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PAPER

Pentaalkylmethylguanidinium methylcarbonates – versatile precursors for the preparation of halide-free and metal-free guanidinium-based ILs†

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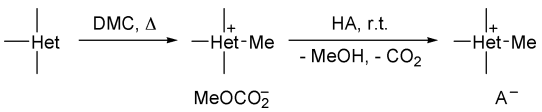
Pentaalkylmethylguanidinium methylcarbonates **6** can easily be prepared from pentaalkylguanidines **5** and dimethyl carbonate (DMC) in a sustainable solvent-free synthesis. Most of the title compounds are room temperature ionic liquids (RTILs) which provide convenient access to halide-free guanidinium-based ILs (GILs) **7** *via* acid–base reactions and subsequent decarboxylation, similar to industrially important imidazolium methylcarbonates **1**.

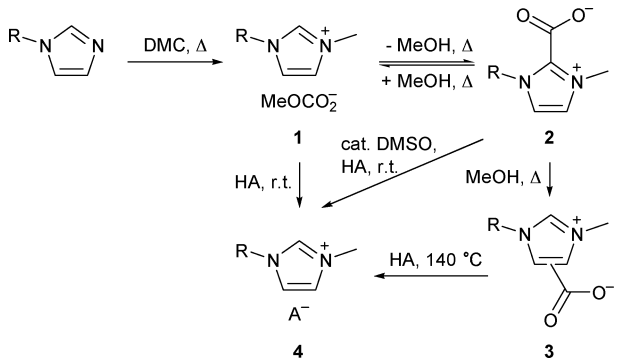
Introduction

Large-scale low waste-producing synthesis of ionic liquids (ILs) avoiding intrinsic impurities is crucial to minimize their production costs and to promote their use as innovative solvents and materials. Large-scale applications for guanidinium- and imidazolium-based ILs are, for example, their use as electrolytes in dye-sensitized solar cells and as cellulose processing solvents.[1,2] Imidazolium-based ionic liquids are usually prepared *via* alkylation of *N*-alkylimidazoles by alkylhalides, followed by an anion exchange reaction.[3] This procedure leads to products more or less contaminated with traces of halide ions and the typically applied group 1 metal cations. Even traces of both minimize their performance in electrochemical devices. Furthermore, this method is unfavourable for ILs with comparatively basic anions, *e.g.* acetate or cyanide. Among the different proposals towards completely halide-free IL syntheses,[4,5] the "methylcarbonate route" is by far the most attractive one because of its simple workup (Scheme 1).[4]



Scheme 1 "Methylcarbonate route" for halide-free ILs.

This strategy makes use of the moderate alkylation power of dialkyl carbonates at higher temperatures[6] and has been described for a variety of group 15 based onium cations, *e.g.* ammonium, phosphonium, pyridinium, imidazolinium, 2*H*-imidazolium and 2-methylimidazolium,[7–11] not only in the context of IL synthesis. In the case of 2*H*-imidazoles as nucleophiles, which is most prominent with regard to IL synthesis, interesting side reactions such as ring carboxylation at different positions can occur (Scheme 2).[12,13]



Scheme 2 "Methylcarbonate route" for 2*H*-imidazolium-based ILs. The primary alkylation product **1** as well as the zwitterion **2** can easily be transformed into the desired ILs **4**. The thermodynamic product **3** is undesired as it is decarboxylated only under harsh conditions.[13]

This sometimes problematic reaction path has been circumvented by diluting the reactants with methanol,[14] thus stabilizing the highly basic methylcarbonate anion *via* hydrogen bridges. However, this strategy necessitates high pressure equipment because of the required reaction temperatures. The resulting 1,3-dialkylimidazolium methylcarbonates **1** or betaines (**2**, **3**) can be reacted with acids HA to give the corresponding imidazolium-based ILs (Scheme 2).[12–14] The acid–base equilibrium is shifted by release of CO_2 if the pK_a value of HA is about the same or smaller than that of unstable methyl carbonic acid (pK_a(H_2O) = 5.6).[15] After evaporation of methanol and carbon dioxide the pure halide-free IL **4** is obtained.

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† Electronic supplementary information (ESI) available: Details on lineshape analysis of **7k** and **7l** and crystal structure analysis of **8**. CCDC reference number 797179. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0gc00698j

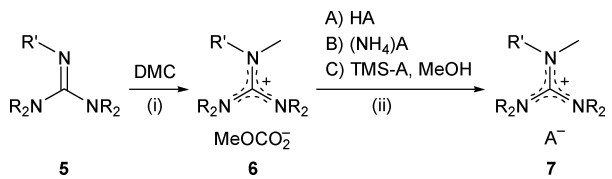
A fully developed synthetic protocol for the preparation of pentaalkylguanidines and hexaalkylguanidinium salts is well-known for more than two decades.[16] Therefore, investigations on guanidinium-based ILs (GILs) have mainly focused on the preparation of low-melting guanidinium salts rather than on the development of new synthetic routes. In most GIL syntheses a halide salt is subjected to anion metathesis in a second step.[17] This methodology leads to the same problems as in the case of imidazolium-based ILs, *i.e.* halide impurities and difficulties in introducing basic anions. Recently, Kunkel and Maas have shown that triflate-GILs can be prepared from the appropriate ureas without involvement of halide-containing intermediates,[18] but this synthetic concept is economically less attractive and fails for anions other than triflate.

Pentaalkylguanidines are well-known as very strong organic bases[19] – their corresponding acids exhibit pK_a values of about 25 in MeCN. Their low nucleophilicity in relation to a high proton affinity led to the development of superbasic proton sponges[20] and extraordinary ligands in transition metal chemistry.[21] While the nucleophilic character of guanidines has been demonstrated by quarternizations using alkyl halides or dialkyl sulfates,[16,22] no such reaction between peralkylated guanidines and dialkylcarbonates has been reported. The only guanidinium alkylcarbonates known have been prepared by a reversible CO_2-scavenging reaction of mixtures of pentaalkylguanidines and alcohols with carbon dioxide.[23] These pentaalkylguanidinium alkylcarbonates are rather labile compounds as they exhibit CO_2-binding energies of less than 10 kJ mol^{-1}. They are no suitable precursors for hexaalkylguanidinium salts because they intrinsically contain at least one protonated nitrogen atom.

Results and discussion

Synthesis

During the search for halide-free synthetic protocols towards GILs, we found that pentaalkylguanidines **5** readily react with dimethyl carbonate (DMC) at elevated temperatures giving pentaalkylmethylguanidinium methylcarbonates **6** in high yield and purity (Scheme 3, Table 1). The reaction can beneficially be performed without additional solvents and optionally by use of microwave-assisted synthesis. Our strategy does not suffer from undesired side reactions, unlike the corresponding reaction of alkylimidazoles, and no high-pressure reactors are necessary.



Scheme 3 Reaction of pentaalkylguanidines **5** with DMC and subsequent anion exchange *via* acid–base reaction. (i) 120 °C, 3 days; (ii) 50 °C, 6 h.

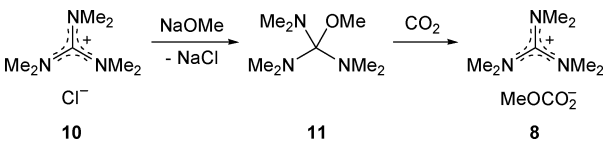
Trying to prepare the simplest possible peralkylated guanidinium methylcarbonate, namely hexamethylguanidinium methylcarbonate (**8**), from pentamethylguanidine and DMC, we were surprised to learn that in this particular case the transformation outlined in Scheme 3 gives rise to side reactions. After three days at 120 °C, the only obtained ether-insoluble product was tetramethylammonium methylcarbonate (**9**)[7] in low yield, identified by its proton and carbon NMR spectra, IR spectrum, ESI mass spectra and elemental analysis. As no other nitrogen sources than pentamethylguanidine were present in the reaction mixture, a degradation of the guanidine motif must have had occurred. It was reasoned that methylation with DMC occurs in a first step giving the desired hexamethylguanidinium methylcarbonate (**8**), readily being followed by some further reaction that is only possible at sterically less crowded guanidinium cations.

Table 1 Pentaalkylmethylguanidinium methylcarbonates **6** prepared by reaction of pentaalkylguanidines **5** with DMC

Product no.	Guanidine	R[a]	R′[a]	Yield [%]
6a	**5a**	Et	Et	94
6b	**5b**	Et	Bu	97
6c	**5c**	Et	*i*Oct[b]	95
6d	**5d**	Bu	Bu	95
6e	**5e**	Bu	*i*Oct[b]	85

[a] *Cf.* Scheme 3. [b] *i*Oct = *rac*-2-ethylhexyl.

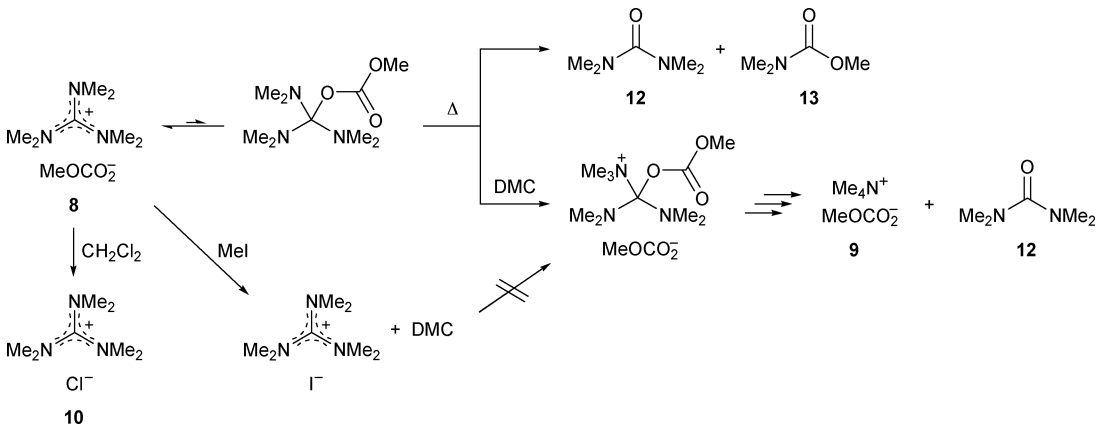
In order to check this reaction pathway, efforts were made to synthesize **8** by other routes. Simple salt metathesis starting from sodium methylcarbonate[24] and hexamethylguanidinium chloride (**10**) proved to be ineffective in methanol, acetonitrile and mixtures of these with ether due to the poor solubility of sodium methylcarbonate in moderately polar solvents. Tris(dimethylamino)methoxymethane (**11**) on the other hand, is known to show basic reactivity like an alkoxide and is thus believed to exist in an equilibrium with a salt-like ionic structure.[25] Because of that we decided to investigate the reactivity of **11** towards carbon dioxide. At room temperature, dry carbon dioxide was passed through a solution of **11** in ether, prepared *in situ* from **10** and sodium methoxide.[26] Instantly a white precipitate of **8** was formed, that was separated by filtration and dried in vacuum (Scheme 4).



Scheme 4 Preparation of **8** *via* carbon dioxide insertion.

When **8** was subsequently reacted with excess DMC at elevated temperatures, the same reactivity as in the case of pentamethylguanidine was observed, leading to the formation of **9**. Spectroscopic investigation of the volatile components of the reaction mixture showed the presence of tetramethyl urea (**12**) as well as *N*,*N*,*O*-trimethyl carbamate (**13**). It was found that these compounds were also obtained by heating **8** in toluene at 120 °C overnight, indicating a second, DMC-independent decomposition route (Scheme 5).

However, when **8** was treated with the much stronger alkylating agent iodomethane in acetonitrile, the formation of DMC and hexamethylguanidinium iodide was observed and no degradation of the guanidinium core could be detected by



Scheme 5 Reactivity of **8** under different conditions, including postulated mechanism for the observed degradation.

NMR spectroscopy. It was also found that **8** slowly reacts with the weak electrophile dichloromethane forming **10** within a few days at room temperature (Scheme 5).

Scheme 5 also outlines the postulated mechanism for the observed reactivity of **8**. The relatively small NMe_2 substituents at the central carbon atom of the hexamethylguanidinium cation lead to little steric hindrance. Thus, a nucleophilic attack of the rather basic methylcarbonate anion at the masked carbenium center can take place. It is proposed, that especially in the absence of solvation by protic solvents a very tight contact ion pair between anion and cation is formed in equilibrium with the dissociated salt, giving rise to a considerable covalent character. Due to the enhanced NMe_2-basicity of this neutral species, it could be prone to further *N*-methylation by DMC and elimination of trimethylamine, finally leading to the tetramethylammonium ion. Contrastingly, **8** is readily methylated by iodomethane at the methylcarbonate anion to yield DMC and hexamethylguanidinium iodide which is inert with respect to excess MeI or DMC. No covalent isomer is available for *N*-alkylation in this case, therefore no degradation of the guanidinium motif can occur despite the much greater methylating power of MeI compared to DMC.

It is interesting to note that the change from methyl to ethyl substituents is sufficient to inhibit decomposition *via* self condensation, thereby allowing for easy preparation of the intermediates **6**. Fortunately, the scope of the given method for preparing GILs is only little limited by the reactions outlined in Scheme 5 as guanidinium salts with more than four methyl substituents are often found to have unacceptably high melting points.[16]

The obtained guanidinium methylcarbonates **6** are mostly RTILs and react with acids HA *via* protonation of the anion and its fragmentation into carbon dioxide and methanol (method A, Scheme 3; Table 2). Since some acids are unstable (*e.g.* HNCO, HNCS), the application of the corresponding ammonium salts in these cases is favorable (method B); ammonia is released. Other acids harmful to handle (*e.g.* HCN, HN_3) are most conveniently prepared *in situ* from their silylated synthons TMS-A in MeOH. Volatile TMS-OMe is released as the new anions are incorporated (method C). All three types of anion metathesis were found to be quantitative reactions. If a volatile anion source is used, a small excess of the reagent will be convenient to assure that no traces of methylcarbonate remain in the product. Water is also usable as the acidic component as shown for entry **7j** of Table 2. In this case, the large excess of water applied shifts the equilibrium between methylcarbonate and similarly basic hydrogen carbonate towards the desired product.[11]

Table 2 GILs containing pentaalkylmethylguanidinium cations prepared by acid–base reaction with various anion sources

Product no.	Reactant	R[a]	R′[a]	Anion A^-	Method[a]	Yield [%]	$T_{5\%}$[b] [°C]	T_{dec}[c] [°C]	T_g[d] [°C]	T_m[e] [°C]
7a	**6d**	Bu	Bu	$[OAc]^-$	A	99	166	250	−68	—
7b	**6d**	Bu	Bu	$[TFA]^-$	A	100	188	227	−66	—
7c	**6d**	Bu	Bu	$[SCN]^-$	B	99	285	326	−62, 43	—
7d	**6d**	Bu	Bu	$[N_3]^-$	C	99	236	273	−63	—
7e	**6d**	Bu	Bu	$[OMs]^-$	A	99	322	375	−55	42
7f	**6d**	Bu	Bu	$[BF_4]^-$	A	99	396	467	−60	—
7g	**6d**	Bu	Bu	$[PF_6]^-$	B	95	367	414	−50	43
7h	**6d**	Bu	Bu	$[Tf_2N]^-$	A	95	378	458	—	38
7i	**6d**	Bu	Bu	$[C_6F_5(Nf)N]^-$	A	98	339	388	−56	—
7j	**6d**	Bu	Bu	$[HCO_3]^-$	D[f]	97	137	162, 225	−58	—
7k	**6c**	Et	*i*Oct[g]	$[Tf_2N]^-$	A	88	412	463	−66	—
7l	**6e**	Bu	*i*Oct[g]	$[Tf_2N]^-$	A	99	402	458	−63, 40	—

[a] *Cf.* Scheme 3. [b] Temperature at which 5% mass loss is observed. [c] Decomposition temperature (temperature of fastest mass loss). [d] Glass transition temperature. [e] Melting temperature. [f] Heating **6d** in excess water at 80 °C for 6 h. [g] *i*Oct = 2-ethylhexyl.

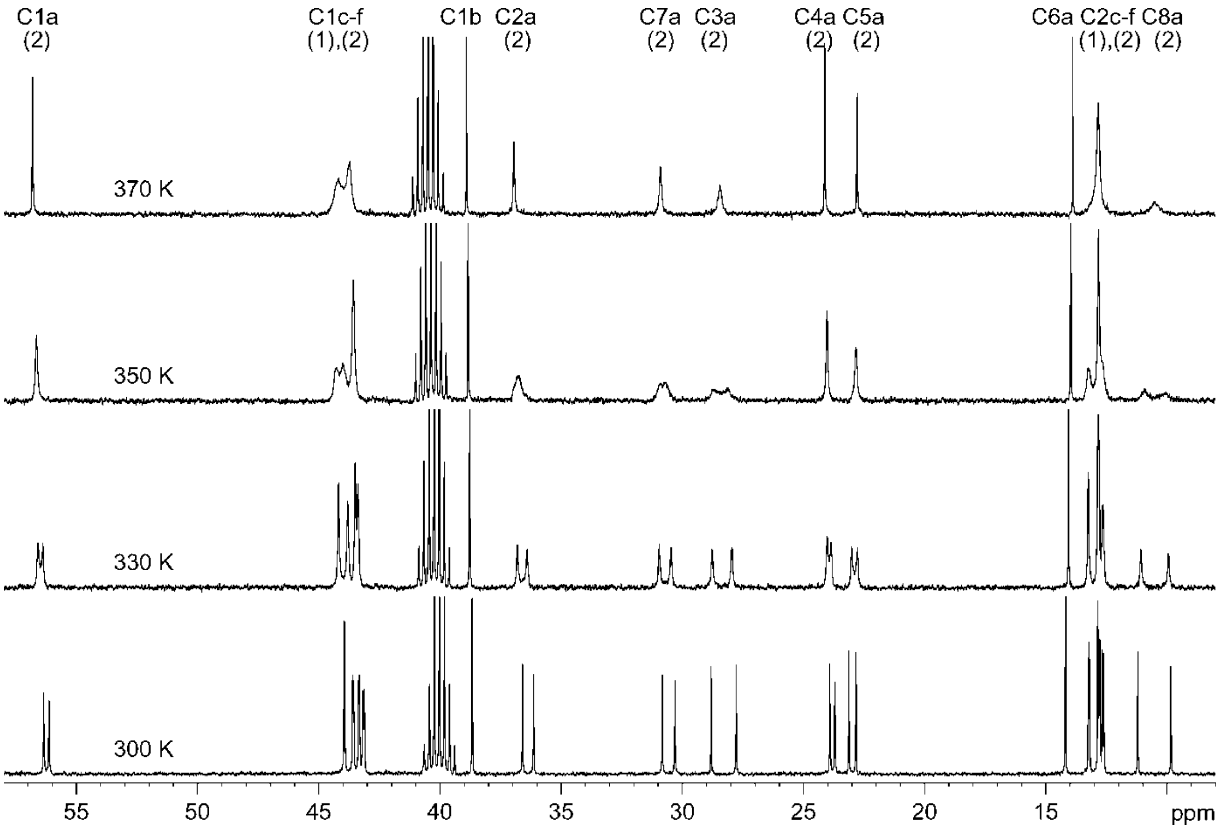
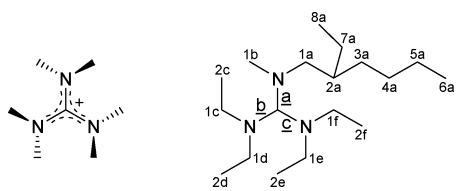


Fig. 1 Temperature dependent ^{13}C NMR spectra of **7k** in DMSO-d_6. Assignment of signals is given as well as the observed exchange processes.

NMR spectroscopy

The proton spectra of all guanidinium methylcarbonates **6** in acetonitrile show a characteristic singlet at 3.29 ppm representing the anion's methyl group. The cation signals are strongly overlapping due to the various alkyl chains. However, the signal of the introduced methyl group is clearly visible at 2.8–2.9 ppm. Some of the smaller cations also show diastereotopic proton signals for the methylene groups in α and β positions, which is caused by a chiral environment around the central carbon atom. Indeed, all guanidinium cations are known to show a propeller-shaped structure (Scheme 6) both in solution[27,18] and in the solid state.[28,29] This deviation from a co-planar orientation of the sp^2-hybridized nitrogen atoms is energetically advantageous because of the steric repulsion even of small substituents.



Scheme 6 Propeller-shaped, chiral structure of guanidinium cations (left) and the numbering scheme for **7k** (cation part, right).

The carbon spectra show characteristic signals for the methylcarbonate anion at 51.8 and 157.6 ppm, respectively. The guanidinium centre is found around 165 ppm, suffering a downfield shift of about six to seven ppm in comparison with the corresponding guanidines as a consequence of the delocalized positive charge. Due to the propeller-shaped, twisted configuration of the central guanidinium motif, all alkyl chains of the pentaalkylmethylguanidinium cations formally become magnetically non-equivalent and give rise to overlapping signals for the outer carbon atoms and narrow signal groups for the inner positions. In addition to that, methylcarbonates **6c** and **6e** as well as their TFSI-analogues **7k** and **7l** show a doubled set of signals. The introduction of the (racemic) 2-ethylhexyl substituent as a second stereogenic element leads to two diastereomeric forms of these cations. This effect was used to determine the energy barrier for the sterically and electronically hindered rotation around the central carbon-nitrogen bonds. Fig. 1 shows details of the temperature-dependent carbon spectra of *N*-(2-ethylhexyl)-*N*′,*N*′,*N*″,*N*″-tetraethyl-*N*-methylguanidinium bis(trifluoromethanesulfonyl)imide (**7k**) in DMSO-d_6. Two different processes are observed, of which (1) involves only the four ethyl groups, whereas (2) affects all diastereomeric signals. A complete line-shape analysis was utilized to elucidate the quantitative features of process (2); details are shown in Table 3. Process (1) could not be quantified reliably because of the small shift differences of the participating signals, however it clearly is somewhat faster than (2), especially for **7k**.

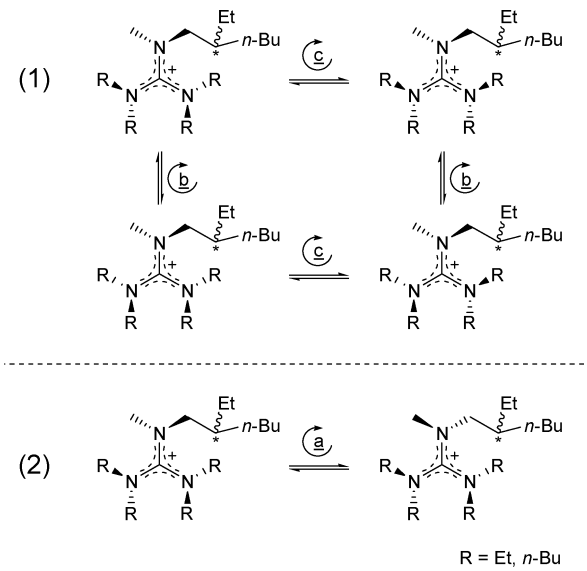
As (1) transforms the ethyl or *n*-butyl groups without changing the diastereomeric signals of the 2-ethylhexyl substituent, we interpret this as a thermally activated rotation around the partial double bonds b and c (Scheme 6, 7). Similarly, the rotation of the third carbon-nitrogen bond a leads to the loss of stereochemical information and thus

Table 3 Activation parameters of (2) for **7k** and **7l**

	E_A[a] [kJ mol^{-1}]	$\Delta H^{\ddagger}$ [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [J mol^{-1} K^{-1}]	$\Delta G^{\ddagger}$[a] [kJ mol^{-1}]
7k	80.0 ± 3.4	77.5 ± 3.4	12.3 ± 9.9	73.8 ± 6.3
7l	104.5 ± 4.0	102.1 ± 4.0	63.4 ± 11.6	83.0 ± 7.5

[a] Calculated for 300 K.

to the collapse of all signals of the diastereomers into an averaged cation structure with a *pseudo*-planar guanidinium centre. The latter process (2) has a higher activation energy because of the bulkier substituent involved. For this reason **7l** shows less separation of the two processes in energy as the difference in size of the corresponding substituents is smaller. The obtained energy barriers are consistent with those reported for *N*,*N*,*N*′,*N*′-tetramethyl-*N*″-arylguanidinium,[30] *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-arylguanidinium[31] and *N*,*N*,*N*′,*N*′-tetramethyl-*N*″,*N*″-bis(benzyl)guanidinium salts,[27] all of which were determined using temperature-dependent proton NMR spectra. *N*,*N*,*N*′,*N*′,*N*″-Pentamethyl-*N*″-(2,4,6-tri-*iso*-propylphenyl)guanidinium iodide was found to have Gibb's free energy barriers of 59 kJ mol^{-1} and 100 kJ mol^{-1} for the rotations involving the NMe_2 and N(Me)Ar substituents, respectively.



Scheme 7 Thermal activation of rotations around the central carbon-nitrogen bonds in **7k** and **7l**; (1) rotations involving NR_2 substituents, (2) rotation involving N(Me)*i*Oct.

In this context it seems likely that using sufficiently bulky substituents, configuratively stable GILs should be accessible. This could lead to chiral GILs bearing no other stereogenic centres in the cation than the guanidinium motif.

Thermal behaviour

Results of the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements are summarized in Table 2. With the exception of the hydrogencarbonate **7j**, all investigated guanidinium salts decompose in a single step, characterized by a single decomposition temperature (temperature of fastest mass loss). High thermal stability of up to 400 °C at 5% decomposition is observed for GILs with weakly coordinating anions such as tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonyl)imide. Similar findings have been reported for a range of GILs, establishing the trend that guanidinium salts are in most cases at least as thermally stable as imidazolium salts with the same anion.

Most of the substances presented in Table 2 are RTILs and show a glass transition in the range of −70 to −50 °C. This behaviour is typical of alkyl-substituted guanidinium salts and is obviously little affected by the commonly used IL anions.[18] Mesylate **7e**, hexafluorophosphate **7g** and bis(trifluoromethanesulfonyl)imide **7h** are solids at room temperature and have melting points of around 40 °C. It is interesting to note that **7l** shows two glass transition temperatures, of which one (−63 °C) is in the above-mentioned temperature range, whereas the second one (40 °C) presumably corresponds to the beginning rotation around the central C–N bonds (*vide supra*). Thiocyanate **7c** also apparently shows two glass transitions (−62 °C and 43 °C), the nature of the less pronounced high-temperature transformation could not be elucidated yet.

Crystal structure of hexamethylguanidinium chloride (10)

Single crystals of **10** were obtained from a concentrated solution of **8** in dichloromethane/ether at room temperature as colourless prisms. **10** crystallizes in the monoclinic space group *C* 2/m with *Z* = 4. The asymmetric unit contains half a formula unit, both crystallographically independent cations are located on special positions, thus showing a fourfold symmetry. The resulting disorder of the cations leads to a characteristic star-shaped appearance that is often found with hexamethylguanidinium salts (Fig. 2).[28] Full details on atomic parameters, bond lengths and angles are given in the ESI,† averaged values are given in Table 4.

Because of the disorder in the cations and (within the measurement's accuracy) the overlapping methyl groups, the individual lengths of chemically equivalent bonds deviate more or less significantly from the averaged values shown in Table 4. However, the mean bond lengths (133.9 pm and 153.3 pm, respectively) are as expected for this cation, as are the NCN and CNC bond angles.[28] As the shortest C . . . Cl distance is 373 pm, no specific cation-anion interaction is present.

Table 4 Averaged bond lengths and angles for **10**[a]

Bond	[pm]	Angle	[°]
C═N	133.9	N–C–N	120.0
N–C	153.3	C═N–C	117.1
		C–N–C	125.5

Torsion	[°]
N═C═N–C	30.4

[a] In this table, "═" represents the partial C–N double bond.

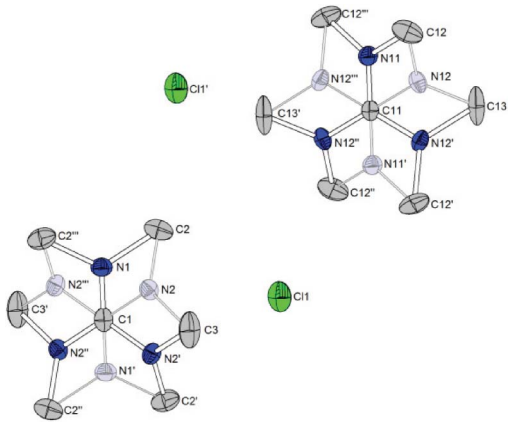


Fig. 2 Molecular structure of **10**. Ellipsoids are shown at 30% probability; hydrogen atoms are omitted for clarity. Nitrogen atoms are disordered between the opaque and shaded positions.

Conclusions

As pentaalkylguanidines can be prepared in large-scale synthesis and purified *via* distillation, this "methylcarbonate route" appears to be the up to date most promising concept for an environmentally friendly synthesis of pure GILs avoiding waste and toxic methylating agents like iodomethane, dimethylsulfate or methyltriflate. The direct accessibility of any guanidinium-based ILs with anions less basic than methylcarbonate, *e.g.* acetate for cellulose processing, the solvent-free synthesis and the completely halide-free and metal-free ionic liquid quality as needed in electrochemical devices offer many perspectives for applications.

Experimental

General remarks

Manipulation of moisture-sensitive guanidinium methylcarbonates was carried out using standard Schlenk- and glovebox-techniques. Pentaalkylguanidines were prepared according to the literature,[16] distilled at reduced pressure and stored under dry nitrogen. Dimethyl carbonate (99%, Aldrich) was used without further purification. Acids and acid generators (Sigma-Aldrich, Merck, Acros) were used as received, the synthesis of *N*-pentafluorophenyl-nonafluoro-*n*-butanesulfonylimine is described elsewhere.[5]

NMR spectra were recorded at 300 K on a Bruker AC 300 or a Bruker DRX 400 for variable-temperature measurements using CD_3CN or DMSO-d_6 as solvent. Chemical shifts are given with respect to tetramethylsilane (^{1}H, ^{13}C), phosphoric acid (^{31}P) and trichlorofluoromethane (^{19}F), respectively. Calibration of ^{1}H and ^{13}C spectra was accomplished with the solvent signals, ^{19}F and ^{31}P spectra were calibrated externally.

The alkyl chains of guanidines and guanidinium cations are numbered beginning with "1" at the innermost position. Each alkyl chain is additionally denoted with a letter, reflecting its position in the IUPAC-conform name, *i.e.* the first substituent at the nitrogen atom with the highest priority has the suffix "a", the second substituent has the suffix "b", and so on. As guanidinium cations are non-planar,[18,27–29] diastereomeric protons can be distinguished in some of the ^{1}H NMR spectra. They are referred to as "Ha" and "Hb", respectively.

TGA measurements were performed using a Mettler TGA/SDTA 851^e apparatus (25 °C – 800 °C, 10 K min^{-1}), DSC curves were measured on a Mettler DSC 821^e, the heating rate was 10 K min^{-1} for all experiments, T_m and T_g are reported as onset values in the second heating cycle.

ESI mass spectra were recorded on a Finnigan TSQ 700 using acetonitrile as solvent. *m*/*z* values are given together with their relative intensities.

All IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using neat samples with an ATR measurement setup. Designation of characteristic bands is given as well as the relative intensities.

Elemental analysis was done on a CHN-Rapid (Heraeus). Values are given in weight percent.

X-ray data collection was performed *via* a STOE IPDS I area detector at 193 K using Mo-Kα-radiation (λ = 71.073 pm). STOE IPDS software[32] was used for integration and data reduction, structure solution and refinement was done with the WinGX program suite[33] using SIR92[34] and SHELX-97.[35]

Pentaalkylguanidines

General procedure for the preparation of pentaalkylguanidines (5). To a solution of the appropriate tetraalkylchloroformamidinium chloride (1.0 eq.) in dry acetonitrile a mixture of the primary amine (1.1 eq.) and triethylamine (1.1 eq.) was added *via* a dropping funnel. The reaction mixture was stirred overnight at room temperature and/or heated at reflux for at least one hour to ensure complete reaction. All volatiles were removed *in vacuo* and to the resulting residue a concentrated aqueous sodium hydroxide solution (>2.5 eq.) was added. The strongly basic mixture was extracted two times with ether. The organic phase was concentrated *in vacuo* and the resulting oily crude product was distilled at reduced pressure giving the pure pentaalkylguanidine, which was stored under dry nitrogen.

***N′*-(2-Ethylhexyl)-*N*,*N*,*N″*,*N″*-tetraethylguanidine (5c) (Gua-2,2-i8-2,2).** Prepared from *N*,*N*,*N′*,*N′*-tetraethylchloroformamidinium chloride (11.36 g, 50.0 mmol, 1.00 eq.), triethylamine (7.0 mL, 50.5 mmol, 1.01 eq.) and 2-ethylhexylamine (8.2 mL, 50.1 mmol, 1.00 eq.). Fractional distillation (75 °C/1.6 × 10^{-1} mbar) gave the guanidine (13.33 g, 94%) as a colourless liquid. Anal. calc. for $C_{17}H_{37}N_3$ (283.50 g mol^{-1}) C 72.02, H 13.15, N 14.82%; found C 71.71, H 12.74, N 15.20%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.85, 0.88 (2 × t, 2 × 3H, $^3J_{HH}$ = 7.1, 6.8 Hz, C6b-H and C8b-H), 0.99, 1.00 (2 × t, 2 × 6H, $^3J_{HH}$ = 7.1, 7.1 Hz, C2a,c-H), 1.22–1.45 (m, 9H, C2b-H to C5b-H and C7b-H), 2.98 (d, 2H, $^3J_{HH}$ = 5.5 Hz, C1b-H), 3.01, 3.09 (2 × q, 2 × 2H, $^3J_{HH}$ = 7.0, 7.1 Hz, C1a,c-H) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 11.7 (C8b), 13.3, 14.3 (C2a,c), 14.5 (C6b), 24.0 (C5b), 25.8 (C4b), 30.1 (C3b), 32.6 (C7b), 42.2 (C1a/c), 43.1 (C2b), 43.7 (C1a/c), 53.0 (C1b), 158.2 (CN_3) ppm. MS (ESI+) *m*/*z* (%) = 284.3058 (100, $C_{17}H_{38}N_3$ requires 284.3060, $[M+H]^+$). IR (neat) ν = 2961 (m, ν_{C-H}), 2927 (m, ν_{C-H}), 2870 (m, ν_{C-H}), 2857 (m, ν_{C-H}), 1610 (vs, $\nu_{C=N}$), 1458 (w), 1400 (m), 1374 (m), 1258 (s, ν_{C-N}), 1219 (m), 1122 (m), 1068 (m), 782 (w) cm^{-1}.

***N*,*N*,*N*′′,*N*′′-Tetra-n-butyl-*N*′-(2-ethylhexyl)-guanidine (5e) (Gua-4,4-i8-4,4).** Prepared from *N*,*N*,*N*′,*N*′-tetra-*n*-butylchloroformamidinium chloride (17.10 g, 50.4 mmol, 1.00 eq.), triethylamine (5.6 g, 55.0 mmol, 1.09 eq.) and 2-ethylhexylamine (7.1 g, 55.0 mmol, 1.09 eq.). Fractional distillation (129 °C/1.7×10^{-1} mbar) gave the guanidine (19.58 g, 98%) as a colourless liquid. Anal. calc. for $C_{25}H_{53}N_3$ (395.71 g mol^{-1}) C 75.88, H 13.50, N 10.62%; found C 76.03, H 13.45, N 10.64%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.83–0.91 (m, 18H, C4a,c-H, C6b-H and C8b-H), 1.18–1.45 (m, 25H, C2a,c-H, C3a,c-H, C2b-H to C5b-H and C7b-H), 2.92–3.04 (m, 10H, C1a-c-H) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 11.8 (C8b), 14.3, 14.4 (C4a,c), 14.5 (C6b), 21.0, 21.2 (C3a,c), 24.0 (C5b), 25.8 (C4b), 30.1 (C3b), 30.7, 31.7 (C2a,c), 32.6 (C7b), 43.3 (C2b), 48.4, 49.7 (C1a,c), 53.1 (C1b), 158.7 (CN_3) ppm. MS (ESI+) *m*/*z* (%) = 396.4311 (100, $C_{25}H_{54}N_3$ requires 396.4312, $[M+H]^+$). IR (neat) *ν* = 2956 (s, ν_{C-H}), 2926 (s, ν_{C-H}), 2859 (s, ν_{C-H}), 1610 (vs, $\nu_{C=N}$), 1459 (m), 1399 (m), 1376 (m), 1285 (w), 1211 (m), 1110 (w), 730 (w) cm^{-1}.

Pentaalkylmethylguanidinium methylcarbonates

General procedure for the preparation of pentaalkylmethylguanidinium methylcarbonates (6). The appropriate pentaalkylguanidine (**5**) (1.0 eq.) and dimethyl carbonate (5–20 eq.) were introduced into a Schlenk-tube with a PTFE valve and degassed two times. The stirred mixture was then heated to 120 °C for three days. Excess dimethyl carbonate was removed *in vacuo*, the crude product was washed two times with dry pentane and finally dried *in vacuo* at 50 °C for at least one hour.

***N*,*N*,*N*′,*N*′,*N*′′-Pentaethyl-*N*′′-methylguanidinium methylcarbonate (6a) [Gua-2,2-2,2-2,1](MeOCO$_2$).** Prepared from *N*,*N*,*N*′,*N*′′,*N*′′-pentaethylguanidine (**5a**) (2.09 g, 10.5 mmol, 1.00 eq.) and dimethyl carbonate (5.0 mL, 59 mmol, 5.6 eq.): 2.87 g (94%) white powder. Anal. calc. for $C_{14}H_{31}N_3O_3$ (289.41 g mol^{-1}) C 58.10, H 10.80, N 14.52%; found C 58.01, H 10.81, N 14.76%. ^{1}H NMR (300 MHz, CD_3CN) δ = 1.08–1.20 (m, 15H, C2a-e-H), 2.83 (s, 3H, C1f-H), 3.03–3.31 (m, 10H, C1a-e-H), 3.27 (s, 3H, OCH_3) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 13.00, 13.04, 13.2, 13.4 (C2a-e), 37.8 (C1f), 44.2, 44.4, 44.5, 44.8 (C1a-d), 48.3 (C1e), 51.7 (OCH_3), 157.5 (CO_3), 164.7 (CN_3) ppm. MS (ESI+) *m*/*z* (%) = 214.2275 (100, $C_{12}H_{28}N_3$ requires 214.2278, $[cation]^+$). IR (neat) *ν* = 2972 (w, ν_{C-H}), 2935 (w, ν_{C-H}), 2890 (w, ν_{C-H}), 1671 (m, $\nu_{C=O}$), 1570 (m, $\nu_{C=N}$), 1538 (s, $\nu_{C=N}$), 1447 (m), 1266 (vs, ν_{C-O}), 1063 (s, ν_{C-O}), 844 (s), 811 (m), 791 (m) cm^{-1}.

***N*-*n*-Butyl-*N*′,*N*′,*N*′′,*N*′′-tetraethyl-*N*-methylguanidinium methylcarbonate (6b) [Gua-4,1-2,2-2,2](MeOCO$_2$).** Prepared from *N*′-*n*-butyl-*N*,*N*,*N*′′,*N*′′-tetraethylguanidine (**5b**) (1.88 g, 8.27 mmol, 1.00 eq.) and dimethyl carbonate (4.49 g, 4.2 mL, 49.84 mmol, 6.03 eq.): 2.53 g (97%) golden yellow oil. Anal. calc. for $C_{16}H_{35}N_3O_3$ (317.47 g mol^{-1}) C 60.53, H 11.11, N 13.24%; found C 60.54, H 11.02, N 13.53%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91 (t, 3H, $^3J_{HH}$ = 7.3 Hz, C4a-H), 1.08–1.17 (m, 12H, C2c-f-H), 1.21–1.36 (m, 2H, C3a-H), 1.43–1.72 (m, 2H, C2a-H), 2.85 (s, 3H, C1b-H), 3.06–3.34 (m, 10H, C1a,c-f-H), 3.28 (s, 3H, OCH_3) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 12.9, 13.1, 13.2, 13.4 (C2c-f), 14.0 (C4a), 20.7 (C3a), 30.0 (C2a), 38.6 (C1b), 44.2, 44.46, 44.61, 44.9 (C1c-f), 51.8 (OCH_3), 53.4 (C1a), 157.6 (CO_3), 164.7 (CN_3) ppm. MS (ESI+) *m*/*z* (%) = 242.2590 (100, $C_{14}H_{32}N_3$ requires 242.2591, $[cation]^+$). IR (neat) *ν* = 2962 (m, ν_{C-H}), 2933 (m, ν_{C-H}), 2874 (m, ν_{C-H}), 1676 (s, $\nu_{C=O}$), 1538 (s, $\nu_{C=N}$), 1439 (m), 1268 (vs, ν_{C-O}), 1064 (s, ν_{C-O}), 838 (m) cm^{-1}.

***N*-(2-Ethylhexyl)-*N*′,*N*′,*N*′′,*N*′′-tetraethyl-*N*-methylguanidinium methylcarbonate (6c) [Gua-i8,1-2,2-2,2](MeOCO$_2$).** Prepared from *N*′-(2-ethylhexyl)-*N*,*N*,*N*′′,*N*′′-tetraethylguanidine (**5c**) (2.26 g, 10.01 mmol, 1.00 eq.) and dimethyl carbonate (4.49 g, 4.2 mL, 49.84 mmol, 4.98 eq.): 2.81 g (95%) golden yellow oil. Anal. calc. for $C_{20}H_{43}N_3O_3$ (373.57 g mol^{-1}) C 64.30, H 11.60, N 11.25%; found C 64.12, H 11.48, N 11.50%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.82–0.94 (m, 6H, C6a-H and C8a-H), 1.02–1.49 (m, 20H, C1c-f-H, C3a-H to C5a-H, C7a-H), 1.65–1.75 (m, 1H, C2a-H), 2.87 (s, 3H, C1b-H), 2.90–3.38 (m, 10H, C1a,c-f-H), 3.29 (s, 3H, OCH_3) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 10.3, 11.4 (C8a, rotamers), 12.8, 12.9, 13.0, 13.1, 13.41, 13.43 (C2c-f, rotamers), 14.3, 14.4 (C6a, rotamers), 23.7, 23.9, 24.7, 24.8 (C4a and C5a, rotamers), 28.8, 29.6 (C3a, rotamers), 31.2, 31.8 (C7a, rotamers), 37.3, 37.8 (C2a, rotamers), 39.4 (C1b), 44.1, 44.3, 44.56, 44.58, 44.9 (C1c-f, rotamers), 51.8 (OCH_3), 57.4, 57.6 (C1a, rotamers), 157.6 (CO_3), 165.2 (CN_3) ppm. MS (ESI+) *m*/*z* (%) = 298.3214 (100, $C_{18}H_{40}N_3$ requires 298.3217, $[cation]^+$). IR (neat) *ν* = 2960 (m, ν_{C-H}), 2930 (m, ν_{C-H}), 2874 (m, ν_{C-H}), 1676 (s, $\nu_{C=O}$), 1537 (s, $\nu_{C=N}$), 1439 (m), 1268 (vs, ν_{C-O}), 1065 (s, ν_{C-O}), 839 (m) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*′′-Penta-*n*-butyl-*N*′′-methylguanidinium methylcarbonate (6d) [Gua-4,4-4,4-4,1](MeOCO$_2$).** Prepared from *N*,*N*,*N*′,*N*′′,*N*′′-penta-*n*-butylguanidine (**5d**) (5.35 g, 15.75 mmol, 1.00 eq.) and dimethyl carbonate (7.09 g, 6.7 mL, 78.75 mmol, 5.00 eq.): 6.44 g (95%) golden yellow oil. Anal. calc. for $C_{24}H_{51}N_3O_3$ (429.68 g mol^{-1}) C 67.09, H 11.96, N 9.78%; found C 66.66, H 11.95, N 10.32%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91, 0.92 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz, C4a-e-H), 1.20–1.49 (m, 15H, C3a-e-H, C2a-e-Ha), 1.56–1.75 (m, 5H, C2a-e-Hb), 2.86 (s, 3H, C1f-H), 2.95–3.26 (m, 10H, C1a-e-Ha and -Hb), 3.29 (s, 3H, OCH_3) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.07, 30.09, 30.2, 30.4, 30.5 (C2a-e), 38.7 (C1f), 49.8, 50.1, 50.2, 50.6 (C1a-d), 51.8 (OCH_3), 53.6 (C1e), 157.6 (CO_3), 165.0 (CN_3) ppm. MS (ESI+) *m*/*z* (%) = 354.3838 (100, $C_{22}H_{48}N_3$ requires 354.3843, $[cation]^+$); MS (ESI−) *m*/*z* (%) = 75.0090 (100, $C_2H_3O_3$ requires 75.0088, $[anion]^-$). IR (neat) *ν* = 2956 (m, ν_{C-H}), 2931 (m, ν_{C-H}), 2872 (m, ν_{C-H}), 1676 (vs, $\nu_{C=O}$), 1534 (s, $\nu_{C=N}$), 1457 (m), 1433 (m), 1269 (vs, ν_{C-O}), 1066 (s, ν_{C-O}), 841 (s) cm^{-1}.

***N*′,*N*′,*N*′′,*N*′′-Tetra-*n*-butyl-*N*-(2-ethylhexyl)-*N*-methylguanidinium methylcarbonate (6e) [Gua-i8,1-4,4-4,4](MeOCO$_2$).** Prepared from *N*,*N*,*N*′′,*N*′′-tetra-*n*-butyl-*N*′-(2-ethylhexyl)-guanidine (**5e**) (2.80 g, 7.07 mmol, 1.00 eq.) and dimethyl carbonate (5.35 g, 5.0 mL, 59.3 mmol, 8.39 eq.): 2.91 g (85%) pale yellow oil. Anal. calc. for $C_{28}H_{59}N_3O_3$ (485.79 g mol^{-1}) C 69.23, H 12.24, N 8.65%; found C 69.14, H 11.99, N 9.25%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.82–0.95 (m, 18H, C4c-f-H, C6a-H and C8a-H), 1.02–1.49 (m, 20H, C3c-f-H, C2c-f-Ha, C3a-H to C5a-H, C7a-H), 1.50–1.79 (m, 5H, C2a-H, C2c-f-Hb), 2.87 (s, 3H, C1b-H), 2.90–3.31 (m, 10H, C1a,c-f-H), 3.29 (s, 3H, OCH_3) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 10.6, 11.2 (C8a,

rotamers), 13.95, 13.98, 14.00, 14.1 (C4c-f), 14.3, 14.4 (C6a, rotamers), 20.7, 20.80, 20.83, 20.9 (C3c-f), 23.7, 24.0, 24.7, 24.8 (C4a and C5a, rotamers), 29.0, 29.5 (C3a, rotamers), 30.2, 30.3, 30.35, 30.39, 30.46, 30.49 (C2c-f, rotamers), 31.1, 32.0 (C7a, rotamers), 37.4, 37.7 (C2a, rotamers), 39.3, 39.4 (C1b, rotamers), 49.9, 50.0, 50.09, 50.10, 50.17, 50.22, 50.7 (C1c-f, rotamers), 51.8 (OCH_3), 57.7, 57.8 (C1a, rotamers), 157.6 (CO_3), 165.4 (CN_3) ppm. MS (ESI+) *m/z* (%) = 410.4466 (100, $C_{26}H_{56}N_3$ requires 410.4469, [cation]$^+$). IR (neat) ν = 2956 (m, ν_{C-H}), 2930 (m, ν_{C-H}), 2872 (m, ν_{C-H}), 1677 (vs, $\nu_{C=O}$), 1532 (s, $\nu_{C=N}$), 1457 (m), 1434 (m), 1269 (vs, ν_{C-O}), 1066 (s, $\nu_{C=O}$), 882 (m) cm^{-1}.

Hexamethylguanidinium methylcarbonate (8)

A suspension of hexamethylguanidinium chloride (**10**) (1.80 g, 10.0 mmol, 1.00 eq.) and sodium methoxide (0.55 g, 10.2 mmol, 1.02 eq.) in ether was stirred at room temperature overnight. Unreacted material and sodium chloride were removed by filtration using diatomaceous earth as filtration aid. Subsequently, P_4O_{10}-dried carbon dioxide was bubbled through the solution for 2 min, resulting in a voluminous precipitation of **8**. The product was isolated by filtration and dried *in vacuo*, giving 1.20 g (55%) **8** as a white powdery solid. Anal. calc. for $C_9H_{21}N_3O_3$ (219.28 g mol^{-1}) C 49.30, H 9.65, N 19.16%; found C 49.44, H 9.90, N 19.61%. ^{1}H NMR (300 MHz, CD_3CN) δ = 2.88 (s, 18H, C1a-f-H), 3.28 (s, 3H, OCH_3) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 40.4 (C1a-f), 51.7 (OCH_3), 157.6 (CO_3), 164.3 (CN_3) ppm. MS (ESI+) *m/z* (%) = 144.1493 (100, $C_7H_{18}N_3$ requires 144.1495, [cation]$^+$). IR (neat) ν = 2936 (w, ν_{C-H}), 2902 (w, ν_{C-H}), 1673 (s, $\nu_{C=O}$), 1599 (s, $\nu_{C=N}$), 1407 (s), 1267 (s, ν_{C-O}), 1258 (s, ν_{C-O}), 1153 (m), 1059 (s, ν_{C-O}), 899 (m), 839 (s) cm^{-1}.

Pentaalkylmethylguanidinium-ILs

General procedure for the preparation of pentaalkylmethylguanidinium salts (7) from the corresponding methylcarbonates (6). The appropriate pentaalkylmethylguanidinium methylcarbonate (**6**) (1–2 mmol, 1.0 eq.) was dissolved in 5 mL of methanol. The appropriate acid or acid generator (1–4 mmol, 1.0–2.0 eq.) was added pure or as a methanolic solution at room temperature. The reaction mixture was stirred at 50 °C overnight. The solution was concentrated *in vacuo* and the product was dried at 10^{-2} mbar.

In the case of water-insoluble or just slightly water-soluble products additional purification was achieved by washing with water. In the case of less volatile acids or ammonium salts as acid generators a precisely stoichiometric ratio of starting materials proved useful, yielding pure products without recrystallization or similar additional purification steps.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium acetate (7a) [Gua-4,4-4,4-4,1](OAc).** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (770 mg, 1.79 mmol, 1.00 eq.) and 1.57 g of a 6.88 wt% solution of acetic acid in methanol (corresponds to 108 mg, 1.80 mmol, 1.01 eq. HOAc): 738 mg (99%) pale brown oil. Anal. calc. for $C_{24}H_{51}N_3O_2$ (413.68 g mol^{-1}) C 69.68, H 12.43, N 10.16%; found C 68.65, H 12.64, N 10.42%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91, 0.92 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz, C4a-e-H), 1.18–1.50 (m, 15H, C3a-e-H, C2a-e-Ha), 1.54–1.75 (m, 5H, C2a-e-Hb), 1.75 (s, 3H, CCH_3), 2.86 (s, 3H, C1f-H), 2.93–3.28 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 24.3 (*C*CH_3), 30.08, 30.10, 30.2, 30.3, 30.5 (C2a-e), 38.7 (C1f), 49.8, 50.16, 50.22, 50.6 (C1a-d), 53.6 (C1e), 165.0 (CN_3), 174.9 (*C*CH_3) ppm. MS (ESI+) *m/z* (%) = 354.3840 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$). IR (neat) ν = 2956 (m, ν_{C-H}), 2931 (m, ν_{C-H}), 2872 (m, ν_{C-H}), 1588 (vs, $\nu_{as}(CO_2^-)$), 1558 (s), 1534 (vs, $\nu_{C=N}$), 1457 (m), 1418 (m), 1362 (s, $\nu_s(CO_2^-)$), 1313 (w), 888 (w) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium trifluoroacetate (7b) [Gua-4,4-4,4-4,1][TFA].** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (605 mg, 1.41 mmol, 1.00 eq.) and trifluoroacetic acid (220 mg, 1.93 mmol, 1.37 eq.): 656 mg (100%) colourless oil. Anal. calc. for $C_{24}H_{48}F_3N_3O_2$ (467.65 g mol^{-1}) C 61.64, H 10.35, N 8.99%; found C 60.94, H 10.04, N 9.07%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91, 0.92 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz, C4a-e-H), 1.20–1.49 (m, 15H, C3a-e-H, C2a-e-Ha), 1.56–1.75 (m, 5H, C2a-e-Hb), 2.86 (s, 3H, C1f-H), 2.95–3.29 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.07, 30.10, 30.2, 30.3, 30.5 (C2a-e), 38.7 (C1f), 49.9, 50.16, 50.22, 50.6 (C1a-d), 53.6 (C1e), 118.7 (q, $^1J_{FC}$ = 299 Hz, C*C*F$_3$), 159.0 (q, $^2J_{FC}$ = 32 Hz, *C*CF$_3$), 165.0 (CN_3) ppm; ^{19}F NMR (282 MHz, CD_3CN) δ = −73.6 (CF_3, $^1J_{FC}$ = 297 Hz) ppm. MS (ESI+) *m/z* (%) = 354.3841 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$); MS (ESI−) *m/z* (%) = 112.9856 (100, $C_2F_3O_2$ requires 112.9856, [anion]$^-$). IR (neat) ν = 2959 (m, ν_{C-H}), 2933 (m, ν_{C-H}), 2874 (w, ν_{C-H}), 1690 (vs, $\nu_{C=O}$), 1535 (s, $\nu_{C=N}$), 1458 (w), 1194 (s, ν_{C-O}), 1149 (s, ν_{C-F}), 1106 (vs, ν_{C-F}), 811 (m, δ_{C-F}), 796 (m, δ_{C-F}), 714 (m, δ_{C-F}) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium thiocyanate (7c) [Gua-4,4-4,4-4,1](SCN).** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (693 mg, 1.61 mmol, 1.00 eq.) and ammonium thiocyanate (123 mg, 1.61 mmol, 1.00 eq.): 660 mg (99%) pale yellow oil. Anal. calc. for $C_{23}H_{48}N_4S$ (412.72 g mol^{-1}) C 66.93, H 11.72, N 13.58%; found C 66.57, H 11.92, N 14.14%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91, 0.92 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz, C4a-e-H), 1.21–1.52 (m, 15H, C3a-e-H, C2a-e-Ha), 1.56–1.77 (m, 5H, C2a-e-Hb), 2.88 (s, 3H, C1f-H), 2.95–3.29 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.07, 30.10, 30.2, 30.3, 30.5 (C2a-e), 38.7 (C1f), 49.8, 50.17, 50.22, 50.6 (C1a-d), 53.6 (C1e), 131.3 (SCN), 165.0 (CN_3) ppm. MS (ESI+) *m/z* (%) = 354.3839 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$); MS (ESI−) *m/z* (%) = 57.9757 (100, CNS requires 57.9757, [anion]$^-$). IR (neat) ν = 2957 (m, ν_{C-H}), 2931 (m, ν_{C-H}), 2871 (m, ν_{C-H}), 2051 (s, $\nu_{C\equiv N}$), 1534 (vs, $\nu_{C=N}$), 1457 (m), 1436 (m), 1417 (m), 1378 (w), 1313 (w), 891 (w), 734 (w) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium azide (7d) [Gua-4,4-4,4-4,1](N_3).** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (883 mg, 2.06 mmol, 1.00 eq.) and trimethylsilyl azide (350 mg, 0.4 mL, 3.05 mmol, 1.48 eq.): 809 mg (99%) light yellow oil. Anal. calc. for $C_{22}H_{48}N_6$ (396.66 g mol^{-1}) C 66.62, H 12.20, N 21.19%; found C 66.24, H 12.27, N 21.69%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91, 0.92 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz,

C4a-e-H), 1.17–1.49 (m, 15H, C3a-e-H, C2a-e-Ha), 1.52–1.74 (m, 5H, C2a-e-Hb), 2.87 (s, 3H, C1f-H), 2.95–3.26 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.10, 30.13, 30.3, 30.4, 30.5 (C2a-e), 38.7 (C1f), 49.9, 50.18, 50.24, 50.6 (C1a-d), 53.6 (C1e), 165.0 (CN_3) ppm. MS (ESI+) *m*/*z* (%) = 354.3841 (100, $C_{22}H_{48}N_3$ requires 354.3848, [cation]$^+$). IR (neat) *ν* = 2956 (m, ν_{C-H}), 2931 (m, ν_{C-H}), 2871 (m, ν_{C-H}), 1990 (vs, $\nu_{N=N=N}$), 1534 (s, $\nu_{C=N}$), 1457 (m), 1436 (m), 1418 (m), 1377 (w), 1314 (w), 890 (w), 738 (w) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium methanesulfonate (7e) [Gua-4,4-4,4-4,1](OMs).** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (679 mg, 1.58 mmol, 1.00 eq.) and 1.48 g of a 10.27 wt% methanolic solution of methanesulfonic acid (corresponds to 152 mg, 1.58 mmol, 1.00 eq. MsOH). The crude product was dried at room temperature/10^{-6} mbar for three hours, yielding 704 mg (99%) **7e** as a white solid. Anal. calc. for $C_{23}H_{51}N_3O_3S$ (449.73 g mol^{-1}) C 61.42, H 11.43, N 9.34%; found C 60.59, H 11.42, N 9.40%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91, 0.92 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz, C4a-e-H), 1.22–1.49 (m, 15H, C3a-e-H, C2a-e-Ha), 1.53–1.74 (m, 5H, C2a-e-Hb), 2.44 (s, 3H, O_3SCH_3), 2.86 (s, 3H, C1f-H), 2.95–3.28 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.0, 30.1, 30.2, 30.3, 30.4 (C2a-e), 38.7 (C1f), 39.9 (O_3SCH_3), 49.8, 50.09, 50.15, 50.5 (C1a-d), 53.6 (C1e), 164.9 (CN_3) ppm. MS (ESI+) *m*/*z* (%) = 354.3840 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 95 (17, [anion]$^-$). IR (neat) *ν* = 2957 (w, ν_{C-H}), 2931 (w, ν_{C-H}), 2871 (w, ν_{C-H}), 1540 (m, $\nu_{C=N}$), 1454 (w), 1197 (vs, $\nu_{S=O}$), 1035 (m), 758 (m), 548 (m), 523 (m) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium tetrafluoroborate (7f) [Gua-4,4-4,4-4,1](BF$_4$).** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (436 mg, 1.01 mmol, 1.00 eq.) and 50% tetrafluoroboric acid in ether (0.2 mL, 1.52 mmol, 1.50 eq.): 441 mg (99%) colourless oil. Anal. calc. for $C_{22}H_{48}BF_4N_3$ (441.44 g mol^{-1}) C 59.86, H 10.96, N 9.52%; found C 59.56, H 11.10, N 9.16%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.92, 0.93 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz, C4a-e-H), 1.20–1.49 (m, 15H, C3a-e-H, C2a-e-Ha), 1.52–1.74 (m, 5H, C2a-e-Hb), 2.86 (s, 3H, C1f-H), 2.95–3.28 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.09, 30.13, 30.2, 30.4, 30.5 (C2a-e), 38.7 (C1f), 49.9, 50.2, 50.3, 50.7 (C1a-d), 53.7 (C1e), 165.0 (CN_3) ppm; ^{19}F NMR (282 MHz, CD_3CN) δ = –150.5 (BF_4) ppm. MS (ESI+) *m*/*z* (%) = 354.3840 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 87.0035 (100, BF_4 requires 87.0035, [anion]$^-$). IR (neat) *ν* = 2959 (w, ν_{C-H}), 2933 (w, ν_{C-H}), 2873 (w, ν_{C-H}), 1536 (m, $\nu_{C=N}$), 1459 (w), 1090 (m), 1047 (vs, ν_{B-F}), 1033 (s), 887 (w), 519 (w) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium hexafluorophosphate (7g) [Gua-4,4-4,4-4,1](PF$_6$).** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (644 mg, 1.50 mmol, 1.00 eq.) and ammonium hexafluorophosphate (266 mg, 1.63 mmol, 1.09 eq.). The product was purified by washing with water. After drying *in vacuo*, 710 mg (95%) of a white powder was obtained. Anal. calc. for $C_{22}H_{48}F_6N_3P$ (499.60 g mol^{-1}) C 52.89, H 9.68, N 8.41%; found C 52.78, H 9.78, N 8.33%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.92, 0.93 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz, C4a-e-H), 1.21–1.52 (m, 15H, C3a-e-H, C2a-e-Ha), 1.54–1.75 (m, 5H, C2a-e-Hb), 2.86 (s, 3H, C1f-H), 2.96–3.29 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.06, 30.09, 30.2, 30.3, 30.5 (C2a-e), 38.7 (C1f), 49.8, 50.15, 50.21, 50.6 (C1a-d), 53.6 (C1e), 165.0 (CN_3) ppm; ^{19}F NMR (282 MHz, CD_3CN) δ = –73.7 (d, $^1J_{FP}$ = 706 Hz, PF_6) ppm; ^{31}P NMR (122 MHz, CD_3CN) δ = –145.4 (sept, $^1J_{FP}$ = 707 Hz, PF_6) ppm. MS (ESI+) *m*/*z* (%) = 354.3835 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 144.9648 (100, F_6P requires 144.9642, [anion]$^-$). IR (neat) *ν* = 2960 (w, ν_{C-H}), 2934 (w, ν_{C-H}), 2874 (w, ν_{C-H}), 1558 (w, $\nu_{C=N}$), 1532 (w, $\nu_{C=N}$), 1458 (w), 1434 (w), 830 (vs, ν_{P-F}), 555 (m) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium bis(trifluoromethanesulfonyl)imide (7h) [Gua-4,4-4,4-4,1](Tf$_2$N).** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (760 mg, 1.77 mmol, 1.00 eq.) and bis(trifluoromethanesulfonyl)amide (572 mg, 2.03 mmol, 1.15 eq.). The product was purified by washing with water. After drying *in vacuo*, 1066 mg (95%) of a white powder was obtained. Anal. calc. for $C_{24}H_{48}F_6N_4O_4S_2$ (634.78 g mol^{-1}) C 45.41, H 7.62, N 8.83%; found C 45.38, H 7.72, N 8.68%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.92, 0.93 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.2 Hz, C4a-e-H), 1.21–1.52 (m, 15H, C3a-e-H, C2a-e-Ha), 1.57–1.75 (m, 6H, C2a-e-Hb), 2.87 (s, 3H, C1f-H), 2.93–3.29 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.09, 30.13, 30.2, 30.4, 30.5 (C2a-e), 38.7 (C1f), 49.9, 50.2, 50.3, 50.7 (C1a-d), 53.7 (C1e), 121.1 (q, $^1J_{CF}$ = 321 Hz, CF_3), 165.0 (CN_3) ppm; ^{19}F NMR (282 MHz, CD_3CN) δ = –80.1 (CF_3, $^1J_{CF}$ = 321 Hz) ppm. MS (ESI+) *m*/*z* (%) = 354.3835 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$); MS (ESI–) *m*/*z* (%) = 279.9178 (100, $C_2F_6NO_4S_2$ requires 279.9178, [anion]$^-$). IR (neat) *ν* = 2962 (w, ν_{C-H}), 2935 (w, ν_{C-H}), 2877 (w, ν_{C-H}), 1544 (m, $\nu_{C=N}$), 1346 (s, $\nu_{as}(SO_2)$), 1196 (vs, ν_{C-F}), 1178 (vs, ν_{C-F}), 1139 (m, $\nu_s(SO_2)$), 1055 (s, ν_{C-F}), 613 (s, δ_{C-F}), 568 (m, δ_{C-F}), 512 (m, δ_{C-F}) cm^{-1}.

***N*,*N*,*N*′,*N*′,*N*″-Penta-*n*-butyl-*N*″-methylguanidinium *N*-pentafluorophenyl-nonafluoro-*n*-butanesulfonylimide (7i) [Gua-4,4-4,4-4,1][C$_6$F$_5$(Nf)N].** Prepared from *N*,*N*,*N*′,*N*′,*N*″-penta-*n*-butyl-*N*″-methylguanidinium methylcarbonate (**6d**) (629 mg, 1.46 mmol, 1.00 eq.) and *N*-pentafluorophenyl-nonafluoro-*n*-butanesulfonylamide[5] (681 mg, 1.46 mmol, 1.00 eq.). The product was purified by washing with water. After drying *in vacuo*, 1173 mg (98%) of a nearly colourless oil was obtained. Anal. calc. for $C_{32}H_{48}F_{14}N_4O_2S$ (818.79 g mol^{-1}) C 46.94, H 5.91, N 6.84%; found C 46.61, H 5.67, N 7.14%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91, 0.92 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.2 Hz, C4a-e-H), 1.23–1.49 (m, 15H, C3a-e-H, C2a-e-Ha), 1.56–1.74 (m, 6H, C2a-e-Hb), 2.87 (s, 3H, C1f-H), 2.96–3.29 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.7 (C3e), 20.8 (C3a-d), 30.12, 30.14, 30.3, 30.4, 30.5 (C2a-e), 38.7 (C1f), 49.9, 50.2, 50.3, 50.7 (C1a-d), 53.7 (C1e), 165.0 (CN_3) ppm; ^{19}F NMR (282 MHz, CD_3CN) δ = –171.3 (t, 1F, $^3J_{FF}$ = 21.2 Hz, C_{para}-F), –169.7 (t, 2F, $^3J_{FF}$ = 20.3

Hz, C_{meta}-F), -152.2 (d, 2F, $^3J_{FF}$ = 22.6 Hz, C_{ortho}-F), −127.5 (tt, 2F, $^3J_{FF}$ = 14.4 Hz, $^4J_{FF}$ = 2.4 Hz, SO_2CF_2), -122.4 (br s, 2F, $CF_2CF_2CF_2$), −115.6 (br s, 2F, CF_2CF_3), −82.6 (tt, 3F, $^3J_{FF}$ = 10.1 Hz, $^4J_{FF}$ = 2.8 Hz, CF_3) ppm. MS (ESI+) *m/z* (%) = 354.3833 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$); MS (ESI−) *m/z* (%) = 463.9436 (100, $C_{10}F_{14}NO_2S$ requires 463.9432, [anion]$^-$). IR (neat) ν = 2963 (w, ν_{C-H}), 2936 (w, ν_{C-H}), 2876 (w, ν_{C-H}), 1537 (m, $\nu_{C=N}$), 1506 (s), 1497 (s), 1458 (m), 1302 (s), 1231 (s), 1207 (vs), 1150 (m), 1131 (m), 1043 (s), 982 (s), 890 (m), 585 (m), 523 (m) cm^{-1}.

***N*,*N*,*N′*,*N′*,*N″*-Penta-*n*-butyl-*N″*-methylguanidinium hydrogen carbonate (7j) [Gua-4,4-4,4-4,1](HCO$_3$).** Prepared by heating *N*,*N*,*N′*,*N′*,*N″*-penta-*n*-butyl-*N″*-methylguanidinium methylcarbonate (**6d**) (710 mg, 1.65 mmol, 1.00 eq.) in 5 mL of water at 80 °C for six hours. The resulting solution was concentrated at reduced pressure and the product dried *in vacuo* at room temperature/10^{-5} mbar, giving 666 mg (97%) of a yellowish oil. Anal. calc. for $C_{23}H_{49}N_3O_3$ (415.65 g mol^{-1}) C 66.46, H 11.88, N 10.11%; found C 66.24, H 11.66, N 10.59%. ^{1}H NMR (300 MHz, CD_3CN) δ = 0.91, 0.92 (2 × t, 15H, $^3J_{HH}$ = 7.2, 7.3 Hz, C4a-e-H), 1.21–1.51 (m, 15H, C3a-e-H, C2a-e-Ha), 1.53–1.74 (m, 5H, C2a-e-Hb), 2.86 (s, 3H, C1f-H), 2.95–3.27 (m, 10H, C1a-e-Ha and -Hb) ppm; ^{13}C NMR (75 MHz, CD_3CN) δ = 14.0 (C4a-e), 20.66 (C3e), 20.74 (C3a-d), 30.0, 30.2, 30.3, 30.4 (C2a-e), 38.7 (C1f), 49.8, 50.1, 50.2, 50.5 (C1a-d), 53.6 (C1e), 164.9 (CN_3) ppm. MS (ESI+) *m/z* (%) = 354.3840 (100, $C_{22}H_{48}N_3$ requires 354.3843, [cation]$^+$). IR (neat) ν = 2956 (m, ν_{C-H}), 2930 (m, ν_{C-H}), 2870 (m, ν_{C-H}), 2680 (br w, ν_{O-H}), 1637 (s, $\nu_{as}(CO_2^-)$), 1535 (s, $\nu_{C=N}$), 1457 (m), 1363 (s, $\nu_s(CO_2^-)$), 1318 (m), 970 (w), 890 (w), 836 (w), 679 (w) cm^{-1}.

***N*-(2-Ethylhexyl)-*N′*,*N′*,*N″*,*N″*-tetraethyl-*N*-methylguanidinium bis(trifluoromethanesulfonyl)imide (7k) [Gua-i8,1-2,2-2,2](Tf$_2$N).** Prepared from *N*-(2-ethylhexyl)-*N′*,*N′*,*N″*,*N″*-tetraethyl-*N*-methylguanidinium methylcarbonate (**6c**) (766 mg, 2.05 mmol, 1.00 eq.) and bis(trifluoromethanesulfonyl)amide (590 mg, 2.10 mmol, 1.03 eq.). The product was purified by washing with water. After drying *in vacuo*, 1050 mg (88%) of a light yellow oil was obtained. Anal. calc. for $C_{20}H_{40}F_6N_4O_4S_2$ (578.68 g mol^{-1}) C 41.51, H 6.97, N 9.68%; found C 41.77, H 6.99, N 9.68%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.77–0.92 (m, 6H, C6a-H and C8a-H), 1.00–1.44 (m, 20H, C1c-f-H, C3a-H to C5a-H, C7a-H), 1.70 (br s, 1H, C2a-H), 2.89 (s, 3H, C1b-H), 2.84–3.38 (m, 10H, C1a,c-f-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6) δ = 9.4, 10.8 (C8a, rotamers), 12.16, 12.22, 12.3, 12.36, 12.41, 12.76, 12.80 (C2c-f, rotamers), 13.7 (C6a), 22.3, 22.6, 23.2, 23.4 (C4a and C5a, rotamers), 27.2, 28.3 (C3a, rotamers), 29.8, 30.3 (C7a, rotamers), 35.6, 36.1 (C2a, rotamers), 38.2 (C1b), 42.6, 42.7, 42.8, 42.9, 43.07, 43.11, 43.5 (C1c-f, rotamers), 55.6, 55.8 (C1a, rotamers), 119.5 (q, $^1J_{CF}$ = 322 Hz, CF_3), 163.3 (CN_3) ppm; ^{19}F NMR (282 MHz, DMSO-d_6) δ = −79.6 (CF_3, $^1J_{CF}$ = 322 Hz) ppm. MS (ESI+) *m/z* (%) = 298.3211 (100, $C_{18}H_{40}N_3$ requires 298.3217, [cation]$^+$); MS (ESI−) *m/z* (%) = 279.9175 (100, $C_2F_6NO_4S_2$ requires 279.9178, [anion]$^-$). IR (neat) ν = 2964 (w, ν_{C-H}), 2935 (w, ν_{C-H}), 2877 (w, ν_{C-H}), 1540 (m, $\nu_{C=N}$), 1348 (m, $\nu_{as}(SO_2)$), 1175 (vs, ν_{C-F}), 1135 (s, $\nu_s(SO_2)$), 1053 (s, ν_{C-F}), 614 (m, δ_{C-F}), 600 (m, δ_{C-F}), 569 (m, δ_{C-F}), 510 (m, δ_{C-F}) cm^{-1}.

***N′*,*N′*,*N″*,*N″*-Tetra-*n*-butyl-*N*-(2-ethylhexyl)-*N*-methylguanidinium bis(trifluoromethanesulfonyl)imide (7l) [Gua-i8,1-4,4-4,4](Tf$_2$N).** Prepared from *N′*,*N′*,*N″*,*N″*-tetra-*n*-butyl-*N*-(2-ethylhexyl)-*N*-methylguanidinium methylcarbonate (**6e**) (342 mg, 0.70 mmol, 1.00 eq.) and bis(trifluoromethanesulfonyl)amide (218 mg, 0.78 mmol, 1.11 eq.). The product was purified by washing with water. After drying *in vacuo*, 480 mg (99%) of a colourless oil was obtained. Anal. calc. for $C_{28}H_{56}F_6N_4O_4S_2$ (690.89 g mol^{-1}) C 48.68, H 8.17, N 8.11%; found C 48.37, H 7.76, N 8.33%. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 0.78–0.92 (m, 18H, C4c-f-H, C6a-H and C8a-H), 0.98–1.44 (m, 20H, C3c-f-H, C2c-f-Ha, C3a-H to C5a-H, C7a-H), 1.50–1.80 (m, 5H, C2a-H, C2c-f-Hb), 2.89 (s, 3H, C1b-H), 2.83–3.33 (m, 10H, C1a,c-f-H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 9.7, 10.5 (C8a, rotamers), 13.27, 13.34 (C4c-f), 13.6, 13.7 (C6a, rotamers), 19.3, 19.38, 19.43, 19.5 (C3c-f), 22.4, 22.7, 23.26, 23.31 (C4a and C5a, rotamers), 27.5, 28.2 (C3a, rotamers), 28.8, 28.97, 29.02, 29.1, 29.2 (C2c-f, rotamers), 29.8, 30.6 (C7a, rotamers), 35.7, 36.1 (C2a, rotamers), 38.1, 38.2 (C1b, rotamers), 48.3, 48.4, 48.5, 48.6, 49.0 (C1c-f, rotamers), 55.9, 56.1 (C1a, rotamers), 119.5 (q, $^1J_{CF}$ = 322 Hz, CF_3), 163.68, 163.71 (CN_3, rotamers) ppm; ^{19}F NMR (282 MHz, DMSO-d_6) δ = −79.5 (CF_3, $^1J_{CF}$ = 322 Hz) ppm. MS (ESI+) *m/z* (%) = 410.4465 (100, $C_{26}H_{56}N_3$ requires 410.4469, [cation]$^+$); MS (ESI−) *m/z* (%) = 279.9179 (100, $C_2F_6NO_4S_2$ requires 279.9178, [anion]$^-$). IR (neat) ν = 2961 (w, ν_{C-H}), 2934 (w, ν_{C-H}), 2875 (w, ν_{C-H}), 1534 (m, $\nu_{C=N}$), 1349 (m, $\nu_{as}(SO_2)$), 1177 (vs, ν_{C-F}), 1135 (s, $\nu_s(SO_2)$), 1055 (s, ν_{C-F}), 615 (m, δ_{C-F}), 600 (m, δ_{C-F}), 569 (m, δ_{C-F}), 511 (m, δ_{C-F}) cm^{-1}.

Crystal structure determination of 10

Crystals were grown from a dichloromethane/ether solution of **8** at room temperature. A colourless block (0.36 × 0.27 × 0.09 mm^3) was transferred to the cold gas stream of the diffractometer and irradiated at 193 K. $C_7H_{18}ClN_3$, M = 179.69 g mol^{-1}, monoclinic, space group C 2/m, Z = 4, a = 13.622(3) Å, b = 7.8211(11) Å, c = 9.8987(17) Å, β = 104.10(2)°, V = 1022.9(3) Å^3. 4051 reflections collected, of which 1080 were independent (R_{int} = 0.0638) and thus used in all calculations. The final wR_2 was 0.2320 (all data).

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