FULL PAPER

Bridgehead Bicyclo[4.4.0]boron Heterocycles: A One-Pot Four-Component Synthesis of Dibenzo[*e*,*i*][1,3,7,2]oxadiazaborecin-8(7*H*)-ones

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A one-pot four-component synthesis of 6-aryl-6*H*-dibenzo[*e*,*i*][1,3,7,2]oxadiazaborecin-8(7*H*)-ones is described. Heating a mixture of isatoic anhydride and a benzylamine afforded the corresponding anthranilamide derivative, which was condensed with a 2-hydroxybenzaldehyde and an arylboronic acid under solvent-free conditions to produce bridgehead bicyclo[4.4.0]-boron heterocycles in good to excellent yields. Single-crystal X-ray analysis conclusively confirms the structures of the obtained bridgehead bicyclic 6–6 heterocyclic compounds.

Keywords: Isatoic anhydride, Benzylamines, 2-Hydroxybenzaldehydes, Arylboronic acids, Bridgehead bicyclo[4.4.0]boron heterocycles, Multicomponent reactions.

Introduction

Nowadays, multicomponent reactions (MCRs) are being used as a powerful tool in synthesis of novel organic and pharmaceutical compounds. MCRs offer significant advantages over classical stepwise approaches, *e.g.*, environmentally friendly conditions, time-saving, simplicity, high efficiency, and high atom economy. MCRs allow the formation of several bonds from simple precursors in a single synthetic operation without any need to isolate reaction intermediates [1].

Organoboron compounds have attracted much synthetic attention because of their wide variety of significant applications in medicinal chemistry for enzyme inhibitory activity and cytotoxic properties. Some of them have been used as antibacterial agents (*e.g.*, **1**, *Fig. 1*). Furthermore, some derivatives have been used as anticancer agents in Boron Neutron Capture Therapy, a binary form of cancer treatment by delivering a compound containing boron-10 selectively to tumor tissues prior to irradiation by neutrons [2 – 5]. In addition, a wide diversity of applications have been reported in organic synthesis, *e.g.*, in *Suzuki Miyaura* cross-coupling reactions [2][6], as compounds with fluorescence, electrooptical, and nonlinear optical characters [7]. Furthermore, recently, four-coordinated organoboron compounds with a π-conjugated chelate backbone have been used in emitters and electron-transport materials for organic light-emitting diodes or organic field effect transistors, photoresponsive materials, sensory and biological imaging compounds [8].

The boronate complexes syntheses from boronic acids using tridentate ligands with N and O donor atoms have been widely presented in several reports. The variants of the ligand's structures allowed the assessment of electronic and steric effects in the corresponding chelate molecules. Further surveys have indicated that the B-atom mostly creates a dative bond with the N-atom and is placed in the tetracoordinated structure [9].

Results and Discussion

As part of our studies on the development of efficient and facile methods for the preparation of biologically active heterocyclic compounds from readily available building blocks [10], we have described a one-pot three-component synthesis of 6-aryl-8*H*-dibenzo[*d*,*h*][1,3,7,2]dioxazaborecin-8-ones from 2-aminobenzoic acids, 2-hydroxybenzaldehydes, and arylboronic acids [11]. Herein, we report a four-component synthesis of a new boronate complex from a 1:1:1:1 addition reaction. Thus,

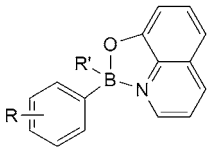

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Fig. 1. An example of biologically active organoboron compounds.

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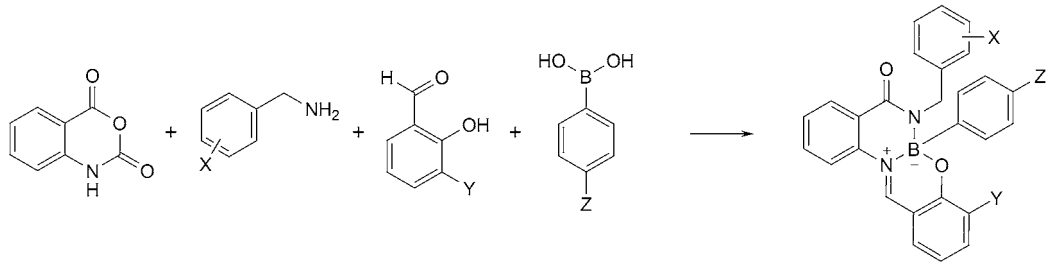
Scheme 1. Four-component reaction between isatoic anhydride **2**, benzylamines **3**, 2-hydroxybenzaldehydes **4**, and aryl boronic acids **5**.



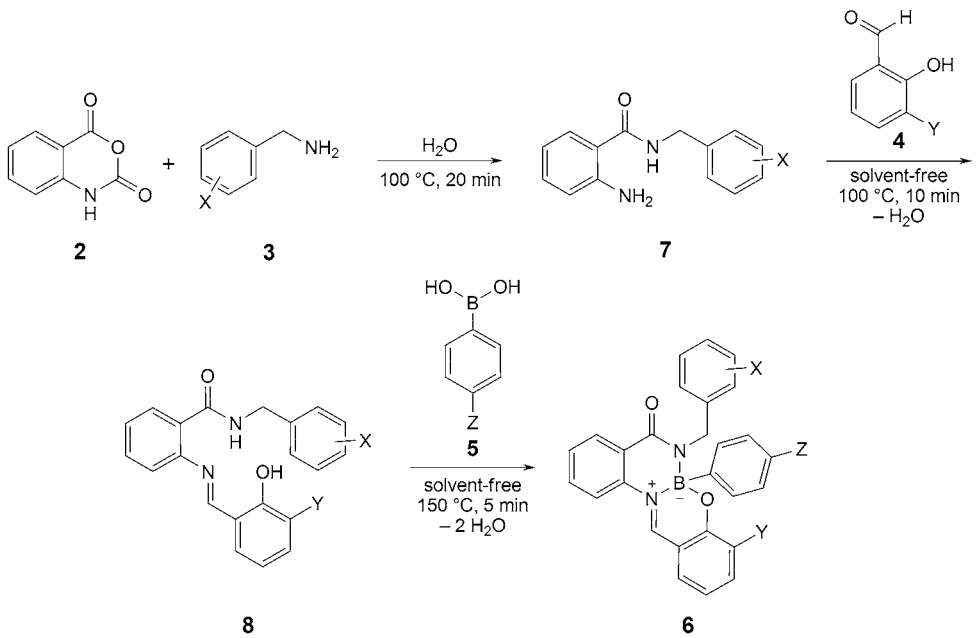
	X	Y	Z
2	**3a** H	**4a** H	**5a** H
	3b 2-Cl	**4b** 3-MeO	**5b** 4-F
	3c 4-Me		**5c** 4-Et
	3d 4-F		

	X	Y	Z	Yield of isolated product [%]
6a	H	H	H	80
6b	H	H	4-Et	95
6c	H	H	4-F	79
6d	H	3-MeO	H	81
6e	2-Cl	H	4-Et	83
6f	4-Me	H	4-F	82
6g	2-Cl	3-MeO	H	84
6h	4-F	3-MeO	H	78
6i	2-Cl	3-MeO	4-Et	90
6j	2-Cl	3-MeO	4-F	85

the *in situ* generated anthranilamide derivatives **7**, from reaction between isatoic anhydride **2** and benzylamines **3a** – **3d**, undergo a condensation reaction with 2-hydroxybenzaldehydes **4a**,**b** to give the corresponding 2-salicylideneanthranilamide derivatives **8**. The latter undergo a condensation-cyclization reaction with aryl boronic acids **5a** – **5c** under solvent-free conditions to afford the corresponding (*N*–*B*)-6-aryl-6*H*-dibenzo[*e*,*i*][1,3,7,2]oxadiazaborecin-8(7*H*)-ones **6a** – **6j** in 78 – 95% yields (see *Experimental Part*). TLC and NMR spectroscopic analysis of the reaction mixtures clearly indicated formation of the corresponding boronate complexes **6** in good to excellent yields. The results are summarized in *Schemes 1* and *2*.

The structures of the isolated products **6** were deduced on the basis of IR, ^{1}H-, and ^{13}C-NMR spectroscopy, mass spectrometry, and elemental analysis. The

Scheme 2. Synthesis of compounds **6**.



IR spectrum of **6b** showed the stretching bands for the C=O and imine functionalities at 1631 and 1595 cm^{-1}, respectively. The mass spectrum of **6b** displayed the molecular ion (M^+) peak at m/z = 444, which was consistent with the 1:1:1:1 adduct of isatoic anhydride, benzylamine, 2-hydroxybenzaldehyde, and 4-ethylphenylboronic acid with the loss of a CO_2 and three H_2O molecules. The fragmentation patterns such as 339 ($[M - EtC_6H_4]^+$), 249 ($[M - (EtC_6H_4+C_6H_5CH_2)]^+$), 106 ($PhCH_2NH^+$), and 91 ($PhCH_2^+$) were consistent with the structure of **6b**. The ^{1}H-NMR spectrum of **6b** exhibited characteristic *multiplet*s at δ(H) 1.14 (t, J = 7.6) and 2.51 (q, J = 7.6) for the Et group, two *doublet*s at δ(H) 4.39 and 5.12 (^2J = 14.0) due to the two diastereotopic H-atoms of NCH_2 moiety as a result of chiral B-atom, as well as characteristic signals with appropriate chemical shifts and coupling constants for the 17 aromatic H-atoms. In NMR spectra of compound **6b**, the characteristic signals at δ(H) 8.33 ppm as a sharp *singlet* in the ^{1}H- and δ(C) 157.4 ppm in the ^{13}C-NMR spectrum confirmed the iminium moiety. The ^{1}H-decoupled ^{13}C-NMR spectrum of **6b** showed the carbonyl signal at δ(C) 162.7 ppm in the expected range for boronate esters. The ipso C-atom attached to B-atom was observed as a broad signal at δ(C) 142.2 ppm. Other 23 distinct resonances were observed in the ^{1}H-decoupled ^{13}C-NMR spectrum of **6b** in agreement with the assigned structure. The ^{11}B-NMR spectrum of **6b** showed a fairly broad signal at 2.85 ppm in agreement with the known tetrahedrally coordinated boronate complexes by the use of tridentate NNO ligands with positively charged B-atom [12]. Partial assignments of these resonances are given in *Experimental Part*.

Single-crystal X-ray analysis of **6c** confirmed conclusively its [4.4.0]bicyclo structure, and by analogy, those of the other products.[1]) An ORTEP diagram of **6c** is shown in *Fig.* 2. Selected bond lengths and bond angles for boronate **6c** are summarized in *Table*.

These bridgehead bicyclo[4.4.0]boronates **6** exhibit transannular N → B fusion with a tetrahedral geometry for B-atom together with six-membered fused rings. The two heterocyclic rings are joined by a dative N–B bond. In agreement with the bond lengths found in similar boronates reported [13], the values of the intramolecular N(1)–B donor-acceptor bond length, B–N(2) and B–O(1) distances found for **6c** are 1.584(3), 1.535(3), and 1.470(2) Å, respectively. The bond angles around the B-atom, are in the range of 106.57(15)° for N(2)–B(1)–N(1) and 113.64(16)° for N(2)–B(1)–C(1), indicative of a distorted tetrahedral geometry of the B-atom. The values are similar to those found in the literature [3].

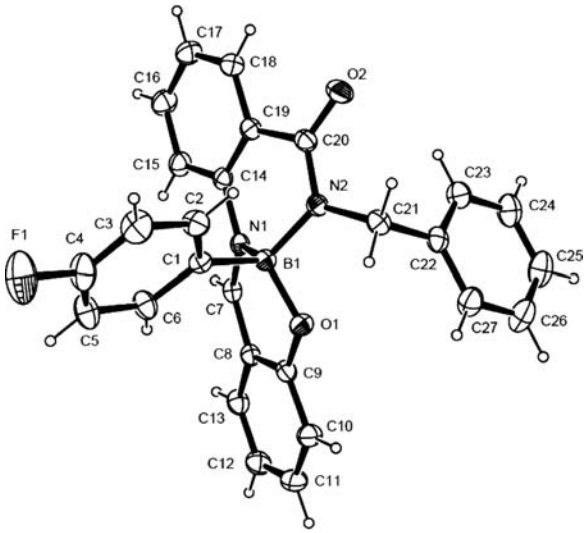


Fig. 2. ORTEP diagram of the molecular structure of **6c**.

Conclusions

In conclusion, we have developed a four-component reaction between isatoic anhydride, benzylamines, 2-hydroxybenzaldehydes, and arylboronic acids for the preparation of a series of boronate esters, 6-aryl-6*H*-dibenzo[*e*,*i*]-[1,3,7,2]oxadiazaborecin-8(7*H*)-ones. The structures of these bridgehead bicyclo[4.4.0]boron heterocycles obtained from tridentate ligands with two N and one O donor atoms and a dative N–B bond have been confirmed by X-ray analysis. The key advantages of our synthesis are high atom economy, use of simple starting materials, and good to excellent yields of the products.

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Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/hlca.201500534.

Experimental Part

General

All the chemicals were obtained from *Merck* (Darmstadt, Germany), and were used without further purification. Column chromatography (CC): silica gel 230 – 240 (*Merck*). M.p.: *Electrothermal 9100* apparatus (Stone, Staffordshire UK); uncorrected. IR Spectra: *Shimadzu IR-460*

[1]) Selected X-ray crystallographic data for compound **6c**: $C_{27}H_{20}BFN_2O_2$, Monoclinic, space group = $P2_1/n$, a = 9.7275(7) Å, b = 13.9047(8) Å, c = 16.3238(11) Å, β = 96.893(7)°, V = 2197.97(19) Å^3, T = 295(2) K, Z = 4, D_{calcd} = 1.316 g/cm^3, μ = 0.089 mm^{-1}, 2593 observed reflections, final R_1 = 0.042, wR_2 = 0.107 and for all data R_1 = 0.075, wR_2 = 0.137. CCDC 968743 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Table. Selected bond distances [Å] and angles [°] for compound **6c**

Bond distances		
B(1)–O(1): 1.470(2)	B(1)–C(1): 1.614(3)	N(2)–C(20): 1.339(2)
B(1)–N(1): 1.584(3)	N(1)–C(7): 1.301(2)	N(2)–C(21): 1.473(2)
B(1)–N(2): 1.535(3)	N(1)–C(14): 1.431(2)	O(1)–C(9): 1.334(2)
Bond angles		
O(1)–B(1)–N(2): 107.01(15)	N(2)–B(1)–C(1): 113.64(16)	C(14)–N(1)–B(1): 115.84(15)
O(1)–B(1)–N(1): 108.95(15)	N(1)–B(1)–C(1): 108.58(15)	C(20)–N(2)–B(1): 121.88(15)
N(2)–B(1)–N(1): 106.57(15)	C(9)–O(1)–B(1): 122.35(14)	C(21)–N(2)–B(1): 119.19(15)
O(1)–B(1)–C(1): 111.88(16)	C(7)–N(1)–B(1): 120.54(16)	

spectrometer (*Shimadzu*, Tokyo, Japan); in cm^{-1}. EI-MS (20 eV): *Agilent Technologies (HP) 5973* mass spectrometer (Santa Clara, CA, USA); in *m*/*z* (rel. %). ^{1}H- and ^{13}C-NMR spectra: *Bruker DPX-250 AVANCE* (at 250.1 and 62.9 MHz, resp.) and *Bruker DRX-500 AVANCE* (at 500.1 and 125.8 MHz, resp.) instruments; in $CDCl_3$ soln.; δ in ppm rel. to Me_4Si (= 0 ppm), *J* in Hz. ^{11}B-NMR spectrum: *Bruker DRX-500 AVANCE* (at 160.5 MHz) instrument (Rheinstetten, Germany); in $CDCl_3$ soln.; δ in ppm rel. to $BF_3{\cdot}OEt_2$ (= 0 ppm). Elemental analyses: *Heraeus CHN-O-Rapid* analyzer. X-ray crystallography: *Bruker SMART* diffractometer; CCD area detector; graphite monochromatized MoK_α radiation.

General Procedure for the Preparation of Compounds **6** (*exemplified with* **6a**)

A mixture of isatoic anhydride (0.163 g, 1 mmol) and benzylamine (0.107 g, 1 mmol) in H_2O (5 ml) was stirred at 100 °C for 20 min. After nearly complete conversion to the corresponding anthranilamide derivative, as was indicated by TLC monitoring, the mixture was cooled to r.t., the aq. phase was separated by suction and the solid residue was dried at 100 °C. Next, 2-hydroxybenzaldehyde (0.122 g, 1 mmol) was added and the mixture was heated at 100 °C for 10 min under solvent-free conditions to give the corresponding 2-salicylideneanthranilamide. Finally, phenyl boronic acid (0.122 g, 1 mmol) was added and the mixture was heated at 150 °C for 5 min. The mixture was cooled to r.t. and the residue was purified by CC using hexane/AcOEt (2:1) as eluent. The solvent was removed and the product was obtained.

[*N*-Benzyl-2-{[2-(hydroxy-κ*O*)benzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](phenyl)boron (**6a**). Orange crystals. Yield: 0.333 g (80%). M.p. 208 °C. IR (KBr): 1636 (C=O), 1609 (C=N), 1545, 1461, 1429, 1384, 1350, 1306, 1275, 1247, 1202, 1170, 1073, 1032, 975, 935, 834, 761, 699. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 4.32 (*d*, ^2J = 14.0, 1 H); 5.03 (*d*, ^2J = 14.0, 1 H); 6.84 (*t*, *J* = 7.3, 1 H); 6.96 (*d*, *J* = 7.8, 1 H); 7.01 – 7.16 (*m*, 7 H); 7.17 (*d*, *J* = 7.3, 1 H); 7.29 (*d*, *J* = 7.8, 2 H); 7.31 – 7.49 (*m*, 4 H); 7.52 (*t*, *J* = 8.3, 1 H); 8.30 – 8.33 (*m*, 1 H); 8.33 (*s*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 46.0; 116.3; 117.5; 119.5; 120.1; 126.4; 127.7; 127.8; 127.9; 128.0; 128.9; 129.8; 130.6; 131.3; 132.4; 133.0; 138.6; 140.3; 141.0; 143.9; 157.6; 160.5; 162.8. EI-MS: 416 (69, M^+), 339 (100), 311 (19), 252 (10), 237 (28), 199 (5), 162 (10), 125 (8), 91 (19), 69 (6), 57 (5). Anal. calc. for $C_{27}H_{21}BN_2O_2$ (416.28): C 77.90, H 5.08, N 6.73; found: C 77.88, H 5.09, N 6.70.

[*N*-Benzyl-2-{[2-(hydroxy-κ*O*)benzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](4-ethylphenyl)boron (**6b**). Orange crystals. Yield: 0.422 g (95%). M.p. 195 °C. IR (KBr): 1631 (C=O), 1595 (C=N), 1565, 1492, 1454, 1369, 1276, 1228, 1152, 1124, 1028, 940, 887, 803, 751, 697. ^{1}H-NMR (500.1 MHz, $CDCl_3$): 1.14 (*t*, *J* = 7.6, 3 H); 2.51 (*q*, *J* = 7.6, 2 H); 4.39 (*d*, ^2J = 14.0, 1 H); 5.12 (*d*, ^2J = 14.0, 1 H); 6.85 (*t*, *J* = 7.4, 1 H); 6.94 (*d*, *J* = 7.7, 2 H); 7.01 (*d*, *J* = 8.4, 1 H); 7.11 (*d*, *J* = 7.8, 2 H); 7.14 (*t*, *J* = 7.8, 1 H); 7.22 (*t*, *J* = 7.4, 2 H); 7.29 – 7.36 (*m*, 2 H); 7.40 – 7.44 (*m*, 2 H); 7.49 – 7.53 (*m*, 1 H); 7.55 (*d*, *J* = 7.7, 2 H); 8.33 (*s*, 1 H); 8.32 – 8.36 (*m*, 1 H). ^{11}B-NMR (160.5 MHz, $CDCl_3$): δ(H) 2.85. ^{13}C-NMR (125.8 MHz, $CDCl_3$): 15.3; 29.6; 45.9; 116.2; 117.4; 119.3; 119.8; 126.1; 127.1; 127.7; 127.8; 128.8; 129.6; 130.4; 131.2; 132.2; 132.9; 138.5; 140.0; 141.0; 142.2; 143.6; 157.4; 160.4; 162.7. EI-MS: EI-MS: 444 (6, M^+), 339 (23), 261 (6), 249 (6), 235 (6) 211 (91), 194 (8), 185 (4), 133 (4), 120 (25), 106 (46), 91 (100), 77 (22), 65 (60), 51 (22). Anal. calc. for $C_{29}H_{25}BN_2O_2$ (444.33): C 78.39, H 5.67, N 6.30; found: C 78.31, H 5.60, N 6.24.

[*N*-Benzyl-2-{[2-(hydroxy-κ*O*)benzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](4-fluorophenyl)boron (**6c**). Orange crystals. Yield: 0.343 g (79%). M.p. 206 °C. IR (KBr): 1640 (C=O), 1609 (C=N), 1550, 1499, 1458, 1388, 1347, 1305, 1244, 1200, 1160, 1127, 1009, 935, 883, 820, 756, 702. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 4.39 (*d*, ^2J = 14.0, 1 H); 5.07 (*d*, ^2J = 14.0, 1 H); 6.75 (*dd*, $^3J_{FH}$ = 9.0, $^3J_{HH}$ = 9.0, 2 H); 6.90 (*t*, *J* = 7.9, 1 H); 7.10 (*d*, *J* = 8.2, 1 H); 7.12 – 7.19 (*m*, 5 H); 7.38 (*d*, *J* = 7.5, 2 H); 7.40 – 7.54 (*m*, 4 H); 7.60 (*t*, *J* = 7.5, 1 H); 8.39 – 7.37 (*m*, 1 H); 8.40 (*s*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 45.8; 114.4 (*d*, $^2J_{FC}$ = 19.5); 116.2; 117.6; 119.4; 120.2; 126.4; 127.8; 128.0; 128.9; 129.9; 130.5; 132.5; 133.0 (*d*, $^3J_{FC}$ = 7.3); 133.2; 138.5; 146.4; 140.4; 140.8; 157.7; 160.2; 162.7; 162.8 (*d*, $^1J_{FC}$ = 245.1). EI-MS: 434 (3, M^+), 339 (81), 329 (8), 249 (17), 235 (13), 220 (8), 169 (7), 152 (9), 120 (8), 106 (22), 91 (100), 77 (20), 58 (14). Anal. calc. for $C_{27}H_{20}BFN_2O_2$ (434.27): C 74.67, H 4.64, N 6.45; found: C 74.71, H 4.67, N 6.42.

[*N*-Benzyl-2-{[2-(hydroxy-κ*O*)-3-methoxybenzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](phenyl)boron (**6d**). Orange crystals. Yield: 0.361 g (81%). M.p. 194 °C. IR (KBr):

1639 (C=O), 1607 (C=N), 1564, 1473, 1465, 1385, 1351, 1259, 1171, 1138, 1078, 1046, 965, 915, 846, 822, 741, 697, 655. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 3.87 (*s*, 3 H); 4.42 (*d*, *J* = 13.5, 1 H); 5.07 (*d*, *J* = 13.5, 1 H); 6.81 (*t*, *J* = 7.8, 1 H); 6.90 (*d*, *J* = 7.6, 1 H); 7.05 – 7.30 (*m*, 10 H); 7.40 – 7.44 (*m*, 2 H); 7.68 (*d*, *J* = 7.5, 2 H); 8.30 (*s*, 1 H); 8.31 – 8.33 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 46.1; 56.7; 116.6; 117.4; 119.7; 121.2; 124.2; 126.4; 127.6; 127.8; 127.9; 128.0; 129.8; 129.9; 130.6; 131.3; 132.4; 138.5; 140.8; 147.1; 149.8; 151.4; 157.5; 162.7. EI-MS: 446 (3, M^+), 416 (18), 400 (17), 369 (36), 339 (11), 313 (12), 297 (40), 248 (21), 219 (25), 207 (34), 194 (39), 169 (35), 103 (97), 91 (100), 77 (87), 65 (21), 51 (32). Anal. calc. for $C_{28}H_{23}BN_2O_3$ (446.30): C 75.35, H 5.19, N 6.28; found: C 75.34, H 5.22, N 6.24.

[*N*-(2-Chlorobenzyl)-2-{[2-(hydroxy-κ*O*)benzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](4-ethylphenyl)boron (6e). Orange crystals. Yield: 0.397 g (83%). M.p. 170 °C. IR (KBr): 1642 (C=O), 1609 (C=N), 1560, 1464, 1276, 1200, 1041, 952, 849, 753, 695, 652. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 1.05 (*t*, *J* = 7.5, 3 H); 2.46 (*q*, *J* = 7.5, 2 H); 4.45 (*d*, *J* = 16.0, 1 H); 5.15 (*d*, *J* = 16.0, 1 H); 6.60 – 7.50 (*m*, 15 H); 8.30 – 8.34 (*m*, 1 H); 8.43 (*s*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 15.2; 28.6; 45.8; 116.2; 117.4; 119.3; 119.9; 126.2; 127.5; 127.6; 127.7; 127.9; 128.8; 129.7; 130.4; 131.2; 132.2; 132.3; 132.9; 144.7; 138.5; 140.2; 140.9; 151.7; 157.4; 160.4; 162.7. EI-MS: 479 (< 1, M^+), 443 (28), 373 (20), 361 (19), 339 (100), 327 (8), 316 (15), 287 (48), 271 (16), 233 (26), 181 (30), 152 (12), 140 (24), 125 (92), 89 (56), 77 (55), 65 (34), 51 (31). Anal. calc. for $C_{29}H_{24}BClN_2O_2$ (478.78): C 72.75, H 5.05, N 5.85; found: C 72.66, H 5.13, N 5.74.

(4-Fluorophenyl)[2-{[2-(hydroxy-κ*O*)benzylidene]amino-κ*N*}-*N*-(4-methylbenzyl)benzamidato(2-)-κ*N*]boron (6f). Orange crystals. Yield: 0.367 g (82%). M.p. 178 °C. IR (KBr): 1631 (C=O), 1610 (C=N), 1605, 1550, 1503, 1462, 1382, 1348, 1304, 1270, 1219, 1158, 1127, 1097, 936, 817, 757, 691. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 2.13 (*s*, 3 H); 4.27 (*d*, ^2J = 13.8, 1 H); 4.91 (*d*, ^2J = 13.8, 1 H); 6.65 (*dd*, $^3J_{FH}$ = 9.0, $^3J_{HH}$ = 9.0, 2 H); 6.83 (*t*, *J* = 7.8, 1 H); 6.89 (*d*, *J* = 7.5, 2 H); 6.90 – 7.15 (*m*, 4 H); 7.24 – 7.36 (*m*, 5 H); 7.49 (*dt*, *J* = 1.5, 8.5, 1 H); 8.18 – 8.23 (*m*, 1 H); 8.29 (*s*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 21.2; 45.7; 114.5 (*d*, $^2J_{FC}$ = 19.4); 116.4; 117.9; 119.4; 120.3; 127.6; 128.8; 128.9; 129.8; 130.3; 132.6; 133.0 (*d*, $^3J_{FC}$ = 6.5); 133.4; 135.8; 137.7; 138.5; 140.4; 141.7; 158.1; 160.2; 162.8 (*d*, $^1J_{FC}$ = 245.4); 162.9. EI-MS: 448 (5, M^+), 366 (39), 353 (90), 343 (17), 325 (12), 249 (46), 227 (12), 200 (12), 122 (30), 105 (100), 91 (18), 77 (55), 65 (18) 51 (22). Anal. calc. for $C_{28}H_{22}BFN_2O_2$ (448.30): C 75.02, H 4.95, N 6.25; found: C 74.91, H 5.14, N 6.18.

[*N*-(2-chlorobenzyl)-2-{[2-(hydroxy-κ*O*)-3-methoxybenzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](phenyl)boron (6 g). Orange crystals. Yield: 0.403 g (84%). M.p. 210 °C. IR (KBr): 1643 (C=O), 1610 (C=N), 1566, 1473, 1382, 1298, 1259, 1171, 1077, 1041, 978, 915, 856, 743, 696, 653. ^{1}H-NMR (500.1 MHz, $CDCl_3$): 3.65 (*s*, 3 H); 4.66 (*d*, ^2J = 16.0, 1 H); 5.20 (*d*, ^2J = 16.0, 1 H); 6.83 (*t*, *J* = 7.8, 1 H); 6.94 (*t*, *J* = 7.9, 1 H); 6.98 – 7.03 (*m*, 2 H); 7.05 – 7.15 (*m*, 4 H); 7.19 (*d*, *J* = 7.7, 2 H); 7.22 (*d*, *J* = 7.7, 1 H); 7.25 (*d*, *J* = 7.9, 1 H); 7.50 – 7.57 (*m*, 3 H); 8.39 – 8.42 (*m*, 1 H); 8.53 (*s*, 1 H). ^{13}C-NMR (125.1 MHz, $CDCl_3$): 43.2; 57.1; 116.7; 117.3; 119.7; 123.0; 124.4; 126.1; 126.8; 127.5; 127.6; 127.7; 128.0; 128.7; 129.8; 130.7; 131.1; 132.4; 132.7; 137.6; 139.0; 145.0; 149.8; 151.7; 157.7; 162.6. EI-MS: 479 (1, M^+ – 1), 445 (37), 403 (100), 369 (65), 325 (25), 280 (35), 236 (15), 184 (60), 125 (93), 89 (30), 77 (42), 51 (23). Anal. calc. for $C_{28}H_{22}BClN_2O_3$ (480.75): C 69.95, H 4.61, N 5.83; found: C 69.93, H 4.62, N 5.79.

[*N*-(4-Fluorobenzyl)-2-{[2-(hydroxy-κ*O*)-3-methoxybenzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](phenyl)boron (6 h). Orange crystals. Yield: 0.362 g (78%). M.p. 155 °C. IR (KBr): 1639 (C=O), 1606 (C=N), 1566, 1506, 1475, 1385, 1348, 1304, 1259, 1219, 1166, 1091, 968, 914, 821, 737, 698. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 3.83 (*s*, 3 H); 4.32 (*d*, ^2J = 13.8, 1 H); 4.94 (*d*, ^2J = 13.8, 1 H),; 6.77 (*dd*, $^3J_{FH}$ = 8.5, $^3J_{HH}$ = 8.5, 2 H); 6.80 (*d*, *J* = 8.0, 1 H); 6.80 – 7.20 (*m*, 7 H); 7.25 – 7.28 (*m*, 1 H); 7.35 – 7.40 (*m*, 2 H); 7.57 (*dd*,$^3J_{HH}$ = 8.5, $^4J_{FH}$ = 5.8, 2 H); 8.28 (*s*, 1 H); 8.27 – 8.31 (*m*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 45.4; 56.6; 114.5 (*d*, $^2J_{FC}$ = 20.8); 116.8; 117.6; 119.9; 120.9; 124.3; 127.7; 127.9; 128.4; 129.8; 130.5; 131.2; 131.7 (*d*, $^3J_{FC}$ = 7.8 Hz); 132.5; 136.5 (*d*, $^4J_{FC}$ = 3.1); 138.5; 144.5; 149.8; 151.1; 157.8; 161.9 (*d*, $^1J_{FC}$ = 243.0); 162.8. EI-MS: 464 (7, M^+), 448 (2), 432 (2), 387 (89), 335 (84), 330 (23), 281 (12) 249 (47), 211 (15), 150 (30), 109 (100), 83 (42), 58 (14). Anal. calc. for $C_{28}H_{22}BFN_2O_3$ (464.30): C 72.43, H 4.78, N 6.03; found: C 72.45, H 4.75, N 6.00.

[*N*-(2-Chlorobenzyl)-2-{[2-(hydroxy-κ*O*)-3-methoxybenzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](4-ethylphenyl)-boron (6i). Orange crystals. Yield: 0.458 g (90%). M.p. 178 °C. IR (KBr): 1641 (C=O), 1609 (C=N), 1568, 1479, 1447, 1302, 1257, 1170, 1047, 971, 813, 745, 688. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 1.10 (*t*, *J* = 7.7, 3 H); 2.52 (*q*, *J* = 7.7, 2 H); 3.87 (*s*, 3 H); 4.56 (*d*, ^2J = 15.8, 1 H); 5.17 (*d*, ^2J = 15.8, 1 H); 6.51 (*d*, *J* = 8.0, 1 H); 6.70 – 6.82 (*m*, 4 H); 6.94 (*d*, *J* = 8.0, 1 H); 6.99 (*t*, *J* = 7.0, 1 H); 7.12 (*d*, *J* = 8.3, 2 H); 7.22 (*d*, *J* = 8.3, 2 H); 7.34 (*t*, *J* = 7.0, 1 H); 7.53 – 7.58 (*m*, 2 H); 8.41 – 8.44 (*m*, 1 H); 8.49 (*s*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 14.4; 31.1; 43.5; 57.2; 116.9; 117.6; 119.9; 123.1; 124.7; 126.3; 127.0; 127.6; 127.7; 128.1; 128.8; 129.6; 129.9; 130.8; 131.2; 132.7; 132.9; 137.7; 138.9; 145.1; 149.9; 151.7; 158.0; 162.9. EI-MS: 508 (< 1, M^+), 473 (3), 403 (8), 369 (4), 339 (36), 302 (2), 275 (23), 150 (83), 125 (100), 107 (33), 77 (38), 65 (38), 51 (36). Anal. calc. for $C_{30}H_{26}BClN_2O_3$ (508.80): C 70.82, H 5.15, N 5.51; found: C 70.68, H 5.24, N 5.36.

[*N*-(2-Chlorobenzyl)-2-{[2-(hydroxy-κ*O*)-3-methoxybenzylidene]amino-κ*N*}benzamidato(2-)-κ*N*](4-fluorophenyl)-boron (6j). Orange crystals. Yield: 0.424 g (85%). M.p. 199 °C. IR (KBr): 1653 (C=O), 1605 (C=N), 1475, 1423, 1229, 1087, 1043, 753, 643. ^{1}H-NMR (250.1 MHz, $CDCl_3$): 3.60 (*s*, 3 H); 4.67 (*d*, ^2J = 16.0, 1 H); 5.17 (*d*, ^2J = 16.0, 1 H); 6.74 (*dd*, $^3J_{FH}$ = 8.8, $^3J_{HH}$ = 8.8, 2 H); 6.86 (*t*, *J* = 7.8, 1 H); 6.90 – 7.23 (*m*, 8 H); 7.52 – 7.60 (*m*, 3 H);

8.40 – 8.44 (*m*, 1 H); 8.51 (*s*, 1 H). ^{13}C-NMR (62.9 MHz, $CDCl_3$): 43.1; 57.0; 114.3 (*d*, $^2J_{FC}$ = 19.0); 116.6; 117.5; 119.9; 122.7; 124.4; 126.1; 126.9; 127.7; 128.1; 128.7; 129.9; 130.7; 132.6 (*d*, $^3J_{FC}$ = 6.4); 132.7; 132.8; 137.4; 138.6; 144.7; 149.8; 151.9; 157.9; 161.5 (*d*, $^1J_{FC}$ = 243.8); 162.4. EI-MS: 499 (1, M^+), 463 (66), 446 (3), 403 (16), 369 (100), 235 (9) 280 (4), 236 (5), 184 (11), 125 (26), 106 (4), 51 (9). Anal. calc. for $C_{28}H_{21}BClFN_2O_3$ (498.74): C 67.43, H 4.24, N 5.62; found: C 67.45, H 4.30, N 5.59.

REFERENCES

[1] 'Multicomponent Reactions', Eds. J. Zhu and H. Bienaymé, Wiley-VCH, Weinheim, 2005; A. Basso, L. Banfi, R. Riva, G. Guanti, *J. Org. Chem.* **2005**, *70*, 575; D. J. Ramón, M. Yus, *Angew. Chem., Int. Ed.* **2005**, *44*, 1602; V. Nair, C. Rajesh, A. U. Vinod, S. Bindu, A. R. Sreekanth, J. S. Mathen, L. Balagopal, *Acc. Chem. Res.* **2003**, *36*, 899; C. Ma, Y. Yang, *Org. Lett.* **2005**, *7*, 1343; Y. Cheng, O. Meth-Cohn, *Chem. Rev.* **2004**, *104*, 2507; C.-F. Lee, L.-M. Yang, T.-Y. Hwu, A.-S. Feng, J.-C. Tseng, T.-Y. Luh, *J. Am. Chem. Soc.* **2000**, *122*, 4992; V. Nair, A. U. Vinod, *Chem. Commun.* **2000**, 1019; R. C. D. Brown, *Angew. Chem., Int. Ed.* **2005**, *44*, 850.

[2] 'Boronic Acids. Preparation and Applications in Organic Synthesis and Medicine', Ed. D. G. Hall, Wiley-VCH, Weinheim, 2005.

[3] S. J. Baker, Y.-K. Zhang, T. Akama, A. Lau, H. Zhou, V. Hernandez, W. Mao, M. R. K. Aller, V. Sander, J. Plattner, *J. Med. Chem.* **2006**, *49*, 4447.

[4] M. F. Hawthorne, M. W. Lee, *J. Neuro-Oncol.* **2003**, *62*, 33.

[5] G. Wu, R. F. Barth, W. Yang, M. Chatterjee, W. Tjarks, M. J. Ciesielski, R. A. Fenstermaker, *Bioconjug. Chem.* **2004**, *15*, 185.

[6] K. Nozaki, T. Tsutsumi, H. Takaya, *J. Org. Chem.* **1995**, *60*, 6668; K. Nozaki, M. Yoshida, H. Takaya, *Angew. Chem., Int. Ed.* **1995**, *33*, 2452.

[7] Z.-Q. Liu, Q. Fang, D.-X. Cao, D. Wang, G.-B. Xu, *Org. Lett.* **2004**, *6*, 2933; C. D. Entwistle, T. B. Marder, *Angew. Chem., Int. Ed.* **2002**, *41*, 2927; H. Reyes, B. M. Muñoz, N. Farfán, R. Santillan, S. Rojas-Lima, P. G. Lacroix, K. J. Nakatani, *J. Mater. Chem.* **2002**, *12*, 2898.

[8] Y.-L. Rao, S. Wang, *Inorg. Chem.* **2011**, *50*, 12263.

[9] Ş. Özçelik, A. Gül, *J. Organomet. Chem.* **2012**, *699*, 87; M. Rodríguez, M. E. Ochoa, C. Rodríguez, R. Santillán, V. Barba, N. Farfán, *J. Organomet. Chem.* **2007**, *692*, 2425; H. I. Beltrán, L. S. Zamudio-Rivera, T. Mancilla, R. Santillán, N. Farfán, *J. Organomet. Chem.* **2002**, *657*, 194; V. Barba, A. Rodríguez, M. E. Ochoa, R. Santillan, N. Farfán, *Inorg. Chim. Acta* **2004**, *357*, 2593; N. Christinat, R. Scopelliti, K. Severin, *J. Org. Chem.* **2007**, *72*, 2192; V. Barba, R. Luna, D. Castillo, R. Santillán, N. Farfán, *J. Organomet. Chem.* **2000**, *604*, 273; V. Barba, D. Cuahutle, M. E. Ochoa, R. Santillan, N. Farfán, *Inorg. Chim. Acta* **2000**, *303*, 7; V. Barba, D. Cuahutle, R. Santillan, N. Farfán, *Can. J. Chem.* **2001**, *79*, 1229; M. Braun, S. M. Schlecht, M. Engelmann, W. Frank, S. Grimme, *Eur. J. Org. Chem.* **2008**, 5221; A. Abreu, S. J. Alas, H. I. Beltrán, R. Santillan, N. Farfán, *J. Organomet. Chem*. **2006**, *691*, 337; N. Christinat, E. Croisier, R. Scopelliti, M. Cascella, U. Röthlisberger, K. Severin, *Eur. J. Inorg. Chem.* **2007**, 5177; P. F. Kaiser, J. M. White, C. A. Hutton, *J. Am. Chem. Soc.* **2008**, *130*, 16450; V. Barba, E. Gallegos, R. Santillan, N. Farfán, *J. Organomet. Chem.* **2001**, *622*, 259; V. Barba, H. Höpfl, N. Farfán, R. Santillan, H. I. Beltran, L. S. Zamudio-Rivera, *Chem. Commun.* **2004**, 2834.

[10] M. Adib, F. Peytam, M. Zainali, L.-G. Zhu, J. Wu, *Tetrahedron Lett.* **2015**, *56*, 4729; M. Adib, H. Janatian Ghazvini, M. Soheilizad, S. Saeedi, M. Tajbakhsh, M. Amanlou, *Helv. Chim. Acta* **2015**, *98*, 1079; M. Adib, M. Soheilizad, L.-G. Zhu, J. Wu, *Synlett* **2015**, *26*, 177; M. Adib, M. Soheilizad, S. Rajai-Daryasarei, P. Mirzaei, *Synlett* **2015**, *26*, 1101; M. H. Sayahi, M. Adib, Z. Hamooleh, L.-G. Zhu, M. Amanlou, *Helv. Chim. Acta* **2015**, *98*, 1231; M. Adib, S. Feizi, M. Shahzad Shirazi, L.-G. Zhu, H. R. Bijanzadeh, *Helv. Chim. Acta* **2014**, *97*, 524.

[11] M. Adib, E. Sheikhi, H. R. Bijanzadeh, L.-G. Zhu, *Tetrahedron* **2012**, *68*, 3377.

[12] P. V. V. N. Kishore, A. Kumar Jami, V. Baskar, *Inorg. Chim. Acta* **2011**, *372*, 321; C. Ikeda, T. Maruyama, T. Nabeshima, *Tetrahedron Lett.* **2009**, *50*, 3349.

[13] H. Höpfl, *J. Organomet. Chem.* **1999**, *581*, 129.

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