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## 2-FUNCTIONALIZED DERIVATIVES OF 2-BROMO-1,3-DIMETHYLIMIDAZOLE

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†Deceased December 22nd 2017. This paper is dedicated to Professor Kiyoshi Tomioka on the occasion of his 70th birthday.

**Abstract** – Attempts at direct bromination of 1,3-dimethylimidazolium salts with bromine were futile. A tribromide or a carbene–lithium–THF adduct were received instead. The quaternary 2-bromo compound was obtained by methylation of 2-bromo-1-methylimidazole and subsequent ion metathesis, which was converted to the corresponding 2-cyano and 2-azido derivatives. Typical reactions of the latter include a dipolar cycloaddition and the Staudinger reaction. Crystal structures of eight compounds have been determined by single-crystal X-ray diffraction.

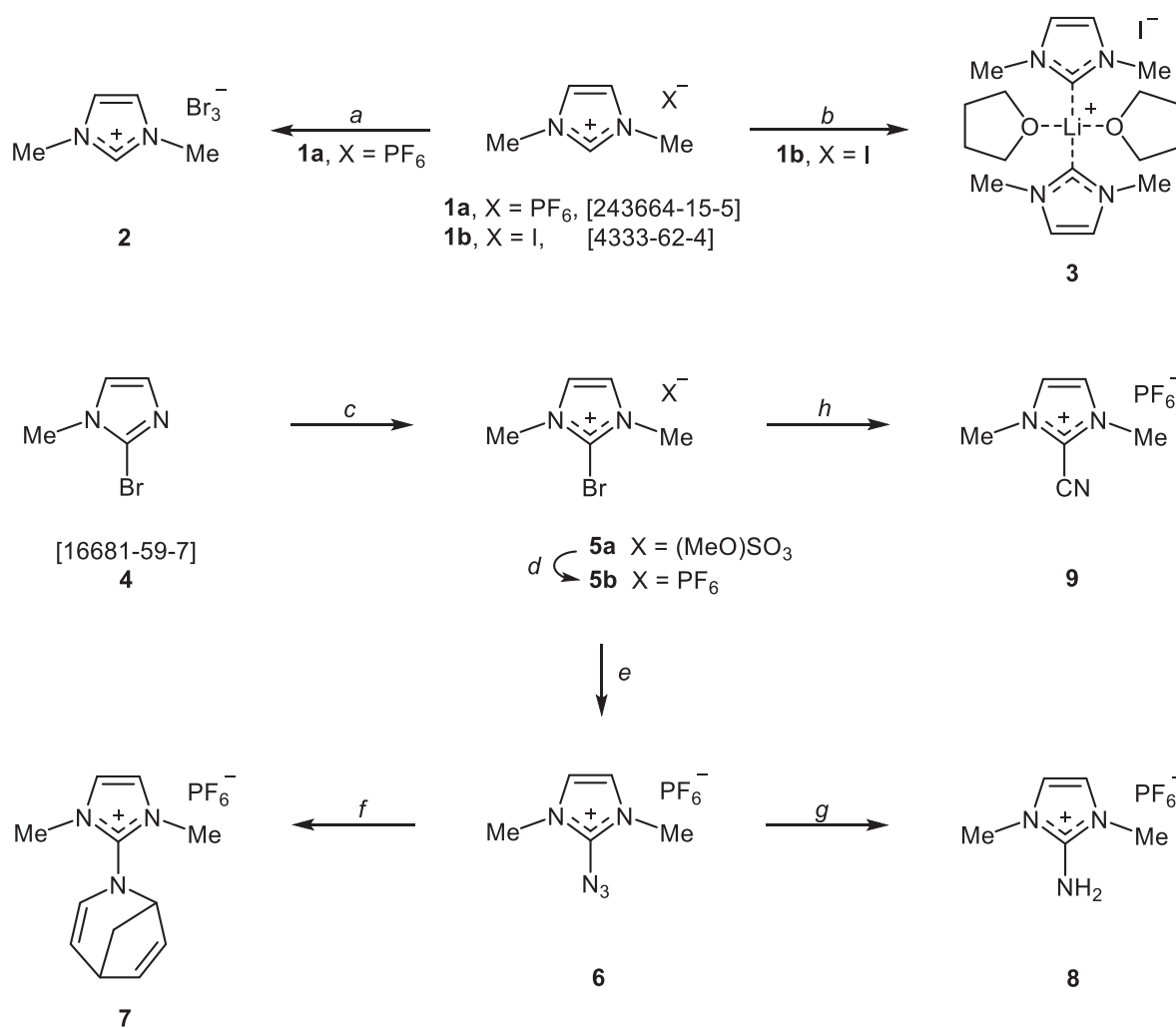
## INTRODUCTION

Salts derived from 2-bromo-1-methylimidazole are the objective of this work. They are presumed to be valuable precursors for various substitution reactions in synthetic organic or metalorganic chemistry. Usually, strongly basic conditions are needed for bromination in position 2 of 1-methylimidazole<sup>1-3</sup> or 1,3-dimethylimidazolium salts.<sup>4</sup> But since brominations in the related 1,3-dimethoxyimidazolium series,<sup>5</sup> and also bromination of 1-hydroxyimidazole 3-oxide<sup>6</sup> gave the respective 2-bromo derivatives, we hoped that a similar, simple reaction with Br<sub>2</sub> would also yield the 2-bromoimidazolium salt without using a strong base. Yet, on attempted reaction of 1,3-dimethylimidazolium hexafluorophosphate<sup>7</sup> (**1a**), no substitution occurred in 2-position as indicated by NMR, and the absence of P–F vibrations in the infrared spectra suggested the formation of a different anion, which was confirmed by X-ray diffraction. However, once the 2-bromo-1,3-dimethylimidazolium salt was obtained *via* alkylation of

2-bromo-1-methylimidazole,<sup>1,2</sup> the way was cleared for the synthesis of several new 2-substituted 1,3-dimethylimidazolium compounds. In contrast to the more complex 2-substituted imidazolium derivatives, these substances, despite their apparent simplicity, have not been described in literature yet.

## RESULTS AND DISCUSSION

To date, no simple synthesis of the 2-bromo-1,3-dimethylimidazolium salt, without the need of a strong base<sup>1-4,8</sup> or the highly toxic cyanogen bromide,<sup>9</sup> is known. Several other routes have been tried, but did not yield the desired product. Therefore, the classical approach had to be used. The resulting 2-bromo salts were then further functionalized (Scheme 1). All substances crystallize readily, and a number of structures have been determined by X-ray diffraction. ORTEP plots and packing diagrams are displayed in Figures 1-8, crystallographic data and structure refinement details are summarized in Table 1.

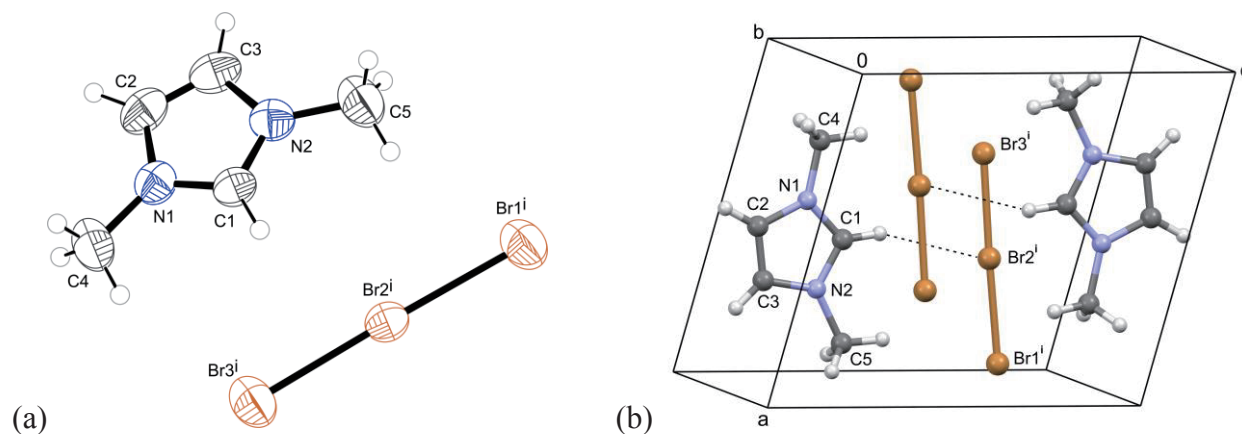


**Scheme 1.** (a) Br<sub>2</sub>, MeOH/H<sub>2</sub>O (40%); (b) LiN(SiMe<sub>3</sub>)<sub>2</sub>, THF; (c) (MeO)<sub>2</sub>SO<sub>2</sub> (72%); (d) NH<sub>4</sub>PF<sub>6</sub>, H<sub>2</sub>O (85%); (e) NaN<sub>3</sub>, acetone (96%); (f) bicyclo[2.2.1]hepta-2,5-diene, acetone (74%); (g) Ph<sub>3</sub>P, acetone/H<sub>2</sub>O (95%); (h) NaCN, MeCN (88%).

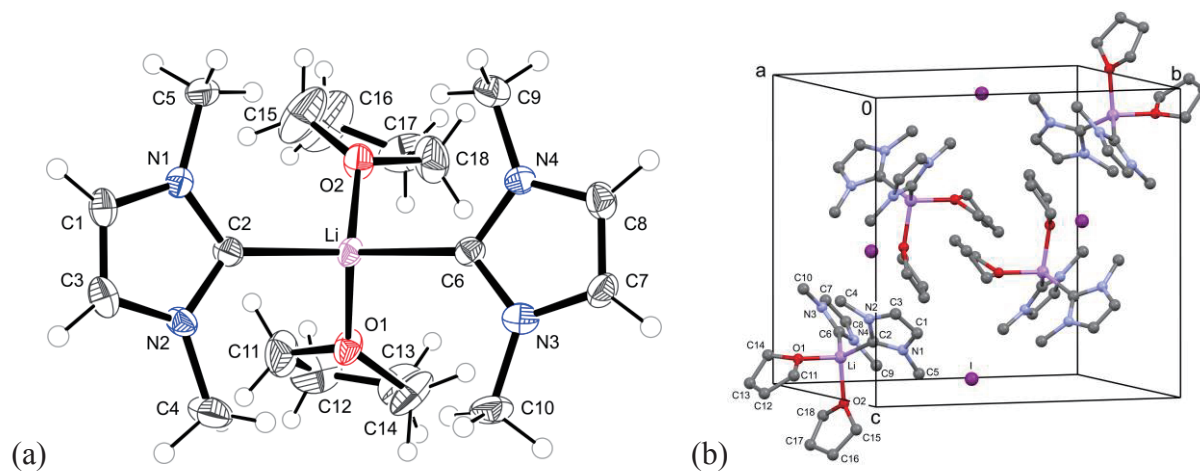
In the crystal structure of what turned out to be 1,3-dimethylimidazolium tribromide (**2**) (Figure 1), the cation is located in a mirror plane perpendicular to [010], and the methyl groups are accordingly disordered with occupancies of 0.5:0.5. The central Br atom accepts a hydrogen bond from the imidazolium ring (H...Br distance 2.8533 Å, C...Br distance 3.746 Å, C–H...Br angle 159.1°). The Br–Br–Br angle in the almost linear anion is 178.5°.

Another synthetic route starting from 1,3-dimethylimidazolium iodide (**1b**),<sup>10,11</sup> *via* the corresponding *N*-heterocyclic carbene (NHC) was considered worth trying since associated imidazolin-2-ylidene–iodine<sup>12</sup> and imidazolin-2-ylidene–bromine<sup>13</sup> coordination compounds have been reported. The unexpected result of the failure of the reaction between the NHC and bromine, bis(1,3-dimethylimidazolin-2-ylidene)-bis(tetrahydrofuran)lithium iodide (**3**), however shattered all hopes. Obviously, the carbene did not attach to the bromine molecule. The structure of **3**, shown in Figure 2, comprises a cationic moiety where the lithium center is coordinated by two neutral NHC ligands and solvated by two tetrahydrofuran molecules. The Li atom is found in a distorted tetrahedral environment, as indicated by the C–Li–C angle (118.1°) and O–Li–O angle (96.8°). As typically observed in NHC complexes,<sup>14</sup> the N–C–N 'carbene angles' of 102.6 and 103.1° are constricted in comparison with 108.7° in the structure of 1,3-dimethylimidazolium iodide,<sup>15</sup> whereas elongated C–N 'carbene bonds' range from 1.347 to 1.366 Å compared with 1.328 and 1.330 Å in the quaternary salt. The NHC ligands are planar, whereas the tetrahydrofuran ligands adopt envelope conformations (O2 and C14 out of the respective planes). The low fraction of independent reflections (0.896) for **3** is due to the fact that the crystal used for data collection was subject to non-merohedral twinning, *i. e.* a larger number of reflections could not be used due to overlapping effects. Related structures of 1,3-disubstituted imidazolin-2-ylidene–lithium complexes<sup>16–18</sup> with a single metalation site and additional ether ligands generally contain large, sterically demanding *N*-substituents. In the present structure, two humble *N*-methyl groups require minimal space. Thus, compound **3** is the smallest and simplest complex of its kind.

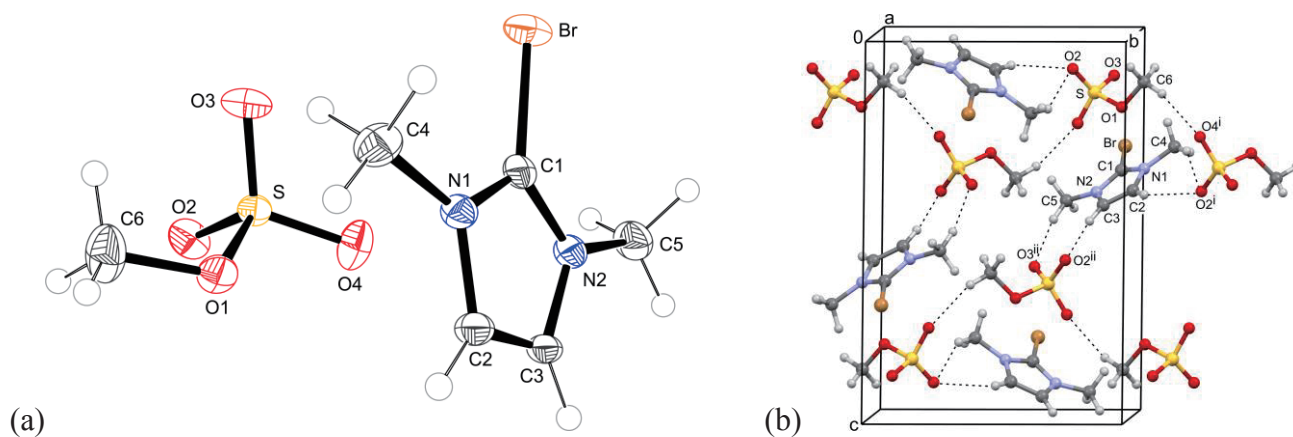
Whereas direct bromination of the quaternary salt with Br<sub>2</sub> did not yield the desired product, an altered sequence of reaction was successful. Thus, the reaction between the 2-lithio derivative of 1-methylimidazole and an equimolar amount of CBr<sub>4</sub><sup>1</sup> or Br<sub>2</sub><sup>2</sup> gave 2-bromo-1-methylimidazole (**4**) in good yield, followed by methylation using dimethyl sulfate to afford the desired quaternary salt (**5a**). A hydrogen-bonded chain of methosulfate ions has been observed in the crystal structure linking the imidazolium rings by C–H...O contacts (Figure 3). Crystal structures of solvates of the respective iodide have been reported recently.<sup>8</sup> Ion metathesis yielded the corresponding hexafluorophosphate **5b**, the cation of which is located near a symmetry center and exhibits disorder with occupation factors of 0.5 (Figure 4).



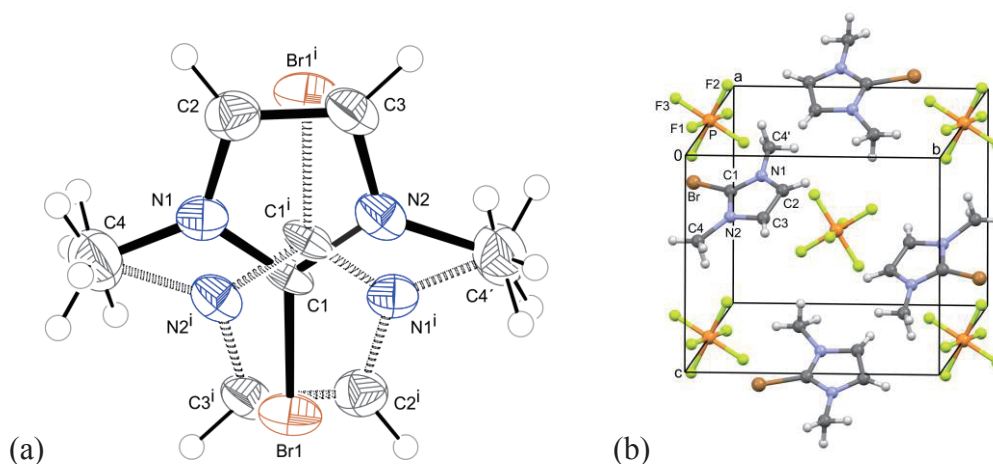
**Figure 1.** (a) Molecular structure and (b) crystal packing of compound **2**, showing the C-H...Br hydrogen bonds. Only one component of the disordered methyl groups shown. Symmetry operation: (i)  $1-x, \frac{1}{2}+y, 1-z$ .



**Figure 2.** The molecular structure of the cation of the carbene complex **3**, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms. The iodide ion is not shown. (b) The crystal packing of compound **3**.



**Figure 3.** (a) The molecular structure of compound **5a** and (b) the crystal packing showing the C-H...O hydrogen bonds. Symmetry operations: (i)  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (ii)  $x, \frac{3}{2}-y, \frac{1}{2}+z$ .

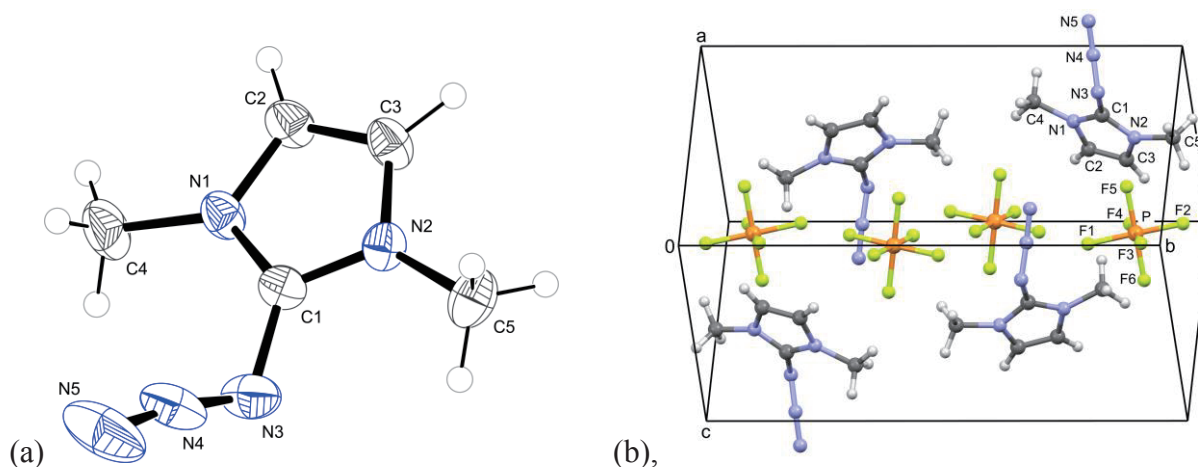


**Figure 4.** (a) Disordered cation in the crystal structure of **5b** with 50% probability displacement ellipsoids for non-H atoms. Hexafluorophosphate ion not shown. Symmetry operation: (i)  $2-x, -y, 1-z$ . (b) Crystal packing of **5b**. Only one component of the disordered cation is shown.

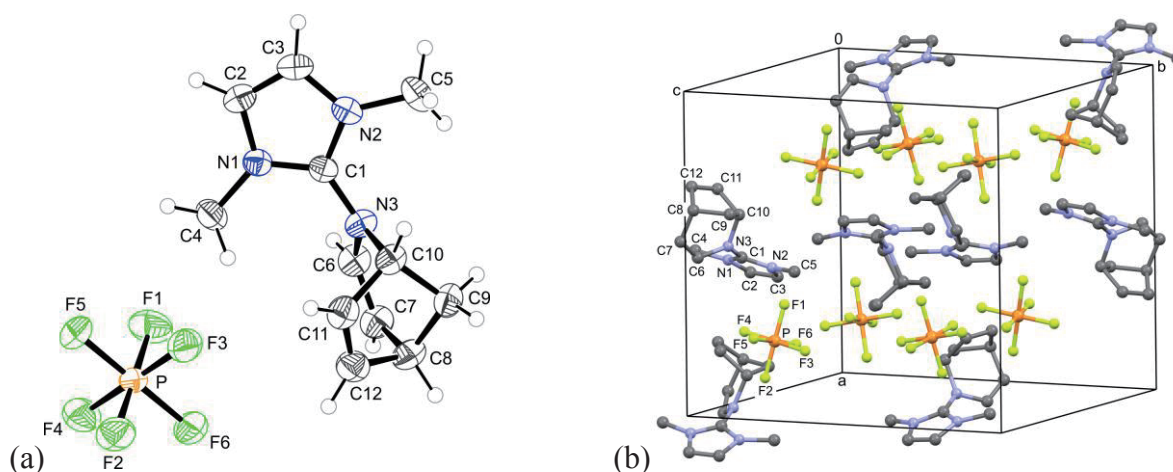
Now that the 2-brominated compound has been secured, further modifications are envisioned, giving access to a plethora of new 2-substituted 1,3-dimethylimidazolium derivatives. One of these modifications is represented by the 2-azido salt **6**. Again, this cation, despite its apparent simplicity, has not been described yet. The molecular structure is depicted in Figure 5 (disordered anion not shown). In the crystal structure of **6**, the N–N–N angle has a value of  $169.9^\circ$ . Derivatives of dipolar cycloaddition of azide with norbornene or norbornadiene have been reported in the 1,3-bis(benzyloxy)<sup>19</sup> or 1,3-bis(methoxy)<sup>20</sup> series, or as 1,2,4-triazole derivative.<sup>21</sup> In the present case, the crystal structure of the corresponding norbornadiene adduct **7** is shown in Figure 6. Another typical reaction of an organic azide is the well-known Staudinger reaction with a phosphane. The resulting iminophosphorane suffered aqueous hydrolysis forming the 2-amino salt **8**, the structure of which is displayed in Figure 7. The asymmetric unit contains 1/8 of the imidazolium molecule, whereas a positional disorder occurs, which is induced by a mirror plane perpendicular to the ring plane, with the imidazolium nitrogen N1 (occupancy of 0.25) lying above and the bridging carbon C1 (occupancy of 0.125 lying on a twofold rotation axis) below this plane. Therefore, all atoms are half occupied. The aforementioned plane belongs to the crystallographic system. Attempts to reduce the symmetry by the use of less high-symmetric space groups resulted in the same disorder or worse R-values and unreasonable displacement parameters. The positions of all hydrogen atoms were identified in difference maps and were refined using riding models or distance restraints. A further, now really positional, disorder caused by a slight twisting of the ring (which lies in a crystallographic mirror plane), could only be solved for the attached amino nitrogen atom N2 by placing the position beside the twofold rotation axis (see C1). This leads to a better R-value, but N2 had to be refined with isotropic parameters. Because of disorder and low electron density (occupancy of 0.25), the hydrogen atoms at N2

could not be localized exactly and had to be refined with bond restraint and a fixed isotropic thermal parameter 1.2 times higher than the value of N2. The high symmetry of this space group also influences the position of the PF<sub>6</sub> anion, which is also disordered, but more in a positional manner. Another modification of the title compound, the 2-cyano salt **9**, is shown in Figure 8. Both, the anion and the methyl groups of the cation are disordered.

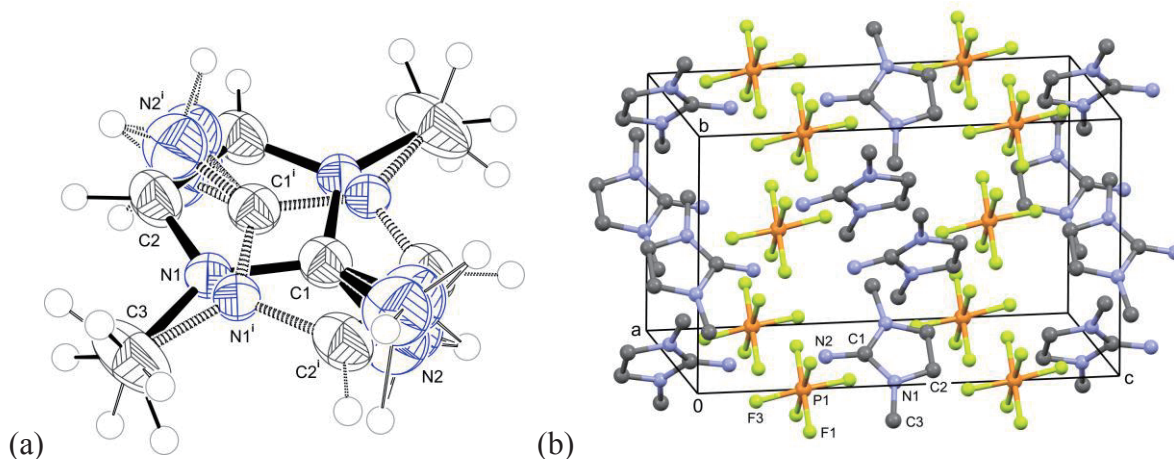
Hence, the functionalization of the 2-position of the 1-methylimidazolium system *via* bromination and subsequent substitution finally was successful.



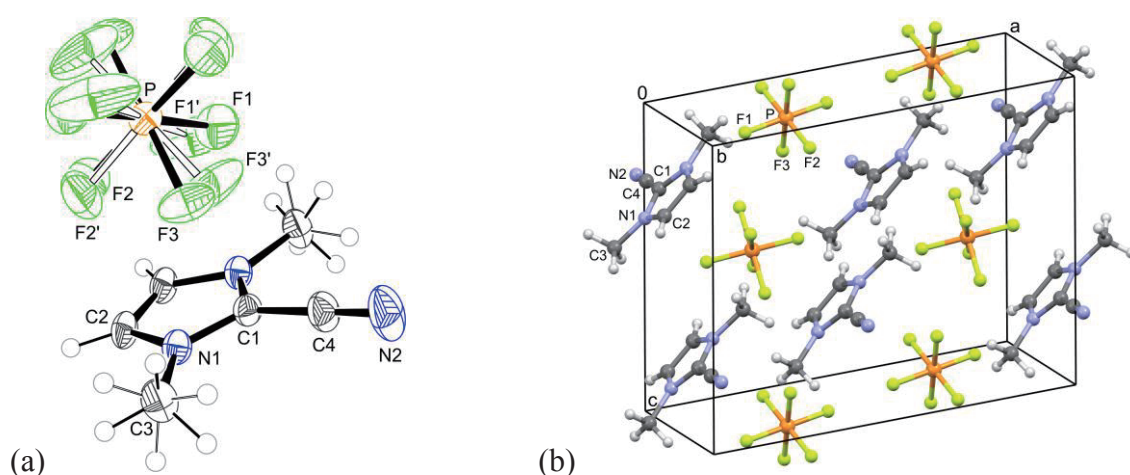
**Figure 5.** (a) The cation in the crystal structure of 2-azido salt **6**, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms. The hexafluorophosphate anion is disordered and not shown. (b) Crystal packing of **6**. Only one component of the disordered anion is shown.



**Figure 6.** (a) Ion pair in the crystal structure, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms and (b) crystal packing of the norbornadiene adduct **7**.



**Figure 7.** (a) Disordered cation in the crystal structure of 2-amino salt **8**, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms. Both the amino and the methyl groups are disordered as well. The disordered hexafluorophosphate anion is not shown. Symmetry operation: (i)  $1-x, 1-y, 1-z$ . (b) Crystal packing of **8**. Only one component of the disordered anion and the disordered cation is shown.



**Figure 8.** (a) Ion pair in the crystal structure of the 2-cyano salt **9**, showing the atom labels and 50% probability displacement ellipsoids for non-H atoms. The hexafluorophosphate anion and the methyl groups of the cation are disordered. (b) Crystal packing of compound **9**. Only one component of the disordered anion and the methyl group of the cation is shown.

Table 1. Crystallographic data and structure refinement details

	2	3	5a	5b	6	7	8	9
Formula	C <sub>8</sub> H <sub>6</sub> N <sub>2</sub> ·Br <sub>3</sub>	C <sub>8</sub> H <sub>8</sub> Li <sub>2</sub> N <sub>2</sub> O <sub>2</sub> ·I	C <sub>5</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>2</sub> ·CH <sub>3</sub> O <sub>4</sub> S	C <sub>5</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>2</sub> ·F <sub>6</sub> P	C <sub>5</sub> H <sub>8</sub> S <sub>2</sub> N <sub>2</sub> ·F <sub>6</sub> P	C <sub>12</sub> H <sub>16</sub> N <sub>3</sub> ·F <sub>6</sub> P	C <sub>3</sub> H <sub>10</sub> N <sub>3</sub> ·F <sub>6</sub> P	C <sub>6</sub> H <sub>8</sub> N <sub>3</sub> ·F <sub>6</sub> P
<i>M<sub>r</sub></i>	336.87	470.32	287.14	321.01	283.13	347.25	257.13	267.12
Cryst. size, mm <sup>3</sup>	0.11×0.08×0.04	0.32×0.26×0.20	0.30×0.20×0.07	0.16×0.06×0.05	0.18×0.16×0.12	0.28×0.18×0.14	0.18×0.18×0.02	0.12×0.05×0.04
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	tetragonal	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> bca	<i>I</i> 4/ <i>mcm</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	8.249(1)	11.656(1)	6.869(1)	6.686(1)	8.122(1)	13.657(1)	8.3547(4)	12.7945(6)
<i>b</i> , Å	6.732(4)	14.149(1)	10.168(2)	10.034(1)	15.975(1)	14.580(1)	14.580(1)	7.7901(4)
<i>c</i> , Å	9.394(2)	13.307(2)	14.900(2)	8.215(1)	8.263(1)	14.799(1)	13.5702(9)	10.5227(5)
$\beta$ , °	104.524(3)	91.01(1)	99.95(1)	111.70(1)	97.500(1)	97.500(1)	947.2(2)	97.021(2)
<i>V</i> , Å <sup>3</sup>	505.00(5)	2194.2(3)	1024.9(2)	512.1(1)	1063.1(1)	2946.9(2)	947.2(2)	1040.9(1)
<i>Z</i>	2	4	4	2	4	8	4	4
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	2.22	1.42	1.86	2.08	1.77	1.57	1.80	1.70
$\mu$ , mm <sup>-1</sup>	11.92	1.48	4.21	4.23	0.33	2.30	0.36	0.33
<i>T</i> , K	233	173	173	203	183	173	173	183
<i>F</i> (000), e	316	960	576	312	568	1424	520	536
<i>hkl</i> range	-9 ≤ <i>h</i> ≤ 9 -7 ≤ <i>k</i> ≤ 7 -11 ≤ <i>l</i> ≤ 11	-15 ≤ <i>h</i> ≤ 15 -18 ≤ <i>k</i> ≤ 18 -15 ≤ <i>l</i> ≤ 17	-6 ≤ <i>h</i> ≤ 8 -12 ≤ <i>k</i> ≤ 11 -17 ≤ <i>l</i> ≤ 17	-7 ≤ <i>h</i> ≤ 7 -11 ≤ <i>k</i> ≤ 11 -9 ≤ <i>l</i> ≤ 9	-9 ≤ <i>h</i> ≤ 9 -19 ≤ <i>k</i> ≤ 19 -10 ≤ <i>l</i> ≤ 10	-16 ≤ <i>h</i> ≤ 16 -17 ≤ <i>k</i> ≤ 17 -14 ≤ <i>l</i> ≤ 17	-10 ≤ <i>h</i> ≤ 10 -9 ≤ <i>k</i> ≤ 10 -16 ≤ <i>l</i> ≤ 16	-15 ≤ <i>h</i> ≤ 15 -9 ≤ <i>k</i> ≤ 9 -12 ≤ <i>l</i> ≤ 12
(( <i>sin</i> θ)/λ) <sub>max</sub> , Å <sup>-1</sup>	0.593	0.674	0.602	0.594	0.606	0.599	0.601	0.601
Ref <sub>l</sub> . measured	3016	7998	6339	6544	25968	19503	7470	8623
Ref <sub>l</sub> . unique / <i>R</i> <sub>int</sub>	960 / 0.035	7998 / -	1872 / 0.043	897 / 0.027	1971 / 0.024	2653 / 0.037	253 / 0.029	921 / 0.027
Ref <sub>l</sub> . observed	793	6017	1524	817	1786	2298	236	793
Parameters	64	240	130	130	181	201	54	107
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 σ( <i>I</i> )]	0.029 / 0.074	0.033 / 0.092	0.031 / 0.059	0.024 / 0.058	0.031 / 0.085	0.035 / 0.090	0.034 / 0.088	0.027 / 0.064
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.037 / 0.077	0.051 / 0.105	0.045 / 0.065	0.028 / 0.059	0.035 / 0.088	0.042 / 0.095	0.036 / 0.090	0.034 / 0.067
Goodness of fit	1.04	1.03	1.07	1.10	1.05	1.03	0.95	1.08
Δρ <sub>max</sub> / min, e Å <sup>-3</sup>	0.45 / -0.65	0.93 / -0.91	0.52 / -0.43	0.32 / -0.17	0.32 / -0.22	0.25 / -0.31	0.14 / -0.21	0.18 / -0.20
CCDC No.	1834818	1834820	1834813	1834819	1834814	1834817	1834815	1834816

## EXPERIMENTAL

Reagents and solvents were purchased from Sigma-Aldrich. 1,3-Dimethylimidazolium hexafluorophosphate<sup>7</sup> (**1a**) and 1,3-dimethylimidazolium iodide<sup>10,11</sup> (**1b**) were prepared according to published procedures. A combination of procedures was used to prepare 2-bromo-1-methylimidazole (**4**).<sup>1,2</sup> NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer. IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument. Diffraction intensity data were recorded with Nonius KappaCCD, Gemini Ultra or Bruker D8 Quest Photon 100 diffractometers using MoK $\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) or CuK $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. The crystal structures were solved by Direct Methods and refined by full-matrix least-squares techniques.<sup>22,23</sup> Visualization of the structures and measurements of distances and angles was performed with the programs Ortep-3<sup>24</sup> and Mercury.<sup>25</sup> CCDC 1834812–20 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](http://www.ccdc.cam.ac.uk/data_request/cif).

**1,3-Dimethylimidazolium tribromide (2).** A mixture of 1,3-dimethylimidazolium hexafluorophosphate (**1a**; 100 mg, 0.41 mmol), H<sub>2</sub>O (0.4 mL), MeOH (0.2 mL), and Br<sub>2</sub> (42  $\mu$ L, 0.83 mmol) was stirred at room temperature for 48 h. The resulting orange crystals were collected, washed with H<sub>2</sub>O (2  $\times$  0.5 mL) and dried under reduced pressure to yield 55 mg (40%), mp 108 °C. – <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  3.84 (s, 6H), 7.68 (s, 2H), 9.04 (s, 1H) ppm. – <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  35.7 (2C), 123.4 (2C), 137.0 ppm. – IR (neat):  $\nu$  3144 (w), 3101 (w), 1562 (m), 1438 (m), 1164 (m), 836 (s), 750 (s), 616 (s) cm<sup>-1</sup>.

**Bis(1,3-dimethylimidazolin-2-ylidene)-bis(tetrahydrofuran)lithium iodide (3).** A suspension of 1,3-dimethylimidazolium iodide (**1b**; 220 mg, 1.0 mmol) in THF (3 mL) was cooled under argon at -120 °C. A solution of 1M lithium bis(trimethylsilyl)amide in THF (1 mL) was added. The mixture was stirred at -120 °C for 20 min, then at room temperature for 2 h. For attempted bromination, Br<sub>2</sub> (50  $\mu$ L) was added, however, without effect. On cooling to -40 °C, the product was obtained as colorless crystals, too unstable for spectroscopic and analytical characterization.

**2-Bromo-1-methylimidazole (4).** 1-Methylimidazole (3.5 g, 42.6 mmol) was dissolved in Et<sub>2</sub>O (150 mL) and cooled with EtOH/N<sub>2</sub>. *n*-Butyllithium (2.5 M, 21.3 mL, 53.15 mmol) was added and stirred for 2 h under Argon at -100 °C. A solution of CBr<sub>4</sub> (14.8 g, 1.1 equiv, 44.8 mmol) in Et<sub>2</sub>O (120 mL) was added dropwise and stirring was continued for 20 min at room temperature. Saturated aqueous NH<sub>4</sub>Cl solution (100 mL) was added and the mixture was filtered. The filtrate was extracted with Et<sub>2</sub>O (2  $\times$  100 mL) and the organic phase was washed with water (100 mL). The solvent was removed under reduced pressure and the resulting brown liquid was distilled (43 °C/0.6 mbar), yielding 4.86 g (71%) of the product as a colorless liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.46 (s, 3H), 6.80 (d, *J* = 1.5 Hz, 1H), 6.82 (d, *J* = 1.5 Hz, 1H) ppm.

–  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  34.4, 119.7, 123.0, 129.4 ppm. – IR (neat):  $\nu$  3112 (w), 2950 (w), 1512 (m), 1471 (m), 1415 (m), 1350 (m), 1273 (m), 1116 (m), 1080 (w), 909 (w), 736 (m), 657 (s)  $\text{cm}^{-1}$ .

**2-Bromo-1,3-dimethylimidazolium methosulfate (5a).** 2-Bromo-1-methylimidazole (**4**; 2.0 g, 12.4 mmol) was cooled with an ice-bath and dimethyl sulfate (1.2 mL, 12.6 mmol) was added under vigorous stirring. The solid formed was recrystallized in  $\text{CHCl}_3$  and dried, yielding 2.6 g (72%) of 2-bromo-1,3-dimethylimidazolium methosulfate (**5a**) as off-white crystals. mp 115.5–116.5 °C. –  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}_d_6$ ):  $\delta$  3.38 (s, 3H), 3.80 (s, 6H), 7.87 (s, 2H) ppm. –  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}_d_6$ ):  $\delta$  36.9 (2C), 53.0, 123.2, 124.8 (2C) ppm. – IR (neat):  $\nu$  3117 (w), 3085 (w), 2949 (w), 1572 (w), 1528 (m), 1458 (w), 1205 (vs), 1055 (m), 1001 (s), 796 (w), 740 (s), 650 (m), 606 (m), 575 (s), 553 (s), 430 (m)  $\text{cm}^{-1}$ .

**2-Bromo-1,3-dimethylimidazolium hexafluorophosphate (5b).** 2-Bromo-1,3-dimethylimidazolium methosulfate (**5a**; 1.51 g, 5.25 mmol) was dissolved in  $\text{H}_2\text{O}$  (3 mL) and a solution of  $\text{NH}_4\text{PF}_6$  (900 mg, 5.53 mmol) in  $\text{H}_2\text{O}$  (2 mL) was added, forming a colorless precipitate. The mixture was stirred overnight at 4 °C, filtered and washed with ice water ( $2 \times 2$  mL) and  $\text{Et}_2\text{O}$  (4 mL). The product was dried under reduced pressure yielding 1.43 g (85%), mp 241–246 °C (dec.). –  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}_d_6$ ):  $\delta$  3.80 (s, 6H), 7.88 (s, 2H) ppm. –  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}_d_6$ ):  $\delta$  36.8 (2C), 123.2, 124.7 (2C) ppm. – IR (neat):  $\nu$  3177 (w), 3153 (w), 1572 (w), 1530 (m), 1410 (w), 1338 (w), 1235 (m), 1169 (w), 1091 (w), 814 (vs), 737 (s), 653 (m), 553 (vs)  $\text{cm}^{-1}$ .

**2-Azido-1,3-dimethylimidazolium hexafluorophosphate (6).** To a solution of 2-bromo-1,3-dimethylimidazolium hexafluorophosphate (**5b**; 120 mg, 0.37 mmol) in acetone (3 mL),  $\text{NaN}_3$  (27 mg, 1.1 equiv) was added. The mixture was stirred for 7 d at –24 °C, the mixture was filtered and the solvent was removed under reduced pressure in an ice-bath to yield 102 mg (96%) of an off-white residue. Single-crystals were obtained by diffusion of  $\text{Et}_2\text{O}$  into a solution in acetone, mp. 88 °C (dec.). –  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}_d_6$ ):  $\delta$  3.74 (s, 6H), 7.53 (s, 2H) ppm. –  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}_d_6$ ):  $\delta$  34.0 (2C), 120.7 (2C), 136.3 ppm. – IR (neat):  $\nu$  2161 (m), 1594 (m), 822 (vs), 740 (m), 555 (s)  $\text{cm}^{-1}$ .

**2-(2-Azabicyclo[3.2.1]octa-3,6-dien-2-yl)-1,3-dimethylimidazolium hexafluorophosphate (norbornadiene adduct) (7).** A solution of azide **6** (100 mg, 0.035 mmol) and bicyclo[2.2.1]hepta-2,5-diene (36 mg, 1.1 equiv) in acetone (3 mL) was stirred overnight at 4 °C. After addition of  $\text{Et}_2\text{O}$  (10 mL), the precipitate was washed with  $\text{Et}_2\text{O}$  and vacuum-dried to give 80 mg (74%) of a light brown solid, mp 161 °C (dec.). –  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}_d_6$ ):  $\delta$  1.89–2.00 (m, 2H), 2.83 (m, 1H), 3.62 (s, 6H), 4.45 (m, 1H), 5.20 (Td,  $J = 6.4$  and 1.2 Hz, 1H), 5.58 (dd,  $J = 5.6$  and 2.3 Hz, 1H), 5.96 (Dt,  $J = 7.6$  and 0.9 Hz, 1H), 6.31 (dd,  $J = 2.8$  and 5.6 Hz, 1H), 7.55 (s, 2H) ppm. –  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO}_d_6$ ):  $\delta$  34.0 (2C), 35.0, 35.2, 63.2, 106.0, 119.9, 120.4 (2C), 124.4, 137.3 ppm. – IR (neat):  $\nu$  3153 (s), 1593 (m),

1531 (m), 829 (vs), 751 (m), 704 (m), 556 (s)  $\text{cm}^{-1}$ .

**2-Amino-1,3-dimethylimidazolium hexafluorophosphate (8).** A solution of azide **6** (98 mg, 0.35 mmol) and triphenylphosphine (103 mg, 1.1 equiv) in acetone (3 mL) was stirred overnight at 4 °C. After addition of  $\text{H}_2\text{O}$  (2 mL), the mixture was stirred for 1 h, the volatiles removed, the residue partitioned between  $\text{Et}_2\text{O}$  ( $5 \times 3$  mL) and  $\text{H}_2\text{O}$  (3 mL) and vacuum-dried to give 85 mg (95%) of a white solid, mp 140-142 °C (dec.). –  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  3.44 (s, 6H), 6.99 (s, 2H), 7.71 (br, 2H) ppm. –  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  32.5 (2C), 116.5 (2C), 145.9 ppm. – IR (neat):  $\nu$  3476 (w), 3388 (w), 1659 (m), 1575 (m), 1435(m), 1267 (m), 1180 (w), 1119 (s), 823 (vs), 746 (m), 724 (s), 686 (s), 555 (s)  $\text{cm}^{-1}$ .

**2-Cyano-1,3-dimethylimidazolium hexafluorophosphate (9).** To a solution of 2-bromo-1,3-dimethylimidazolium hexafluorophosphate (**5b**; 100 mg, 0.31 mmol) in MeCN (abs.) (2 mL), NaCN (18 mg, 1.15 equiv) was added. The mixture was stirred for 31 h under inert gas at room temperature. The solvent was removed under reduced pressure. Acetone (3 mL) was added to the residue, it was filtered and washed with acetone (2 mL). The solvent of the filtrate was removed under reduced pressure and the residue was vacuum-dried to yield 73 mg (88%) of the crude product as off-white solid. Single-crystals were obtained by diffusion of  $\text{Et}_2\text{O}$  into a solution in acetone, mp 242 °C (dec.). –  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  4.02 (s, 6H), 8.06 (s, 2H) ppm. –  $^{13}\text{C}$  NMR (75 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  36.9 (2C), 105.2, 120.4, 126.8 (2C) ppm. – IR (neat):  $\nu$  3179 (w), 3161 (w), 2259 (w), 1581 (w), 1543 (m), 1444 (m), 1243 (m), 1092 (w), 1046 (w), 824 (vs), 685 (m), 556 (s), 456 (m)  $\text{cm}^{-1}$ .

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