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Facile and Reliable Synthesis of Tetraphenoxyborates and Their Properties

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Tetraphenoxyborates are reliably prepared in a two-step sequence, exploiting less corrosive reagents like boric acid and the corresponding phenols. The broad scope of this transformation is demonstrated in 22 examples. Several solid-state structures reveal the preferential conformation of the phenoxy moieties allowing cation interaction. Furthermore, a novel architecture of a phenoxy-substituted tetraborate was found. Surprisingly, the tetraphenoxyborates exhibit a good stability in neutral and basic media.

Introduction

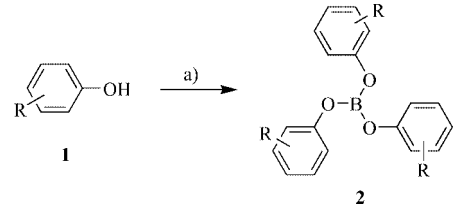
Tetracoordinated borates play an important role in nature.[1] In particular, these natural products are involved in the communication among bacterial microorganisms.[2] Size, oxophilic nature, and a maximum coordination number of four predestine boron for templating alkoxy or phenoxy moieties in an efficient manner. The synthesis and properties of tetracoordinated borates are well established, whereas the corresponding tetraphenoxy derivatives are only little explored. Tetraphenoxyborates are commonly used as bulky and inert counterions for catalysts[3] or as electrolytes in batteries.[4]

The formation of such tetragonal-coordinated compounds involves the reaction of Lewis acidic boron species with a nucleophilic phenoxy system. If very electron-deficient boranes are applied with no additional base, a tetragonal boron derivative is observed, incorporating an unusual tautomeric form of the phenolate.[5] Treatment of the corresponding phenol with boron trichloride in the presence of a nitrogen base leads to the triphenoxyborane by a direct displacement of chlorine and subsequently to the anionic tetragonal derivative. This approach requires very electron-deficient phenols and a highly corrosive boron reagent.[6] When employing sodium tetrahydridoborate as boron source in the reaction with phenol a variety of different borates is observed. Herein the counterion plays a crucial role, because the sodium cations link the borate subunits to infinite polymeric structures.[7] The stepwise formation of tetraphenoxyborates requires the prior construction of the triesters of boric acid followed by the conversion with phenolates. In order to obtain soluble phenolate equivalents of divalent cations like barium, sophisticated reagent mixtures were applied.[8] However, the direct use of barium metal ameliorated the process to barium-linked dimeric borates.[9]

We present a reliable protocol for the synthesis of a wide scope of tetraphenoxyborates. The simple two-step sequence can be performed in a one-pot process and is feasible for large quantities of the desired tetragonal boron compound.

Results and Discussion

The synthesis of tetraphenoxyborates began with the esterification of the corresponding phenol with boric acid (Scheme 1). The transformation was performed in refluxing toluene with the use of a Dean–Stark trap. With the removal of water the reaction mixture became homogeneous. The amount of water received was slightly lower than anticipated from a stoichiometric condensation reaction.



Scheme 1. a) $B(OH)_3$, toluene, 12 h reflux with a Dean–Stark trap.

Removal of the solvent under reduced pressure yielded a mixture of phenyl esters of boric acid. Mass spectrometric investigation of the crude product indicated the presence of several trigonal boron species as depicted in Figure 1.

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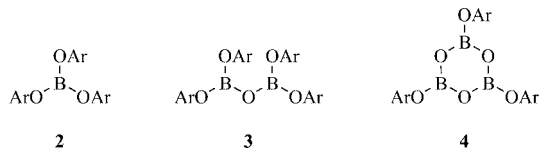
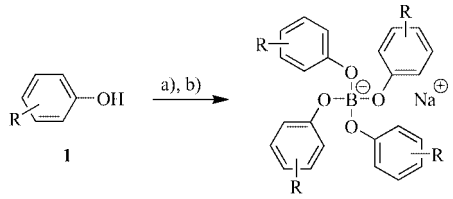


2 3 4

Figure 1. Major products by the condensation reaction of **1** with boric acid.

The presence of abundant **1** gives rise to a fast equilibrium among the ester species **2**–**4**.[10] When the crude material was carefully distilled under high vacuum (10^{-4}–10^{-5} mbar), the pure triester **2** could be obtained. However, this step turned out to be time-consuming. Furthermore, it was only feasible on smaller quantities, limited to substrates of low molecular weight and involved an unacceptable loss of material. Therefore, the crude mixture was directly subjected to the corresponding phenolate in THF (Scheme 2).



1 5

Scheme 2. a) $B(OH)_3$, toluene, 12 h reflux with a Dean–Stark trap; b) Na, **1**, THF, room temp.

THF proved to be the appropriate solvent for this particular transformation including the reaction of phenol with sodium as well as the formation of the desired tetraphenoxyborate **5**, which precipitated and could easily be isolated by simple filtration. The formation of anionic borates results in a fast equilibrium of the corresponding trigonal compounds **2**–**4** and strongly favours the formation of the mononuclear borate species **5**. Noteworthy, performing the transformation at high concentration led almost exclusively to **5**. However, application of 4-methoxyphenol in this reaction sequence yielded the desired borate **9** besides the tetranuclear borate **28** as by-product in very low yields. Fortunately, a suitable single crystal for X-ray analysis was obtained (Figure 2). Further spectroscopic investigation was not possible because not sufficient pure material of **28** was available.

Compound **28** represents an intermediate in the formation of **5** from higher aggregates similar to **3** or **4**. The molecular structure reveals a mixed tetraborate. In the centre, a trigonal boric anhydride unit is connected to three tetragonal anionic borate moieties. The tetrahedral symmetry of the borates is distorted and shows two pairs of angles

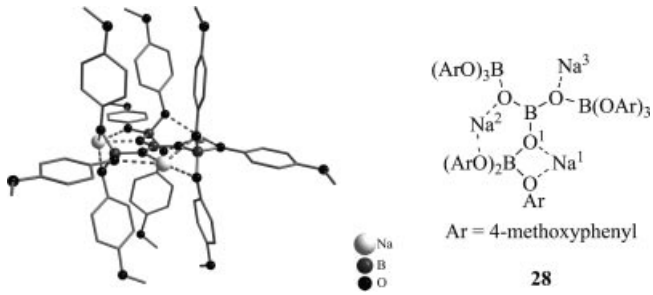


Figure 2. Left: X-ray structure of the tetraborate **28**; right: coordination pattern.

(Table 1). Three sodium cations link the borate fragments through the phenol oxygen atoms and compensate the negative charge. In addition, each sodium cation is coordinated by two THF molecules, which are omitted in Figure 2 for clarity. The architecture of the depicted tetraborate **28** is unique. Remarkably, **28** exhibits no C_3 symmetry, due to the deviated orientation of the methoxy substituents in its periphery.

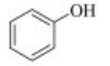
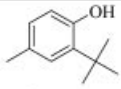
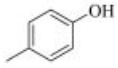
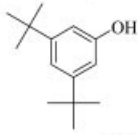
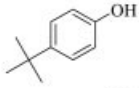
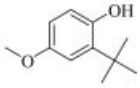
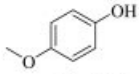
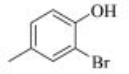
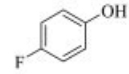
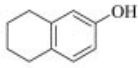
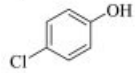
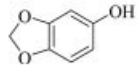
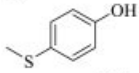
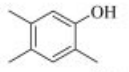
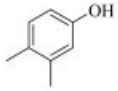
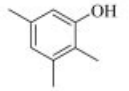
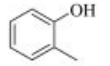
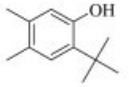
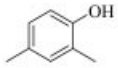
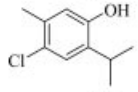
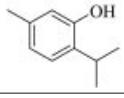
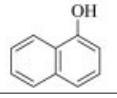
As shown in Table 2, the parent phenol (Entry 1) as well as mono-, di- and trisubstituted substrates were applied in the synthesis of their tetraphenoxyborates in moderate to excellent yields. The reaction outcome is determined by the steric demand and electronic nature of the individual phenol derivative. The conversion of *para*- and *ortho*-cresol to the corresponding borates **7** and **14**, respectively, shows a lower yield for the latter one, due to the steric demand close to the borate centre (Entries 2 and 9). This trend is reflected in the conversion of almost all *ortho*-alkyl-substituted phenols compared to the congeners with free *ortho* positions. Interestingly, thymol and 4-chlorothymol, both exhibiting an isopropyl group at C-2, provide the borates **16** and **26** in high yields (Entries 11 and 21).

Phenols with a single *tert*-butyl substituent were successfully subjected to the condensation reaction with boric acid followed by salt formation to yield **8**, **17**, **19** or **25** in good yields (Entries 3, 12, 14 and 20), whereas two *tert*-butyl groups dramatically disfavour the arrangement of four phenolates around the boron centre (Entry 13). Furthermore, electronic effects can lower the nucleophilicity of the intermediate sodium phenolate, resulting in a lower yield for the desired borate. Therefore, substrates like 4-fluorophenol, 4-chlorophenol and 2-bromo-4-methylphenol were converted into the corresponding borates **10**, **11** and **20**, respectively, in moderate yields (Entries 5, 6 and 15). In contrast, tetraphenoxyborates of electron-rich phenols were obtained in good to excellent yields (Entries 4, 7 and 17).

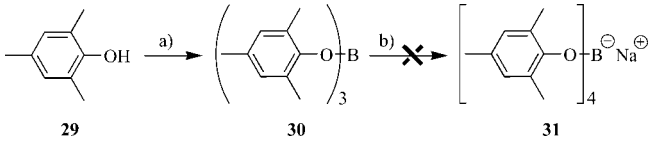
Table 1. Selected geometric parameters [Å, °] for a subunit of **28**.

B^{trig}–O^1	1.3624(1)	O–B^{trig}–O	119.542(5)
B^{tetr}–O(Ar)	1.4630(1), 1.4647(1), 1.4888(1)	B^{trig}–O^1–B^{tetr}	126.218(10)
B^{tetr}–O^1	1.4610(1)	O^1–B^{tetr}–O(Na^1)	102.450(8)
Na^1–O^1	2.3255(2)	(Na^2)O–B^{tetr}–O(Na^2)	99.389(12)
Na^1–O(Ar)	2.6439(2)	(Na^1)O–B^{tetr}–O(Na^2)	113.274(5), 115.317(5)
Na^2–O(Ar)	2.4078(2), 2.4635(2)		

Table 2. Substrates for the synthesis of tetraphenoxyborates.

Entry	Phenol	Yield borate	Entry	Phenol	Yield borate
1		82% (**6b**)	12		63% (**17**)
2		84% (**7**)	13		37% (**18**)
3		57% (**8**)	14		57% (**19**)
4		66% (**9**)	15		43% (**20**)
5		37% (**10**)	16		62% (**21**)
6		41% (**11**)	17		82% (**22**)
7		99% (**12**)	18		71% (**23**)
8		83% (**13**)	19		68% (**24**)
9		64% (**14**)	20		64% (**25**)
10		75% (**15**)	21		93% (**26**)
11		90% (**16**)	22		57% (**27**)

Phenols with two *ortho* substituents smoothly undergo the condensation reaction to the triphenoxyborane, whereas the subsequent formation of the tetraphenoxyborates was not observed (Scheme 3).

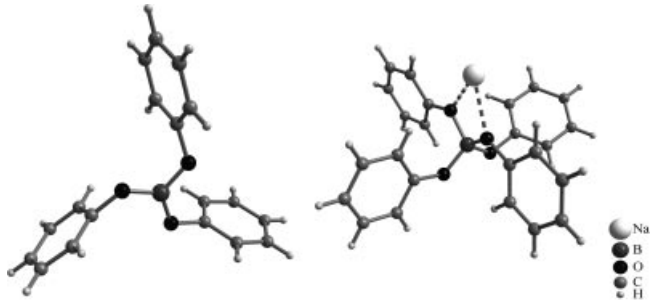


29 **30** **31**

Scheme 3. a) $B(OH)_3$, toluene, 24 h reflux with a Dean–Stark trap; b) **29**, NaH, THF.

The conversion of 2,4,6-trimethylphenol (**29**) with sodium metal was sluggish, therefore sodium hydride was employed for deprotonation. Still, the addition of **30** to the phenolate of **29** gave no indication for the formation of the sodium tetraphenoxyborate **31**. The reaction mixture was analyzed by ^{11}B NMR spectroscopy, as the signals for a trigonal and a tetragonal boron atom clearly differ from each other. Only a broad signal at δ = 15.89 ppm was observed, indicating the triphenoxyborane **30**. Remarkably, compound **30** could easily be separated from the phenolate of **29** by chilling the reaction mixture. Compound **30** was filtered off and obtained as pure colourless solid. Thus, triphenoxyboranes of phenol derivatives exhibiting two alkyl substituents in the *ortho* positions are far too shielded to undergo addition with a further phenolate equivalent.

Because suitable crystals for X-ray analysis of both, triphenoxyborane (**6a**) and the corresponding tetraphenoxyborate (**6b**) were available, a direct comparison of the structural features was possible (Figure 3). The obtained geometric data are representative for most analogues.



6a **6b**

Figure 3. Molecular structure of triphenoxyborane (**6a**) and the tetraphenoxyborate (**6b**) determined by X-ray analysis.

Triphenoxyborane (**6a**) exhibits a trigonal-planar boron centre with three phenyl units symmetrically arranged around the boron atom. The planes of the aromatic rings are oriented almost perpendicular to the BO_3 plane, resulting in a water-wheel-shaped molecule. Three almost similar distances of about 2.35 Å between the oxygen atoms of **6a** emphasise the expected C_3 symmetry of **6a**. In contrast, the tetraphenoxyborate (**6b**) reveals a slight deviation from the tetrahedral symmetry by elongation in one direction. The pair of oxygen atoms bridged by the sodium cation forms the shorter side of the tetrahedron and exhibits an interatomic distance of about 2.26 Å. Interestingly, the opposite side shows the same oxygen–oxygen distance without a coordinating counterion. The corresponding interatomic distances on the longer side are in the range of 2.44–2.48 Å. Compared to **6a**, neighboured *ortho*-carbon atoms come closer to each other up to 4.28 Å. The sodium cation in **6b** has in fact a coordination number of five. Two positions are held by phenoxy oxygen atoms, represented in Figure 3 by dashed lines. The remaining three ligands are THF molecules, which are omitted for clarity. Almost the same assembly can be found in the X-ray structure of tetraphenoxyborate **10** as shown in Figure 4. Again, THF molecules are not depicted for clarity.

The tetraphenoxyborate **10** exhibits very similar structural features compared to **6b** according to geometry and complexation of the sodium cation by the substrate and three THF molecules. In contrast, the tetranaphthoxyborate **27** (Figure 4) is no longer able to coordinate to the sodium cation itself, due to the highly crowded boron centre. Therefore, the cation is coordinated by five THF molecules

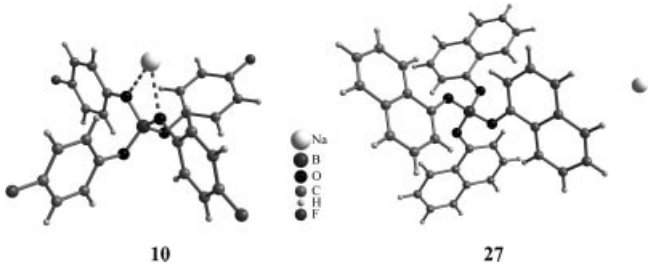


Figure 4. Molecular structures of tetraphenoxyborates **10** and **27** determined byX-ray analysis.

and reveals a boron–sodium distance of 8.97 Å, which is about 3 times longer than for **6b** or **10**. The boron–oxygen bond lengths in **27** are comparable with those observed for **6b** and **10**, whereas the distance between the phenoxy carbon atoms increases by 6% (Table 3). The oxygen atoms in **27** are almost equidistant, resulting in a consistent tetrahedral symmetry of the BO_4 unit.

Table 3. Selected geometric parameters [Å (shortest), ° (largest)] for **6a**, **6b**, **10** and **27**.

	6a	**6b**	**10**	**27**
B–O	1.3570(1)	1.4505(1)	1.4500(1)	1.4595(1)
O–Na	–	2.3422(2)	2.3469(2)	8.1432(5)
C^1–$C^{1'}$	4.1062(4)	3.5017(2)	3.4752(2)	3.6991(2)
O–B–O	120.454(20)	98.510(4)[a]	99.052(4)[a]	114.254(4)
		102.130(4)[b]	103.291(4)[b]	
		115.489(5)	114.775(4)	
B–O–C^1	122.382(15)	126.445(4)	126.102(4)	126.247(4)

[a] Sodium-bridged pair of oxygen atoms. [b] Non-bridged pair of oxygen atoms.

The geometric data for the described sodium tetraphenoxyborates correspond to earlier reports on complex architectures of sodium hydrido(phenoxy)borates concerning oxygen–boron and oxygen–sodium bond lengths as well as the angle for the sodium-chelating oxygen–boron–oxygen cleft at about 100°.[7] In contrast to sodium borates, the non-coordinating oxygen atoms in barium-linked dimeric borates span a significantly wider oxygen–boron–oxygen angle than the opposite angle between the cation-bridged oxygen atoms.[9]

It turned out that tetraphenoxyborates are much less prone to hydrolysis than the corresponding trigonal triphenoxyborane species. Consequently, **5** can be handled for short times at ambient conditions,[11] whereas the triphenyl ester of boric acid is almost immediately affected by moisture. The enhanced stability of the tetragonal boron systems is based on the saturated coordination sphere of the boron centre. However, protic media or strongly coordinating solvents like methanol or acetonitrile might affect the stability of **5**. In this context, ^{11}B NMR studies proved to be a versatile tool. Besides the chemical shift as an indicator for the electronic properties, the line full width at half maximum can individually characterize the structure of a specific borate derivative. The comparison of different triphenoxyboranes is not facile to accomplish, due to extremely broad signals. However, triphenoxyboranes and tetraphenoxyborates can easily be distinguished as presented in Figure 5.

The ^{11}B NMR spectrum of triphenoxyborane in chloroform (Figure 5, top) shows a broad signal at $\delta \approx 15$ ppm with a line full width at half maximum of 320 Hz, which represents a typical value for a trigonal boron species. When the same substrate is recorded in methanol, a shift to $\delta \approx 18$ ppm is observed accompanied by a significantly decreased line full width at half maximum of 85 Hz. Methanol is a particular solvent since an adduct formation with the ester of boric acid can occur.[12] Thus, the electrophilic boron centre experiences a tetragonal environment which is clearly supported by the NMR spectroscopic data. Interestingly, only a single species is detected revealing that no exchange of the phenolate groups occurs. When recording the corresponding tetraphenoxyborate in methanol, the protic and nucleophilic properties have no significant impact on the NMR spectroscopic data. The chemical shift as well as the line width of the signal correspond to the data collected for a THF solution. Furthermore, the typical line full width at half maximum for a tetraphenoxyborate of 20–40 Hz in THF or MeOH was also observed in acetonitrile (Figure 5, bottom).

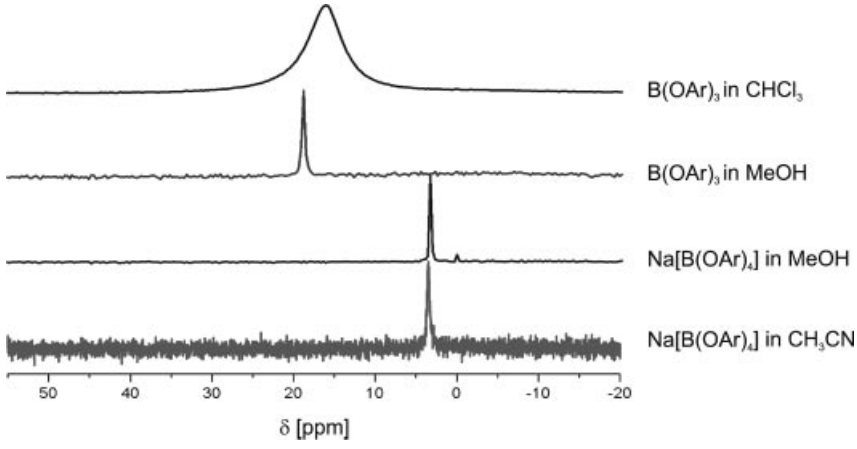


Figure 5. ^{11}B NMR studies of trigonal and tetragonal boron species (Ar = 2,4-dimethylphenyl).

Conclusion

A reliable and easy to perform two-step-one-pot sequence for the synthesis of tetraphenoxyborates was elaborated. The protocol is applicable to a broad scope of phenols and useful for larger scale as well. Interestingly, the tetraphenoxyborates exhibit a much higher stability than the trigonal congeners. Consequently, tetraphenoxyborates can be handled in methanol, THF and acetonitrile.

Furthermore, a novel tetranuclear borate system was found, consisting of trigonal and tetragonal boron moieties. The structural comparison of the corresponding tetraphenoxyborates and triphenyl esters of boric acid reveals that the tetragonal arrangement yields in a superb organisation of the *ortho* positions in the aryl moieties. Oxidative coupling reactions of these boron-templated phenolates are currently studied and will be reported in due course.

Experimental Section

General Remarks: All reagents were used in analytical grades. Solvents were desiccated if necessary by standard methods. Microanalyses were performed with a Vario EL III (Elementar-Analysensysteme, Hanau, D). ^{1}H and ^{13}C NMR spectra were recorded at 25 °C with a Bruker ARX 300, AM 360 or AMX 400. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of $CHCl_3$, [D_7]THF or CD_2HCN in the corresponding deuterated solvents. ^{11}B NMR spectra were recorded at 25 °C with a Bruker AC 200 by external calibration. Mass spectra were obtained with a Quattro LC (Waters-Micromass) or Micro TOF (Bruker) by employing ESI and HRMS (negative mode).

Triphenoxyborane (6a): Phenol (9.4 g, 0.10 mol) and boric acid (2.1 g, 0.03 mol) were suspended in toluene (50 mL) and the reaction mixture was heated for a period of 12 h (Dean–Stark trap). Toluene was removed under reduced pressure and the crude product was purified by distillation to yield a colourless oil, which solidified upon cooling; yield 5.8 g, 67%. B.p. 150 °C, $5\cdot10^{-6}$ mbar; m.p. 82 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94–6.99 (m, 3 H, 4-H), 7.00–7.04 (m, 6 H, 2-H), 7.15–7.21 (m, 6 H, 3-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.20 (C-2), 123.50 (C-4), 129.26 (C-3), 152.85 (C-1) ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 15.65 ppm. MS (EI = 70 eV): *m/z* (%) = 290.0 (100) $[M]^{+\cdot}$, 197.0 (44) $[M - C_6H_5O]^{+\cdot}$, 94.0 (75) $[C_6H_5O]^{+\cdot}$, 77.0 (81) $[C_6H_5]^{+\cdot}$.

General Procedure for the Preparation of Sodium Tetraphenoxyborates: A suspension of the corresponding phenol derivative (0.32 mol) and boric acid (0.10 mol) in toluene (200 mL) was heated for a period of 12 h (Dean–Stark trap). Toluene was removed under reduced pressure and the excess of phenol was removed by distillation, solid phenols were removed by sublimation. The crude product was dissolved in THF (40 mL) and added dropwise to a solution of the sodium phenolate, which was prepared by deprotonation of the corresponding phenol (0.09 mol) with 1 equiv. of sodium (0.09 mol) in THF (70 mL). After stirring for additional 1–12 h, the precipitated product was filtered off and washed subsequently with diethyl ether (40 mL) and pentane (40 mL). The filtrate was stored at 4 °C for another 12 h and a second crop was isolated as described above. Drying under high vacuum provided the desired products as colourless solids that were stored under inert conditions at ambient temperature. For **10**, **11**, **12**, **17**, **20**, **21** and **26** the scale of the protocol was reduced by a factor of three. All borates decomposed at temperatures above 200 °C under change of colour. The obtained tetraphenoxyborates exhibit good stability. However, the microanalyses of most borates show slight deviations from ±0.4% and therefore, HRMS data are given.[13]

Sodium Tetraphenoxyborate (6b): 33.3 g, 82%. ^{1}H NMR (300 MHz, CD_3CN): δ = 6.64–6.70 (m, 4 H, 4-H), 7.06–7.08 (m, 16 H, 2-H, 3-H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 119.26 (C-4), 120.14 (C-2), 129.64 (C-3), 158.93 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.79 ppm. HRMS: calcd. for $C_{24}H_{20}BO_4$ 383.1453 $[M - Na^+]^-$; found 383.1417.

Sodium Tetrakis(4-methylphenoxy)borate (7): 38.8 g, 84%. ^{1}H NMR (400 MHz, [D_8]THF): δ = 2.14 (s, 12 H, CH_3), 6.74–6.78 (m, 8 H, 2-H), 6.87–6.91 (m, 8 H, 3-H) ppm. ^{13}C NMR (75 MHz, [D_8]-THF): δ = 20.76 (CH_3), 120.62 (C-2), 127.56 (C-4), 129.53 (C-3), 156.62 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.34 ppm. HRMS: calcd. for $C_{28}H_{28}BO_4$ 439.2080 $[M - Na^+]^-$; found 439.2066.

Sodium Tetrakis(4-*tert*-butylphenoxy)borate (8): 35.9 g, 57%. ^{1}H NMR (300 MHz, [D_8]THF): δ = 1.22 (s, 36 H, CH_3), 6.90–6.93 (m, 8 H, 2-H), 6.99–7.02 (m, 8 H, 3-H) ppm. ^{13}C NMR (75 MHz, [D_8]-THF): δ = 32.16 (CH_3), 34.45 [$C(CH_3)_3$], 120.27 (C-2), 125.64 (C-3), 141.07 (C-4), 156.67 (C-1) ppm. ^{11}B NMR (64 MHz, [D_8]-THF): δ = 2.04 ppm. HRMS: calcd. for $C_{40}H_{52}BO_4$ 607.3971 $[M - Na^+]^-$; found 607.3979.

Sodium Tetrakis(4-methoxyphenoxy)borate (9): 34.7 g, 66%. ^{1}H NMR (300 MHz, CD_3CN): δ = 3.79 (s, 12 H, OCH_3), 6.75–6.78 (m, 8 H, arom. H), 7.07–7.10 (m, 8 H, arom. H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 56.16 (OCH_3), 114.92, 120.65 (C-2, C-3), 152.69, 153.33 (C-1, C-4) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.30 ppm. MS (ESI): *m/z* (%) = 503 (100) $[M - Na^+]^-$. $C_{28}H_{28}BNaO_8$ (526.2): calcd. C 63.90, H 5.36; found C 63.60, H 5.26.

Sodium Tetrakis(4-fluorophenoxy)borate (10): 5.9 g, 37%. ^{1}H NMR (300 MHz, CD_3CN): δ = 6.77–6.83 (m, 8 H, 2-H), 6.97–7.02 (m, 8 H, 3-H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 115.61 [d, ^2J(F,C) = 24.8 Hz, C-3], 120.79 [d, ^3J(F,C) = 7.9 Hz, C-2], 155.20 (C-1), 156.85 [d, ^1J(F,C) = 247.4 Hz, C-4] ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.66 ppm. HRMS: calcd. for $C_{24}H_{16}BF_4O_4$ 455.1072 $[M - Na^+]^-$; found 455.1103.

Sodium Tetrakis(4-chlorophenoxy)borate (11): 7.4 g, 41%. ^{1}H NMR (300 MHz, CD_3CN): δ = 6.98–7.06 (m, 16 H, 2-H, 3-H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 121.51 (C-2), 123.41 (C-4), 129.38 (C-3), 157.75 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.57 ppm. HRMS: calcd. for $C_{24}H_{16}BCl_4O_4$ 517.9927 $[M - Na^+]^-$; found 517.9906.

Sodium Tetrakis(4-methylthiophenoxy)borate (12): 19.5 g, 99%. ^{1}H NMR (400 MHz, CD_3CN): δ = 2.05 (s, 12 H, SCH_3), 6.64–6.70 (m, 16 H, 2-H, 3-H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 18.37 (SCH_3), 120.85 (C-2), 126.78 (C-3), 130.66 (C-4), 157.09 (C-1) ppm. ^{11}B NMR (128 MHz, CD_3CN): δ = 4.07 ppm. HRMS: calcd. for $C_{28}H_{28}BO_4S_4$ 567.0969 $[M - Na^+]^-$; found 567.0955.

Sodium Tetrakis(3,4-dimethylphenoxy)borate (13): 43.0 g, 83%. ^{1}H NMR (300 MHz, CD_3CN): δ = 2.04 (s, 12 H, 4-CH_3), 2.07 (s, 12 H, 3-CH_3), 6.72–6.76 (m, 8 H, 5-H, 6-H), 6.78 (s, 4 H, 2-H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 18.84 (3-CH_3), 20.18 (4-CH_3), 117.27 (C-6), 121.35 (C-2), 126.54 (C-4), 130.49 (C-5), 137.19 (C-3), 156.94 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.60 ppm. HRMS: calcd. for $C_{32}H_{36}BO_4$ 495.2718 $[M - Na^+]^-$; found 495.2720.

Sodium Tetrakis(2-methylphenoxy)borate (14): 29.6 g, 64%. ^{1}H NMR (400 MHz, [D_8]THF): δ = 2.10 (s, 12 H, CH_3), 6.51 [dd,

$^3J_{3,4}$(H,H) = $^3J_{4,5}$(H,H) = 7.4 Hz, 4 H, 4-H], 6.76 [ddd, $^3J_{4,5}$(H,H) = 7.4 Hz, $^3J_{5,6}$(H,H) = 8.4 Hz, $^4J_{3,5}$ = 1.6 Hz, 4 H, 5-H], 6.87 [d, $^3J_{3,4}$(H,H) = 7.4 Hz, 4 H, 3-H], 7.19 [d, $^3J_{5,6}$(H,H) = 8.4 Hz, 4 H, 6-H] ppm. ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 17.78 (CH_3), 118.86 (C-4), 120.59 (C-6), 126.38 (C-5), 129.11 (C-2), 130.19 (C-3), 157.55 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.92 ppm. HRMS: calcd. for $C_{28}H_{28}BO_4$ 439.2080 [M – Na$^+$]$^-$; found 439.2065.

Sodium Tetrakis(2,4-dimethylphenoxy)borate (15): 38.9 g, 75%. ^{1}H NMR (360 MHz, [D$_8$]THF): δ = 2.03 (s, 12 H, 2-CH_3), 2.10 (s, 12 H, 4-CH_3), 6.55 [dd, $^3J_{5,6}$(H,H) = 8.3 Hz, $^4J_{3,5}$(H,H) = 1.8 Hz, 4 H, 5-H], 6.68 [d, $^4J_{3,5}$(H,H) = 1.8 Hz, 4 H, 3-H], 6.98 [d, $^3J_{5,6}$(H,H) = 8.3 Hz, 4 H, 6-H] ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 17.56 (2-CH_3), 20.57 (4-CH_3), 119.06 (C-6), 126.49 (C-5), 127.02 (C-2), 127.94 (C-4), 131.05 (C-3), 155.62 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 3.21 ppm. HRMS: calcd. for $C_{32}H_{36}BO_4$ 494.2737 [M – Na$^+$]$^-$; found 494.2785.

Sodium Tetrakis[5-methyl-2-(1-methylethyl)phenoxy]borate (16): 56.8 g, 90%. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.35 [d, ^3J(H,H) = 6.9 Hz, 24 H, CH(CH_3)$_2$], 2.23 (s, 12 H, 5-CH_3), 3.64 [sept, ^3J(H,H) = 6.9 Hz, 4 H, CH(CH_3)$_2$], 6.48 [d, $^3J_{3,4}$(H,H) = 7.8 Hz, 4 H, 4-H], 6.99 [d, $^3J_{3,4}$(H,H) = 7.5 Hz, 4 H, 3-H], 7.52 (s, 4 H, 6-H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 21.62 [CH(CH_3)$_2$], 23.79 [CH(CH$_3$)$_2$], 27.98 (5-CH_3), 118.24 (C-6), 120.22 (C-4), 125.64 (C-3), 135.16 (C-2), 135.55 (C-5), 156.98 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 3.22 ppm. HRMS: calcd. for $C_{40}H_{52}BO_4$ 607.3971 [M – Na$^+$]$^-$; found 607.3981.

Sodium Tetrakis(2-*tert*-butyl-4-methylphenoxy)borate (17): 14.4 g, 63%. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 1.58 [s, 36 H, C(CH_3)$_3$], 2.04 (s, 12 H, CH_3), 6.40 [dd, $^3J_{5,6}$(H,H) = 8.6 Hz, $^4J_{3,5}$(H,H) = 2.1 Hz, 4 H, 5-H], 6.70 [d, $^4J_{3,5}$(H,H) = 2.1 Hz, 4 H, 3-H], 7.64 [d, $^3J_{5,6}$(H,H) = 8.6 Hz, 4 H, 6-H] ppm. ^{13}C NMR (100 MHz, [D$_8$]-THF): δ = 21.20 (CH_3), 31.47 [C(CH$_3$)$_3$], 35.42 [C(CH$_3$)$_3$], 120.21 (C-6), 123.29 (C-3), 125.98 (C-5), 126.62 (C-4), 136.99 (C-2), 156.04 (C-1) ppm. ^{11}B NMR (128 MHz, [D$_8$]THF): δ = 4.87 ppm. HRMS: calcd. for $C_{44}H_{60}BO_4$ 663.4590 [M – Na$^+$]$^-$; found 663.4571.

Sodium Tetrakis(3,5-di-*tert*-butylphenoxy)borate (18): 31.6 g, 37%. ^{1}H NMR (300 MHz, CD_3CN): δ = 1.21 [s, 72 H, C(CH_3)$_3$], 6.71 [d, $^4J_{2,4}$(H,H) = 1.5 Hz, 4 H, 4-H], 6.98 [d, $^4J_{2,4}$(H,H) = 1.5 Hz, 8 H, 2-H] ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 32.13 [C(CH$_3$)$_3$], 35.47 [C(CH$_3$)$_3$], 112.63 (C-2), 114.86 (C-4), 151.49 (C-3), 159.14 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.75 ppm. HRMS: calcd. for $C_{56}H_{84}BO_4$ 831.6468 [M – Na$^+$]$^-$; found 831.6431.

Sodium Tetrakis(2-*tert*-butyl-4-methoxyphenoxy)borate (19): 42.8 g, 57%. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.57 [s, 36 H, C(CH_3)$_3$], 3.56 (s, 12 H, OCH_3), 6.29 [dd, $^3J_{5,6}$(H,H) = 8.8 Hz, $^4J_{3,5}$(H,H) = 2.6 Hz, 4 H, 5-H], 6.64 [d, $^4J_{3,5}$(H,H) = 2.6 Hz, 4 H, 3-H], 7.64 [d, $^3J_{5,6}$(H,H) = 8.8 Hz, 4 H, 6-H] ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 31.15 [C(CH$_3$)$_3$], 35.91 (OCH_3), 56.45 [C(CH$_3$)$_3$], 110.77 (C-5), 113.98 (C-6), 120.18 (C-3), 139.29 (C-2), 151.73 (C-1), 152.34 (C-4) ppm. ^{11}B NMR (128 MHz, CD_3CN): δ = 2.99 ppm. HRMS: calcd. for $C_{44}H_{60}BO_8$ 727.4387 [M – Na$^+$]$^-$; found 727.4364.

Sodium Tetrakis(2-bromo-4-methylphenoxy)borate (20): 11.1 g, 43%. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 2.12 (s, 12 H, CH_3), 6.78 [dd, $^3J_{5,6}$(H,H) = 8.4 Hz, $^4J_{3,5}$(H,H) = 1.7 Hz, 4 H, 5-H], 7.13 [d, $^4J_{3,5}$(H,H) = 1.7 Hz, 4 H, 3-H], 7.46 [d, $^3J_{5,6}$(H,H) = 8.4 Hz, 4 H, 6-H] ppm. ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 20.26 (CH_3), 114.29 (C-2), 120.95(C-6), 129.29 (C-5), 129.82 (C-4), 132.96 (C-3), 152.24 (C-1) ppm. ^{11}B NMR (128 MHz, [D$_8$]THF): δ = 2.12 ppm. HRMS: calcd. for $C_{28}H_{24}BBr_4O_4$ 750.8507 [M – Na$^+$]$^-$; found 750.8503.

Sodium Tetrakis(5,6,7,8-tetrahydro-2-naphthoxy)borate (21): 12.9 g, 62%. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 1.79 (m, 16 H, 7-H, 6-H), 2.67 (m, 16 H, 8-H, 5-H), 6.54 [d, $^4J_{1,3}$(H,H) = 1.7 Hz, 4 H, 1-H], 6.75 [dd, $^3J_{3,4}$(H,H) = 8.4 Hz, $^4J_{1,3}$(H,H) = 1.7 Hz, 4 H, 3-H], 6.88 [d, $^3J_{3,4}$(H,H) = 8.4 Hz, 4 H, 4-H] ppm. ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 26.68, 29.72 (C-6, C-7), 29.83, 30.76 (C-5, C-8), 118.84 (C-3), 121.26 (C-1), 127.11 (C-4), 129.53 (C-4a), 137.06 (C-8a), 156.88 (C-2) ppm. ^{11}B NMR (100 MHz, [D$_8$]THF): δ = 3.99 ppm. HRMS: calcd. for $C_{40}H_{44}BO_4$ 599.3338 [M – Na$^+$]$^-$; found 599.3312.

Sodium Tetrakis(1,3-benzodioxol-5-yloxy)borate (22): 47.7 g, 82%. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 5.83 (s, 8 H, OCH_2O), 6.48 [dd, $^3J_{6,7}$(H,H) = 8.4 Hz, $^4J_{4,6}$(H,H) = 2.2 Hz, 4 H, 6-H], 6.55 [d, $^3J_{6,7}$(H,H) = 8.4 Hz, 4 H, 7-H], 6.74 [d, $^4J_{4,6}$(H,H) = 2.2 Hz, 4 H, 4-H] ppm. ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 101.39 (OCH_2O), 102.96 (C-4), 107.88 (C-6), 112.00 (C-7), 141.09 (C-7a), 148.50 (C-3a), 153.88 (C-5) ppm. ^{11}B NMR (128 MHz, [D$_8$]THF): δ = 4.03 ppm. HRMS: calcd. for $C_{28}H_{20}BO_{12}$ 559.1053 [M – Na$^+$]$^-$; found 559.1033.

Sodium Tetrakis(2,4,5-trimethylphenoxy)borate (23): 40.8 g, 71%. ^{1}H NMR (300 MHz, CD_3CN): δ = 2.03 (s, 12 H, 5-CH_3), 2.04 (s, 12 H, 4-CH_3), 2.09 (s, 12 H, 2-CH_3), 6.67 (s, 4 H, 3-H), 7.19 (s, 4 H, 6-H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 17.22 (2-CH_3), 18.94 (4-CH_3), 19.99 (5-CH_3), 121.08 (C-6), 125.16 (C-4), 124.43 (C-2), 131.72 (C-3), 133.88 (C-5), 155.99 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.85 ppm. HRMS: calcd. for $C_{36}H_{44}BO_4$ 551.3344 [M – Na$^+$]$^-$; found 551.3342.

Sodium Tetrakis(2,3,5-trimethylphenoxy)borate (24): 39.1 g, 68%. ^{1}H NMR (300 MHz, CD_3CN): δ = 2.06 (s, 12 H, 5-CH_3), 2.07 (s, 12 H, 3-CH_3), 2.11 (s, 12 H, 2-CH_3), 6.25 (s, 4 H, 6-H), 7.14 (s, 4 H, 4-H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 12.54 (2-CH_3), 20.63 (3-CH_3), 21.59 (5-CH_3), 118.11 (C-6), 120.43 (C-4), 123.61 (C-2), 134.67 (C-3), 136.67 (C-5), 157.95 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 2.99 ppm. HRMS: calcd. for $C_{36}H_{44}BO_4$ 551.3344 [M – Na$^+$]$^-$; found 551.3352.

Sodium Tetrakis(2-*tert*-butyl-4,5-dimethylphenoxy)borate (25): 47.5 g, 64%. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 1.63 [s, 36 H, C(CH_3)$_3$], 1.91 (s, 12 H, 5-CH_3), 1.93 (s, 12 H, 4-CH_3), 6.63 (s, 4 H, 3-H), 7.61 (s, 4 H, 6-H) ppm. ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 19.08 (5-CH_3), 19.33 (4-CH_3), 31.80 [C(CH$_3$)$_3$], 35.24 [C-(CH$_3$)$_3$], 121.70 (C-6), 121.76 (C-5), 126.70 (C-3), 132.81 (C-4), 134.81 (C-2), 156.17 (C-1) ppm. ^{11}B NMR (64 MHz, [D$_8$]THF): δ = 2.75 ppm. HRMS: calcd. for $C_{48}H_{68}BO_4$ 719.5205 [M – Na$^+$]$^-$; found 719.5225.

Sodium Tetrakis[4-chloro-5-methyl-2-(1-methylethyl)phenoxy]borate (26): 23.8 g, 93%. ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 1.18 [d, ^3J(H,H) = 6.9 Hz, 24 H, CH(CH_3)$_2$], 2.09 (s, 12 H, 5-CH_3), 3.47 [sept, ^3J(H,H) = 6.9 Hz, 4 H, CH(CH_3)$_2$], 6.80 (s, 4 H, 3-H), 7.42 (s, 4 H, 6-H) ppm. ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 20.00 (5-CH_3), 22.93 [CH(CH$_3$)$_2$], 28.09 [CH(CH$_3$)$_2$], 121.76 (C-6), 121.82 (C-4), 125.58 (C-3), 132.05 (C-2), 137.62 (C-5), 155.53 (C-1) ppm. ^{11}B NMR (64 MHz, [D$_8$]THF): δ = 2.54 ppm. HRMS: calcd. for $C_{40}H_{48}BCl_4O_4$ 743.2405 [M – Na$^+$]$^-$; found 743.2378.

Sodium Tetrakis(1-naphthoxy)borate (27): Boric acid (0.62 g, 0.01 mol) was added to a solution of 1-naphthol (4.61 g, 0.032 mol) in toluene (40 mL) and the reaction mixture was heated for 12 h (Dean–Stark trap). Toluene was removed under reduced pressure and the crude product was dissolved in THF (15 mL). First, 1-naphthol (1.33 g, 0.9 mol) and then sodium hydride (0.37 g, 60% suspension in paraffin, 0.9 mol) was added to the solution at 0 °C. After completion of the reaction, the solution was stored at 4 °C

for 12 h. The precipitated product was isolated by filtration and subsequent washing with diethyl ether (5 mL) and pentane (5 mL); yield: 3.4 g, 57%. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.13–7.18 (m, 8 H, 7-H and 8-H), 7.36–7.41 (m, 8 H, 4-H and 5-H), 7.67–7.72 (m, 8 H, 2-H and 6-H), 8.55–8.57 (m, 4 H, 3-H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 112.28 (C-2), 117.60 (C-8), 124.58 (C-3), 124.74 (C-5), 126.30 (C-4), 127.74 (C-7 and C-8a), 128.14 (C-6), 135.92 (C-4a), 155.63 (C-1) ppm. ^{11}B NMR (64 MHz, CD_3CN): δ = 4.05 ppm. HRMS: calcd. for $C_{40}H_{28}BO_4$ 583.2086 $[M - Na^+]^-$; found 583.2090.

Tris(2,4,6-trimethylphenoxy)borane (30): 2,4,6-Trimethylphenol (**29**) (15 g, 0.11 mol) and boric acid (2.1 g, 0.03 mol) were suspended in toluene (100 mL) and the reaction mixture was heated for a period of 24 h (Dean–Stark trap). Toluene was distilled off under reduced pressure and excess of **29** was removed by sublimation. The crude product was purified by crystallisation in toluene to yield a colourless solid; yield 9.1 g, 64%; m.p. 245 °C (toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 9 H, 4-CH_3), 2.28 (s, 18 H, 2-CH_3 and 6-CH_3), 6.80 (s, 6 H, 3-H and 5-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.95 (2-CH_3 and 6-CH_3), 20.59 (4-CH_3), 127.71 (C-2 and C-6), 129.15 (C-3 and C-5), 132.45 (C-4), 148.26 (C-1) ppm. ^{11}B NMR (64 MHz, $CDCl_3$): δ = 15.89. MS (EI = 70 eV): *m*/*z* (%) = 416.2 (100) $[M]^{+\cdot}$, 281.2 (12) $[M - (CH_3)_3C_6H_2O]^{+\cdot}$.

X-ray Crystal Structure Analysis for 6a: $C_{18}H_{15}BO_3$ (290.11), colourless crystal 0.30 × 0.25 × 0.15 mm, a = 11.650(1), b = 15.897(2), c = 19.724(2) Å, α = 113.31(1), β = 106.59(1), γ = 90.19(1)°, V = 3186.9(6) Å^3, $\rho_{calcd.}$ = 1.209 g cm^{-3}, μ = 0.648 mm^{-1}, empirical absorption correction based on ψ scan data (0.829 ≤ T ≤ 0.909), Z = 8, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223 K, ω/2θ scans, 13476 reflections collected (±h, +k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 12986 independent (R_{int} = 0.043) and 8143 observed reflections [$I \geq 2\sigma(I)$], 794 refined parameters, R = 0.049, wR_2 = 0.143, max. residual electron density 0.23 (–0.27) e·Å^{-3}, four almost identical independent molecules in the asymmetric unit, hydrogen atoms calculated and refined as riding atoms.

X-ray Crystal Structure Analysis for 6b: $C_{36}H_{44}BNaO_7$ (622.51), colourless crystal 0.70 × 0.50 × 0.30 mm, a = 18.299(1), b = 9.803(1), c = 19.287(1) Å, β = 100.09(1)°, V = 3406.3(4) Å^3, $\rho_{calcd.}$ = 1.214 g cm^{-3}, μ = 0.772 mm^{-1}, empirical absorption correction (0.614 ≤ T ≤ 0.801), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 1.54178 Å, T = 223 K, ω and φ scans, 25313 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 5816 independent (R_{int} = 0.055) and 4546 observed reflections [$I \geq 2\sigma(I)$], 481 refined parameters, R = 0.051, wR_2 = 0.153, max. residual electron density 0.30 (–0.27) e·Å^{-3}, two of the three THF solvent molecules are disordered and refined with split positions, hydrogen atoms calculated and refined as riding atoms.

X-ray Crystal Structure Analysis for 10: $C_{36}H_{40}BF_4NaO_7$ (694.48), colourless crystal 0.60 × 0.60 × 0.45 mm, a = 12.955(1), b = 17.126(1), c = 16.242(1) Å, β = 99.17(1)°, V = 3557.5(4) Å^3, $\rho_{calcd.}$ = 1.297 g cm^{-3}, μ = 0.963 mm^{-1}, empirical absorption correction (0.596 ≤ T ≤ 0.671), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 1.54178 Å, T = 223 K, ω and φ scans, 10815 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 6038 independent (R_{int} = 0.026) and 4264 observed reflections [$I \geq 2\sigma(I)$], 443 refined parameters, R = 0.053, wR_2 = 0.163, max. residual electron density 0.38 (–0.32) e· Å^{-3}, the THF solvent molecules are partly disordered, refinement with split positions did not improve the model, hydrogen atoms calculated and refined as riding atoms.

X-ray Crystallography Study: Data sets were collected with Enraf Nonius CAD4 and Nonius KappaCCD diffractometers. For the programs used see ref.[14] CCDC-285239 to -285243 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.

X-ray Crystal Structure Analysis for 27: $C_{60}H_{68}BNaO_9$ (966.94), colourless crystal 0.30 × 0.25 × 0.15 mm, a = 17.904(1), b = 17.710(1), c = 16.789(1) Å, β = 91.69(1)°, V = 5321.1(5) Å^3, $\rho_{calcd.}$ = 1.207 g cm^{-3}, μ = 0.703 mm^{-1}, empirical absorption correction (0.817 ≤ T ≤ 0.902), Z = 4, monoclinic, space group $C2/c$ (no. 15), λ = 1.54178 Å, T = 223 K, ω and φ scans, 16055 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 4362 independent (R_{int} = 0.034) and 2748 observed reflections [$I \geq 2\sigma(I)$], 323 refined parameters, R = 0.075, wR_2 = 0.258, max. residual electron density 0.56 (–0.28) e·Å^{-3}, the THF solvent molecules are heavily disordered, refinement with split positions did not improve the model, hydrogen atoms calculated and refined as riding atoms.

X-ray Crystal Structure Analysis for 28: $C_{87}H_{111}B_4Na_3O_{27}$ (1700.97), colourless crystal 0.40 × 0.30 × 0.30 mm, a = 14.658(1), b = 16.913(1), c = 19.312(1) Å, α = 85.15(1), β = 87.80(1), γ = 70.01(1)°, V = 4482.9(5) Å^3, $\rho_{calcd.}$ = 1.260 g cm^{-3}, μ = 0.878 mm^{-1}, empirical absorption correction (0.720 ≤ T ≤ 0.779), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223 K, ω and φ scans, 17206 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 14334 independent (R_{int} = 0.040) and 10777 observed reflections [$I \geq 2\sigma(I)$], 1156 refined parameters, R = 0.055, wR_2 = 0.164, max. residual electron density 0.33 (–0.25) e· Å^{-3}, C67 and THF molecule O211–C215 disordered and refined with split positions, hydrogen atoms calculated and refined as riding atoms.

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