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Highly Efficient Synthesis of 5-Substituted 1*H*-Tetrazoles Catalyzed by Cu–Zn Alloy Nanopowder, Conversion into 1,5- and 2,5-Disubstituted Tetrazoles, and Synthesis and NMR Studies of New Tetrazolium Ionic Liquids

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A series of 5-substituted 1*H*-tetrazoles were synthesized through [3+2] cycloaddition reactions between nitriles RCN and NaN_3 in the presence of Cu–Zn alloy nanopowder as catalyst. The 1,5-dibutyl, 1-butyl-5-hexyl, 2,5-dibutyl, and 2-butyl-5-hexyl derivatives were then used as building blocks to synthesize several novel tetrazolium ionic liquids (ILs) with $EtSO_4^-$, OTf^-, and NTf_2^- counterions. Whereas alkylation of the 2,5-dialkyltetrazoles selectively gave the N-4 alkylated onium salts, with the 1,5-dialkyl derivatives approximately 1:1 mixtures of two tetrazolium salts were formed by alkylation at N-3 and N-4. The triflate and ethyl sulfate salts are room-temperature ILs that are hydrophilic, whereas the NTf_2 salts are low-melting ILs and are hydrophobic. The resulting tetrazolium-based ionic liquids were studied by various multinuclear and 2D NMR techniques including natural abundance ^{15}N and $^1H/^{15}N$ correlations.

Introduction

The 1*H*-tetrazole functional group is recognized as a highly versatile moiety in organic, organometallic, and medicinal chemistry.[1] With a high nitrogen content and low molecular weight, the tetrazole moiety – in particular its amino and nitro derivatives, and their derived onium salts – have become interesting targets for possible application in high-energy chemistry.[2]

Various methods for the synthesis both of 5-substituted and of 1-substituted 1*H*-tetrazoles have been developed. For the 1-substituted systems, treatment of primary amines with orthocarboxylic acid ester/sodium azide and employment of metallic triflates or imidazolium ionic liquids (ILs) are among the more recently reported methods.[3] In a recent study from this laboratory[4] we reported on the use of orthocarboxylic acid esters/$TMSN_3$ in Brønsted acidic ILs – namely $[EtNH_3][NO_3]$ and $[PMIM(SO_3H)][OTf]$ – for the facile construction of 1-substituted 1*H*-1,2,3,4-tetrazoles, with recycling and reuse of the ILs. [3+2] Cycloadditions between nitriles and azides constitute an efficient and widely used preparative method for the construction of 5-substituted-1*H*-tetrazoles. Since the 2001 paper by Demko and Sharpless on the use of $NaN_3/ZnBr_2$ in water,[5] several other preparative methods have been reported. These include $TMSN_3$/TBAF/solventless,[6] NaN_3/Zn/Al hydrotalcite/DMF,[7] $TMSN_3/Cu_2O$/DMF/MeOH,[8a] $TMSN_3/Me_3Al$/toluene/reflux,[8b] NaN_3/tungstates/DMF,[9] $TMSN_3$/iron salts/DMF,[10] and NaN_3/mesoporous ZnS nanospheres/HCl/DMF systems.[11] Application of a scalable high-temperature microreactor for the synthesis of 5-substituted 1*H*-tetrazoles in either a batch or a continuous flow system utilizing NaN_3/AcOH has also been reported.[12]

Although copper- and zinc-based molecular catalysts have been employed for decades in a wide variety of organic transformations, there has been intense recent research interest in their more efficient application in the nanoparticulate forms.[11,13] The utility of bimetallic catalysts has been demonstrated in important transformations such as Ullmann reactions (Cu–Zn nanocatalyst),[14] propargylation of ketones (Cu–Zn couple),[15] industrial methanol synthesis (ZnO supported Cu),[16] and in certain cross-coupling reactions (Cu–Ni–C).[17] The potential for synergic effects between two metals led us to explore the efficacy of bimetallic Cu–Zn nanoparticles in [3+2] cycloaddition reactions between nitriles and azides for the construction of 5-substituted 1*H*-tetrazoles.

In this two-part study we first report on a convenient, high-yielding synthesis of a host of 5-substituted 1*H*-tetrazoles through the employment of commercially available, cheap, Cu–Zn alloy nanopowder. This procedure offers easy product isolation and reuse of the catalyst. In the second part we report on the synthesis and characterization of a series of new tetrazole-based onium salts with OTf, $EtSO_4$, and NTf_2 counterions as room-temperature or low-melting ionic liquids.

A number of energetic tetrazolium salts with 3,5-dinitro-1,2,4-triazolate and other counterions have been reported in several recent papers by Shreeve et al., who used 5-ami-

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notetrazole as a key building block.[2] The focus of the current study was to exploit the widely applicable method for the preparation of the 5-substituted 1*H*-tetrazoles reported here in order to gain access to tetrazolium-based ILs that might find applications as catalysts and solvents in organic synthesis.

Results and Discussion

Synthesis of 5-Substituted 1H-Tetrazoles

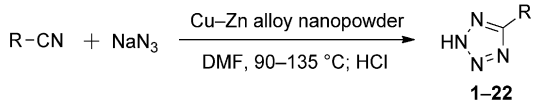
Initially, a comparative study focusing on the synthesis of 5-phenyltetrazole was carried out with use of three different heterogeneous catalysts – Cu–Sn alloy, Cu–Zn couple, and Cu–Zn alloy nanopowder – and NaN_3 in DMF at reflux (Table 1). The results indicated that Cu–Zn alloy was superior, providing higher isolated yields in shorter times and with smaller quantities of the catalysts. Recycling and reuse of the catalyst was also tested in two subsequent cycles and showed minimal decreases in the isolated yields (see Table 1). Under these conditions, NaN_3 was found to be superior to $TMSN_3$.

Table 1. Comparative study of catalysts for the synthesis of 5-phenyltetrazole.[a]

Entry	Catalyst	Azide source	Time [h]	Yield [%]
1	Cu–Sn alloy[b] (100 mg)	NaN_3	28	52
2	Cu–Zn couple[c] (100 mg)	NaN_3	20	78
3	Cu–Zn alloy[d] (100 mg)	NaN_3	10	89
4	Cu–Zn alloy[d] (50 mg)	NaN_3	10	92
5	Cu–Zn alloy[d] (38 mg)[e]	NaN_3	10	95 (92[f], 84[g])
6	Cu–Zn alloy[d] (38 mg)	$TMSN_3$	24	53

[a] Benzonitrile (2 mmol) + azide source (2.8 mmol) + catalyst (*x* mg) + DMF (6 mL) at 120 °C. [b] Bronze – spherical powder – 200 mesh (Product No. 520365, Aldrich). [c] Prepared by the reported procedure.[15] [d] Nanopowder, <150 nm particle size, 56–60% (Cu basis), 37–41% (Zn basis) (procured from Aldrich product No. 593583). [e] Further decreases in catalyst amount lowered the yields and increased the reaction times. [f, g] These yields correspond to the second and third runs, respectively, with the recycled catalyst.

On the basis of this survey study, the RCN/NaN_3/Cu–Zn alloy nanopowder/DMF system was selected as the method of choice (Scheme 1) for examination of the scope of this transformation (Table 2). Benzonitrile derivatives bearing a host of activating and deactivating substituents reacted efficiently, forming the corresponding 5-aryl-1*H*-tetrazoles with isolated yields in the 68–96% range (Table 2, Entries 2–8). With phthalonitrile, the isolated monotetrazole product reacted further under the same set of conditions to give the corresponding bis-tetrazole (Table 2, Entries 9 and 10). Tetrazole derivatives of bicyclic and polycyclic aromatics were synthesized conveniently by this method (Table 2, Entries 11–13). Representative heterocyclic aromatic tetrazoles were also prepared in respectable isolated yields (Table 2, Entries 14–16). Benzylnitrile reacted efficiently, allowing the synthesis of the 5-benzylic derivative (Table 2, Entry 17). In representative cases, aliphatic nitriles also reacted, but with heptanenitrile the isolated yield was lower (Table 2, Entries 18 and 19).[18] With *p*-aminobenzonitrile only a trace of the tetrazole was obtained (Table 2, Entry 20),[19] and with cyclohexanecarbonitrile and adamantane-1-carbonitrile the reactions did not proceed (Table 2, Entries 21 and 22). The reported yields for *o*-nitrobenzonitrile[1c,9,10] and *o*-methoxybenzonitrile[8b] do not indicate any noticeable drop in the levels of conversion due to steric effects, but a low yield reported for *o*-bromobenzonitrile[10] and the lack of reaction with cyclohexanecarbonitrile and adamantane-1-carbonitrile in this study do suggest that increased steric crowding can have a notable effect on the yields.

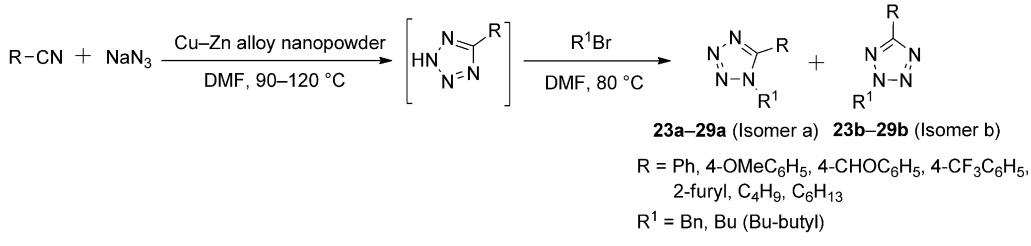


Scheme 1. Synthesis of 5-substituted tetrazoles catalyzed by Cu–Zn alloy nanopowder.

Synthesis of 1,5- and 2,5-Substituted Tetrazoles

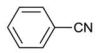
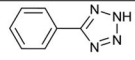
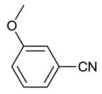
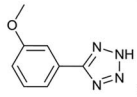
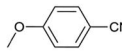
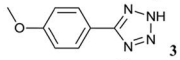
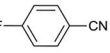
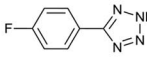
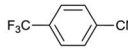
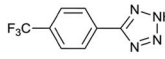
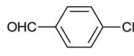
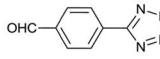
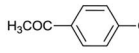
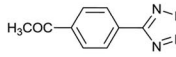
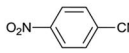
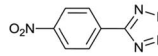
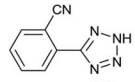
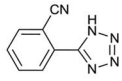
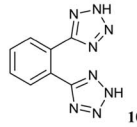
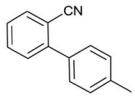
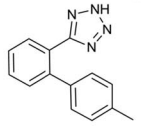
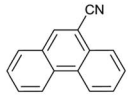
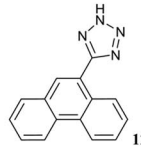
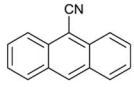
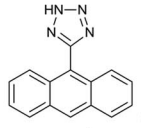
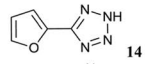
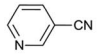
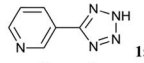
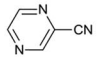
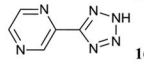
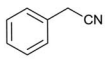
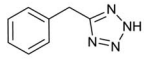
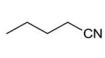
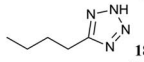
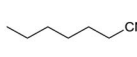
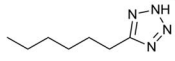
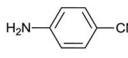
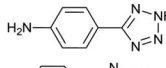
Treatment of 5-substituted 1*H*-tetrazoles, prepared in situ as shown in Scheme 2, with benzyl bromide or *n*-butyl bromide gave the corresponding 1,5- (isomers **a**) and 2,5-disubstituted (isomers **b**) derivatives as mixtures in which the **b** isomers were the major products. The highest percentage of an **a** isomer was obtained in the case of furanyltetrazole (Table 3, Entry 5).

Dialkylated tetrazole derivatives were also synthesized by treatment of the corresponding tetrazoles with Et_3N/*n*BuBr in acetonitrile as solvent (see Experimental Section and Table 3). The resulting isomeric dialkylated mixtures were



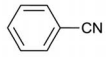
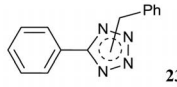
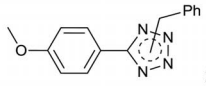
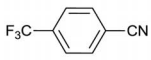
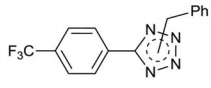
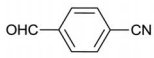
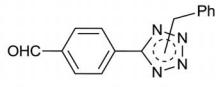
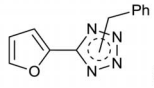
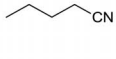
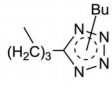
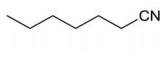
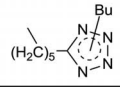
Scheme 2. One-pot syntheses of isomeric 1,5- and 2,5-disubstituted tetrazoles.

Table 2. Scope of [3+2] cycloaddition reactions between nitriles and NaN_3 catalyzed by Cu–Zn alloy nanopowder.

Entry	Nitrile	Tetrazole	*T* [°C]	Time [h]	M.p. [°C]	Yield [%]
1		 **1**	120	10	215–216	95
2		 **2**	120	9	158	89
3		 **3**	120	11	230–232	90
4		 **4**	130	15	191–192	68
5		 **5**	100	10	220–221	93
6		 **6**	120	10	184–185	91
7		 **7**	120	8	171–173	77
8		 **8**	100	7	217	96
9		 **9**	120	12	220–221	75[a]
10		 **10**	120	11	226–229	88
11		 **11**	135	37	151	82
12		 **12**	135	29	239–241	78
13		 **13**	135	35	270–271	14
14		 **14**	90	2	206–208	92
15		 **15**	110	12	241–242	72
16		 **16**	120	3	187–188	81
17		 **17**	120	22	124–125	80
18		 **18**	120	27	42	84
19		 **19**	120	36	oil	62
20		 **20**	–	–	–	trace
21		**21**	–	–		NR
22		**22**	–	–		NR

[a] A trace of bis-tetrazole derivative was formed with a 1:1 molar ratio of nitrile to sodium azide. An increase in the molar ratio of azide resulted in increased formation of the monotetrazole derivative with only 15% of the disubstitution product. NR – no reaction.

Table 3. One-pot syntheses of 1,5- (**a**) and 2,5-substituted (**b**) tetrazoles catalyzed by Cu–Zn alloy nanopowder.

Entry	Nitrile	RBr	Tetrazole (isomers **a** & **b**)	Isomer ratio **b/a**[a]	Time [h]	Overall yield of **b/a** [%]
1			 **23**	1:0.26	12.5	70/13
2			 **24**	1:0.27	14	65/14
3			 **25**	1:0.09	13	77/5
4			 **26**	1:0.20	13	64/10
5			 **27**	1:0.67	4.5	48/30
6		C_4H_9Br	 **28**	1:0.22[b]	30.5	51/11
7		C_4H_9Br	 **29**	1:0.33[c]	42	33/11

[a] Isomer ratio determined by GC–MS. [b] With NEt_3, isomers were formed in 1:0.57 ratio (relative yield: 62:34). [c] With NEt_3, isomers were formed in 1:0.73 ratio (relative yield: 52:38).

conveniently separated by conventional chromatography. In the ^{13}C NMR spectra the tetrazole ring carbons are very distinct, appearing at ca. 155 ppm in isomers **a** and at ca. 167 ppm in isomers **b**.

With the 1,5- and 2,5-disubstituted derivatives at hand we focused our attention on the synthesis of tetrazolium-based ionic liquids for possible application as catalysts and solvents in organic synthesis.

Synthesis of New Tetrazolium-Based Ionic Liquids

Four dialkyltetrazoles bearing aliphatic chains – 1,5-dibutyl- (**28a**, Scheme 3), 1-butyl-5-hexyl- (**29a**), 2,5-dibutyl- (**28b**), and 2-butyl-5-hexyltetrazole (**29b**) – were selected as building blocks for the synthesis of ionic liquids.

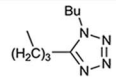
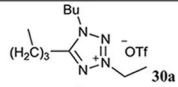
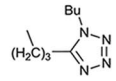
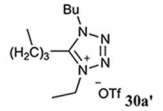
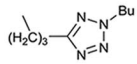
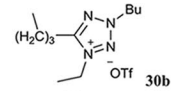
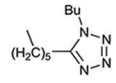
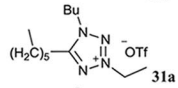
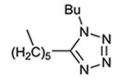
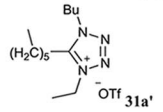
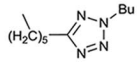
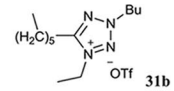
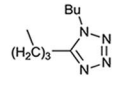
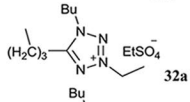
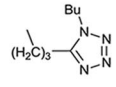
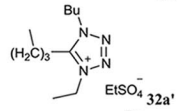
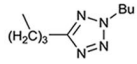
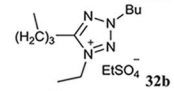
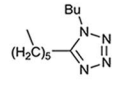
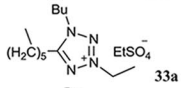
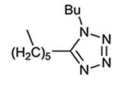
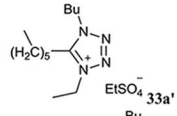
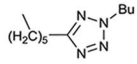
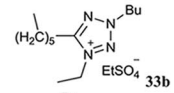
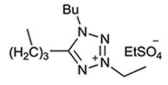
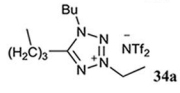
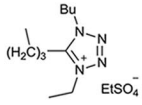
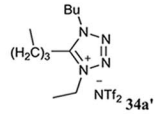
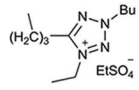
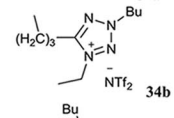
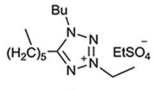
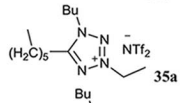
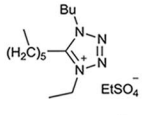
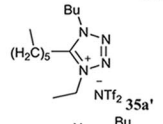
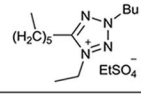
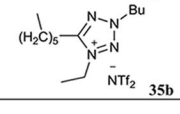
Whereas alkylation of the 2,5-dialkyltetrazoles selectively gave onium salts alkylated at N-4, with the 1,5-dialkyl derivatives almost 1:1 mixtures of two tetrazolium salts were formed by alkylation at N-3 and N-4 (Table 4). The triflate salts were prepared by treatment with EtOTf in DCM, whereas the ethyl sulfate salts were synthesized by alkylation with diethyl sulfate in toluene. Metathesis with $LiNTf_2$ furnished the corresponding NTf_2 salts. The triflate and ethyl sulfate salts were room-temperature ionic liquids, whereas the NTf_2 salts were low-melting ILs (see Experimental). As with most imidazolium and pyridinium ILs, the tetrazolium salts prepared in this study exhibit good solubility in acetonitrile, acetone, and dichloromethane (Table 5). The NTf_2 salts are hydrophobic and partially miscible with Et_2O, whereas the triflates and ethyl sulfate salts are hydrophilic and immiscible with Et_2O. These attributes make them promising as solvents/catalysts for organic synthesis, offering the possibility for simple workup procedures, in line with those of imidazolium ILs.

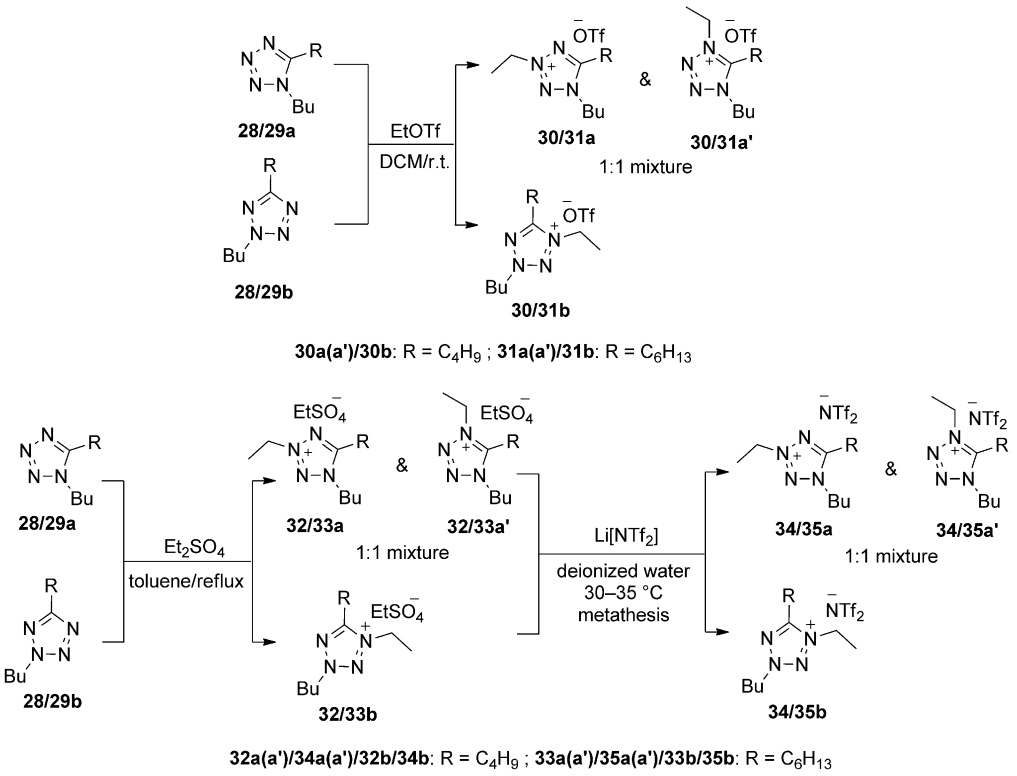
The ethyl sulfate salts **32a/32a′** (1:1) and the NTf_2 salts **34a/34a′** (1:1) were subjected to a detailed 2D NMR study (TOCSY, COSY, NOESY, HSQC, and HMBC – Figures S1–S7 in the Supporting Information) to allow specific assignment of the positions of the ethyl groups and the proton signals in the 1:1 mixtures (Tables S1 and S2 in the Supporting Information).

Formation of pairs of isomeric onium salts was further confirmed by ^{15}N NMR, which showed two sets of four nitrogen resonances (Table 6). Unambiguous assignment of the individual nitrogen resonances was achieved through the $^1H/^{15}N$ HMBC spectra (Figures S12/S13 and S25/S26 in the Supporting Information) recorded for compounds **28a/28b**, **32a/32a′**, and **32b** (HMBC correlations are given in Tables S3–S5 in the Supporting Information).

In the ^{15}N NMR spectrum of **32a/32a′** (Figure S18/Table S4 in the Supporting Information), one of the nitrogen signals (N-1) is buried under the signal from CD_3CN solvent. This was confirmed by re-recording the spectrum in $CDCl_3$ (Figure S19 in the Supporting Information). In the $^1H/^{15}N$ HMBC spectrum (Figure S25 in the Supporting Information) the nitrogen resonance at –91.73 ppm exhibited a strong cross-peak with the ethyl protons, whereas no such correlation was detected with either of the *n*-butyl groups

Table 4. Synthesis of tetrazolium-based ionic liquids.

Entry	Starting material	Counterion source	IL	Time [h]	Yield [%]
1		EtOTf	 **30a**	9	96
2		EtOTf	 **30a'**		
3		EtOTf	 **30b**	9	95
4		EtOTf	 **31a**	9	95
5		EtOTf	 **31a'**		
6		EtOTf	 **31b**	9	96
7		Et_2SO_4	 **32a**	6	77
8		Et_2SO_4	 **32a'**		
9		Et_2SO_4	 **32b**	6	79
10		Et_2SO_4	 **33a**	6	73
11		Et_2SO_4	 **33a'**		
12		Et_2SO_4	 **33b**	6	75
13		$LiNTf_2$	 **34a**	7	98
14		$LiNTf_2$	 **34a'**		
15		$LiNTf_2$	 **34b**	7	97
16		$LiNTf_2$	 **35a**	7	98
17		$LiNTf_2$	 **35a'**		
18		$LiNTf_2$	 **35b**	7	98



Scheme 3. Synthesis of isomeric 1,5- and 2,5-disubstituted tetrazole-based ionic liquids.

Table 5. Miscibilities of tetrazolium ILs in various solvents.[a]

Entry	Ionic liquid	Toluene	DCM	Hexane	Acetone	Acetonitrile	Water	Ether
1	**30a/a′** and **30b**	NM	M	NM	M	M	M	NM
2	**31a/a′** and **31b**	NM	M	NM	M	M	M	NM
3	**32aa′** and **32b**	NM	M	NM	M	M	M	NM
4	**33a/a′** and **33b**	NM	M	NM	M	M	M	NM
5	**34a/a′** and **34b**	M	M	NM	M	M	NM	PM
6	**35a/a′** and **35b**	M	M	NM	M	M	NM	PM

[a] M – miscible; NM – not miscible; PM – partially miscible.

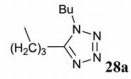
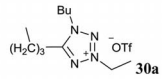
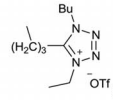
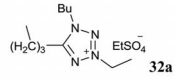
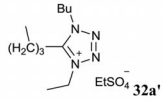
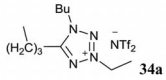
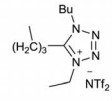
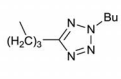
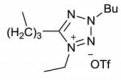
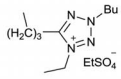
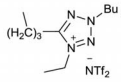
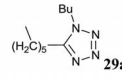
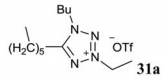
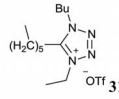
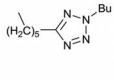
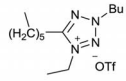
(of the major isomer). On this basis, this signal was assigned to N-3. In the other isomer, the signal at –135.02 ppm showed a strong cross-peak with the ethyl protons in addition to the *n*-butyl CH_2 group (attached directly to the ring carbon), so this nitrogen signal was assigned to N-4 (which bears the ethyl group). A clear trend of substituent effects on the ^{15}N NMR chemical shifts is observed in going from the dialkyltetrazole precursors to the *N*-ethylated salts (see Table 6). Except for N_1, which is somewhat deshielded, the $\Delta\delta^{15}N$ values exhibit an upfield trend in going from dialkyltetrazoles to the tetrazolium ILs (the upfield shifts in the ^{15}N values are most pronounced for the nitrogen atoms undergoing alkylation), whereas $\Delta\delta^{13}C$ values for the ring carbon remain relatively unchanged. Similar anion deshielding and cation shielding trends can be deduced from the ^{15}N NMR spectra of systems reported by Shreeve et al.[2f,2g,2h]

Electrospray mass spectra of the ILs in the positive ion mode showed intense signals for intact cations and relatively less intense cation/molecule cluster ions. In the negative ion mode, apart from the anions, observation of anion/molecule cluster ions was noteworthy.

Summary

The facile and quite general method for the synthesis of 5-substituted 1*H*-tetrazoles described above, together with the relatively straightforward syntheses of 1,5- and 2,5-dialkyl derivatives, provided the starting points for the synthesis of new tetrazolium-based ionic liquids with OTf, $EtSO_4$, and NTf_2 counterions. Natural-abundance ^{15}N NMR and $^1H/^{15}N$ 2D NMR correlations were successfully utilized to analyze the resulting tetrazolium ILs and for specific assignment of the nitrogen chemical shifts.

Table 6. ^{15}N (and ^{13}C) NMR chemical shifts for the tetrazole moiety in *N*-alkyltetrazoles and their ionic liquids.[a,b]

Entry	Compound	N_1 ($\Delta\delta^{15}N$)	N_2 ($\Delta\delta^{15}N$)	N_3 ($\Delta\delta^{15}N$)	N_4 ($\Delta\delta^{15}N$)	^{13}C of ring carbon
1	 **28a**	–147.02	–12.51	7.51	–55.8	154.86
2	 **30a**	–136.86 (10.16)	–20.31 (–7.8)	–91.39 (–98.9)	–69.96 (–14.16)	162.60
3	 **30a'**	–136.87 (10.15)	–16.96 (–4.45)	–17.66 (–25.17)	–134.90 (–79.1)	154.40
4	 **32a**	–137.30 (9.72)	–20.65 (–8.14)	–91.73 (–99.24)	–70.62 (–14.82)	162.62
5	 **32a'**	–136.72 (10.3)	–17.56 (–5.05)	–18.22 (–25.73)	–135.02 (–79.22)	154.52
6	 **34a**	–137.25 (9.77)	–20.24 (–7.73)	–91.24 (–98.75)	–69.77 (–13.97)	162.62
7	 **34a'**	–136.55 (10.47)	–16.71 (–4.2)	–17.44 (–24.95)	–134.92 (–79.12)	154.34
8	 **28b**	–81.65	–96.54	–1.68	–51.21	166.94
9	 **30b**	–69.40 (12.25)	–93.43 (3.11)	–20.24 (–18.56)	–135.19 (–83.98)	162.54
10	 **32b**	–69.87 (11.78)	–93.75 (2.79)	–20.45 (–18.77)	–135.16 (–83.95)	162.51
11	 **34b**	–69.28 (12.37)	–93.44 (3.1)	–20.25 (–18.57)	–135.49 (–84.28)	162.58
12	 **29a**	–147.24	–12.68	7.12	–56.17	154.79
13	 **31a**	–137.13 (10.11)	–20.45 (–7.77)	–91.51 (–98.63)	–70.11 (–13.94)	162.61
14	 **31a'**	–137.13 (10.11)	–17.08 (–4.44)	–17.78 (–24.9)	–135.02 (–78.85)	154.39
15	 **29b**	–80.96	–96.17	–0.45	–49.72	166.88
16	 **31b**	–69.23 (11.73)	–93.21 (2.96)	–20.14 (–19.69)	–135.09 (–85.37)	162.52

[a] $\Delta\delta^{15}N$ NMR values: cation minus neutral. [b] To the best of our knowledge the ^{15}N NMR chemical shift of NTf_2^- has not been reported. In the ^{15}N NMR spectrum of **34a**/**34a′** in CD_3CN (Figure S21 in the Supporting Information) and in $CDCl_3$ (Figure S22 in the Supporting Information) no signal attributable to the anion was detectable. For the tetrazolium salt **34b** (Figure S23 in the Supporting Information) the ^{15}N spectrum recorded in CD_3CN did not exhibit a signal for the anion, whereas in $CDCl_3$, (Figure S24 in the Supporting Information) a small peak at –243.07 was observed. This chemical shift is close to the reported value of –237.1 ppm for $(C_2F_5SO_2)_2N^-$.[27]

We plan to incorporate these ILs into our synthetic/mechanistic projects that continue to focus on electrophilic and onium ion chemistry in ILs.[4,20]

Experimental Section

General: The reagents employed were high-purity commercial samples and were used without further purification. Column chromatography was performed on silica gel (32–63 particle size). Melting points were recorded with a MEL-TEMP apparatus and are uncorrected. Both 1D and 2D NMR spectra were recorded in $CDCl_3$, CD_3CN, or [D_6]DMSO with a Varian INOVA 500 MHz instrument. Chemical shifts were referenced to internal solvent signals: ^1H at δ = 7.26 ppm/^{13}C at δ = 77.16 ppm for $CDCl_3$, ^1H at δ = 1.94 ppm/^{13}C at 1.32 and 118.26 ppm for CD_3CN, and ^1H at 2.50 ppm/^{13}C at δ = 39.52 ppm for [D_6]DMSO. ^{19}F spectra were referenced relative to external $CFCl_3$. The ^{15}N NMR spectra were recorded at 50.66 MHz with CD_3CN and $CDCl_3$ as solvents. Chemical shift values are referenced to external nitromethane (neat). IR spectra (solution) were obtained with a SHIMADZU FT-IR spectrophotometer. The IR and mass data for the new compounds are reported. GC–MS analyses were performed with a HP 5890 series II GC coupled to a HP 5972 series mass selective detector instrument. Electrospray mass spectra were recorded with a Bruker-Esquire system in both positive and negative ion modes. The designations C^+ (cation) and A^- (anion) are used in reporting of electrospray-MS data.

General Procedure for the Synthesis of 5-Substituted Tetrazoles (Compounds 1–22): Cu–Zn alloy nanopowder (38 mg) was added to a mixture of the nitrile (2 mmol) and sodium azide (2.8 mmol) in DMF (6 mL) and the mixture was stirred under ambient conditions for the specified time and temperature (Table 2, monitoring by TLC). After completion, the resulting mixture was allowed to cool to room temperature and the catalyst was separated by centrifugation and washed with ethyl acetate (three times). The resulting centrifugate was treated with HCl (5 N, 10 mL) and ethyl acetate (used to wash the catalyst) with stirring. The organic layer was separated and the aqueous solution left behind was extracted further with ethyl acetate. The combined organic extracts were washed with water and concentrated to furnish the desired tetrazole. Most of the compounds were obtained in pure form after simple trituration with hexane, whereas a few others were purified by column chromatography (32–63 particle size; hexane/ethyl acetate 1:1). In a representative case (Table 1), the recovered catalyst was reused in two successive runs without any significant decrease in the product yields.

5-Phenyltetrazole (1):[6] Yield 95% (0.27 g), white solid, m.p. 215–216 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 7.57–7.63 (m, 3 H), 8.01–8.03 (m, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 124.56, 127.41, 129.88, 131.71, 155.76 (br.) ppm.

5-(3-Methoxyphenyl)tetrazole (2):[6] Yield 89% (0.31 g), off-white solid, m.p. 158 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 3.83 (s, 3 H, –OCH_3), 7.19 (dd, J = 2.5 8.5 Hz, 1 H), 7.54 (t, J = 8.1 Hz, 1 H), 7.55–7.60 (m, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 55.81 (OCH_3), 111.82, 116.81, 119.43, 125.01, 131.12, 155.43 (br.), 159.70 ppm.

5-(4-Methoxyphenyl)tetrazole (3):[5] Yield 90% (0.32 g), white solid, m.p. 230–232 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 3.82 (s, 3 H, –OCH_3); 7.14 (d, J = 9.0 Hz, 2 H), 7.96 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 55.46 (OCH_3), 114.87, 116.29, 128.65, 154.72 (br.), 161.48 ppm.

5-(4-Fluorophenyl)tetrazole (4): Yield 68% (0.22 g), off-white solid, m.p. 191–192 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 7.46 (t, J = 9.0 Hz, 2 H), 8.08–8.10 (m, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]-DMSO): δ = 116.61 (d, J = 22.25 Hz), 128.66 (d, J = 4.25 Hz), 129.48 (d, J = 8.75 Hz), 154.79 (br.), 163.65 (d, J = 247.63 Hz, C–F) ppm. ^{19}F NMR (470.2 MHz, $CDCl_3$): δ = –109.62 (m) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2924, 1663, 1611, 1499, 1242, 1161 cm^{-1}. MS (EI): m/z (%) = 164 $[M]^+$, 136 (100) $[M - N_2]^+$, 121 $[M - HN_3]^+$, 109, 95 $[M$ – tetrazole$]^+$, 75, 57.

5-[4-(Trifluoromethyl)phenyl]tetrazole (5):[10] Yield 93% (0.39 g), white solid, m.p. 220–221 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 7.98 (d, J = 8.0 Hz, 2 H), 8.25 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 123.87 (q, J = 271 Hz, CF_3), 126.43 (q, J = 3.75 Hz), 127.79, 128.46, 130.99 (q, J = 31.94 Hz), 155.30 (br.) ppm. ^{19}F NMR (470.2 MHz, $CDCl_3$): δ = –61.58 (s) ppm.

4-(Tetrazol-5-yl)benzaldehyde (6):[21] Yield 91% (0.31 g), white solid, m.p. 184–185 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 8.11 (d, J = 8.0 Hz, 2 H), 8.24 (d, J = 8.0 Hz, 2 H), 10.08 (s, 1 H, –CHO) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 127.60, 129.53, 130.37, 137.60, 155.40 (br.), 192.69 (–CHO) ppm.

5-(4-Acetylphenyl)tetrazole (7):[6] Yield 77% (0.29 g), white solid, m.p. 171–173 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 2.64 (s, 3 H, –$COCH_3$), 8.14–8.19 (m, 4 H) ppm. ^{13}C NMR (125 MHz, [D_6]-DMSO): δ = 26.90 (CO*C*H_3), 127.20, 129.18, 130.15, 138.44, 155.31 (br.), 197.45 (*C*OCH_3) ppm.

5-(4-Nitrophenyl)tetrazole (8):[6] Yield 96% (0.37 g), yellow solid, m.p. 217 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 8.28 (d, J = 8.8 Hz, 2 H), 8.42 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 124.57, 128.17, 130.63, 148.71, 155.41 (br., *C*-N_4) ppm.

5-(2-Benzonitrile)tetrazole (9):[22] Yield 75% (0.26 g), white solid, m.p. 220–221 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 7.77 (dt, J = 1, 7.8 Hz, 1 H), 7.92 (dt, J = 1.2, 7.8 Hz, 1 H), 8.07 (t, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 110.69 (*C*–CN), 117.72 (C–*CN*), 128.05, 130.18, 131.86, 134.29, 135.43, 156.00 (br., *C*-N_4) ppm.

1,2-Bis(5-tetrazolyl)benzene (10):[5,22] Yield 88% (0.38 g), yellow solid, m.p. 226–229 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 7.80–7.83 (m, 2 H), 7.90–7.93 (m, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]-DMSO): δ = 124.55, 130.77, 131.34, 154.87 (br., *C*-N_4) ppm.

5-[2-(4′-Methyl)biphenyl]tetrazole (11):[6] Yield 82% (0.39 g), pale yellow solid, m.p. 151 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 2.30 (s, 3 H, –CH_3), 6.97 (d, J = 7.9 Hz, 2 H), 7.13 (d, J = 7.9 Hz, 2 H), 7.55 (t, J = 6.8 Hz, 2 H), 7.63–7.71 (m, 2 H) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 20.89 (CH_3), 123.33, 127.77, 128.69, 129.12, 130.86, 131.10, 131.29, 136.52, 137.10, 141.67, 155.12 (br., *C*-N_4) ppm.

5-(Phenanthren-9-yl)tetrazole (12):[23] Yield 78% (0.38 g), white solid, m.p. 239–241 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 7.76 (t, J = 7.5 Hz, 2 H), 7.84 (q, J = 8.3 Hz, 2 H), 8.13 (d, J = 8.0 Hz, 1 H), 8.37 (s, 1 H), 8.49 (d, J = 8.00 Hz, 1 H), 8.95 (d, J = 8.18 Hz, 1 H), 9.0 (d, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, [D_6]-DMSO): δ = 120.60, 123.14, 123.58, 125.95, 127.70, 127.73, 127.75, 128.31, 128.88, 129.41, 130.05, 130.20, 130.68, 155.13 (br., *C*-N_4, two coinciding carbon resonances) ppm.

5-(9-Anthryl)tetrazole (13):[23] Yield 14% (0.07 g), yellow solid, m.p. 270–271 °C. ^1H NMR (500 MHz, [D_6]DMSO): δ = 7.44 (d, J =

8.5 Hz, 2 H), 7.54–7.61 (m, 4 H), 8.22 (d, *J* = 8.5 Hz, 2 H), 8.91 (s, 1 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 118.08, 124.41, 125.87, 127.72, 128.77, 129.66, 130.39, 130.50, 152.54 (br., *C*-N$_4$) ppm.

5-(2-Furyl)tetrazole (14):[6] Yield 92% (0.25 g), off-white solid, m.p. 206–208 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.76 (dd, *J* = 2.0, 3.0 Hz, 1 H), 7.25 (dd, *J* = 0.5, 3.5 Hz, 1 H), 8.02 (dd, *J* = 0.5, 1.5 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 112.91, 113.43, 140.34, 146.53, 148.73 (br., *C*-N$_4$) ppm.

3-(Tetrazol-5-yl)pyridine (15):[6] Yield 72% (0.21 g), white solid, m.p. 241–242 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.64 (dd, *J* = 5.0, 8.0 Hz, 1 H), 8.39 (dt, *J* = 1.5, 8.0 Hz, 1 H), 8.76 (br. s, 1 H), 9.22 (br. s, 1 H) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ = 121.45, 124.38, 134.47, 147.60, 151.63, 154.46 (br., *C*-N$_4$) ppm.

2-(2*H*-tetrazol-5-yl)pyrazine (16):[5] Yield 81% (0.24 g), off-white solid, m.p. 187–188 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.88 (s, 2 H), 9.40 (s, 1 H) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ = 140.00, 143.39, 144.89, 146.83, 153.55 (br.) ppm.

5-Benzyltetrazole (17):[6] Yield 80% (0.26 g), white solid, m.p. 124–125 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 4.29 (s, 2 H, –*CH*$_2$Ph), 7.24–7.27 (m, 3 H), 7.32–7.35 (m, 2 H) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ = 28.91 (–*CH*$_2$Ph), 127.04, 128.67, 128.74, 136.00, 155.17 (br., *C*-N$_4$) ppm.

5-Butyltetrazole (18):[6] Yield 84% (0.21 g), white crystalline solid, m.p. 42 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.88 (t, *J* = 7.5 Hz, 3 H, –CH$_2$CH$_2$CH$_2$*CH*$_3$), 1.3 (sextet, *J* = 7.3 Hz, 2 H, –CH$_2$CH$_2$*CH*$_2$CH$_3$), 1.66 (quint., *J* = 7.5 Hz, 2 H, –CH$_2$*CH*$_2$CH$_2$CH$_3$), 2.86 (t, *J* = 7.5 Hz, 2 H, –*CH*$_2$CH$_2$-CH$_2$CH$_3$) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ = 13.48 (–CH$_2$CH$_2$CH$_2$*CH*$_3$), 21.51 (–CH$_2$CH$_2$*CH*$_2$CH$_3$), 22.36 (–CH$_2$*CH*$_2$CH$_2$CH$_3$), 29.09 (–*CH*$_2$CH$_2$CH$_2$CH$_3$), 155.73 (*C*-N$_4$) ppm.

5-Hexyltetrazole (19): Yield 62% (0.19 g), colorless oil, ^{1}H NMR (500 MHz, CDCl$_3$): δ = 0.84 (t, *J* = 7.0 Hz, 3 H, –CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$), 1.24–1.3 (m, 4 H, –CH$_2$CH$_2$*CH*$_2$-*CH*$_2$CH$_2$CH$_3$), 1.36–1.40 (m, 2 H, –CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_2$CH$_3$), 1.86 (quint., *J* = 7.5 Hz, 2 H, –CH$_2$*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.1 (t, *J* = 7.8 Hz, 2 H, –*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$) ppm. ^{13}C NMR (500 MHz, CDCl$_3$): δ = 14.06 (–CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$), 22.51 (–CH$_2$*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 23.60 (–CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_2$-CH$_3$), 27.76 (–*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 28.79 (–CH$_2$CH$_2$-*CH*$_2$CH$_2$CH$_2$CH$_3$), 31.34 (–CH$_2$CH$_2$CH$_2$*CH*$_2$CH$_2$CH$_3$), 157.08 (*C*-N$_4$) ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2957, 2928, 2859, 1668, 1559, 1460, 1254, 1057 cm^{-1}. MS (EI): *m*/*z* (%) = 111 [M – propyl]$^+$, 97 [M – butyl]$^+$, 84 [M – tetrazole]$^+$, 69 [M – hexyl]$^+$, 55 (100), 43, 39.

General Procedure for the Synthesis of 1,5- and 2,5-Disubstituted Tetrazoles (23a/23b to 29a/29b)

1) One-Pot Reaction Starting from a Nitrile: Cu–Zn alloy nanopowder (38 mg) was added to a mixture of a nitrile (2 mmol) and sodium azide (2.8 mmol) in DMF (6 mL) and the mixture was stirred at 90–120 °C until the TLC confirmed complete conversion of the nitrile. At that point the reaction mixture was allowed to cool to room temperature and benzyl bromide (1.2 equiv. relative to tetrazole product) or butyl bromide (1.2 equiv. relative to tetrazole product) was added. The contents were further stirred at 80 °C until completion (monitoring by TLC; see Table 3). After completion, the catalyst was separated off by centrifugation and washed with ethyl acetate (3 times). Water was added to the centrifugate and organics were extracted into ethyl acetate (three times). The combined organic extracts was then washed with water, hydrogencarbonate, and brine and dried with MgSO$_4$. The solvent was removed under reduced pressure to furnish the corresponding *N*-alkylated tetrazole as a mixture of two isomers. The individual isomers were conveniently separated by chromatography with hexane/ethyl acetate (1:0.5).

2) Starting from a Tetrazole: Compounds **28a/28b** and **29a/29b** can also be prepared by starting from the corresponding tetrazoles with use of NEt$_3$ as catalyst. Triethylamine (1 mmol) was added to the appropriate tetrazole **18** or **19** (2 mmol) in MeCN, and the reaction mixture was stirred initially for about half an hour. *n*BuBr [(2.1 mmol)] was then added dropwise with stirring at room temp. followed by reflux for 3 to 4 h. Upon completion of reaction, the resulting mixture was allowed to cool to room temp., poured into cold water, and extracted three times with ethyl acetate. The combined organic phase was washed with water and brine and dried with Na$_2$SO$_4$. Upon removal of solvent under reduced pressure the desired *N*-butyltetrazoles were isolated as isomeric mixtures, which were then separated as described above.

1-Benzyl-5-phenyltetrazole (23a):[24] Yield 13% (0.06 g), white microcrystals, m.p. 87–88 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.61 (s, 2 H, –CH$_2$), 7.14–7.16 (m, 2 H), 7.32–7.36 (m, 3 H), 7.48–7.51 (m, 2 H), 7.54–7.59 (m, 3 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 51.46 (CH$_2$), 123.88, 127.27, 128.87, 128.97, 129.29, 129.30, 131.45, 134.03, 154.81 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3063, 3032, 2918, 2849, 1472, 1454, 1402, 1107 cm^{-1}. MS (EI): *m*/*z* (%) = 236 [M]$^+$, 179, 91 (100) [C$_7$H$_7$]$^+$, 77, 65, 51.

2-Benzyl-5-phenyltetrazole (23b):[25] The literature did not provide NMR spectroscopic data. Yield 70% (0.33 g), white microcrystals, m.p. 61–62 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.81 (s, 2 H, –CH$_2$), 7.34–7.44 (m, 5 H), 7.45–7.50 (m, 3 H), 8.13–8.15 (m, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 56.95 (CH$_2$), 127.01, 127.50, 128.51, 128.98, 129.08, 129.15, 130.44, 133.50, 165.59 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3067, 3034, 1530, 1497, 1466, 1449, 1044, 1028 cm^{-1}. MS (EI): *m*/*z* (%) = 236 [M]$^+$, 207, 179 (100), 165, 91 [C$_7$H$_7$]$^+$, 77, 63, 51.

1-Benzyl-5-(4-methoxyphenyl)tetrazole (24a):[24] Yield 14% (0.07 g), white solid, m.p. 105–106 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.86 (s, 3 H, –OCH$_3$); 5.61 (s, 2 H, –CH$_2$), 6.99 (d, *J* = 8.8 Hz, 2 H), 7.15–7.17 (m, 2 H), 7.34–7.38 (m, 3 H), 7.54 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 51.39 (CH$_2$), 55.60 (OCH$_3$), 114.79, 115.86, 127.17, 128.84, 129.33, 130.50, 134.21, 154.66, 162.02 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2922, 2841, 1611, 1478, 1447, 1258, 1179, 1020 cm^{-1}. MS (EI): *m*/*z* (%) = 266 [M]$^+$, 224 [M – N$_3$]$^+$, 209, 195, 119 [M – BnN$_2$]$^+$, 91 (100) [C$_7$H$_7$]$^+$, 65.

2-Benzyl-5-(4-methoxyphenyl)tetrazole (24b): Yield 65% (0.35 g), spongy, white solid, m.p. 117–118 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.86 (s, 3 H, –OCH$_3$); 5.78 (s, 2 H, –CH$_2$), 6.98 (d, *J* = 8.8 Hz, 2 H), 7.34–7.42 (m, 5 H), 8.07 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 55.50 (CH$_2$), 56.84 (OCH$_3$), 114.37, 120.11, 128.49, 128.52, 129.03, 129.13, 133.61, 161.37, 165.48 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2924, 1614, 1466, 1254, 1028, 833 cm^{-1}. MS (EI): *m*/*z* (%) = 207, 180, 165, 103, 91 (100) [C$_7$H$_7$]$^+$, 77, 63, 50.

1-Benzyl-5-[4-(trifluoromethyl)phenyl]tetrazole (25a): Yield 5% (0.03 g), white solid, m.p. 103–104 °C. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 5.64 (s, 2 H, CH$_2$), 7.14–7.16 (m, 2 H), 7.36–7.38 (m, 3 H), 7.72 (d, *J* = 8.3 Hz, 2 H), 7.77 (d, *J* = 8.3 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 51.75 (CH$_2$), 123.56 (q, *J* = 271.7 Hz, –CF$_3$), 126.34 (q, *J* = 3.6 Hz), 127.16, 129.18, 129.50, 129.52, 133.45 (q, *J* = 32.4 Hz), 133.67, 153.72 (two coinciding car-

bon resonances) ppm. ^{19}F NMR (470.2 MHz, $CDCl_3$): δ = –63.17 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2922, 2851, 1449, 1425, 1323, 1171, 1123, 1067 cm^{-1}. MS (EI): *m/z* (%) = 304 $[M]^+$, 275, 248, 179, 91 (100) $[C_7H_7]^+$, 77, 65, 51.

2-Benzyl-5-[4-(trifluoromethyl)phenyl]tetrazole (25b): Yield 77% (0.47 g), white solid, m.p. 73–74 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.83 (s, 2 H, –CH_2), 7.36–7.45 (m, 5 H), 7.73 (d, *J* = 8.3 Hz, 2 H), 8.26 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 57.16 (CH_2), 124.01 (q, *J* = 270.3 Hz, –CF_3), 125.99 (q, *J* = 3.7 Hz), 127.31, 128.60, 129.23, 129.25, 130.87, 132.21 (q, *J* = 32.4 Hz), 133.22, 164.41 ppm. ^{19}F NMR (470.2 MHz, $CDCl_3$): δ = –62.90 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2924, 1545, 1427, 1323, 1167, 1125, 1067, 853 cm^{-1}. MS (EI): *m/z* (%) = 275, 248, 179, 91 (100) $[C_7H_7]^+$, 77, 65, 51.

4-(1-Benzyltetrazol-5-yl)benzaldehyde (26a): Yield 10% (0.05 g), white solid, m.p. 117–118 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.66 (s, 2 H, –CH_2), 7.14–7.16 (m, 2 H), 7.35–7.37 (m, 3 H), 7.78 (d, *J* = 8.3 Hz, 2 H), 8.01 (d, *J* = 8.6 Hz, 2 H), 10.10 (s, 1 H, –CHO) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 51.85 (CH_2), 127.22, 129.19, 129.50, 129.75, 130.29, 133.64, 138.13, 154.55 (br.), 191.20 (two coinciding carbon resonances, –CHO) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2922, 2851, 1703 (–C=O), 1614, 1449, 1206 cm^{-1}. MS (EI): *m/z* (%) = 264 $[M]^+$, 235 $[M – CHO]^+$, 208, 179, 130, 91 (100) $[C_7H_7]^+$, 77, 65, 51.

4-(2-Benzyltetrazol-5-yl)benzaldehyde (26b): Yield 64% (0.34 g), white solid, m.p. 239–241 °C (dec.). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.83 (s, 2 H, CH_2), 7.35–7.45 (m, 5 H), 7.99 (d, *J* = 8.5 Hz, 2 H), 8.32 (d, *J* = 8.5 Hz, 2 H), 10.07 (s, 1 H, –CHO) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 57.20 (CH_2), 127.55, 128.61, 129.23, 129.26, 130.33, 132.92, 133.18, 137.53, 164.52, 191.78 (–CHO) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3032, 2922, 2832, 1699 (–C=O), 1613, 1535, 1202, 835 cm^{-1}. MS (EI): *m/z* (%) = 235 $[M – CHO]^+$, 208, 178, 104, 91 (100) $[C_7H_7]^+$, 77, 63, 50.

1-Benzyl-5-(2-furyl)tetrazole (27a): Yield 30% (0.14 g), white solid, m.p. 86 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.87 (s, 2 H, –CH_2), 6.62 (dd, *J* = 1.80, 3.5 Hz, 1 H), 7.23 (dd, *J* = 0.7, 3.7 Hz, 1 H), 7.26–7.30 (m, 2 H), 7.31–7.35 (m, 3 H), 7.68 (dd, *J* = 0.7, 1.9 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.09 (CH_2), 112.58, 115.16, 127.75, 128.83, 129.13, 134.02, 139.63, 145.52, 146.47 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3134, 1620, 1518, 1456, 1445, 1223, 1163, 1009 cm^{-1}. MS (EI): *m/z* (%) = 226 $[M]^+$, 169, 141, 91 (100) $[C_7H_7]^+$, 77, 65, 53.

2-Benzyl-5-(2-furyl)tetrazole (27b):[26] The literature ref. did not provide characterization data. Yield 48% (0.22 g), pale red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.79 (s, 2 H, –CH_2), 6.54 (dd, *J* = 1.8, 3.5 Hz, 1 H), 7.11 (dd, *J* = 0.9, 3.55 Hz, 1 H), 7.34–7.42 (m, 5 H), 7.57 (dd, *J* = 0.8, 1.8 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 57.02 (CH_2), 111.53, 111.81, 128.56, 129.15, 133.16, 142.94, 144.36, 158.69 (two coinciding carbon resonances) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3131, 1630, 1514, 1499, 1456, 1431, 1227, 1179, 1003 cm^{-1}. MS (EI): *m/z* (%) = 226 $[M]^+$, 170, 141, 115, 91 (100) $[C_7H_7]^+$, 65, 53, 39.

1,5-Dibutyltetrazole (28a): Yield 11% (0.04 g), with NEt_3 as catalyst: Yield 34% (0.12 g), colorless liquid, ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3 H), 0.93 (t, *J* = 7.3 Hz, 3 H), 1.30–1.44 (m, 4 H), 1.74–1.88 (m, 4 H), 2.79 (t, *J* = 7.8 Hz, 2 H), 4.21 (t, *J* = 7.0 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 13.50, 13.68, 19.72, 22.32, 22.93, 29.26, 31.70, 46.78, 154.86 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2961, 2934, 2874, 1518, 1462, 1424, 1381, 1238, 1086 cm^{-1}. MS (EI): *m/z* (%) = 183 $[M + 1]^+$, 153 $[M – ethyl]^+$, 140 $[M – N_3]^+$, 125 $[M – butyl]^+$, 112, 84, 55, 41 (100).

2,5-Dibutyltetrazole (28b): Yield 51% (0.19 g), with NEt_3 as catalyst: Yield 62% (0.23 g), colorless liquid, ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90* (t, *J* = 7.0 Hz, 3 H), 0.91* (t, *J* = 7.0 Hz, 3 H), 1.28–1.40 (m, 4 H), 1.73** (quint., *J* = 8.2 Hz, 2 H), 1.94** (quint., *J* = 7.5 Hz, 2 H), 2.84 (t, *J* = 7.8 Hz, 2 H), 4.52 (t, *J* = 7.3 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 13.44, 13.78, 19.67, 22.30, 25.21, 30.26, 31.35, 52.66, 166.94 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2961, 2934, 2874, 1495, 1466, 1402, 1358, 1026 cm^{-1}. MS (EI): *m/z* (%) = 183 $[M + 1]^+$, 154 $[M – N_2]^+$, 111 (100) $[M – C_5H_{12}]^+$, 84, 57, 41. * Overlapping signals; ** partially resolved.

1-Butyl-5-hexyltetrazole (29a): Yield 11% (0.05 g), with NEt_3 as catalyst: Yield 38% (0.13 g), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82* (t, *J* = 7.0 Hz, 3 H), 0.90 (t, *J* = 7.5 Hz, 3 H), 1.23–1.37 (m, 8 H), 1.75 (quint., *J* = 7.7 Hz, 2 H), 1.82 (quint., *J* = 7.5 Hz, 2 H), 2.76 (t, *J* = 8 Hz, 2 H), 4.19 (t, *J* = 7.5 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 13.43, 13.97 19.66, 22.42, 23.17, 27.15, 28.80, 31.31, 31.64, 46.71, 154.79 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2959, 2932, 2872, 2860, 1518, 1462, 1464, 1092 cm^{-1}. MS (EI): *m/z* (%) = 211 $[M + 1]^+$, 153 $[M – butyl]^+$, 112, 85, 55, 41 (100). * Partially resolved.

2-Butyl-5-hexyltetrazole (29b): Yield 33% (0.14 g) [with NEt_3 as catalyst: Yield 52% (0.22 g)], colorless liquid, ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.3 Hz, 3 H), 0.91 (t, *J* = 7.3 Hz, 3 H), 1.24–1.35 (m, 8 H), 1.73 (quint., *J* = 7.5 Hz, 2 H), 1.90–1.96 (m, 2 H), 2.83 (t, *J* = 7.8 Hz, 2 H), 4.52 (t, *J* = 7.0 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, $CDCl_3$): δ = 13.43, 14.08, 19.66, 22.56, 25.51, 28.14, 28.86, 31.35, 31.49, 52.64, 166.88 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2959, 2930, 2872, 2860, 1495, 1466, 1358, 1026 cm^{-1}. MS (EI): *m/z* (%) = 211 $[M + 1]^+$, 167 $[M – propyl]^+$, 153 $[M – butyl]^+$, 139 $[M – pentyl]^+$, 112, 97, 69, 55, 41 (100).

General Procedure for the Synthesis of Tetrazolium Triflates (Table 4): Ethyl triflate (1.1 mmol) was slowly added under nitrogen to the appropriate 1,5- (**28a**, **29a**) and 2,5-disubstituted tetrazole (**28b**, **29b**) (1 mmol) in dry DCM with stirring at ambient temperature. Stirring was continued for about 9 h (a purple color developed after an hour and the color became more intense over time). Upon completion, the excess solvent was removed under reduced pressure, leaving behind the purple colored triflate salt as a resinous liquid. This was washed with toluene and dried under reduced pressure and in vacuo at 60 °C to furnish **30a/30b** and **31a/31b** salts as pale brown liquids (room-temperature ILs).

1,5-Dibutyl-3-ethyltetrazolium Triflate (30a) and 1,5-Dibutyl-4-ethyltetrazolium Triflate (30a′): Isomeric mixture (1:1). Yield 96% (0.35 g), pale brown liquid, ^{1}H NMR (500 MHz, CD_3CN): δ = 0.97 (t, *J* = 7.3 Hz, 6 H), 0.98 (t, *J* = 7.5 Hz, 6 H), 1.40–1.55 (m, 8 H), 1.61 (t, *J* = 7.3 Hz, 3 H), 1.65 (t, *J* = 7.3 Hz, 3 H), 1.63–1.70 (m, 2 H), 1.77–1.83 (m, 2 H), 1.91–2.00 (m, 4 H), 3.04 (t, *J* = 7.7 Hz, 2 H), 3.17 (t, *J* = 8.2 Hz, 2 H), 4.48 (t, *J* = 7.3 Hz, 2 H), 4.49 (t, *J* = 7.5 Hz, 2 H), 4.54 (q, *J* = 7.3 Hz, 2 H), 4.82 (q, *J* = 7.3 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.49, 13.63, 13.66, 13.68, 13.78, 13.99, 20.07, 20.14, 22.36, 22.54, 23.10, 23.76, 28.57, 28.81, 30.87, 31.11, 47.04, 51.06, 51.24, 53.92, 121.89 (q, *J* = 318.4 Hz, -CF_3), 154.40, 162.60 ppm. ^{19}F NMR (470.2 MHz, CD_3CN): δ = –79.37 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3422, 2967, 2878, 1466, 1262, 1225, 1161, 1030 cm^{-1}. MS (ESI+): *m/z* (%) = 571 [CA/C]$^+$, 211 (100) $[C]^+$, 155 $[M – butyl]^+$, 84. MS (ESI–): *m/z* (%) = 509 $[CA/A]^–$, 149 (100) $[A]^–$.

2,5-Dibutyl-4-ethyltetrazolium Triflate (30b): Yield 95% (0.34 g), pale brown liquid, ^{1}H NMR (500 MHz, CD_3CN): δ = 0.97 (t, *J* = 7.3 Hz, 3 H), 0.98 (t, *J* = 7.4 Hz, 3 H), 1.38–1.51 (m, 4 H), 1.59 (t, *J* = 7.2 Hz, 3 H), 1.78–1.84 (m, 2 H), 2.01–2.07 (m, 2 H), 3.03 (t, *J* = 7.7 Hz, 2 H), 4.54 (q, *J* = 7.3 Hz, 2 H), 4.78 (q, *J* = 7.2 Hz, 2

H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.52, 13.67, 13.77, 19.91, 22.56, 23.77, 28.46, 30.85, 47.26, 57.94, 121.43 (q, J = 317.9 Hz, $–CF_3$), 162.54 ppm. ^{19}F NMR (470.2 MHz, CD_3CN): δ = –79.43 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3414, 2967, 2880, 1535, 1470, 1279, 1242, 1225, 1167, 1030 cm^{-1}. MS (ESI+): *m*/*z* (%) = 571 [CA/C]$^+$, 211 [C]$^+$ (100), 155 [C – butyl]$^+$, 84. MS (ESI–): *m*/*z* (%) = 509 [CA/A]$^-$, 149 (100) [A]$^-$.

1-Butyl-3-ethyl-5-hexyltetrazolium Triflate (31a) and 1-Butyl-4-ethyl-5-hexyltetrazolium Triflate (31a′): Isomeric mixture (1:1). Yield 95% (0.37 g), brown liquid, ^{1}H NMR (500 MHz, CD_3CN): δ = 0.90 (t, J = J = 7.2 Hz, 3 H), 0.91 (t, J = J = 7.2 Hz, 3 H), 0.97 (t, J = 7.3 Hz, 3 H), 0.98 (t, J = 7.3 Hz, 3 H), 1.32–1.37 (m, 8 H), 1.42–1.51 (m, 8 H), 1.61 (t, J = 7.4 Hz, 3 H), 1.65 (t, J = 7.4 Hz, 3 H), 1.65–1.72 (m, 2 H), 1.82 (quint., J = 7.6 Hz, 2 H), 1.91–2.00 (m, 4 H), 3.03 (t, J = 7.7 Hz, 2 H), 3.16 (t, J = 8.3 Hz, 2 H), 4.48 (t, J = 7.5 Hz, 2 H), 4.49 (t, J = 7.5 Hz, 2 H), 4.54 (q, J = 7.4 Hz, 2 H), 4.81 (q, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.49, 13.63, 13.65, 13.99, 14.25, 14.28, 20.06, 20.13, 22.56, 23.08, 23.12, 24.01, 26.53, 26.88, 28.99, 29.48, 30.89, 31.12, 31.81, 31.89, 47.03, 51.06, 51.23, 53.91, 121.64 (q, J = 319.3 Hz, $–CF_3$), 154.39, 162.61 ppm. ^{19}F NMR (470.2 MHz, CD_3CN): δ = –79.44 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3408, 2963, 2936, 2876, 1533, 1464, 1275, 1225, 1163, 1030 cm^{-1}.

2-Butyl-4-ethyl-5-hexyltetrazolium Triflate (31b): Yield 96% (0.38 g), brown liquid, ^{1}H NMR (500 MHz, CD_3CN): δ = 0.91 (t, J = 7.1 Hz, 3 H), 0.97 (t, J = 7.8 Hz, 3 H), 1.32–1.37 (m, 4 H), 1.39–1.48 (m, 4 H), 1.58 (t, J = 7.4 Hz, 3 H), 1.82 (quint., J = 7.6 Hz, 2 H), 2.00–2.06 (m, 2 H), 3.02 (t, J = 7.7 Hz, 2 H), 4.53 (q, J = 7.3 Hz, 2 H), 4.78 (t, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.50, 13.69, 14.27, 19.88, 23.13, 23.99, 26.41, 28.99, 30.85, 31.88, 47.23, 57.92, 121.69 (q, J = 319.3 Hz, $–CF_3$), 162.52 ppm. ^{19}F NMR (470.2 MHz, CD_3CN): δ = –79.44 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3414, 2961, 2936, 2876, 1535, 1468, 1277, 1225, 1163, 1030 cm^{-1}.

General Procedure for the Synthesis of Tetrazolium Ethyl Sulfates (Table 4): Diethyl sulfate (1.2 mmol) was slowly added with stirring at ambient temperature to a solution of the appropriate 1,5- (**28a**, **29a**) or 2,5-disubstituted tetrazole (**28b**, **29b**) (1 mmol) in toluene, followed by stirring under reflux for about 8 h. Upon cooling to room temp. the corresponding tetrazolium salts separated out as insoluble liquids. They were further washed with toluene and dried under reduced pressure and in vacuo at 60 °C to furnish the onium salts **32a/32a′** (1:1 isomer mixture), **32b** and **33b** as room-temperature ILs.

1,5-Dibutyl-3-ethyltetrazolium Ethyl Sulfate (32a) and 1,5-Dibutyl-4-ethyltetrazolium Ethyl Sulfate (32a′): Isomeric mixture (1:1). Yield 77% (0.26 g), pale brown liquid, ^{1}H NMR (500 MHz, CD_3CN): δ = 0.98 (t, J = 7.3 Hz, 6 H), 0.99 (t, J = 7.3 Hz, 6 H), 1.20 (t, J = 7.2 Hz, 6 H), 1.42–1.55 (m, 8 H), 1.61–1.70 (m, 2 H), 1.62 (t, J = 7.3 Hz, 3 H), 1.66 (t, J = 7.3 Hz, 3 H), 1.78–1.84 (m, 2 H), 1.92–2.01 (m, 4 H), 3.05 (t, J = 7.7 Hz, 2 H), 3.20 (t, J = 8.2 Hz, 2 H), 3.91 (q, J = 7.2 Hz, 4 H), 4.50 (t, J = 7.6 Hz, 2 H), 4.51 (t, J = 7.5 Hz, 2 H), 4.55 (q, J = 7.2 Hz, 2 H), 4.82 (q, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.51, 13.66, 13.68, 13.71, 13.80, 13.99, 15.48, 20.1, 20.17, 22.45, 22.57, 23.13, 23.80, 28.58, 28.83, 30.88, 31.10, 47.06, 51.09, 51.28, 53.92, 63.98, 154.52, 162.62 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3433, 2963, 2938, 2876, 1535, 1466, 1242, 1167, 1017, 916 cm^{-1}. MS (ESI+): *m*/*z* (%) = 547 [CA/C]$^+$, 211 (100) [C]$^+$, 155 [C – butyl]$^+$, 84. MS (ESI–): *m*/*z* (%) = 125 [A]$^-$, 97 (100).

2,5-Dibutyl-4-ethyltetrazolium Ethyl Sulfate (32b): Yield 79% (0.27 g), pale brown liquid, ^{1}H NMR (500 MHz, CD_3CN): δ = 0.99 (t, J = 7.5 Hz, 3 H), 1.0 (t, J = 3.5, J = 7.6 Hz, 3 H), 1.24 (t, J = 7.0 Hz, 3 H), 1.42–1.55 (m, 4 H), 1.61 (t, J = 7.3 Hz, 3 H), 1.80–1.86 (m, 2 H), 2.03–2.09 (m, 2 H), 3.07 (t, J = 7.7 Hz, 2 H), 3.97 (q, J = 7.3 Hz, 2 H), 4.58 (q, J = 7.2 Hz, 2 H), 4.81 (t, J = 7.1 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.54, 13.67, 13.80, 15.37, 19.91, 22.56, 23.76, 28.42, 30.81, 47.25, 57.89, 64.55, 162.51 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3426, 2963, 2936, 2876, 1535, 1466, 1167, 1017, 916 cm^{-1}. MS (ESI+): *m*/*z* (%) = 547 [CA/C]$^+$, 211 (100) [C]$^+$, 155 [M – butyl]$^+$, 127, 84. MS (ESI–): *m*/*z* (%) = 125 [A]$^-$, 111, 97 (100).

1-Butyl-3-ethyl-5-hexyltetrazolium Ethyl Sulfate (33a) and 1-Butyl-4-ethyl-5-hexyltetrazolium Ethyl Sulfate (33a′): Isomeric mixture (1:1). Yield 73% (0.26 g), pale brown liquid, ^{1}H NMR (500 MHz, CD_3CN): δ = 0.93 (t, J = 7.1 Hz, 6 H), 0.99 (t, J = 7.4 Hz, 3 H), 1.0 (t, J = 7.3 Hz, 3 H), 1.21 (t, J = 7.1 Hz, 6 H), 1.34–1.39 (m, 8 H), 1.44–1.53 (m, 8 H), 1.63 (t, J = 7.3 Hz, 3 H), 1.68 (t, J = 7.3 Hz, 3 H), 1.67–1.73 (m, 2 H), 1.84 (quint., J = 7.6 Hz, 2 H), 1.94–2.03 (m, 4 H), 3.07 (t, J = 7.7 Hz, 2 H), 3.23 (t, J = 8.3 Hz, 2 H), 3.89 (q, J = 7.1 Hz, 4 H), 4.52 (q, J = 6.9 Hz, 4 H), 4.57 (q, J = 7.4 Hz, 2 H), 4.84 (q, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.49, 13.66, 13.69, 13.98, 14.27, 14.29, 15.50, 20.08, 20.15, 22.65, 23.09, 23.13, 24.04, 26.50, 26.87, 29.02, 29.50, 30.85, 31.09, 31.83, 31.90, 47.00, 51.03, 51.22, 53.85, 63.63 (two coinciding carbon resonances), 154.51, 162.59 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3408, 2959, 2934, 2874, 1535, 1466, 1246, 1225, 1167, 1020, 916 cm^{-1}.

2-Butyl-4-ethyl-5-hexyltetrazolium Ethyl Sulfate (33b): Yield 75% (0.27 g), pale brown liquid, ^{1}H NMR (500 MHz, CD_3CN): δ = 0.91 (t, J = 7.5 Hz, 3 H), 0.97 (t, J = 7.4 Hz, 3 H), 1.25 (t, J = 7.1 Hz, 3 H), 1.33–1.36 (m, 4 H), 1.41–1.48 (m, 4 H), 1.59 (t, J = 7.1 Hz, 3 H), 1.82 (quint., J = 7.7 Hz, 2 H), 2.04 (quint., J = 7.4 Hz, 2 H), 3.03 (t, J = 7.6 Hz, 2 H), 4.02 (q, J = 7.1 Hz, 2 H), 4.55 (q, J = 7.3 Hz, 2 H), 4.78 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.53, 13.69, 14.29, 15.26, 19.90, 23.13, 24.01, 26.38, 29.00, 30.82, 31.89, 47.25, 57.91, 65.45, 162.52 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3406, 2959, 2934, 2874, 1535, 1462, 1234, 1161, 1044, 860 cm^{-1}.

General Procedure for the Synthesis of Tetrazolium Bis(trifluoromethanesulfonyl)imides (Table 4): The metathesis reaction was carried out by addition of an aqueous solution of Li[NTf_2] (1 mmol in 8 mL of deionized H_2O) to an aqueous solution of the appropriate tetrazolium ethyl sulfate **32a/32a′**, **32b**, **33a/33a′**, or **33b** (1 mmol, 8 mL of deionized H_2O) and stirred at 30–35 °C. Upon completion (turbid solution turns to clear, 7–8 h), the onium salts **34a/34a′**, **34b**, **35a/35a′**, and **35b** separated as sticky semi-solids. After repeated washing with water, the salts were dissolved in toluene or MeCN and evaporated to remove the last traces of water. Final vacuum drying at 80 °C gave colorless semi-solids upon standing at room temperature.

1,5-Dibutyl-3-ethyltetrazolium Bis(trifluoromethanesulfonyl)imide (34a) and 1,5-Dibutyl-4-ethyltetrazolium Bis(trifluoromethanesulfonyl)imide (34a′): Isomeric mixture (1:1): Yield 98% (0.48 g), colorless semi-solid, m.p. 60 °C. ^{1}H NMR (500 MHz, CD_3CN): δ = 0.97 (t, J = 7.3 Hz, 6 H), 0.98 (t, J = 7.3 Hz, 6 H), 1.41–1.55 (m, 8 H), 1.61 (t, J = 7.3 Hz, 3 H), 1.66 (t, J = 7.3 Hz, 3 H), 1.61–1.70 (m, 2 H), 1.77–1.84 (m, 2 H), 1.91–2.00 (m, 4 H), 3.03 (t, J = 7.7 Hz, 2 H), 3.14 (t, J = 8.3 Hz, 2 H), 4.47 (t, J = 7.6 Hz, 2 H), 4.48 (t, J = 7.4 Hz, 2 H), 4.53 (q, J = 7.3 Hz, 2 H), 4.81 (q, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.53, 13.60, 13.63, 13.65, 13.76, 14.03, 20.07, 20.14, 22.32, 22.54, 23.12, 23.76, 28.61, 28.83, 30.93, 31.15, 47.08, 51.11, 51.27, 53.98, 120.94 (q, J = 318.4 Hz, $–CF_3$), 154.34, 162.62 ppm. ^{19}F NMR (470.2 MHz,

CD_3CN): δ = –80.17 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2967, 2940, 2880, 1533, 1468, 1348, 1186, 1136, 1055 cm^{-1}.

2,5-Dibutyl-4-ethyltetrazolium Bis(trifluoromethanesulfonyl)imide (34b): Yield 97% (0.47 g), colorless semi-solid, m.p. 32 °C. ^1H NMR (500 MHz, CD_3CN): δ = 0.97 (t, J = 7.5 Hz, 3 H), 0.98 (t, J = 7.3 Hz, 3 H), 1.40–1.53 (m, 4 H), 1.59 (t, J = 7.3 Hz, 3 H), 1.78–1.84 (m, 2 H), 2.01–2.07 (m, 2 H), 3.03 (t, J = 7.7 Hz, 2 H), 4.53 (q, J = 7.2 Hz, 2 H), 4.78 (q, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.52, 13.72, 13.77, 19.93, 22.57, 23.79, 28.50, 30.88, 47.31, 58.02, 120.98 (q, J = 319.4 Hz, $–CF_3$), 162.58 ppm. ^{19}F NMR (470.2 MHz, CD_3CN): δ = –80.13 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2963, 2936, 2876, 1533, 1468, 1351, 1186, 1136, 1057 cm^{-1}.

1-Butyl-3-ethyl-5-hexyltetrazolium Bis(trifluoromethanesulfonyl)-imide (35a) and 1-Butyl-4-ethyl-5-hexyltetrazolium Bis(trifluoromethanesulfonyl)imide (35a′): Isomeric mixture (1:1): Yield 98% (0.51 gm), colorless semi-solid, m.p. 45 °C. ^1H NMR (500 MHz, CD_3CN): δ = 0.91 (t, J = 7.1 Hz, 3 H), 0.92 (t, J = 7.1 Hz, 3 H), 0.98 (t, J = 7.5 Hz, 3 H), 0.99 (t, J = 7.5 Hz, 3 H), 1.32–1.37 (m, 8 H), 1.43–1.51 (m, 8 H), 1.61 (t, J = 7.2, 3 H), 1.66 (t, J = 7.4 Hz, 3 H), 1.65–1.70 (m, 2 H), 1.82 (quint., J = 7.6 Hz, 2 H), 1.91–2.00 (m, 4 H), 3.03 (t, J = 7.6 Hz, 2 H), 3.14 (t, J = 8.3 Hz, 2 H), 4.48 (t, J = 7.5 Hz, 2 H), 4.49 (t, J = 7.5 Hz, 2 H), 4.53 (q, J = 7.2 Hz, 2 H), 4.82 (q, J = 7.3 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.52, 13.62, 13.65, 14.03, 14.26, 14.29, 20.08, 20.15, 22.55, 23.10, 23.14, 24.04, 26.56, 26.92, 29.01, 29.52, 30.93, 31.18, 31.81, 31.90, 47.10, 51.13, 51.29, 53.99, 120.96 (q, J = 318.9 Hz, $–CF_3$), 154.37, 162.66 ppm. ^{19}F NMR (470.2 MHz, CD_3CN): δ = –80.12 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2963, 2936, 2876, 1466, 1351, 1188, 1136, 1057 cm^{-1}. MS (ESI+): m/z (%) = 757 $[CA/C]^+$, 239 (100) $[C]^+$, 183 [C – butyl]$^+$, 155. MS (ESI–): m/z (%) = 799 ($[C]^+$ and 2$[A]^-$), 280 (100) $[A]^-$.

2-Butyl-4-ethyl-5-hexyltetrazolium Bis(trifluoromethanesulfonyl)-imide (35b): Yield 98% (0.51 g), colorless semi-solid, m.p. 36 °C. ^1H NMR (500 MHz, CD_3CN): δ = 0.91 (t, J = 7.1 Hz, 3 H), 0.97 (t, J = 7.5 Hz, 3 H), 1.32–1.37 (m, 4 H), 1.39–1.48 (m, 4 H), 1.58 (t, J = 7.2 Hz, 3 H), 1.82 (quint., J = 7.4 Hz, 2 H), 2.00–2.06 (m, 2 H), 3.02 (t, J = 7.7 Hz, 2 H), 4.52 (q, J = 7.3 Hz, 2 H), 4.78 (t, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (500 MHz, CD_3CN): δ = 13.49, 13.72, 14.26, 19.88, 23.13, 23.98, 26.43, 28.99, 30.86, 31.87, 47.24, 57.96, 120.93 (q, J = 318.8 Hz, -CF_3), 162.53 ppm. ^{19}F NMR (470.2 MHz, CD_3CN): δ = –80.19 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2963, 2936, 2876, 1533, 1468, 1348, 1186, 1136, 1055 cm^{-1}. MS (ESI+): m/z (%) = 757 $[CA/C]^+$, 239 $[C]^+$ (100), 183 [C – butyl]$^+$, 155. MS (ESI–): m/z (%) = 799 ($[C]^+$ and 2$[A]^-$), 280 (100) $[A]^-$.

Supporting Information (see footnote on the first page of this article): NMR spectra and the 2D NMR correlations for representative compounds.

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[18] Acetonitrile and propionitrile did not react. Similar results (<5% conversion) with propionitrile and isopropyl nitrile in the presence of tungstates were reported in ref.[9]

[19] Similar results were reported previously (see ref.[21]) for *p*-amino- and *o*-aminobenzonitrile in the presence of NaN_3/montmorillonitrile K-10 or kaolin.

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