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Hexaalkylguanidinium Trifluoromethanesulfonates – A General Synthesis from Tetraalkylureas and Triflic Anhydride, and Properties as Ionic Liquids

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More than thirty hexaalkylguanidinium trifluoromethanesulfonates **12** were prepared from *N*,*N*-diethyl-*N*′,*N*′-dimethylurea, *N*,*N*-dibutyl-*N*′,*N*′-diethylurea, or tetrabutylurea, triflic anhydride, and a dialkylamine or cyclic *sec*-amine in two steps. The combination of the urea and triflic anhydride first yields a bis(tetraalkylamidinio)ether bis(triflate) **10**, which is then converted into a salt **12** by reaction with the amine component. The reaction sequence can also be carried out as a one-pot procedure. Eighteen of the prepared guanidinium triflates **12** constitute room-temperature ionic liquids, which were characterized for their melting point, glass transition temperature, viscosity, and refractive index.

Introduction

Ionic liquids (ILs), salts with melting points below about 100 °C, are currently attracting much interest in both academic and industrial laboratories. Some of their unique properties,[1,2] such as very low vapor pressure, high thermal stability, a wide electrochemical window, and tunable miscibility with other liquid phases, recommend them as alternatives to the traditional organic liquids for several different purposes. ILs are currently widely evaluated and used as reaction media in synthesis,[1,3] as electrolytes for electrochemical processes and devices,[4] for applications in separation and analytical techniques,[5] and as engineering liquids with various industrial applications.[6]

For practical reasons, ILs with melting points around room temperature or below are preferred for most applications. These room-temperature ILs (RTILs) typically consist of an organic cation bearing alkyl substituents of variable chain length and an inorganic or organic anion. Although a great number of charge-stabilized organic cations are known, *N*,*N*′-dialkylimidazolium, *N*-alkylpyridinium, and quaternary ammonium or phosphonium ions are currently the most common cations in RTILs. Recently, increasing interest in guanidinium-based ILs can be noticed, some of which are already commercially available.[7] Guanidinium salts, where the parent $^{+}C(NH_2)_3$ cation is not fully alkylated, retain Brönsted acidity due to the remaining NH bond(s) and may be used as task-specific ILs catalyzing specific transformations.[8] We focus here, however, on hexaalkylguanidinium salts as ILs, including those which contain an *N*,*N*′-dialkylimidazoline or a related ring system. Many of them have a high thermal stability[9–11] and, due to the effective dissipation of the positive charge in the cation, a better chemical stability than some of the other common classes of ILs.[12] Various uses of hexaalkylguanidinium-based RTILs as reaction media have been reported recently.[13] Hexaalkylguanidinium iodides and tricyanomethanides have been considered as electrolytes in dye-sensitized solar cells.[14] Further applications of guanidinium ILs have been proposed in the patent literature, for example as surfactants in the preparation of mesoporous metal oxides,[15] as electrolytes in electrochemical sensors,[16] and as hydraulic fluids.[17] The ability of hexaalkylguanidinium to act as a phase-transfer catalyst[18] can also be a useful property of a guanidinium-based RTIL.[13a]

The major approaches to hexaalkylguanidinium salts are summarized in Scheme 1. Probably the shortest pathway consists of the reaction of chloroformamidinium salts **1a**, obtained by the chlorination of tetraalkylureas or their cyclic relatives (such as *N*,*N*′-dialkylimidazolin-2-ones) with phosgene, phosphorus oxychloride, or oxalyl chloride, with a *sec*-amine[14,19,20] or a dialkyl(trimethylsilyl)amine.[21] Kantlehner and coworkers were the first to use the phosgene route to prepare a number of peralkylated guanidinium salts from various tetraalkylureas ($R^{1–4}$ = Me, Et, Bu; $R^1 = R^2$ = Et, $R^3 = R^4$ = Pr, Bu, allyl).[19] Tetramethylisothiuronium salt **1b** ($R^{1–4}$ = Me, X = CH_3SO_4) reacts with dimethylamine to yield hexamethylguanidinium methylsulfate **4**;[19b] however, the full potential of this method has not yet been exploited. *O*-Alkyluronium salts **1c**, easily obtained by the *O*-alkylation of tetraalkylureas, are only partially suited as precursors to guanidinium salts **4** because *O*-ethyl-*N*,*N*′-tetramethyluronium tetrafluoroborate reacts in the expected manner with dimethylamine and pyrrolidine, but suffers *O*-dealkylation when exposed to dipropylamine or morpholine.[22]

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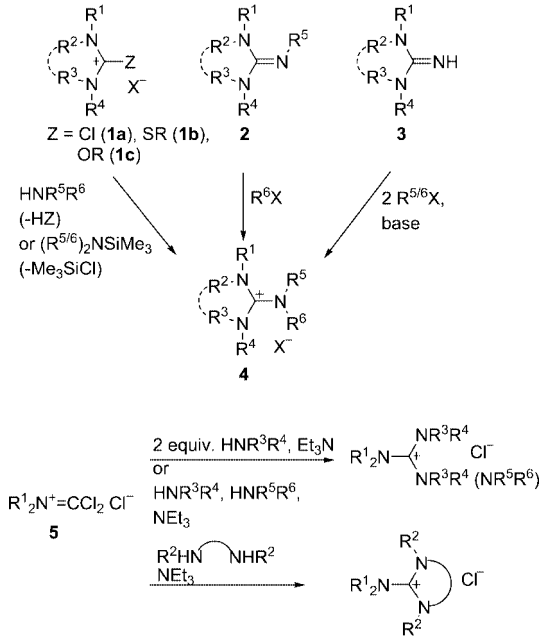


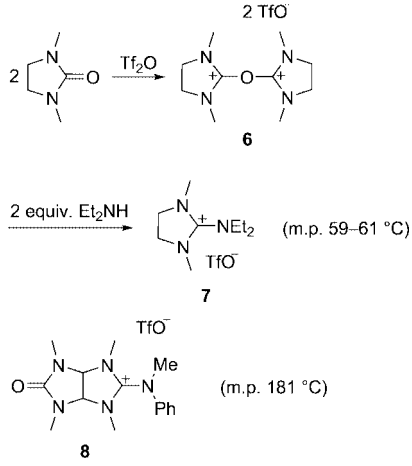
Scheme 1. Synthetic pathways to hexaalkylguanidinium salts.

Instead of the direct reaction between chloroformamidinium salts **1a** and amines HNR^5R^6, a two-step procedure is often chosen which allows a wider variation of alkyl substituents R^5 and R^6. To this end, salt **1a** or **1b** is first combined with a primary amine to yield a pentaalkylguanidine **2** which can be alkylated with a wide range of alkyl halides.[10,13a,19b,20,23,24] The twofold alkylation of *N*,*N*,*N*′,*N*′-tetraalkylguanidines, on the other hand, is preferentially used to prepare guanidinium salts **4** with two equal *N*′′,*N*′′-substituents.[25,26]

Hexaalkylguanidinium salts can also be obtained from *N*,*N*-dialkylphosgeniminium salts **5** (Scheme 1), either by reaction with a bis(*sec*-amine)[27] or with 2 equiv. of a *sec*-amine;[9] successive treatment of **5** with 1 equiv. each of R^3R^4NH and R^5R^6NH is also possible and enhances the structural diversity.[9,27]

Hexaalkylguanidinium salts **4** prepared by one of the above methods in most cases contain a halide or methylsulfate anion. In order to fine tune other solvent properties such as melting point, viscosity, and miscibility, an anion exchange is usually required to introduce the often-encountered RTIL anions such as BF_4, PF_6, CF_3SO_3, $N(SO_2CF_3)_2$, $N(CN)_2$, and $B(OR)_4$.

Some time ago, P. Stang et al.[28] observed that tetraalkylureas react with triflic anhydride to give dication ether bis(triflates) which can be cleaved with a variety of nucleophiles. Thus, the reaction of dication ether salt **6** with diethylamine generated the low-melting cyclic guanidinium salt **7** (Scheme 2), which in retrospect constitutes one of the early examples of a guanidinium-based IL. The analogously prepared *N*-phenylated guanidinium salt **8**, on the other hand, is a high-melting solid.[29] We have now returned to these isolated observations to develop a general synthesis of hexaalkylguanidinium triflates from tetraalkylureas, and have found that many of these salts are room-temperature ILs. Only a few other hexaalkylguanidinium triflates have been reported in the meantime;[21b,30] in those cases, the triflate ion was introduced by anion exchange at one or the other stage of the synthesis.

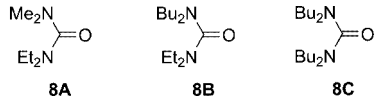


Scheme 2. Cyclic hexasubstituted guanidinium triflates **7** and **8**.

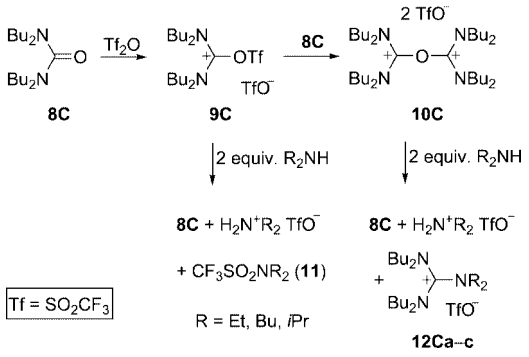
Results and Discussion

Synthetic Work

The tetraalkylureas **8A**–**C** served as starting materials for the synthesis of hexasubstituted guanidinium triflates.

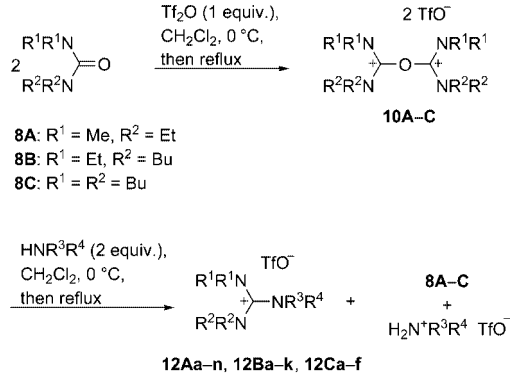


As described earlier for tetramethylurea,[28] the reaction of tetrabutylurea (**8C**) with triflic anhydride occurs in two steps (Scheme 3). In the first step, the urea is *O*-sulfonylated to give the trifloxy salt **9C** which can be isolated (as an extremely moisture-sensitive RTIL!) when the reaction is carried out with 1:1 stoichiometry in CH_2Cl_2 at ≤ 0 °C. This salt reacts with an additional equiv. of urea **8C** to form dication ether salt **10C** which is also obtained directly from **8C** and Tf_2O in a 2:1 ratio at room temperature. We speculated that the triflate anion could also be displaced from **9C** with secondary amines to provide hexaalkylguanidinium salts **12**. However, the reaction of **9C** with 2 equiv. of diethylamine, dibutylamine, or diisopropylamine resulted in the formation of *N*,*N*-dialkyl-trifluoromethanesulfonamides **11** and urea **8C**, indicating that the amine nucleophile had attacked the sulfur rather than the uronium carbon. On the other hand, the same amines smoothly reacted with dication ether salt **10C** to form the desired hexaalkyl-substituted guanidinium triflates **12C** and urea **8C**. Analogous results were obtained with ureas **8A** and **8B** as starting materials.



Scheme 3. Reaction of uronium salts **9C** and **10C** with *sec*-amines.

Having established the reaction pathway, we synthesized a number of hexasubstituted guanidinium triflates **12** as shown in Scheme 4. Dication salts **10A**–**C** were prepared in one step from ureas **8A**–**C** and were isolated. They were combined with a broad range of *sec*-amines to provide the guanidinium triflates **12** listed in Table 1, generally in fair to good yields. As can be seen, not only dialkylamines, with linear and branched chains, but also cyclic amines (pyrrolidine) and benzylamines can be introduced. The reaction of **10A** with (*S*)-(1-phenylethyl)amine furnished the chiral salt **12Ah**. The separation of guanidinium salts **12** from the accompanying products, urea **8** and *sec*-amine hydrotriflate, was possible by extractive workup; the urea can be recovered from the product mixture by extraction into pentane and vacuum distillation, and treatment of the salt mixture with aqueous NaOH removes selectively the ammonium salt, while guanidinium salts **12** are stable to aqueous base under these conditions.



Scheme 4. Synthesis of guanidinium triflates **12**.

Table 1. Hexaalkylguanidinium triflates $[(NR^1{}_2)(NR^2{}_2)(NR^3R^4)C^+\ CF_3SO_3^-]$ prepared and their physical data.

Entry	Salt	R^1	R^2	R^3	R^4	T_m/T_g [°C][a]	T_{dec} [°C][b]	$n_D{}^{20}$[c]	Miscibility with[d] CH_2Cl_2/EtOH	H_2O	Et_2O/C_6H_{14}
1	**12Aa**	Me	Et	Et	Et	240/–	461	–	+	+	–
2	**12Ab**	Me	Et	Pr	Pr	210/–	457	–	+	+	–
3	**12Ac**	Me	Et	Bu	Bu	–/–65	452	1.460	+	–	–
4	**12Ad**	Me	Et	Hex	Hex	–/–66	446	1.461	+	–	–
5	**12Ae**	Me	Et	R[e]	R[e]	–/–51	432	1.466	+	–	–
6	**12Af**	Me	Et	Bu	Me	61/–78	458	–	+	+	–
7	**12Ag**	Me	Et	Cy	Me	–/–45	392	1.475	+	–	–
8	**12Ah**	Me	Et	Me	R[f]	45/–42	389	–	+	–	–
9	**12Ai**	Me	Et	–$(CH_2)_4$–		12/–38	457	1.470	+	+	–
10	**12Aj**	Me	Et	Bn	Me	88/–30	407	–	+	–	–
11	**12Ak**	Me	Et	Bn	Et	–/–40	397	1.501	+	–	–
12	**12Al**	Me	Et	Bn	Bu	–/–32	391/452	1.495	+	–	–
13	**12Am**	Me	Et	Bn	Bn	74/–17	401/510	–	+	–	–
14	**12An**	Me	Et	R[g]	R[g]	–/–66	409	1.458	+	+	–
15	**12Ba**	Et	Bu	Et	Et	–/–55	375	1.465	+	–	–
16	**12Bb**	Et	Bu	Pr	Pr	33/–58	435	1.465	+	–	–
17	**12Bc**	Et	Bu	Hex	Hex	–/–69	430	1.464	+	–	–
18	**12Bd**	Et	Bu	Bu	Me	–/–56	442	1.461	+	–	–
19	**12Be**	Et	Bu	Cy	Me	–/–43	392	1.475	+	–	–
20	**12Bf**	Et	Bu	–$(CH_2)_4$–		21/–60	448	1.472	+	–	–
21	**12Bg**	Et	Bu	Bn	Me	–/–38	396	1.495	+	–	–
22	**12Bh**	Et	Bu	Bn	Et	–/–38	396	1.496	+	–	–
23	**12Bi**	Et	Bu	Bn	Bu	–/–32	385	1.493	+	–	–
24	**12Bj**	Et	Bu	Bn	Bn	79/–26	381/511	–	+	–	–
25	**12Bk**	Et	Bu	R[g]	R[g]	52/–20	412	–	+	–	–
26	**12Ca**	Bu	Bu	Et	Et	58/–56	438	–	+	–	–
27	**12Cb**	Bu	Bu	Pr	Pr	64/–51	433	–	+	–	–
28	**12Cc**	Bu	Bu	Bu	Bu	89/–	431	–	+	–	–
29	**12Cd**	Bu	Bu	Hex	Hex	49/–	427	–	+	–	–
30	**12Ce**	Bu	Bu	Bu	Me	–/–59	439	1.463	+	–	–
31	**12Cf**	Bu	Bu	Cy	Me	76/–37	394	–	+	–	–
32	**12Cg**	Bu	Bu	–$(CH_2)_4$–		–/–59	445	1.472	+	–	–
33	**12Ch**	Bu	Bu	Bn	Et	87/–32	379/408	–	+	–	–
34	**12Cf**	Bu	Bu	R[g]	R[g]	81/–	410	–	+	–	–

[a] T_m = melting point, T_g = glass transition temperature. [b] T_{dec} = decomposition temperature under N_2 atmosphere. [c] Refractive index at 20 °C. [d] Visually observed miscibility (solubility in the case of solids) at room temp.; + miscible, – immiscible, C_6H_{14} = cyclohexane. [e] R = 2-ethylhexyl. [f] R = (*S*)-(–)-phenylethyl. [g] R = 2-methoxyethyl.

The preparation of salts **12** could be simplified further by carrying out the two-step transformation as a one-pot procedure, without the isolation of dication ether salts **10** (as we show for **12Ac** in the Experimental Section). As ILs are often placed in the context of green chemistry,[31] their production should also be carried out under environmentally benign conditions. Therefore, we checked whether CH_2Cl_2 can be replaced by non-chlorinated solvents. We found that for the one-pot synthesis of **12Ac** from urea **8A**, CH_2Cl_2 can be replaced by cyclohexane as the reaction medium, and it can also be eliminated from the workup procedure. However, we had to accept that the yield dropped from 56% to 45%.

All guanidinium triflates prepared were fully characterized by their ^1H and ^{13}C NMR spectroscopic data. In agreement with earlier observations,[9,32] the hexaalkylguanidinium salts showed restricted rotation around the C^+–NR_2 partial double bonds, giving rise to the magnetic nonequivalence of the chemically equivalent nuclei in the two alkyl chains of a symmetrically substituted NR_2 group. For example, the following δ (^{13}C) values were observed for **12Ac**: 40.4/40.6 (NCH_3), 43.4/43.9 (NCH_2, ethyl), and 48.9/49.6 (NCH_2, butyl). In addition, for guanidinium salts containing an asymmetrical NR^1R^2 group, *E*/*Z* isomerism around the iminium partial double bond can give rise to two diastereomers which in some cases were clearly recognized in the spectra (e.g., **12Af**–**h**, **12Ak**, **12Bg**, **12Bh**) while in some other cases extensive signal overlap prevented a clear conclusion. Furthermore, the benzylic protons of all $PhCH_2$-substituted guanidinium salts were observed to be diastereotopic at about 30 °C. This phenomenon was observed and studied before and has been attributed to a chiral non-planar (propeller-like) structure of hexalkylguanidinium ions.[32] In the meantime, this has been confirmed even for the hexamethylguanidinium cation, the simplest of the hexaalkylguanidinium cations, in several solid-state structures[33] and in DFT calculations of the gas-phase structure.[33a]

In the IR spectra, all guanidinium salts showed, besides the typical bands associated with the triflate anion (around 1265, 1150, and 1031 cm^{-1}), strong absorption bands characterizing the guanidinium (CN_3^+) moiety. In series **12A**, two such absorptions were found at 1575–1588 cm^{-1} and 1542–1558 cm^{-1}; in the two series **12B** and **12C**, only one, somewhat broadened, absorption was observed in the range 1535–1544 cm^{-1} which in some cases was accompanied by another strong band at wavenumbers higher by 10–20 cm^{-1}.

Ionic Liquid Properties

Table 1 provides information on phase transitions, thermal stability, refractive indices, and miscibility in common solvents of the newly prepared guanidinium salts **12**. It can be seen that, with the exception of **12Aa** and **12Ab**, all of them can be classified as ILs (melting points below 100 °C), and that the majority of these salts are room-temperature ILs. A rule of thumb is confirmed, namely that a more unsymmetrical substitution in the guanidinium cation tends to lower the melting point. For example, the melting point decreases in the sequence **12Cc** (hexabutylguanidinium), **12Cb** (tetrabutyl-dipropylguanidinium), **12Ca** (tetrabutyl-diethylguanidinium), **12Cd** (tetrabutyl-dihexylguanidinium). On the other hand, benzyl and 2-methoxyethyl substituents tend to increase the melting point of the salt. The triflate counterion also has an influence; as Table 2 shows, the melting point of the triflate salts is significantly lower than that of the halide or PF_6^- salts with the same guanidinium cation, while the triflate and tetrafluoroborate salts share the RTIL property.

DSC measurements revealed that most guanidinium triflates **12** also show a glass transition. As with other hexaalkylguanidinium salts,[9] the glass temperature of the salts bearing simple alkyl groups is typically in the range from –50 to –78 °C. The presence of cyclohexyl and especially of phenyl rings brings this phase transition in the range of –20 to –45 °C.

Thermogravimetric analyses indicated the high thermal stability of hexaalkylguanidinium triflates **12**. A typical TGA curve is shown in Figure 1. The decomposition temperatures T_{dec} (defined here as the temperature of fastest mass loss at a heating rate of 10 °C/min) range from 380 °C to 460 °C, and complete decomposition in one step takes place in almost all cases.

Most of the salts **12** in Table 1 are hydrophobic. Only the salts with the smallest alkyl groups (**12Aa**, **12Ab**, **12Af** and **12Ai**) were found to be water soluble. Interestingly, **12Ac** (containing NMe_2,NEt_2, and NBu_2) is water insoluble, but the replacement of one CH_2 unit by O in the butyl chains

Table 2. Influence of the anion on the melting point of hexaalkylguanidinium salts.

Entry	Cation	M.p. [°C] or physical state at 20 °C for salt with the given anion				
		CF_3SO_3[a]	BF_4[b]	PF_6[b]	Br[b]	Other anion
1	$(NMe_2)(NEt_2)(NBu_2)C^+$	liquid	liquid	66–67	70–71	–
2	$(NEt_2)(NEt_2)(NBu_2)C^+$	liquid	liquid	88–89	–	Cl: 55–58[c]
3	$(NEt_2)(NPr_2)(NBu_2)C^+$	33	–	–	–	Cl: 55–56[c] Ph_4B: 203[c]
4	$(NPr_2)(NBu_2)(NBu_2)C^+$	64	–	–	–	Cl: 85[c]
5	$(NBu_2)(NBu_2)(NBu_2)C^+$	89	–	–	–	Cl: 147[c]
6	$(NMe_2)(NBu_2)(Pyr)C^+$[d]	12	liquid	104–106	76–77	–
7	$(NEt_2)(NBu_2)(NMeHex)C^+$	liquid	–	–	–	I: highly viscous oil[e]

[a] This work. [b] Ref.[26b]. [c] Ref.[19b]. [d] Pyr = pyrrolidin-1-yl. [e] W. Kantlehner et al., unpublished results.

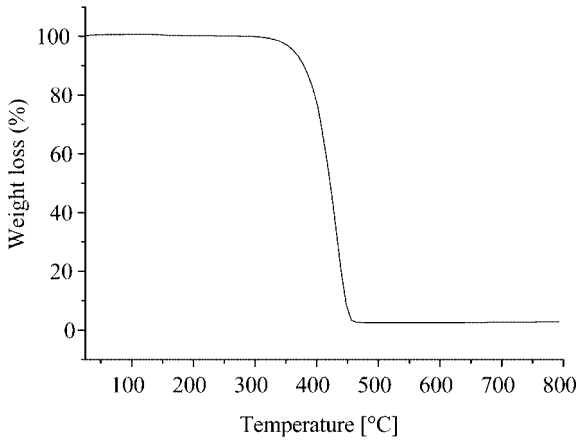


Figure 1. TGA curve for salt **12Bc**.

is sufficient to make **12An** water soluble. It should be noted that even the salts called "hydrophobic" contain traces of water and are hygroscopic to some extent. For example, the water content of a dried sample of **12Ac** increased from 420 ppm to 1310 ppm when kept in contact with air for 15 h.

The refractive index data given in Table 1 characterize the ILs as obtained from the synthesis described in the Experimental Section. Because of the difficulty in rigorously purifying these ILs, the values may be somewhat affected by remaining impurities, including the residual water content. Nevertheless, it can be stated that the refractive indices are distinctly higher than in some of the commercially available imidazolium-based ILs (e.g. $[C_4mim]X$ shows refractive indices of 1.433 when X = OTf, 1.451 when X = NTf_2, and 1.410 when X = BF_4).[34]

Viscosity data for some RTILs **12** are presented in Table 3 and Figure 2. Again, it should be kept in mind that these ILs contain traces of water, and as shown for other ILs, the presence of water can affect the viscosity significantly.[35,36] As could be expected, these liquids are rather viscous; on the other hand, they are less viscous at room temperature than glycerol (934 mPa s at 20 °C), with the exception of **12Be**. Since viscous reaction media are in general not welcome, the considerable decrease of viscosity observed in the often-used temperature range of 60–80 °C is certainly a bonus. The viscosities at 60 °C (Table 3) are in the range measured at 20 °C for 1,3-dialkylimidazolium triflates bearing short alkyl substituents.[36] The viscosities of salts **12** increase roughly with the length of the alkyl chains in the cation, although the last three entries in Table 3 deviate somewhat from this trend. The influence of the triflate anion on the viscosity cannot be illustrated, since data for hexaalkylguanidinium ILs with the same cation but different anions are not available. For $[(NHex)_4(NMe)_2C]$-NTf_2, viscosities of 346 mPa s (25 °C) and 124 mPa s (60 °C) have been reported.[9] The viscosities of 1-methyl-3-butylimidazolium Ils decrease in the anion sequence I > PF_6 > BF_4 >> OTf > NTf_2.[35,37] Although it is likely that in these ILs the viscosity is more strongly affected by the cation-anion interactions (because of the acidity of the C2–H bond) compared to salts **12**, it is obvious that the triflate anion contributes to a decrease in viscosity.

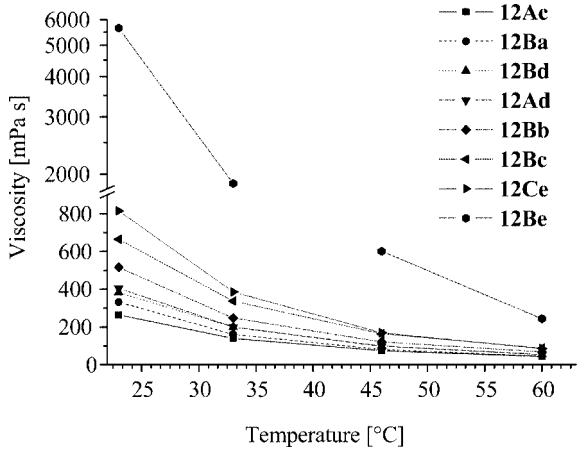


Figure 2. Viscosity of some salts **12** as a function of temperature.

The dependence of the viscosities of the ILs in Table 3 on shear rate and time was also studied. In each case, the viscosity remained constant with shear rates increasing from 10 s^{-1} to 150 s^{-1}. Furthermore, the viscosity was independent of time for measurements carried out with shear rates that were kept constant (10 s^{-1} and 100 s^{-1}). In other words, no thixotropic or rheopectic behavior was observed. Both results are typical for Newtonian fluids.

Table 3. Dynamic viscosity of hexaalkylguanidinium triflates at different temperatures.[a]

Entry	Salt	Viscosity η [mPa s] at 23 ± 0.01 °C	at 60 ± 0.01 °C
1	$[(NMe_2)(NEt_2)(NBu_2)C]$OTf (**12Ac**)	263	44
2	$[(NEt_2)(NEt_2)(NBu_2)C]$OTf (**12Ba**)	332	45
3	$[(NEt_2)(NBu_2)(NMeBu)C]$OTf (**12Bd**)	382	55
4	$[(NMe_2)(NEt_2)(NHex_2)C]$OTf (**12Ad**)	406	53
5	$[(NEt_2)(NPr_2)(NBu_2)C]$OTf (**12Bb**)	516	67
6	$[(NEt_2)(NBu_2)(NHex_2)C]$OTf (**12Bc**)	665	88
7	$[(NBu_2)(NBu_2)(NMeBu)C]$OTf (**12Ce**)	815	85
8	$[(NEt_2)(NBu_2)(NCyMe)C]$OTf (**12Be**)	5647	244

[a] Data were measured on samples which had a water content in the range of 400–700 ppm (**12Bd**: 970 ppm; **12Be**: 1070 ppm) according to coulometric Karl-Fischer titration.

Conclusion and Outlook

We have reported here that a wide range of hexaalkylguanidinium triflates **12**, most of which are room-temperature ILs, can be prepared from tetraalkylureas, triflic anhydride and dialkylamines in two steps. We have also shown that isolation of the first-step products, dication ether triflates **10**, is not necessary, so that the synthesis can be carried out as an operationally simple one-pot process. This procedure is a chloride-free alternative to the preparation from chloroformamidinium chlorides **1a** or *N*,*N*-dialkylphosgeniminium chlorides **5** followed by anion exchange with the obtained hexaalkylguanidinium chlorides to get the triflate salts. Moreover, it is possible to replace CH_2Cl_2 by non-chlorinated solvents as the reaction medium and for workup. Thus, the preparation of guanidinium triflates **12** can be conducted in a completely chlorine-free manner; as ILs are often put in the context of green chemistry, this might be an additional benefit of our method.

It has been reported that hexaalkylguanidinium triflates are converted efficiently into the corresponding tris(pentafluoroethyl)trifluorophosphate salts when treated with the acid $H[(C_2F_5)_3PF_3]\cdot 5H_2O$.[21b] The combination of this anion-exchange reaction with our synthesis of guanidinium triflates **12** would also render chloride-free the synthesis of hexaalkylguanidinium salts with $[(C_2F_5)_3PF_3]^-$ and similar low-nucleophilicity anions.

The hexaalkylguanidinium triflates reported here can be expected to find several applications as ILs, based in particular on the low nucleophilicity and hydrolytic stability of the triflate anion, the better chemical stability of the cations as compared to the usual 1,3-dialkylimidazolium-based ILs[9] and the high thermal stability of these salts. As reaction media, the low nucleophilicity recommends them for processes in which short-lived electron-deficient intermediates (e.g. carbocations and onium ions) are involved.[38] Furthermore, the ability of the triflate anion to act as a weak hydrogen-bond acceptor and the absence of a hydrogen-bond donor moiety in the cation (as opposed to 1,3-dialkylimidazolium cations) are features which they have in common with the IL, 1-butyl-1-methylpyrrolidinium triflate, for example. It has been suggested that these features contribute to the fact that S_N2 reactions using mono-, di-, and tributylamine as nucleophiles, occur significantly faster in the last-mentioned IL than in [bmim]OTf or in acetonitrile and CH_2Cl_2 solutions.[39] These are only two out of several more possible applications for ILs consisting of hexaalkylguanidinium triflate salts.

Experimental Section

General Remarks: Rigorously dried organic solvents were used. All amines were dried with KOH pellets and in most cases distilled. NMR spectra were recorded using a Bruker DRX 400 spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz, ^{19}F: 376.46 MHz). ^{1}H NMR spectra were referenced to the proton signal of the solvent [δ ($CDCl_3$) = 7.26 ppm, δ (CD_3CN) = 1.94 ppm], ^{13}C spectra were referenced to the solvent signal [δ ($CDCl_3$) = 77.0 ppm, δ (CD_3CN) = 118.26 ppm], and ^{19}F spectra were referenced to C_6F_6 in $CDCl_3$ [δ (C_6F_6) = –162.9 ppm]. IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer. Mass spectra were recorded with a Finnigan MAT SSQ-7000 spectrometer (CI = 100 eV). Microanalyses were carried out with an Elementar vario MICRO cube instrument.

***O*-Trifluoromethylsulfonyl-*N*,*N*,*N*′,*N*′-tetrabutyluronium Triflate (9C):** To a solution of triflic anhydride (0.85 g, 0.50 mL, 3.00 mmol) in $CHCl_3$ (6 mL), cooled to 0 °C and kept under argon, was added *N*,*N*,*N*′,*N*′-tetrabutylurea (0.85 g, 0.97 mL, 3.00 mmol) in $CHCl_3$ (6 mL). Evaporation of the solvent at 0.001 mbar left a yellow oil, which was not purified further due to its extreme moisture sensitivity. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, 6 H, CH_2CH_3), 1.33–1.39 (m, 4 H, CH_2CH_3), 1.68–1.74 (m, 4 H, $CH_2CH_2CH_3$), 3.56–3.59 (m, 4 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.3 (CH_3), 19.7, 29.1 [$(CH_2)_2CH_3$], 52.5 (NCH_2), 152.2 (CN_2) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –67.5 (covalent OTf), –74.7 (anionic OTf) ppm.

Reaction of 9C with Et_2NH: A solution of **9C** in $CHCl_3$ (12 mL) was cooled to 0 °C, and diethylamine (0.44 g, 0.62 mL, 6.00 mmol) was added. After the addition was completed, the crystallization of diethylammonium triflate started. The mixture was allowed to stand in a refrigerator at 4 °C for 3 d, and then the solid was removed by filtration (0.31 g, 46% yield). The residual oil consisted of *N*,*N*,*N*′,*N*′-tetrabutylurea (**8C**), residual ammonium salt and *N*,*N*-diethyl-trifluoromethanesulfonamide (**11**). Fractional distillation in a kugelrohr apparatus furnished **11** (80 °C/0.092 mbar, colorless liquid, 0.34 g, 55% yield) and *N*,*N*,*N*′,*N*′-tetrabutylurea (200 °C/0.092 mbar, yellowish oil, 0.63 g, 74% yield).

Spectroscopic and Analytical Data for 11: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.2 Hz, 6 H, CH_2CH_3), 3.45 (broadened q, 4 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (CH_3), 42.7 (NCH_2), 120.0 (q, $^1J_{C,F}$ = 323.4 Hz, CF_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –72.8 ppm. IR (NaCl): $\tilde{\nu}$ = 1386 (vs) (RSO_2N), 1226 (vs), 1184 (vs), 1132 (vs) (RSO_2N), 1020 (s), 951 (s) cm^{-1}. MS (CI): *m*/*z* (%) = 206 (100) $[M + H]^+$. $C_5H_{10}F_3NO_2S$ (205.50): calcd. C 29.27, H 4.91, N 6.83; found C 29.28, H 4.96, N 7.20.

Bis(*N*,*N*-diethyl-*N*′,*N*′-dimethylamidinio) Ether Bis(trifluoromethanesulfonate) (10A). Typical Procedure: In a 100 mL Schlenk vessel purged with argon was placed triflic anhydride (2.82 g, 1.65 mL, 10.0 mmol) and dry CH_2Cl_2 (15 mL). The solution was cooled to 0 °C and *N*,*N*-diethyl-*N*′,*N*′-dimethylurea (**8A**, 2.88 g, 20 mmol) in CH_2Cl_2 (10 mL) was added dropwise. After the addition was complete, the reaction mixture was kept at 0 °C for 1 h with magnetic stirring, brought to room temp., and finally heated at reflux for 12 h. After cooling to room temp., the colorless precipitate was isolated by filtration and dried (0.001 mbar/8 h) to yield 3.81 g (67% yield) of **10A**, m.p. 170–176 °C. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.32 (t, 12 H, CH_2CH_3), 3.15 (s, 12 H, NCH_3), 3.57 (q, 8 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 12.6 (CH_2CH_3), 42.1 (NCH_3), 46.0 (NCH_2), 156.9 (CN_3) ppm. ^{19}F NMR (376 MHz, CD_3CN): δ = –75.6 ppm. IR (KBr): $\tilde{\nu}$ = 1687 (s), 1666 (s), 1459 (m), 1266 (vs), 1155 (s), 1033 (s), 638 (s) cm^{-1}. $C_{16}H_{32}F_6N_4O_7S_2$ (570.57): calcd. C 33.68, H 5.65, N 9.82; found C 33.67, H 5.85, N 9.82.

Bis(*N*,*N*-dibutyl-*N*′,*N*′-diethylamidinio) Ether Bis(trifluoromethanesulfonate) (10B): Prepared according to the typical procedure from *N*,*N*-dibutyl-*N*′,*N*′-diethylurea (**8B**, 4.56 g, 20 mmol) and triflic anhydride (2.82 g, 1.65 mL, 10.0 mmol). Yield: 6.35 g (86%), m.p. 76–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 [t, 12 H, $(CH_2)_3CH_3$], 1.38–1.45 (m, 20 H, $CH_2CH_2CH_3$, NCH_2CH_3), 1.74–1.78 (m, 8 H,

$CH_2CH_2CH_2CH_3$), 3.55 (t, 8 H, NCH_2 ethyl), 3.64 (q, 8 H, NCH_2 butyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8 [$(CH_2)_3CH_3$], 13.5 (NCH_2CH_3), 19.9 ($CH_2CH_2CH_3$), 29.1 (NCH_2CH_2), 46.2, 51.5 (NCH_2CH_3, NCH_2CH_2), 156.0 (CN_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.6 ppm. IR (KBr): $\tilde{\nu}$ = 1666 (s), 1635 (s), 1476 (m), 1431 (m), 1261 (vs), 1224 (s), 1152 (s), 1032 (s), 638 (s) cm^{-1}. $C_{28}H_{56}F_6N_4O_7S_2$ (738.89): calcd. C 45.51, H 7.64, N 7.58; found C 45.17, H 7.76, N 7.16.

Bis(tetrabutylamidinio) Ether Bis(trifluoromethanesulfonate) (10C): Prepared from *N*,*N*,*N*′,*N*′-tetrabutylurea (**8C**, 14.20 g, 16.10 mL, 50.0 mmol) and triflic anhydride (7.05 g, 4.12 mL, 25.0 mmol) according to the typical procedure. As the product did not crystallize directly from the reaction solution, the solvent was evaporated, pentane (20 mL) was added to the residue, and the mixture was stirred for 30 min. A microcrystalline solid formed, which was allowed to deposit and was isolated by decantation of the liquid phase. This purification procedure was repeated three times. The product was finally isolated by filtration and dried (0.001 mbar/8 h), giving a yellowish solid (17.8 g, 84% yield), m.p. 47–55 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, 24 H, CH_2CH_3), 1.38–1.47 (m, 16 H, CH_2CH_3), 1.70–1.78 (m, 16 H, NCH_2CH_2), 3.56 (broad t, 16 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (CH_3), 19.9 (CH_2CH_3), 29.5 (NCH_2CH_2), 51.6 (NCH_2), 156.0 (CN_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.6 ppm. IR (KBr): $\tilde{\nu}$ = 1659 (s), 1632 (s), 1466 (m), 1423 (m), 1259 (vs), 1154 (s), 1031 (s), 638 (s) cm^{-1}. $C_{36}H_{72}F_6N_4O_7S_2$ (851.10): calcd. C 50.80, H 8.53, N 6.58; found C 50.54, H 8.57, N 6.57.

***N*,*N*,*N*′,*N*′,*N*″,*N*″-Hexaalkylguanidinium Trifluoromethanesulfonates 12. General Procedure:** A suspension of a bis(amidinio)ether bis(trifluoromethanesulfonate) **10** (ca. 1.5–5 mmol) in dry CH_2Cl_2 (20–25 mL) was prepared and cooled to 0 °C. A solution of a *sec*-amine (2–2.05 equiv. relative to **10**) in CH_2Cl_2 (ca. 5 mL) was added. After 30 min at 0 °C, the mixture was brought to room temp., stirred for 1 h and finally heated at reflux for 1–72 h. After cooling to room temp., the solution was concentrated, and *n*-pentane (10 mL) was added in order to extract the formed urea **8**, which was recovered from the pentane phase by vacuum distillation. The second liquid (oily) phase was dissolved in CH_2Cl_2 (15 mL) and extracted with 0.1 M NaOH (20 mL), and the organic phase was then dried with Na_2SO_4. After removal of the solvent, salt **12** was obtained. To remove the remaining traces of volatiles the salt was kept at 0.001 mbar/20 °C for 5 h.

***N*,*N*,*N*′,*N*′-Tetraethyl-*N*″,*N*″-dimethylguanidinium Trifluoromethanesulfonate (12Aa):** Prepared from **10A** (2.00 g, 3.51 mmol) in CH_2Cl_2 (20 mL) and diethylamine (0.51 g, 0.72 mL, 7.02 mmol) in CH_2Cl_2 (5 mL); 1 h at reflux. Yellowish solid (0.55 g, 45% yield), m.p. 240 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.17–1.23 (m, 12 H, CH_2CH_3), 2.98 (s, 6 H, CH_3), 3.15–3.19 (m, 2 H, CH_2CH_3), 3.25–3.30 (m, 6 H, CH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 13.0 (CH_2CH_3), 40.3 (NCH_3), 43.3, 43.8 (NCH_2), 163.4 (CN_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.6 ppm. IR (KBr): $\tilde{\nu}$ = 2981 (m), 2942 (m), 1580 (s), 1553 (s), 1463 (m), 1423 (m), 1271 (vs), 1222 (m), 1147 (s), 1031 (s) cm^{-1}. MS (CI): *m*/*z* (%) = 200 (100) [cation]$^+$. $C_{12}H_{26}F_3N_3O_3S$ (349.41): calcd. C 41.25, H 7.50, N 12.03; found C 41.07, H 7.49, N 11.99.

***N*,*N*-Diethyl-*N*′,*N*′-dimethyl-*N*″,*N*″-dipropylguanidinium Trifluoromethanesulfonate (12Ab):** Prepared from **10A** (1.14 g, 2.00 mmol) in CH_2Cl_2 (20 mL) and dipropylamine (0.40 g, 0.60 mL, 4.20 mmol); 11 h at reflux temp. White solid (0.55 g, 75% yield), m.p. 211 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.89–0.94 (m, 6 H, $CH_2CH_2CH_3$), 1.16–1.23 (m, 6 H, CH_2CH_3), 1.50–1.83 (m, 4 H, $CH_2CH_2CH_3$), 2.990 and 2.994 (2 s, 3 H each, NCH_3), 3.02–3.34 (m, 8 H, $NCH_2CH_2CH_3$, NCH_2CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.0, 11.2 ($CH_2CH_2CH_3$), 12.6, 13.0 (CH_2CH_3), 20.7, 21.0 ($CH_2CH_2CH_3$), 40.3, 40.5 (NCH_3), 43.4, 44.1 (NCH_2CH_3), 51.0, 51.6 ($NCH_2CH_2CH_3$), 120.9 (q, $^1J_{C,F}$ = 320.9 Hz, CF_3), 163.4 (CN_3) ppm. MS (CI): *m*/*z* (%) = 228 (100) [cation]$^+$. $C_{14}H_{30}F_3N_3O_3S$ (377.47): calcd. C 44.55, H 8.01, N 11.13; found C 44.24, H 7.97, N 11.05.

***N*,*N*-Dibutyl-*N*′,*N*′-diethyl-*N*″,*N*″-dimethylguanidinium Trifluoromethanesulfonate (12Ac):** Prepared from **10A** (1.78 g, 3.12 mmol) in CH_2Cl_2 (20 mL) and dibutylamine (0.81 g, 1.06 mL, 6.24 mmol); 5 h at reflux temp. Yellowish oil (0.86 g, 68% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 [t, 6 H, $CH_2(CH_2)_2CH_3$], 1.18–1.72 (several m, 14 H, NCH_2CH_3, $CH_2CH_2CH_2CH_3$), 3.004 and 3.010 (2 s, 3 H each, NCH_3), 3.17–3.32 (2 m, 8 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 13.0, 13.6, 13.7 [$(CH_2)_nCH_3$], 19.8, 20.1, 29.4, 29.6 [$CH_2(CH_2)_2CH_3$], 40.4, 40.6 (NCH_3), 43.3, 43.9 (NCH_2CH_3), 48.9, 49.6 (NCH_2 butyl), 163.5 (CN_3) ppm. MS (CI): *m*/*z* (%) = 256 (100) [cation]$^+$. $C_{16}H_{34}F_3N_3O_3S$ (405.52): calcd. C 47.39, H 8.45, N 10.36; found C 47.31, H 8.46, N 10.30.

***N*,*N*-Diethyl-*N*′,*N*′-dihexyl-*N*″,*N*″-dimethylguanidinium Trifluoromethanesulfonate (12Ad):** Prepared from **10A** (3.42 g, 6.00 mmol) in CH_2Cl_2 (40 mL) and dihexylamine (2.22 g, 2.80 mL, 12.0 mmol); 25 h at reflux temp. Colorless oil (1.55 g, 57% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 [t, 6 H, $(CH_2)_5CH_3$], 1.18–1.70 [several m, 22 H, $CH_2(CH_2)_4CH_3$, NCH_2CH_3], 3.00 and 3.01 (2 s, 3 H each, NCH_3), 3.14–3.35 (2 m, 8 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 13.0, 13.9 (CH_2CH_3), 22.4, 22.5, 26.3, 26.5, 27.4, 27.6, 31.2, 31.3 [$(CH_2)_4CH_3$], 40.4, 40.6 (NCH_3), 43.4, 44.0 (NCH_2 ethyl), 49.3, 49.9 (NCH_2 hexyl), 163.5 (CN_3) ppm. MS (CI): *m*/*z* (%) = 312 (100) [cation]$^+$. $C_{20}H_{42}F_3N_3O_3S$ (461.29): calcd. C 52.04, H 9.17, N 9.10; found C 51.53, H 9.02, N 9.11.

***N*,*N*-Diethyl-*N*′,*N*′-bis(2-ethylhexyl)-*N*″,*N*″-dimethylguanidinium Trifluoromethanesulfonate (12Ae):** Prepared from **10A** (0.86 g, 1.50 mmol) in CH_2Cl_2 (20 mL) and bis(2-ethylhexyl)amine (0.72 g, 0.91 mL, 3.00 mmol); 44 h at reflux temp. Colorless oil (0.21 g, 27% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.78–0.90 (m, 12 H, CH_2CH_3), 1.15–1.53 [several m, 24 H, NCH_2CH_3, $(CH_2)_3CHCH_2CH_3$], 2.75–3.34 (m, 14 H, NCH_2, NCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.7, 10.08, 10.10, 11.0, 11.20, 11.22, 12.4, 12.70, 12.74, 12.8, 12.9, 13.79, 13.84, 13.9 (C-CH_3), 22.7, 22.8, 23.0, 23.77, 23.82, 23.84, 24.1, 24.2, 28.0, 28.2, 28.88, 28.94, 29.06, 29.11, 30.3, 31.0, 31.1, 31.2, 37.0, 37.06, 37.14, 37.3, 37.4, 37.5, 40.18, 40.23, 40.5, 40.6 (NCH_3), 43.5, 43.6, 43.9, 44.0 (NCH_2), 52.7, 53.85, 53.91, 54.0 (NCH_2CH), 120.8 (q, $^1J_{C,F}$ = 320.9 Hz, CF_3), 163.9 (CN_3) ppm. MS (CI): *m*/*z* (%) = 368 (100) [cation]$^+$. $C_{24}H_{50}F_3N_3O_3S$ (517.73): calcd. C 55.68, H 9.73, N 8.12; found C 55.34, H 9.38, N 8.30.

***N*-Butyl-*N*′,*N*′-diethyl-*N*,*N*″,*N*″-trimethylguanidinium Trifluoromethanesulfonate (12Af):** Prepared from **10A** (1.16 g, 2.03 mmol) in CH_2Cl_2 (20 mL) and *N*-butyl-*N*-methylamine (0.38 g, 0.51 mL, 4.30 mmol); 9 h at reflux temp. White solid (0.34 g, 46% yield), m.p. 61 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, 3 H, butyl-CH_3), 1.12–1.25 (m, 8 H, NCH_2CH_3, $CH_2CH_2CH_3$), 1.47–1.60 (m, 2 H, NCH_2CH_2), 2.94–3.01 (several s, 9 H, NCH_3), 3.07–3.23 (m, 6 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7 (CH_2CH_3), 13.4 (butyl-CH_3), 19.7, 19.8 ($NCH_2CH_2CH_2$), 29.1, 29.3 (NCH_2CH_2), 37.76, 37.82, 39.9, 40.2, 43.37, 43.45, 43.94 (NCH_3, NCH_2CH_3), 52.2, 52.6 (NCH_2 butyl), 120.8 (q, $^1J_{C,F}$ = 320.9 Hz, CF_3), 163.2 (CN_3) ppm. MS (CI): *m*/*z* (%) = 214 (100) [cation]$^+$. $C_{13}H_{28}F_3N_3O_3S$ (363.44): calcd. C 42.96, H 7.77, N 11.56; found C 42.41, H 7.70, N 11.49.

***N*-Cyclohexyl-*N′*,*N′*-diethyl-*N*,*N′′*,*N′′*-trimethylguanidinium Trifluoromethanesulfonate (12Ag):** Prepared from **10A** (1.17 g, 2.05 mmol) in CH_2Cl_2 (20 mL) and *N*-cyclohexyl-*N*-methylamine (0.52 g, 0.60 mL, 4.50 mmol); 12 h at reflux temp. Yellowish oil (0.56 g, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95–1.87 (m, 16 H, NCH_2CH_3, CH_2 cy), 2.72–2.90 (10 H, NCH_3, CH cy), 2.99–3.21 (m, 4 H, NCH_2CH_3) ppm; all multiplets were unstructured, indicating dynamic processes. MS (CI): *m*/*z* (%) = 240 (100) [cation]$^+$. $C_{15}H_{30}F_3N_3O_3S$ (389.48): calcd. C 46.26, H 7.76, N 10.79; found C 46.11, H 7.53, N 10.75.

***N*,*N*-Diethyl-*N′*,*N′′*,*N′′*-trimethyl-*N′*-[(*S*)-1-phenylethyl]guanidinium Trifluoromethanesulfonate (12Ah):** Prepared from **10A** (1.14 g, 2.00 mmol) in CH_2Cl_2 (15 mL) and (*S*)-(–)-*N*-methyl-*N*-(1-phenylethyl)amine (0.55 g, 4.10 mmol); 20 h at reflux temp. Yellowish solid (0.19 g, 24% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89–1.26 (m, 6 H, CH_2CH_3), 1.60 (d, 3 H, $CHCH_3$), 2.28–3.38 (several m and s, 13 H, NCH_3, NCH_2CH_3), 4.67 (m, 1 H, NCH), 7.18–7.39 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.3, 12.7, 12.9, 15.2, 15.6 (CH_2CH_3, $CHCH_3$), 32.6, 40.3, 40.6, 42.1, 43.2, 43.7, 44.1 (NCH_3, NCH_2CH_3), 59.9 (NCH), 120.9 (q, $^1J_{C,F}$ = 321.0 Hz, CF_3), 125.5, 126.5, 128.9, 129.0, 129.2, 138.2 (Ar-C), 163.6 (CN_3) ppm. MS (CI): *m*/*z* (%) = 262 (100) [cation]$^+$. $[\alpha]_D^{20}$ = 28.7 (*c* = 7.7, EtOH). $C_{17}H_{28}F_3N_3O_3S$ (411.48): calcd. C 49.62, H 6.86, N 10.21; found C 49.44, H 6.80, N 10.28.

***N*,*N*-Diethyl-*N′*,*N′*-dimethyl-*N′′*,*N′′*-tetramethyleneguanidinium Trifluoromethanesulfonate (12Ai):** Prepared from **10A** (1.37 g, 2.40 mmol) in CH_2Cl_2 (20 mL) and pyrrolidine (0.36 g, 0.42 mL, 5.05 mmol); 6 h at reflux temp. Yellowish oil (0.26 g, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (t, 6 H, NCH_2CH_3), 2.01 (m, 4 H, CH_2CH_2), 2.97 (s, 6 H, NCH_3), 3.24 (q, 4 H, NCH_2CH_3), 3.41 (br. s, 2 H, NCH_2 ring), 3.48 (br. s, 2 H, NCH_2 ring) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0 (NCH_2CH_3), 24.8, 25.2 (CH_2CH_2), 40.3 (NCH_3), 43.5 (NCH_2), 49.6, 49.7 (NCH_2), 160.0 (CN_3) ppm. MS (CI): *m*/*z* (%) = 198 (100) [cation]$^+$. $C_{11}H_{24}F_3N_3O_3S$ (347.40): calcd. C 41.49, H 6.96, N 12.10; found C 41.74, H 7.20, N 12.24.

***N*-Benzyl-*N′*,*N′*-diethyl-*N*,*N′′*,*N′′*-trimethylguanidinium Trifluoromethanesulfonate (12Aj):** Prepared from **10A** (2.09 g, 3.60 mmol) in CH_2Cl_2 (40 mL) and *N*-benzyl-*N*-methylamine (0.89 g, 0.95 mL, 7.32 mmol); 12 h at reflux temp. White solid (0.57 g, 39% yield), m.p. 88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (broadened t, 6 H, NCH_2CH_3), 2.78–3.45 (several m and s, 13 H, 3 NCH_3, 2 NCH_2), 4.12–4.24 (m, 1 H, NCH_2Ph), 4.40–4.49 (m, 1 H, NCH_2Ph), 7.21–7.23 (m, 2 H, Ar-H), 7.26–7.38 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 12.9 (NCH_2CH_3), 38.0, 38.3, 39.8, 40.5, 40.7 (NCH_3), 43.1, 43.4, 43.6, 44.3 (NCH_2CH_3), 56.4, 56.8 (NCH_2Ph), 120.9 (q, $^1J_{C,F}$ = 320.7 Hz, CF_3), 128.5, 128.6, 128.7, 128.8, 128.9, 129.1, 129.3, 133.9 (Ar-C), 163.1 (CN_3) ppm. MS (CI): *m*/*z* (%) = 248 (100) [cation]$^+$. $C_{16}H_{26}F_3N_3O_3S$ (397.46): calcd. C 48.35, H 6.59, N 10.57; found C 48.77, H 6.72, N 10.61.

***N*-Benzyl-*N*,*N′*,*N′*-triethyl-*N′′*,*N′′*-dimethylguanidinium Trifluoromethanesulfonate (12Ak):** Prepared from **10A** (1.71 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and *N*-benzyl-*N*-ethylamine (0.82 g, 0.91 mL, 6.10 mmol); 72 h at reflux temp. Orange oil (0.86 g, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13–1.28 (m, 9 H, NCH_2CH_3), 2.85/2.91/3.01/3.08 [4 s, 6 H, $N(CH_3)_2$], ca. 3.0–3.36 (m, 6 H, 3 NCH_2CH_3), 4.26–4.34 (m, 2 H, NCH_2Ph), 7.19–7.23 (m, 2 H, Ar-H), 7.33–7.38 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.5, 12.7, 13.1, 13.3 (NCH_2CH_3), 39.9, 40.2, 40.6, 43.4, 44.1, 44.2, 45.1 (NCH_3, NCH_2CH_3), 52.7, 53.2 (NCH_2Ph), 120.9 (q, $^1J_{C,F}$ = 321.0 Hz, CF_3), 128.4, 128.9, 129.1, 129.2, 129.3 (Ar-C), 163.1 (CN_3) ppm. MS (CI): *m*/*z* (%) = 262 (100) [cation]$^+$. $C_{17}H_{28}F_3N_3O_3S$ (411.48): calcd. C 49.62, H 6.86, N 10.21; found C 49.45, H 6.93, N 10.11.

***N*-Benzyl-*N*-butyl-*N′*,*N′*-diethyl-*N′′*,*N′′*-dimethylguanidinium Trifluoromethanesulfonate (12Al):** Prepared from **10A** (1.71 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and *N*-benzyl-*N*-butylamine (0.99 g, 1.09 mL, 6.10 mmol); 22 h at reflux temp. Yellow oil (0.74 g, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89–0.92 (m, 3 H, butyl-CH_3), 1.13–1.91 (several m, 10 H, 2 NCH_2CH_3, $NCH_2CH_2CH_2CH_3$), 2.88–3.33 [4 s and several m, 12 H, NCH_2-$CH_2CH_2CH_3$, $N(CH_3)_2$, 2 NCH_2CH_3], 4.20–4.39 (m, 2 H, NCH_2Ph), 7.19–7.23 (m, 2 H, Ar-H), 7.33–7.38 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 12.8, 12.9, 13.3 (NCH_2CH_3, butyl-CH_3), 19.5, 19.7, 28.9, 29.4 (NCH_2-$CH_2CH_2CH_3$), 39.7, 40.0, 40.1, 40.3 (NCH_3), 43.1, 43.2, 43.4, 43.9 (NCH_2CH_3), 48.7, 49.8 (NCH_2 butyl), 53.1, 53.6 (NCH_2Ph), 120.7 (q, $^1J_{C,F}$ = 320.9 Hz, CF_3), 128.27, 128.32, 128.7, 128.9, 129.1, 133.8, 133.9 (Ar-C), 162.78, 162.86 (CN_3) ppm. MS (CI): *m*/*z* (%) = 290 (100) [cation]$^+$. $C_{19}H_{32}F_3N_3O_3S$ (439.54): calcd. C 51.92, H 7.34, N 9.56; found C 51.41, H 7.34, N 9.81.

***N*,*N*-Dibenzyl-*N′*,*N′*-diethyl-*N′′*,*N′′*-dimethylguanidinium Trifluoromethanesulfonate (12Am):** Prepared from **10A** (1.71 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and dibenzylamine (1.20 g, 1.18 mL, 6.10 mmol); 24 h at reflux temp. White solid (0.76 g, 53% yield), m.p. 74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 and 1.25 (2 t, 6 H, NCH_2CH_3), 3.03 (s, 3 H, NCH_3), 3.10 (s, 3 H, NCH_3), 3.17–3.57 (4 m, 4 H, NCH_2CH_3), 3.97–4.00 (m, 2 H, CH_2Ph), 4.23–4.32 (m, 2 H, CH_2Ph), 7.18–7.26 (m, 4 H, Ar-H), 7.41–7.46 (m, 6 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.5, 13.1 (NCH_2CH_3), 40.3, 40.7 (NCH_3), 43.5, 43.6 (NCH_2CH_3), 53.3, 54.1 (NCH_2Ph), 120.9 (q, $^1J_{C,F}$ = 320.6 Hz, CF_3), 128.7, 128.8, 129.1, 129.2, 129.4, 133.8, 133.9 (Ar-C), 163.0 (CN_3) ppm. MS (CI): *m*/*z* (%) = 324 (100) [cation]$^+$. $C_{22}H_{30}F_3N_3O_3S$ (473.55): calcd. C 55.80, H 6.39, N 8.87; found C 55.77, H 6.38, N 8.73.

***N*,*N*-Dimethyl-*N′*,*N′*-diethyl-*N′′*,*N′′*-bis(2-methoxyethyl)guanidinium Trifluoromethanesulfonate (12An):** Prepared from **10A** (1.71 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and bis(2-methoxyethyl) amine (0.81 g, 0.90 mL, 6.10 mmol); 22 h at reflux temp. Yellow oil (0.74 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16/1.18 (2 t, 6 H, NCH_2CH_3), 2.92/3.00 (2 s, 3 H each, OCH_3), 3.30 [s, 6 H $N(CH_3)_2$], 3.15–3.70 (several m, 12 H, NCH_2CH_3, $NCH_2CH_2OCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.1, 12.7 (NCH_2CH_3), 39.7, 40.3 (NCH_3), 43.2, 43.8 (NCH_2CH_3), 48.8, 49.9 ($NCH_2CH_2OCH_3$), 58.7 ($NCH_2CH_2OCH_3$), 68.6, 68.8 ($NCH_2CH_2OCH_3$), 164.6 (CN_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.6 ppm. IR (KBr): $\tilde{\nu}$ = 2979 (m), 2938 (m), 2898 (m), 2831 (m), 1584 (s), 1547 (s), 1460 (m), 1422 (m), 1270 (vs), 1223 (m), 1151 (s), 1118 (s), 1031 (s) cm^{-1}. MS (CI): *m*/*z* (%) = 260 (100) [cation]$^+$. $C_{14}H_{30}F_3N_3O_5S$ (409.47): calcd. C 41.07, H 7.38, N 10.26; found C 40.81, H 7.30, N 10.51.

***N*,*N*-Dibutyl-*N′*,*N′*,*N′′*,*N′′*-tetraethylguanidinium Trifluoromethanesulfonate (12Ba):** Prepared from **10B** (1.48 g, 2.00 mmol) in CH_2Cl_2 (20 mL) and diethylamine (0.30 g, 0.42 mL, 4.10 mmol); 17 h at reflux temp. Yellow oil (0.26 g, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, 6 H, $CH_2CH_2CH_3$), 1.19–1.73 (several m, 20 H, $CH_2CH_2CH_3$, NCH_2CH_3), 3.03–3.43 (several m, 12 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 12.9, 13.6 ($CH_2CH_2CH_3$), 20.0, 29.5 ($CH_2CH_2CH_3$), 43.9 (NCH_2 ethyl), 49.5 (NCH_2 butyl), 163.8 (CN_3) ppm. MS (CI): *m*/*z* (%) = 284 (100) [cation]$^+$. $C_{18}H_{38}F_3N_3O_3S$ (433.57): calcd. C 49.86, H 8.83, N 9.69; found C 49.80, H 8.90, N 9.67.

***N*,*N*-Dibutyl-*N*′,*N*′-diethyl-*N*′′,*N*′′-dipropylguanidinium Trifluoromethanesulfonate (12Bb):** Prepared from **10B** (1.48 g, 2.00 mmol) in CH_2Cl_2 (20 mL) and dipropylamine (0.43 g, 0.56 mL, 4.20 mmol); 24 h at reflux temp. A yellowish oil was obtained which solidified over two weeks. Yield: 0.21 g (23% yield); m.p. 33 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 [2 t, 12 H, $(CH_2)_2CH_3$], 1.16–1.23 [2 m, 14 H, NCH_2CH_3, $NCH_2(CH_2)_2$], 1.46–1.79 (2 m, 4 H, $NCH_2CH_2CH_3$), 2.91–3.39 (m, 12 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 12.6, 12.7, 13.4, 13.5 (CH_3), 19.9, 20.7, 20.8, 29.3, 29.4 [NCH_2CH_2, $NCH_2(CH_2)_2$], 43.8, 49.3, 49.4, 51.3 (NCH_2), 120.9 (q, $^1J_{C,F}$ = 321.1 Hz, CF_3), 163.8 (CN_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.6 ppm. IR (NaCl): $\tilde{\nu}$ = 2965 (s), 2937 (s), 2876 (m), 1539 (s), 1461 (m), 1440 (m), 1270 (vs), 1222 (m), 1146 (s), 1031 (s) cm^{-1}. MS (CI): *m*/*z* (%) = 312 (100) [cation]$^+$. $C_{20}H_{42}F_3N_3O_3S$ (461.63): calcd. C 52.04, H 9.17, N 9.10; found C 51.67, H 9.05, N 9.17.

***N*,*N*-Dibutyl-*N*′,*N*′-diethyl-*N*′′,*N*′′-dihexylguanidinium Trifluoromethanesulfonate (12Bc):** Prepared from **10B** (1.48 g, 2.00 mmol) in CH_2Cl_2 (20 mL) and dihexylamine (0.78 g, 0.98 mL, 4.20 mmol); 17 h at reflux temp. Yellowish oil (0.61 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, 6 H, CH_3), 0.88 (s, 3 H, CH_3), 0.89 (s, 3 H, CH_3), 1.14 (s, 6 H, CH_3 ethyl), ca. 1.20–1.70 [m, 24 H, $CH_2(CH_2)_4CH_3$, NCH_2CH_3 and $CH_2(CH_2)_2CH_3$], 3.00–3.38 (several m, 12 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.61, 12.64, 13.38, 13.41, 13.7 (CH_3), 19.82, 19.85, 22.3, 22.9, 26.28, 26.33, 27.26, 27.29, 29.24, 29.41, 31.04, 31.08 [$(CH_2)_nCH_3$, *n* = 2,4], 43.71, 43.74 (NCH_2 ethyl), 49.25, 49.35, 49.49, 49.53 (NCH_2 butyl, hexyl), 120.9 (q, $^1J_{C,F}$ = 320.9 Hz, CF_3), 163.7 (CN_3) ppm. MS (CI): *m*/*z* (%) = 396 (100) [cation]$^+$, 544 (3) [M]$^+$. $C_{26}H_{54}F_3N_3O_3S$ (545.79): calcd. C 57.22, H 9.97, N 7.70; found C 56.99, H 9.85, N 7.68.

***N*,*N*,*N*′-Tributyl-*N*′′,*N*′′-diethyl-*N*′-methylguanidinium Trifluoromethanesulfonate (12Bd):** Prepared from **10B** (1.48 g, 2.00 mmol) in CH_2Cl_2 (20 mL) and *N*-butyl-*N*-methylamine (0.36 g, 0.48 mL, 4.10 mmol); 10 h at reflux temp. Colorless oil (0.61 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82–0.88 (overlapping triplets, 9 H, 3 CH_2CH_3), 1.09–1.61 [m, 18 H, 2 CH_3, $(CH_2)_2CH_3$], 2.89 (s, 3 H, NCH_3), 2.90–3.31 (m, 10 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 12.5, 12.6, 12.8, 13.29, 13.32, 13.4, 19.6, 19.69, 19.73, 19.76, 19.81 (CH_3), 29.0, 29.1, 29.2, 29.3, 29.5 [$(CH_2)_2CH_3$], 37.9, 38.1 (NCH_3), 43.2, 43.6, 43.7, 43.8 (NCH_2 ethyl), 48.8, 49.2, 49.3, 49.4, 52.48, 52.51 (NCH_2 butyl), 120.7 (q, $^1J_{C,F}$ = 321.0 Hz, CF_3), 163.53, 163.54 (CN_3) ppm. MS (CI): *m*/*z* (%) = 298 (100) [cation]$^+$. $C_{19}H_{40}F_3N_3O_3S$ (447.60): calcd. C 50.98, H 9.01, N 9.39; found C 50.51, H 8.98, N 9.42.

***N*,*N*-Dibutyl-*N*′-cyclohexyl-*N*′′,*N*′′-diethyl-*N*′-methylguanidinium Trifluoromethanesulfonate (12Be):** Prepared from **10B** (1.51 g, 2.05 mmol) in CH_2Cl_2 (20 mL) and *N*-cyclohexyl-*N*-methylamine (0.46 g, 0.54 mL, 4.10 mmol); 12 h at reflux temp. Yellowish oil (0.62 g, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91/0.92 [2 t, 3 H each, $N(CH_2)_2CH_3$], 1.18–1.93 (several m, 24 H, NCH_2CH_3, 9 CH_2), 2.86 (s, 3 H, NCH_3), 3.01–3.32 (m, 9 H, 4 NCH_2, NCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 12.7, 12.8, 13.49, 13.55 [$(CH_2)_nCH_3$], 19.9, 20.0, 24.79, 24.82, 25.6, 25.7, 25.8, 29.2, 29.26, 29.28, 29.31, 29.37, 29.40, 31.57, 31.63, 33.5, 33.6 [CH_2CH_3, CH_2 cy, $(CH_2)_nCH_3$], 43.1, 43.6, 43.9, 44.1, 48.8, 49.2, 49.5, 49.6 (NCH_2, NCH_3), 61.7, 61.8 (NCH), 120.9 (q, $^1J_{C,F}$ = 321.2 Hz, CF_3), 164.2, 164.3 (CN_3) ppm. MS (CI): *m*/*z* (%) = 324 (100) [cation]$^+$. $C_{21}H_{42}F_3N_3O_3S$ (473.64): calcd. C 53.25, H 8.94, N 8.87; found C 53.48, H 8.92, N 8.93.

***N*,*N*-Dibutyl-*N*′,*N*′-diethyl-*N*′′,*N*′′-tetramethyleneguanidinium Trifluoromethanesulfonate (12Bf):** Prepared from **10B** (2.22 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and pyrrolidine (0.43 g, 0.50 mL, 6.10 mmol); 20 h at reflux temp. Yellowish oil (0.42 g, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, 6 H, CH_3), 1.18 (t, 6 H, CH_3), 1.28 (m, 4 H, $CH_2CH_2CH_2CH_3$), 1.50 (m, 4 H, $CH_2CH_2CH_2CH_3$), 2.03 (m, 4 H, $CH_2CH_2CH_2$ ring), 3.11 (t, 4 H, NCH_2 butyl), 3.23 (br. q, 4 H, NCH_2CH_3), 3.40 (m, 4 H, NCH_2 ring) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 13.6 (CH_3), 19.9, 24.8, 24.9, 29.3 (CH_2), 43.7 (NCH_2 ethyl), 49.3, 49.7, 50.1 (NCH_2 butyl, ring), 120.7 (q, $^1J_{C,F}$ = 320.8 Hz, CF_3), 160.0 (CN_3). MS (CI): *m*/*z* (%) = 282 (100) [cation]$^+$. $C_{18}H_{36}F_3N_3O_3S$ (431.56): calcd. C 50.10, H 8.41, N 9.74; found C 50.10, H 8.30, N 9.74.

***N*-Benzyl-*N*′,*N*′-dibutyl-*N*′′,*N*′′-diethyl-*N*-methylguanidinium Trifluoromethanesulfonate (12Bg):** Prepared from **10B** (2.22 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and *N*-benzyl-*N*-methylamine (0.74 g, 0.79 mL, 6.10 mmol); 72 h at reflux temp. Yellow oil (1.09 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88–0.96 (several t, 6 H, 2 CH_2CH_3), 1.17–1.67 (several m, 14 H, 2 CH_2CH_3, 2 $CH_2(CH_2)_2CH_3$), 2.77/2.79 (2 s, 3 H together, NCH_3), 2.91–3.64 (m, 8 H, NCH_2), 4.29–4.41 (m, 2 H, CH_2Ph), 7.18–7.20 (m, 2 H, Ar-H), 7.35–7.38 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.74, 12.79, 13.49, 13.53, 13.57 (CH_2CH_3), 19.75, 19.89, 19.99, 20.09, 29.49, 29.52 [$CH_2(CH_2)_2CH_3$], 38.2, 38.3 (NCH_3), 42.8, 43.7, 43.8, 44.1 (NCH_2 ethyl), 48.5, 49.3, 49.4, 49.6 (NCH_2 butyl), 56.6, 56.8 (NCH_2Ph), 120.9 (q, $^1J_{C,F}$ = 320.9 Hz, CF_3), 122.5, 128.6, 128.7, 128.9, 129.2, 129.3, 133.6, 133.8 (Ar-C), 163.3, 163.5 (CN_3) ppm. MS (CI): *m*/*z* (%) = 332 (100) [cation]$^+$. $C_{22}H_{38}F_3N_3O_3S$ (481.62): calcd. C 54.86, H 7.95, N 8.72; found C 54.12, H 7.78, N 8.65.

***N*-Benzyl-*N*′,*N*′-dibutyl-*N*,*N*′′,*N*′′-triethylguanidinium Trifluoromethanesulfonate (12Bh):** Prepared from **10B** (2.22 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and *N*-benzyl-*N*-ethylamine (0.82 g, 0.91 mL, 6.10 mmol); 72 h at reflux temp. Yellow oil (0.95 g, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88–0.99 (several t, 6 H, CH_3 butyl), 1.17–1.64 [m, 17 H, NCH_2CH_3, $CH_2(CH_2)_2CH_3$], 2.80–3.49 (m, 10 H, 5 NCH_2), 4.25–4.42 (2 overlapping AB spin systems, 2 H, NCH_2Ph), 7.17–7.18 (m, 2 H, Ar-H), 7.36–7.40 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.69, 12.72, 12.86, 12.91, 13.54, 13.58, 13.61 (CH_3), 19.37, 19.7, 20.0, 20.1, 29.3, 29.4, 29.5, 29.6 [$CH_2(CH_2)_2CH_3$], 43.3, 43.91, 43.98, 44.2, 44.6, 44.7 (NCH_2 ethyl), 49.0, 49.4, 49.5, 49.6, 53.1 (NCH_2 butyl, NCH_2Ph), 122.5, 124.8, 128.3, 128.4, 129.0, 129.1, 129.3, 129.4, 133.8 (Ar-C), 163.5 (CN_3) ppm. MS (CI): *m*/*z* (%) = 346 (100) [cation]$^+$. $C_{23}H_{40}F_3N_3O_3S$ (495.64): calcd. C 55.73, H 8.13, N 8.48; found C 55.35, H 8.15, N 8.44.

***N*-Benzyl-*N*-butyl-*N*′,*N*′-diethyl-*N*′′,*N*′′-dibutylguanidinium Trifluoromethanesulfonate (12Bi):** Prepared from **10B** (2.21 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and *N*-benzyl-*N*-butylamine (0.99 g, 1.09 mL, 6.10 mmol); 22 h at reflux temp. Yellow oil (0.74 g, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94–1.01 (several t, 9 H, butyl-CH_3), 1.24–1.84 (several m, 18 H, 2 NCH_2CH_3, 3 $NCH_2CH_2CH_2CH_3$), 2.94–3.56 (several m, 10 H, NCH_2), 4.31–4.42 (m, 2 H, NCH_2Ph), 7.19–7.22 (m, 2 H, Ar-H), 7.40–7.44 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 12.8, 12.9, 13.5, 13.55, 13.57, 13.6 (NCH_2CH_3, $NCH_2CH_2CH_2CH_3$), 19.9, 20.0, 20.1 ($NCH_2CH_2CH_2CH_3$), 29.2, 29.27, 29.29, 29.3, 29.7 ($NCH_2CH_2CH_2CH_3$), 43.4, 43.8, 44.0, 44.1 (NCH_2 ethyl), 49.1, 49.3, 49.44, 49.46, 49.50, 49.6, 53.68, 53.71 (NCH_2 butyl, NCH_2Ph), 128.3, 128.4, 129.1, 129.2, 129.3, 133.7 (Ar-C), 163.5 (CN_3) ppm. MS (CI): *m*/*z* (%) = 374 (100) [cation]$^+$. $C_{25}H_{44}F_3N_3O_3S$ (523.70): calcd. C 57.34, H 8.47, N 8.02; found C 57.19, H 8.32, N 8.36.

***N*,*N*-Dibenzyl-*N*′,*N*′-dibutyl-*N*′′,*N*′′-diethylguanidinium Trifluoromethanesulfonate (12Bj):** Prepared from **10B** (2.22 g, 3.00 mmol) in

CH_2Cl_2 (20 mL) and dibenzylamine (1.20 g, 1.18 mL, 6.10 mmol); 72 h at 80 °C in a closed Schlenk tube. White solid (0.50 g, 30% yield), m.p. 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97, 1.00, 1.29, 1.35 (4 t, 3 H each, CH_3), ca. 1.15–1.87 [m, 8 H, $CH_2(CH_2)_2$-CH_3], 3.04–3.56 (several m, 8 H, 4 NCH_2), 4.01–4.25 (2 overlapping AB spin systems, 4 H, NCH_2Ph), 4.23 (d, J = 14.0 Hz, 2 H, NCH_2Ph), 7.16 (d, 4 H, Ar-H), 7.44–7.48 (m, 6 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 13.0, 13.65, 13.68 (CH_3), 20.0, 20.2, 29.3, 29.8 [$CH_2(CH_2)_2CH_3$], 43.7, 44.3 (NCH_2 ethyl), 49.2, 49.7 (NCH_2 butyl), 53.7, 53.8 (NCH_2Ph), 128.6, 128.7, 129.3, 129.4, 129.5, 129.6, 133.5, 133.6 (Ar-C), 163.3 (CN_3) ppm. MS (CI): m/z (%) = 408 (100) [cation]$^+$. $C_{28}H_{42}F_3N_3O_3S$ (557.71): calcd. C 60.30, H 7.59, N 7.53; found C 60.19, H 7.45, N 7.63.

***N*,*N*-Dibutyl-*N*′,*N*′-diethyl-*N*′′,*N*′′-bis(2-methoxyethyl)guanidinium Trifluoromethanesulfonate (12Bk):** Prepared from **10B** (2.21 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and bis(2-methoxyethyl)amine (0.81 g, 0.90 mL, 6.10 mmol); 22 h at reflux temp. Yellow solid (1.02 g, 69% yield), m.p. 57 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91/0.93 (2 t, 3 H each, CH_3 butyl), 1.13–1.20 (2 t, 6 H, NCH_2CH_3), 1.29–1.63 (several m, 8 H, $NCH_2CH_2CH_2CH_3$), 2.91–3.74 (several m, 22 H, NCH_2CH_3, $NCH_2CH_2CH_2CH_3$, $NCH_2CH_2OCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9, 12.2, 13.5, 13.7 (NCH_2CH_3, $NCH_2CH_2CH_2CH_3$), 19.9, 20.0, 28.6, 29.3 ($NCH_2CH_2CH_2CH_3$), 43.3, 43.4 (NCH_2 ethyl), 48.9, 49.0, 49.3, 49.4 (NCH_2 butyl, NCH_2CH_2O), 58.61, 58.63 ($NCH_2CH_2OCH_3$), 68.2, 68.4 ($NCH_2CH_2OCH_3$), 165.2 (CN_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.6 ppm. IR (KBr): $\tilde{\nu}$ = 2962 (m), 2936 (m), 2876 (m), 1544 (s), 1461 (m), 1435 (m), 1271 (vs), 1222 (m), 1150 (s), 1118 (s), 1031 (s) cm^{-1}. MS (CI): m/z (%) = 344 (100) [cation]$^+$. $C_{20}H_{42}F_3N_3O_5S$ (493.62): calcd. C 48.66, H 8.58, N 8.51; found C 48.33, H 8.50, N 8.52.

***N*,*N*,*N*′,*N*′-Tetrabutyl-*N*′′,*N*′′-diethylguanidinium Trifluoromethanesulfonate (12Ca):** Prepared from **10C** (2.55 g, 3.00 mmol) in CH_2Cl_2 (15 mL) and diethylamine (0.44 g, 0.62 mL, 6.00 mmol); 2 h at reflux temp. An oil was obtained, which solidified over 1 d, yielding a white solid (0.68 g, 46% yield), m.p. 58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.97 (2 t, 12 H, CH_3 butyl), 1.24 (t, 6 H, NCH_2CH_3), 1.31–1.46 (m, 12 H) and 1.64–1.78 (m, 4 H, $CH_2CH_2CH_2CH_3$), 3.02–3.11 (m, 4 H, NCH_2CH_3), 3.15–3.44 (m, 8 H, NCH_2 butyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 13.60, 13.63 (CH_3), 20.04, 20.07 ($CH_2CH_2CH_2CH_3$), 29.48, 29.53 ($CH_2CH_2CH_2CH_3$), 43.9 (NCH_2 ethyl), 49.4, 49.5 (NCH_2 butyl), 163.9 (CN_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.5 ppm. IR (KBr): $\tilde{\nu}$ = 2962 (s), 2936 (s), 2876 (s), 1539 (vs), 1460 (m), 1270 (vs), 1223 (m), 1150 (s), 1032 (s) cm^{-1}. MS (CI): m/z (%) = 340 (100) [cation]$^+$. $C_{22}H_{46}F_3N_3O_3S$ (489.32): calcd. C 53.96, H 9.47, N 8.58; found C 53.93, H 9.46, N 8.40.

***N*,*N*,*N*′,*N*′-Tetrabutyl-*N*′′,*N*′′-dipropylguanidinium Trifluoromethanesulfonate (12Cb):** Prepared from **10C** (1.70 g, 2.00 mmol) in CH_2Cl_2 (20 mL) and di-*n*-propylamine (0.41 g, 0.56 mL, 4.10 mmol); 3 h at reflux temp. White solid (0.48 g, 46% yield), m.p. 64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89–0.98 (m, 18 H, CH_3), 1.25–1.35 (m, 14 H) and 1.68–1.86 [m, 6 H, $CH_2(CH_2)_nCH_3$, n = 1,2], 2.97–3.25 (m, 6 H, NCH_2), 3.25–3.34 (m, 6 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 13.6, 13.7 (CH_3), 20.4, 20.8 (CH_2CH_3), 29.4, 29.6 ($CH_2CH_2CH_2CH_3$), 49.4, 49.5, 51.4 (NCH_2), 164.2 (CN_3) ppm. MS (CI): m/z (%) = 368 (100) [cation]$^+$. $C_{24}H_{50}F_3N_3O_3S$ (517.73): calcd. C 55.68, H 9.73, N 8.12; found C 56.02, H 9.89, N 8.23.

***N*,*N*,*N*′,*N*′,*N*′′,*N*′′-Hexabutylguanidinium Trifluoromethanesulfonate (12Cc):** Prepared from **10C** (1.69 g, 2.00 mmol) in CH_2Cl_2 (20 mL) and dibutylamine (0.51 g, 0.67 mL, 4.00 mmol). Colorless crystalline solid (0.52 g, 48% yield), m.p. 89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, 18 H, CH_3), 1.27–1.43 (m, 18 H, $CH_2CH_2CH_2CH_3$) 1.66–1.78 (m, 6 H, $CH_2CH_2CH_2CH_3$), 3.01–3.09 (m, 6 H, NCH_2), 3.25–3.32 (m, 6 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (CH_3), 20.0 (CH_2CH_3), 29.5 ($CH_2CH_2CH_3$), 49.5 (NCH_2), 164.1 (CN_3) ppm. MS (CI): m/z (%) = 396 (100) [cation]$^+$. $C_{26}H_{54}F_3N_3O_3S$ (545.79): calcd. C 57.22, H 9.97, N 7.70; found C 57.15, H 9.96, N 7.75.

***N*,*N*,*N*′,*N*′-Tetrabutyl-*N*′′,*N*′′-dihexylguanidinium Trifluoromethanesulfonate (12Cd):** Prepared from **10C** (1.28 g, 1.50 mmol) in CH_2Cl_2 (20 mL) and dihexylamine (0.56 g, 0.70 mL, 3.00 mmol); 21 h at reflux temp. Colorless solid (0.32 g, 35% yield), m.p. 50 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, 6 H, CH_3 hexyl), 0.95 (t, 12 H, CH_3 butyl), 1.28–1.71 [several m, 32 H, $CH_2(CH_2)_nCH_3$, n = 2,4], 3.02–3.29 (2 m, 12 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.62, 13.64, 13.8 (CH_3), 20.0, 22.5, 26.5, 27.5, 29.5, 31.3 [$CH_2(CH_2)_nCH_3$, n = 2,4], 49.49, 49.51, 49.7 (NCH_2), 164.1 (CN_3) ppm. MS (CI): m/z (%) = 452 (100) [cation]$^+$. $C_{30}H_{62}F_3N_3O_3S$ (601.89): calcd. C 59.86, H 10.38, N 6.98; found C 59.76, H 10.16, N 6.96.

***N*,*N*,*N*′,*N*′,*N*′′-Pentabutyl-*N*′′-methylguanidinium Trifluoromethanesulfonate (12Ce):** Prepared from **10C** (1.14 g, 1.30 mmol) in CH_2Cl_2 (20 mL) and *N*-butyl-*N*-methylamine (0.23 g, 0.30 mL, 2.60 mmol); 7 h at reflux temp. Yellow oil (0.33 g, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90–0.94 (t, 15 H, CH_3 hexyl) 1.22–1.81 (m, 20 H, $CH_2CH_2CH_2CH_3$), 2.96 (s, 3 H, NCH_3), 2.99–3.31 (m, 10 H, NCH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.53, 15.56 (CH_2CH_3), 19.8, 19.9, 20.0 ($CH_2CH_2CH_3$), 29.3, 29.4, 29.5, 29.7 ($CH_2CH_2CH_3$), 38.2 (NCH_3), 48.9, 49.4, 49.5, 49.6, 52.8 (NCH_2), 164.0 (CN_3) ppm. MS (CI): m/z (%) = 354 (100) [cation]$^+$. $C_{23}H_{48}F_3N_3O_3S$ (503.71): calcd. C 54.84, H 9.61, N 8.34; found C 54.97, H 9.52, N 8.21.

***N*,*N*,*N*′,*N*′-Tetrabutyl-*N*′′-cyclohexyl-*N*′′-methylguanidinium Trifluoromethanesulfonate (12Cf):** Prepared from **10C** (1.17 g, 2.00 mmol) in CH_2Cl_2 (20 mL) and *N*-cyclohexyl-*N*-methylamine (0.52 g, 0.60 mL, 4.50 mmol); 12 h at reflux temp. White solid (0.48 g, 46% yield), m.p. 76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.97 (overlapping triplets, 12 H, CH_2CH_3), 1.30–1.71 (m, 16 H, $CH_2CH_2CH_2CH_3$), 1.71–1.99 (m, 10 H, CH_2 cy) 2.91 (s, 3 H, NCH_3), 2.99–3.34 (m, 9 H, NCH_2, NCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.0 (CH_2CH_3), 19.9, 20.1 ($CH_2CH_2CH_2CH_3$), 24.9, 25.8, 29.36, 29.38, 29.5, 29.51, 31.6 (CH_2 cy, $CH_2CH_2CH_2CH_3$), 33.8 (NCH_3), 48.9, 49.4, 49.6, 49.7 (NCH_2), 61.9 (NCH), 164.5 (CN_3) ppm. MS (CI): m/z (%) = 380 (100) [cation]$^+$. $C_{25}H_{50}F_3N_3O_3S$ (529.35): calcd. C 56.68, H 9.51, N 7.93; found C 56.39, H 9.42, N 8.05.

***N*,*N*,*N*′,*N*′-Tetrabutyl-*N*′′,*N*′′-tetramethyleneguanidinium Trifluoromethanesulfonate (12Cg):** Prepared from **10C** (2.55 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and pyrrolidine (0.43 g, 0.50 mL, 6.1 mmol); 20 h at reflux temp. Yellowish oil (0.66 g, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, 12 H, CH_3), 1.24–1.34 (m, 8 H, CH_2CH_3), 1.45–1.55 (m, 8 H, $CH_2CH_2CH_3$), 2.05 (broad signal, 4 H, 3-H_2-, 4-H_2 ring), 3.11–3.15 (m, 8 H, NCH_2 butyl), 3.41 (broad signal, 4 H, NCH_2 ring) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (CH_3), 19.9 (CH_2CH_3), 24.8 (NCH_2CH_2 ring), 29.4 ($CH_2CH_2CH_3$), 49.4, 50.9 (NCH_2), 120.9 (q, $^1J_{C,F}$ = 320.9 Hz, CF_3), 160.2 (CN_3) ppm. MS (CI): m/z (%) = 338 (100) [cation]$^+$. $C_{22}H_{44}F_3N_3O_3S$ (487.66): calcd. C 54.18, H 9.09, N 8.62; found C 54.64, H 9.10, N 8.72.

***N*-Benzyl-*N*′,*N*′,*N*′′,*N*′′-tetrabutyl-*N*-ethylguanidinium Trifluoromethanesulfonate (12Ch):** Prepared from **10C** (1.70 g, 2.00 mmol) in CH_2Cl_2 (25 mL) and *N*-benzyl-*N*-ethylamine (0.55 g, 0.61 mL,

4.10 mmol); 48 h at reflux temp. Yellowish solid (0.49 g, 44% yield), m.p. 87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94–0.99 (several t, 6 H, CH_3 butyl), 1.25–1.77 [several m, 19 H, NCH$_2$CH_3, CH$_2$(CH_2)$_2$-CH$_3$], 2.80–3.43 (several m, 10 H, 5 NCH_2), 4.28/4.43 (AB system, J = 14.0 Hz, 2 H, NCH_2Ph), 7.17–7.20 (m, 2 H, Ar-H), 7.38–7.40 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8, 13.62, 13.65, 13.67 (butyl-CH$_3$, CH$_2$CH_3), 19.9, 20.01, 20.05, 20.17, 29.4, 29.5, 29.8 (NCH$_2$CH_2CH_2CH$_3$), 44.6 (NCH$_2$ ethyl), 49.0, 49.5, 49.6, 53.1 (NCH$_2$ butyl, NCH_2Ph), 128.5, 129.1, 129.3, 133.7 (Ar-C), 163.7 (CN$_3$) ppm. MS (CI): m/z (%) = 402 (100) [cation]$^+$. $C_{27}H_{48}F_3N_3O_3S$ (551.75): calcd. C 58.77, H 8.77, N 7.62; found C 58.64, H 8.72, N 7.49.

***N*,*N*,*N*′,*N*′′-Tetrabutyl-*N*′′,*N*′′-bis(2-methoxyethyl)guanidinium Trifluoromethanesulfonate (12Ci):** Prepared from **10C** (2.55 g, 3.00 mmol) in CH_2Cl_2 (25 mL) and bis(2-methoxyethyl)amine (0.81 g, 0.90 mL, 6.10 mmol); 48 h at reflux temp. Yellowish solid (1.12 g, 68% yield), m.p. 80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91–0.93 (2 t, 12 H, butyl-CH$_3$), 1.26–1.67 (several m, 16 H, NCH$_2$CH_2CH_2CH$_3$), 2.89–3.70 (16 H NCH_2CH$_2$CH$_2$CH$_3$, NCH_2CH_2OCH_3), 3.27 (s, 6 H, OCH$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 13.6 (NCH$_2$CH$_2$CH$_2$CH_3), 19.89, 19.93, 28.7, 29.3 (NCH$_2$CH_2CH_2CH$_3$), 48.9, 49.1 (NCH$_2$, NCH_2CH$_2$O), 58.6 (NCH$_2$CH$_2$OCH_3), 68.0 (NCH$_2$CH_2OCH$_3$), 120.9 (q, $^1J_{C,F}$ = 320.9 Hz, CF$_3$), 165.3 (CN$_3$) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.6 ppm. IR (KBr): $\tilde{\nu}$ = 2961 (s), 2933 (s), 2875 (s), 1539 (s), 1459 (m), 1436 (m), 1263 (vs), 1224 (m), 1150 (s), 1118 (s), 1031 (s) cm^{-1}. MS (CI): m/z (%) = 400 (100) [cation]$^+$. $C_{24}H_{50}F_3N_3O_5S$ (549.73): calcd. C 52.44, H 9.17, N 7.64; found C 52.95, H 9.14, N 7.65.

One-Pot Synthesis of 12Ac: In a 50 mL Schlenk vessel purged with argon was placed triflic anhydride (1.41 g, 0.82 mL, 5.0 mmol) and dry CH_2Cl_2 (15 mL). The solution was cooled to 0 °C, and *N*,*N*-diethyl-*N*′,*N*′-dimethylurea (**8A**, 1.44 g, 10 mmol) in CH_2Cl_2 (10 mL) was added dropwise. After the addition was complete, the reaction mixture was kept at 0 °C for 30 min with magnetic stirring, brought to room temp. and finally heated at reflux for 12 h. After cooling to room temp., a solution of a dibutylamine (1.29 g, 1.70 mL, 10.0 mmol) in CH_2Cl_2 (10 mL) was added. After the addition was complete, the mixture was heated at reflux for 5 h. After cooling to room temp. the solution was concentrated, and pentane (10 mL) was added. A second liquid (oily) phase formed, which was separated, dissolved in CH_2Cl_2 (10 mL), and extracted with 0.1 M NaOH, and the organic phase was dried with Na_2SO_4. After evaporation of the solvent, a yellow oil was obtained, which was kept at 0.001 mbar for 5 h to eliminate the remaining traces of volatiles. Yield: 1.13 g (56%).

Chlorine-Free One-Pot Synthesis of 12Ac: In a 50 mL Schlenk vessel purged with argon was placed triflic anhydride (1.41 g, 0.82 mL, 5.0 mmol) and dry cyclohexane (10 mL). The solution was cooled to 14 °C and *N*,*N*-diethyl-*N*′,*N*′-dimethylurea (**8A**, 1.44 g, 10 mmol) in cyclohexane (10 mL) was added dropwise. After the addition was complete, the reaction mixture was kept at 14 °C for 30 min with magnetic stirring, brought to room temp. and finally heated at reflux for 3 h. After cooling to room temp., dibutylamine (1.29 g, 1.70 mL, 10.0 mmol) was added. The mixture was then heated at reflux for 3 h, followed by cooling to room temp. and removal of the solvent. The oily phase was extracted with 1 M NaOH (5 mL), washed with water (3 × 10 mL), dissolved in EtOH (15 mL) and dried with Na_2SO_4. Evaporation of the solvent yielded a yellow oil, which was kept at 0.001 mbar for 5 h to remove the remaining traces of volatiles; yield: 0.91 g (45%).

Thermal Analysis: The thermal behavior of the salts was characterized by differential scanning calorimetry (DSC). The DSC experiments were performed using two different Perkin–Elmer DSC 7 systems. For measurements below room temperature down to –140 °C, an instrument with helium cooling was used. For the temperature range between –70 and +120 °C, one with nitrogen cooling was used. The heating and cooling rates for both were 10 °C min^{-1}. Glass transition temperatures (T_g) and melting points (T_m) were defined as peak maxima. Temperature calibration was performed on a sample of indium. The thermal stability of the salts was determined by thermogravimetric analysis using a Mettler–Toledo TGA/SDTA 851 instrument. In each experiment, the sample was heated under a N_2 atmosphere, and the temperature was linearly increased in steps of 10 °C min^{-1} from 30 °C to 800 °C.

Refractive Index Data: Refractive indices were determined using an Abbé refractometer Type G. The instrument was calibrated by measuring the refractive index of some common organic solvents. Each sample was dried at 50 °C/0.001 mbar for 3 h. All measurements were performed at 20 ± 1 °C.

Viscosity: The viscosity of RTILs was measured with a Haake Mars II modular advanced rheometer system (Thermo Electron Corporation). All measurements were performed at 23 ± 0.01 °C on samples that had been dried at 70 °C/15–30 mbar for 4–5 h. For each analysis, a 2–3 mL sample was used, and the tests were carried out with a 60 mm titanium plate. The analyses were performed in controlled rate (CR) mode with a shear rate of 10 s^{-1} and 100 s^{-1}, but also in CR mode with a starting shear rate of 10 s^{-1} up to a shear rate of 150 s^{-1}. In accordance with these results, the zero shear viscosity was fixed. The temperature-dependent experiments were performed with a constant shear rate of 10 s^{-1} in the temperature range 20–60 °C.

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