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Chelated Boronate–Imine and Boronate–Amine Complexes as Chiral Dopants for Nematic Liquid Crystals

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Enantiomerically and diastereomerically pure chelated boronate–imine complexes **5** and a library of boronate–amine complexes **8** have been synthesized by taking advantage of a modular concept based on aromatic aldehydes, aminoethanols and boronic acids. The configuration of the amine complexes **8** featuring stable stereogenic boron and nitrogen centers are assigned based upon crystal structure analyses of the representative compounds **8aaa** and **8acj** and the comparison of the CD spectra of all complexes **8**. They serve as colorless, stable dopants for nematic liquid crystals and provide high helical twisting power. The interaction of boronates **8** with nematic compounds ZLI-1840 and 5-CB featuring a benzonitrile moiety is studied by ^{19}F and ^{1}H NMR spectroscopy. A strong π-stacking between the arylboronate residue and the nematic compound as well as a hydrogen bond are indicated by the spectroscopic data. Based thereupon, a model is proposed that correlates the configuration of the dopant with the sign of the helix formed by twisting the nematic phase.

Introduction

Among the various liquid-crystalline compounds, the cholesteric or chiral nematic phase meets particular interest due to its manifold applications in displays, polarizers, certain polymers and paints and as color-effect materials.[1] The cholesteric phase is essentially a twisted nematic phase with a nematic arrangement in each individual layer, wherein the molecules are aligned along a common direction, the so called director. From one layer to the next, the director rotates about a certain angle, thus creating a helical arrangement.[2] The most elegant way to produce a cholesteric phase was discovered more than 80 years ago by the French physicist G. Friedel[3] who found that the addition of a small amount of a chiral, nonracemic compound, a dopant, to a nematic liquid crystal converts it into a cholesteric phase (Figure 1).[1d] Later, the phenomenon was carefully studied by the research groups of Buckingham, Stegemeyer, and Baesseler.[4] As shown by Stegemeyer and Mainusch,[4c] an enantiomerically pure compound that, itself, does not form a mesophase is nevertheless able to function as a dopant and thus introduce a helical structure in a nematic phase. Chiral doping can even serve for the determination of the absolute configuration and the enantiomeric purity of dopants.[2c]

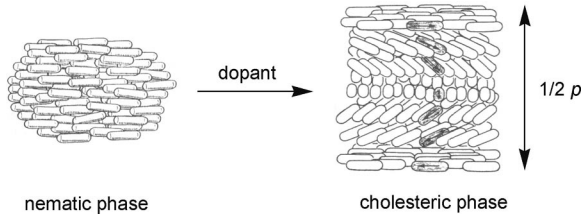

Figure 1. Conversion of a nematic phase into a cholesteric phase by the addition of a dopant.[1d]

A measure of the efficiency of a chiral dopant is the so-called helical twisting power (HTP). It is defined for small concentrations of the dopant according to Equation (1). Therein, p is the pitch of the induced helix, and x is the molar fraction of the dopant, dissolved in the nematic phase. Given the HTP of an individual dopant, the appropriate ratio of the dopant to the nematic liquid-crystalline compound provides a hight of the pitch that is in the range of the wavelength of visible light. This property is desirable for most applications. In general, one aims at a high HTP value, so that the smallest amount possible of the valuable dopant has to be used.

$$HTP = \lim_{x \to 0} \frac{1}{p \cdot x} \quad (1)$$

In the beginning, readily available natural products were used as dopants, mainly terpenes and steroids, and derivatives thereof.[4c] Among the numerous synthetic compounds used as dopants later, biphenyls,[5a] binaphthol-derived esters[5b] and, in particular, TADDOLs[6] displayed remark-

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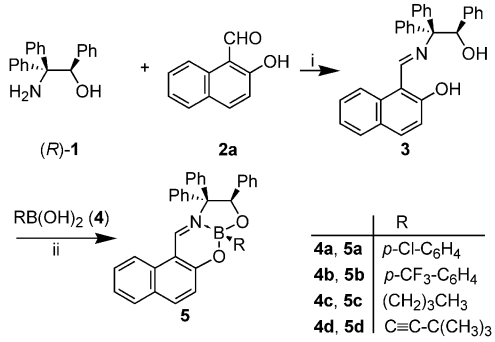
ably high values of helical twisting power. Metal complexes featuring a stereogenic metal center in addition to chiral ligands seem to open an entry to a large variety of chiral dopants due to the manifold combinations of different ligands and central atoms. This concept has been realized by using tris(dionato)metal complexes of chromium, cobalt, rhodium and ruthenium[7a,7b] as well as binaphthol-derived titanium complexes.[7c] The fact that bis(chelated) alkoxy(imine)titanium complexes developed by us[7d–7f] and, more recently, tetrapyrrol-derived zinc complexes[7g] gave the so far highest HTP values (up to 740 μm^{-1} and 920 μm^{-1}, respectively) may illustrate the efficiency of metal-containing dopants. The disadvantages, which will hamper their application, are not only the toxicity of the transition metals but even more the fact that most of them are colored, partly due to the ligand, partly due to the metal ion according to its oxidation stage. We were interested whether the environmentally benign and safe half-metal boron will be a suitable central atom in chelate complexes. Having recently observed[8] that boron functions as a configurationally stable stereogenic center in boronate–imine complexes, we show here that diastereomerically and enantiomerically pure boronate–amine complexes are readily accessible. For the first time colorless, air- and moisture-stable boronate–amine complexes are demonstrated to serve as chiral dopants with significant helical twisting power.

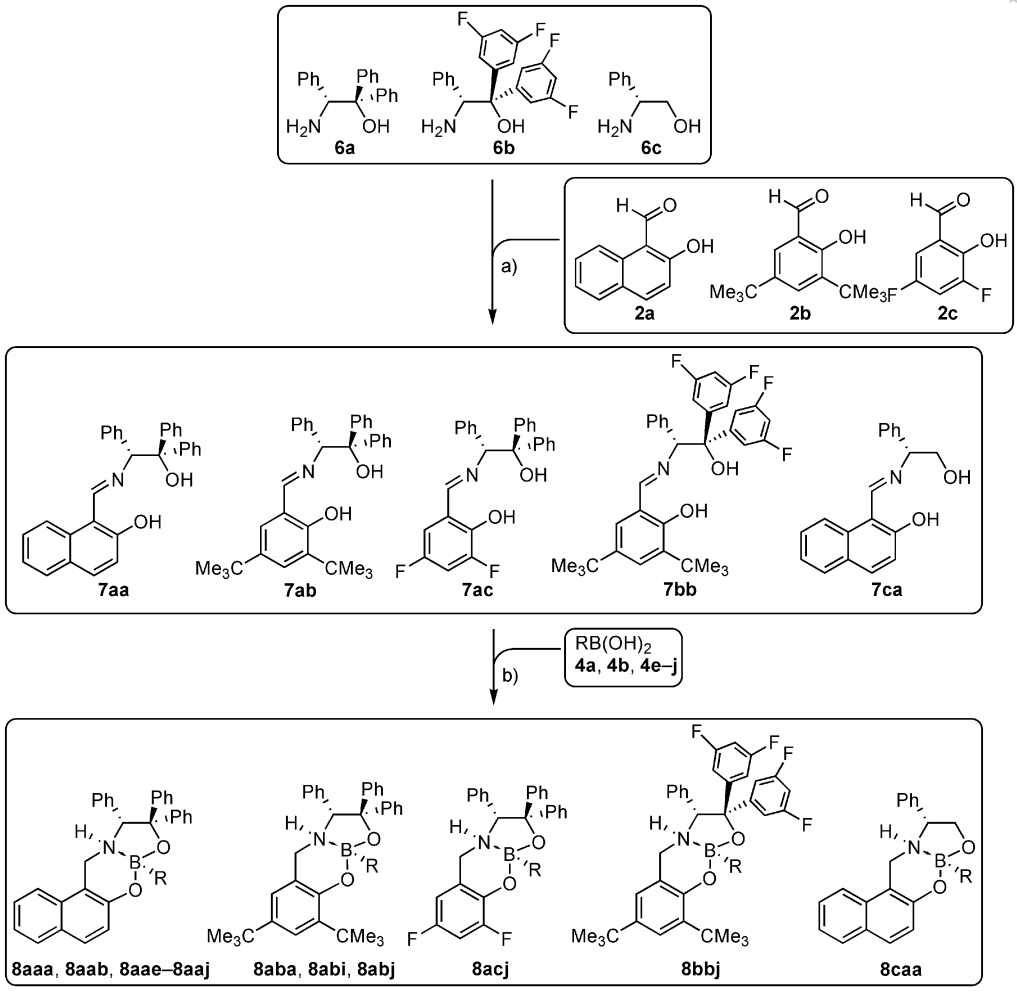
Results and Discussion

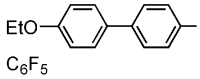
The novel boronate–imine complexes[8] and boronate–amine complexes were obtained by modular syntheses, combining a chiral 2-aminoethanol with 2-hydroxy-1-naphthaldehyde or aromatic *ortho*-hydroxy aldehydes as the second component and a boronic acid as the third one. Based on this concept, a variety of boronate complexes with a substantial diversity became available. (*R*)-2-Amino-1,2,2-triphenylethanol (**1**), readily accessible from methyl mandelate,[9] was chosen as the starting material for the synthesis of boronate–imine complexes **5**. As illustrated in Scheme 1, the amino alcohol **1** was treated with 2-hydroxy-1-naphthaldehyde (**2a**) to give the imine **3** whose condensation with boronic acids **4a**–**d** was easily accomplished by heating a solution in toluene in the presence of molecular sieves. Thereby, boron is expected to become a stereogenic center in the imine complexes **5a**–**d**, and the question of diastereoselectivity and configurational stability arises. The role of boron as a stereogenic center has been studied occasionally[8,10] in acyclic and cyclic complexes, and the barrier of inversion was determined in enantiomeric acyloxyboranes[10g–10i] and boronate–imine complexes.[8,10j] Remarkably, all the complexes **5a**–**d** were obtained in a completely diastereoselective manner. The formation of a single diastereomer is clearly demonstrated by NMR spectroscopy. In particular, the ^{11}B NMR spectra of the individual complexes display a single resonance (see Exp. Sect.) in the shift range that is typical for tetracoordinated boron.[11] The crystal structure of the representative compound **5a** revealed the relative configuration and allows to assign the (R_C,R_B) configuration to the complex **5a**.[8] The boron–nitrogen distance of 1.588 Å confirms the existence of a coordinative bond. The CD spectra and the accordance of the Cotton effects for all the complexes **5a**–**d** demonstrate the homochirality at the boron atom and makes it plausible to consider the complexes **5b**–**d** as the (R_C,R_B) stereoisomers as well.



Scheme 1. Synthesis of boronate–imine complexes **5a**–**d**. Reagents and conditions: (i) methanol/THF (1:1), Na_2SO_4, reflux 12 h, 55%; (ii) molecular sieves (3 Å), toluene, reflux 12 h, 54% (**5a**), 44% (**5b**), 86% (**5c**), 92% (**5d**).

The bright yellow color of the boronate–imine complexes **5** is a clear disadvantage with respect to their application as chiral dopants, in particular if they are intended to serve as effect colors.[1e] Therefore, we replaced the imine by colorless amine ligands and designed enantiomerically and diastereomerically pure boronate–amine complexes. The synthesis shown in Scheme 2 uses the same type of building blocks, but involves as an additional step the reduction of the imine to the amine moiety. The amino alcohols (*R*)-**6a**–**c** with a stereogenic center adjacent to the amino group served as the starting materials. Aminotriphenylethanol **6a**[12] and the amino alcohol **6b** featuring geminal *meta*-difluorophenyl substituents are readily available from (*R*)-phenylglycine, whereas 2-amino-2-phenylethanol (**6c**) is a commercial product. They were condensed with the aldehydes **2a**–**c** to give the imines **7aa**–**7ca**. In order to avoid any racemization that could occur due to an imine/enamine tautomerism, the reaction was run at low temperature (–15 °C for 72 h).[13] Upon reduction with sodium cyanoborohydride,[14] the corresponding amines were isolated as their hydrochlorides, which turned out to decompose when stored for a longer time. Therefore, they were converted immediately by treatment with boronic acids **4a**, **4b**, and **4e**–**j** in the presence of sodium hydrogen carbonate that served to liberate in situ the amine from the hydrochloride. The yields of the products **8** over two steps varied considerably, but were fair in most cases. The novel boronate–amine complexes were found to be air- and moisture-stable compounds. Their ^{11}B resonances again indicate the existence of *tetra*-coordinated boron compounds[11] (see Exp. Sect.). Aside from the boron atom, the amine nitrogen atom becomes a stereogenic center during the formation of the chelate. Here again, the condensation was found to be com-



	R
4a, **8aaa**, **8aba**, **8caa**	4-Cl-C_6H_4
4b, **8aab**	4-CF_3-C_6H_4
4e, **8aae**	C_6H_5
4f, **8aaf**	4-NC-C_6H_4
4g, **8aag**	4-Me_3Si-C_6H_4
4h, **8aah**	
4i, **8aai**, **8abi**	
4j, **8aaj**, **8abj**, **8acj**, **8bbj**	C_6F_5

Scheme 2. Synthesis of a library of boronate–amine complexes **8**. Reagents and conditions: (a) methanol/THF (1:1), Na_2SO_4, –15 °C, 72 h, 93% (**7aa**), 88% (**7ab**), 30% (**7ac**), 69% (**7bb**), 61% (**7ca**); (b) (i) $NaCNBH_3$, methanol, 25 °C, then dilute HCl, (ii) toluene, $NaHCO_3$, reflux, 4 h, 46% (**8aaa**), 65% (**8aab**), 33% (**8aae**), 41% (**8aaf**), 90% (**8aag**), 13% (**8aah**), 38% (**8aai**), 55% (**8aaj**), 63% (**8aba**), 45% (**8abi**), 54% (**8abj**), 50% (**8acj**), 64% (**8bbj**), 37% (**8caa**).

pletely diastereoselective. The ^1H, ^{13}C, and ^{11}B NMR spectra clearly show that a single diastereomer has formed, and even traces of epimers could not be detected.

The question of the configurations at the stereogenic boron and nitrogen atoms is answered by crystal structure analyses of the representative compounds **8aaa** and **8acj** shown in Figures 2 and 3. In both compounds, the junction of the fused five- and six-membered ring is *cis*, thus minimizing the strain. The nitrogen and boron atoms are found to be pyramidal, and the (R_B,R_C,S_N) configuration is assigned to the complex **8aaa**, whereas complex **8acj** adopts the (S_B,R_C,S_N) configuration. Nevertheless, both complexes are homochiral, and the alternative configuration at the stereogenic boron atoms is a formal one, due to the change of priorities according to the Cahn–Ingold–Prelog rules.[15] At a glance, the heterochirality at the boron atom in the imine complex **5a** on the one hand and the amine complexes **8aaa** and **8acj** on the other hand might be surprising, in view of the identical configuration of the chiral backbone. One should be aware, however, that the amino alcohols (*R*)-**1** and (*R*)-**6a** are regioisomers. In all the three complexes **5a**, **8aaa**, and **8acj**, the aryl substituent at the boron atom and

the phenyl group at the stereogenic center of the amino alcohol moiety are *cis*-configured. In the crystal of compound **8aaa**, one molecule of methanol is included due to the medium used for the crystallization. As shown in Figure 2, the alcohol is bound to the nitrogen atom by a hydrogen bond, wherein the NH group is the hydrogen donor rather than the OH group. This observation can be interpreted as a consequence of the enhanced acidity of the amine hydrogen atom due to the complexation with the boron atom. In both boronate–amine complexes **8aaa** and **8acj**, the heterocyclic six-membered ring adopts a chair-like configuration, presumably to avoid steric congestion caused by the accumulation of aryl residues. The configurations of the other boronate–amine complexes were again assigned by the accordance of their Cotton effects in the CD spectra.

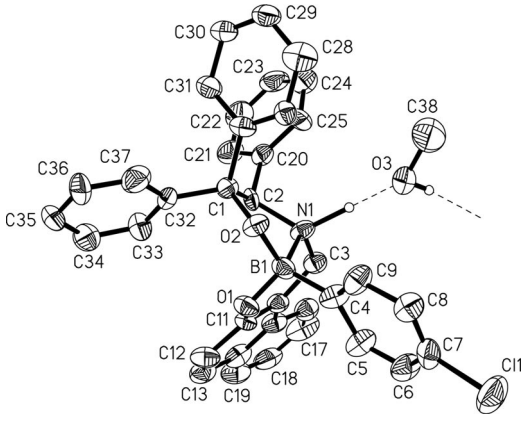


Figure 2. Diagram of the chosen asymmetric unit of the crystal structure of **8aaa**·CH_3OH. Dashed lines indicate hydrogen bonds. Displacement ellipsoids are set at 30% probability, hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Distances [Å] and angles [°]: B1–O1 1.472(5), B1–O2 1.468(5), B1–N1 1.619(6), B1–C4 1.622(6), O1–C11 1.356(5), O2–C1 1.460(4), N1–C2 1.522(4), N1–C3 1.512(5), C1–C2 1.583(6), C3–C10 1.496(5), C10–C11 1.390(6); O1–B1–O2 110.2(3), O1–B1–N1 107.4(3), O1–B1–C4 112.2(3), O2–B1–N1 99.4(3), O2–B1–C4 112.9(3), N1–B1–C4 114.0(3); N1–H2 1.00(3), H2···O3 1.96(3), N1–H2···O3 166(3), N1···O3 2.936(4); O3–C38 1.404(5), O3–H1 0.82, H1···O2i 2.03, O3–H1···O2i 172, O3···O2i 2.842(4) (i: 1 – *x*, –0.5 + *y*, 1 – *z*).

The helical twisting power of the boronates **5** and **8** used as dopants was determined in two different host compounds, the commercial nematic phases ZLI-1840 and 5-CB, whose structures are shown in Scheme 3. ZLI-1840 is a mixture of eight alkyl-substituted cyclohexylphenyl and cyclohexylbiphenyl cyanides. It is used as a component in LC displays. 5-CB, on the other hand, is a mesophase that consists of a single compound, 4-(4′-pentyl-phenyl)benzonitrile.[16] The boronates **5** and **8** were dissolved in the nematic compounds at different concentrations in the range of 10^{-2} to 10^{-3} mol fraction of the dopant. As expected, imine complexes **5** gave yellowish mixtures, whereas the mixtures of amine complexes **8** with the nematic compounds were colorless. The HTP values were determined by the Grandjean-Cano wedge method,[17] that permits to determine the hight of the pitch *p*. The 1/*p* values were measured at different concentrations of the dopant, and the gradient of the plot

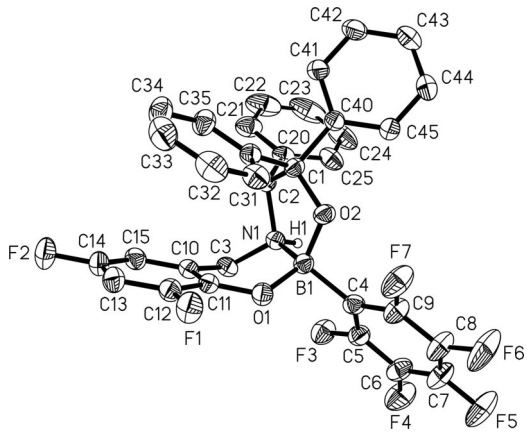
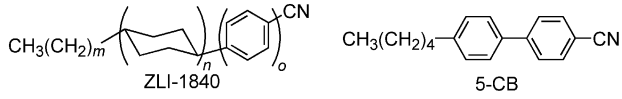


Figure 3. Molecular structure of **8acj** in the crystal. Displacement ellipsoids are set at 30% probability, hydrogen atoms bonded to carbon atoms are omitted for clarity. Bond lengths [Å] and angles [°]: B1–O1 1.463(3), B1–O2 1.426(3), B1–N1 1.654(3), B1–C4 1.642(3), O1–C11 1.349(3), O2–C1 1.414(2), N1–C2 1.519(2), N1–C3 1.501(3), C1–C2 1.593(3), C3–C10 1.498(3), C10–C11 1.394(3); O1–B1–O2 117.99(17), O1–B1–N1 108.12(15), O1–B1–C4 106.66(15), O2–B1–N1 100.12(14), O2–B1–C4 108.64(16), N1–B1–C4 115.65(15); N1–H1 0.85(2).

of 1/*p* vs. the molar fraction equals the HTP value. The sign of the helicity was determined from the motion of the colored interference rings during the rotation of the azimuth of the polarizer in the microscope to higher values. If the colored rings move outwards, this indicates a left-handed helix, moving inwards a right-handed one.[7e,18] The HTP values are shown in Table 1. It turned out that negative HTP values (*M*) resulted in all measurements, indicating a left-handed helix.



Scheme 3. Nematic phases used for HTP measurements of the dopants **5** and **8**.

Except for a few cases where a low HTP value was obtained in one of the nematic phases (Entries 3, 10, 18) the Grandjean-Cano measurement was performed in ZLI-1840 and 5-CB. As the induction of helicity by the dopant, which plays the role of the guest in the nematic host, is based on noncovalent interactions, it is not surprising that an individual dopant exhibits different twisting powers in different nematic compounds, depending on their functional groups, the number of their aromatic and/or cycloaliphatic rings and the molecular size and extension. Here, we have chosen two nematic phases that have an identical functional group, the benzonitrile, but differ in the number of aromatic rings, the incorporation of cyclohexyl rings and the extension of the aliphatic side chain. As shown in Table 1, the HTP values for the two nematic compounds ZLI-1840 and 5-CB roughly parallel the different dopants. For an individual dopant, both nematic phases are in the same order of magnitude. In the series of dopants, the HTP values varied considerably, ranging from values below 10 up to over

Table 1. HTP values of boronate–imine complexes **5** and boronate–amine complexes **8** in nematic phases ZLI-1840 and 5-CB.

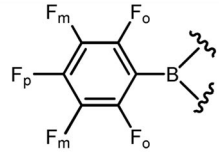
Entry	Boronate complex	HTP [μm^{-1}] ZLI-1840	5-CB
1	**5a**	–12	–19
2	**5b**	–10	–17
3	**5c**	[a]	–5
4	**5d**	–2	–6
5	**8aaa**	–32	–50
6	**8aab**	–58	–46
7	**8aae**	–12	–30
8	**8aaf**	–42	–43
9	**8aag**	–72	–60
10	**8aah**	–22	[a]
11	**8aai**	–95	–40
12	**8aaj**	–61	–25
13	**8aba**	–45	–67
14	**8abi**	–96	–115
15	**8abj**	–12	–11
16	**8acj**	–30	–32
17	**8bbj**	–35	–44
18	**8caa**	–5	[a]

[a] Not determined.

100 μm^{-1}. Imine complexes gave only moderate HTP values (Entries 1–4), and dopants with aliphatic residues at the boron atom (Entries 3 and 4) display only marginal twisting power. Therefore, aryl–boron residues were implemented in all the amine complexes (Entries 5–18). It turned out that the substitution pattern of the aryl group at the boron atom had a strong influence on the HTP values. This becomes in particular evident from the series of dopants **8aaa**–**8aaj** (Entries 5–12) featuring a naphthyl moiety. Neither the pure phenyl (Entry 7) nor the 3-thienyl substitution (Entry 10) gave a good performance as dopants. A *p*-phenyl substituent turned out to be favorable (Entries 5, 6, 8, 9, 11), as well as the pentafluorophenyl moiety (Entry 12), and the biphenyl-substituted boron complex **8aai** gave a high HTP value of 95 μm^{-1} in ZLI-1840. When changing the naphthyl moiety, derived from 2-hydroxy-1-naphthaldehyde, against a di-*tert*-butyl-substituted aromatic backbone (Entries 13–15), again a high HTP value was obtained with the *p*-ethoxybiphenyl derivative **8abi** (Entry 14), leading to the best results in ZLI-1840 (–96 μm^{-1}) and 5-CB (–115 μm^{-1}). The pentafluorophenyl residue at the boron atom gave only a poor result (Entry 15). Further variation in the phenolic backbone with the difluoro derivative **8acj** (Entry 16) and replacement of the geminal diphenyl group by the corresponding (3,5-difluoro)phenyl derivative **8bbj** (Entry 17) did not have exceptional influence on the HTP values (Entries 16 and 17 vs. Entries 12 and 15). All the amine complexes listed in Entries 5–17 feature the chiral aminotriarylethanol pattern in the backbone and include a geminal diarylhydroxymethyl unit. In contrast, dopant **8caa** is missing this pattern. When comparing the marginal HTP values of **8caa** (Entry 18) with otherwise identical compound **8aaa** (Entry 5), the importance of the geminal diarylhydroxymethyl group, well known from asymmetric synthesis,[19] becomes evident also in the context of induced helicity.

Various attempts have been made in order to understand, on a supramolecular level, the interaction between the chiral dopant and the nematic phase, and different models have been developed, based on theoretical calculations and spectroscopic information.[2b,2c,7b,7h,20] In order to investigate the noncovalent interaction of the nematic compounds ZLI-1840 and 5-CB with the new, colorless broronate–amine complexes **8**, we took advantage of their modular synthesis that permits to introduce probes at different sites of the molecules. As a tool, we used ^{19}F NMR shifts of boronate–amine complexes **8aaj**, **8abj**, **8acj** and **8bbj** and the alterations in the shift values that occurred after the nematic compounds ZLI-1840 and 5-CB had been added. The results are shown in Table 2. First the effect of the solvent was studied with boronate complex **8aaj** that was measured in chloroform, toluene and [D_{12}]cyclohexane (Entries 1, 4, 7), whereas compound **8abj** was measured in toluene (Entry 9), and **8acj** and **8bbj** in [D_{12}]cyclohexane exclusively (Entries 12 and 14). As expected, compound **8aaj** displays in all solvents separate signals for the three groups of anisochronous fluorine atoms in *ortho*, *meta*, and *para* position of the (pentafluorophenyl)boronate moiety. In the absence of an additive, the chemical shifts were not influenced significantly by the solvent. In order to obtain insight in the interaction of dopant and nematic phase, the shift differences were determined that occurred upon addition of the additives ZLI-1840 and 5-CB.

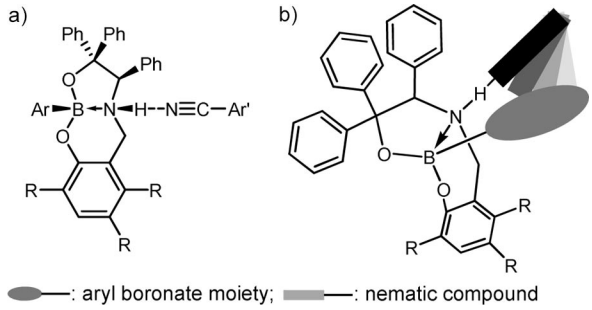
Table 2. Influence of the additives ZLI-1840 and 5-CB on the ^{19}F resonances in the pentafluorophenyl ring of boronate–amine complexes **8aaj**, **8abj**, **8acj** and **8bbj**.

Entry	Boronate	Solvent/Additive				
			^{19}F NMR	*o*	*m*	*p*
1	**8aaj**	$CHCl_3$/–	δ	–135.7	–162.1	–155.5
2	**8aaj**	$CHCl_3$/ZLI-1840	$\Delta\delta$	0.1	–0.4	–0.5
3	**8aaj**	$CHCl_3$/5-CB	$\Delta\delta$	0.1	–0.3	–0.4
4	**8aaj**	toluene/–	δ	–135.2	–161.5	–154.7
5	**8aaj**	toluene/ZLI-1840	$\Delta\delta$	0.2	–1.6	–1.9
6	**8aaj**	toluene/5-CB	$\Delta\delta$	0.4	–1.7	–2.0
7	**8aaj**	C_6D_{12}/–	δ	–136.7	–163.8	–157.6
8	**8aaj**	C_6D_{12}/5-CB	$\Delta\delta$	1.9	–0.1	–0.2
9	**8abj**	toluene/–	δ	–140.7	–167.7	–162.4
10	**8abj**	toluene/ZLI-1840	$\Delta\delta$	0.7	–0.2	–0.3
11	**8abj**	toluene/5-CB	$\Delta\delta$	0.6	–0.2	–0.2
12	**8acj**	C_6D_{12}/–	δ	–136.2	–163.7	–157.4
13	**8acj**	C_6D_{12}/5-CB	$\Delta\delta$	2.6	–0.5	–0.4
14	**8bbj**	C_6D_{12}/–	δ	–136.7	–163.2	–157.5
15	**8bbj**	C_6D_{12}/5-CB	$\Delta\delta$	3.0	–0.6	–0.6

In Table 2, the shift differences $\Delta\delta$ are given, defined as the difference of the shifts in the presence and in the absence of the nematic compounds. Accordingly, a positive value indicates a downfield, a negative value an upfield shift that is induced by the additive. In the first series (Entries 1–3), where chloroform was used as the solvent, the high-field and low-field shift differences are relatively small, with a

maximum upfield shift of the *p*-fluorine substituents of 0.5 ppm. It seems to be plausible that the relatively polar solvent chloroform prevents the nematic compounds from forming stable aggregates with the boronate **8aaj**. Accordingly, significantly higher shift differences are observed in the hydrocarbons toluene (Entries 5 and 6) and cyclohexane (Entries 7 and 8). Thus, upfield shifts up to 2.0 ppm were observed for the *p*-fluorine atoms in the boronate **8aaj** in toluene, and downfield shifts up to 1.9 ppm for the *o*-fluorine position in [D_{12}]cyclohexane. The comparison of ZLI-1840 and 5-CB gave very similar shift differences, indicating that both nematic compounds interact in the same way with the boronate **8aaj** (Entry 5 vs. 6 and 10 vs. 11). The measurements of the remaining complexes **8abj**, **8acj**, and **8bbj** were restricted to the solvents toluene (Entries 9–11) or [D_{12}]cyclohexane (Entries 12–15). Here again, remarkable upfield and downfield shifts were determined. A clear and constant tendency becomes obvious from the comparison of the *o*- with the *m*- and *p*-fluorine shift differences: in all experiments, the signals of the *o*-fluorine atoms are shifted downfield, whereas the signals of the fluorine atoms in *meta* and *para* position display an upfield shift. Two additional resonances in the ^{19}F NMR spectra have to be taken into account in the boronate complexes **8acj** and **8bbj** due to the *m*-difluoro substitution pattern in the phenolic part of **8acj** and the pair of diastereotopic fluorine atoms in the geminal 3,5-difluorophenyl group of **8bbj**, respectively. It turned out that in toluene or [D_{12}]cyclohexane the addition of 5-CB led to a small upfield shift in the case of **8bbj** (0.4 and 0.5 ppm). In the phenolate moiety of compound **8acj**, the *p*-fluorine signal is shifted by 0.6 ppm, the *o*-fluorine signal by 1.2 ppm upon addition of 5-CB. Both resonances are shifted to higher field. The effect of the nematic compounds to the geminal diaryl group as well as the phenolate moiety can be explained by a nonspecific effect of the co-solvent that leads to an upfield shift of all ^{19}F resonances. In contrast, the nematic compounds ZLI-1840 and 5-CB *influence the aryl residue at the boron atom in a very specific way*, as it becomes evident from a discrimination between the *o*- (downfield shifted signals) and the *m*- and *p*- fluorine atoms (upfield shifted signals). One can conclude thereupon that a π–π interaction between the aromatic rings of the nematic compounds and the arylboronic moiety occurs. This is in accordance with the results of the measurement of the HTP values, shown in Table 1: The strongest influence on the helical twisting power originates from the arylboronate moiety.

Aside from π-stacking, another noncovalent interaction between the nematic phase and the boronate–amine complexes is taken into account. Both ZLI-1840 and 5-CB are similar in their HTP values and in the effect on the fluorine resonances on the arylboronic moiety. This could correspond to the cyano group, a common feature of both nematic compounds. As demonstrated by the crystal structure of boronate complex **8aaa**, the amino group becomes a hydrogen-bond donor upon complexation with the boron atom. When a benzonitrile is offered as an acceptor,[21] a hydrogen bond might form, as shown in Scheme 4a. In order to prove this assumption, ^1H NMR spectra of boronate **8aaj** in [D_{12}]cyclohexane were measured at different amounts of the additive 5-CB. Figure 4 shows the relevant part of the NMR spectra displaying the signals of the NH groups, the tertiary benzylic proton and the diastereotopic NCH_2 protons. The downfield shift of the NH signal at increasing concentrations of the nitrile 5-CB clearly indicates a hydrogen bond.[22] The model deduced thereof also explains for the complex **8aaj** the upfield shift of the *m*- and *p*-fluorine signals. Due to the attachment of the benzonitrile moiety to the amino group, they become influenced by the diamagnetic field originating from the first benzene ring in 5-CB and ZLI-1840. The downfield shift of the *o*-fluorine signals, on the other hand, is caused by the proximity to the cyano group.



Scheme 4. (a) Hydrogen-bonded cyano group of the nematic compounds at the boronate–amine complexes **8**; (b) model of (*M*) helicity of the nematic compound induced by dopants **8**.

The π-stacking and hydrogen-bond formation will not only occur in the nonpolar solvent cyclohexane but also in the mixture of dopants **8** in the pure nematic phase 5-CB or ZLI-1840. As seen from Table 1, all the homochiral boronate–amine complexes induce a left-handed helix of the nematic phase. That means that the configuration of dopant clearly correlates with the (*M*) helix. Taking into account the noncovalent interactions between the dopant and the nematic compound 5-CB, we propose a model for the origin of the (*M*) helicity, deduced from the structure of the dopant. As illustrated in Scheme 4b, the arylboronic residue prevents the nematic compound from forming a stack towards the front side. There remain two directions of a stacking on the rear side. A turn to the right, however, will be disfavored by the aryl groups of the amino alcohol moiety, in particular the one at the stereogenic amine carbon atom, and the *cis*-oriented one of the geminal phenyl groups. As a consequence, the stacking turns to the left, "open" rear side of the complex. The fact that this part of the molecule does not influence the stacking significantly, is demonstrated by the HTP values of dopants with a naphthyl and a di-*tert*-butylphenyl moiety, which turn out to be rather similar (Table 2, Entry 5 vs. 13). Thus, stacking to the left side can be interpreted as the first steps of the left-handed helix. The plausible correlation between the configuration of the boronate–amine complexes and the (*M*) helicity is illustrated by the mnemonic shown in Scheme 4b.

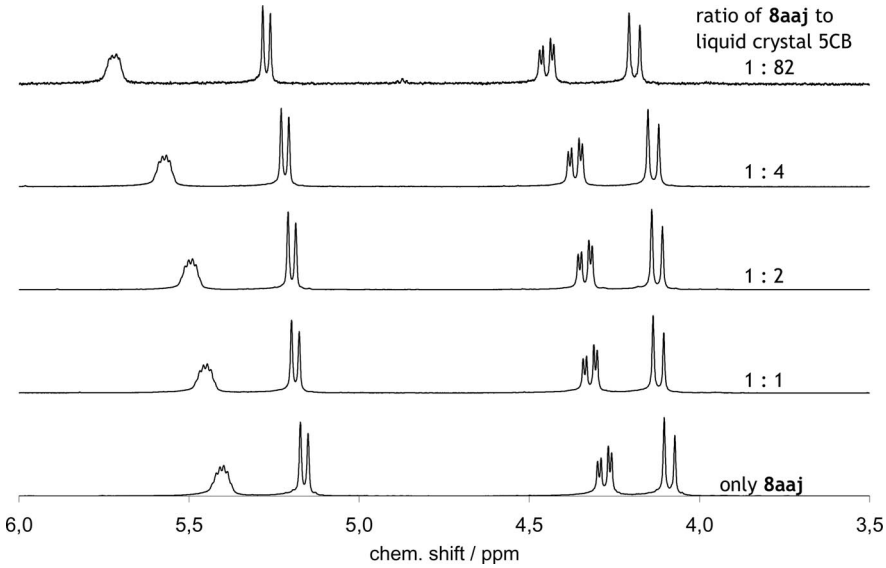


Figure 4. ^{1}H NMR shifts of **8aaj** in different solutions of 5-CB in [D_{12}]cyclohexane. Assignment of signals (from left to right): NH, benzylic H and diastereotopic NCH_2.

Conclusions

We have synthesized a series of diastereomerically and enantiomerically pure boronate–imine and boronate–amine complexes. Their configurations are determined by representative crystal structure analyses. For the first time, it is shown that boronate–amine complexes **8** are suitable, colorless, air-stable dopants for nematic liquid-crystalline phases. Based on NMR studies of the boronate–amine complexes in the presence of nematic compounds ZLI-1840 and 5-CB, an interpretation of their noncovalent interaction is given, and a rationale is offered that correlates the configuration of the dopant with the sense of helicity in the induced cholesteric phase.

Experimental Section

General: Melting points (uncorrected) were determined with a Büchi 540 melting point apparatus. Optical rotations were measured with a Perkin-Elmer 341 polarimeter. $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. NMR spectra were recorded at 25 °C with a Varian VXR 200 or 300 or a Bruker DRX 500 spectrometer. Mass spectra (ESI) were measured with a Finnigan LCQDECA spectrometer. All boronate complexes display the typical isotope pattern of the [M + H] peak in the ESI mass spectra. CD spectra were measured with a Jasco J-600 spectropolarimeter. Silica gel 60 F254 TLC plates (Merck) were used. Elemental analyses were carried out with a Perkin-Elmer CHN-Analysator 263 at the Institut für Pharmazeutische Chemie (Universität Düsseldorf). All reactions involving organometallic compounds or metal complexes were carried out under anhydrous nitrogen.

Procedure for the Determination of the HTP Values: See ref.[7d,7e]

Imines 3, 7aa, 7ab and Boronate–Imine Complex 5a: These were prepared as described previously.[13,9,8]

Amino Alcohol 6b: This was obtained as yellowish solid from 1-bromo-3,5-difluorobenzene and methyl (*R*)-2-amino-2-phenylacetate hydrochloride according to the procedure given in ref.[13], yield 2.0 g (58%), R_f = 0.6 (hexane/ethyl acetate, 2:1), m.p. 39 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.52 (s, 3 H), 1.97 (s, 2 H), 5.04 (s, 1 H), 6.20 (s, 1 H), 6.84–7.50 (m, 11 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 61.9, 79.1, 102.3, 103.7, 109.3, 110.1, 128.3–128.7, 139.0, 147.3, 150.4, 161.8, 162.8, 163.8, 164.8 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –110.5, –108.8 ppm. $C_{20}H_{15}F_4NO{\cdot}H_2O$ (378.34): calcd. C 63.32, H 4.52, N 3.69; found C 63.09, H 4.26, N 3.59.

General Procedure for the Preparation of Imines 7ac, 7ca and 7bb: Amino alcohol **6** (5.0 mmol), the corresponding aldehyde **2** (5.5 mmol, 1.1 equiv.) and sodium sulfate (3.5 g, 25.0 mmol) were suspended in a solution of dry methanol (50 mL) and dry tetrahydrofuran (50 mL). The mixture was cooled to –15 °C and stirred for 72 h. After filtration, the solvent was removed in a rotary evaporator, and the residue was purified by column chromatography to deliver imines **7ac** and **7ca** as yellow, solid compounds.

7ac: Yield 0.8 g (30%), R_f = 0.73 (chloroform/ethyl acetate, 10:1), m.p. 123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.7 (s, 1 H), 5.4 (s, 1 H), 6.56 (m, 1 H), 6.81 (m, 1 H), 7.0–7.3 (m, 13 H), 7.5 (d, *J* = 8.5 Hz, 2 H), 8.14 (s, 1 H), 12.9 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 78.9, 80.6, 107.6, 111.7, 126.4–129.6, 137.5, 143.5, 144.2, 165.7 ppm. $C_{27}H_{21}F_2NO_2$ (429.46): calcd. C 75.51, H 4.93, N 3.26; found C 75.73, H 4.77, N 3.24.

7ca: Yield 3.2 g (61%), R_f = 0.1 (chloroform/ethyl acetate, 10:1), m.p. 186 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.6 (s, 1 H), 3.9 (m, *J* = 12, *J* = 8.7 Hz, 2 H), 4.6 (dd, *J* = 8.2, *J* = 8.7 Hz, 1 H), 6.8 (d, *J* = 9.2 Hz, 1 H), 7.1 (t, *J* = 7.8 Hz, 1 H), 7.25–7.37 (m, 7 H), 7.4 (d, *J* = 9.2 Hz, 1 H), 7.7 (d, *J* = 8.4 Hz, 1 H), 8.8 (s, 1 H), 14.8 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 67.4, 71.3, 107.1, 118.1, 122.8, 123.1, 126.4, 126.8–129.2, 133.3, 136.9, 137.8, 159.3, 173.4 ppm. $C_{19}H_{17}NO_2$ (291.35): calcd. C 78.33, H 5.88, N 4.81; found C 78.13, H 5.93, N 4.72.

7bb: Yield 0.96 g (69%), R_f = 0.55 (hexane/ethyl acetate, 10:1), m.p. 92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19 (s, 9 H), 1.33 (s, 9 H), 3.19 (s, 1 H), 5.24 (s, 1 H), 6.49–7.32 (m, 13 H), 8.33 (s, 1 H), 12.51 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.7, 31.7, 34.5, 35.5, 78.5, 80.0, 103.3, 110.5, 127.1–129.9, 137.5, 141.1, 148.9, 158.1, 162.0, 162.5, 164.5, 170.0 ppm. ^{19}F NMR (470 MHz,

$CDCl_3$): δ = –109.7, –108.9 ppm. $C_{35}H_{35}F_4NO_2$ (577.66): calcd. C 72.77, H 6.11, N 2.42; found C 73.00, H 6.19, N 2.32.

General Procedure for the Preparation of Boronate–Imine Complexes 5b, 5c and 5d: The imine **3** (0.44 g, 1.0 mmol), the corresponding boronic acid (1.5 mmol) and molecular sieves (3 Å) (1.0 g) were suspended in dry toluene (100 mL) and refluxed for 20 h. After filtration, the solvent was removed in a rotary evaporator, and the residue was purified by column chromatography (chloroform/ethyl acetate, 10:1) to deliver boronates **5b**–**d** as yellow, solid compounds. For the preparation of boronate **7c**, the imine **5b** was treated with (iPrO)$_2$B(nBu) in an analogous way, however, in the absence of molecular sieves. According to this procedure, the following compounds were obtained.

5a: Yellow solid, yield 791 mg (55%), R_f = 0.61 (chloroform/ethyl acetate, 10:1), m.p. 214 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.19 (s, 1 H), 6.4 (s, 2 H), 6.87 (t, J = 7.6 Hz, 2 H), 6.9 (d, J = 8.0 Hz, 2 H), 7.09 (d, J = 8.0 Hz, 2 H), 7.12 (m, 5 H), 7.17 (m, 3 H), 7.27 (m, 3 H), 7.30 (d, J = 9.0 Hz, 1 H), 7.32 (t, J = 7.6 Hz, 1 H), 7.39 (t, J = 8.0 Hz, 1 H), 7.45 (d, J = 8.1 Hz, 1 H), 7.74 (d, J = 8.0 Hz, 1 H), 7.98 (d, J = 9.1 Hz, 1 H), 8.0 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 82.8, 87.2, 113.5, 120.6, 121.4, 124.7, 126.7, 126.8–129.0, 127.7, 129.1, 129.4, 131.8, 133.1, 134.4, 138.7, 139.0, 139.6, 156.2, 163.6 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 6.8 ppm. MS (ESI): m/z (%) = 563 (24), 564 (100), 565 (48) [M + H]$^+$.

5b: Yellow solid, yield 261 mg (44%), R_f = 0.83 (chloroform/ethyl acetate, 10:1), m.p. 216 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.2 (s, 1 H), 6.4 (d, J = 6.1 Hz, 2 H), 6.85 (t, J = 7.0 Hz, 2 H), 7.12–7.18 (m, 6 H), 7.18 (d, J = 8.2 Hz, 2 H), 7.28 (d, J = 7.0 Hz, 2 H), 7.30 (d, J = 9.1 Hz, 1 H), 7.31 (m, 3 H), 7.32 (m, 1 H), 7.4 (d, J = 7.4 Hz, 2 H), 7.49 (d, J = 7.8 Hz, 1 H), 7.72 (d, J = 8.3 Hz, 1 H), 7.74 (d, J = 8.1 Hz, 1 H), 8.0 (d, J = 9.1 Hz, 1 H), 8.05 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 82.9, 87.3, 113.5, 120.6, 121.4, 123.3, 124.8, 126.7–130.5, 127.8, 129.5, 131.8, 132.9, 135.1, 138.6, 138.9, 139.8, 156.4, 163.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 6.1 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.4 ppm. MS (ESI): m/z (%) = 597 (22), 598 (100), 599 (40) [M + H]$^+$.

5c: Yellow solid, yield 495 mg (86%), R_f = 0.69 (chloroform/ethyl acetate, 10:1), m.p. 197 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.7 (t, J = 7.1 Hz, 3 H), 1.18 (m, 6 H), 6.07 (s, 1 H), 7.0–7.3 (m, 15 H), 7.2 (d, J = 9.1 Hz, 1 H), 7.28 (t, J = 7.1 Hz, 1 H), 7.38 (t, J = 7.7 Hz, 1 H), 7.5 (d, J = 8.2 Hz, 1 H), 7.7 (d, J = 7.9 Hz, 1 H), 7.86 (s, 1 H), 7.9 (d, J = 9.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 26.1, 27.4, 82.1, 88.1, 114.0, 120.6, 121.8, 124.2, 126.8–130.1, 127.5, 128.6, 129.2, 132.0, 136.1, 138.5, 139.1, 139.3, 155.0, 163.4 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 8.8 ppm. MS (ESI): m/z (%) = 509 (28), 510 (100), 511 (40) [M + H]$^+$.

5d: Yellow solid, yield 555 mg (92%), R_f = 0.53 (chloroform/ethyl acetate, 10:1), m.p. 211 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.0 (s, 9 H), 6.15 (s, 1 H), 6.9 (d, J = 7.6 Hz, 2 H), 7.02 (m, 6 H), 7.1 (t, J = 6.7 Hz, 1 H), 7.17 (t, J = 7.0 Hz, 1 H), 7.26 (d, J = 9.0 Hz, 1 H), 7.29 (m, 6 H), 7.41 (t, J = 7.0 Hz, 1 H), 7.53 (d, J = 8.0 Hz, 1 H), 7.72 (d, J = 7.5 Hz, 1 H), 7.82 (s, 1 H), 7.92 (d, J = 9.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.6, 31.2, 82.6, 87.6, 105.2, 114.1, 120.7, 121.7, 124.4, 126.4–130.8, 127.7, 128.6, 129.2, 131.8, 135.9, 138.6, 139.2, 155.1, 162.6 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 2.0 ppm. MS (ESI): m/z (%) = 533 (24), 534 (100), 535 (39) [M + H]$^+$.

General Procedure for the Preparation of Boronate–Amine Complexes 8: Imines **7aa**–**7ca** (1.0 mmol) and sodium cyanoborohydride (0.19 g, 3.0 mmol) were dissolved in absolute methanol (75 mL). After the addition of hydrochloric acid (10%) (5 mL), the yellow solution was stirred at room temperature for 1 h, while it turned colorless gradually. Distilled water (50 mL) was added, and the solution was extracted three times with chloroform. The combined organic layers were dried with sodium sulfate, and the solvent was removed in a rotary evaporator. Immediately, the crude colorless, product thus obtained, the corresponding boronic acid **4a**, **4b**, **4e**–**j** (1.0 mmol) and sodium hydrogen carbonate (0.13 g, 1.5 mmol) were suspended in dry toluene (100 mL) and refluxed for 4 h. After the addition of distilled water, the layers were separated, and the aqueous phase was extracted with chloroform. The combined organic layers were dried with sodium sulfate, and the solvent was removed in a rotary evaporator. The residue was purified by column chromatography to deliver boronates **8** as colorless, solid materials. According to this procedure, the following compounds were obtained.

8aaa: Yield 260 mg (46%), R_f = 0.82 (chloroform/ethyl acetate, 10:1), m.p. 142 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.1 (d, J = 15.3 Hz, 1 H), 4.23 (dd, J = 15.3, J = 4.4 Hz, 1 H), 4.4 (dd, J = 11, J = 4.4 Hz, 1 H), 5.17 (d, J = 11 Hz, 1 H), 6.66 (d, J = 6.9 Hz, 2 H), 6.85 (d, J = 8.9 Hz, 1 H), 7.03 (m, 3 H), 7.08 (m, 3 H), 7.16 (m, 4 H), 7.22 (m, 3 H), 7.24 (d, J = 8.02 Hz, 2 H), 7.26 (t, J = 7.0 Hz, 1 H), 7.49 (d, J = 7.4 Hz, 2 H), 7.56 (d, J = 8.9 Hz, 1 H), 7.67 (d, J = 7.3 Hz, 1 H), 7.72 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.1, 72.3, 85.4, 103.6, 119.7, 121.9, 122.7, 126.1–129.1, 127.9, 128.2, 129.0, 130.1, 131.7, 133.8, 134.0, 143.8, 147.9, 153.7 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 5.1 ppm. MS (ESI): m/z (%) = 565 (30), 566 (100), 567 (48) [M + H]$^+$.

8aab: Yield 234 mg (65%), R_f = 0.81 (chloroform/ethyl acetate, 10:1), m.p. 143 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.09 (d, J = 15.4 Hz, 1 H), 4.19 (dd, J = 15.4, J = 4.0 Hz, 1 H), 4.44 (dd, J = 11.3, J = 4.0 Hz, 1 H), 5.18 (d, J = 11.3 Hz, 1 H), 6.69 (d, J = 7.0 Hz, 2 H), 6.85 (d, J = 9.0 Hz, 1 H), 7.02 (m, 3 H), 7.06 (m, 3 H), 7.10 (d, J = 7.0 Hz, 1 H), 7.12–7.20 (m, 6 H), 7.22 (t, J = 7.0 Hz, 1 H), 7.48 (d, J = 8.2 Hz, 2 H), 7.49 (d, J = 7.7 Hz, 2 H), 7.53 (d, J = 9.0 Hz, 1 H), 7.64 (d, J = 8.1 Hz, 1 H), 7.89 (d, J = 7.7 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.2, 72.4, 85.5, 103.7, 119.7, 121.8, 122.8, 124.6, 126.7–129.2, 128.2, 128.8, 130.1, 131.6, 132.5, 133.8, 143.7, 147.8, 153.6 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 5.0 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.9 ppm. MS (ESI): m/z (%) = 599 (29), 600 (100), 601 (40) [M + H]$^+$.

8aae: 175 mg (33%), R_f = 0.73 (chloroform/ethyl acetate, 10:1), m.p. 140 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.08 (d, J = 15.4 Hz, 1 H), 4.25 (dd, J = 15.4, J = 4.0 Hz, 1 H), 4.53 (dd, J = 11.4, J = 3.8 Hz, 1 H), 5.17 (d, J = 11.4 Hz, 1 H), 6.67 (br. s, 2 H), 6.87 (d, J = 9.0 Hz, 1 H), 7.04 (m, 2 H), 7.08 (t, J = 7.6 Hz, 2 H), 7.14 (d, J = 7.8 Hz, 1 H), 7.15 (m, 2 H), 7.18 (t, J = 8.0 Hz, 1 H), 7.24 (m, 3 H), 7.26 (m, 2 H), 7.39 (t, J = 8.0 Hz, 1 H), 7.51 (d, J = 7.3 Hz, 2 H), 7.54 (d, J = 9.0 Hz, 1 H), 7.66 (d, J = 7.8 Hz, 1 H), 7.69 (d, J = 7.1 Hz, 1 H), 7.8 (d, J = 7.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.1, 72.2, 85.3, 103.7, 119.8, 122.0, 122.5, 126.2–129.9, 128.0, 128.1, 128.8, 130.0, 131.8, 132.3, 134.2, 143.1, 144.0, 148.2, 153.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 5.2 ppm. MS (ESI): m/z (%) = 531 (23), 532 (100), 533 (38) [M + H]$^+$.

8aaf: Yield 234 mg (41%), R_f = 0.65 (chloroform/ethyl acetate, 10:1), m.p. 176 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.14 (d, J = 15.7 Hz, 1 H), 4.29 (dd, J = 15.7, J = 4.0 Hz, 1 H), 4.96 (dd, J = 11.3, J = 4.0 Hz, 1 H), 5.21 (d, J = 11.4 Hz, 1 H), 6.69 (d, J = 6.9 Hz, 2 H), 6.87 (d, J = 8.9 Hz, 1 H), 7.06–7.14 (m, 6 H), 7.16–

7.24 (m, 7 H), 7.28 (t, J = 7.0 Hz, 1 H), 7.44 (d, J = 7.5 Hz, 2 H), 7.51 (d, J = 7.4 Hz, 2 H), 7.57 (d, J = 9.0 Hz, 1 H), 7.69 (d, J = 7.9 Hz, 1 H), 7.9 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.2, 72.6, 85.5, 103.7, 119.8, 121.8, 122.8, 126.2–129.2, 128.3, 128.8, 130.1, 131.3, 131.6, 132.9, 133.5, 143.6, 147.6, 153.3 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 4.5 ppm. MS (ESI): m/z (%) = 556 (26), 557 (100), 558 (38) $[M + H]^+$.

8aag: Yield 543 mg (90%), R_f = 0.75 (chloroform/ethyl acetate, 10:1), m.p. 228 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.2 (s, 9 H), 4.09 (d, J = 15.3 Hz, 1 H), 4.29 (dd, J = 15.2, J = 4.0 Hz, 1 H), 4.48 (dd, J = 11.2, J = 4.0 Hz, 1 H), 5.17 (d, J = 11.3 Hz, 1 H), 6.66 (br. s, 2 H), 6.88 (d, J = 9.0 Hz, 1 H), 7.04 (m, 4 H), 7.09 (m, 4 H), 7.15 (d, J = 7.8 Hz, 1 H), 7.19 (t, J = 7.3 Hz, 1 H), 7.26 (m, 4 H), 7.47 (d, J = 7.6 Hz, 2 H), 7.52 (d, J = 7.4 Hz, 2 H), 7.54 (d, J = 9.0 Hz, 1 H), 7.67 (d, J = 8.0 Hz, 1 H), 7.79 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –1.1, 42.1, 72.3, 85.3, 103.7, 119.7, 122.1, 122.5, 126.2–129.0, 128.1, 128.8, 129.9, 131.6, 131.8, 133.0, 134.2, 139.8, 144.0, 148.2, 153.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 5.0 ppm. MS (ESI): m/z (%) = 603 (25), 604 (100), 605 (46) $[M + H]^+$.

8aah: Yield 70 mg (13%), R_f = 0.64 (chloroform/ethyl acetate, 10:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.1 (d, J = 15.4 Hz, 1 H), 4.3 (dd, J = 15.4, J = 4.2 Hz, 1 H), 4.45 (dd, J = 11.6, J = 4.2 Hz, 1 H), 5.17 (d, J = 11.6 Hz, 1 H), 6.6 (br. s, 2 H), 6.9 (d, J = 9.0 Hz, 1 H), 7.1 (m, 4 H), 7.19 (m, 1 H), 7.2 (m, 4 H), 7.25 (m, 4 H), 7.26 (d, J = 4.5 Hz, 1 H), 7.33 (d, J = 4.7 Hz, 1 H), 7.53 (d, J = 7.8 Hz, 2 H), 7.56 (d, J = 9.0 Hz, 1 H), 7.61 (d, J = 2.1 Hz, 1 H), 7.68 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.0, 71.9, 85.3, 103.8, 119.8, 122.2, 122.6, 125.3, 126.4–129.3, 128.2, 128.8, 129.1, 129.9, 131.1, 131.6, 133.6, 143.6, 147.5, 153.4 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 4.4 ppm. MS (ESI): m/z (%) = 537 (24), 538 (100), 539 (43) $[M + H]^+$.

8aai: Yield 250 mg (38%), R_f = 0.71 (chloroform/ethyl acetate, 10:1), m.p. 144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (t, J = 7.0 Hz, 3 H), 3.96 (q, J = 7.0 Hz, 2 H), 4.09 (d, J = 15.4 Hz, 1 H), 4.29 (dd, J = 15.4, J = 4.2 Hz, 1 H), 4.48 (dd, J = 11.2, J = 4.0 Hz, 1 H), 5.18 (d, J = 11.3 Hz, 1 H), 6.66 (br. s, 2 H), 6.86 (d, J = 8.7 Hz, 2 H), 6.88 (d, J = 9.1 Hz, 1 H), 7.0–7.3 (m, 12 H), 7.15 (d, J = 7.7 Hz, 1 H), 7.18 (t, J = 7.8 Hz, 1 H), 7.44 (d, J = 8.7 Hz, 2 H), 7.47 (d, J = 7.9 Hz, 2 H), 7.52 (d, J = 7.7 Hz, 2 H), 7.54 (d, J = 9.1 Hz, 1 H), 7.66 (d, J = 8.0 Hz, 1 H), 7.84 (d, J = 7.9 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.9, 42.1, 63.4, 72.2, 85.3, 103.7, 114.7, 119.8, 122.0, 122.5, 126.2, 126.3–129.0, 127.9, 128.1, 128.8, 129.9, 131.8, 132.7, 133.9, 134.2, 140.4, 144.0, 148.1, 153.9, 158.3 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 6.0 ppm. MS (ESI): m/z (%) = 651 (25), 652 (100), 653 (50) $[M + H]^+$.

8aaj: Yield 343 mg (55%), R_f = 0.79 (chloroform/ethyl acetate, 10:1), m.p. 114 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.14 (d, J = 16.0 Hz, 1 H), 4.44 (dd, J = 15.9, J = 5.3 Hz, 1 H), 5.26 (d, J = 11.7 Hz, 1 H), 5.45 (m, 1 H), 6.68 (d, J = 7.4 Hz, 2 H), 6.98 (d, J = 7.3 Hz, 2 H), 7.04 (d, J = 9.0 Hz, 1 H), 7.05 (d, J = 7.8 Hz, 2 H), 7.09 (d, J = 7.3 Hz, 1 H), 7.12 (d, J = 8.2 Hz, 1 H), 7.15 (m, 3 H), 7.21 (d, J = 7.8 Hz, 3 H), 7.25 (m, 2 H), 7.51 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 9.0 Hz, 1 H), 7.66 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.8, 72.1, 86.2, 104.7, 119.8, 122.2, 123.1, 126.5–129.5, 128.5, 128.8, 130.0, 131.1, 132.6, 142.0, 146.5, 151.8 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 4.3 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –135.7 (d, J = 23 Hz, 2 F), –155.5 (t, J = 21 Hz, 1 F), –162.1 (m, 2 F) ppm. MS (ESI): m/z (%) = 621 (27), 622 (100), 623 (38) $[M + H]^+$.

8aba: Yield 380 mg (63%), R_f = 0.76 (chloroform/ethyl acetate, 10:1), m.p. 187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 (s, 9 H), 1.18 (s, 9 H), 3.41 (d, J = 13.6 Hz, 1 H), 4.12 (d, J = 13.6 Hz, 1 H), 4.14 (s, 1 H), 5.12 (d, J = 11.6 Hz, 1 H), 6.53 (d, J = 2 Hz, 1 H), 6.65 (d, J = 7.3 Hz, 2 H), 7.05 (m, 4 H), 7.12 (m, 5 H), 7.14 (d, J = 2 Hz, 1 H), 7.22 (m, 2 H), 7.25 (d, J = 8.1 Hz, 2 H), 7.51 (d, J = 7.7 Hz, 2 H), 7.7 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.4, 31.6, 34.1, 34.9, 45.4, 70.9, 85.0, 112.2, 121.7, 124.0, 126.4–129.3, 127.7, 133.8, 133.9, 138.2, 140.2, 144.2, 148.2, 151.3 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 4.9 ppm. MS (ESI): m/z (%) = 627 (23), 628 (100), 629 (53) $[M + H]^+$.

8abi: 321 mg (45%), R_f = 0.67 (chloroform/ethyl acetate, 10:1), m.p. 187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 9 H), 1.19 (s, 9 H), 1.36 (t, J = 7.0 Hz, 3 H), 3.40 (d, J = 14.0 Hz, 1 H), 3.99 (q, J = 7.0 Hz, 2 H), 4.20 (d, J = 14.0 Hz, 1 H), 4.22 (m, 1 H), 5.13 (d, J = 12.0 Hz, 1 H), 6.54 (d, J = 2.0 Hz, 1 H), 6.66 (d, J = 7.3 Hz, 2 H), 6.88 (d, J = 8.8 Hz, 2 H), 7.06 (m, 2 H), 7.09 (d, J = 7.5 Hz, 2 H), 7.12 (d, J = 2.0 Hz, 1 H), 7.14 (m, 2 H), 7.19 (t, J = 7.5 Hz, 1 H), 7.30 (m, 2 H), 7.40 (t, J = 7.7 Hz, 1 H), 7.47 (d, J = 8.8 Hz, 2 H), 7.50 (d, J = 8.1 Hz, 2 H), 7.54 (d, J = 7.4 Hz, 2 H), 7.71 (d, J = 8.2 Hz, 1 H), 7.85 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.9, 29.4, 31.6, 34.1, 34.9, 45.4, 63.5, 70.8, 85.0, 112.2, 114.7, 121.7, 123.9, 126.1, 126.4–132.4, 128.0, 132.9, 134.0, 138.1, 139.9, 140.1, 144.4, 148.5, 151.5, 158.3 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 5.4 ppm. MS (ESI): m/z (%) = 713 (20), 714 (100), 715 (51) $[M + H]^+$.

8abj: Yield 369 mg (54%), R_f = 0.75 (chloroform/ethyl acetate, 10:1), m.p. 196 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (s, 9 H), 1.29 (s, 9 H), 3.50 (d, J = 13.7 Hz, 1 H), 4.33 (dd, J = 13.7, J = 3.0 Hz, 1 H), 4.70 (d, J = 11.4 Hz, 1 H), 5.53 (q, J = 8.0 Hz, 1 H), 6.57 (d, J = 7.4 Hz, 2 H), 6.59 (d, J = 2.2 Hz, 1 H), 6.82 (d, J = 8.3 Hz, 2 H), 6.94 (t, J = 7.3 Hz, 2 H), 7.05 (t, J = 7.3 Hz, 2 H), 7.08 (d, J = 7.3 Hz, 3 H), 7.19 (d, J = 7.4 Hz, 3 H), 7.24 (d, J = 2.2 Hz, 1 H), 7.3 (t, J = 7.4 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.5, 31.6, 34.2, 34.9, 46.4, 71.0, 85.4, 115.9, 122.4, 124.7, 126.8–129.4, 132.2, 139.1, 141.0, 141.9, 145.5, 151.1 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 5.1 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –140.7 (d, J = 17 Hz, 2 F), –162.4 (t, J = 20 Hz, 1 F), –167.7 (m, 2 F) ppm. MS (ESI): m/z (%) = 683 (24), 684 (100), 685 (44) $[M + H]^+$.

8acj: Yield 304 mg (50%), R_f = 0.75 (chloroform/ethyl acetate, 10:1), m.p. 167 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.66 (d, J = 15.4 Hz, 1 H), 4.26 (dd, J = 15.4, J = 4.6 Hz, 1 H), 5.02 (d, J = 10.7 Hz, 1 H), 5.37 (m, 1 H), 6.28 (d, J = 8.0 Hz, 1 H), 6.63 (dd, J = 9.0, J = 2.8 Hz, 1 H), 6.71 (d, J = 7.3 Hz, 2 H), 6.97 (d, J = 7.3 Hz, 2 H), 7.12 (t, J = 7.2 Hz, 1 H), 7.19 (d, J = 7.8 Hz, 2 H), 7.27 (t, J = 7.3 Hz, 1 H), 7.40 (t, J = 7.7 Hz, 2 H), 7.46 (d, J = 8.2 Hz, 2 H), 7.51 (t, J = 7.4 Hz, 1 H), 7.72 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 45.5, 72.6, 86.2, 105.1, 108.1, 117.5, 126.2–132.4, 132.6, 139.2, 141.7, 146.0, 153.9 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 4.8 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –124.5 (t, J = 8.4 Hz, 1 F), –130.7 (d, J = 10.7 Hz, 1 F), –138.0 (d, J = 19 Hz, 2 F), –158.2 (t, J = 20 Hz, 1 F), –164.9 (m, 2 F) ppm. MS (ESI): m/z (%) = 607 (23), 608 (100), 609 (35) $[M + H]^+$.

8bbj: Yield 484 mg (64%), R_f = 0.78 (chloroform/ethyl acetate, 10:1), m.p. 153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19 (s, 9 H), 1.28 (s, 9 H), 3.54 (d, J = 13.6 Hz, 1 H), 4.35 (dd, J = 13.6, J = 3.2 Hz, 1 H), 4.67 (d, J = 10.6 Hz, 1 H), 5.54 (q, J = 7.4 Hz, 1 H), 6.34 (d, J = 8.9 Hz, 2 H), 6.52 (t, J = 8.6 Hz, 1 H), 6.55 (t, J = 8.4 Hz, 1 H), 6.64 (d, J = 2.3 Hz, 1 H), 6.69 (d, J = 7.3 Hz, 2 H), 6.67 (d, J = 8.7 Hz, 2 H), 7.26 (d, J = 2.4 Hz, 1 H), 7.31 (t, J = 7.3 Hz, 2 H), 7.39 (t, J = 7.4 Hz, 1 H) ppm. ^{13}C NMR (125 MHz,

$CDCl_3$): δ = 29.5, 31.5, 34.3, 34.9, 47.1, 71.3, 84.4, 103.1, 109.6, 111.1, 115.7, 122.4, 125.2, 128.4, 129.6, 130.3, 131.4, 139.3, 142.5, 145.0, 149.1, 150.8 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 5.1 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ = –109.4 (t, J = 8.0 Hz, 2 F), –109.5 (t, J = 8.0 Hz, 2 F), –135.5 (d, J = 24 Hz, 2 F), –156.8 (t, J = 21 Hz, 1 F), –162.9 (m, 2 F) ppm. MS (ESI): m/z (%) = 755 (23), 756 (100), 757 (43) $[M + H]^+$.

8caa: Yield 153 mg (37%), R_f = 0.4 (chloroform/ethyl acetate, 10:1), m.p. 224 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.02 (d, J = 15.0 Hz, 1 H), 4.06 (m, 1 H), 4.1 (m, 2 H), 4.2 (d, J = 15.0 Hz, 1 H), 4.59 (dd, J = 10.0, J = 3.0 Hz, 1 H), 7.08 (d, J = 8.3 Hz, 2 H), 7.15 (d, J = 6.6 Hz, 2 H), 7.21 (d, J = 8.9 Hz, 1 H), 7.26 (t, J = 7.0 Hz, 1 H), 7.28 (m, 4 H), 7.36 (t, J = 7.0 Hz, 1 H), 7.4 (d, J = 8.2 Hz, 2 H), 7.73 (d, J = 8.9 Hz, 1 H), 7.74 (d, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.1, 63.6, 68.8, 106.1, 119.8, 121.8, 122.9, 126.9, 127.8, 127.9–129.7, 128.5, 129.0, 130.4, 131.9, 133.6, 134.1, 154.2 ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ = 5.9 ppm. MS (ESI): m/z (%) = 413 (24), 414 (100), 415 (39) $[M + H]^+$.

Crystal Structure Determinations of Compounds 8aaa·CH_3OH and 8acj: Crystals suitable for X-ray study were selected by means of a polarisation microscope and investigated with a STOE IPDS by using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å). Unit-cell parameters were determined by least-squares refinements on the positions of 8000 and 8000 reflections in the range 5.20° < θ <18.35° and 5.20° < θ < 21.20°, respectively. As nonracemic substances were used for the preparation of the crystals, with respect to the monoclinic symmetries and the systematic extinctions space group type No. 4 was uniquely determined in both cases. Lp corrections were applied to the intensity data. The structures were solved by direct methods,[23] and the positions of all hydrogen atoms were found in subsequent ΔF maps. Refinements by full-matrix least-squares calculations on F^2[24] converged to the indicators given in Table 3 [**8aaa**·CH_3OH: S = 0.78, $(\Delta/\sigma)_{max}$ = 0.000; **8acj**: S = 1.05, $(\Delta/\sigma)_{max}$ = 0.000]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. All atom coordinates and isotropic displacement parameters were refined for the hydrogen atoms bonded to nitrogen atoms. The length of the O–H bond of the methanol solvent molecule was restrained to 0.82 Å within a standard deviation of 0.02. Idealized bond lengths and angles were used for the CH_3, CH_2 and CH fragments; the riding model was applied for their H atoms. Isotropic displacement parameters of the H atoms were kept equal to 120% of the equivalent isotropic displacement parameters of the parent secondary, tertiary, or "aromatic" carbon atoms. The refined Flack parameter [–0.11(10)] clearly indicated the choice of the correct enantiomorph in the case of the chlorine-containing compound. CCDC-753266 (**8aaa**·CH_3OH), and -753267 (**8acj**) contain 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.

Table 3. Summary of crystal data, details of intensity measurements and structure refinements of **8aaa**·CH_3OH, and **8acj**.

	8aaa·CH_3OH	**8acj**
Empirical formula	$C_{38}H_{33}BClNO_3$	$C_{33}H_{21}BF_7NO_2$
Formula mass	597.91	607.32
Crystal system	monoclinic	monoclinic
Space group; no.	$P2_1$; 4	$P2_1$; 4
a [Å]	10.3282(10)	8.1899(5)
b [Å]	12.2347(8)	18.7018(9)
c [Å]	12.7875(12)	9.5680(6)
β [°]	92.521(12)	107.030(7)
V [Å^3]	1614.3(2)	1401.23(15)
Z	2	2
F(000)	628	620
$D_{calcd.}$ [Mg m^{-3}]	1.230	1.439
μ (Mo-K_α) [mm^{-1}]	0.156	0.121
Crystal size [mm]	0.30 × 0.30 × 0.30	0.30 × 0.18 × 0.18
T [K]	291(2)	291(2)
θ range [°]	1.97 < θ < 25.00	2.18 < θ < 25.91
hkl ranges	–12 ≤ h ≤ 12	–10 ≤ h ≤ 10
	–14 ≤ k ≤ 14	–22 ≤ k ≤ 22
	–15 ≤ l ≤ 15	–11 ≤ l ≤ 11
No. of reflns. measd.	21114	19937
No. of unique reflns.	5667	5378
No. of reflns. obsd. [$I > 2\sigma(I)$]	2653	4259
No. of param./restraints	402/2	401/1
R_1 [$I > 2\sigma(I)$][a]	0.0535	0.0345
wR_2 (all data)[a]	0.1131	0.0897
Max./min. $\Delta\rho$ [e Å^{-3}]	0.28/–0.18	0.18/–0.18

[a] As defined in SHELXL97-2.

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