Supporting Information

for

$Na[B(hfip)_4]$ (hfip = $OC(H)(CF_3)_2$): A Weakly Coordinating Anion Salt and its First Application to Prepare Ionic Liquids

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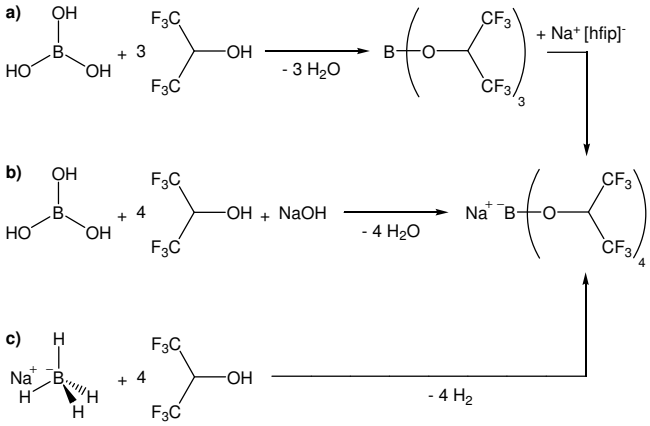
1 Synthesis and Characterization of $Na^+[B(hfip)_4]^-.(Solvent)_x$

The synthesis of $Na^+[B(hfip)_4]^-$ was investigated by three reaction pathways (Scheme S1).



Scheme S1: The three pathways tested for the synthesis of the $Na^+[B(hfip)_4]^-$ salt. **a)** Using boric acid, hfipH and $Na^+[hfip]^-$ in two reaction steps, **b)** Using boric acid, hfipH and NaOH in a batch reaction, **c)** Using $NaBH_4$ and hfipH in a one pot reaction.

a) With Boric Acid, hfipH and $Na^+[hfip]^-$ as Starting Materials

In the first step, the Lewis acid $[B(hfip)_3]$ should be synthesized using boric acid and hfipH as starting materials (Scheme S1a). The synthesis of $[B(hfip)_3]$ using the more expensive borane-methyl sulfide complex $[BH_3.S(CH_3)_2]$ and hfipH was already reported,[1] but we hoped for an easier and cheaper synthesis of $[B(hfip)_3]$. From $[B(hfip)_3]$ and known $Na^+[hfip]^-$,[2, 3] the $Na^+[B(hfip)_4]^-$ salt should be prepared.

Table S1: Preparation attempts of $[B(hfip)_3]$ according Scheme S1a using several solvents and reaction-conditions.

Nr.	$n_{(boric\ acid)}$:$n_{(hfipH)}$	Solvent	Remarks
(1)	1:5	none	hfipH was added to the boric acid. Immediate heating of the reaction flask was observed. The reaction mixture was stirred for 48 h at r.t.
(2)	1:8	none	hfipH was added to the boric acid. Immediate heating of the reaction flask was observed. The reaction mixture was refluxed for 4 h.
(3)	1:4.5	water	hfipH was added dropwise to a solution of boric acid in water. Immediate heating of the reaction flask was observed. The reaction mixture was stirred for 6 h at r.t.

b) With Boric Acid, hfipH and NaOH as Starting Materials – Batch Reactions

The preparation of $Na^+[B(hfip)_4]^-$ was also tested from boric acid, hfipH and NaOH as starting materials. In Table S2, the batch reactions carried out in various solvents are summarized.

Table S2: Preparation attempts of $Na^+[B(hfip)_4]^-$ according Scheme S1b using several solvents and conditions.

Nr.	$n_{(boric\ acid)}$:$n_{(NaOH)}$:$n_{(hfipH)}$	Solvent	Remarks
(4)	1:1:4.5	water	hfipH was added dropwise to a solution/suspension of boric acid and NaOH in the solvent used. Immediate heating of the reaction flask was observed. The reaction mixture was stirred for 24 h at r.t.
(5)	1:1:4.5	hexane	
(6)	1:1:4.5	CH_3CN	

All reactions given in Table S1 and Table S2 were studied by multinuclear NMR, but no formation of $[B(hfip)_3]$ or $[B(hfip)_4]^-$ was observed. The product of reaction 1 in Table S1 was also investigated by ESI- and APCI-MS, but no signals for the expected products were observed and the high number of signals suggests that several products are generated by this reaction. In conclusion, we have to note that the synthesis of $[B(hfip)_3]$ or $Na^+[B(hfip)_4]^-$ according to Scheme S1a-b and using boric acid as a starting material were not successful.

c) With $NaBH_4$ and hfipH as Starting Materials

The next tested synthesis of $Na^+[B(hfip)_4]^-$ started from $NaBH_4$ and hfipH (Scheme S1c). The synthesis of $Li^+[Al(OR^F)_4]^-$ (R^F = $C(H)(CF_3)_2$, $C(CH_3)(CF_3)_2$ or $C(CF_3)_3$) works well using $LiAlH_4$ and the fluorinated alcohol as starting materials in hexane or heptane as reaction medium.[4] Non-polar solvents are very helpful for an easy separation of the products after reaction. However, here we found two distinct differences between the synthesis of aluminate and borate salts: *i*) the basicity of the hydrides in $[BH_4]^-$ is lower than that in $[AlH_4]^-$; *ii*) boron is smaller than aluminum and thus a higher steric impediment can be expected when binding four large alkoxy groups to a central boron atom.

Both differences are negative for the synthesis of the $Na^+[B(hfip)_4]^-$ salt: Uncompleted conversions of the substitution of the fourth hydride of $NaBH_4$ were observed in many cases (see Table S3; ^{11}B- and ^{19}F-NMR analysis). ^{11}B-NMR is very helpful and allows for an easy differentiation between the intermediate $Na^+[H\text{-}B(hfip)_3]^-$ and the desired $Na^+[B(hfip)_4]^-$ product through the $^1J(B, H)$ and the $^3J(B, H)$ coupling constants. In all reactions given in Table S3, except that in hexane, the first three hydrides reacted fast and completely. However,

in ether solvents with long reflux times the main product was $Na^+[B(hfip)_4]^-$, and $Na^+[H\text{-}B(hfip)_3]^-$ was observed only as an intermediate.

Table S3: Attempts for the synthesis of $Na^+[B(hfip)_4]^-$ according Scheme S1c by using various solvents; their boiling points T_b, reaction-conditions and the conversions for main product and intermediate.

Nr.	$n_{(NaBH4)}$:$n_{(hfipH)}$	**Solvent**[a]	T_b [°C]	**Refluxing-time [h]**	**Conversion [%]**[b] $Na^+[H\text{-}B(hfip)_3]^-$	$Na^+[B(hfip)_4]^-$
(7)	1:25	none	59[c]	6	47	53
(8)	1:4.5	*n*-hexane	69	6	11	< 1[d]
(9)	1:4.5	Et_2O	35	60[e]	41	59
(10)	1:4.5	THF	66	40[f]	–	100
(11)	1:4.5	DME	85	4	–	100

[a] Et_2O: diethyl ether, THF: tetrahydrofuran, DME: 1,2-dimethoxyethane. [b] The conversions were determined from the integrals of the corresponding signals in the ^{11}B-NMR spectra. [c] T_b of hfipH, which was used in high excess in reaction 7. [d] The remaining $NaBH_4$ (88%) did not react. [e] The reaction lasted 7 d, altogether 60 h under reflux and was stirred in the remaining time at r.t. [f] The reaction lasted 36 d, altogether 40 h under reflux and was stirred in the remaining time at r.t.

In the reactions 7 to 9 in Table S3, no complete conversions were observed. The reaction in *n*-hexane gives the lowest conversion and in contrast to the reactions in other solvents a high amount (88%) of non-reacted $NaBH_4$ was observed. Due to the non-solubility and low basicity of $NaBH_4$ in *n*-hexane, the reaction was slow and incomplete. The 34 °C lower boiling donor solvent Et_2O that dissolves $NaBH_4$ allows for a better conversion, but the reaction does not go to completion (cf. Figure S1, reaction in Et_2O monitored by ^{11}B-NMR analysis).

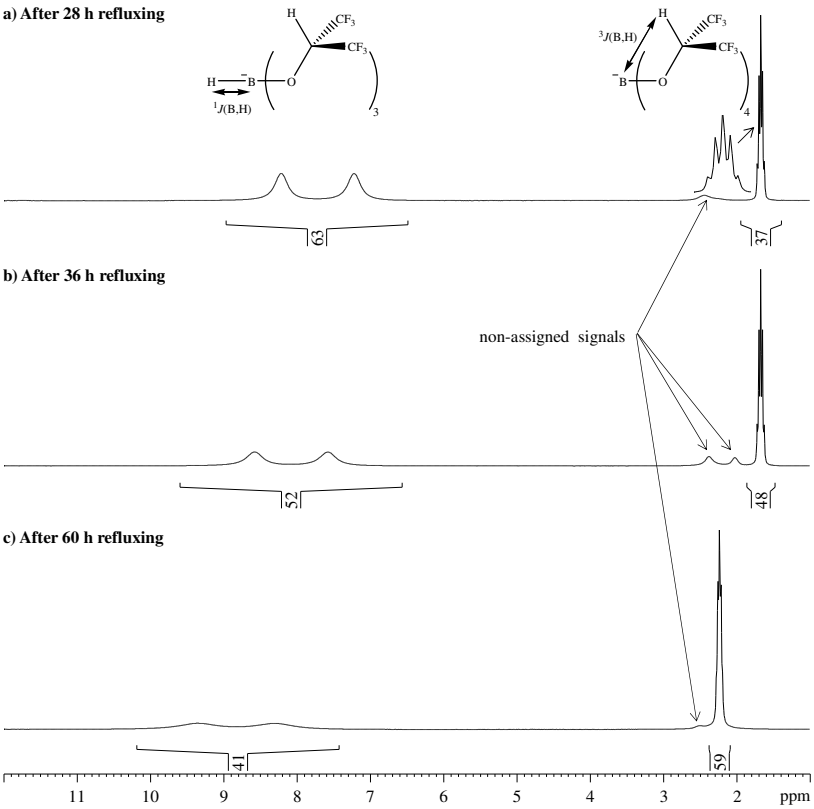


Figure S1: ^{11}B-NMR spectra during the reaction of $NaBH_4$ and hfipH according to Scheme S1c in Et_2O (reaction 9 in Table S3). [D_6]acetone for a) and b), and CD_2Cl_2 for c) were used as NMR solvents. Under each signal, the integral value given corresponds to the percentage of $Na^+[BH(hfip)_3]^-$ (doublet, higher chemical shift) and $Na^+[B(hfip)_4]^-$ (quintet, lower chemical shift), respectively.

Aside from $[H\text{-}B(hfip)_3]^-$ and $[B(hfip)_4]^-$ species, we recognize in the ^{11}B-NMR spectra (Figure S1) other non-assigned boron species of minor intensities, which appear and disappear in the course of the reaction. THF provides comparable solubilities as Et_2O, but boils 31 °C higher and thus reaction 10 in THF leads to completion after 40 h reflux. 1,2-dimethoxyethane (DME), offers both, very good solubilities for $NaBH_4$ / intermediates and an even higher b.p. of 85 °C, so that complete conversion was observed in only 4 h.

2 NMR Spectra of $Na^+[B(hfip)_4]^-.(THF)_2$ (1) and $Na^+[B(hfip)_4]^-.(DME)$ (2)

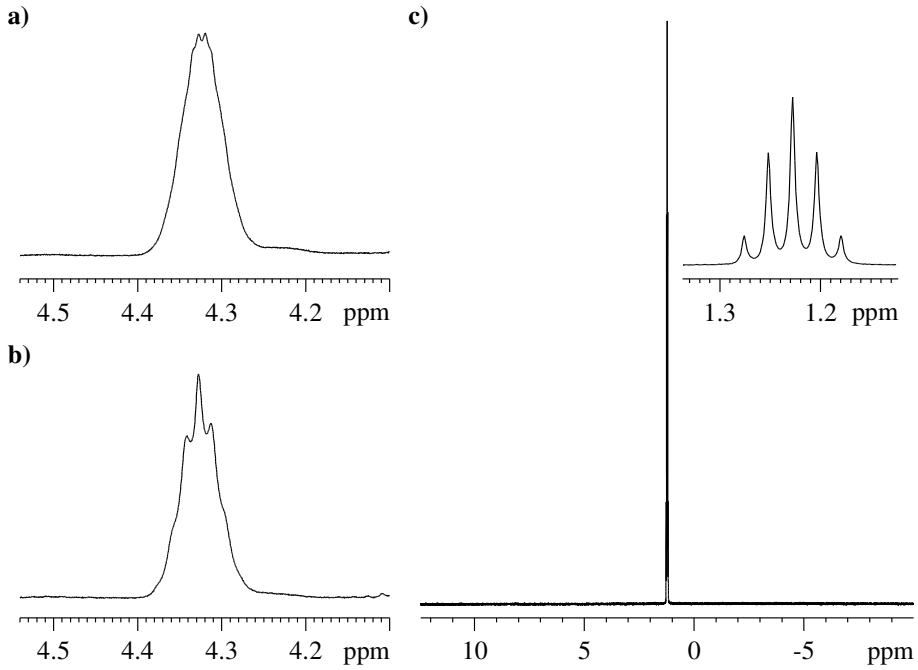


Figure S2: a) ^{1}H-, **b)** ^{1}H{^{11}B}- and **c)** ^{11}B-NMR spectra of **1** in $CDCl_3$.

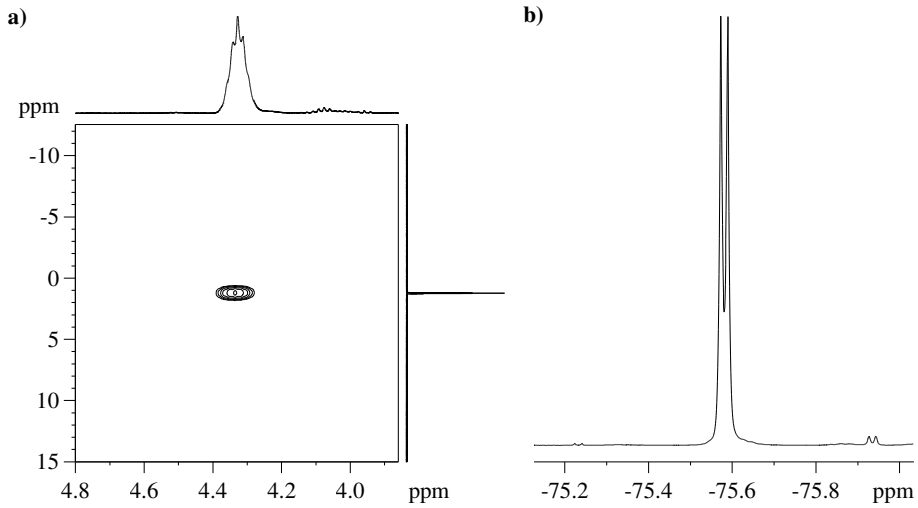


Figure S3: a) ^{11}B, ^{1}H HSQC- and **b)** ^{19}F-NMR spectra of **1** in $CDCl_3$.

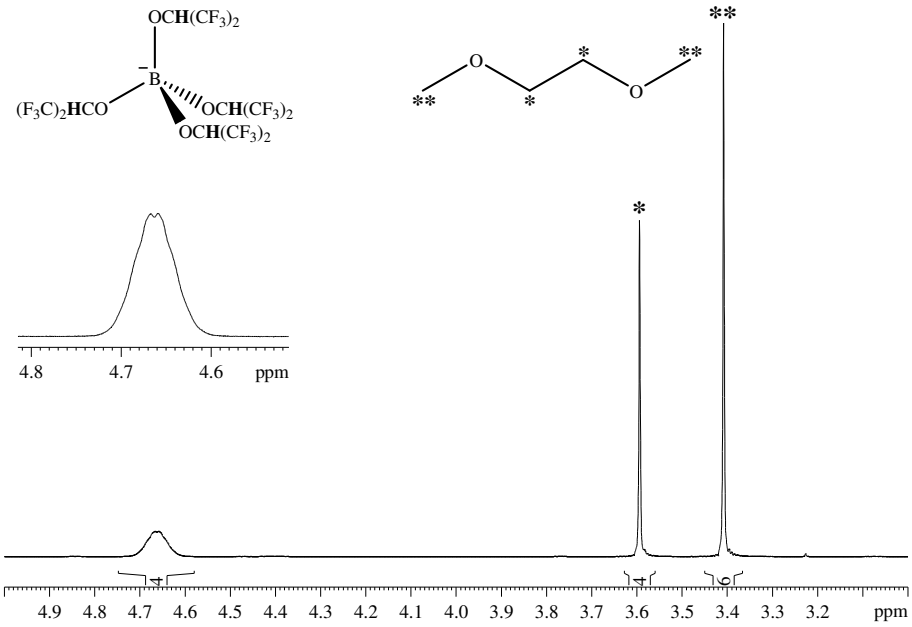


Figure S4: ^{1}H-NMR spectrum of **2** in $CDCl_3$ after 10 h drying in vacuum (0.1 Pa) at 40–45 °C.

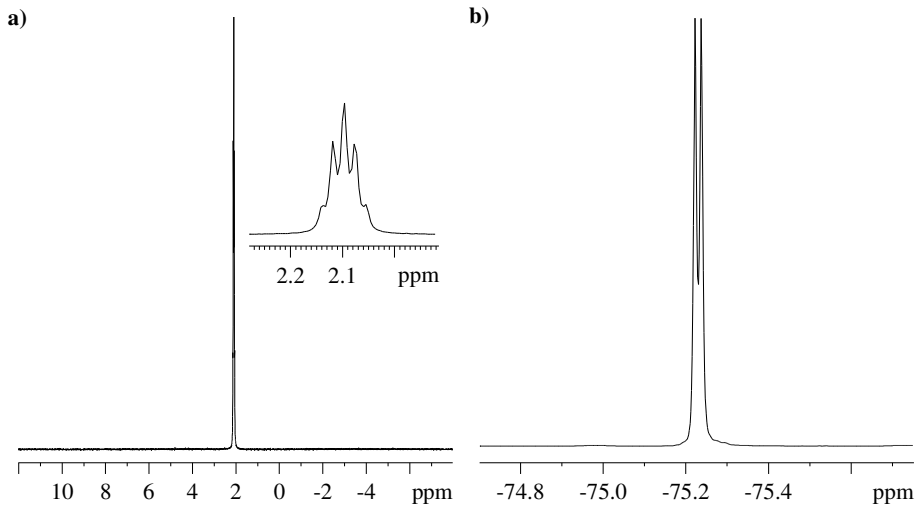


Figure S5: a) ^{11}B- and **b)** ^{19}F-NMR spectra of **2** in $CDCl_3$ after 10 h drying in vacuum (0.1 Pa) at 40–45 °C.

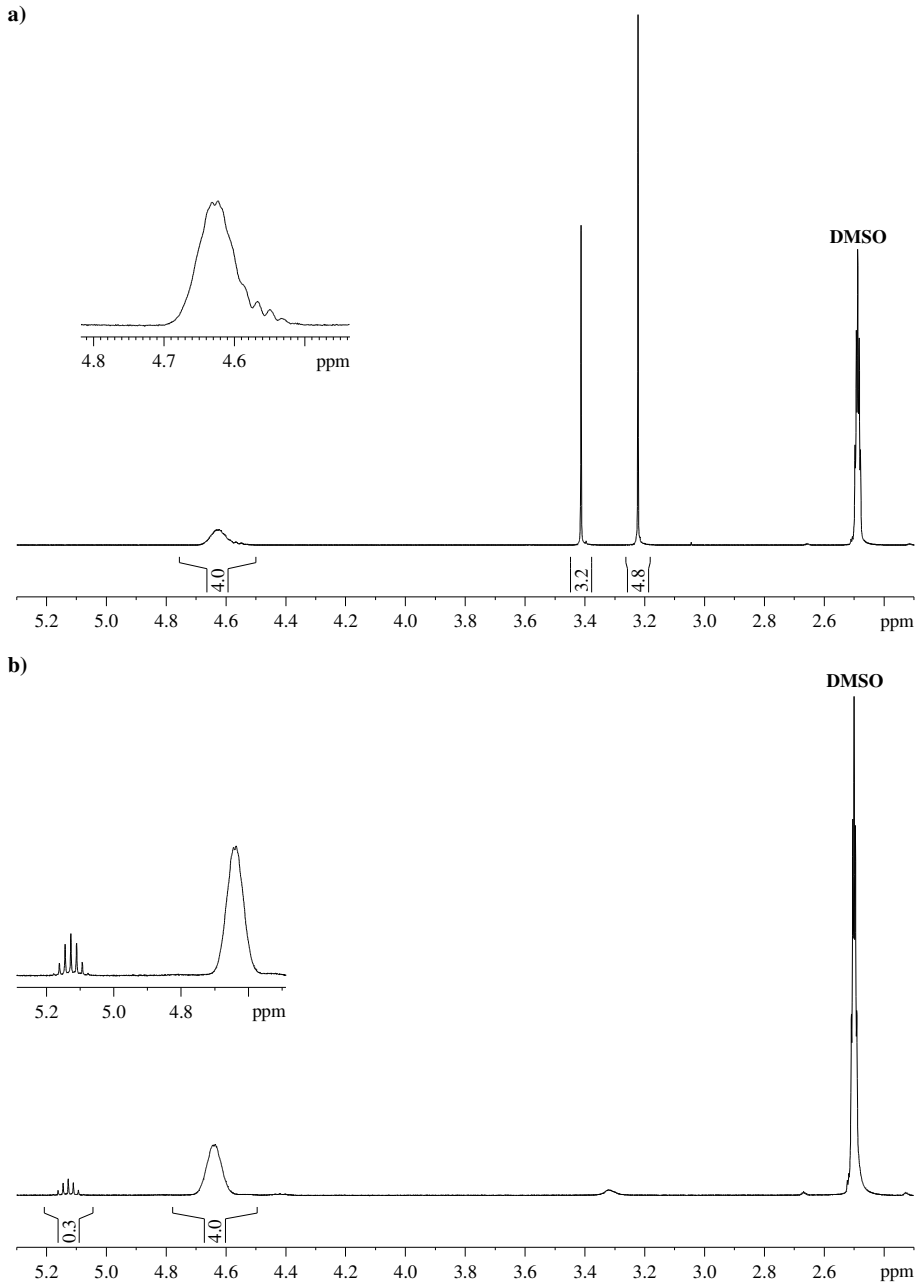


Figure S6: ^{1}H-NMR spectra of **2** in [D_6]DMSO after drying in vacuum (0.1 Pa) **a)** at 60 °C (5–6 h), **b)** at 80 °C (4–5 h).

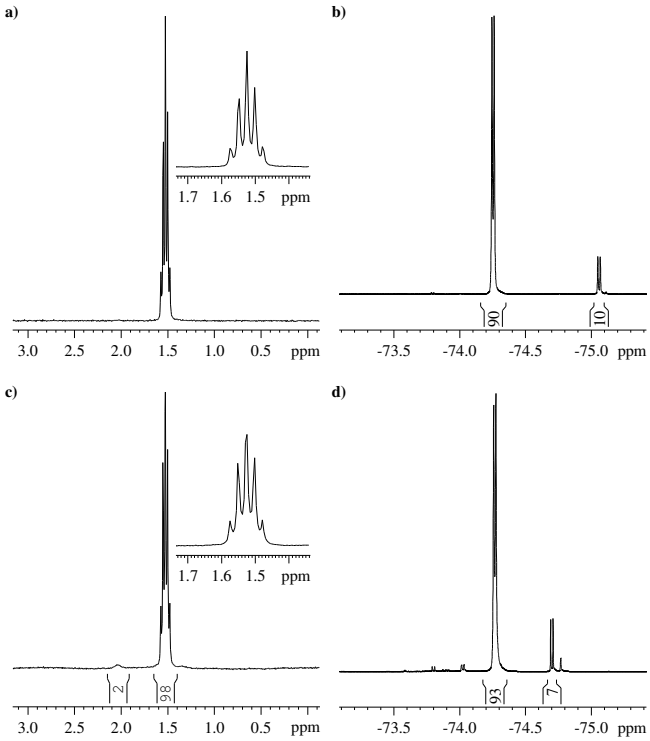


Figure S7: ^{11}B- (left) and ^{19}F- (right) NMR spectra of **2** in [D_6]DMSO after drying in vacuum (0.1 Pa) **a-b)** at 60 °C (5–6 h), **c-d)** at 80 °C (4–5 h).

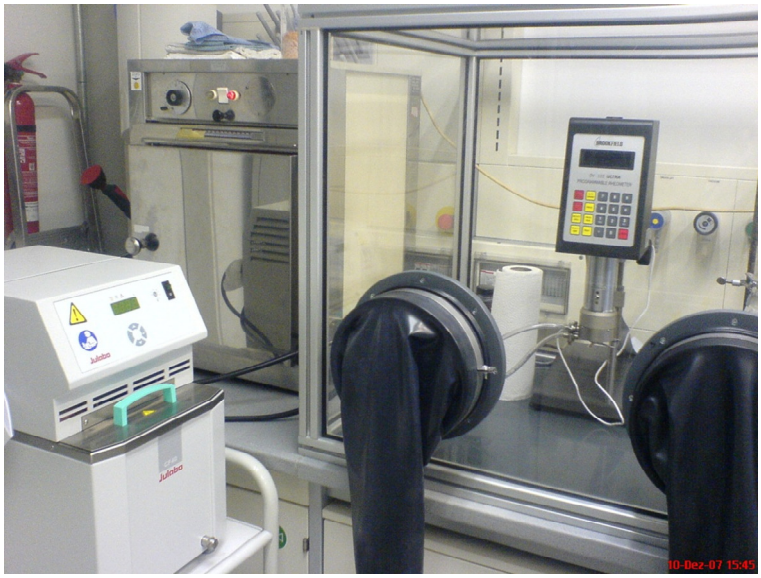
3 Elemental Analysis of $[B(hfip)_4]^-$ Ionic Liquids

Table S4: The results of the elemental analysis for **4**, **5** and **7** (average values of two measurements).

Salt	**C**	**H**	**N**
	Exp (Calc) [%]	**Exp (Calc) [%]**	**Exp (Calc) [%]**
$[C_4MIM]^+[B(hfip)_4]^-$ (**4**)	29.72 (29.36)	2.34 (2.34)	3.36 (3.42)
$[C_4MMIM]^+[B(hfip)_4]^-$ (**5**)	30.43 (30.31)	2.59 (2.54)	3.35 (3.37)
$[C_6MIM]^+[B(hfip)_4]^-$ (**7**)	31.33 (31.23)	2.73 (2.74)	3.30 (3.31)

4 Temperature dependent viscosity measurements

Programmable rotation viscosimeter from Brookfield (RVDV-III UCP) in an atmosphere of dry air in a specifically purpose-built glove box (relative humidity below 0.1%), connected with a cryostat for the tempering of the samples (accuracy about ± 0.1 °C).



5 Temperature dependent conductivity measurements

Metrohm 712 conductometer in an argon filled glove box (water and oxygen content below 1 ppm) and a metal thermostat for the tempering of the samples (accuracy about ± 0.1 °C).

6 Crystal Data

Table S5: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Na(1)	7416(1)	4588(1)	2624(1)	31(1)
B(1)	5680(2)	7193(2)	2373(1)	24(1)
O(1)	6743(1)	6669(1)	3013(1)	26(1)
O(2)	4525(1)	8134(1)	2753(1)	27(1)
O(3)	6433(1)	7727(1)	1642(1)	25(1)
O(4)	5178(1)	6076(1)	2127(1)	25(1)
O(5)	8357(2)	3283(1)	3675(1)	41(1)
O(6)	7800(2)	2957(1)	1736(1)	40(1)
F(1)	9514(2)	7355(2)	2522(1)	60(1)
F(2)	9808(2)	7577(2)	3829(1)	70(1)
F(3)	9506(2)	5815(2)	3387(1)	70(1)
F(4)	5453(2)	7612(2)	4498(1)	66(1)
F(5)	7395(2)	8187(2)	4831(1)	86(1)
F(6)	7408(2)	6254(2)	4739(1)	81(1)
F(7)	1963(2)	10478(1)	1724(1)	55(1)
F(8)	1523(1)	9163(1)	2710(1)	50(1)
F(9)	2517(1)	8517(1)	1515(1)	50(1)
F(10)	5426(1)	10226(1)	3252(1)	47(1)
F(11)	3222(2)	10136(1)	3733(1)	59(1)
F(12)	3587(2)	11436(1)	2722(1)	60(1)
F(13)	8558(1)	5599(1)	1406(1)	38(1)
F(14)	9289(1)	7167(1)	768(1)	42(1)
F(15)	8545(1)	5822(1)	50(1)	47(1)
F(16)	7117(1)	9076(1)	218(1)	41(1)
F(17)	6649(2)	7722(1)	-595(1)	51(1)
F(18)	4936(2)	8685(1)	254(1)	54(1)
F(19)	4949(1)	4027(1)	3095(1)	45(1)
F(20)	4022(2)	5636(1)	3809(1)	49(1)
F(21)	2600(1)	4557(1)	3316(1)	51(1)
F(22)	3341(2)	5991(1)	910(1)	57(1)
F(23)	4163(2)	4170(1)	1419(1)	58(1)
F(24)	1918(2)	5061(2)	1720(1)	61(1)
C(1)	7404(2)	7441(2)	3461(1)	34(1)
C(2)	9077(3)	7042(2)	3304(1)	46(1)
C(3)	6915(3)	7359(3)	4392(1)	51(1)
C(4)	4031(2)	9303(2)	2385(1)	31(1)

C(5)	2496(2)	9372(2)	2087(1)	38(1)
C(6)	4049(2)	10280(2)	3029(1)	40(1)
C(7)	6710(2)	7160(2)	869(1)	26(1)
C(8)	8289(2)	6453(2)	763(1)	32(1)
C(9)	6368(2)	8166(2)	179(1)	34(1)
C(10)	3777(2)	5842(2)	2349(1)	29(1)
C(11)	3814(2)	5006(2)	3146(1)	35(1)
C(12)	3286(2)	5252(2)	1599(1)	40(1)
C(13)	7761(3)	3146(2)	4527(1)	47(1)
C(14)	9717(3)	2387(2)	3620(2)	47(1)
C(15)	8037(3)	1756(2)	4703(2)	47(1)
C(16)	9449(3)	1279(2)	4170(2)	49(1)
C(17)	8747(3)	2665(2)	985(2)	49(1)
C(18)	7137(3)	1901(2)	1986(2)	50(1)
C(19)	8143(3)	807(2)	1616(2)	49(1)
C(20)	8684(3)	1350(2)	779(2)	47(1)

Table S6: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

	x	**y**	**z**	**U(eq)**
H(1A)	7190(20)	8310(20)	3263(14)	43(6)
H(4A)	4650(20)	9492(17)	1916(12)	25(5)
H(7A)	6080(20)	6568(18)	780(11)	25(5)
H(10A)	3070(20)	6554(19)	2473(12)	27(5)
H(13A)	8310(30)	3580(20)	4907(17)	62(8)
H(13B)	6710(30)	3540(30)	4553(17)	65(8)
H(14A)	9990(30)	2220(30)	3016(19)	70(8)
H(14B)	10440(30)	2800(20)	3843(16)	57(8)
H(15A)	7220(30)	1420(30)	4525(17)	67(8)
H(15B)	8080(30)	1580(30)	5292(18)	66(8)
H(16A)	9290(30)	640(30)	3804(17)	64(8)
H(16B)	10250(30)	1010(30)	4524(18)	67(8)
H(17A)	8430(30)	3240(30)	565(19)	73(9)
H(17B)	9850(40)	2730(30)	1160(20)	87(10)
H(18A)	7030(30)	1870(20)	2595(16)	46(6)
H(18B)	6170(40)	1860(30)	1630(20)	110(12)
H(19A)	7610(30)	150(20)	1559(15)	52(7)
H(19B)	9020(30)	580(30)	2080(20)	83(9)
H(20A)	8030(30)	1380(20)	384(17)	55(8)
H(20B)	9610(40)	930(30)	595(19)	74(9)

Table S7: Bond lengths [Å] and angles [°] for **1**.

Na(1)-O(5)	2.2589(17)	O(3)-B(1)-O(1)	110.58(14)
Na(1)-O(6)	2.2852(16)	O(4)-B(1)-O(1)	101.85(14)
Na(1)-O(1)	2.3436(15)	O(2)-B(1)-Na(1)	143.69(12)
Na(1)-F(13)	2.4607(15)	O(3)-B(1)-Na(1)	105.33(11)
Na(1)-O(4)	2.5282(16)	O(4)-B(1)-Na(1)	56.74(8)
Na(1)-F(19)	2.5357(16)	O(1)-B(1)-Na(1)	49.59(8)
Na(1)-F(3)	2.929(2)	C(1)-O(1)-B(1)	120.82(14)
Na(1)-B(1)	3.016(2)	C(1)-O(1)-Na(1)	133.92(12)
B(1)-O(2)	1.450(2)	B(1)-O(1)-Na(1)	101.53(10)
B(1)-O(3)	1.467(2)	C(4)-O(2)-B(1)	124.18(14)
B(1)-O(4)	1.472(2)	C(7)-O(3)-B(1)	122.70(14)
B(1)-O(1)	1.487(2)	C(10)-O(4)-B(1)	123.52(13)
O(1)-C(1)	1.388(2)	C(10)-O(4)-Na(1)	119.88(11)
O(2)-C(4)	1.390(2)	B(1)-O(4)-Na(1)	94.13(10)
O(3)-C(7)	1.388(2)	C(13)-O(5)-C(14)	104.82(16)
O(4)-C(10)	1.390(2)	C(13)-O(5)-Na(1)	128.94(13)
O(5)-C(13)	1.437(3)	C(14)-O(5)-Na(1)	126.24(13)
O(5)-C(14)	1.438(3)	C(17)-O(6)-C(18)	108.75(16)
O(6)-C(17)	1.437(2)	C(17)-O(6)-Na(1)	132.83(13)
O(6)-C(18)	1.441(3)	C(18)-O(6)-Na(1)	117.95(12)
F(1)-C(2)	1.329(3)	C(2)-F(3)-Na(1)	109.48(13)
F(2)-C(2)	1.337(3)	C(8)-F(13)-Na(1)	144.24(11)
F(3)-C(2)	1.329(3)	C(11)-F(19)-Na(1)	114.53(11)
F(4)-C(3)	1.329(3)	O(1)-C(1)-C(3)	109.72(17)
F(5)-C(3)	1.333(3)	O(1)-C(1)-C(2)	107.99(16)
F(6)-C(3)	1.318(3)	C(3)-C(1)-C(2)	111.96(18)
F(7)-C(5)	1.337(2)	F(3)-C(2)-F(1)	106.4(2)
F(8)-C(5)	1.332(2)	F(3)-C(2)-F(2)	108.4(2)
F(9)-C(5)	1.333(2)	F(1)-C(2)-F(2)	107.20(18)
F(10)-C(6)	1.342(3)	F(3)-C(2)-C(1)	111.62(18)
F(11)-C(6)	1.330(2)	F(1)-C(2)-C(1)	110.91(18)
F(12)-C(6)	1.337(2)	F(2)-C(2)-C(1)	112.1(2)
F(13)-C(8)	1.355(2)	F(6)-C(3)-F(4)	109.0(2)
F(14)-C(8)	1.327(2)	F(6)-C(3)-F(5)	106.8(2)
F(15)-C(8)	1.336(2)	F(4)-C(3)-F(5)	106.48(19)
F(16)-C(9)	1.329(2)	F(6)-C(3)-C(1)	112.40(19)
F(17)-C(9)	1.332(2)	F(4)-C(3)-C(1)	110.31(19)
F(18)-C(9)	1.338(2)	F(5)-C(3)-C(1)	111.6(2)
F(19)-C(11)	1.349(2)	O(2)-C(4)-C(6)	108.56(16)
F(20)-C(11)	1.331(2)	O(2)-C(4)-C(5)	109.67(16)

F(21)-C(11)	1.321(2)	C(6)-C(4)-C(5)	111.77(16)
F(22)-C(12)	1.335(3)	F(8)-C(5)-F(9)	106.58(17)
F(23)-C(12)	1.330(3)	F(8)-C(5)-F(7)	107.33(16)
F(24)-C(12)	1.326(2)	F(9)-C(5)-F(7)	106.98(17)
C(1)-C(3)	1.519(3)	F(8)-C(5)-C(4)	112.79(17)
C(1)-C(2)	1.533(3)	F(9)-C(5)-C(4)	110.44(16)
C(4)-C(6)	1.519(3)	F(7)-C(5)-C(4)	112.37(17)
C(4)-C(5)	1.521(3)	F(11)-C(6)-F(12)	107.43(17)
C(7)-C(8)	1.518(3)	F(11)-C(6)-F(10)	107.06(19)
C(7)-C(9)	1.524(3)	F(12)-C(6)-F(10)	106.42(17)
C(10)-C(12)	1.521(3)	F(11)-C(6)-C(4)	113.07(17)
C(10)-C(11)	1.528(3)	F(12)-C(6)-C(4)	112.28(19)
C(13)-C(15)	1.511(3)	F(10)-C(6)-C(4)	110.22(16)
C(14)-C(16)	1.512(3)	O(3)-C(7)-C(8)	111.07(15)
C(15)-C(16)	1.522(3)	O(3)-C(7)-C(9)	107.93(14)
C(17)-C(20)	1.507(3)	C(8)-C(7)-C(9)	111.73(15)
C(18)-C(19)	1.484(3)	F(14)-C(8)-F(15)	107.72(15)
C(19)-C(20)	1.522(3)	F(14)-C(8)-F(13)	106.70(16)
		F(15)-C(8)-F(13)	106.50(15)
O(5)-Na(1)-O(6)	89.87(6)	F(14)-C(8)-C(7)	113.94(16)
O(5)-Na(1)-O(1)	113.49(6)	F(15)-C(8)-C(7)	111.91(16)
O(6)-Na(1)-O(1)	156.56(6)	F(13)-C(8)-C(7)	109.67(14)
O(5)-Na(1)-F(13)	132.81(6)	F(16)-C(9)-F(17)	107.07(16)
O(6)-Na(1)-F(13)	82.27(5)	F(16)-C(9)-F(18)	107.17(16)
O(1)-Na(1)-F(13)	80.25(5)	F(17)-C(9)-F(18)	107.15(16)
O(5)-Na(1)-O(4)	145.98(6)	F(16)-C(9)-C(7)	113.04(16)
O(6)-Na(1)-O(4)	105.50(6)	F(17)-C(9)-C(7)	112.67(15)
O(1)-Na(1)-O(4)	56.10(5)	F(18)-C(9)-C(7)	109.43(16)
F(13)-Na(1)-O(4)	80.09(5)	O(4)-C(10)-C(12)	107.49(15)
O(5)-Na(1)-F(19)	86.70(6)	O(4)-C(10)-C(11)	109.66(16)
O(6)-Na(1)-F(19)	87.75(6)	C(12)-C(10)-C(11)	112.48(16)
O(1)-Na(1)-F(19)	95.22(5)	F(21)-C(11)-F(20)	108.06(15)
F(13)-Na(1)-F(19)	138.84(5)	F(21)-C(11)-F(19)	107.25(16)
O(4)-Na(1)-F(19)	64.33(5)	F(20)-C(11)-F(19)	106.04(17)
O(5)-Na(1)-F(3)	73.95(6)	F(21)-C(11)-C(10)	113.56(17)
O(6)-Na(1)-F(3)	130.82(6)	F(20)-C(11)-C(10)	109.97(16)
O(1)-Na(1)-F(3)	59.19(5)	F(19)-C(11)-C(10)	111.60(15)
F(13)-Na(1)-F(3)	76.67(5)	F(24)-C(12)-F(23)	108.03(18)
O(4)-Na(1)-F(3)	113.72(5)	F(24)-C(12)-F(22)	107.30(18)
F(19)-Na(1)-F(3)	135.39(5)	F(23)-C(12)-F(22)	106.56(18)
O(5)-Na(1)-B(1)	139.67(6)	F(24)-C(12)-C(10)	112.71(17)

O(6)-Na(1)-B(1)	129.12(6)	F(23)-C(12)-C(10)	111.83(18)
O(1)-Na(1)-B(1)	28.88(5)	F(22)-C(12)-C(10)	110.13(17)
F(13)-Na(1)-B(1)	71.13(5)	O(5)-C(13)-C(15)	104.44(18)
O(4)-Na(1)-B(1)	29.13(5)	O(5)-C(14)-C(16)	106.03(19)
F(19)-Na(1)-B(1)	85.26(6)	C(13)-C(15)-C(16)	103.62(19)
F(3)-Na(1)-B(1)	84.59(6)	C(14)-C(16)-C(15)	104.83(19)
O(2)-B(1)-O(3)	110.39(14)	O(6)-C(17)-C(20)	106.73(19)
O(2)-B(1)-O(4)	114.30(15)	O(6)-C(18)-C(19)	105.71(19)
O(3)-B(1)-O(4)	109.93(14)	C(18)-C(19)-C(20)	102.0(2)
O(2)-B(1)-O(1)	109.50(14)	C(17)-C(20)-C(19)	103.32(18)

Table S8: Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	**y**	**z**	**U(eq)**
Na(1)	1561(1)	4103(1)	2621(1)	25(1)
B(1)	3509(2)	1708(2)	2622(1)	17(1)
O(1)	3678(1)	3102(1)	2570(1)	17(1)
O(2)	2207(1)	1855(1)	2287(1)	18(1)
O(3)	3506(1)	957(1)	3698(1)	18(1)
O(4)	4534(1)	1130(1)	1916(1)	18(1)
O(5)	1084(1)	6168(1)	1670(1)	27(1)
O(6)	-347(1)	5039(1)	3518(1)	26(1)
F(1)	5632(1)	3655(1)	981(1)	34(1)
F(2)	4818(1)	5434(1)	1496(1)	38(1)
F(3)	6687(1)	4468(1)	1896(1)	44(1)
F(4)	4136(1)	3404(1)	4574(1)	33(1)
F(5)	3465(1)	5132(1)	3499(1)	36(1)
F(6)	5464(1)	4798(1)	3785(1)	42(1)
F(7)	505(1)	589(1)	711(1)	51(1)
F(8)	806(1)	-93(1)	2320(1)	47(1)
F(9)	-260(1)	1793(1)	1841(1)	54(1)
F(10)	1165(1)	3787(1)	800(1)	43(1)
F(11)	1699(1)	2638(1)	-397(1)	42(1)
F(12)	3179(1)	3238(1)	280(1)	42(1)
F(13)	1535(1)	2665(1)	4427(1)	33(1)
F(14)	2445(1)	1532(1)	5740(1)	39(1)
F(15)	575(1)	1134(1)	5502(1)	48(1)
F(16)	3843(1)	-827(1)	5463(1)	38(1)
F(17)	1862(1)	-1270(1)	5724(1)	43(1)
F(18)	3172(1)	-1735(1)	4384(1)	51(1)
F(19)	6866(1)	642(1)	718(1)	36(1)

F(20)	7576(1)	-854(1)	1965(1)	37(1)
F(21)	7117(1)	1145(1)	2156(1)	35(1)
F(22)	5545(1)	-2311(1)	2378(1)	46(1)
F(23)	5156(1)	-1121(1)	884(1)	44(1)
F(24)	3652(1)	-1231(1)	2207(1)	37(1)
C(1)	4823(1)	3442(1)	2779(1)	19(1)
C(2)	5498(2)	4263(2)	1777(1)	26(1)
C(3)	4482(2)	4203(2)	3663(1)	26(1)
C(4)	2033(2)	1564(2)	1342(1)	20(1)
C(5)	756(2)	966(2)	1547(1)	32(1)
C(6)	2015(2)	2813(2)	492(1)	27(1)
C(7)	2407(2)	493(2)	4317(1)	21(1)
C(8)	1744(2)	1446(2)	5014(1)	28(1)
C(9)	2827(2)	-845(2)	4982(1)	30(1)
C(10)	5342(1)	-12(1)	2240(1)	20(1)
C(11)	6733(2)	229(2)	1757(1)	26(1)
C(12)	4932(2)	-1178(2)	1916(1)	28(1)
C(13)	1935(2)	6930(2)	894(2)	39(1)
C(14)	144(2)	6952(2)	2245(1)	28(1)
C(15)	-909(2)	6139(2)	2818(1)	29(1)
C(16)	-1325(2)	4352(2)	4210(2)	43(1)

Table S9: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2**.

	x	**y**	**z**	**U(eq)**
H(1A)	5445(15)	2718(16)	2998(12)	14(4)
H(4A)	2736(16)	929(16)	1093(12)	16(4)
H(7A)	1758(17)	371(17)	3947(13)	22(4)
H(10A)	5374(15)	-255(15)	2953(13)	13(4)
H(13A)	1430(20)	7530(20)	370(18)	50(6)
H(13B)	2550(20)	6320(20)	538(18)	49(6)
H(13C)	2450(20)	7350(20)	1202(19)	59(7)
H(14A)	-229(19)	7720(20)	1775(15)	35(5)
H(14B)	549(19)	7260(19)	2746(16)	35(5)
H(15A)	-1341(19)	5800(20)	2318(16)	38(5)
H(15B)	-1590(20)	6690(20)	3249(16)	39(5)
H(16A)	-910(20)	3700(20)	4699(17)	44(6)
H(16B)	-1970(20)	4940(20)	4591(19)	60(7)
H(16C)	-1840(30)	3990(30)	3800(20)	66(8)

Table S10: Bond lengths [Å] and angles [°] for **2**.

Na(1)-O(5)	2.2854(14)	F(10)-Na(1)-C(15)	92.99(5)
Na(1)-O(1)	2.3083(13)	F(5)-Na(1)-C(15)	103.45(5)
Na(1)-O(6)	2.3496(14)	B(1)-Na(1)-C(15)	167.17(5)
Na(1)-O(2)	2.4824(13)	C(14)-Na(1)-C(15)	27.80(5)
Na(1)-F(13)	2.5224(14)	O(4)-B(1)-O(3)	110.49(12)
Na(1)-F(10)	2.6098(14)	O(4)-B(1)-O(2)	112.85(12)
Na(1)-F(5)	2.9160(14)	O(3)-B(1)-O(2)	111.09(12)
Na(1)-B(1)	3.000(2)	O(4)-B(1)-O(1)	110.41(12)
Na(1)-C(14)	3.1168(19)	O(3)-B(1)-O(1)	110.46(12)
Na(1)-C(15)	3.121(2)	O(2)-B(1)-O(1)	101.20(11)
B(1)-O(4)	1.4567(19)	O(4)-B(1)-Na(1)	140.07(10)
B(1)-O(3)	1.4636(19)	O(3)-B(1)-Na(1)	109.07(9)
B(1)-O(2)	1.4807(18)	O(2)-B(1)-Na(1)	55.53(7)
B(1)-O(1)	1.4913(18)	O(1)-B(1)-Na(1)	48.79(6)
O(1)-C(1)	1.3905(17)	C(1)-O(1)-B(1)	121.30(11)
O(2)-C(4)	1.3963(17)	C(1)-O(1)-Na(1)	133.69(9)
O(3)-C(7)	1.3834(18)	B(1)-O(1)-Na(1)	102.13(8)
O(4)-C(10)	1.3900(17)	C(4)-O(2)-B(1)	122.12(11)
O(5)-C(14)	1.422(2)	C(4)-O(2)-Na(1)	120.42(9)
O(5)-C(13)	1.426(2)	B(1)-O(2)-Na(1)	95.02(8)
O(6)-C(16)	1.424(2)	C(7)-O(3)-B(1)	123.51(11)
O(6)-C(15)	1.430(2)	C(10)-O(4)-B(1)	123.32(11)
F(1)-C(2)	1.3283(19)	C(14)-O(5)-C(13)	112.42(14)
F(2)-C(2)	1.337(2)	C(14)-O(5)-Na(1)	112.35(9)
F(3)-C(2)	1.3374(18)	C(13)-O(5)-Na(1)	127.75(11)
F(4)-C(3)	1.3350(19)	C(16)-O(6)-C(15)	111.30(13)
F(5)-C(3)	1.346(2)	C(16)-O(6)-Na(1)	126.52(12)
F(6)-C(3)	1.3334(18)	C(15)-O(6)-Na(1)	108.90(9)
F(7)-C(5)	1.331(2)	C(3)-F(5)-Na(1)	108.94(9)
F(8)-C(5)	1.335(2)	C(6)-F(10)-Na(1)	110.43(9)
F(9)-C(5)	1.335(2)	C(8)-F(13)-Na(1)	147.69(10)
F(10)-C(6)	1.344(2)	O(1)-C(1)-C(3)	108.31(12)
F(11)-C(6)	1.3299(19)	O(1)-C(1)-C(2)	109.31(12)
F(12)-C(6)	1.328(2)	C(3)-C(1)-C(2)	111.54(12)
F(13)-C(8)	1.3518(19)	F(1)-C(2)-F(3)	107.50(13)
F(14)-C(8)	1.329(2)	F(1)-C(2)-F(2)	107.29(13)
F(15)-C(8)	1.338(2)	F(3)-C(2)-F(2)	107.65(13)
F(16)-C(9)	1.333(2)	F(1)-C(2)-C(1)	110.58(13)
F(17)-C(9)	1.340(2)	F(3)-C(2)-C(1)	111.62(13)
F(18)-C(9)	1.332(2)	F(2)-C(2)-C(1)	111.98(13)

F(19)-C(11)	1.3342(19)	F(6)-C(3)-F(4)	107.59(13)
F(20)-C(11)	1.3408(19)	F(6)-C(3)-F(5)	107.14(13)
F(21)-C(11)	1.338(2)	F(4)-C(3)-F(5)	106.55(13)
F(22)-C(12)	1.3355(19)	F(6)-C(3)-C(1)	113.07(13)
F(23)-C(12)	1.334(2)	F(4)-C(3)-C(1)	110.56(13)
F(24)-C(12)	1.340(2)	F(5)-C(3)-C(1)	111.62(13)
C(1)-C(3)	1.526(2)	O(2)-C(4)-C(5)	106.64(13)
C(1)-C(2)	1.536(2)	O(2)-C(4)-C(6)	109.51(12)
C(4)-C(5)	1.524(2)	C(5)-C(4)-C(6)	112.34(13)
C(4)-C(6)	1.528(2)	F(7)-C(5)-F(8)	107.21(14)
C(7)-C(8)	1.527(2)	F(7)-C(5)-F(9)	107.57(14)
C(7)-C(9)	1.530(2)	F(8)-C(5)-F(9)	107.08(16)
C(10)-C(11)	1.526(2)	F(7)-C(5)-C(4)	112.52(15)
C(10)-C(12)	1.529(2)	F(8)-C(5)-C(4)	109.90(14)
C(14)-C(15)	1.498(2)	F(9)-C(5)-C(4)	112.28(14)
		F(12)-C(6)-F(11)	107.95(14)
O(5)-Na(1)-O(1)	120.94(5)	F(12)-C(6)-F(10)	106.71(14)
O(5)-Na(1)-O(6)	73.22(5)	F(11)-C(6)-F(10)	107.31(13)
O(1)-Na(1)-O(6)	151.21(5)	F(12)-C(6)-C(4)	110.20(13)
O(5)-Na(1)-O(2)	137.74(5)	F(11)-C(6)-C(4)	112.70(14)
O(1)-Na(1)-O(2)	57.15(4)	F(10)-C(6)-C(4)	111.72(13)
O(6)-Na(1)-O(2)	131.30(5)	O(3)-C(7)-C(8)	110.86(13)
O(5)-Na(1)-F(13)	146.06(5)	O(3)-C(7)-C(9)	107.91(13)
O(1)-Na(1)-F(13)	77.92(5)	C(8)-C(7)-C(9)	110.76(13)
O(6)-Na(1)-F(13)	78.70(5)	F(14)-C(8)-F(15)	107.70(13)
O(2)-Na(1)-F(13)	75.82(4)	F(14)-C(8)-F(13)	106.75(14)
O(5)-Na(1)-F(10)	74.44(5)	F(15)-C(8)-F(13)	106.13(13)
O(1)-Na(1)-F(10)	97.30(5)	F(14)-C(8)-C(7)	113.24(14)
O(6)-Na(1)-F(10)	111.11(5)	F(15)-C(8)-C(7)	112.48(15)
O(2)-Na(1)-F(10)	64.81(4)	F(13)-C(8)-C(7)	110.14(12)
F(13)-Na(1)-F(10)	134.84(4)	F(18)-C(9)-F(16)	107.12(15)
O(5)-Na(1)-F(5)	88.08(5)	F(18)-C(9)-F(17)	107.43(14)
O(1)-Na(1)-F(5)	59.92(4)	F(16)-C(9)-F(17)	107.37(13)
O(6)-Na(1)-F(5)	98.67(4)	F(18)-C(9)-C(7)	110.41(13)
O(2)-Na(1)-F(5)	115.12(4)	F(16)-C(9)-C(7)	112.50(14)
F(13)-Na(1)-F(5)	77.58(4)	F(17)-C(9)-C(7)	111.75(15)
F(10)-Na(1)-F(5)	138.59(5)	O(4)-C(10)-C(11)	107.46(12)
O(5)-Na(1)-B(1)	141.67(5)	O(4)-C(10)-C(12)	110.98(12)
O(1)-Na(1)-B(1)	29.08(4)	C(11)-C(10)-C(12)	111.64(13)
O(6)-Na(1)-B(1)	145.12(5)	F(19)-C(11)-F(21)	107.14(14)
O(2)-Na(1)-B(1)	29.45(4)	F(19)-C(11)-F(20)	107.35(13)

F(13)-Na(1)-B(1)	68.41(5)	F(21)-C(11)-F(20)	106.89(13)
F(10)-Na(1)-B(1)	85.70(5)	F(19)-C(11)-C(10)	113.18(13)
F(5)-Na(1)-B(1)	85.68(4)	F(21)-C(11)-C(10)	110.13(13)
O(5)-Na(1)-C(14)	24.95(4)	F(20)-C(11)-C(10)	111.83(14)
O(1)-Na(1)-C(14)	137.38(5)	F(23)-C(12)-F(22)	107.56(14)
O(6)-Na(1)-C(14)	49.21(5)	F(23)-C(12)-F(24)	106.71(14)
O(2)-Na(1)-C(14)	155.77(5)	F(22)-C(12)-F(24)	107.29(14)
F(13)-Na(1)-C(14)	122.18(5)	F(23)-C(12)-C(10)	113.47(14)
F(10)-Na(1)-C(14)	91.81(5)	F(22)-C(12)-C(10)	111.48(13)
F(5)-Na(1)-C(14)	86.32(5)	F(24)-C(12)-C(10)	110.04(13)
B(1)-Na(1)-C(14)	164.81(5)	O(5)-C(14)-C(15)	108.45(13)
O(5)-Na(1)-C(15)	49.05(5)	O(5)-C(14)-Na(1)	42.70(7)
O(1)-Na(1)-C(15)	162.70(5)	C(15)-C(14)-Na(1)	76.26(9)
O(6)-Na(1)-C(15)	25.68(4)	O(6)-C(15)-C(14)	108.77(13)
O(2)-Na(1)-C(15)	140.15(5)	O(6)-C(15)-Na(1)	45.42(7)
F(13)-Na(1)-C(15)	104.37(5)	C(14)-C(15)-Na(1)	75.95(9)

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