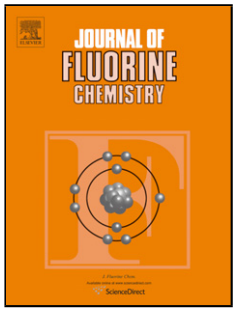

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Synthetic and structural studies on pentafluorobenzylated imidazole systems

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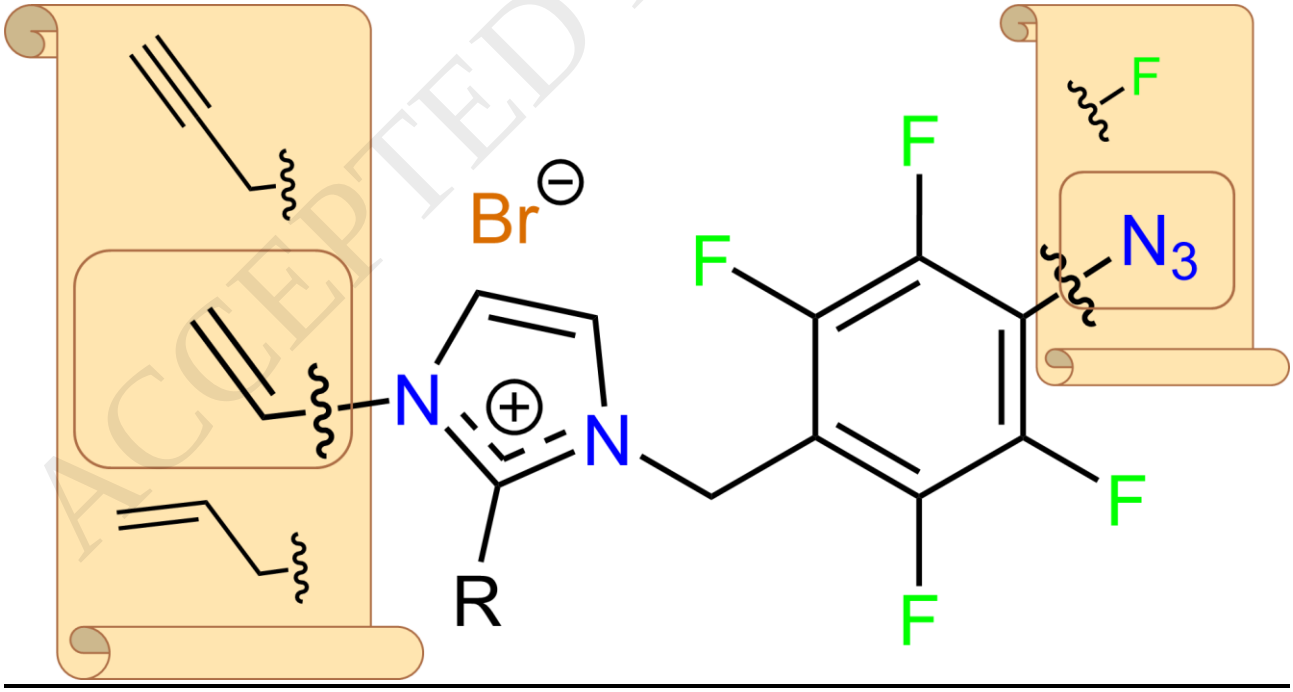
Graphical abstract



Highlights:

- Synthesis of different amphiphilic compounds *via* well-known S- and/or N- alkylation routes.
- Characterisation of several pentafluorobenzylated imidazole compounds and their reaction intermediates by single crystal analysis, IR- and NMR-spectroscopy, and mass spectrometry.
- Performance of surface tension experiments for key substances.
- Functionalisation of the pentafluorobenzyl subunit using azide, and thermochemical investigations of the product (TGA/DSC).
- Investigation of Staudinger and copper-catalysed azide-alkyne cycloaddition reactions with azide derivative.

ABSTRACT

Quaternization of common N-functionalized imidazoles (vinyl-, allyl-, propargyl-) with pentafluorobenzyl bromide afforded the respective series of differently substituted imidazolium salts. Likewise, chemospecific S- and N-alkylation of the commercial medicinal drug methimazole (1-methyl-3*H*-imidazole-2-thione) and its vinylated relative 1-vinyl-3*H*-imidazole-2-thione yielded N,S-bis(pentafluorobenzyl)-2-mercaptoimidazole derivatives.

In order to illustrate the proven feasibility of perfluorophenyl moieties to undergo further nucleophilic aromatic substitution, one member of this newly conceived family of fluorinated salts was converted to the *4*-azido derivative, namely 3-(4-azido-2,3,5,6-tetrafluorobenzyl)-1-vinylimidazolium bromide. Staudinger and copper-catalyzed azide-alkyne cycloaddition reactions were performed as well in an initial investigation into azide follow-up chemistry. All target compounds, including new intermediates, were characterized by routine spectroscopy and mass spectrometry. Additionally, X-ray single crystal structure determinations were performed for 14 substances.

Surfactant properties were investigated for selected representatives through surface tension measurements. Lastly, the thermal stability of the azido compound was evaluated by thermoanalysis (TGA /DSC).

Keywords: pentafluorobenzyl imidazoles; crystal structure analysis; surface tension; nucleophilic aromatic azidation, Staudinger reaction, CuAAC click reaction

1. INTRODUCTION

Ever since Heinrich Debus discovered glyoxaline (imidazole) in 1858,[1] the scientific world continues to be intrigued by this simple aromatic heterocycle, an amphoteric molecule frequently referred to as "organic water". Like imidazole itself, which is a natural product occurring in edible lentils,[2] countless derivatives have been identified as active principles of medicinal and biological relevance. Due to their exceptional chemical tailorability, azolium heterocycles, including polymerizable ones, have conquered many different technical fields [3] and applications spanning from cosmetic hair care [4] to electrochemical processes.[5]

In the closely interrelated areas of N-heterocyclic carbene (NHC) complexes and imidazole-based ionic liquid (IL) chemistry, materials science and catalysis are continuously advancing.[6-13] In particular, azolium compounds bearing unsaturated side chains, such as 1-allyl-, 1-vinyl- or 1-propargylimidazole, had a profound impact.[4,5,14]

As is generally known, the incorporation of perfluoroalkyl or (perfluoroalkyl)alkyl moieties results in physicochemical properties that significantly differ from those of their respective hydrocarbon parent structures. Perfluoroalkyl and (perfluoroalkyl)alkyl compounds are famous for their water and/or oil repellency, thermal stability, oxygen affinity, and surfactant properties.[15-17]

In contrast, the formally related perfluoroaryl or (perfluoroaryl)alkyl groups are not necessarily linked to high surface activity. However, Broniatowski & Dynarowicz-Łatka [18] recently reported on non-ionic surfactants based on a perfluorobenzyl system. In the same vein, we set out to conduct an investigation focused on the combination of hydrophobic, lipophilic (perfluoroaryl)alkyl moieties with several polar, hydrophilic imidazolium cores.

2. RESULTS AND DISCUSSION

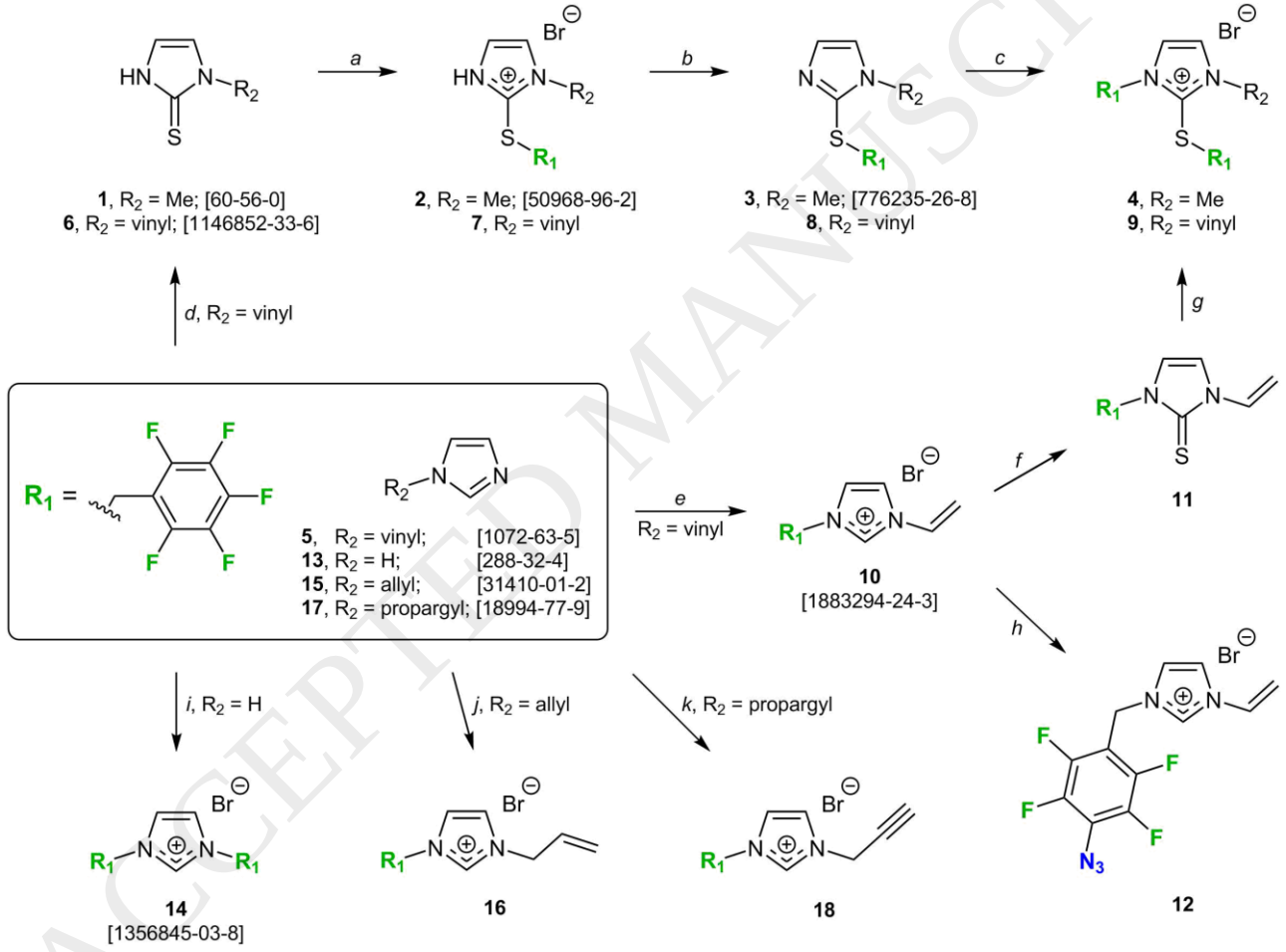
2.1 Synthetic considerations

Quaternization of amine or imine systems is mainly achieved by the well-known Menshutkin reaction,[19,20] yielding N-quaternized organic cations. In comparison to standard N-alkylation reactions, perfluoralkyl and (perfluoroalkyl)alkyl halides of the types Rf_nX and Rf_nCH_2X show a significantly decreased propensity towards S_N2 reactions due to the electron withdrawing effect of the fluorine atoms, rendering the terminal halide a bad leaving group.[21] The introduction of an ethylene spacer to Rf_nX compounds, giving reactants of the type $Rf_nCH_2CH_2X$, mitigates this deactivating effect and allows for S_N2-typical use as alkylating agent.[10]

However, quaternization reactions of amines or imines with such 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl halides may be rivalled by base-promoted elimination reactions and might predominantly result in 1*H*,1*H*,2H,2*H*-perfluoroalk-1-enes and ammonium or iminium halides.[22,23] In contrast, no eliminative side reactions are to be expected for the highly reactive and commercially available

2,3,4,5,6-pentafluorobenzyl bromide (PFB-Br).

In analogy to our previous efforts in the field of (perfluoroalkyl)alkylimidazolium salts,[9] we again chose the affordable medical drug methimazole (1-methyl-3*H*-imidazole-2-thione) as starting material. As MacFarlane and co-workers have shown, methimazole regioselectively reacts with alkyl halides via S-alkylation to the respective 2-alkylmercaptoimidazolium halides.[12-13] Accordingly, the alkylation of methimazole with PFB-Br leads to the formation of 1-methyl-2-[(2,3,4,5,6-pentafluorobenzyl)thio]-3*H*-imidazolium bromide (**2**). This substance was one of many compounds tested for antimicrobial behaviour, but no further analytical characterization (e.g. NMR spectroscopy, X-ray diffraction) has been reported.[24] Deprotonation of **2**, resulting in compound **3**, and subsequent N-functionalization affords the doubly alkylated S,N-bis(pentafluorobenzyl) salt **4** in high yields (Scheme 1).



Scheme 1. Synthetic approaches to multiply functionalized pentafluorobenzylated imidazole systems. (*a*) PFB-Br, MeCN; (*b*) $NaHCO_3$, MeOH; (*c*) PFB-Br, MeCN; (*d*) ^{i}Pr-MgCl, S_8, THF, HCl/H_2O; (*e*) PFB-Br, MeCN; (*f*) S_8, NEt_3, pyridine; (*g*) PFB-Br, MeCN; (*h*) NaN_3, $CaBr_2$, MeCN; (*i*) PFB-Br (2 equiv.), $NaHCO_3$, MeCN; (*j*) PFB-Br, MeCN; (*k*) PFB-Br, MeCN.

In recent literature,[25-27] the N,N-bispentafluorobenzylated imidazolium salt **14** [1356845-03-8] has proven to be a valuable precursor in the synthesis of palladium or rhodium NHC complexes for catalytic purposes or the fabrication of perrhenate salts. A new preparative strategy was conceived, and **14** was obtained in excellent yields via a one-pot reaction of imidazole with a mild base and PFB-Br (2 equiv.).

According to a procedure published by Vereshchagin *et al.* (2006) [28] and Wang *et al.* (2016),[29] propargyl imidazole (**17**) was synthesised from imidazole and propargyl bromide in the presence of KOH under mild conditions. Inspired by this work, both 1-propargyl- and 1-allylimidazole were functionalized as well, resulting in their respective N-pentafluorobenzyl salts **16** and **18**.

In order to access the doubly N- and S-pentafluorobenzylated vinylimidazolium bromide **9**, two different routes, starting with vinylimidazole, are viable. The first route begins with the thionation of vinylimidazole using a published procedure.[30] S-Pentafluorobenzylation of **6** resulted in the hydrobromide salt **7**, which was neutralized to give **8**. The second route comprises N-pentafluorobenzylation of vinylimidazole,[31] yielding compound **10**, followed by thionation at position 2, in turn forming the thione **11**. Subsequent alkylation of **8** or **11** afforded the S,N-bis(pentafluorobenzyl)ated compound **9** in comparatively low yields. In search of a reason for such poor conversions, we found that the S-pentafluorobenzyl moiety of **9** exhibits a certain instability in solution and is readily attacked by nucleophiles. It is likely that, at elevated temperatures or long reaction times, even bad nucleophiles such as bromide, suffice to abstract the S-pentafluorobenzyl group, thus reversing the desired reaction.

The aforementioned peculiarity was confirmed by ^{1}H-NMR experiments (Figure 1). In the presence of moderately nucleophilic pyridine, **9** reacts to the thione **11**, and the respective pentafluorobenzylated pyridinium salt is formed to the same extent. The first two NMR spectra display the proton signals of **9** before (A) and directly after (B) the addition of pyridine. After 24 hours at room temperature, the spectrum exhibits additional peaks at 9.17, 8.70, 8.23 and 6.18 ppm, corresponding to the newly formed pyridinium salt, whereas the peaks at 4.96, 5.30, 5.49, 7.27 – 7.42 and 7.64 ppm belong to thione **11**. Approximately 30 % of **9** are still left in the sample (C). After 12 days at room temperature, the S-pentafluorobenzyl moiety was fully transferred to pyridine. The ^{1}H-NMR spectrum shows only the signals of the thione **11**, the pyridinium salt and an excess of pyridine (D). The reference spectra of the thione **11** and the pure pyridinium salt, obtained via equimolar reaction of pyridine with PFB-Br at room temperature overnight, are shown in E and F, respectively. Similar findings in recent literature regarding thioimidazolium ionic liquids [32] suggest that S-alkylated thioimidazolium salts may, generally, react as alkylating agents.

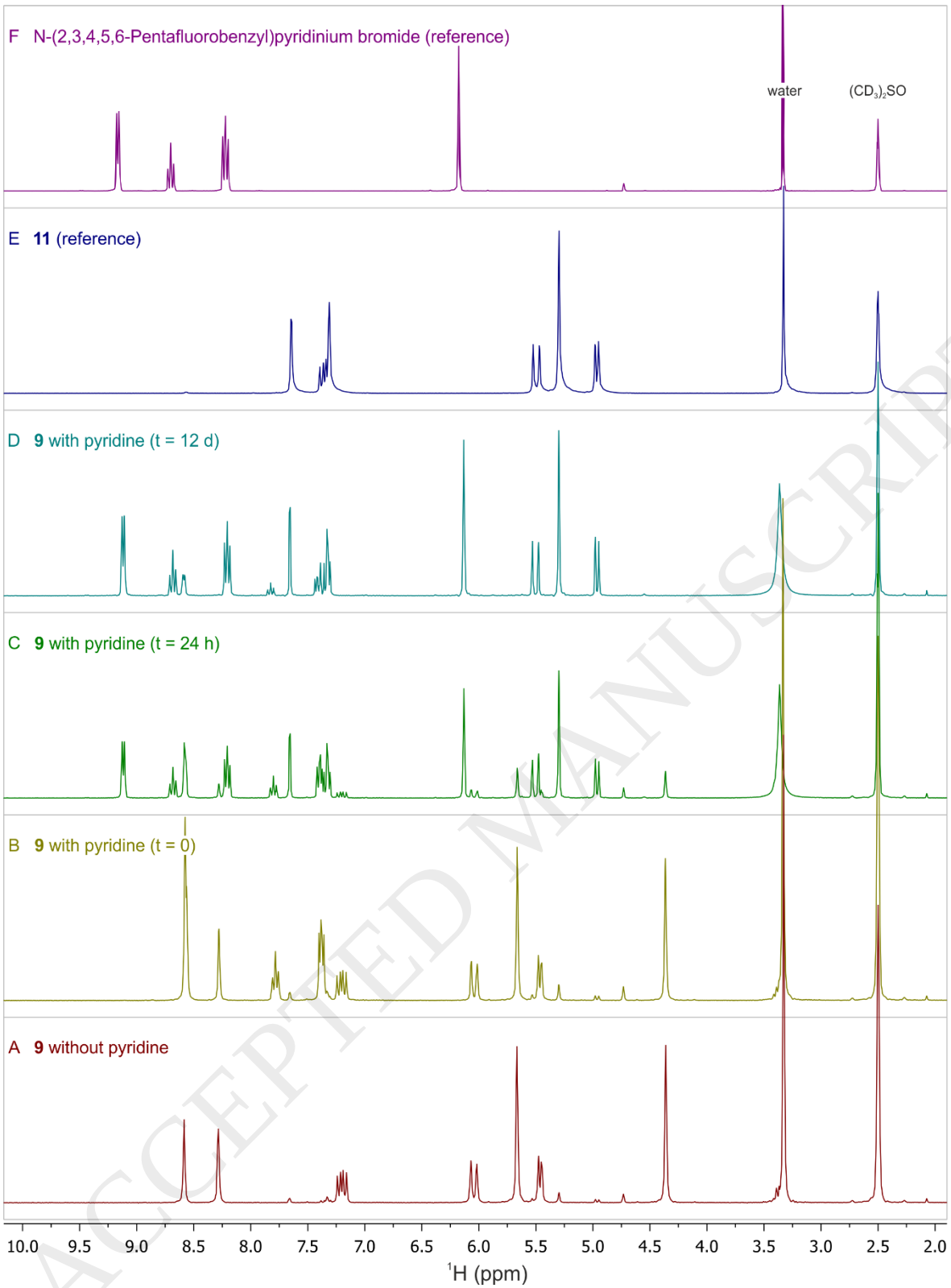


Figure 1. Transfer of the S-pentafluorobenzyl moiety from the both N- and S-pentafluorobenzylated salt **9** to pyridine, forming the N-pentafluorobenzylated vinylimidazolinethione **11** and N-pentafluorobenzylated pyridinium bromide.

Furthermore, conversion of the pentafluorobenzyl moiety into a 4-azidotetrafluorobenzyl group via well-established S_NAr reactions,[33-37] forming compound **12**, underline their synthetic modularity (Scheme 1). The thermal properties of the introduced azide functionality were characterized by DSC and TGA analysis (Figure 2). Thermal decomposition of **12** starts at approximately 125 °C and undergoes an apparent interconnected two-step process (125 – 159 °C, 159 – 180 °C), followed by continuous mass loss. This result is in accordance with the DSC analysis, in which a single exothermic event peaking at around 159 °C occurs, thus reflecting the onset of rapid decomposition typically observed in azide-containing energetic compounds. Considering the two steps observed in the TGA curve and the corresponding mass loss, there is evidently a more complex degradation-polymerisation cascade involved than the mere elimination of N_2.[38-40]

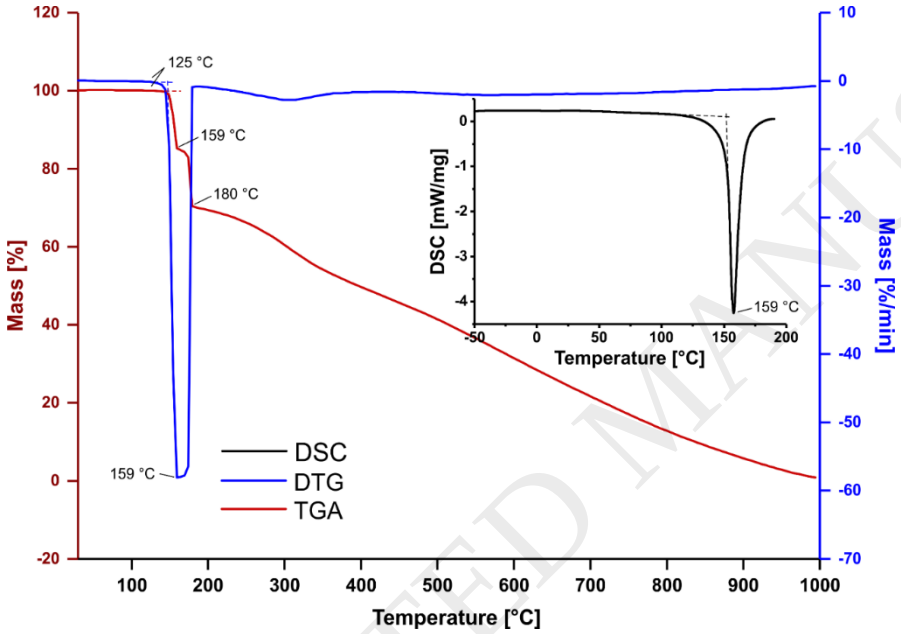
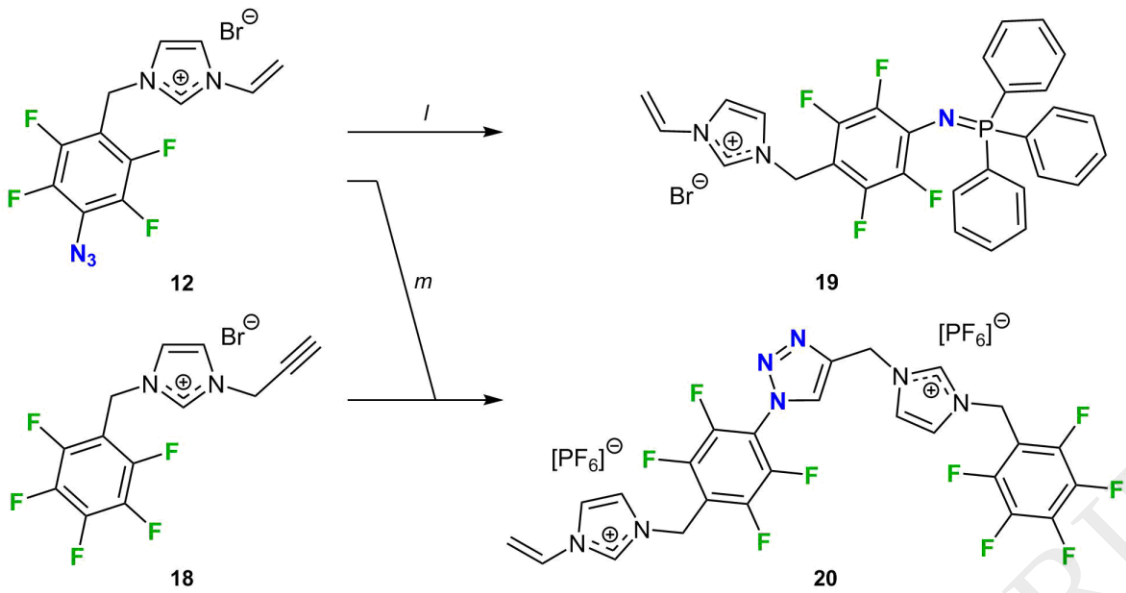


Figure 2. TG, DTG and DSC analyses of azide compound **12**.

The implementation of an azide moiety opens up a plethora of further derivation options, two of which were explored, namely a Staudinger reaction and a copper-catalysed azide-alkyne cycloaddition (CuAAC) (Scheme 2).[34,35,41,42] Addition of triphenylphosphine to a solution of **12** results in the formation of the corresponding phosphazene **19**, which proved to be rather stable against hydrolysis.

The CuAAC reaction was performed using reactants **12** and **18**, yielding triazole **20**. Of course, these model reactions should be understood as proof of principle and merely aim to illustrate the rich follow-up chemistry that was made accessible through azidation of the pentafluorophenyl moiety.



Scheme 2. Representative follow-up chemistry based on azide intermediate **12**. (*l*) PPh_3, MeCN; (*m*) 1. $CuSO_4 \cdot 5\ H_2O$ (cat.), sodium ascorbate (0.2 equiv.), $^{i}PrOH$ / H_2O 2:1, 2. $(NH_4)PF_6$, H_2O.

2.2 Structural analyses

All investigated substances were found to crystallize readily, thus enabling the structure determination of **2** – **4**, **7**, **8**, **9 · CHCl$_3$**, **10 · 2 H$_2$O**, **11**, **12**, **14**, **16**, **18, 19 · CH$_3$CN· 0.22 H$_2$O** and **20** (Scheme 1 and 2) from single-crystal X-ray data (see Table S1 and Figures S1 – S14 in section 2 of the supporting information). The bond distances and angles observed for these compounds do not exhibit any uncommon features. The bromide salts **2** and **7**, whose cations differ only in their N-1 substituent (Me or vinyl), are isostructural (Figure 3). The corresponding *XPac* comparison [43] of the cation packing gives a dissimilarity index [44] of 5.4 (for details, see section 3 of the supporting information).

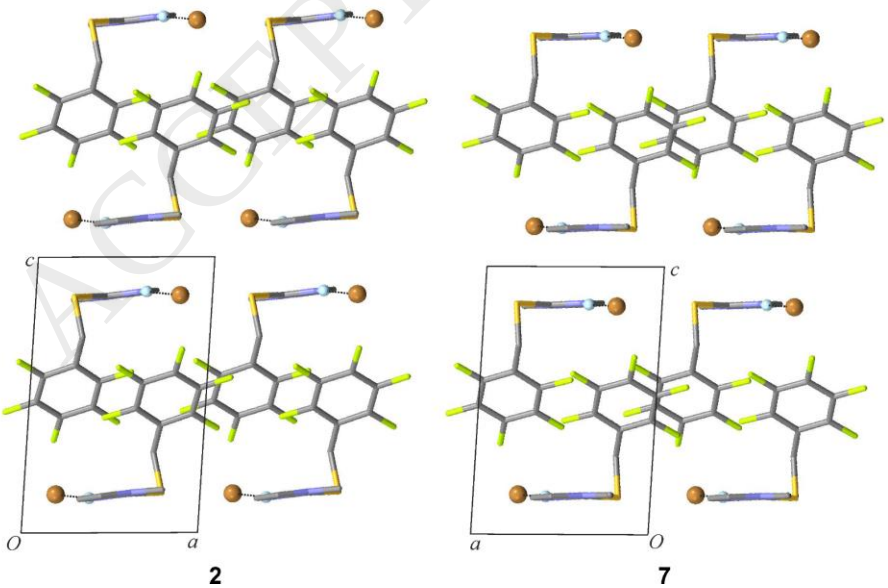


Figure 3. Molecular packing of **2** and **7**, viewed along the respective *b* axis in the crystal structures, illustrating their isostructural relationship. Cations and Br^- are connected by an N–H···O bond. H atoms not involved in H-bonds are omitted for clarity.

Variations in molecular conformation can be rationalized in terms of the 2-[(pentafluorobenzyl)thio]imidazole fragment I (Figure 4a) present in compounds **2** – **4** and **7** – **9** or the 1-(pentafluorobenzyl)imidazole fragment II, which is found in **4**, **14**, **16**, **18** and **9** – **12** (Figure 4b). In the first set, the molecular geometry of the isostructural analogues of **2** and **7** differs from that of **8** in a 180° rotation about the central S–C(benzyl) bond. By contrast, the imidazole ring of compound **3** is approximately coplanar with the C–S–C–C fragment linking the imidazole and phenyl rings. **4** and **9** are close chemical analogues displaying very similar type-I geometries but fundamentally different type-II-conformations. As a result, the two phenyl rings of **4** are almost parallel, while those of **9** form a 54° angle. Fragment II occurs in a range of conformations in which the angle formed by the planes of the imidazole and phenyl rings range between 59° (in **4**) and 82° (in **11**). Compounds **2** and **7** display the expected intermolecular (imidazole) N–H···Br bond.

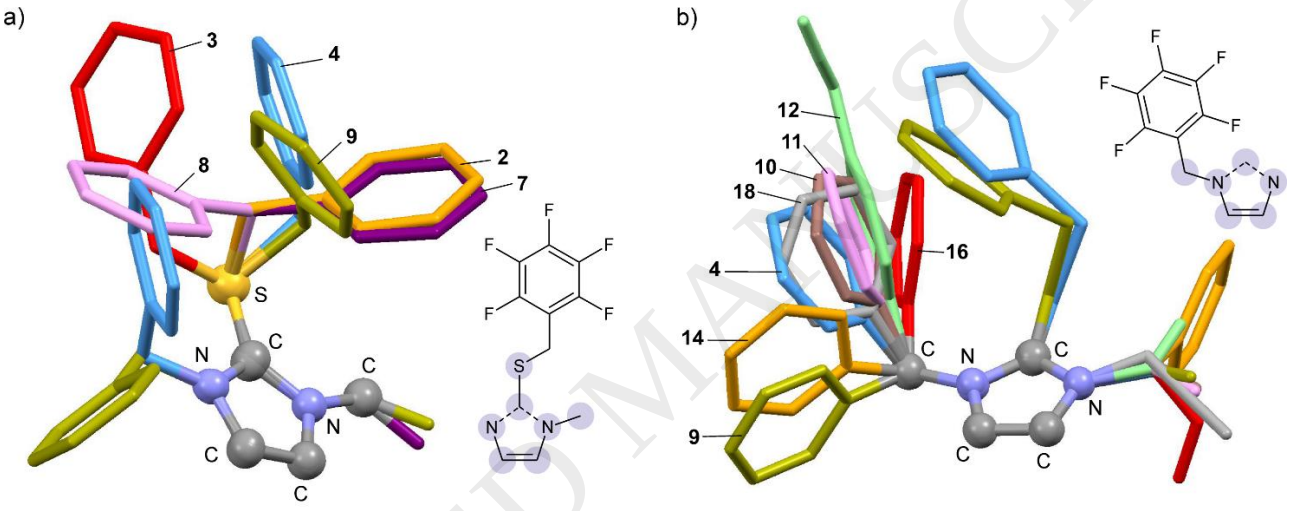


Figure 4. Comparison of molecular geometries. a) Overlay of 2-[(pentafluorobenzyl)thio]imidazole fragments I present in compounds **2**, **3**, **4**, **7**, **8** and **9**, obtained by least-squares fitting a rigid fragment composed of the imidazole ring, the S atom of the thio substituent and a C atom of either the Me or vinyl substituent. b) Overlay of 1-(pentafluorobenzyl)imidazole fragments II present in compounds **4**, **14**, **16**, **18** and **9** – **12**, obtained by least-squares fitting a rigid fragment composed of the imidazole ring and the first C atom of the pentafluorobenzyl group. Fitted fragments are shown in balls and sticks style, F and H atoms are omitted for clarity. Only one of two independent cations of **18** is shown.

In the dihydrate **10 · 2H$_2$O**, water molecules (*w*1, w2) and Br$^-$ anions are linked into a (*w*2)O–H···O(*w*1) and (*w*1)O–H···Br-bonded chain structure, which propagates parallel to the *a* axis (Figure 5). This chain can be described as an …*ABAB*… sequence of two types of symmetrical, vertex-sharing rings, each having the graph set symbol $R^2_4(8)$.[45] Ring type *A* is formed by two *w*1 water molecules and two Br$^-$ anions, with each of the former donating an H bond to each of the latter. Moreover, each water molecule *w*1 also belongs to a homodromic ring of type *B* within which it accepts an H-bond from each of two *w*2 water molecules.

The asymmetric unit of the acetonitrile solvate **19 · CH$_3$CN · 0.22 H$_2$O** contains two units of **19**, two solvent molecules and additionally one partially occupied water site with an occupancy of 0.44(1).

The vacancy/occupation of the water site is correlated with the adoption of two alternative positions by one Br^- ion. The presence of water in this crystal structure was confirmed *via* Karl-Fischer titration.

The quality of diffraction data of **20** was negatively affected by multiple twinning. However, the obtained molecular structure is consistent with expected geometrical features (see Figure 6).

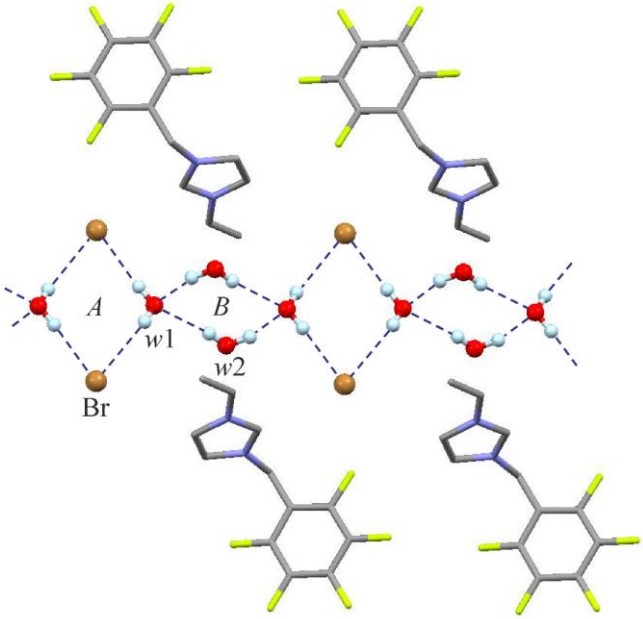


Figure 5. Packing of cations and an H-bonded homodromic chain propagating parallel to the *a* axis in the structure of **10 · 2H₂O**. The O–H···Br and O–H···O bonded chain displays two types of $R^2_4(8)$ ring with ring *A* being composed of two water molecules and two bromide ions and ring *B* connecting four water molecules.

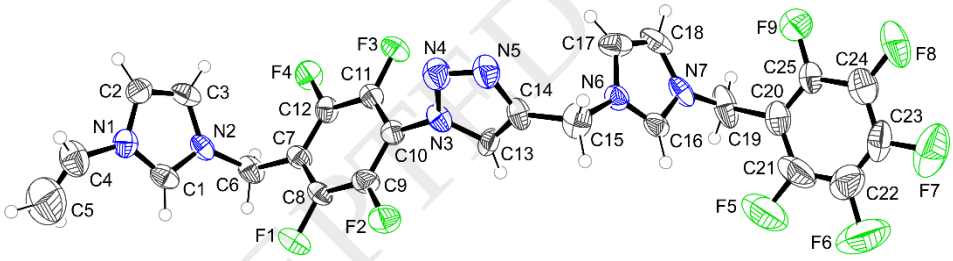


Figure 6. Molecular structure of **20** showing the atom labels and non-H-atoms with displacement ellipsoids drawn at the 50% probability level. The PF_6-anions were omitted.

2.3 Surface tension experiments

In order to assess whether pentafluorobenzylated imidazolium salts display any appreciable surface activity, aqueous surface tension measurements were conducted. While it was deemed unlikely that their surfactancy is in the same order of magnitude as for (perfluoroalkyl)alkyl imidazolium salts,[9] these compounds still contain the key moieties often employed in surfactant design: a hydrophobic (perfluorophenyl) part and a hydrophilic (imidazolium) counterpart. In the measured concentration range, the compounds **4**, **7** and **18** reduced aqueous surface tension values the most (Figure 7) but did not influence it to the same extent as commercial (fluoro)surfactants.[46] In case of compound **18**, a

concentration of 43.6 mmol/L led to a value of 59.0 mN/m. Only the generation of a saturated solution (c = 164 mmol/L) helped to bring the surface tension down to 49.0 mN/m (Table 1). Concentrated solutions of the other tested substances, namely the S-alkylated compound **2**, the doubly N-alkylated salt **14** and the N-alkylated compounds **10** and **16**, hardly influenced the average surface tension or even did not affect it at all. Consequently, their measurements were not included in the graph. Conclusively, these findings further emphasize that sp^2-hybridized perfluorophenyl groups contribute far less to aqueous surfactancy than sp^3 perfluoroalkyl substituents.

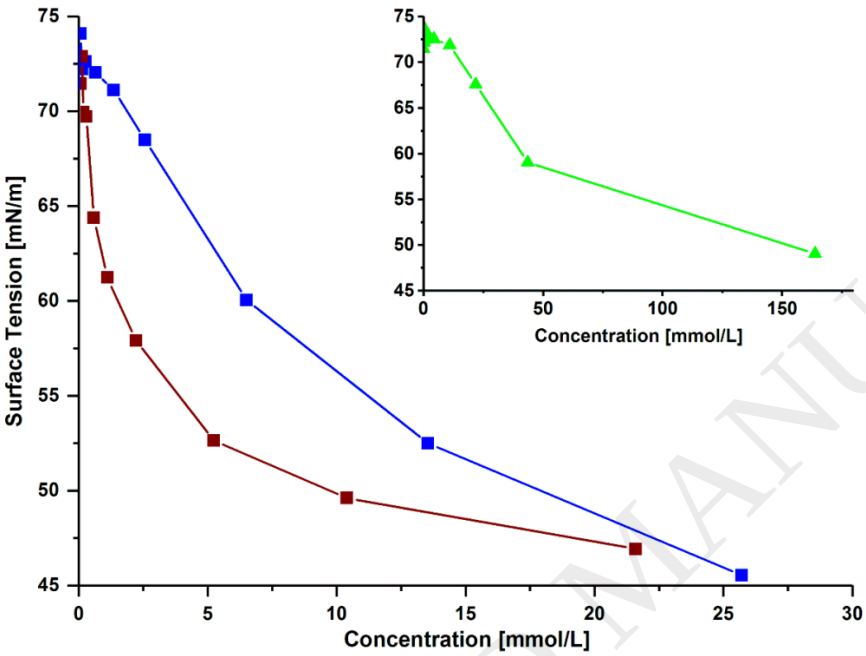


Figure 7. Surface tension data of selected compounds (–■– compound **4**, –■– compound **7,** –▲– compound **18**).

3. CONCLUSION

A series of pentafluorobenzylated imidazole compounds has been conceived and prepared in order to evaluate their synthetic accessibility, stability, structural features and surfactancy. Simple aromatic nucleophilic substitution at the pentafluorophenyl subunit by azide [33] yielded the *p*-substituted derivative (**12**) almost quantitatively. Through this, new avenues of follow up derivations have been opened and were exemplified by a Staudinger as well as a CuAAC reaction.[34,35,41,42] In conclusion, the molecular assemblies of allyl, vinyl, or propargyl side chains paired with functionalized pentafluorobenzyl groups allow access to a plethora of application-tailorable materials such as functional ionic liquids and related salts, polyelectrolytes,[47-52] or nitrene-mediated covalent grafts.[53,54]

4. EXPERIMENTAL

Reagents and solvents were purchased from commercial suppliers and used without further purification. Propargylimidazole (**17**) [28,29] and 1-vinyl-4-imidazoline-2-thione (**6**) [30] were

prepared according to published procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 300, ^{19}F spectra with a Bruker 600 MHz Avance II+ spectrometer and analyzed using the MestReNova software (version 9.0.1).[55] IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument and analyzed with the Bruker Opus software (version 7.2).[56] Mass spectrometry was performed on a Thermo Finnigan Q Exactive Orbitrap spectrometer and melting points were determined on a Leica Galen III Kofler microscope. Thermogravimetric measurements were carried out on a Netzsch TG209 F1 analyzer. 8-12 mg of the sample was heated in an atmosphere of nitrogen from room temperature to 900 °C at a rate of 20 °C/min with a flow rate of 30 mL/min. DSC measurements were performed on a Netzsch DSC 200 F3 Maia differential scanning calorimeter. 3-5 mg of the sample was weighed into a standard 40 µL aluminum crucible, which was sealed afterwards. The lid was pricked prior to measurement allowing evaporation of volatile substances. The sample was subjected to a temperature range between −55 and 200 °C with a heating rate of 5 °C/min. Dry nitrogen was used as the purge gas (purge: 10 mL/min). Thermogravimetric analyses (TGA, DTG) and differential scanning calorimetry (DSC) scans were recorded and analyzed by the Netzsch Proteus software (version 6.1.0). Surface tension measurements were carried out on a Krüss (DSA25E) drop shape analyzer. At a temperature of 25 °C at the tip of a needle (1.83 mm external diameter), a suspended drop of a liquid is generated, pictures were recorded by an Allied Vision camera (GuppyPro) and the surface tension calculated via Krüss Advance software (Version 1.6-03) using the Young-Laplace method. Diffraction intensity data were recorded with a Bruker D8 Quest Photon 100 diffractometer using Mo$K\alpha$ (λ = 0.7107 Å) radiation. The crystal structures were solved using Direct Methods and refined by full-matrix least-squares techniques.[57,58] The structures were visualized and the distances and angles calculated with the programs Ortep-3 [59] and Mercury.[60] CCDC 1856823–34, 1882203 and 1882204 contain the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif).

4.1 1-Methyl-2-[(2,3,4,5,6-pentafluorobenzyl)thio]-3*H*-imidazolium bromide (2)

1-Methyl-4-imidazoline-2-thione (**1**; 1.0 g, 8.8 mmol) was dissolved in anhydrous acetonitrile (10 mL). 2,3,4,5,6-pentafluorobenzyl bromide (1.4 mL, 1.05 equiv., 9.3 mmol) was added and the mixture was stirred for 24 h under argon at room temperature, forming a white precipitate. Subsequently, diethyl ether (5 mL) was added and the mixture was cooled to -24 °C. Immediately after, the product was filtered off, washed twice with diethyl ether (2 × 10 mL) and dried under reduced pressure, yielding 3.2 g (97 %) of 1-methyl-2-[(2,3,4,5,6-pentafluorobenzyl)thio]-3*H*-imidazolium bromide (**2**) as a white powder. Single-crystals were obtained by diffusion of Et_2O into a methanolic solution of **2**. M.p. 175 °C (dec.). – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 3.83 (s, 3H, MeH), 4.42 (s, 2H, N-BnH), 7.83 (d, J = 2.0 Hz, 1H, ImH), 7.97 (d, J = 2.0 Hz, 1H, ImH) ppm. – ^{13}C

NMR (75 MHz, $(CD_3)_2SO$): δ 26.3 (N-BnC), 35.2 (MeC), 110.6-111.3 (m, BnC), 121.9 (ImC), 126.4 (ImC), 135.0 – 135.7 (m, BnC), 136.7 (ImC), 138.3 – 139.3 (m, BnC), 141.7 – 142.2 (m, BnC), 142.5 – 143.0 (m, BnC), 145.8 – 146.3 (m, BnC) ppm. – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -162.3 – -162.1 (m, BnF), -154.7 (t, J = 22.3 Hz, BnF), -143.9 – -143.8 (m, BnF) ppm. – FT-IR (ATR): ν 3154 (w), 3088 (w), 2919 (w), 2873 (w) (νCH), 2649 (br, νNH), 1738 (w), 1703 (w), 1659 (w), 1571 (w), 1527 (m), 1504 (s), 1480 (m) (νC=N, νC=C), 1296 (m), 1131 (m) (νCF), 994 (s), 964 (s), 918 (m), 885 (m), 775 (s) (δ_oCH), 676 (m), 644 (m) (νCS) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* [M^+] = 295.0323, found *m/z* [$C_{11}H_8F_5N_2S^+$] = 295.0307.

4.2 1-Methyl-2-[(2,3,4,5,6-pentafluorobenzyl)thio]imidazole (3)

To a solution of 1-methyl-2-[(2,3,4,5,6-pentafluorobenzyl)thio]-3*H*-imidazolium bromide (**2**; 650 mg, 1.7 mmol) in methanol (3 mL), sodium hydrogen carbonate (161 mg, 1.1 equiv., 1.9 mmol) was added. The mixture was stirred under argon at room temperature for 17 h. Afterwards, diethyl ether (10 ml) was added, the white precipitate removed by filtration and the filtrate concentrated under reduced pressure. The resulting colorless liquid was dried *in vacuo*, which led to its crystallization. Yield: 499 mg (98 %). M.p. 34 – 35 °C. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 3.58 (s, 3H, MeH), 4.17 (s, 2H, N-BnH), 6.94 (s, 1H, ImH), 7.31 (s, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 25.5 (N-BnC), 33.1 (MeC), 111.9 – 112.8 (m, BnC), 124.5 (ImC), 129.3 (ImC), 134.5 – 135.5 (m, BnC), 136.8 (ImC), 137.4 – 139.0 (m, BnC), 140.8 – 141.9 (m, BnC), 142.3 – 143.1 (m, BnC), 145.4 – 146.4 (m, BnC) ppm. – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -163.3 – -163.1 (m, BnF), -156.0 (t, J = 21.7 Hz, BnF), -143.7 – -143.6 (m, BnF) ppm. – FT-IR (ATR): ν 3115 (w), 2994 (w), 2952 (w) (νCH), 1657 (m), 1521 (m), 1500 (s), 1463 (m) (νC=N, νC=C), 1275 (m), 1121 (s) (νCF), 983 (s), 968 (s), 913 (m), 889 (m), 728 (s), 677 (m) (δ_oCH), 645 (m) (νCS) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* [M + H^+] = 295.0323, found *m/z* [$C_{11}H_7F_5N_2S$ + H^+] = 295.0302, calcd. *m/z* [M + Na^+] = 317.0142, found *m/z* [$C_{11}H_7F_5N_2S$ + Na^+] = 317.0119.

4.3 3-Methyl-1-(2,3,4,5,6-pentafluorobenzyl)-2-[(2,3,4,5,6-pentafluorobenzyl)thio]-imidazolium bromide (4)

(a) To a solution of 1-methyl-4-imidazoline-2-thione (**1**; 250 mg, 2.2 mmol) in anhydrous acetonitrile (2 mL), 2,3,4,5,6-pentafluorobenzyl bromide (728 µL, 2.2 equiv., 4.8 mmol) was added. The mixture was stirred for 24 h under argon at room temperature. Next, sodium hydrogen carbonate (220 mg, 1.2 equiv., 2.6 mmol) and anhydrous acetonitrile were added and stirring was continued for 4 days. Afterwards, acetone (5 mL) was added, the solids were removed by filtration and the solvent was removed under reduced pressure. The crude product was dissolved in acetone (2 mL) and reprecipitated via the addition of diethyl ether (10 mL), filtered and dried *in vacuo*, yielding 1.1 g

(92 %) of 3-methyl-1-(2,3,4,5,6-pentafluorobenzyl)-2-[(2,3,4,5,6-pentafluorobenzyl)thio]-imidazolium bromide (**4**) as a white powder.

(b) To a solution of 1-methyl-2-[(2,3,4,5,6-pentafluorobenzyl)thio]imidazole (**3**, 499 mg, 1.7 mmol) in anhydrous acetonitrile (1 mL), 2,3,4,5,6-pentafluorobenzyl bromide (282 µL, 1.1 equiv., 1.9 mmol) was added. The solution was stirred under argon at room temperature for 6 d, forming a white precipitate. Diethyl ether (5 mL) was added for complete precipitation. The product was filtered, washed with diethyl ether (2 × 2 mL) and dried *in vacuo*, yielding 920 mg (98 %).

Single-crystals of **4** were obtained by diffusion of Et_2O into a solution of **4** in acetonitrile. M.p. 109.5 °C (dec.). – ^{1}H NMR (300 MHz, Methanol-d_4): δ 3.97 (s, 3H, MeH), 4.40 – 4.47 (m, 2H, N-BnH), 5.65 (s, 2H, S-BnH), 7.94 – 7.98 (m, 2H, ImH) ppm. – ^{13}C NMR (75 MHz, Methanol-d_4): δ 27.4 (N-BnC), 37.5 (MeC), 42.5 (S-BnC), 108.6 – 109.3 (m, BnC), 111.1 – 111.7 (m, BnC), 126.6 (ImC), 127.8 (ImC), 137.3 – 137.9 (m, BnC), 140.8 (ImC), 140.6 – 141.2 (m, BnC), 141.4 – 141.7 (m, BnC), 141.9 – 142.4 (m, BnC), 144.7 – 145.1 (m, BnC), 145.4 – 145.8 (m, BnC), 147.9 – 148.4 (m, BnC), 148.7 – 149.1 (m, BnC) ppm. – ^{19}F NMR (376 MHz, Methanol-d_4): δ -163.7 – -163.6 (m, BnF), -163.4 – -163.2 (m, BnF), -155.1 (t, J = 19.9 Hz, BnF), -154.2 – -154.1 (m, BnF), -145.3 – -145.2 (m, BnF), -142.3 – -142.2 (m, BnF) ppm. – FT-IR (ATR): ν 3151 (w), 3092 (w), 3020 (w), 2997 (w), 2969 (w), 2922 (w) (νCH), 1657 (m), 1564 (w), 1529 (m), 1500 (s) (νC=N, νC=C), 1428 (m), 1247 (m), 1133 (m) (ν CF), 1013 (m), 989 (s) (δ_iCH), 969 (s), 910 (m), 787 (m) (δ_oCH), 697 (m), 637 (m) (νCS) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* [M^+] = 475.0321, found *m/z* [$C_{18}H_9F_{10}N_2S^+$] = 475.0265.

4.4 1-Vinyl-4-imidazoline-2-thione (6) [1146852-33-6] (according to [30])

1-Vinylimidazole (**5**; 7.5 g, 79.7 mmol) was dissolved in anhydrous tetrahydrofuran (THF; 60 mL) and cooled in an ice bath. Isopropylmagnesium chloride solution (42 mL, 2 *M* in THF, 1.05 equiv., 84.0 mmol) was added and the mixture was stirred at room temperature under an argon atmosphere for 2 d. Then, elemental sulfur (S_8, 2.7 g, 1.05 equiv., 84.2 mmol) was added to the solution and stirring was continued at room temperature for 24 h. Next, water (25 mL) was added and the mixture was acidified with HCl (50 mL, 1 *M*, 50.0 mmol). The mixture was extracted with chloroform (3 × 100 mL) and the combined organic layers were washed with brine (100 mL). The solvent was removed under reduced pressure, yielding 7.5 g (74 %) of 1-vinyl-4-imidazoline-2-thione (**6**) as an off-white solid. M.p. 143-144 °C. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 4.92 (dd, J = 9.0, 1.1 Hz, 1H, VinH), 5.43 (dd, J = 16.1, 1.2 Hz, 1H, VinH), 7.04 (t, J = 2.5 Hz, 1H, ImH), 7.38 (dd, J = 16.1, 9.1 Hz, 1H, VinH), 7.53 (t, J = 2.2 Hz, 1H, ImH), 12.35 (br s, 1H, N-H) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 100.9 (VinC), 113.8 (ImC), 116.3 (ImC), 129.0 (VinC), 161.8 (ImC) ppm. – FT-IR (ATR): ν 3120 (m), 3018 (m), 2916 (w), 2704 (w) (νCH, νNH), 1646 (m), 1570 (m), 1463 (s), 1415

(m) (νC=N, νC=C), 1286 (m), 1269 (s), 1245 (m) (νC=S), 961 (m), 877 (m), 775 (m), 745 (s), 684 (m), 653 (m) (δ_oCH) cm^{-1}.

4.5 2-[(2,3,4,5,6-Pentafluorobenzyl)thio]-1-vinyl-3*H*-imidazolium bromide (7)

To a solution of 1-vinyl-4-imidazoline-2-thione (**6**; 500 mg, 4.0 mmol) in anhydrous acetonitrile (10 mL), 2,3,4,5,6-pentafluorobenzyl bromide (634 µL, 1.05 equiv., 4.2 mmol) was added. The mixture was stirred under inert gas at room temperature for 2 d, forming a white precipitate. Then, diethyl ether (20 mL) was added and the mixture was cooled to -24 °C in order to complete precipitation. The white crystalline product was filtered off, washed with diethyl ether (2 × 5 mL) and dried, yielding 1.4 g (93 %) of 2-[(2,3,4,5,6-pentafluorobenzyl)thio]-1-vinyl-3*H*-imidazolium bromide (**7**). Single-crystals were obtained by diffusion of Et_2O into a methanolic solution of **7**. M.p. 172 °C (dec.). – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 4.35 (s, 2H, S-BnH), 5.35 (dd, J = 8.8, 2.0 Hz, 1H, VinH), 5.89 (dd, J = 15.4, 2.0 Hz, 1H, VinH), 7.26 (dd, J = 15.5, 8.8 Hz, 1H, VinH), 7.81 (d, J = 2.0 Hz, 1H, ImH), 8.32 (d, J = 2.0 Hz, 1H, ImH), 10.76 (br s, 1H, N-H) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 26.7 (S-BnC), 109.5 (VinC), 110.6 – 111.4 (m, BnC), 121.2 (ImC), 124.2 (ImC), 127.6 (VinC), 135.0 – 135.6 (m, BnC), 136.8 (ImC), 138.3 – 138.9 (m, BnC), 141.7 – 142.2 (m, BnC), 142.5 – 143.0 (m, BnC), 145.8 – 146.3 (m, BnC) ppm. – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -162.4 – -162.2 (m, BnF), -155.0 (t, J = 22.3 Hz, BnF), -143.8 – -143.6 (m, BnF) ppm. – FT-IR (ATR): ν 3160 (w), 3085 (w), 2988 (w), 2935 (w), 2906 (w) (νCH), 2653 (br m) (νNH), 1738 (w), 1705 (w), 1657 (w), 1646 (w), 1568 (w), 1525 (m), 1503 (s), 1468 (s) (νC=N, νC=C), 1313 (m), 1131 (m) (νCF), 996 (s), 965 (s), 931 (s), 915 (m), 885 (m), 770 (s), 660 (m), 643 (m) (νCS, δCH) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* $[M^+]$ = 307.0323, found *m/z* $[C_{12}H8F_5N_2S^+]$ = 307.0302.

4.6 2-[(2,3,4,5,6-Pentafluorobenzyl)thio]-1-vinylimidazole (8)

To 2-[(2,3,4,5,6-pentafluorobenzyl)thio]-1-vinyl-3*H*-imidazolium bromide (**7**; 600 mg, 1.5 mmol) and sodium hydrogen carbonate (145 mg, 1.1 equiv., 1.7 mmol), methanol (3 mL) was added and the mixture stirred under inert gas at room temperature for 1d. Next, diethyl ether (10 mL) was added, the precipitate removed by filtration and the filtrate concentrated under reduced pressure. The colorless residue was dissolved in heptane (1 mL) and slowly cooled to -24 °C, which led to phase separation and crystallization. The heptane layer was removed and the product was dried *in vacuo*, yielding 334 mg (96 %) of 2-[(2,3,4,5,6-pentafluorobenzyl)thio]-1-vinylimidazole (**8**) as a white crystalline solid. M.p. 33 – 34 °C. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 4.18 (s, 2H, S-BnH), 4.91 (dt, J = 8.8, 1.1 Hz, 1H, VinH), 5.47 (dt, J = 15.7, 1.0 Hz, 1H, VinH), 7.02 – 7.14 (m, 2H, VinH and ImH), 7.82 (d, J = 1.6 Hz, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 25.9 (S-BnC), 102.7 (VinC), 111.7 – 112.5 (m, BnC), 119.2 (ImC), 128.3 (ImC), 130.8 (VinC), 134.8 – 135.5 (m, BnC), 137.1 (ImC), 137.8 – 138.8 (m, BnC), 141.2 – 141.8 (m, BnC), 142.5 – 143.1 (m, BnC), 145.7 –

146.4 (m, BnC) ppm. – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -163.3 – -163.1 (m, BnF), -156.2 (t, J = 21.9 Hz, BnF), -143.6 – -143.4 (m, BnF) ppm. – FT-IR (ATR): ν 3157 (w), 3124 (w), 3097 (w), 2979 (w), 2934 (w) (νCH), 1729 (w), 1647 (m), 1580 (w), 1500 (s), 1438 (s) (νC=N, νC=C), 1273 (s), 1125 (m), 1106 (m) (νCF), 991 (s), 959 (s), 869 (s), 745 (s) (δ_oCH), 676 (m), 644 (m) (νCS) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* [M + H$^+$] = 307.0323, found *m/z* [$C_{12}H_7F_5N_2S$ + H$^+$] = 307.0301, calcd. *m/z* [M + Na$^+$] = 329.0142, found *m/z* [$C_{12}H_7F_5N_2S$ + Na$^+$] = 329.0119.

4.7 3-(2,3,4,5,6-Pentafluorobenzyl)-2-[(2,3,4,5,6-pentafluorobenzyl)thio]-1-vinylimidazolium bromide (9)

(a) 2,3,4,5,6-Pentafluorobenzyl bromide (176 µL, 2.0 equiv., 1.2 mmol) was added to a solution of 2-[(2,3,4,5,6-pentafluorobenzyl)thio]-1-vinylimidazole (**8**, 178 mg, 0.58 mmol) in anhydrous acetonitrile (1 mL). The solution was concentrated under reduced pressure after stirring at 50 °C under inert gas for 1.5 d. Finally, diethyl ether (10 mL) was added and the precipitate was isolated by filtration, washed with diethyl ether (2 × 5 mL) and dried *in vacuo*, yielding 330 mg (38 %) of 3-(2,3,4,5,6-pentafluorobenzyl)-2-[(2,3,4,5,6-pentafluorobenzyl)thio]-1-vinylimidazolium bromide (**9**) as a white powder.

(b) 2,3,4,5,6-Pentafluorobenzyl bromide (127 µL, 1.2 equiv., 0.84 mmol) was added to 3-(2,3,4,5,6-pentafluorobenzyl)-1-vinylimidazoline-2-thione (**11**, 215 mg, 0.70 mmol) in anhydrous diethyl ether (4 mL). The mixture was stirred under argon atmosphere at room temperature for 24 h. Then, the resulting precipitate was filtered, washed with diethyl ether (2 × 5 mL) and dried under reduced pressure, yielding 120 mg (30 %) of **9**.

Single-crystals were obtained by crystallization from slow evaporation of a solution of **9** in chloroform. M.p. 108 °C (dec.). The substance decomposes in solution over time, resulting in additional peaks in the ^{1}H- and ^{13}C-NMR spectra, assignable to compound **11** and other by-products. Due to the decomposition, no ^{19}F-spectrum was recorded. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 4.36 (s, 2H, S-BnH), 5.46 (dd, J = 8.7, 2.3 Hz, 1H, VinH), 5.66 (s, 2H, N-BnH), 6.04 (dd, J = 15.3, 2.3 Hz, 1H, VinH), 7.20 (dd, J = 15.3, 8.7 Hz, 1H, VinH), 8.28 (d, J = 2.2 Hz, 1H, ImH), 8.58 (d, J = 2.3 Hz, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 26.2 (S-BnC), 40.9 (N-BnC), 111.3 (VinC), 121.1 (ImC), 126.5 (ImC), 127.7 (VinC), 138.5 (ImC) ppm (Quaternary C-atoms of the benzyl ring were not observed due to low concentration). – FT-IR (ATR): ν 3094 (w), 3026 (w), 2947 (w) (νCH), 1658 (w), 1644 (w), 1546 (w), 1519 (s), 1505 (s) (νC=N, νC=C), 1456 (w), 1401 (w), 1312 (w) (δSCH$_2$), 1226 (w), 1130 (m) (νCF), 1042 (m) (δ_iCH), 995 (m), 969 (s), 930 (m), 811 (m) (δ_oCH), 716 (w), 693 (w), 648 (w) (νCS) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* [M$^+$] = 487.0321, found *m/z* [$C_{19}H_9F_{10}N_2S^+$] = 487.0277.

4.8 3-(2,3,4,5,6-Pentafluorobenzyl)-1-vinylimidazolium bromide (10)

To a cooled (ice-bath) solution of 1-vinylimidazole (**5**; 2.0 g, 21.3 mmol) in anhydrous acetonitrile (10 mL), 2,3,4,5,6-pentafluorobenzyl bromide (3.4 mL, 1.05 equiv., 22.5 mmol) was added. The mixture was allowed to warm up to room temperature and was stirred under inert gas for 2 d. Diethyl ether (50 mL) was added and the product precipitated by storing at -24 °C. The solid was filtered off, washed with diethyl ether (2 × 20 mL) and dried, yielding 7.4 g (99 %) of 3-(2,3,4,5,6-pentafluorobenzyl)-1-vinylimidazolium bromide (**10**) as a white product. Single-crystals of the dihydrate were obtained by diffusion of Et_2O into a methanolic solution of **10**. M.p. 114.5 – 116 °C. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 5.44 (dd, J = 8.8, 2.5 Hz, 1H, VinH), 5.72 (s, 2H, N-BnH), 6.08 (dd, J = 15.7, 2.5 Hz, 1H, VinH), 7.38 (dd, J = 15.6, 8.8 Hz, 1H, VinH), 8.03 (t, J = 1.9 Hz, 1H, ImH), 8.39 (t, J = 1.9 Hz, 1H, ImH), 9.82 (s, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 40.3 (N-BnC), 107.5 – 108.2 (m, BnC), 109.2 (VinC), 119.3 (ImC), 123.5 (ImC), 128.6 (VinC), 135.1 – 135.8 (m, BnC), 136.1 (ImC), 138.3 – 139.2 (m, BnC), 139.3 – 140.1 (m, BnC), 142.6 – 143.4 (m, BnC), 143.4 – 143.9 (m, BnC), 146.6 – 147.3 (m, BnC) ppm. – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -162.0– -161.8 (m, BnF), -153.2 (t, J = 22.0 Hz, BnF), -140.9 – -140.7 (m, BnF) ppm. – IR (ATR): ν 3117 (w), 3093 (w), 3063 (w), 3033 (w), 2985 (w), 2951 (w), 2898 (w) (νCH), 1655 (m), 1566 (m), 1544 (m), 1529 (s), 1507 (s) (νC=N, νC=C), 1170 (s), 1134 (s) (νCF), 1037 (s), 1017 (m) (δ_iCH), 969 (s), 924 (s), 849 (m), 785 (m), 673 (s) (δ_oCH) cm^{-1}. – HRMS (ESI pos.): calcd. m/z [M^+] = 275.0602, found m/z [$C_{12}H_8F_5N_2^+$] = 275.0583.

4.9 3-(2,3,4,5,6-Pentafluorobenzyl)-1-vinylimidazoline-2-thione (11)

To 3-(2,3,4,5,6-pentafluorobenzyl)-1-vinylimidazolium bromide (**10**; 1.0 g, 2.8 mmol) and elemental sulfur (91 mg, 1.0 equiv.,2.8 mmol), pyridine (3 mL) and trimethylamine (311 mg, 1.1 equiv., 3.1 mmol) were added. The mixture was stirred at 70 °C under inert gas for 2 h. After cooling to room temperature, activated charcoal was added to remove discoloration. Then, the mixture was filtered and washed with pyridine (2 mL). Water (8 mL) was added, forming an off-white precipitate. The mixture was cooled to 4 °C in order to complete precipitation. Finally, the precipitate was filtered off, washed with ice-cold water (2 × 5 mL) and dried under reduced pressure, yielding 695 mg (81 %) of 3-(2,3,4,5,6-pentafluorobenzyl)-1-vinylimidazoline-2-thione (**11**). Single-crystals were obtained from slow evaporation of a solution of **11** in methanol/water. M.p. 99 – 100 °C. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 4.96 (dd, J = 9.1, 1.5 Hz, 1H, VinH), 5.30 (s, 2H, N-BnH), 5.49 (dd, J = 16.1, 1.5 Hz, 1H, VinH), 7.27 – 7.42 (m, 2H, VinH and ImH), 7.64 (d, J = 2.7 Hz, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 101.6 (VinC), 109.2 – 109.8 (m, BnC), 113.3 (ImC), 119.5 (ImC), 129.4 (VinC), 135.0 – 135.6 (m, BnC), 138.3 – 138.6 (m, BnC), 138.7 – 139.0 (m, BnC), 141.8 – 142.4 (m, BnC), 143.1 – 143.6 (m, BnC), 146.3 – 147.0 (m, BnC), 162.4 (ImC) ppm (N-BnC hidden by solvent). – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -164.6– -161.5 (m, BnF), -154.7 (t, J = 22.4 Hz,

BnF), -142.6 – -139.5 (m, BnF) ppm. – FT-IR (ATR): *ν* 3170 (w), 3135 (w), 3109 (w), 2992 (w), 2976 (w), 2943 (w) (*ν*CH), 1655 (w), 1640 (m), 1524 (m), 1500 (s), 1454 (m) (*ν*C=N, *ν*C=C), 1420 (m), 1403 (s), 1371 (m), 1301 (m), 1246 (m) (*ν*C=S), 1200 (m), 1128 (m) (*ν*CF), 1067 (m), 1012 (m), 1000 (m) (δ_iCH), 967 (m), 958 (m), 923 (m), 890 (m), 803 (m), 727 (m), 714 (m), 703 (m), 683 (m), 667 (m) (δ_oCH) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* [M + H^+] = 307.0323, found *m/z* [$C_{12}H_7F_5N_2S$ + H^+] = 307.0309.

4.10 3-(4-Azido-2,3,5,6-tetrafluorobenzyl)-1-vinylimidazolium bromide (12)

An Ar-purged Schlenk round-bottom flask was charged with 1-(2,3,4,5,6-pentafluorobenzyl)-3-vinylimidazolium bromide (**10**, 1.4 g, 4.0 mmol), dissolved in acetonitrile (150 ml). Then, sodium azide (390 mg, 1.5 equiv, 6.0 mmol) and calcium bromide (601 mg, 0.75 equiv, 3.0 mmol) were added and the reaction mixture was stirred under reflux protected from light and air for 5 d (**Warning**: *It is advised to comply with the described conditions to avoid multiple fluorine substitution and thus the formation of explosive side products* [37]). The solids were removed by filtration and the solvent was evaporated. The crude product was taken up in acetonitrile and filtered a second time. The filtrate was overlaid with diethyl ether (300 ml) and cooled to -20 °C overnight. The product was separated from the solvents and by-products by filtration. Last traces of contaminants were removed by a second precipitation in a mixture of methylene chloride / n-hexane (1:7). Finally, the desired product was filtered off and washed with diethyl ether and n-hexane, yielding a yellow solid 1.3 g (87 %). Single-crystals were obtained by slow evaporation of a solution of **12** in methylene chloride covered with n-hexane or n-heptane. M.p. 128 °C (dec.). – ^{1}H NMR (300 MHz, MeOH-*d4*): *δ* 5.48 (dd, *J* = 8.7, 2.7 Hz, 1H, N-BnH), 5.66 (s, 2H, N-BnH), 5.95 (dd, *J* = 15.6, 2.8 Hz, 1H, VinH), 7.25 (dd, *J* = 15.6, 8.7 Hz, 1H, VinH), 7.80 (d, *J* = 2.3 Hz, 1H, ImH), 8.07 (d, *J* = 2.2 Hz, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, MeOH-*d4*): *δ* 42.0 (N-BnC), 108.3 – 108.8 (m, BnC), 110.8 (VinC), 121.4 (ImC), 121.9 (ImC), 124.7 (ImC), 129.8 (VinC) ppm. ^{19}F NMR (376 MHz, Acetone-*d6*): *δ* -152.9 – -152.8 (m, BnF), -143.7 – -1143.5 (m, BnF) ppm. – FT-IR (ATR): *ν* 3120, 3080, 2975, 2948, 2920, 2816 (νCH), 2179, 2162, 2120 (νN=N), 1652, 1567, 1550 (νC=C, νC=N),1491, 1225 (νCF), 1164, 1019 (δ_iCH), 943, 922, 786, 662 (δ_oCH) cm^{-1} – HRMS (ESI pos): calcd. *m/z* [M^+] = 298.0710, found *m/z* [$C_{12}H_8F_4N_5^+$] = 298.0696.

4.11 1,3-Bis(2,3,4,5,6-pentafluorobenzyl)imidazolium bromide (14)

To a solution of imidazole (**13**; 475 mg, 7.0 mmol) in anhydrous acetonitrile (10 mL), sodium hydrogen carbonate (685 mg, 1.2 equiv., 8.2 mmol) and 2,3,4,5,6-pentafluorobenzyl bromide (2.2 mL, 2.1 equiv., 14.6 mmol) were added. The mixture was stirred under argon at room temperature for 5 d. After filtration, the solvent was removed under reduced pressure, yielding 2.9 g (81 %) of 1,3-bis(2,3,4,5,6-pentafluorobenzyl)imidazolium bromide (**14**) as a white powder. Single-crystals

were obtained by diffusion of Et_2O into a methanolic solution of **14**. M.p. 184.5 – 185.0 °C. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 5.70 (s, 4H, N-BnH), 7.89 (d, J = 1.6 Hz, 2H, ImH), 9.63 (s, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 40.3 (N-BnC), 107.2 – 108.6 (m, BnC), 123.0 (ImC), 135.2 – 135.8 (m, BnC), 137.6 (ImC), 138.4 – 139.1 (m, BnC), 139.3 – 139.9 (m, BnC), 142.7 – 143.3 (m, BnC), 143.3 – 143.9 (m, BnC), 146.5 – 147.2 (m, BnC) ppm. – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -162.0 – -161.7 (m, BnF), -152.9 (t, J = 21.9 Hz, BnF), -141.2 – -141.0 (m, BnF) ppm. – FT-IR (ATR): ν 3185 (w), 3059 (m), 2980 (w), 2955 (m), 2919 (w), 2871 (w) (νCH), 1761 (w), 1656 (w), 1631 (w), 1578 (w), 1563 (w), 1525 (m), 1502 (s) (νC=N, νC=C), 1174 (m), 1129 (m) (νCF), 1031 (m), 1020 (s) (δ_iCH), 968 (m), 931 (s), 799 (m) (δ_oCH) cm^{-1}. – HRMS (ESI pos.): calcd. m/z [M^+] = 429.0444, found m/z [$C_{17}H_7F_{10}N_2^+$] = 429.0409.

4.12 3-Allyl-1-(2,3,4,5,6-pentafluorobenzyl)imidazolium bromide (16)

To a solution of 1-allylimidazole (**15**; 420 mg,3.9 mmol) in acetonitrile (anhydrous, 5 mL) 2,3,4,5,6-pentafluorobenzyl bromide (580 µL, 0.99 equiv., 3.8 mmol) was added. The mixture was refluxed under inert gas for 2 d. After cooling to room temperature, diethyl ether (20 mL) was added and the mixture stored at -24 °C for a few hours. After filtration of the cold mixture, the product was washed with diethyl ether (2 × 10 mL) and dried, yielding 1.3 g (93 %) of 3-allyl-1-(2,3,4,5,6-pentafluorobenzyl)imidazolium bromide (**16**) as a white crystalline solid. Single-crystals were obtained by diffusion of Et_2O into a solution in acetonitrile. M.p. 108 – 109°C. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 4.88 (dt, J = 6.0, 1.5 Hz, 2H, AllH), 5.30 (dd, J = 17.1, 1.5 Hz, 1H, AllH), 5.36 (dd, J = 10.2, 1.3 Hz, 1H, AllH), 5.68 (s, 2H, N-BnH), 6.05 (ddt, J = 16.4, 10.3, 6.0 Hz, 1H, AllH), 7.84 (dt, J = 11.4, 1.9 Hz, 2H, ImH), 9.41 (s, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 51.0 (AllC), 107.7 – 108.5 (m, BnC), 120.3 (AllC), 122.8 (AllC), 122.9 (ImC), 131.6 (ImC), 135.3 – 135.8 (m, BnC), 136.8 (ImC), 138.5 – 139.1 (m, BnC), 139.4 – 139.8 (m, BnC), 142.7 – 143.1 (m, BnC), 143.3 – 143.9 (m, BnC), 146.5 – 147.1 (m, BnC) ppm (N-BnC hidden by solvent peak). – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -161.8 – -161.7 (m, BnF), -153.0 (t, J = 22.0 Hz, BnF), -141.3 – -141.2 (m, BnF) ppm. – FT-IR (ATR): ν 3177 (w), 3128 (w), 3065 (m), 3972 (m), 2862 (w) (νCH), 1754 (w), 1660 (m), 1634(w), 1569 (m), 1524 (s), 1502 (s) (νC=N, νC=C),1453 (m), 1420 (m), 1349 (m), 1305 (m), 1175 (s), 1129 (s) (νCF), 1028 (s), 970 (s) (δ_iCH), 945 (s), 931 (s), 762 (s), 655 (s) (δ_oCH) cm^{-1}. – HRMS (ESI pos.): calcd. m/z [M^+] = 289.0759, found m/z [$C_{13}H_{10}F_5N_2^+$] = 289.0739.

4.13 1-Propargylimidazole (17) [18994-77-9] (modified procedure according to [28, 29])

Imidazole (**13**; 8.3 g, 122 mmol) was added to a solution of KOH (15.2 g, 270.9 mmol) in water (24 mL) and combined with acetone (75 mL) under vigorous stirring. After 20 min the mixture was cooled in an ice-NaCl-bath, then propargyl bromide (9.6 mL, 1.04 equiv., 127 mmol) was added dropwise. After stirring for 1 h, the biphasic mixture was allowed to warm to room temperature and

stirred for another 1.5 h. The organic layer was separated and the aqueous layer was extracted with chloroform (3 × 50 ml). The solvents of the combined organic layers were removed by evaporation under reduced pressure. The product was purified by silica gel flash column chromatography (petroleum ether/EtOAc 2/1), yielding 6.8 g (52 %) of 1-propargylimidazole (**17**). – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 3.50 (t, J = 2.6 Hz, 1H, PpgH), 4.93 (d, J = 2.6 Hz, 2H, PpgH), 6.94 (t, J = 1.3 Hz, 1H, ImH), 7.21 (t, J = 1.3 Hz, 1H, ImH), 7.70 (s, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 35.4 (PpgC), 76.1 (PpgC), 78.7 (Ppg C), 119.3 (ImC), 128.7 (ImC), 137.0 (ImC) ppm. – FT-IR (ATR): ν 3289 (m), 3113 (m), 2960 (w), 2927 (w), 2120 (w) (νCH), 1504 (s) (νC=N, νC=C), 1281 (m), 1228 (s) (νCH), 1107 (m), 1074 (s) (δ_iCH), 906 (m), 818 (m), 732 (s), 658 (s), 612 (s) (δ_oCH) cm^{-1}.

4.14 1-(2,3,4,5,6-pentafluorobenzyl)-3-propargylimidazolium bromide (18)

2,3,4,5,6-Pentafluorobenzyl bromide (392 µL, 1.1 equiv., 2.6 mmol) was added to a solution of 1-propargylimidazole (**17**; 250 mg, 2.4 mmol) in anhydrous acetonitrile (3 mL). The mixture was stirred under argon at room temperature for 3 d. Diethyl ether (10 mL) was added and the white precipitate was filtered, washed with ether (2 × 5 mL) and dried under reduced pressure, yielding 832 mg (96 %) of 1-(2,3,4,5,6-pentafluorobenzyl)-3-propargylimidazolium bromide (**18**) as a white crystalline solid. Single-crystals of **18** were obtained by diffusion of Et_2O into a solution in acetonitrile. M.p. 124 – 125 °C. – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 3.87 (t, J = 2.5 Hz, 1H, PpgH), 5.26 (d, J = 2.6 Hz, 2H, PpgH), 5.72 (s, 2H, N-BnH), 7.89 (dt, J = 9.4, 1.9 Hz, 2H, ImH), 9.52 (s, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 38.8 (PpgC), 40.2 (N-BnC), 75.9(PpgC), 79.1 (PpgC), 107.7 – 108.4 (m, BnC), 122.6 (ImC), 123.1 (ImC), 135.1 – 135.8 (m, BnC), 136.9 (ImC), 138.4 – 139.1 (m, BnC), 139.3 – 139.9 (m, BnC), 142.6 – 143.3 (m, BnC), 143.3 – 143.9 (m, BnC), 146.6 – 147.2 (m, BnC) ppm. – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -161.9 – -161.7 (m, BnF), -153.0 (t, J = 22.2 Hz, BnF), -141.2 – -141.1 (m, BnF) ppm. – FT-IR (ATR): ν 3164 (w), 3122 (m), 3050 (m), 3017 (m), 2918 (w), 2843 (w), 2116 (w) (νCH), 1749 (w), 1660 (m), 1569 (m), 1525 (s), 1505 (s) (νC=N, νC=C), 1173 (s), 1124 (s) (νCF), 1040 (s), 1029 (s) (δ_iCH), 960 (s), 911 (s), 788 (m), 760 (s), 660 (s) (δ_oCH) cm^{-1}. – HRMS (ESI pos.): calcd. m/z [M^+] = 287.0602, found m/z [$C_{13}H_8F_5N_2^+$] = 287.0582.

4.15 3-{2,3,5,6-Tetrafluoro-4-[(triphenylphosphoranylidene)amino]benzyl}-1-vinyl-imidazolium bromide (19)

3-(4-Azido-2,3,5,6-tetrafluorobenzyl)-1-vinylimidazolium bromide (**12**; 100 mg, 0.26 mmol) and triphenylphosphine (70 mg, 1.03 equiv., 0.27 mmol) were dissolved in acetonitrile (3 ml) and stirred under an argon atmosphere at room temperature for 3 d. Via addition of diethyl ether (10 ml), the desired product precipitated. The solid was collected and dried under reduced pressure, yielding

138 mg (85 %) of 3-{2,3,5,6-tetrafluoro-4-[(triphenylphosphoranylidene)amino]benzyl}-1-vinylimidazolium bromide (**19**) as a pale yellow solid. Single-crystals of the acetonitrile/water adduct were obtained by diffusion of diethyl ether into a solution of **19** in acetonitrile. M.p. 216 – 219 °C (dec). – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 5.41 (dd, J = 8.7, 2.4 Hz, 1H, VinH), 5.46 (s, 2H, N-BnH), 5.98 (dd, J = 15.7, 2.5 Hz, 1H, VinH), 7.27 (dd, J = 15.7, 8.8 Hz, 1H, VinH), 7.52 – 7.81 (m, 15H, PhH), 7.91 (s, 1H, ImH), 8.24 (s, 1H, ImH), 9.52 (s, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 40.7 (N-BnC), 97.07 – 97.8 (m, BnC), 108.9 (VinC), 119.2 (ImC), 123.3 (ImC), 128.7 (VinC), 129.0 (d, J = 12.4 Hz, PhC), 130.2 (d, J = 102.9 Hz, PhC), 131.8 (d, J = 10.1 Hz, PhC), 132.4 (ImC) (d, J = 2.9 Hz, PhC), 135.7 (ImC), 139.4 – 140.4 (m, BnC), 142.8 – 144.2 (m, BnC), 146.7 – 147.4 (m, BnC) ppm. – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -153.0 – -152.9 (m, BnF), -146.8 – -146.7 (m, BnF) ppm. – FT-IR (ATR): ν 3400 (br w) (water), 3038 (w), 2987 (w) (νCH), 1648 (m), 1527 (s), 1486 (s), 1435 (m) (νC=C, νC=N, νN=P), 1223 (s), 1159 (m), 1110 (m) (νCF, νPPh), 1027 (m), 1008 (m), 965 (w), 910 (m), 876 (w), 853 (w) (δ_iCH), 763 (m), 719 (s), 694 (s), 675 (m) (δ_oCH), 626 (m), 598 (w), 560 (m), 529 (s) ($\delta_{oop/ip}$ring) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* [M^+] = 532.1560, found *m/z* [$C_{30}H_{23}F_4N_3P^+$] = 532.1551.

4.16 1-(2,3,4,5,6-Pentafluorobenzyl)-3-[(1-{2,3,5,6-tetrafluoro-4-[(3-vinylimidazolium-1-yl)-methyl]phenyl}-1,2,3-triazol-4-yl]methyl]imidazolium bis(hexafluoridophosphate) (20)

1-(2,3,4,5,6-pentafluorobenzyl)-3-propargylimidazolium bromide (**18**; 100 mg, 0.27 mmol) and 3-(4-azido-2,3,5,6-tetrafluorobenzyl)-1-vinylimidazolium bromide (**12**; 103 mg, 1.0 equiv., 0.27 mmol) were dissolved in an isopropanol/water 2:1 mixture (4.5 ml). Copper(II) sulfate pentahydrate (5 mg, 0.07 equiv.) and sodium ascorbate (12 mg, 0.22 equiv.) were added and the mixture was stirred under an argon atmosphere at room temperature for 4 days. Then, the solvents were removed under reduced pressure. After re-dissolving the residue in water (2 ml), a solution of ammonium hexafluorophosphate in water (1 ml) was added. The precipitate was collected by filtration and dried *in vacuo*, yielding 188 mg (79 %) of the crude 1-(2,3,4,5,6-pentafluorobenzyl)-3-((1-(2,3,5,6-tetrafluoro-4-((3-vinylimidazolium-1-yl)-methyl)-phenyl)-1,2,3-triazol-4-yl)methyl)-imidazolium bis(hexafluoridophosphate) (**20**) as a pale yellow solid. Single-crystals were obtained by diffusion of diethyl ether into a solution of **20** dissolved in acetonitrile. M.p. 202 – 204 °C (dec.) – ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ 5.47 (dd, J = 8.7, 2.5 Hz, 1H, VinH), 5.69 (s, 2H, N-BnH), 5.71 (s, 2H, N-BnH), 5.79 (s, 2H, CH2), 6.00 (dd, J = 15.6, 2.5 Hz, 1H, VinH), 7.31 (dd, J = 15.6, 8.8 Hz, 1H, VinH), 7.83 (t, J = 1.7 Hz, ImH), 7.90 (t, J = 1.8 Hz, ImH), 7.99 (t, J = 1.9 Hz, ImH), 8.26 (t, J = 1.9 Hz, ImH), 8.78 (s, 1H, TrH), 9.49 (s, 1H, ImH), 9.59 (s, 1H, ImH) ppm. – ^{13}C NMR (75 MHz, $(CD_3)_2SO$): δ 40.5 (CH_2), 43.5 (N-BnC), 107.7 – 108.5 (m, BnC), 109.4 (VinC) , 114.1 – 114.8 (m, BnC), 116.8 – 117.3 (m, BnC), 119.3 (ImC), 123.1 (ImC), 123.8 (ImC), 127.4 (TrC) , 128.7 (VinC), 135.2 – 135.9 (m,

BnC), 136.4 (ImC), 137.3 (ImC), 138.3 – 139.2 (m), 139.3 – 139.8 (m), 141.4 (TrC), 142.6 – 143.2 (m), 143.2 – 143.9 (m), 146.6 – 147.2 (m)ppm. (One of the benzylic CH_2 is hidden by solvent peak, see C,H-HETCORR). – ^{19}F NMR (376 MHz, $(CD_3)_2SO$): δ -161.8 – -161.6 (m, BnF), -152.8 (t, J = 22.2 Hz, BnF), -147.3 – -147.1 (m, BnF), -141.4 – -141.2 (m, BnF), -139.8 – -139.7 (m, BnF), -70.3 (d, J = 710.0 Hz, PF_6^-) ppm. – FT-IR (ATR): ν 3161 (w) (νCH), 1661 (w), 1559 (w), 1506 (m), 1453 (w) (νC=C, νC=N, νN=N), 1162 (m), 1129 (m) (νCF), 1038 (m), 1017 (m), 970 (w), 920 (m) (δ_iCH), 824 (s) (PF_6^-), 740 (m), 680 (m), 654 (m) (δ_oCH), 556 (s) ($\delta_{oop/ip}$ring) cm^{-1}. – HRMS (ESI pos.): calcd. *m/z* $[M^+]$ = 730.0960, found *m/z* $[C_{25}H_{16}F_{15}N_7P^+]$ = 730.0943.

Statement of significance:

In order to further explore the applicative potential of imidazoles with novel substitution patterns, several polymerisable and pentafluorobenzylated derivatives thereof were synthesised and thoroughly characterised. *Via* well-established thionation to S-nucleophilic imidazolinethiones, the incorporation of a second side-chain was achieved. Even further derivatisation options were demonstrated through nucleophilic aromatic substitution at the pentafluorophenyl moiety. This remarkably versatile family of fluorinated imidazoles may be chemically tailored to numerous applications, amongst which are e.g. N-heterocyclic carbene pre-catalysts, energetic materials, polyelectrolytes and ionic liquids

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Table 1. Minimal aqueous surface tension values at a given concentration for compounds **2**, **4**, **7**, **10**, **14**, **16** and **18**.

Compound	Concentration [mmol/L]	Min. Surface Tension [mN/m]
2	133.3	67.66 ± 0.11
4	25.70	45.53 ± 0.13
7	21.54	46.94 ± 0.10
10	169.4	62.08 ± 0.09
14	197.9	60.44 ± 0.08
16	136.8	60.09 ± 0.09
18	163.8	49.04 ± 0.06