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Azolium Salts Functionalized with Cyanomethyl, Vinyl, or Propargyl Substituents and Dicyanamide, Dinitramide, Perchlorate and Nitrate Anions

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A series of functionalized imidazolium and 1,2,4-triazolium salts with cyanomethyl, vinyl and propargyl substituents coupled with energetic anions, viz., perchlorate, nitrate, dicyanamide and dinitramide were prepared and characterized by NMR and IR spectroscopy, and elemental analyses. Since some melt < 100 °C, they can be classed as ionic liquids. Their densities range between 1.25–1.76 g cm^{-3}. The standard enthalpies of formation of the salts were calculated by using the computationally feasible DFT(B3LYP) and MP2 methods in conjunction with an empirical approach based on calculated densities of the salts. These values range from $\Delta H°_f$ = –56 (**12a**) to 851 (**21c**) kJ mol^{-1}. Of the salts synthesized, the dicyanamides exhibit the highest positive heats of formation, but also the lowest densities.

Introduction

Ionic liquids have been extensively studied, e.g., as novel solvents,[1] in separation processes,[2] in electrochemistry,[3] and as lubricants.[4] The introduction of functional groups into the azolium cation modifies the properties of the salt which enables the enhancement of certain characteristics which may be tailored to particular applications.[1g–1i]

Syntheses of energetic materials continue to attract considerable interest. Salt-based energetic materials often possess some advantage over molecular compounds since they tend to have lower vapor pressures and higher densities.[5–7] Many new members of heterocyclic-based energetic, low-melting salt families have been reported. Theoretical calculations of enthalpies of formation of salts, based on the heats of formation of cation, anion, and lattice energy, show that when ΔH_f for analogous species with various functional groups are determined, the values decrease CN > NO_2 > NH_2 > H.[8a–8d] Initially, this appears to suggest that introduction of the nitrile moiety would give rise to the most energetic species, i.e., a compound with the highest detonation pressure and velocity. However, nearly invariably and not surprisingly, the density of the nitrile is less than that of the nitro or amino-substituted salt and thus detonation properties are diminished given that the detonation pressure is dependent on the square of the density and detonation velocity is proportional to the density. Calculations show that $\Delta H°_f$ for the vinyl group is also slightly higher than that of hydrogen; $\Delta H°_f$ for ethylene is 52.4 kJ mol^{-1}; and $\Delta H°_f$ for acetylene is 226.7 kJ mol^{-1}.[8d] Therefore, $\Delta H°_f$ for propargyl is expected to be higher than vinyl.

This paper describes the synthesis and characterization of a series of azolium salts with cyanomethyl-, vinyl- and propargyl-substituted imidazolium and 1,2,4-triazolium cations coupled with energetic inorganic anions – nitrate, perchlorate, dicyanamide and dinitramide. Their thermal properties were determined and the standard enthalpies of formation calculated.

Results and Discussion

1-Substituted 1,2,4-triazoles, **1**, **2**, and **19**, were obtained by reacting sodium triazolate with methyl iodide, chloroacetonitrile and propargyl bromide. The remaining starting materials, 4-amino triazole, 1-vinyl imidazole, 1-methyl imidazole, 1-methyl triazole are commercially available. Compounds **3**, **4**, **7**, **9**, **10**, **11**, **15**, **16**, and **20** were obtained via quaternization reactions between the azole and the corresponding halide. These were then metathesized with silver nitrate, silver perchlorate, silver dicyanamide[9] or silver dinitramide[10] to give salts **5**, **6**, **8**, **12**, **13**, **14**, **17**, **18**, or **21** (Scheme 1).

Phase-transition temperatures (midpoints of melting points, T_m, or glass transition temperature, T_g) for all the salts were determined using differential scanning calorimetry (DSC) (Table 1). Most of the phase-transition temperatures are lower than 100 °C, and some of the salts are room temperature ionic liquids. With a common cation, phase-transition temperatures recorded for perchlorates > nitrates (with the exception of **8** and **12**) > dicyanamides > dinitra-

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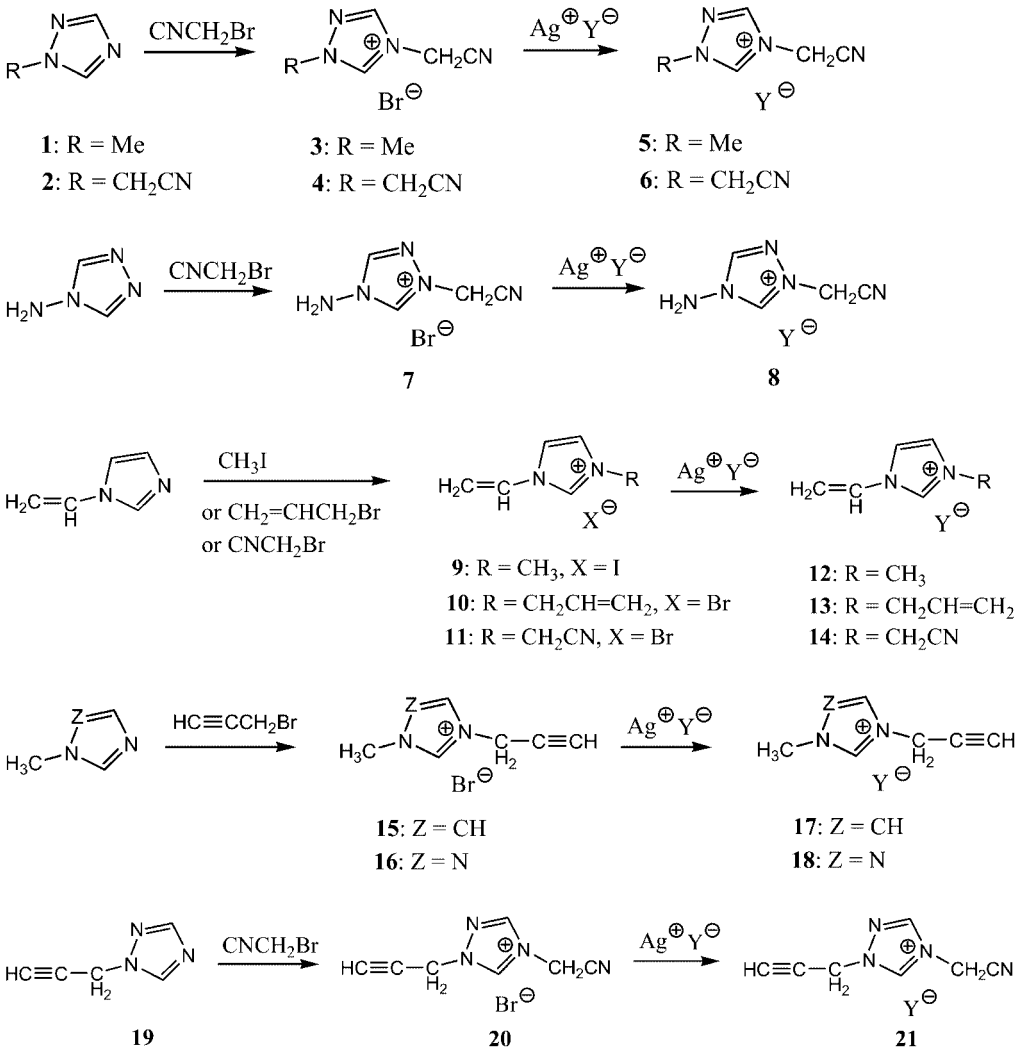


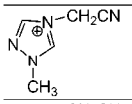
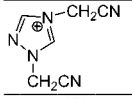
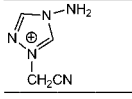
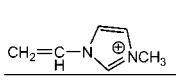
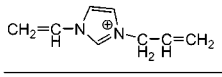
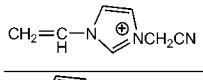
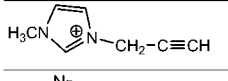
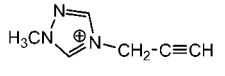
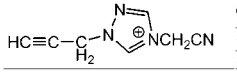
Scheme 1.

mides (with the exception of **8** and **17**). Invariably the perchlorate salts are the most thermally stable, sometimes by > 100 °C and with thermal decomposition temperatures ≥ 200 °C. Comparing compounds **5**, **6**, and **8** that have common anions, the melting points or phase transition points (T_m/T_g) of the triazolium salts substituted with two cyanomethyl ($CNCH_2$-) groups were highest (**6a**–**d**). When the substituents were one $CNCH_2$– group and 1-methyl (**5a**–**d**) or 4-amino (**8a**–**d**), the T_m/T_g decreased, and the latter two sets were similar (except **8b**). For vinyl imidazolium salts, **14a**–**d** with a $CNCH_2$– substituent exhibit the highest T_m/T_g followed by the salts with a methyl group (**12a**, **d**), and finally the allyl-substituted salts (except **12b**). Similar relationships were observed for propargyl-substituted salts **18** and **21**.

When comparing densities, it is seen that the 1-methylcyano-4-aminotriazolium salts (**8a**–**d**) exhibit the highest values, from perchlorate (1.76 g cm^{-3}) to dicyanamide (1.43 g cm^{-3}).[11–13] Not surprisingly, the presence of the amino-substituted cation with its enhanced proclivity to form hydrogen bonds gives rise to higher density followed by $CNCH_2^- > CH_3$. Similar ordering is observed in moving from **14a**–**d** > **12a**,**b**,**d** > **13a**–**d** as the cation substituent changes from $CNCH_2^-$ to CH_3 to allyl. Densities of **21a**–**c** exceed those of **18a**–**d** due to the presence of the dicyanomethyl vis-à-vis methyl. The densities of **18a**–**d** > **17a**–**d** because, in general, the densities of triazolium salts are higher than imidazolium. Regardless of the cation, with few exceptions, the density order is $ClO_4^- > N(NO_2)_2^- > NO_3^- > N(CN)_2^-$.

One of the purposes of this work is to compare the energetic properties of salts that contain the dicyanamide anion with their dinitramide analogues. As predicted,[8] the calculated heats of formation for the dicyanamide salts are invariably more positive than those of the analogous dinitramide salts, and, in fact, the dicyanamides have values higher than any of their counterparts in this study followed by dinitramides > perchlorates > nitrates in each of the cation

Table 1. Properties of azolium salts.

Cation	Anion		T_m /°C	T_d[a] /°C	D[b] /g·cm^{-3}	? H_f[298][c] /kJ·mol^{-1}
	NO_3^-	**5a**	115	152	1.51	167
	ClO_4^-	**5b**	140	250	1.65	209
	$N(CN)_2^-$	**5c**	66	115	1.35	605
	$N(NO_2)_2^-$	**5d**	–45[d]	143	1.55	336
	NO_3^-	**6a**	133	135	1.53	359
	ClO_4^-	**6b**	147	220	1.66	400
	$N(CN)_2^-$	**6c**	114	114	1.39	796
	$N(NO_2)_2^-$	**6d**	–22[d]	141	1.57	526
	NO_3^-	**8a**	93	158	1.61	267
	ClO_4^-	**8b**	–23[d]	193	1.76	310
	$N(CN)_2^-$	**8c**	66	105	1.43	707
	$N(NO_2)_2^-$	**8d**	–41[d]	180	1.64	438
	NO_3^-	**12a**	70	155	1.41	–56
	ClO_4^-	**12b**	–63[d]	207	1.57	–14
	$N(NO_2)_2^-$	**12d**	50	145	1.47	113
	NO_3^-	**13a**	17	85	1.39	26
	ClO_4^-	**13b**	70	225	1.53	66
	$N(CN)_2^-$	**13c**	2[d]	168	1.27	462
	$N(NO_2)_2^-$	**13d**	–	127	1.45	191
	NO_3^-	**14a**	83	161	1.44	156
	ClO_4^-	**14b**	130	225	1.58	197
	$N(CN)_2^-$	**14c**	73	155	1.31	593
	$N(NO_2)_2^-$	**14d**	70	153	1.50	323
	NO_3^-	**17a**	63	180	1.38	104
	ClO_4^-	**17b**	74	221	1.52	144
	$N(CN)_2^-$	**17c**	17	131	1.25	540
	NO_3	**18a**	74	176	1.42	205
	ClO_4^-	**18b**	98	236	1.57	246
	$N(CN)_2^-$	**18c**	–54[d]	119	1.28	642
	$N(NO_3)_2$	**18d**	–59[d]	121	1.48	372
	NO_3^-	**21a**	112	134	1.45	415
	ClO_4^-	**21b**	125	139	1.59	455
	$N(CN)_2$	**21c**	–23[d]	101	1.32	851
	$N(NO_2)_2^-$	**21d**	–31[d]	136	1.50	581

[a] Thermal degradation. [b] Calculated density, references.[11–13] [c] Molar enthalpy of formation, calcd. [d] T_g.

families. As is usually the case, the nitrate salts have the lowest heats of formation.

However, the performance of energetic materials is measured by detonation pressure and detonation velocity where the former is dependent on the square of the density and the latter is proportional to the density.[14] Some of these values (based on the traditional Chapman–Jouget thermodynamic detonation theory) were obtained by using CHEETAH 4.0 (Table 2).[15]

As is shown in Table 1, the dicyanamide salts exhibit the lowest densities of the anion salts studied. The importance of density in performance is easily seen since in every case, while the dinitramide is more dense and exhibits a lower heat of formation than its dicyanamide counterpart, it displays an appreciably higher detonation pressure and velocity. It should be noted that **5d**, **6d**, **8d**, **18d**, and **21d** have performance characteristics resembling those of TNT. None of the dicyanamides approaches this value.

Comparing the heats of formation of **5**, **6**, and **8**, it can be seen that the $CNCH_2$– group contributes most, greater than NH_2 with the CH_3 substituent contributing least. From **12**–**14**, the order of the heats of formation is **14** > **13** > **12**, once again indicating that the $CNCH_2$-substituent contributes most, greater than allyl with CH_3– last. Based on **17**, **18**, and **21**, the results further indicate that the 1,2,4-triazolium cation contributes more positively to the heat of formation of a salt than imidazolium does, and again the $CNCH_2$– group is a stronger contributor than methyl.

Table 2. Comparison of detonation pressures and velocities for dicyanamide and dinitramide salts with common cations.[a]

Compd.	Anion	Detonation pressure[b]	Detonation velocity[c]
5c	$N(CN)_2^-$	11.60	6.21
5d	$N(NO)_2^-$	21.53	7.51
6c	$N(CN)_2^-$	11.64	6.21
6d	$N(NO)_2^-$	21.38	7.44
8c	$N(CN)_2^-$	14.83	6.88
8d	$N(NO)_2^-$	24.82	7.85
14c	$N(CN)_2^-$	9.27	5.65
14d	$N(NO)_2^-$	17.28	6.97
18c	$N(CN)_2^-$	10.05	5.89
18d	$N(NO)_2^-$	18.72	7.16
21c	$N(CN)_2^-$	10.16	5.90
21d	$N(NO)_2^-$	18.87	7.13

[a] TNT: 19.53 GPa, 6.88 m/s. [b] Detonation pressure, GPa. [c] Detonation velocity, m/s.

Thermochemistry

Computations were performed with the Gaussian 03 (Revision D.01) suite of programs.[16] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses are carried out by using B3LYP functional with 6-31+G** basis set,[17] and single energy points were calculated at the MP2(full)/6-311++G** level.[18,19] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Based on Born–Haber energy cycles, the heats of formation of an ionic salt can be simplified by the formula:

$$\Delta H_f^\circ \text{ (ionic salt, 298 K)} = \Delta H_f^\circ \text{ (cation, 298 K)} + \Delta H_f^\circ \text{ (anion, 298 K)} - \Delta H_L$$

where ΔH_L is the lattice energy of the ionic salt which can be predicted by the formula suggested by Jenkins[20] as:

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$$

where n_M and n_X depend on the nature of the ions M_p^+ and Xq^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form

$$U_{POT}/\text{kJ mol}^{-1} = \gamma\,(\rho_m/M_m)^{1/3} + \delta$$

where ρ_m [g/cm^3] density, M_m [g] is the chemical formula mass of the ionic material, and the coefficients γ [kJ/mol cm] and δ [kJ/mol] take the values from the literature.[20]

For NO_3^-, ClO_4^-, and $N(NO_2)_2^-$, the proton affinities (PA) were taken from literature results calculated by using the G2 or G3 method.[21] For $N(CN)_2^-$, the PA was calculated by using G2. The heats of formation of NO_3^-, ClO_4^-, $N(NO_2)_2^-$, and $N(CN)_2^-$ were calculated to be –308, –278, –162, and 113 kJ mol^{-1}, respectively. Thus with a common

cation, the heats of formation of these salts (positive to negative) is $N(CN)_2^- > N(NO_2)_2^- > ClO_4^- > NO_3^-$.

Conclusions

A series of imidazolium and 1,2,4-triazolium salts functionalized with vinyl, propargyl and cyanomethyl substituents and paired with nitrate, perchlorate, dicyanoamide, and dinitroamide anions have been prepared and characterized. Some of them melt at less than 100 °C and can be classified as ionic liquids. The densities of these salts range between 1.25–1.76 g cm^{-3} with those of the dicyanamides being the lowest. The heats of formation for these salts which were calculated with the Gaussian 03 (Revision D.01) suite of programs indicate that the dicyanamides have the highest values. However, they unfortunately show the least promise for useful applications since they have the lowest energetic performance characteristics which are primarily a function of density.

Experimental Section

Caution: While we have experienced no difficulties with shock and friction sensitivity of these compounds that have high nitrogen content and rather high heats of formation, they must be synthesized in mmol amounts and handled with extreme care.

General Methods: ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AMX 300) spectrometer operating at 300.1 and 75.5 MHz, respectively. Chemical shifts are reported in parts per million relative to the appropriate standard (Me_4Si for ^{1}H and ^{13}C NMR spectra). Phase-transition temperatures and decomposition temperatures were determined by using a differential scanning calorimeter (DSC, TA Instruments TA10) at a scan rate of 10 °C min^{-1}. IR spectra (BioRad FTS 3000 Excalibur series infrared spectrometer) were measured by using KBr pellets. Elemental analyses were carried out by using a CE-440 elemental analyzer (EAI Exeter Analytical). In some cases the experimental values for nitrogen are lower than the required values. This is sometimes observed for compounds with large amounts of nitrogen.

1-Substituted 1,2,4-triazoles, **1**, **2** and **19**, were obtained by reacting sodium triazolate with methyl iodide, chloroacetonitrile and propargyl bromide. The remaining starting materials, 4-aminotriazole, 1-vinylimidazole, 1-methylimidazole, 1-methyltriazole are commercially available. Compounds **3**, **4**, **7**, **9**, **10**, **11**, **15**, **16**, and **20** were obtained via quaternization reactions between the azole and the corresponding halide. These were then metathesized with silver nitrate, silver perchlorate, silver dicyanamide[9] or silver dinitramide[10] to give salts **5**, **6**, **8**, **12**, **13**, **14**, **17**, **18**, or **21**.

Sodium hydride (25 mmol, 1.00 g, 60% yield) in dry THF (40 mL) was added to a two-necked round-bottomed flask (100 mL) maintained under N_2 and containing a magnetic stir bar. 1,2,4-Triazole (25 mmol, 1.70 g) in THF (5 mL) was then added slowly to the stirring solution and the mixture was refluxed for 12 h and then cooled to room temp. Chloroacetonitrile (40 mmol, 3.12 g) was added and the mixture was refluxed for 12 h. Then the mixture was cooled to room temp. filtered. The filtrate was concentrated under vacuum then isolated by chromatography (silica gel column), eluted by hexane/ethyl acetate (80:20). The light brown solid **2** was obtained (1.9 g, 70% yield), T_m = 60 °C.

Sodium 1,2,4-triazolate (25 mmol) was prepared as above. Propargyl bromide (40 mmol, 4.72 g) was added and the mixture was refluxed for 12 h. Workup was similar to above. A light brown liquid **19** (1.6 g, 60% yield), ^{1}H NMR ($CHCl_3$): δ = 2.60 (t, J = 2.6 Hz, 1 H), 5.40 (d, J = 2.6 Hz, 2 H), 7.97 (s, 1 H), 8.30 (s, 1 H) ppm. ^{13}C NMR ($CHCl_3$): δ = 153.2, 143.6, 76.7, 75.8, 40.3 ppm.

A typical preparation of an iodide salt was to dissolve **1** (10 mmol, 0.83 g) and methyl iodide (20 mmol, 2.8 g) in ethyl acetate (5 mL) in a Pyrex glass tube (20 mL) that was subsequently evacuated, sealed, and stirred at 60 °C for 24 h. The precipitate was washed with ethyl acetate (3 × 5 mL) and dried under vacuum for 24 h to give the colorless solid 3-cyanomethyl-1-methyl-1,2,4-triazolium iodide (**3**) (1.8 g, 80% yield), T_m = 168 °C. IR (KBr): $\tilde{\nu}$ = 3062, 2953, 2906, 1580, 1402, 1227, 1163, 1070 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 4.22 (s, 3 H), 5.67 (s, 2 H), 9.10 (s, 1 H), 10.10 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 145.7, 144.4, 114.2, 40.5, 37.1 ppm. $C_5H_7BrN_4$ (203.04): calcd. C 29.58, H 3.47, N 27.59; found C 29.53, H 3.33, N 26.80.

1,4-Bis(cyanomethyl)-1,2,4-triazolium Bromide (4): 1.6 g, 70% yield, grey solid; T_m = 184 °C. IR (KBr): $\tilde{\nu}$ = 3113, 2965, 2918, 1788, 1570, 1537, 1421, 1382, 1342, 1231, 1155, 1035, 1003 cm^{-1}. ^{1}H NMR (H_2O/D_2O): δ = 5.78 (s, 2 H), 5.89 (s, 2 H), 9.33 (s, 1 H), 10.50 (s, 1 H) ppm. ^{13}C NMR (H_2O/D_2O): δ = 146.2, 145.6, 113.4, 113.1, 41.4, 37.1 ppm. $C_6H_6BrN_5$ (228.05): calcd. C 31.60, H 2.65, N 30.71; found C 31.54, H 2.54, N 30.84.

1-Cyanomethyl-1,2,4-triazolium Bromide (7): 1.8 g, 90% yield, colorless solid; T_m = 102 °C. IR (KBr): $\tilde{\nu}$ = 3107, 2932, 2071, 1638, 1560, 1520, 1406, 1287, 1162, 1034, 998 cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): δ = 5.92 (s, 2 H), 7.22 (s, 2 H), 9.35 (s, 1 H), 10.37 (s, 1 H) ppm. ^{13}C NMR (DMSO): δ = 147.2, 145.3, 115.1, 41.7 ppm. $C_4H_6BrN_5$ (204.03): calcd. C 23.55, H 2.96, N 34.33; found C 23.45, H 2.86, N 34.43.

3-Methyl-1-vinylimidazolium Iodide (9):[22] 2.3 g, 96% yield, light yellow liquid, T_m = 75 °C.

3-Allyl-1-vinyl-imidazolium Bromide (10): 1.8 g, 85% yield, orange solid, T_m = 253 °C. IR (KBr): $\tilde{\nu}$ = 3124, 3065, 2994, 1651, 1549, 1423, 1370, 1308, 1172 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 4.97 (d, J = 6.2 Hz, 2 H), 5.33–5.49 (m, 3 H), 6.01 (dd, J = 2.7, J = 15.6 Hz, 1 H), 6.10 (tdd, J = 6.2, J = 10.3, J = 17.0 Hz, 1 H), 7.39 (dd, J = 8.7, J = 15.6 Hz, 1 H), 7.67 (t, J = 1.8 Hz, 1 H), 8.02 (t, J = 1.8 Hz, 1 H), 10.06 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 136.3, 131.5, 129.5, 123.7, 122.0, 120.6, 109.9, 52.4 ppm. $C_8H_{11}BrN_2$ (215.09): calcd. C 44.67, H 5.15, N 13.02; found C 44.40, H 5.03, N 12.34.

3-Cyanomethyl-1-vinylimidazolium Bromide (11): 1.5 g, 70% yield, colorless solid, T_m = 148 °C. IR (KBr): $\tilde{\nu}$ = 3103, 3063, 3034, 2983, 1647, 1555, 1406, 1177 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 5.53 (dd, J = 3.0, J = 8.7 Hz, 1 H), 5.55 (s, 2 H), 5.89 (dd, J = 3.0, J = 15.5 Hz, 1 H), 7.20 (dd, J = 8.7, J = 15.5 Hz, 1 H), 7.79 (t, J = 1.8 Hz, 1 H), 7.91 (t, J = 1.8 Hz, 1 H), 9.31 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 136.6, 128.9, 124.1, 121.4, 114.5, 111.9, 38.3 ppm. $C_7H_8BrN_3$ (214.06): calcd. C 39.28, H 3.77, N 19.63; found C 39.19, H 3.68, N 19.31.

1-Methyl-3-propargylimidazolium Bromide (15): 1.8 g, 90% yield, colorless solid, T_m = 68 °C. IR (KBr): $\tilde{\nu}$ = 3196, 3086, 2126, 1627, 1570, 1437, 1342, 1164 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 3.23 (t, J = 2.6 Hz, 1 H), 3.95 (s, 3 H), 5.33 (d, J = 2.6 Hz, 2 H), 7.63 (s, J = 1.8 Hz, 1 H), 7.72 (s, J = 1.8 Hz, 1 H), 9.54 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 137.6, 124.9, 122.9, 78.4, 75.9, 40.0, 37.1 ppm. $C_7H_9BrN_2$ (201.06): calcd. C 41.82, H 4.51, N 13.93; found C 41.31, H 4.50, N 13.42.

1-Methyl-4-propargyl-1,2,4-triazolium Bromide (16): 1.4 g, 70% yield, colorless solid, T_m = 201 °C. IR (KBr): $\tilde{\nu}$ = 3223, 3011, 2939, 1566, 1425, 1356, 1230, 1199, 1153 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 3.20 (t, J = 2.6 Hz, 1 H), 4.18 (s, 3 H), 5.25 (d, J = 2.6 Hz, 2 H), 8.99 (s, 1 H), 9.95 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 145.0, 143.4, 79.4, 74.5, 39.9, 39.1 ppm. $C_6H_8BrN_3$ (202.05): calcd. C 35.67, H 3.99, N 20.80; found C 35.83, H 3.86, N 20.19.

4-Cyanomethyl-1-propargyl-1,2,4-triazolium Bromide (20): 1.4 g, 62% yield, light brown solid, T_m = 179 °C. IR (KBr): $\tilde{\nu}$ = 3123, 2965, 2117, 1570, 1412, 1379, 1341, 1231, 1152, 1069 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 3.23 (t, J = 2.6 Hz, 1 H), 5.40 (d, J = 2.6 Hz, 2 H), 5.69 (s, 2 H), 9.18 (s, 1 H), 10.36 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 146.0, 144.3, 113.8, 80.0, 73.7, 43.9, 36.9 ppm. $C_7H_7BrN_4$ (227.06): calcd. C 37.03, H 3.11, N 24.67; found C 37.38, H 3.04, N 24.44.

All metathesis reactions were carried out by using halide salts (1 mmol) reacted with silver nitrate or silver perchlorate or silver dicyanoamide or silver dinitroamide (1 mmol) in water (10 mL) in a test tube (100 mL). The mixture was filtered, the water pumped off, and the remaining residue dried under vacuum at 40 °C for 24 h. The yields were essentially quantitative.

4-Cyanomethyl-1-methyl-1,2,4-triazolium Nitrate (5a): Colorless solid, T_m = 115 °C. IR (KBr): $\tilde{\nu}$ = 3059, 2952, 2395, 1761, 1580, 1380, 1163 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 4.21 (s, 3 H), 5.66 (s, 2 H), 9.09 (s, 1 H), 10.08 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 145.7, 144.4, 114.2, 40.4, 36.9 ppm. $C_5H_7N_5O_3$ (185.14): calcd. C 32.44, H 3.81, N 37.83; found C 32.46, H 3.67, N 38.01.

4-Cyanomethyl-1-methyl-1,2,4-triazolium Perchlorate (5b): Colorless solid, T_m = 140 °C. IR (KBr): $\tilde{\nu}$ = 3059, 2951, 2904, 1578, 1466, 1363, 1072 cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 4.12 (s, 3 H), 5.40 (s, 2 H), 8.81 (s, 1 H), 9.59 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]-acetone): δ = 145.2, 144.0, 113.7, 40.5, 37.0 ppm. $C_5H_7ClN_4O_4$ (222.59): calcd. C 26.98, H 3.17, N 25.17; found C 27.09, H 3.14, N 24.49.

4-Cyanomethyl-1-methyl-1,2,4-triazolium Dicyanamide (5c): Colorless solid, T_m = 66 °C. IR (KBr): $\tilde{\nu}$ = 3082, 3019, 2239, 2198, 2136, 1582, 1418, 1318, 1161, 1071 cm^{-1}. ^{1}H NMR ([D$_6$]acetonitrile): δ = 4.12 (s, 3 H), 5.47 (s, 2 H), 8.89 (s, 1 H), 9.82 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]acetonitrile): δ = 145.3, 144.1, 120.7, 113.8, 40.4, 37.0 ppm. $C_7H_7N_7$ (189.18): calcd. C 44.44, H 3.73, N 51.83; found C 43.88, H 3.65, N 49.59.

4-Cyanomethyl-1-methyl-1,2,4-triazolium Dinitramide (5d): Colorless liquid, T_g = –45 °C. IR (KBr): $\tilde{\nu}$ = 3091, 2997, 1584, 1518, 1434, 1182, 1013 cm^{-1}. ^{1}H NMR ([D$_6$]acetonitrile): δ = 4.11 (s, 3 H), 5.44 (s, 2 H), 8.87 (s, 1 H), 9.75 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]-acetonitrile): δ = 145.2, 144.1, 113.7, 40.3, 36.8 ppm. $C_5H_7N_7O_4$ (229.15): calcd. C 26.21, H 3.08, N 42.79; found C 25.45, H 2.85, N 42.92.

1,4-Bis(cyanomethyl)-1,2,4-triazolium Nitrate (6a): Colorless solid, T_m = 133 °C. IR (KBr): $\tilde{\nu}$ = 3101, 3003, 2957, 2378, 2264, 1755, 1574, 1355, 1073, 934 cm^{-1}. ^{1}H NMR (H_2O/D_2O): δ = 5.70 (s, 2 H), 5.82 (s, 2 H), 9.25 (s, 1 H), 10.44 (s, 1 H) ppm. ^{13}C NMR (H_2O/D_2O): δ = 146.1, 145.5, 113.3, 113.0, 41.1, 36.8 ppm. $C_6H_6N_6O_3$ (210.15): calcd. C 34.29, H 2.88, N 39.99; found C 34.46, H 2.70, N 39.83.

1,4-Bis(cyanomethyl)-1,2,4-triazolium Perchlorate (6b): Colorless solid, T_m = 147 °C. IR (KBr): $\tilde{\nu}$ = 3116, 2925, 2364, 1572, 1419, 1386, 1068 cm^{-1}. ^{1}H NMR ([D$_3$]acetone): δ = 5.93 (s, 2 H), 6.04 (s, 2 H), 9.51 (s, 1 H), 10.53 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetone): δ = 146.4, 146.3, 113.4, 112.9, 41.3, 37.2 ppm. $C_6H_6ClN_5O_4$ (247.61): calcd. C 29.11, H 2.44, N 28.29; found C 29.12, H 2.15, N 27.72.

1,4-Bis(cyanomethyl)-1,2,4-triazolium Dicyanamide (6c): Colorless solid, T_m = 114 °C. IR (KBr): $\tilde{\nu}$ = 3121, 2991, 2245, 2201, 2139, 1576, 1318, 1161, 1069 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 5.53 (s, 2 H), 5.64 (s, 2 H), 9.05 (s, 1 H), 10.09 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 146.1, 145.5, 120.6, 113.4, 113.0, 41.5, 37.3 ppm. $C_8H_6N_8$ (214.19): calcd. C 44.86, H 2.82, N 52.32; found C 44.43, H 3.01, N 51.98.

1,4-Bis(cyanomethyl)-1,2,4-triazolium Dinitramide (6d): Colorless liquid, T_g = –22 °C. IR (KBr): $\tilde{\nu}$ = 3135, 3080, 2997, 1578, 1518, 1433, 1337, 1179, 1015 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 5.56 (s, 2 H), 5.66 (s, 2 H), 9.06 (s, 1 H), 10.11 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 146.1, 145.7, 113.3, 112.9, 41.5, 37.2 ppm. $C_6H_6N_8O_4$ (254.16): calcd. C 28.35, H 2.38, N 44.09; found C 27.87, H 2.21, N 44.09.

4-Amino-1-cyanomethyl-1,2,4-triazolium Nitrate (8a): Colorless solid, T_m = 93 °C. IR (KBr): $\tilde{\nu}$ = 3201, 3103, 2988, 1701, 1626, 1562, 1366, 1166, 1071 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 5.61 (s, 2 H), 6.60 (s, 2 H), 8.81 (s, 1 H), 10.16 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]-acetonitrile): δ = 146.8, 145.6, 113.4, 41.3 ppm. $C_4H_6N_6O_3$ (186.13): calcd. C 25.81, H 3.25, N 45.15; found C 25.62, H 3.12, N 45.00.

4-Amino-1-cyanomethyl-1,2,4-triazolium Perchlorate (8b): Colorless liquid, T_g = –23 °C. IR (KBr): $\tilde{\nu}$ = 3345, 3140, 2962, 2023, 1634, 1567, 1418, 1360, 1171, 1095 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 5.49 (s, 2 H), 6.10 (s, 2 H), 8.76 (s, 1 H), 9.59 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 147.2, 145.4, 113.4, 41.7 ppm. $C_4H_6ClN_5O_4$ (223.57): calcd. C 21.49, H 2.70, N 31.32; found C 21.47, H 2.66, N 31.49.

4-Amino-1-cyanomethyl-1,2,4-triazolium Dicyanamide (8c): Light yellow solid, T_m = 66 °C. IR (KBr): $\tilde{\nu}$ = 3278, 2985, 2237, 2196, 2136, 1638, 1527, 1330, 1180, 1021 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 5.55 (s, 2 H), 6.44 (s, 2 H), 8.80 (s, 1 H), 9.79 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 146.9, 145.0, 121.1, 113.4, 41.6 ppm. $C_6H_6N_8$ (190.17): calcd. C 37.90, H 3.18, N 58.92; found C 37.76, H 3.09, N 58.49.

4-Amino-1-cyanomethyl-1,2,4-triazolium Dinitramide (8d): Colorless liquid, T_g = –41 °C. IR (KBr): $\tilde{\nu}$ = 3322, 3134, 2998, 1632, 1518, 1433, 1336, 1181, 1017 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 5.55 (s, 2 H), 6.32 (s, 2 H), 8.81 (s, 1 H), 9.79 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 146.9, 145.2, 113.1, 41.3 ppm. $C_4H_6N_8O_4$ (230.14): calcd. C 20.88, H 2.63, N 48.69; found C 20.39, H 2.50, N 48.02.

3-Methyl-1-vinylimidazolium Nitrate (12a): Colorless solid, T_m = 70 °C. IR (KBr): $\tilde{\nu}$ = 3144, 3097, 1655, 1581, 1553, 1346, 1176 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 3.91 (s, 3 H), 5.29 (dd, J = 2.6, J = 8.7 Hz, 1 H), 5.82 (dd, J = 2.6, J = 15.6 Hz, 1 H), 7.19 (dd, J = 8.7, J = 15.6 Hz, 1 H), 7.64 (t, J = 1.8 Hz, 1 H), 7.93 (t, J = 1.8 Hz, 1 H), 9.41 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 137.0, 129.5, 125.3, 120.1, 109.4, 36.8 ppm. $C_6H_9N_3O_3$ (171.15): calcd. C 42.11, H 5.30, N 24.55; found C 41.68, H 5.29, N 23.63.

3-Methyl-1-vinylimidazolium Perchlorate (12b): Light yellow liquid, T_g = –63 °C. IR (KBr): $\tilde{\nu}$ = 3117, 3157, 1657, 1583, 1555, 1369, 1177, 1092 cm^{-1}. ^{1}H NMR ([D$_3$]acetone): δ = 4.03 (s, 3 H), 5.46 (dd, J = 2.7, J = 8.7 Hz, 1 H), 5.97 (dd, J = 2.7, J = 15.6 Hz, 1 H), 7.32 (dd, J = 8.7, J = 15.6 Hz, 1 H), 7.75 (t, J = 1.8 Hz, 1 H), 8.02 (t, J = 1.8 Hz, 1 H), 9.22 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetone): δ = 136.7, 129.6, 125.5, 120.2, 109.8, 37.0 ppm. $C_6H_9ClN_2O_4$ (208.60): calcd. C 34.55, H 4.35, N 13.43; found C 3.92, H 4.34, N 13.36.

3-Methyl-1-vinylimidazolium Dinitramide (12d): Colorless solid, T_m = 50 °C. IR (KBr): $\tilde{\nu}$ = 3154, 3097, 1659, 1518, 1434, 1227, 1190,

1011 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 4.00 (s, 3 H), 5.47 (dd, J = 2.7, J = 8.7 Hz, 1 H), 5.84 (dd, J = 2.7, J = 15.7 Hz, 1 H), 7.20 (dd, J = 8.7, J = 15.7 Hz, 1 H), 7.58 (t, J = 1.8 Hz, 1 H), 7.80 (t, J = 1.8 Hz, 1 H), 9.02 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 136.2, 129.3, 125.3, 120.4, 110.3, 37.2 ppm. $C_6H_9N_5O_4$ (215.17): calcd. C 33.49, H 4.22, N 32.55; found C 32.83, H 4.05, N 32.42.

3-Allyl-1-vinylimidazolium Nitrate (13a): Light yellow liquid, T_g = –64 °C; T_m = 17 °C. IR (KBr): $\tilde{\nu}$ = 3134, 3091, 1651, 1552, 1377, 1171 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 4.88 (d, J = 6.2 Hz, 2 H), 5.45–5.44 (m, 3 H), 5.90 (dd, J = 2.6, J = 15.6 Hz, 1 H), 6.05 (tdd, J = 6.2, J = 10.3, J = 17.1 Hz, 1 H), 7.25 (dd, J = 8.7, J = 15.6 Hz, 1 H), 7.63 (t, J = 1.8 Hz, 1 H), 7.94 (t, J = 1.8 Hz, 1 H), 9.61 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 136.7, 131.6, 129.6, 123.9, 121.8, 120.6, 109.7, 52.5 ppm. $C_8H_{11}N_3O_3$ (197.19): calcd. C 48.73, H 5.62, N 21.31; found C 48.32, H 5.53, N 21.18.

3-Allyl-1-vinylimidazolium Perchlorate (13b): Colorless solid, T_m = 70 °C. IR (KBr): $\tilde{\nu}$ = 3142, 3099, 1652, 1578, 1549, 1425, 1368, 1169, 1096 cm^{-1}. ^{1}H NMR ([D$_3$]acetone): δ = 5.02 (d, J = 6.2 Hz, 2 H), 5.42–5.57 (m, 3 H), 6.01 (dd, J = 2.5, J = 15.6 Hz, 1 H), 6.17 (tdd, J = 6.4, J = 10.3, J = 16.9 Hz, 1 H), 7.36 (dd, J = 8.7, J = 15.6 Hz, 1 H), 7.80 (t, J = 1.8 Hz, 1 H), 8.10 (t, J = 1.8 Hz, 1 H), 9.35 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetone): δ = 136.2, 131.6, 129.7, 124.2, 122.3, 120.6, 109.9, 52.8 ppm. $C_8H_{11}ClN_2O_4$ (234.64): calcd. C 40.95, H 4.73, N 11.92; found C 40.73, H 4.68, N 11.76.

3-Allyl-1-vinylimidazolium Dicyanamide (13c): Brown liquid, T_g, 2 °C. IR (KBr): $\tilde{\nu}$ = 3096, 3019, 2235, 2195, 2134, 1652, 1552, 1311, 1171 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 4.84 (d, J = 6.3 Hz, 2 H), 5.39–5.48 (m, 3 H), 5.86 (dd, J = 2.6, J = 15.6 Hz, 1 H), 6.06 (tdd, J = 6.2, J = 10.1, J = 17.3 Hz, 1 H), 7.18 (dd, J = 8.7, J = 15.6 Hz, 1 H), 7.55 (t, J = 1.8 Hz, 1 H), 7.82 (t, J = 1.8 Hz, 1 H), 9.08 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 135.8, 131.2, 129.4, 124.0, 122.4, 120.6, 118.4, 110.2, 52.7 ppm. $C_{10}H_{11}N_5$ (201.23): calcd. C 59.69, H 5.51, N 34.80; found C 59.24, H 5.45, N 34.73.

3-Allyl-1-vinylimidazolium Dinitramide (13d): No T_g. IR (KBr): $\tilde{\nu}$ = 3141, 3100, 1653, 1514, 1429, 1184, 1007 cm^{-1}. ^{1}H NMR ([D$_3$]-acetonitrile): δ = 4.83 (d, J = 6.2 Hz, 2 H), 5.40–5.45 (m, 3 H), 5.91 (dd, J = 2.7, J = 15.6 Hz, 1 H), 6.04 (tdd, J = 6.3, J = 10.1, J = 17.3 Hz, 1 H), 7.17 (dd, J = 8.7, J = 15.6 Hz, 1 H), 7.52 (t, J = 1.8 Hz, 1 H), 7.78 (t, J = 1.8 Hz, 1 H), 8.98 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 135.9, 131.3, 129.5, 124.1, 122.5, 120.7, 110.4, 52.9 ppm. $C_8H_{11}N_5O_4$ (241.20): calcd. C 39.84, H 4.60, N 29.03; found C 39.83, H 4.64, N 28.61.

3-Cyanomethyl-1-vinylimidazolium Nitrate (14a): Colorless solid, T_m = 83 °C. IR (KBr): $\tilde{\nu}$ = 3109, 3032, 1647, 1561, 1371, 1177 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 5.55 (dd, J = 3.0, J = 8.7 Hz, 1 H), 5.57 (s, 2 H), 5.90 (dd, J = 3.0, J = 15.6 Hz, 1 H), 7.22 (dd, J = 8.7, J = 15.6 Hz, 1 H), 7.81 (t, J = 1.8 Hz, 1 H), 7.92 (t, J = 1.8 Hz, 1 H), 9.32 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 136.7, 128.9, 124.1, 121.4, 114.5, 111.8, 38.2 ppm. $C_7H_8N_4O_3$ (196.16): calcd. C 42.87, H 4.11, N 28.56; found C 43.05, H 3.94, N 28.37.

3-Cyanomethyl-1-vinylimidazolium Perchlorate (14b): Colorless solid, T_m = 130 °C. IR (KBr): $\tilde{\nu}$ = 3154, 3098, 3063, 2983, 1652, 1555, 1406, 1368, 1177, 1104 cm^{-1}. ^{1}H NMR ([D$_3$]acetone): δ = 5.57 (dd, J = 3.1, J = 8.7 Hz, 1 H), 5.77 (s, 2 H), 6.10 (dd, J = 3.1, J = 15.5 Hz, 1 H), 7.46 (dd, J = 8.7, J = 15.5 Hz, 1 H), 8.09 (t, J = 1.8 Hz, 1 H), 8.24 (t, J = 1.8 Hz, 1 H), 9.66 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetone): δ = 137.6, 129.6, 124.5, 121.3, 114.2, 111.0, 38.2 ppm. $C_7H_8ClN_3O_4$ (233.61): calcd. C 35.99, H 3.45, N 17.99; found C 35.89, H 3.32, N 17.60.

3-Cyanomethyl-1-vinylimidazolium Dicyanamide (14c): Colorless solid, T_m = 73 °C. IR (KBr): $\tilde{\nu}$ = 3105, 2239, 2197, 2135, 1653, 1557, 1425, 1313, 1175 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 5.59 (dd, J = 3.0, J = 8.7 Hz, 1 H), 5.60 (s, 2 H), 5.95 (dd, J = 3.0, J = 15.5 Hz, 1 H), 7.26 (dd, J = 8.7, J = 15.5 Hz, 1 H), 7.85 (t, J = 1.8 Hz, 1 H), 7.98 (t, J = 1.8 Hz, 1 H), 9.36 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 136.7, 129.0, 124.2, 121.5, 120.9, 114.5, 112.0, 38.3 ppm. $C_9H_8N_6$ (200.20): calcd. C 53.99, H 4.03, N 41.98; found C 53.70, H 4.01, N 41.82.

3-Cyanomethyl-1-vinylimidazolium Dinitramide (14d): Colorless solid, T_m = 70 °C. IR (KBr): $\tilde{\nu}$ = 3144, 3075, 2996, 1652, 1557, 1515, 1434, 1336, 1182, 1011 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 5.45 (s, 2 H), 5.48 (dd, J = 2.8, J = 8.8 Hz, 1 H), 5.88 (dd, J = 2.8, J = 15.6 Hz, 1 H), 7.20 (dd, J = 8.8, J = 15.6 Hz, 1 H), 7.74 (t, J = 1.8 Hz, 1 H), 7.85 (t, J = 1.8 Hz, 1 H), 9.21 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 137.0, 129.2, 124.2, 121.2, 114.1, 111.5, 38.3 ppm. $C_7H_8N_6O_4$ (240.19): calcd. C 35.01, H 3.36, N 34.99; found C 34.37, H 3.15, N 34.74.

1-Methyl-3-propargylimidazolium Nitrate (17a): Colorless solid, T_m = 63 °C. IR (KBr): $\tilde{\nu}$ = 3222, 3151, 3104, 1570, 1378, 1164 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 3.17 (t, J = 2.6 Hz, 1 H), 3.97 (s, 3 H), 5.14 (d, J = 2.6 Hz, 2 H), 7.54 (t, J = 1.8 Hz, 1 H), 7.64 (t, J = 1.8 Hz, 1 H), 8.93 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 137.1, 124.9, 123.0, 78.5, 75.7, 40.0, 36.9 ppm. $C_7H_9N_3O_3$ (183.16): calcd. C 45.90, H 4.95, N 22.94; found C 45.04, H 4.93, N 22.53.

1-Methyl-3-propargylimidazolium Perchlorate (17b): Colorless solid, T_m = 74 °C. IR (KBr): $\tilde{\nu}$ = 3268, 3150, 2984, 1607, 1566, 1442, 1387, 1355, 1165, 1093 cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 3.35 (t, J = 2.6 Hz, 1 H), 4.10 (s, 3 H), 5.30 (d, J = 2.6 Hz, 2 H), 7.76 (t, J = 1.8 Hz, 1 H), 7.81 (t, J = 1.8 Hz, 1 H), 9.13 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 137.7, 125.2, 123.2, 78.6, 75.8, 39.8, 36.9 ppm. $C_7H_9ClN_2O_4$ (220.61): calcd. C 38.11, H 4.11, N 12.70; found C 37.85, H 4.02, N 12.62.

1-Methyl-3-propargylimidazolium Dicyanamide (17c): Colorless liquid, T_m = 17 °C. IR (KBr): $\tilde{\nu}$ = 3233, 3106, 2236, 2195, 2135, 1570, 1440, 1312, 1164 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 3.16 (t, J = 2.6 Hz, 1 H), 3.88 (s, 3 H), 5.07 (d, J = 2.6 Hz, 2 H), 7.47 (t, J = 1.8 Hz, 1 H), 7.55 (t, J = 1.8 Hz, 1 H), 8.84 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 137.2, 125.0, 123.0, 120.4, 78.6, 75.5, 40.0, 37.0 ppm. $C_9H_9N_5$ (187.20): calcd. C 57.74, H 4.85, N 37.41; found C 58.28, H 4.89, N 38.27.

1-Methyl-3-propargylimidazolium Dinitramide (17d): T_m = 62 °C. IR (KBr): $\tilde{\nu}$ = 3258, 3153, 2978, 1515, 1434, 1339, 1183, 1008 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 3.10 (t, J = 2.6 Hz, 1 H), 3.87 (s, 3 H), 5.05 (d, J = 2.6 Hz, 2 H), 7.44 (t, J = 1.8 Hz, 1 H), 7.52 (t, J = 1.8 Hz, 1 H), 8.76 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 137.4, 125.1, 123.1, 78.5, 75.6, 40.0, 37.1 ppm. IR (KBr): $\tilde{\nu}$ = 3258, 3153, 2978, 1515, 1434, 1339, 1183, 1008 cm^{-1}. $C_7H_9N_5O_4$ (227.18): calcd. C 37.01, H 3.99, N 30.83; found C 36.43, H 3.97, N 30.78.

1-Methyl-4-propargyl-1,2,4-triazolium Nitrate (18a): Colorless solid, T_m = 74 °C. IR (KBr): $\tilde{\nu}$ = 3267, 3085, 2994, 2395, 2130, 1757, 1577, 1375, 1155, 1070 cm^{-1}. ^{1}H NMR (D_2O/H_2O): δ = 3.16 (t, J = 2.6 Hz, 1 H), 4.14 (s, 3 H), 5.21 (d, J = 2.6 Hz, 2 H), 8.95 (s, 1 H), 9.91 (s, 1 H) ppm. ^{13}C NMR (D_2O/H_2O): δ = 145.0, 143.4, 79.2, 74.4, 39.7, 38.9 ppm. $C_6H_8N_4O_3$ (184.15): calcd. C 39.13, H 4.38, N 30.42; found C 39.15, H 4.34, N 29.58.

1-Methyl-4-propargyl-1,2,4-triazolium Perchlorate (18b): Colorless solid, T_m = 98 °C. IR (KBr): $\tilde{\nu}$ = 3289, 3102, 2988, 1573, 1439, 1373, 1153, 1096 cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 3.39 (t, J = 2.6 Hz, 1 H), 4.26 (s, 3 H), 5.37 (d, J = 2.6 Hz, 2 H), 9.09 (s, 1 H), 9.94 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 144.9, 143.8, 79.6,

74.7, 39.9, 38.8 ppm. $C_6H_8ClN_3O_4$ (221.60): calcd. C 32.52, H 3.64, N 18.96; found C 32.52, H 3.45, N 18.89.

1-Methyl-4-propargyl-1,2,4-triazolium Dicyanamide (18c): Colorless liquid, T_g = –54 °C. IR (KBr): $\tilde{\nu}$ = 3252, 3067, 2237, 2196, 2135, 1580, 1440, 1314, 1158, 1069 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 3.21 (t, J = 2.6 Hz, 1 H), 4.10 (s, 3 H), 5.17 (d, J = 2.6 Hz, 2 H), 8.83 (s, 1 H), 9.77 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 144.7, 143.3, 120.4, 79.3, 74.5, 39.9, 39.0 ppm. $C_8H_8N_6$ (188.19): calcd. C 51.06, H 4.28, N 44.66; found C 51.35, H 4.33, N 43.88.

1-Methyl-4-propargyl-1,2,4-triazolium Dinitramide (18d): Colorless liquid, T_g = –59 °C. IR (KBr): $\tilde{\nu}$ = 3265, 3091, 1582, 1518, 1437, 1184, 1012 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 3.13 (t, J = 2.6 Hz, 1 H), 4.11 (s, 3 H), 5.18 (d, J = 2.6 Hz, 2 H), 8.80 (s, 1 H), 9.68 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 144.8, 143.5, 79.3, 74.6, 40.1, 39.1 ppm. $C_6H_8N_6O_4$ (228.17): calcd. C 31.58, H 3.53, N 36.83; found C 30.97, H 3.42, N 37.22.

4-Cyanomethyl-1-propargyl-1,2,4-triazolium Nitrate (21a): Colorless solid, T_m = 112 °C. IR (KBr): $\tilde{\nu}$ = 3135, 2951, 1683, 1569, 1347, 1151, 1070 cm^{-1}. ^{1}H NMR (D$_2$O/H$_2$O): δ = 3.18 (t, J = 2.6 Hz, 1 H), 5.36 (d, J = 2.6 Hz, 2 H), 5.64 (s, 2 H), 9.13 (s, 1 H), 10.31 (s, 1 H) ppm. ^{13}C NMR (D$_2$O/H$_2$O): δ = 146.1, 144.5, 113.9, 80.0, 73.9, 44.0, 36.9 ppm. $C_7H_7N_5O_3$ (209.16): calcd. C 40.20, H 3.37, N 33.48; found C 40.10, H 3.45, N 33.68.

4-Cyanomethyl-1-propargyl-1,2,4-triazolium Perchlorate (21b): Colorless solid, T_m = 125 °C. IR (KBr): $\tilde{\nu}$ = 3271, 3135, 2988, 1574, 1423, 1348, 1100 cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 3.45 (t, J = 2.6 Hz, 1 H), 5.57 (d, J = 2.6 Hz, 2 H), 5.87 (s, 2 H), 9.40 (s, 1 H), 10.45 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 146.0, 144.7, 113.6, 79.5, 74.2, 43.5, 36.9 ppm. $C_7H_7ClN_4O_4$ (246.61): calcd. (246.61) C, 34.09; H, 2.86; N, 22.72. Found: C, 34.14; H, 2.49; N, 21.99.

4-Cyanomethyl-1-propargyl-1,2,4-triazolium Dicyanamide (21c): Colorless liquid, T_g = –23 °C. IR (KBr): $\tilde{\nu}$ = 3126, 2985, 2239, 2131, 1673, 1574, 1428, 1317, 1154 cm^{-1}. ^{1}H NMR ([D$_3$]acetonitrile): δ = 3.18 (t, J = 2.6 Hz, 1 H), 5.31 (d, J = 2.6 Hz, 2 H), 5.48 (s, 2 H), 8.97 (s, 1 H), 10.03 (s, 1 H) ppm. ^{13}C NMR ([D$_3$]acetonitrile): δ = 145.9, 144.3, 121.5, 113.7, 79.7, 74.0, 43.9, 37.2 ppm. $C_9H_7N_7$ (213.20): calcd. C 50.70, H 3.31, N 45.99; found C 50.16, H 3.04, N 44.10.

4-Cyanomethyl-1-propargyl-1,2,4-triazolium Dinotramide (21d): Colorless solid, T_m = 100 °C. IR (KBr): $\tilde{\nu}$ = 3140, 2955, 1697, 1570, 1349, 1152, 1071 cm^{-1}. ^{1}H NMR (D$_2$O/H$_2$O): δ = 3.12 (t, J = 2.6 Hz, 1 H), 5.30 (d, J = 2.6 Hz, 2 H), 5.59 (s, 2 H), 9.08 (s, 1 H), 10.26 (s, 1 H) ppm. ^{13}C NMR (D$_2$O/H$_2$O): δ = 145.9, 144.2, 113.6, 79.7, 73.6, 43.7, 36.7 ppm. $C_7H_7N_7O_4$ (253.17): calcd. C 33.21, H 2.79, N 38.73; found C 33.07, H 2.73, N 37.52.

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