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Synthesis of functionalized diarylborinic 8-oxyquinolates *via* bimetallic boron–lithium intermediates

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ABSTRACT

The simple one-pot approach to functionalized diarylborinic 8-oxyquinolates has been developed starting with selected dihalobenzenes (Hal = Br, I) and (dialkoxy)phenylboranes $PhB(OR)_2$ (R = Me, Et). The initial step results in halogenated diarylborinic "ate" complexes which are prone to halogen–lithium exchange when treated with *t*-BuLi. The resultant dianionic lithiated diarylborinic "ate" complexes of the type $[(LiAr)PhB(OR)_2]Li$ were reacted with selected electrophiles followed by hydrolysis to give unsymmetrically substituted diarylborinic acids isolated in the form of respective 8-hydroxyquinoline complexes as the final products in moderate to good yields. The crystal structure of (2-fluoro-4-formylphenyl)(phenyl)borinic 8-oxyquinolinate has been determined by X-ray diffraction. The alternative method involving the lithiation of *B*-protected bis(halophenyl)borinic *N*,*N*-dimethylethanolamine esters followed by the quench with electrophiles has also been investigated.

1. Introduction

Recently, arylborinic complexes have attracted a special attention due to their promising applications in materials chemistry and engineering – especially, in the construction of luminescent devices as a part of emitting layers, electron transport materials, and as sensors for inorganic ions [1]. There are also examples of potent biological activity of selected borinic derivatives [2]. These compounds were examined as ligands for lithium, zinc, and magnesium complexes [3], as catalysts in boron-catalyzed aldol reaction [4], and as reagents in the asymmetric synthesis [5]. In this context, the improvement of the synthetic chemistry of diarylborinic derivatives is highly desirable. There are various approaches to these compounds. Classically, they can be obtained with varying yields by reacting organolithium or organomagnesium compounds with borate esters $B(OR)_3$ followed by hydrolysis and esterification with *O*,*N*-chelating ligands such as ethanolamine, 8-hydroxyquinoline and their analogues [6] (Scheme 1a). However, the method suffers from the selectivity problems due to the formation of other arylboron products such as arylboronic esters and tetraarylborates. Symmetrical arylborinic azaesters can also be formed in the reaction of triarylborane with appropriate ligand due to the cleavage of one phenyl group [1f,g,3] (Scheme 1b). Another method is based on the treatment of organolithium or organomagnesium compounds with arylboronic esters $ArB(OR)_2$ and hydrolysis followed by esterification [2a,7] (Scheme 1c). This approach can provide an access to unsymmetrical borinic acid derivatives. However, the method is limited to derivatives lacking sensitive functional groups which can react with aryllithiums or Grignard compounds. Alternatively, diarylborinic complexes were obtained by transmetalation of aryltin or arylsilicon compounds with appropriate bromoborane derivatives followed by addition of complexing agent [1d,e] (Scheme 1d). In a few cases polymeric unsymmetrical borinic complexes were obtained using the latter method [1h–j,8a,b].

Recently, our group has focused on the generation of bimetallic aromatic boron–lithium reagents and their application to the synthesis of functionalized arylboronic acids and esters [9]. In this paper, we present our results concerning related bimetallic systems and their applications in the synthesis of novel unsymmetrically functionalized diarylborinic esters. They were isolated as well-defined and relatively stable 8-hydroxyquinoline (**Q**) complexes.

2. Results and discussion

It was shown previously that the protection of the boron atom against nucleophilic attack is mandatory for the successful

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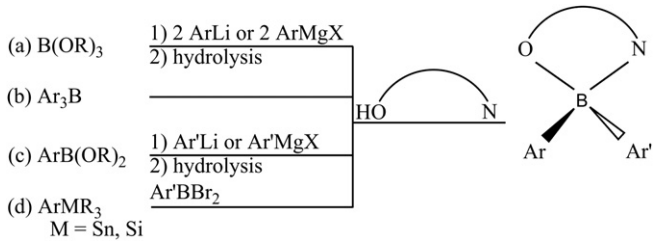


Scheme 1. Synthetic approaches to diarylborinic *O*,*N*-chelate complexes.

generation of aromatic boron–lithium reagents [9]. We have investigated two different strategies of the protection. The first one involved the *in situ* formation of halogenated borinic anionic "ate" complexes, featuring the tetra-coordinate boron atom and, hence, reasonably resistant against lithiating reagents. The second approach relies on the formation of the halogenated diarylborinic ester with *N*,*N*-dimethylethanolamine (DMAE) possessing B–N dative bond as the boron protection.

2.1. Synthesis via lithiated diarylborinic "ate" complexes

We have focused especially our attention on a protocol that can provide unsymmetrical borinic derivatives as they are in many cases difficult to obtain using known procedures. Thus, we referred to our previous work [9], where the protection of the boron atom in the form of the anionic boronic "ate" complex was successfully used to generate bimetallic lithium–boron aromatic reagents. This one-pot protocol was based on the formation of haloarylboronic "ate" complex from an appropriate dihalobenzene, and subsequent lithiation followed by reaction with an electrophile. We have decided to check whether a similar synthetic sequence can be employed for the synthesis of unsymmetrically functionalized diarylborinic derivatives isolated as final product in the form of stable **Q** complexes (Scheme 2). In our first approach, 4-iodophenyllithium was obtained from 1,4-diiodobenzene and *n*-BuLi in Et_2O at −78 °C. A subsequent reaction with diethyl phenylboronate $PhB(OEt)_2$ resulted in an efficient formation of the iodinated diarylborinic "ate" complex **ate-I**. The consecutive step involved attempted *in situ* lithiation of **ate-I** *via* iodine/lithium exchange. Unfortunately, *n*-BuLi (Scheme 2, reaction 3a) proved ineffective even at +15 °C. After addition of DMF followed by hydrolysis with aq. H_2SO_4 and complexation with **Q**, we obtained monoiodinated **Q** complex containing only *ca.* 5% of the expected formylated derivative **1**. We have modified this protocol as we have added THF in order to promote halogen/lithium exchange. Unfortunately, this modification did not improve the course of the latter reaction. Thus we decided to use *t*-BuLi in order to perform iodine–lithium exchange. The addition of *t*-BuLi was performed at low temperature −110 °C (Scheme 2, reaction 3b). After the addition of *t*-BuLi, the reaction mixture was consecutively treated with *ca.* 20% (v/v) THF, to promote the halogen–lithium interconversion, and then allowed to warm up to −75 °C. The resultant lithiated diarylborinic reagent **ate-Li** was quenched with DMF to afford **1** in good yield. This protocol was successfully extended by employing other electrophiles (Me_2S_2, TMSCl, *t*-BuNCO, $PhB(OEt)_2$) to give corresponding well-defined **Q** complexes. Our protocol was successfully applied also with 1,3-diiodobenzene as well as 1,4-dibromo-2-fluorobenzene as starting materials. The results are collected in Table 1.

Specifically, the use of $PhB(OEt)_2$ as the electrophile for quenching the lithiated borinic "ate" complexes resulted in the formation of symmetrical bis(diarylborinic) bis(oxyquinolinates) $PhB(Q)C_6H_4B(Q)Ph$ **11** (with central *para*-phenylene core) and **12** (with *meta*-phenylene core). They are very poorly soluble in common solvents but their composition was confirmed unambigously by photospray MS.

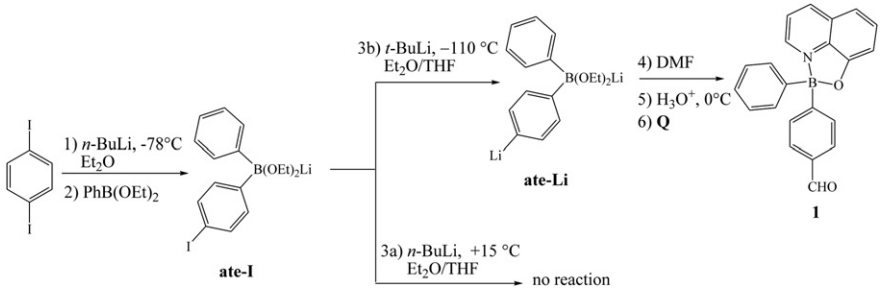
It should be noted that the usefulness of $PhB(OMe)_2$ as the borylating reagent in our protocol proved troublesome in most cases. To our surprise we found that with an exception for *ortho*-fluorinated compounds **9** and **10**, all other attempts were unsuccessful. This may be due to the insufficient protection of the boron atom in dimethoxydiphenyl borinic "ate" complexes against nuclephilic attack during the generation of bimetallic lithium–boron reagents.

2.2. Generation of lithiated borinic azaesters and subsequent reactions with electrophiles

It has been reported that selected lithiated arylboronic *N*-alkyldiethanolamine esters can be generated due to the effective protection of the boron atom achieved by the intramolecular coordination with nitrogen donor atom [10]. This has prompted us to study the analogous approach employing selected halogenated diarylborinic DMAE esters as starting materials. They were obtained by combining appropriate halophenyllithiums with dialkyl phenylboronates followed by a careful hydrolysis (Table 2). The resulting crude borinic acids were subjected to the reaction with DMAE in Et_2O to give respective crystalline esters **13**–**17** only sparingly soluble in this solvent, and thus, easily collected by filtration. The tetrahedral environment of the boron atom in **13**–**17** was clearly evidenced by the ^{11}B NMR spectroscopy showing the resonances in the range 6–8 ppm.

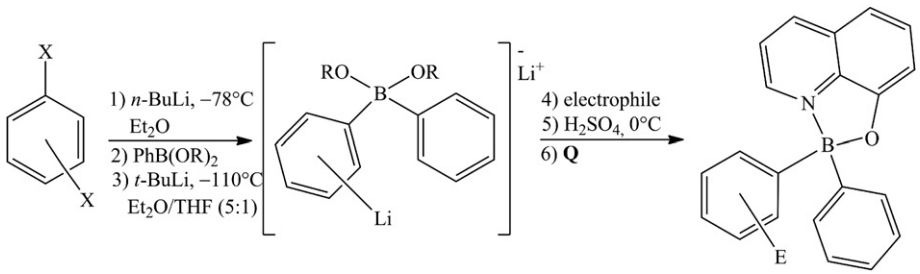
In the next step we performed the halogen–lithium exchange reactions in halogenated azaesters **13**–**17** using *n*-BuLi as well as *t*-BuLi (Scheme 3).

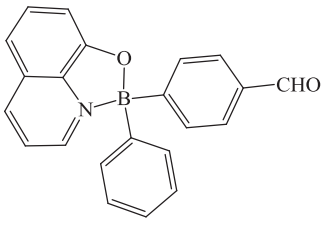
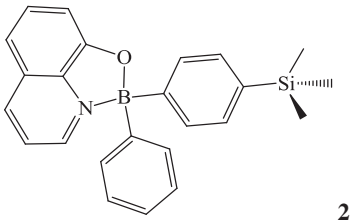
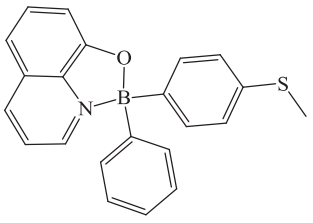
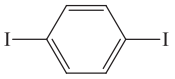
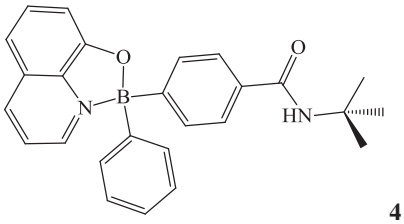
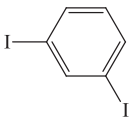
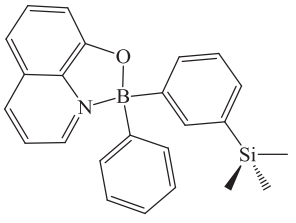
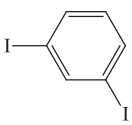
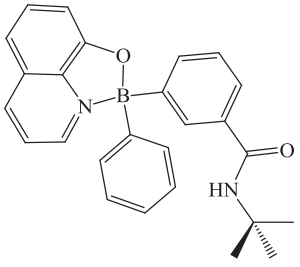
In our first approach we have performed bromine–lithium interconversion reactions involving dibrominated ester **13** in order to generate dilithiated borinic intermediate *en route* to symmetrically difunctionalized borinic esters. Initially, we started with the stoichiometric amount of *n*-BuLi in THF at −90 °C. The low



Scheme 2. Synthesis of functionalized borinic 8-oxyquinolinate **1** *via* lithiated diarylborinic "ate" complex.

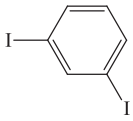
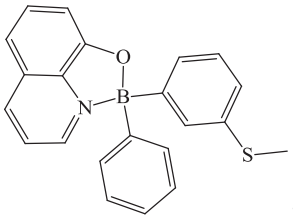
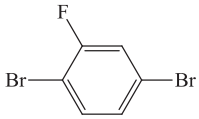
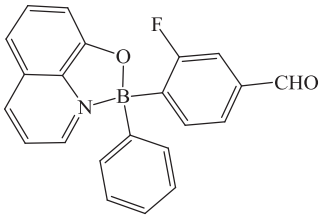
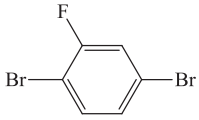
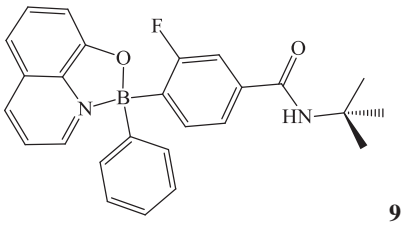
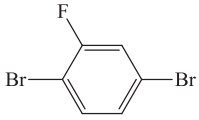
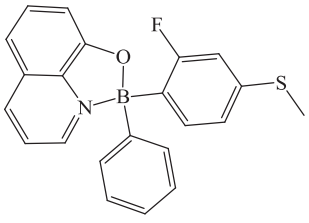
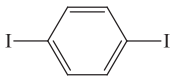
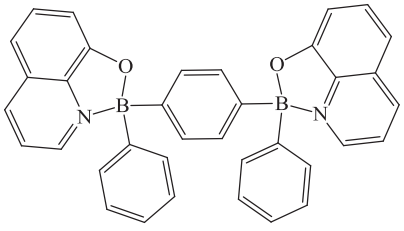
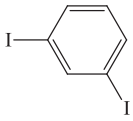
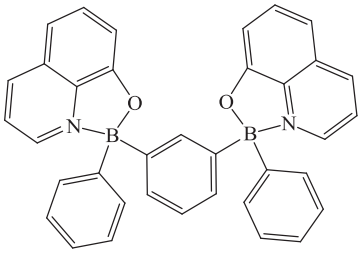
Table 1
Synthesis of borinic **Q**-esters *via* "ate" complex functionalization.



Dihalobenzene	Boron reagent/electrophile	Product	Yield [%]
	$PhB(OEt)_2$ DMF	 **1**	70
	$PhB(OEt)_2$ TMSCl	 **2**	77
	$PhB(OEt)_2$ Me_2S_2	 **3**	75
	$PhB(OEt)_2$ *t*-BuNCO	 **4**	70
	$PhB(OEt)_2$ TMSCl	 **5**	67
	$PhB(OEt)_2$ *t*-BuNCO	 **6**	61

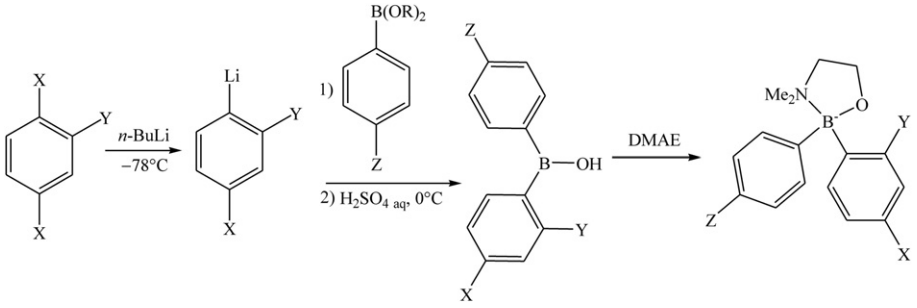
(*continued on next page*)

Table 1 (*continued*)

Dihalobenzene	Boron reagent/electrophile	Product	Yield [%]
	$PhB(OEt)_2$ Me_2S_2	 **7**	76
	$PhB(OEt)_2$ DMF	 **8**	81
	$PhB(OMe)_2$ *t*-BuNCO	 **9**	40
	$PhB(OMe)_2$ Me_2S_2	 **10**	72
	$PhB(OEt)_2$ $PhB(OEt)_2$	 **11**	86
	$PhB(OEt)_2$ $PhB(OEt)_2$	 **12**	80

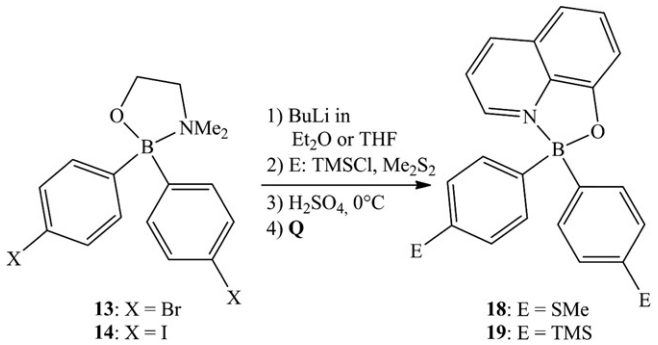
temperature was kept in order to minimize the possibility of the cleavage of the B—N bond. The reaction mixture was quenched with an excess of dimethyl disulfide followed by hydrolysis and addition of **Q**. We have found that the lithiation did not occur at all as the complex of the starting bis(4-bromophenyl)borinic acid with **Q** was isolated. When we repeated procedure at −70 °C the reaction occurred to give the expected disubstituted product **18** in moderate yield (42%). It was contaminated with substantial amounts of impurities such as monosubstituted product and dibrominated ester, which could not be quantitatively removed by recrystallization. A large 2.5-fold excess of *n*-BuLi was not sufficient to complete the Br—Li exchange. When we used the iodo precursor **14** then we

Table 2
Synthesis of halogenated diarylborinic DMAE complexes **13**–**17**.



Product	X	Y	Z	Yield [%]
13	Br	H	Br	78
14	I	H	I	78
15	I	H	Br	75
16	Br	F	H	76
17	I	H	H	80

obtained **18** in a higher yield (ca 60%) when compared with the synthesis starting with **13** but again the product was significantly impure. The use of TMSCl electrophile resulted in the isolation of an impure bis(silylated) derivative **19** in 60% yield. Finally, we tried to generate monolithiated arylborinic azaesters from the corresponding monohalogenated precursors **16** and **17** using a high (5-fold) excess of *n*-BuLi in THF at −70 °C. Again, the Hal/Li exchange reactions were not complete as the crude functionalized products contained *ca.* 10% of halogenated esters. Similar results were obtained with *t*-BuLi as the lithiating agent. Procedures repeated in less polar solvent (Et_2O) gave similar results. There may be a few reasons of the problems encountered in the approach to functionalized borinic derivatives *via* halogen/lithium exchange in the *B*-protected DMAE azaesters. The low solubility of halogenated diarylborinic azaesters at low temperature may be an important case as it can significantly decrease the extent of lithiation. Secondly, our previous results [11] indicated a possible labile character of the dative B—N bond at −78 °C in halogenated arylboronic *N*-alkyldiethanolamine azaesters. In these compounds, the boron atom is susceptible to alkylation with *n*-BuLi and thus, deprotonative lithiation was performed more selectively with weakly nucleophilic lithium amide bases (LDA and LTMP) [12]. Such labile behaviour may also be present in DMAE diarylborinic complexes, resulting in the competitive attack of *n*-BuLi or the carbanionic centre of the generated lithiated diarylborinic complex on the boron atom of the other molecule.



Scheme 3. The approach to diarylborinic **Q** complexes *via* halogen–lithium exchange in the corresponding *N,N*-dimethylethanolamine esters.

2.3. The crystal structure of compound *8*

We have performed single crystal X-ray analysis of compound **8** to additionally confirm the structure of obtained product. Single crystals suitable for structure determination were obtained by slow evaporation of the solution of **8** in CH_2Cl_2. Compound crystallizes in the triclinic *P*−1 space group with one molecule of compound **8** and one molecule of the solvent in the asymmetrical part of the unit cell. The position of the solvent molecule is strongly disordered. The molecular structure of **8** is presented in Fig. 1.

As expected, the intramolecular coordination of the boron atom by **Q**-yl nitrogen atom results in the formation of the central five-membered ring. The tetrahedral geometry of the boron atom is slightly disordered with the THC index of 74% [13]. The most important structural parameters are summarized in Table 3. The supramolecular architecture of **8** is based on C—H···O, C—H···π and π···π interactions. There are two relatively short C—H···O contacts involving both types of oxygen atoms (Fig. 2, Table 4 – intermolecular contacts). One of them connects the H atom in the α position to the **Q**-yl N atom with the formyl O atom. The characteristic

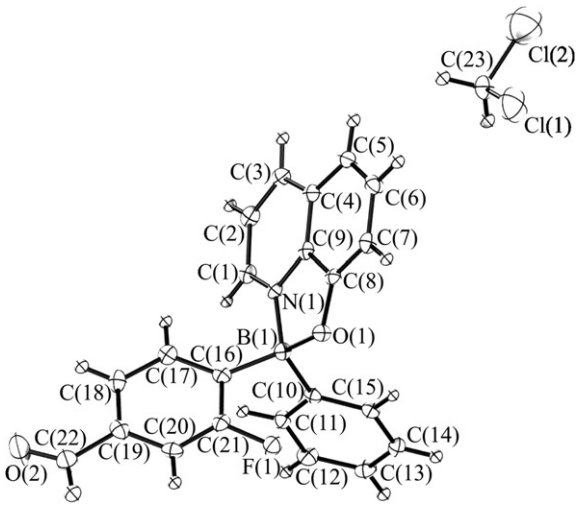


Fig. 1. Ortep-like plot of the solid state structure of **8** showing atom numbering scheme. Displacement ellipsoids were drawn at the 50% level of probability.

Table 3
Selected bond lengths (Å) and angles (°) for **8**.

B(1)–O(1)	1.514(3)	C(16)–B(1)–C(10)	112.0(2)
B(1)–N(1)	1.619(3)	C(10)–B(1)–O(1)	112.7(2)
B(1)–C(16)	1.614(3)	O(1)–B(1)–N(1)	99.3(2)
B(1)–C(10)	1.606(4)	N(1)–B(1)–C(16)	111.3(2)
		C(16)–B(1)–O(1)	112.0(2)
		N(1)–B(1)–C(10)	108.8(2)

Table 4
C–H···O and C–H···π interactions for **8** (in Å and deg.).[a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	D–H···A	Symmetry operator
C(7)–H(7)···O(7)	0.950(3)	2.464(2)	3.409(3)	172.7(2)	$-x, -y, 1-z$
C(1)–H(1)···O(2)	0.950(3)	2.376(3)	3.016(4)	124.4(2)	$-x, 1-y, -z$
C(22)–H(22)···Cg(1)	1.00(3)	2.454	3.410	159.08	$-x, -y, -z$
C(3)–H(3)···Cg(1)	0.949(3)	2.487	3.381	156.74	$1-x, 1-y, 1-z$

[a] Cg(1) is the centroid of the C(10)–C(15) ring.

centrosymmetric dimeric motif occurs due to the interaction between the H atom in the *ortho* position to the **Q**-yl O atom with the **Q**-yl O atom of the adjacent molecule: as a result an eight-membered ring is formed. There is also a set of C–H···π interactions: the shortest ones involve the unsubstituted Ph ring and the formyl H atom from one side as well as the H atom in the γ position to the **Q**-yl N atom from the other side of the aromatic ring.

Two types of π···π stacking motifs are observed in the crystal structure of **8**. The first motif is based on a close assembly of the pyridine rings (symmetry operator: $1-x, 1-y, 1-z$) of two neighboring molecules and the other engages both 8-hydroxyquinoline rings in such a manner that the pyridine ring from one molecule is located near the phenol ring from the other one, and *vice-versa*, the phenol ring from the latter molecule is located near the pyridine ring from the first one (symmetry operator: $-x, 1-y, 1-z$). Vertical distances within the first and second motifs are 3.470 Å and 3.367 Å, respectively.

3. Conclusions

In conclusion, we have evaluated the potential of two different approaches to functionalized diarylborinic acid derivatives. The first one is the simple one-pot protocol which uses readily available starting materials. It is based on the generation of bimetallic lithiated diarylborinic "ate" complexes as a key step. These reagents were successfully treated with electrophiles to produce some hitherto unknown unsymmetrical diarylborinic **Q** complexes, which are not easily accessible by other methods. This includes especially derivatives bearing reactive functionalities such as amide and formyl groups. The alternative approach involved the formation of lithiated diarylborinic DMAE azaesters as reactive intermediates but several attempts indicate that it is less selective resulting in the less satisfactory purity of final products.

4. Experimental section

4.1. General comments

All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. Et_2O and THF were stored over sodium wire before use. Starting materials: diiodobenzenes, 1,4-dibromo-2-fluorobenzene, and other important reagents including *tert*-butyl isocyanate, *N*,*N*-dimethylformamide, dimethyl disulfide, *n*-BuLi (10 M in hexanes), *t*-BuLi (1.7 M in hexanes), $B(OR)_3$ (R = Me, Et) were received from Aldrich and used without further purification. Phenylboronic esters were prepared as described previously [14]. The NMR chemical shifts are given relative to TMS by using known chemical shifts of residual proton (^1H) or carbon (^{13}C) solvent resonances. In the ^{13}C NMR spectra of arylborinic complexes, the resonances of boron-bound carbon atoms were not observed in most cases as a result of broadening owing to partially relaxed $^{13}C-^{11}B$ spin–spin coupling (^{11}B: $I = 3/2$).

4.2. Crystal structure determination of compound *8*

Single crystal X-ray data collection for **8** were performed on a Bruker AXS Kappa APEX II Ultra diffractometer equipped with a TXS rotating anode (Mo–K_α radiation, $\lambda = 0.71073$ Å), Helios multi-layer optics and an Oxford Cryosystems nitrogen gas-flow low temperature device (700 Series Cryostream). Single crystals

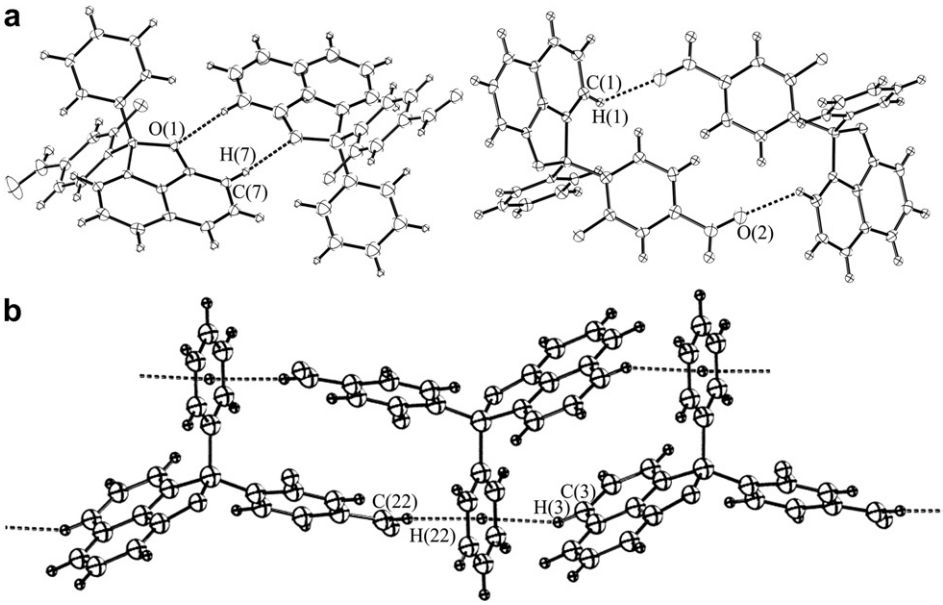


Fig. 2. Crystal packing motifs for **8** based on a) C–H···O; b) C–H···π and π···π interactions. Displacement ellipsoids were drawn at the 50% probability level.

of suitable sizes were attached to a goniometer head using the *Paratone® N* oil (from Hampton Research) and maintained at a constant temperature of 100 K. The data collection strategies were optimized and monitored using the appropriate algorithms implemented by the *APEX2* [15] program package. Only the ω scans were taken into account using 0.5° intervals. Determination of the unit cell parameters and integration of the raw images was performed with the *APEX2* suite of programs (integration was done by *SAINT* [15]). The data set was corrected for Lorentz and polarization effects. The multi-scan absorption correction, scaling and merging of reflections were done with *SADABS* [15].

The structure was solved by direct methods algorithm using *SHELXS* [16]. The IAM refinements, based on F^2, were performed with the *SHELXL* [16] program. In all cases statistical weights were applied. Atomic scattering factors, in their analytical form, were taken from the International Tables for Crystallography [17]. All non-hydrogen atoms were refined anisotropically and most of the hydrogen atoms were placed in idealized positions (with 0.96 Å for C–H bond distances) within the riding model for ADPs (with $U^H_{iso} = 1.2 \cdot U^C_{eq}$). The positions of hydrogen atom were clearly visible on the residual density maps. Positions of the solvent molecules were strongly disordered and the refinement led to *ca.* 0.5:0.5 occupancies. Additional constraints covering ADPs were applied (Table 5).

4.3. Description of syntheses and compound characterization

4.3.1. Syntheses of functionalized diarylborinic 8-oxyquinolates involving lithiated diarylborinic "ate" complexes

*4.3.1.1. B(4-Formylphenyl)(phenyl)**Q* ***(1)***. *n*-BuLi (1 mL, 10 M, 0.01 mol) was added to a stirred suspension of 1,4-diiodobenzene (3.3 g, 0.01 mol) in Et_2O (50 mL) at −78 °C. After 1 h $PhB(OEt)_2$ (1.9 mL, 0.01 mol) was added and mixture was stirred for 1 h. At −110 °C *t*-BuLi (11.8 mL, 1.7 M, 0.02 mol) was added, followed by THF (10 mL). The mixture was allowed to warm up to −75 °C during 1 h followed by dropwise addition of DMF (0.8 mL, 0.01 mol). After 1 h the solvent was removed under vacuum, and the obtained residue was dissolved in Et_2O (50 mL). The mixture was cooled down to −15 °C and hydrolyzed with aq. sulfuric acid (20 mL, 1.5 M). Phases were separated and the organic phase was added to Et_2O (10 mL) solution of **Q** (1.45 g, 0.01 mol). The resulting yellow solution was stirred for 2 h and then concentrated in vacuo. The crude product was obtained by filtration. It was washed with Et_2O (20 mL) to give a green powder. It was dried under vacuum at rt for 24 h. Yield of **1**: 4.8 g (70%), m.p. 146–147 °C ^{1}H NMR (400 MHz, [D_6]DMSO) δ: 9.93 (1H, s, CHO), 9.23 (1H, dd, *J* 5.1 Hz, *J* 0.7 Hz, Q), 8.81 (1H, dd, *J* 8.3 Hz, *J* 0.8 Hz, Q), 7.93 (1H, dd, *J* 8.3 Hz, *J* 5.1 Hz, Ar), 7.76 (2H, m, Ar), 7.72 (1H, t, *J* 8.0 Hz, Ph), 7.64 (2H, d, *J* 8.1 Hz, Ph), 7.45 (1H, d, *J* 8.1 Hz, Ar), 7.34 (2H, m, Ar), 7.23–7.15 (4H, m, Ar); ^{13}C{^{1}H}NMR (100.6 MHz, [D_6]DMSO) δ: 193.3, 157.5, 141.6, 140.3, 136.3, 134.9, 132.4, 131.9, 131.3, 128.5, 128.1, 127.5, 126.8, 124.3, 113.3, 109.0; ^{11}B NMR (64.16 MHz, $CDCl_3$) δ: 12 ($w_{1/2}$ = 1600 Hz). Anal. Calcd. for $C_{22}H_{16}BNO_2$ (337.18): C 78.37, N 4.15, H 4.78%, found C 78.21, N 4.53, H 4.83%.

All other compounds in this section were prepared as described for the preparation of **1**.

*4.3.1.2. B(4-trimethylsilylphenyl)(phenyl)**Q* ***(2)***. Starting materials: 1,4-diiodobenzene (3.3 g, 0.01 mol), $PhB(OEt)_2$ (1.9 mL, 0.01 mol), Me_3SiCl (1.13 mL, 0.01 mol). Yield: 2.95 g (77%), m.p. 201–202 °C ^{1}H NMR (400 MHz, [D_6]DMSO) δ: 9.13 (1H, dd, *J* 5.1 Hz, *J* 0.9 Hz, Q), 8.77 (1H, dd, *J* 8.4 Hz, *J* 0.9 Hz, Q), 8.64–8.50 (1H, m, Ar), 8.24–8.09 (1H, m, Ar), 7.89 (1H, dd, *J* 8.3 Hz, *J* 5.1 Hz, Ph), 7.70 (1H, t, *J* 2.0 Hz, Ph), 7.61–7.49 (1H, m, Ar), 7.68–7.34 (3H, m, Ar), 7.27–7.14 (3H, m, Ar), 7.10–6.55 (2H, m, Ph), 0.18 (9H, s, $SiMe_3$); ^{13}C{^{1}H}NMR (100.6 MHz, [D_6]DMSO) δ: 157.8, 141.3, 140.0, 137.3, 136.4, 136.1, 132.4, 132.2, 131.4, 130.9, 128.0, 127.3, 126.6, 124.2, 112.9, 108.7, −1.04; ^{11}B NMR (64.16 MHz, $CDCl_3$) δ: 10 ($w_{1/2}$ = 1800 Hz). Anal. Calcd. for $C_{24}H_{24}BNOSi$ (283.13): calcd. C 75.59, N 3.67, H 6.34%, found C 75.26, N 3.94, H 6.25%.

*4.3.1.3. B(4-methylthiophenyl)(phenyl)**Q* ***(3)***. Starting materials: 1,4-diiodobenzene (3.3 g, 0.01 mol), $PhB(OEt)_2$ (1.9 mL, 0.01 mol), Me_2S_2 (0.9 mL, 0.01 mol). Yield: 2.67 g (75%), m.p. 162–164 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56 (1H, d, *J* 5.0 Hz, Q), 8.41 (1H, d, *J* 8.3 Hz, Q), 7.69–7.61 (2H, m, Ar), 7.44 (2H, d, *J* 6.4 Hz, Ar), 7.37 (2H, d, *J* 7.6 Hz, Ar), 7.30–7.17 (7H, m, Ar), 2.44 (3H, s, SMe); ^{13}C{^{1}H}NMR (100.6 MHz, [D_6]DMSO) δ: 157.7, 141.3, 140.0, 136.3, 135.9, 132.4, 132.1, 131.4, 128.0, 127.4, 126.6, 125.4, 124.2, 113.0, 108.7, 14.8; ^{11}B NMR (64.2 MHz, [D_6]acetone) δ: 9 ($w_{1/2}$ = 1800 Hz). $C_{22}H_{18}BNOS$ (355.26): C 74.38, N 3.94, H 5.11%, found C 74.31, N 4.18, H 5.07%.

*4.3.1.4. B(4-tert-butylcarbamoylphenyl)(phenyl)**Q* ***(4)***. Starting materials: 1,4-diiodobenzene (3.3 g, 0.01 mol), $PhB(OEt)_2$ (1.9 mL, 0.01 mol), *t*-BuNCO (1.2 mL, 0.01 mol). Yield: 2.88 g (70%), m.p. 208–209 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.14 (1H, *J* 5.0 Hz, Q) 8.55 (1H, d, *J* 8.2 Hz, Q), 7.91 (1H, dd, *J* 8.4 Hz, *J* 5.1 Hz, Ar), 7.71 (1H, t, *J* 8.0 Hz, Ar), 7.61 (2H, d, *J* 8.0, Ph), 7.56 (1H, s, NH), 7.43 (3H, m, Ar), 7.33–7.31 (2H, m, Ar), 7.31–7.14 (4H, m, Ar), 1.33 (9H, s, CMe_3); ^{13}C{^{1}H}NMR (100.6 MHz, [D_6]DMSO) δ: 166.9, 157.7, 141.4, 140.1, 136.3, 134.4, 132.4, 131.4, 130.9, 128.0, 127.4, 126.7, 126.3, 124.2, 113.1, 108.8, 50.6, 28.6; ^{11}B NMR (64.2 MHz, [D_6]acetone) δ: 9 ($w_{1/2}$ = 640 Hz). Anal. Calcd. for $C_{26}H_{25}BN_2O_2$ (408.30): C 76.48, N 6.86, H 6.17%, found C 76.75, N 6.53, H 6.11%.

*4.3.1.5. B(3-trimethylsilylphenyl)(phenyl)**Q* ***(5)***. Starting materials: 1,3-diiodobenzene (3.3 g, 0.01 mol), $PhB(OEt)_2$ (1.9 mL, 0.01 mol), Me_3SiCl (1.3 mL, 0.01 mol). Yield: 2.56 g (67%), m.p. 167–169 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.13 (1H, dd, *J* 5.1, *J* 0.8 Hz, Q), 8.77 (1H, dd, *J* 8.3 Hz, *J* 0.8 Hz, Q), 7.90 (1H, dd, *J* 8.3 Hz, *J* 5.1 Hz, Ar), 7.70 (1H, *J* 7.9 Hz, Ar), 7.55 (1H, s, Ph), 7.42 (1H, d, *J* 8.4 Hz, Ar), 7.39–7.28 (4H, m, Ar), 7.28–7.11 (5H, m, Ph), 0.14 (9H, s, $SiMe_3$); ^{13}C{^{1}H}NMR (100.6 MHz, [D_6]DMSO) δ: 178.8, 157.8, 141.3, 140.0, 137.9, 136.4, 136.1, 136.0, 132.4, 132.1, 131.5, 131.4, 128.0, 127.3, 126.8, 126.6, 124.2, 120.8, 112.9, 108.7, −1.0; ^{11}B NMR (64.2 MHz, $CDCl_3$) δ: 10 ($w_{1/2}$ = 1200 Hz). Anal. Calcd. for $C_{24}H_{24}BNSiO$ (381.35): C 75.59, N 3.67, H 6.34%, found, C 75.40, N 3.84, H 5.98%.

*4.3.1.6. B(3-tert-butylcarbamoylphenyl)(phenyl)**Q* ***(6)***. Starting materials: 1,3-diiodobenzene (3.3 g, 0.01 mol), $PhB(OEt)_2$ (1.9 mL, 0.01 mol), *t*-BuNCO (1.2 mL, 0.01 mol). Yield: 2.50 g (61%), m.p. 168–169 °C ^{1}H NMR (400 MHz, [D_6]DMSO) δ: 9.15 (1H, d, *J* 4.8 Hz, Q) 8.78 (1H, d, *J* 8.0 Hz, Q), 7.91 (1H, dd, *J* 8.4 Hz, *J* 5.2 Hz, Ar), 7.75 (1H, s, Ar), 7.71 (1H, t, *J* 8.0 Hz, Ar), 7.61 (2H, m, Ph), 7.50 (1H, m, Ar), 7.43 (1H,

Table 5
Selected crystal data for compound **8**.

Chemical formula	$C_{45}H_{32}B_2Cl_2F_2N_2O_4$
M_r	795.25
Crystal system, space group	Triclinic, *P*−1
Temperature (K)	100
a, *b*, *c* (Å)	8.1868 (2), 9.2398 (3), 12.9267 (4)
α, β, γ (°)	92.856 (2), 105.140 (2), 96.713 (2)
V (Å^3)	934.12 (5)
Z	1
T_{min}, T_{max}	0.951, 0.977
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19677, 4393, 2993
R_{int}	0.038
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.058, 0.148, 1.22
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.78, −0.91

d, *J* 8.4 Hz Ar), 7.33–7.31 (2H, dd, *J* 8 Hz, *J* 2 Hz, Ar), 7.27–7.10(5H, m, Ar), 1.32 (9H, s, CMe_3); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ: 167.3, 157.7, 147.2, 141.4, 140.1, 136.4, 134.9, 134.0, 132.4, 131.4, 130.4, 128.1, 127.4, 126.9, 124.6, 125.5, 124.2, 50.6, 28.6; ^{11}B NMR (64.2 MHz, [D_6]DMSO) δ: 11 ($w_{1/2} = 1900$ Hz). Anal. Calcd. for $C_{26}H_{25}BN_2O_2$ (408.30): C 76.48, N 6.86, H 6.17%, found C 76.45, N 6.79, H 6.15%.

*4.3.1.7. B(3-methylthiophenyl)(phenyl)**Q*** ***(7)***. Starting materials: 1,3-diiodobenzene (3.3 g, 0.01 mol), $PhB(OEt)_2$ (1.9 mL, 0.01 mol), Me_2S_2 (0.9 mL, 0.01 mol). Yield: 2.71 g (76%), m.p. 142–143 °C.

^1H NMR (400 MHz, [D_6]DMSO) δ: 9.16 (1H, d, *J* 5.1 Hz, Q), 8.77 (1H, d, *J* 8.0 Hz, Q), 7.90 (1H, dd, *J* 8.3 Hz, *J* 5.1 Hz, Ar), 7.70 (1H, t, *J* 8.0 Hz, Ar), 7.42 (1H, d, *J* 8.4 Hz, Ar),7.37–34 (2H, m, Ar), 7.24–7.16 (7H, m, Ar), 7.09–7.06 (1H, m, Ar), 2.36 (3H, s, SMe); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ: 157.7, 141.5, 140.1, 136.6, 136.3, 132.4, 131.8, 129.4, 128.2, 128.0, 127.4, 127.3, 126.6, 124.3, 124.2, 113.1, 108.8, 14.8; ^{11}B NMR (64.2 MHz, [D_6]DMSO) δ: 10 ($w_{1/2} = 1200$ Hz). $C_{22}H_{18}BNOS$ (355.26): C 74.38, N 3.94, H 5.11%, found C 74.11, N 3.59, H 5.10%.

*4.3.1.8. B(2-fluoro-4-formylphenyl)(phenyl)**Q*** ***(8)***. Starting materials: 1,4-dibromo-2-fluorobenzene (2.54 g, 0.01 mol), $PhB(OEt)_2$ (1.5 mL, 0.01 mol), DMF (0.8 mL, 0.01 mol). Yield: 2.87 g (81%), m.p. 158–160 °C ^1H NMR (400 MHz, [D_6]DMSO) δ: 9.93 (1H, s, CHO), 9.11 (1H, d, *J* 4.8 Hz, Q), 8.82 (1H, dd, *J* 8.6 Hz, *J* 0.8 Hz, Q), 7.94 (1H, dd, *J* 8.3 Hz, *J* 5.2 Hz, Ar), 7.71 (1H, t, *J* 8.0 Hz, Ar), 7.66–7.64 (1H, m, Ar), 7.60–7.57 (1H, m, Ar), 7.47–7.45 (2H, m, Ar), 7.32 (2H, dd, *J* 7.9 Hz, *J* 1.6 Hz, Ar), 7.27–7.14 (4H, m, Ar); $^{13}C\{^1H\}$ NMR (100.6 MHz, [D_6]DMSO) δ: 192.3, 165.8 (d, *J* 242 Hz), 157.3, 142.3 (d, *J* 6 Hz), 140.6, 137.7 (d, *J* 7 Hz), 136.5, 135.3 (d, *J* 11 Hz), 132.3, 131.0, 128.0, 127.6, 127.0, 125.1 (d, *J* 2 Hz), 124.4, 114.7 (d, *J* 26 Hz), 113.5, 109.1; ^{11}B NMR (64.2 MHz, [D_6]DMSO) δ: 12. Anal. Calcd. for $C_{22}H_{15}BFNO_2$ (355.17): C 74.40, N 3.94, H 4.26%, found C 73.95, N 3.87, H 4.65%.

*4.3.1.9. B(2-fluoro-4-tert-butylcarbamoylphenyl)(phenyl)**Q*** ***(9)***. Starting materials: 1,4-dibromo-2-fluorobenzene (2.54 g, 0.01 mol), $PhB(OMe)_2$ (1.5 mL, 0.01 mol), *t*-BuNCO (1.2 mL, 0.01 mol). Yield: 1.7 g (40%), m.p. 183–185 °C ^1H NMR (400 MHz, [D_6]DMSO) δ: 9.04 (1H, d, *J* 5.2 Hz, Q), 8.81 (1H, dd, *J* 8.4 Hz, *J* 0.9 Hz, Q), 7.93 (1H, dd, *J* 8.34 Hz, *J* 5.2 Hz, Ar), 7.79–7.64 (2H, m, Ar), 7.57–7.42 (2H, m, Ar), 7.42–7.34 (2H, m, Ar), 7.34–7.27 (2H, m, Ar), 7.13–6.99 (3H, m, Ar), 1.33 (9H, s, *t*-Bu); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ: 165.4, 165.2 (d, *J* 237 Hz), 157.4, 148.2, 142.0 (d, *J* 7 Hz), 140.4, 137.3 (d, *J* 7 Hz), 136.5, 134.1 (d, *J* 11 Hz), 132.4, 131.1, 128.0, 127.4, 126.8, 124.3, 122.5 (d, *J* 2 Hz), 113.6 (d, *J* 28 Hz), 113.3, 108.9, 50.8, 28.5; ^{11}B NMR (64.2 MHz, [D_6]DMSO) δ: 10 ($w_{1/2}$ = 1800 Hz). Anal. Calcd. for $C_{26}H_{24}BFN_2O_2$ (426.29): calcd. C 73.25, N 6.57, H 5.67%, found C 72.92, N 6.38, H 5.78%.

*4.3.1.10. B(2-fluoro-4-methylthiophenyl)(phenyl)**Q*** ***(10)***. Starting materials: 1,4-dibromo-2-fluorobenzene (2.54 g, 0.01 mol), $PhB(OMe)_2$ (1.5 mL, 0.01 mol), Me_2S_2 (0.9 mL, 0.01 mol). Yield: 2.69 g (72%), m.p. 164–166 °C ^1H NMR (400 MHz, [D_6]DMSO) δ: 9.03 (1H, d, *J* 5.1 Hz, Q), 8.78 (1H, dd, *J* 8.4 Hz, *J* 0.8 Hz, Q), 7.90 (1H, dd, *J* 8.3 Hz, *J* 5.1 Hz, Ar), 7.69 (1H, t, *J* 7.9 Hz, Ar), 7.42 (1H, d, *J* 7.9 Hz, Ar), 7.33 (2H, dd, *J* 7.9 Hz, *J* 1.5 Hz, Ar), 7.24–7.14 (5H, m, Ar), 6.96 (1H, dd, *J* 7.9 Hz, *J* 1.7 Hz, Ar), 6.86 (1H, dd, *J* 10.0 Hz, *J* 1.7 Hz, Ar), 2.42 (3H, s, SMe); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ: 166.0 (d, *J* 242 Hz), 157.5, 141.8 (d, *J* 6 Hz), 140.2, 139.5 (d, *J* 9 Hz), 136.5, 135.0 (d, *J* 12 Hz), 132.3, 131.1, 127.9, 127.4, 126.7, 124.2, 121.1 (d, *J* 2 Hz), 113.2, 112.0 (d, *J* 28 Hz), 108.8, 14.5; ^{11}B NMR (64.2 MHz, [D_6]DMSO) δ: 12 ($w_{1/2} = 1400$ Hz). Anal. Calcd. for $C_{22}H_{17}BFONS$ (373.25): C 70.79, H 4.59, N 3.75%, found C 70.62, H 4.75, N 3.83%.

*4.3.1.11. 1,4-Bis[B(phenyl)**Q**]benzene (**11**).* Starting materials: 1,4-diiodobenzene (3.3 g, 0.01 mol), $PhB(OEt)_2$ (3.8 mL, 0.02 mol). Yield: 4.66 g (86%), m.p. 365–366 °C. MS (Photospray, $CH_3COOC_2H_5$): *m*/*z*: Calcd. $C_{36}H_{27}B_2N_2O_2$ ($MH^{\pm}$, 541.2), $C_{30}H_{21}B_2N_2O_2$ (463.2), $C_{24}H_{17}B_2N_2O_2$ (387.1), $C_{15}H_{11}BNO$ (232.1); found: 541.3, 463.4, 387.6, 232.2. Anal. Calcd. for $C_{36}H_{26}B_2N_2O_2$ (540.22): C 80.04, H 4.85, N 5.19%, found C 80.32, H 4.83, N 5.12%.

*4.3.1.12. 1,3-Bis[B(phenyl)**Q**]benzene (**12**).* Starting materials: 1,3-diiodobenzene (3.3 g, 0.01 mol), $PhB(OEt)_2$ (3.8 mL, 0.02 mol). Yield: 4.32 g (80%), m.p. 149–150 °C. MS (Photospray, $CH_3COOC_2H_5$): *m*/*z*: Calcd. $C_{36}H_{27}B_2N_2O_2$ ($MH^{\pm}$, 541.2), $C_{30}H_{21}B_2N_2O_2$ (463.2), $C_{24}H_{17}B_2N_2O_2$ (387.1), $C_{15}H_{11}BNO$ (232.1); found. 541.5, 463.4, 387.5, 232.2 Anal. Calcd. for $C_{36}H_{26}B_2N_2O_2$ (540.22): C 80.04, H 4.85, N 5.19%, found C 79.95, H 4.80, N 5.17%.

4.3.2. Synthesis of halogenated diarylborinic DMAE azaesters

*4.3.2.1. B(4-bromophenyl)$_2$(N,N-dimethylethanolamine) (**13**).* *n*-BuLi (5 mL, 10 M, 0.05 mol) was added dropwise to a stirred suspension of 1,4-dibromobenzene (11.8 g, 0.05 mol) in Et_2O (50 mL) at −70 °C. The mixture was stirred for 1 h followed by a dropwise addition of dimethyl 4-bromophenylboronate (11.5 g, 0.05 mol). The mixture was stirred for 1 h at −70 °C and then warmed up to 0 °C. After addition of aq. H_2SO_4 (15 mL, 1.5 M) the organic phase was separated. The aqueous phase was extracted with Et_2O (2 × 15 mL) and the extract was combined with the organic phase. DMAE (4.45 g, 0.05 mol) was added to the organic phase to give a white slurry. It was stirred at rt for 6 h and filtered. The product was washed with Et_2O and dried under vacuum at rt for 24 h. Yield 15.9 g (78%), m.p. 164–165 °C ^1H NMR (400 MHz, [D_6]DMSO) δ: 7.56 (4H, d, *J* 8.0 Hz, Ph), 7.34 (4H d, *J* 8.0 Hz, Ph), 4.07 (2H, s, br, CH_2), 2.93 (2H, m, CH_2), 2.49 (6H, s, NMe_2); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ: 134.5. 129.6, 119.5, 60.1, 46.6, 39.5; ^{11}B NMR (64.16 MHz, [D_6]DMSO) δ: 10 ($w_{1/2}$ = 960 Hz). Anal. Calcd. for $C_{16}H_{18}BBr_2NO$ (410.94): C 46.76, N 3.41, H 4.41%. Found: C 46.64, N 3.45 H, 4.40%.

*4.3.2.2. B(4-iodophenyl)$_2$(N,N-dimethylethanolamine) (**14**).* The synthesis was performed as described for **1** starting with 1,4-diiodobenzene (16.5 g, 0.05 mol) and dimethyl 4-iodophenylboronate (13.8 g, 0.05 mol). Yield: 19.6 g (78%), m.p. 202–203 °C ^1H NMR (400 MHz, [D_6]DMSO) δ: 7.52 (4H, d, *J* 8.4 Hz, Ph), 7.41 (4H, d, *J* 8.0 Hz, Ph), 4.05 (2H, t, *J* 6.8 Hz, CH_2), 2.92 (2H, t, *J* 6.8 Hz, CH_2), 2.49 (6H, s, NMe_2); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ: 135.5, 134.7, 92.4, 60.1, 46.6, 39.5; ^{11}B NMR (64.16 MHz, [D_6]DMSO) δ: 9 ($w_{1/2}$ = 640 Hz). Anal. Calcd. for $C_{16}H_{18}BI_2NO$ (504.94): C 38.06, N 2.77, H 3.59%, found: C 38.04, N 2.71, H 3.50%.

*4.3.2.3. B(4-bromophenyl)(4-iodophenyl)(N,N-dimethylethanolamine) (**15**).* The synthesis was performed as described for **1** starting with 1,4-diiodobenzene (16.5 g, 0.05 mol) and dimethyl 4-bromophenylboronate (11.4 g, 0.05 mol). Yield: 17.1 g (75%), m.p. 179–181 °C ^1H NMR (400 MHz, [D_6]DMSO) δ: 7.55 (4H, m, Ph), 7.42 (2H, d, *J* 7.2 Hz, Ph), 7.34 (2H, d, *J* 8.0 Hz, Ph), 4.06 (2H, s, br, CH_2), 2.92 (2H, s, br, CH_2), 2.49 (6H, s, NMe_2); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ: 135.5, 134.7, 134.5, 129.6, 119.5, 92.4, 39.5; ^{11}B NMR (64.16 MHz, [D_6]DMSO) δ: 6 ($w_{1/2}$ = 1200 Hz). Anal. Calcd. for $C_{16}H_{18}BBrINO$ (457.94): C 41.96, N 3.06, H 3.96%, found: C 41.64, N 2.71, H 3.59%.

*4.3.2.4. B(4-bromo-2-fluorophenyl)(phenyl)(N,N-dimethylethanolamine) (**16**).* The synthesis was performed as described for **1** starting with 1,4-dibromo-2-fluorobenzene (15.1 g, 0.05 mol) and dimethyl phenylboronate (7.5 g, 0.05 mol). Yield: 13.2 g (76%), m.p. 194–196 °C ^1H NMR (400 MHz, [D_6]DMSO) δ: 7.61 (2H, dd, *J* 8.4 Hz, *J* 1.6 Hz, Ph), 7.52 (2H, d, *J* 8.0, Ph), 7.45 (2H, d, *J* 7.5, Ph), 7.17 (2H, d, *J* 7.2 Hz, Ph), 7.08

(1H, t, *J* 7.2 Hz, Ph), 4.08 (2H, t, *J* 6.4 Hz, CH_2), 2.92 (2H, t, *J* 6.4 Hz, CH_2), 2.48 (6H, s, NMe_2); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ :163.7 (d, *J* 241 Hz), 137.2 (d, *J* 14 Hz), 132.4, 126.8, 126.7, 119.3, 117.5, 60.5, 39.5; ^{11}B NMR (64.2 MHz, [D_6]DMSO) δ: 7 ($w_{1/2}$ = 1400 Hz). Anal. Calcd. for $C_{16}H_{18}BBrFNO$ (350.03): C 54.90, N 4.00, H 5.18%, found: C 54.55, N 3.69, H 4.99%.

*4.3.2.5. B(4-iodophenyl)(phenyl)(N,N-dimethylethanolamine) (**17**).* The synthesis was performed as described for **1** starting with bromobenzene (7.85 g, 0.05 mol) and dimethyl 4-bromophenylboronate (11.4 g, 0.05 mol). Yield: 15.1 g (80%), m.p. 165–166 °C ^1H NMR (400 MHz, [D_6]DMSO) δ: 7.61 (2H, dd, *J* 8.4 Hz, *J* 1.6 Hz, Ph), 7.52 (2H, d, *J* 8.1 Hz, Ph), 7.45 (2H, d, *J* 7.6 Hz, Ph), 7.17 (2H, d, *J* 7.2 Hz, Ph), 7.08 (1H, t, *J* 7.2 Hz), 4.08 (2H, t, *J* 6.4 Hz, CH_2), 2.92 (2H, t, *J* 6.4 Hz, CH_2), 2.49 (6H, s, NMe_2); $^{13}C\{^1H\}$NMR (100.6 MHz, [D_6]DMSO) δ: 135.5, 134.9, 132.2, 126.9, 125.6, 92.2, 39.5; ^{11}B NMR (64.2 MHz, [D_6]DMSO) δ: 7 ($w_{1/2}$ = 1200 Hz). Anal. Calcd. for $C_{16}H_{19}BINO$ (379.04): C 50.70, N 3.70, H 5.05%, found: C 50.45, N 3.67, H 4.79%.

4.3.3. Syntheses of functionalized diarylborinic 8-oxyquinolates via halogen/Li exchange in halogenated diarylborinic DMAE azaesters

*4.3.3.1. B(4-(methylthio)phenyl)$_2$**Q** **(18).*** Compound **13** (1.23 g, 3.0 mmol) was dissolved in 50 mL of THF and cooled to −78 °C followed by dropwise addition of *n*-BuLi (1.5 mL, 10 M, 15 mmol). The mixture was stirred for 1 h at −75 °C, followed by dropwise addition of Me_2S_2 (1.50 g, 16 mmol). After 1 h the mixture was warmed up to 0 °C. The solvent was removed under vacuum. The residue was dissolved in 50 mL of Et_2O and the solution was cooled to −20 °C followed by hydrolysis with aq. H_2SO_4 (6 mL, 1.5 M). The aqueous phase was extracted with Et_2O (2 × 15 mL) and the extract was combined with the organic phase. **Q** was added (0.44 g, 3.0 mmol) to the organic phase. The resulting yellow solution was stirred at rt for 2 h and concentrated in vacuo. The crude product was obtained by filtration. It was washed with dichloromethane (5 mL) and dried in vacuo at rt for 24 h. Yield: 0.51 g (42%). ^1H NMR (400 MHz, [D_6]DMSO) δ: 9.11 (1H, d, *J* 5.2 Hz, Q), 8.78 (1H, d, *J* 7.6 Hz, Q), 7.90 (1H, dd, *J* 8.1 Hz, *J* 5.2 Hz, Ar), 7.70 (1H, t, *J* 8.2 Hz, Ph), 7.43 (1H, d, *J* 8.0 Hz, Ar), 7.40 (1H, d, *J* 8.4 Hz, Ar), 7.27 (4H, m, Ar), 7.18 (2H, d, *J* 8.4 Hz, Ph), 7.12 (2H, d, *J* 8.4 Hz, Ph), 2.40 (6H, s, SMe); ^{11}B NMR (64.2 MHz, $CDCl_3$) δ: 11 ($w_{1/2}$ = 1200 Hz).

*4.3.3.2. B(4-(trimethylsilyl)phenyl)$_2$**Q** **(19).*** The synthesis was performed as described for **18** with azaester **14** and TMSCl as electrophile (1.9 mL, 0.015 mol). Yield: 0.81 g (60%). ^1H NMR (400 MHz, [D_6]DMSO) δ: 9.13 (1H, d, *J* 6.8 Hz, Q), 8.77 (1H, d, *J* 7.8 Hz, Q), 7.89 (1H, dd, *J* 6.8 Hz, *J* 4.8 Hz, Ar), 7.70 (1H, t, *J* 8.0 Hz, Ar), 7.42 (1H, d, *J* 8.4 Hz, Ar), 7.36–7.05 (8H, m, Ar), 7.17 (1H, d, *J* 7.6 Hz, Ar), 0.18 (18H, s, $SiMe_3$); ^{11}B NMR (64.2 MHz, [D_6]DMSO) δ: 9 ($w_{1/2}$ = 1800 Hz).

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Appendix A. Supplementary material

CCDC 856215 (**8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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