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## **Supporting Information**

# Syntheses, Characterisation and Solid-State Study of Alkali and Ammonium BArF Salts.

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# **Supporting Information**

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#### 1. General considerations:

All syntheses were carried out using chemicals as purchased from commercial sources unless otherwise stated. All manipulations and reactions were performed under inert atmosphere. Glassware was dried in vacuo before use with a hot air gun. All solvents were dried and deoxygenated by using a solvent purification system (SPS). NMR spectra were recorded in 400 MHz or 500 MHz Ultrashield spectrometers in CD<sub>2</sub>Cl<sub>2</sub> or C<sub>4</sub>D<sub>8</sub>O unless otherwise cited. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are quoted in ppm relative to residual solvent peaks. <sup>11</sup>B chemical shifts are quoted in ppm relative to trimethyl borate (TMB) as external reference standard in C<sub>4</sub>D<sub>8</sub>O ( $\delta$  in C<sub>4</sub>D<sub>8</sub>O = 16.586 ppm) using a coaxial insert for NMR tubes. <sup>7</sup>Li shifts are quoted in ppm relative to LiCl as external reference standard in D<sub>2</sub>O ( $\delta$  in D<sub>2</sub>O = 0 ppm) using a coaxial insert for NMR tubes. <sup>19</sup>F shifts are quoted in ppm relative to trifluoroacetic acid (TFA) as external reference standard in C<sub>4</sub>D<sub>8</sub>O ( $\delta$  in C<sub>4</sub>D<sub>8</sub>O = -77.052 ppm) using a coaxial insert for NMR tubes. <sup>133</sup>Cs shifts are quoted in ppm relative to CsNO<sub>3</sub> as external reference standard in D<sub>2</sub>O ( $\delta$  in D<sub>2</sub>O = 0 ppm) using a coaxial insert for NMR tubes. The content of the alkali metals was determined by ICP (Inductively Coupled Plasma based analytical techniques), with an optical emission spectrometer (ICP-OES, Perkin-Elmer Optima 4300DV), with a mass spectrometer (ICP-MS, Agilent 7500 ce), and with an atomic emission spectrometer (ICP-AES). Mass spectra for the ammonium BArF salts were recorded using ESI ionization method in positive mode (MS-ESI, MaXis Impact spectrometer, Bruker Daltonics). IR spectra were recorded using Attenuated Total Reflection (ATR) technique unless otherwise cited.

NaBArF was purchased from Alfa Aesar (content stated by the supplier for the batches used = 97%) and dried in vacuo (120 °C) prior to its use. HBArF·2Et<sub>2</sub>O (9),<sup>1</sup>

RbBArF,<sup>2</sup> CsBArF,<sup>2</sup> dibenzylammonium BArF (6)<sup>3</sup> and (*S*,*S*)-bis-(1-phenylethyl)ammonium BArF (8)<sup>4</sup> were prepared following reported synthetic methods and were subsequently characterised.

**NaBArF.** <sup>1</sup>H NMR (C<sub>4</sub>D<sub>8</sub>O, 400 MHz):  $\delta$  7.78 (br s, 8H), 7.56 (br s, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 126 MHz):  $\delta$  162.8 (q,  $J_{C-B} = 50$  Hz), 135.6, 130.0 (qm,  $J_{C-F} =$ 32 Hz), 125.5 (q,  $J_{C-F} = 272$  Hz), 118.2 (m) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 376 MHz):  $\delta$ -63.2 (24F) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 128 MHz):  $\delta$  -8.6 ppm. IR (neat, cm<sup>-1</sup>): 1629, 1611, 1357, 1280, 1116, 1102. M.p. = 305 °C (decomposes). IR and <sup>1</sup>H NMR data were in agreement with those previously reported.<sup>5</sup>

**RbBArF.**<sup>2</sup> <sup>1</sup>H NMR (C<sub>4</sub>D<sub>8</sub>O, 400 MHz):  $\delta$  7.78 (br s, 8H), 7.57 (br s, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 126 MHz):  $\delta$  162.8 (q,  $J_{C-B} = 50$  Hz), 135.6, 130.1 (qm,  $J_{C-F} =$ 32 Hz), 125.5 (q,  $J_{C-F} = 270$  Hz), 118.2 (m) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 376 MHz):  $\delta$ -63.3 (24F) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 128 MHz):  $\delta$  -8.6 ppm. IR (neat, cm<sup>-1</sup>): 1612, 1357, 1281, 1122, 1084. M.p. = >350 °C.<sup>6</sup> Content in Rb by ICP-OES: calcd. 9.01%, found 8.90%.

**CsBArF.**<sup>2</sup> <sup>1</sup>H NMR (C<sub>4</sub>D<sub>8</sub>O, 400 MHz): δ 7.78 (br s, 8H), 7.57 (br s, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 126 MHz): δ 162.8 (q,  $J_{C-B} = 50$  Hz), 135.6, 130.0 (qm,  $J_{C-F} = 32$  Hz), 125.5 (q,  $J_{C-F} = 270$  Hz), 118.2 (m) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 376 MHz): δ -63.1 (24F) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>4</sub>D<sub>8</sub>O, 128 MHz): δ -8.6 ppm. <sup>133</sup>Cs NMR (D<sub>2</sub>O, 53

<sup>&</sup>lt;sup>1</sup> M. Brookhart, B. Grant and A. F. Volpe, Jr., Organometallics, 1992, 11, 3920-3922.

<sup>&</sup>lt;sup>2</sup> A. Vidal-Ferran, I. Mon, A. Bauzá, A. Frontera and L. Rovira, Chem. - Eur. J., 2015, 21, 11417-11426.

<sup>&</sup>lt;sup>3</sup> C. R. South, M. N. Higley, K. C. F. Leung, D. Lanari, A. Nelson, R. H. Grubbs, J. F. Stoddart and M. Weck, *Chem. – Eur. J.*, 2006, **12**, 3789-3797.

<sup>&</sup>lt;sup>4</sup> H. Fernández-Pérez, I. Mon, A. Frontera and A. Vidal-Ferran, *Tetrahedron*, 2015, 71, 4490-4494.

<sup>&</sup>lt;sup>5</sup> H. Nishida, N. Takada, M. Yoshimura, T. Sonoda and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1984, 57, 2600-2604.

<sup>&</sup>lt;sup>6</sup> The upper temperature limit of the melting point apparatus was 350 °C.

MHz):  $\delta$  -23.02 ppm. IR (neat, cm<sup>-1</sup>): 1612, 1357, 1281, 1184, 1117, 1087. M.p. = >350 °C.<sup>6</sup> Content in Cs by ICP-MS: calcd. 13.34%, found 13.20%.

**Dibenzylammonium tetrakis**[3,5-bis(trifluoromethyl)phenyl]borate (6).<sup>3</sup> <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  7.73 (br s, 8H), 7.61-7.52 (m, 10H), 7.40-7.37 (br d, J = 7.4 Hz, 4H), 5.94 (br s, 2H), 4.45 (s, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta$  162.2 (q, J = 50 Hz), 135.3, 132.3, 131.0, 129.8, 129.3 (qm,  $J_{C-F} = 32$  Hz), 127.8, 125.1 (q,  $J_{C-F} = 271$  Hz), 117.9 (m), 54.2 ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 376 MHz):  $\delta$  –63.0 (24F) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 128 MHz):  $\delta$  –8.5 ppm. IR (neat, cm<sup>-1</sup>): 3700, 3616, 3280, 3044, 1611, 1354, 1272, 1113. M.p. = 118-122 °C. MS (ESI): *m/z* calcd. for C<sub>14</sub>H<sub>16</sub>N: 198.3; found: 198.1 [*M*–BArF]<sup>+</sup>. <sup>1</sup>H NMR data was in agreement with those previously reported.<sup>3</sup>

(*S*,*S*)-bis-(1-phenylethyl)ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (8).<sup>4</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.70 (br s, 8H), 7.55-7.45 (m, 10H), 7.21-7.14 (m, 4H), 5.32 (br t, *J* = 51 Hz, 2H) 4.25 (m, 2H), 1.61 (d, *J* = 6.8 Hz, 6H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.8 (q, *J* = 50 Hz), 135.0, 132.4, 132.1, 131.0, 129.1 (qm, *J* = 30 Hz), 126.4, 124.8 (q, *J* = 273 Hz), 117.7 (m), 60.1, 20.3 ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 376 MHz):  $\delta$  -63.3 (24F) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 128 MHz):  $\delta$ -8.7 ppm. IR (neat, cm<sup>-1</sup>): 1611, 1578, 1353, 1273, 1094. M.p. = 117-119 °C. [ $\alpha$ ]<sub>D</sub><sup>25</sup> +19.7 (*c* 0.56, CH<sub>3</sub>OH). MS (ESI): *m*/*z* calcd. for C<sub>16</sub>H<sub>20</sub>N: 226.3; found: 226.2 [*M*–BArF]<sup>+</sup>. Elemental analysis calcd. (%) for C<sub>48</sub>H<sub>32</sub>BF<sub>24</sub>N: C 52.91, H 2.96, N 1.29; found: C 53.03, H 3.07, N 1.48. IR, [ $\alpha$ ]<sub>D</sub><sup>25</sup>, <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR data were in agreement with those previously reported.<sup>4</sup>

#### 2. General Structural Comments on X-ray Crystals:

**Determination of single crystal X-ray diffraction structure.** Crystals of the alkali metal BArF salts were obtained by slow evaporation in  $CH_2Cl_2$  at room temperature under inert atmosphere. Crystals of **6** and **8** were obtained by solvent diffusion in the gas phase, using CHCl<sub>3</sub> and *n*-pentane at room temperature under inert atmosphere. Crystals of **7** were obtained by slow evaporation in CDCl<sub>3</sub> at room temperature under inert atmosphere. THF-solvates of the BArF salts were obtained by slow evaporation in THF at room temperature under inert atmosphere. The measured crystals were prepared under inert conditions immersed in perfluoropolyether as a protecting oil for manipulation.

All crystal structures for LiBArF, LiBArF·4H<sub>2</sub>O, LiBArF·4THF, NaBArF, NaBArF·6THF, KBArF, CsBArF·7THF, **6** and **7** were determined using an Apex DUO diffractometer equipped with a Kappa 4-axis goniometer, an APEX II 4K CCD area detector, a Microfocus Source E025 IuS using MoK<sub> $\alpha$ </sub> radiation, Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = -173 °C). Crystal structures for RbBArF and CsBArF were determined using a Bruker-Nonius diffractometer equipped with an APEX II 4K CCD area detector, a FR591 rotating anode with MoK<sub> $\alpha$ </sub> radiation, Montel mirrors as monochromator, a Kappa 4-axis goniometer and an Oxford Cryosystems low temperature for **8** was determined using a Rigaku MicroMax 007HF diffractometer equipped with a 1/4chi goniometer, a PILATUS 200K area detector, a Microfocus rotating anode X-ray tube using MoK<sub> $\alpha$ </sub> radiation, Confocal Max Flux optic as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = -173 °C). Full-sphere

data was collected with  $\omega$  and  $\varphi$  scans. Programs used in the Bruker devices: Data collection APEX-2,<sup>7</sup> data reduction Bruker Saint<sup>8</sup> V/.60A and absorption correction SADABS.<sup>9</sup> Programs used in the Rigaku device: Data collection CrystalClear,<sup>10</sup> data reduction with CrysAlisPro<sup>11</sup>and absorption correction with Scale3 Abspack scaling algorithm.<sup>12</sup>

Crystal structure solution was achieved using direct methods as implemented in SHELXTL<sup>13</sup> and visualised using the program SHELXIe.<sup>14</sup> Missing atoms were subsequently located using difference Fourier synthesis and added to the atom list. Least-squares refinement on F<sup>2</sup> using all measured intensities was carried out using the program SHELXL 2015.<sup>15</sup> All non-hydrogen atoms were refined including anisotropic displacement parameters.

**General structural comments:** LiBArF: The aromatic rings of the BArF anion are disordered over two orientations (ratio 62:38). One of the CF<sub>3</sub> groups is disordered over three positions with a ratio 55:38:7. NaBArF: The aromatic groups of the BArF anion are disordered over two orientations with a ratio of 70:30. KBArF: The CF<sub>3</sub> groups in the phenyl rings are rotationally disordered with a 75:25 ratio. RbBArF: The CF<sub>3</sub> groups in the phenyl rings are rotationally disordered with a ratio of 90:10. CsBArF: In the BArF unit, the aromatic rings and the corresponding trifluoromethyl groups are

 <sup>&</sup>lt;sup>7</sup> Data collection with: APEX II versions v2009.1-02, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
<sup>8</sup> Data reduction with: SAINT versions V7.60A, Bruker AXS Inc., Madison, Wisconsin, USA, 2003/2007.

<sup>&</sup>lt;sup>9</sup> SADABS, V2008/1, Bruker AXS Inc., Madison, Wisconsin, USA, 2003/2001, see: R. H. Blessing, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1995, **A51**, 33-38.

<sup>&</sup>lt;sup>10</sup> Data collection with CrystalClear-SM Expert 2.1 b29. Rigaku 2013.

<sup>&</sup>lt;sup>11</sup> Data reduction with CrysAlisPro 1.171.38.37f (Rigaku OD, 2015).

<sup>&</sup>lt;sup>12</sup> Empirical absorption correction using spherical harmonics implemented in a Scale3 Abspack scaling algorithm, CrysAlisPro 1.171.38.37f (Rigaku OD, 2015).

<sup>&</sup>lt;sup>13</sup> SHELXT; G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8.

<sup>&</sup>lt;sup>14</sup> SHELXle; C. B. Huebschle, G. M. Sheldrick and B. Dittrich, J. Appl. Cryst., 2011, 44, 1281-1284.

<sup>&</sup>lt;sup>15</sup> SHELXL; G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.

disordered over two orientations in a 55:45 ratio. One of the trifluoromethyl groups is additionally rotationally disordered. The dichloromethane molecule, which is located on a four-fold rotation axis, is also disordered over two orientations in a 50:50 ratio. Dibenzylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate: One of the CF<sub>3</sub> is disordered over two positions with ratio 75:25. groups а (R)-(1phenylethyl)ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (7): One of the  $CF_3$  groups (F7A-F9A) is disordered in three orientations with a ratio 50:30:20. (S,S)bis-(1-phenylethyl)ammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (8): Four of the CF<sub>3</sub> groups, as it is common in the solid state for such moieties, are disordered. F4, F5 and F6 are disordered in three positions with a ratio 45:45:10. F10, F11, F12 and F13, F14, F15 are disordered in two positions with a ratio 50:50. Finally F22, F23, F24 atoms are disordered over two positions with a ratio of 45:55. One of the phenyl rings of the (S,S)-bis-(1-phenylethyl)ammonium is disordered in two positions (C3A, C4A, C5A, C6A, C7A, C8A) with a ratio of 70:30.

For compounds **7** and **8** a determination of the absolute structure was not performed since the data collected were not suitable for this type of determination. Compound **8** crystallised as a multicomponent crystal. Only non-overlapping reflections of the measured crystals were taken in account for refinement.<sup>16</sup>

LiBArF·4H<sub>2</sub>O: One of the CF<sub>3</sub> groups is disordered over two orientations with a ratio 90:10.

LiBArF·4THF: The compound crystallised as a two component crystal with a ratio of 51:49. The collected data was processed with TWINABS taking into account overlapping reflections.<sup>16</sup>

<sup>&</sup>lt;sup>16</sup> TWINABS Version 2008/4 Bruker AXS; R. H. Blessing, Acta Cryst., 1995, A51, 33-38.

NaBArF·6THF: This compound crystallised as a two component crystal with a ratio 59:41. The collected data was processed with TWINABS taking into account overlapping reflections.<sup>16</sup>

CsBArF·7THF: This substance crystallised with four independent BArF anions and four independent  $Cs \cdot (THF)_7$  cations in the unit cell. The major part of the CF<sub>3</sub> groups of the **BArF** anions and the THF molecules are disordered in two orientations/conformations. This structure refines in the triclinic chiral space group P1 as a racemic twin (ratio 47:53). Refinement in the space group P-1 was also attempted leading to a much higher R1 value than in P1.

Details of the crystal parameters, data collection and refinement are summarised in Table S1, Table S2 and Table S3, respectively.

Compound	LiBArF	NaBArF	KBArF	RbBArF	CsBArF
Formula	C <sub>32</sub> H <sub>17,44</sub> BF <sub>24</sub> LiO <sub>2,72</sub>	C <sub>32</sub> H <sub>18.76</sub> BF <sub>24</sub> NaO <sub>2.38</sub>	$C_{32}H_{13}BF_{24}KO_{0.5}$	C <sub>32</sub> H <sub>14</sub> BF <sub>24</sub> RbO	$C_{33}H_{14}BF_{24}Cl_2Cs$
Solvent	DCM	DCM	DCM	DCM	DCM
Formula weight	919.17	931.11	911.33	966.71	1081.06
Crystal size (mm <sup>3</sup> )	0.20 x 0.10 x 0.07	0.30 x 0.18 x 0.10	0.30 x 0.30 x 0.20	0.20 x 0.20 x 0.20	0.30 x 0.20 x 0.05
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless
Ťemp (K)	100	100	100	100	100
Crystal system	Tetragonal	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Space group	P4/n	P4/n	P4/n	<i>P</i> 4/n	P4/ncc
A (Å)	13.5464(8)	13.5537(7)	13.5095(5)	13.5956(17)	13.7562(4)
B (Å)	13.5464(8)	13.5537(7)	13.5095(5)	13.5956(17)	13.7562(4)
C (Å)	9.5297(5)	9.7850(7)	9.2868(4)	9.2978(18)	19.0303(7)
$\alpha$ (deg)	90	90	90	90	90
$\beta$ (deg)	90	90	90	90	90
$\gamma$ (deg)	90	90	90	90	90
$V(Å^3)$	1748.7(2)	1798.5(2)	1695.9(15)	1719.6(5)	3601.2(2)
Z	2	2	2	2	4
$\rho$ (g/cm <sup>3</sup> )	1.746	1.720	1.786	1.868	1.994
$\mu (\text{mm}^{-1})$	0.196	0.202	0.317	1.600	1.329
$\theta_{\rm max}$ (°)	28.003	28.503	36.405	32.723	30.176
Reflec. measured	20179	9218	21387	6734	9253
Unique reflections	$2113[R_{int} = 0.039]$	$2249[R_{int}=0.031]$	$4145[R_{int} = 0.027]$	3049[R <sub>int</sub> =0.035]	$2373[R_{int}=0.025]$
Absorpt. correct.	Multi-scan	Empirical	Empirical	Empirical	Empirical
Parameters/Restrains	264/527	277/283	195/180	160/103	296/356
$R1/wR2 [I > 2\sigma(I)]$	0.051/0.129	0.062/0.173	0.054/0.164	0.055/0.142	0.038/0.094
R1/wR2 [all data]	0.069/0.141	0.089/0.198	0.061/0.169	0.077/0.151	0.052/0.102
Goodness-of-fit $(F^2)$	1.069	1.042	1.112	1.054	1.067
Peak/hole $(e/Å^3)$	0.432/-0.440	0.467/-0.406	1.162 /-0.657	0.863 /-0.545	0.936/-0.910

Table S1. Selected crystallographic data for the alkali metal salts.

Camera d	Dibenzyl ammonium	( <i>R</i> )-(1-phenylethyl)	(S,S)-Bis-(1-phenylethyl)	
Compound	<b>B</b> ArF ( <b>6</b> )	ammonium BArF (7)	ammonium BArF (8)	
Formula	C <sub>46</sub> H <sub>28</sub> BF <sub>24</sub> N	C <sub>40</sub> H <sub>26</sub> BF <sub>24</sub> NO	C <sub>48</sub> H <sub>32</sub> BF <sub>24</sub> N	
Solvent	CHCl <sub>3</sub>	CDCl <sub>3</sub>	CHCl <sub>3</sub>	
Formula weight	1061.50	1003.43	1089.55	
Crystal size (mm <sup>3</sup> )	0.40 x 0.20 x 0.15	0.25 x 0.25 x 0.20	0.30 x 0.20 x 0.05	
Crystal colour	Colourless	Colourless	Colourless	
Ťemp (K)	100	100	100	
Crystal system	Monoclinic	Monoclinic	Triclinic	
Space group	P2/c	C2	<i>P</i> 1	
A (Å)	19.2714(8)	22.752(5)	11.0125(5)	
B (Å)	9.2919(4)	9.487(2)	11.2448(6)	
C (Å)	24.3117(9)	19.182(4)	11.4104(7)	
$\alpha$ (deg)	90.00	90.00	109.792(5)	
$\beta$ (deg)	92.9513(14)	94.351(7)	100.616(4)	
$\gamma$ (deg)	90.00	90.00	105.928(4)	
$V(Å^3)$	4347.7(3)	4128.7(15)	1217.0(12)	
Z	4	4	1	
$\rho$ (Mg/m <sup>3</sup> )	1.622	1.614	1.487	
$\mu (\text{mm}^{-1})$	0.166	0.172	0.151	
$\theta_{max}$ (°)	29.862	29.988	30.037	
Reflec. measured	36587	25002	21568	
Unique reflections	$12160 [R_{int} = 0.042]$	$10245 [R_{int} = 0.046]$	$10916 [R_{int} = 0.113]$	
Absorpt. correct.	Empirical	Empirical	Multi-scan	
Parameters/Restrains	677/132	667/121	846/605	
$R1/wR2 [I > 2\sigma(1)]$	0.0548/0.1304	0.0493/0.1256	0.0739/0.1906	
R1/wR2 [all data]	0.0965/0.1490	0.0570/0.1325	0.0818/0.1945	
Goodness-of-fit (F <sup>2</sup> )	1.043	1.041	1.030	
Peak/hole (e/ Å <sup>3</sup> )	0.476/-0.412	0.416/-0.365	0.550/-0.448	

Table	<b>S2.</b>	Selected	crystallographic	data	for	studied	ammonium s	alts.
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Table S3. Selected crystallographic data for studied tetrahydrate and THF-solvated salts.

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Compound	L1BArF·4H <sub>2</sub> O	L1BArF 4THF	NaBArF 6THF	CsBArF 7THF
Formula	$C_{32}H_{20}BF_{24}LiO_4$	C <sub>32</sub> H <sub>29.33</sub> B <sub>0.67</sub> F <sub>16</sub> Li <sub>0.67</sub> O <sub>2.67</sub>	$C_{28}H_{30}B_{0.5}F_{12}Na_{0.5}O_3$	$C_{60}H_{68}BCsF_{24}O_7$
Solvent	THF	THF	THF	THF
Formula weight	942.23	772.39	659.42	1500.86
Crystal size (mm <sup>3</sup> )	0.15 x 0.20 x 0.20	0.15 x 0.10 x 0.06	0.15 x 0.15 x 0.08	0.25 x 0.25 x 0.10
Crystal colour	Colourless	Colourless	Colourless	Colourless
Ťemp (K)	100	100	100	100
Crystal system	Tetragonal	Triclinic	Monoclinic	Triclinic
Space group	<i>I</i> 4(1)/a	<i>P</i> 1	C2/c	P2
A (Å)	15.9430(4)	16.4686(13)	17.9001(8)	13.0651(15)
B (Å)	15.9430(4)	17.9533(15)	18.5829(8)	13.0711(14)
C (Å)	14.8521(5)	19.0631(13)	35.8142(16)	38.978(4)
$\alpha$ (deg)	90	77.610(3)	90	87.174(3)
$\beta$ (deg)	90	69.759(2)	90.5574(14)	84.108(3)
$\gamma$ (deg)	90	77.079(2)	90	89.978(3)
$V(Å^3)$	3775.1(2)	5096.0(7)	11912.5(9)	6613.1(13)
Z	4	6	16	4
$\rho$ (Mg/m <sup>3</sup> )	1.658	1.510	1.471	1.507
$\mu$ (mm <sup>-1</sup> )	0.186	0.153	0.150	0.676
$\theta_{max}$ (°)	32.450	24.959	25.064	27.669
Reflec. measured	3220	29063	19343	49448
Unique reflections	$2594 [R_{int} = 0.0275]$	$16077 [R_{int} = 0.1186]$	$14906 [R_{int} = 0.0370]$	$42676 [R_{int} = 0.0531]$
Absorpt. correct.	Multi-scan	Multi-scan	Empirical	Empirical
Parameters/Restrains	173/99	1741/1068	975/608	4592/5956
$R1/wR2 [I > 2\sigma(1)]$	0.0489/0.1294	0.0548/0.1304	0.0779/0.2036	0.0879/0.2286
R1/wR2 [all data]	0.0620/0.1387	0.1418/0.2094	0.0984/0.2213	0.0967/0.2359
Goodness-of-fit (F <sup>2</sup> )	1.055	1.031	1.078	1.023
Peak/hole (e/ Å <sup>3</sup> )	0.475/-0.406	0.584/-0.429	0.754/-0.562	2.489/-1.757

### 3. Spectroscopic Data for Alkali Metal BArF Salts:



Figure S2. <sup>13</sup>C $\{^{1}H\}$  NMR spectrum (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of LiBArF·2Et<sub>2</sub>O.



90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm Figure S4. <sup>11</sup>B{<sup>1</sup>H} NMR spectrum (128 MHz,  $C_4D_8O$ ) of LiBArF 2Et<sub>2</sub>O (TMB = Trimethyl borate).



















Figure S11. IR spectrum of NaBArF (spectra recorded from the sample as received from the supplier).





























#### 4. Spectroscopic Data for Ammonium Metal BArF Salts:





90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm **Figure S31.**  ${}^{11}B{}^{1}H{}$  NMR spectrum (128 MHz,  $CD_2Cl_2$ ) of dibenzylammonium BArF (6) (TMB = Trimethyl borate).











**Figure S36.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum (128 MHz,  $CD_2Cl_2$ ) of (*R*)-(1-phenylethyl)ammonium BArF (7) (TMB = Trimethyl borate).



Figure S37. IR spectrum of (*R*)-(1-phenylethyl)ammonium BArF (7).



Supplementary Material (ESI) for RSC Advances

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm Figure S39.  ${}^{13}C{}^{1}H$  NMR spectrum (100 MHz, CDCl<sub>3</sub>) of (*S*,*S*)-bis-(1-phenylethyl)ammonium BArF (8).

![](_page_30_Figure_1.jpeg)

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm **Figure S41.** <sup>11</sup>B{<sup>1</sup>H} NMR spectrum (128 MHz,  $CD_2Cl_2$ ) of (*S*,*S*)-bis-(1-phenylethyl)ammonium BArF (8) (TMB = Trimethyl borate).

![](_page_31_Figure_1.jpeg)

Figure S42. IR spectrum of (*S*,*S*)-bis-(1-phenylethyl)ammonium BArF (8).

### 5. ORTEP Figures for Alkali Metal BArF Salts:

![](_page_32_Figure_2.jpeg)

**Figure S43.** Crystal structure of the LiBArF salt. Colour scheme: C: black, H: blue, B: orange, F: green, L: violet, O: red. Atomic displacement ellipsoids are drawn at a 50% probability level.

![](_page_32_Figure_4.jpeg)

**Figure S44.** Crystal structure of the NaBArF salt. Colour scheme: C: black, H: blue, B: orange, F: green, Na: purple, O: red. Atomic displacement ellipsoids are drawn at a 50% probability level.

![](_page_33_Figure_1.jpeg)

**Figure S45.** Crystal structure of KBArF. Colour scheme: C: black, H: blue, B: orange, F: green, K: purple, O: red. Atomic displacement ellipsoids are drawn at a 50% probability level.

![](_page_33_Figure_3.jpeg)

**Figure S46.** Crystal structure of RbBArF. Colour scheme: C: black, H: blue, B: orange, F: green, Rb: purple, O: red. Atomic displacement ellipsoids are drawn at a 50% probability level.

![](_page_34_Figure_1.jpeg)

**Figure S47.** Crystal structure of CsBArF. Colour scheme: C: black, H: blue, B: orange, F: green, Cs: purple, Cl: green. Atomic displacement ellipsoids are drawn at a 50% probability level.