Supporting Information

A General Design Platform for Ionic Liquid Ions Based on Bridged Multi-Heterocycles with Flexible Symmetry and Charge

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MATERIALS AND METHODS:

Commercial reagents were used directly as obtained from commercial sources (Aldrich) unless otherwise noted. All solvents were 'solvent grade' and used as received without additional purification. BioRad AG 1-X8 strongly basic anion exchange resin was prepared according to manufacturer's specifications.

Single-crystal X-ray diffraction data were collected on a Bruker CCD area detector-equipped diffractometer (Madison, WI) with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystals of **2, 3, 7**·$2H_2O$**,** and **8** were cooled to -100 ^oC with a stream of nitrogen gas, whereas the analysis of **4** was performed at room temperature. Data were collected using graphite monochromated MoK_α radiation. SHELXTL-5 software was used for structure solution and refinement.[†] Each structure was refined by using full-matrix least-squares methods on F^2. All atoms were readily located and the positions of all non-hydrogen atoms were refined anisotropically. All hydrogens were placed in calculated positions and allowed to ride on the bonded atom.

Melting point/glass transition analyses were performed by Differential Scanning Calorimetry (DSC) using a DSC 2920 Modulated DSC, TA Instruments, Inc. (New Castle, DE) cooled with a liquid nitrogen cryostat. The calorimeter was calibrated for temperature and cell constants using indium (melting point 156.61 ^oC; H = 28.71 J g^{-1}). Data were collected at constant atmospheric pressure, with heating at a rate of 5 ^oC min^{-1} using samples between 5-15 mg in aluminum sample pans (sealed then perforated with a pin-hole to equilibrate pressure from potential expansion of evolved gases). The DSC was adjusted so that zero heat flow was between 0 and -0.5 mW, and the baseline drift was less than 0.1 mW over the temperature range of 0-180 ^oC. An empty sample pan served as the reference.

Thermogravimetric analyses (TGA) was performed using a TGA 2950, TA Instruments, Inc. (New Castle, DE). These experiments were conducted under air atmosphere and measured in the dynamic heating regime. Samples between 5-15 mg were heated from 30-600 ^oC under constant heating ramp of 5 ^oC min^{-1} with a 30 minute isotherm at 75 ^oC.

The ^1H and ^{13}C NMR spectra were recorded using a Bruker spectrometer operating at 500 or 360 MHz and 90 or 125 MHz, respectively. Infrared (IR) analyses were obtained by direct measurement of the neat samples by utilizing a Perkin-Elmer 100 FT-IR instrument featuring an ATR force gauge, and spectra were obtained in the range of ν_{max} = 650 – 4000 cm^{-1}.

[†] (a) G. M. Sheldrick, Program for Semiempirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1997 (b) G. M. Sheldrick, SHELXTL, Version 6.14, Bruker AXS Inc., Madison, WI, 2003.

SYNTHETIC PROTOCOLS FOR THE FORMATION OF REPORTED MAJOR PRODUCTS:

***A. Preparation of 1-cyanomethyl-3-methylimidazolium chloride precursor salt* (1):** Compound **1** was prepared by a solvent-free adaptation of a previously reported method.[‡] Yields and reaction times are unoptimized. The following serves as general procedure. In a 50 mL round bottom flask with magnetic stirbar, chloroacetonitrile (2.867 g, 37.9 mmol) was slowly added to 1-methylimidazole (2.87 g, 35 mmol). The mixture was stirred at room temperature overnight, and the resulting white solid precipitate washed with ethyl acetate (4 x 10 mL) followed by rotary evaporation and then high vacuum at room temperature for 24 h to remove residual solvent. White solid, water soluble, 90% yield, mp (DSC) $\boldsymbol{T}_{m}$ = 178.7 ^{o}C, onset for 5% decomposition $\boldsymbol{T}_{5\%onset}$ = 221.1 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) $\boldsymbol{\delta}$ ppm 9.56 (s, 1H), 8.00 (t, J = 1.73 Hz, 1H), 7.87 (t, J = 1.64 Hz, 1H), 5.82 (s, 2H), 3.92 (s, 3H); ^{13}C (125 MHz, DMSO-d_6) $\boldsymbol{\delta}$ ppm 138.29, 124.80, 123.03, 115.34, 37.21, 36.64. FT-IR ($\boldsymbol{\nu}_{max}$): 3392 (w), 3032 (s), 2977 (s), 2906 (s), 1575 (s), 1565 (s), 1439 (m), 1337 (m), 1254 (s), 1168 (s), 915 (m).

***B. Preparation of 1-(5-tetrazolidyl)methyl-3-methylimidazolium•(ZnBrCl) and recrystallization as* catena*-poly[(bromochlorozinc)-μ-[1-(5-tetrazolato)methyl-3-methylimidazolium]-N^{1}:N^{4}] coordination polymer* (2)[§]:** Compound **2** was prepared by modifying the methods of Sharpless and coworkers[**] from the halide salt 1-cyanomethyl-3-methylimidazolium chloride (**1**). Yields and reaction times are unoptimized. The following serves as a general procedure. Subsequent monitoring of the reaction by way of ^{1}H-NMR spectroscopy resulted in ~ 85% conversion of **1** to product **2** under room temperature conditions with all other factors the same.

1-cyanomethyl-3-methylimidazolium chloride (**1**) (2.81 g, 17.2 mmol) was combined with NaN_3 (1.30 g, 20 mmol) in a 100 mL round-bottom flask with 50 mL water and stirred to dissolve with a magnetic stir bar. Zinc bromide was added (4.49 g, 20 mmol), and the mixture stirred to reflux overnight. The resultant white solid was rinsed with water and filtered. The final product was dried at 60 ^{o}C for 24 h in an oven. White powder, 80% yield, glass transition temperature (DSC) $\boldsymbol{T}_{m}$ = at decomposition temperature; onset for 5% decomposition, $\boldsymbol{T}_{5\%onset}$ = 306.9 ^{o}C; ^{1}H NMR (360 MHz, DMSO-d_6) $\boldsymbol{\delta}$ ppm 9.18 (s, 1H), 7.75 (t, J = 1.72 Hz, 1H), 7.68 (t, J = 1.74 Hz, 1H), 5.57 (s, 2H); 3.87 (3H, s); ^{13}C NMR (125 MHz, DMSO-d_6) $\boldsymbol{\delta}$ ppm 154.17, 138.06, 124.44, 123.56, 42.92, 36.56. FT-IR ($\boldsymbol{\nu}_{max}$): 3498 (w), 3103 (s), 3078 (s), 2076 (s), 16128 (w), 1572 (s), 1446 (s), 1433 (s), 1421 (s), 1340 (m),

‡ W. A. Herrmann, L. J. Goossen, M. Spiegler, *Organometallics*, 1998, **17**, 2162.

§ Nomenclature for these coordination polymers constructed based upon guidelines from *Nomenclature of Inorganic Chemistry II: IUPAC Recommendations 2000*, eds. J. A. McCleverty and N. G. Connelly, Royal Chemical Society Publishing, Cambridge, UK, 2001, 130 pp.

** Z. P. Demko, K. B. Sharpless, *J. Org. Chem.*, 2001, **66**, 7945.

1171 (s), 1072 (m), 839 (s), 816 (s), 776 (s), 692 (s). **2** was crystallized for X-ray diffraction analysis by dissolution in a minimum amount of concentrated HNO_3, evaporating the resulting mixture to near dryness, washing the residual with dry acetone, and then slow evaporation in air.

***C. Isolation and recrystallization of 1-(5-1H-tetrazolyl)methyl-3-methylimidazolium chloride as zinc-free salt* (3):** Compound **3** was obtained from the Zn-coordination polymer (**2**) via a preparatory adaptation of an anion exchange resin technique reported to remove trace Zn selectively from water and industrial waste samples[††]. Yields and reaction times are unoptimized.

Conditioning of anion exchange resin: To 15.167 g of BioRad AG 1-X8 strongly basic anion exchange resin (100-200 mesh), 40 mL D.I. water was added and the resin stirred in a 125 mL flask to a slurry for 20 min. The slurry was then introduced into a glass column (~ 0.5 cm ID, 40 cm length; prewashed with 9 N HCl and rinsed several times with D.I. water) with a sand and glass wool plug. 9 N HCl was then eluted through the column (2 x 30 mL) and discarded upon neutralization.

Sample preparation for anion exchange: The Zn-coordination polymer **2** was added to a 50 mL Erlenmeyer flask (0.508 g, 1.473 mmol) and 15 mL of 9 N HCl was added and stirred to dissolve the solid material. The solution was sonicated briefly to break up residual solids suspended in the acidic solution, and an additional 10 mL 9 N HCl was added to completely dissolve the material.

*Zn separation from **2** by anion exchange resin:* 10 mL collection vials were numbered and arranged to collect eluted fractions from the column, and **2** dissolved in minimal 9 N HCl was introduced by 3 mL increments to the top of the resin bed and eluted at a rate of ~1 drop/sec (controlled by positive pressure introduced to top of column). When sample introduction was complete, 9 N HCl was eluted for complete removal of the salt **3**. After this step, the column was eluted with 0.005 M HCl followed by eluting the column with enough water until elution had tested negative for chloride by silver nitrate spot test (~1:1 v/v ratio of eluted fraction to 0.1 M $AgNO_3$). In all, 24 vials were collected from the exchange resin, where each vial contained approximated 5-10 mL of eluted material.

Qualitative analysis of Zn removal by pH measurement and $K_2[Hg[CNS)_4]$ spot test: Determination of Zn in eluted fractions was estimated by two methods. First, the approximate pH of the elution in each collected vial was obtained by pH indicator paper (Vials 1-19, pH < 1; Vial 20, pH ~ 3-5; Vials 21-24, pH ~ 5). As the $[ZnCl_4]^{2-}$ anion is present at high chloride concentrations, the zinc should remain supported on the resin and it may be assumed that the earlier elution volumes were relatively Zn-free.

[††] (a) K. Krausa, G. Moore, *J. Amer. Chem. Soc.*, 1953, **75**, 1460 (b) S. Kallmann, C. G. Steele, N. Y. Chui, *Anal. Chem.*, 1954, **28**, 230 (c) T. Z. Bishay, *Anal. Chem.*, 1972, **44**, 1087 (d) F. W. E. Strelow, *Anal. Chem.*, 1978, **50**, 1359 (e) J. A. Sweileh, E. M. El-Nemma, *Anal. Chim. Acta*, 2004, **523**, 287 (f) C. Archer, D. J. Vance, *Anal. At. Spectrom.*, 2004, **19**, 656 (g) D. M. Borrok, R. B. Wanty, W. I. Ridley, R. Wolf, P. J. Lamothe, M. Adams, *Chem. Geol.,* 2007, **242**, 400.

Next, a solution of $K_2[Hg(CNS)_4]$ (prepared the previous day by established methods,[‡‡] 2.7% $HgCl_2$ and 3.9% in D.I. water) was used to test each of the eluted fractions for Zn by spot test (1:1 ratio of 0.5 mL each, sample to test solution; concentration limit = 1/10,000). A white precipitate indicating the presence of Zn formed quickly (less than 1 min) for elution vials #14-22, where 14-16 only had a slight precipitate. To ensure the quality of the samples, only vials 2-5 and 7-11 were included for sample collection. Vials #1 and #6 seemed to visually contain column impurity (yellow coloring) and were stored separately. Vials 12 and 13, although not obviously precipitating, were kept separate as well to increase the window between the eluted sample and Zn-containing eluted solution.

*Isolation of 1-(5-1*H*-tetrazolyl)methyl-3-methylimidazolium chloride* **(3)***:* Each of the eluted fractions of **3** was heated (~60 °C, 24 h) to remove water and excess HCl, and the residual solids were triturated with dry ethanol. From evaporating the reserved ethanol solution, the product was obtained as a white solid. White solid, 71% yield, mp (DSC) $\boldsymbol{T}_m$ = 155.5 °C (melts during early onset of decomposition); onset for 5% decomposition, $\boldsymbol{T}_{5\%onset}$ = 213.1 °C, ^{1}H-NMR (500 MHz, DMSO-d_6) $\boldsymbol{\delta}$ ppm 9.35 (s, 1H), 7.86 (t, J = 1.65 Hz, 1H), 7.77 (t, J = 1.61 Hz, 1H), 5.89 (s, 2H), 3.89 (s, 3H); ^{13}C-NMR (125 MHz, DMSO-d_6) $\boldsymbol{\delta}$ ppm 153.38, 137.56, 123.84, 122.96, 42.29, 36.91. FT-IR ($\boldsymbol{\nu}_{max}$): 3107 (m), 3001 (s), 2468 (w), 2395 (s), 1801 (m), 1668 (w), 1584 (m), 1552 (s), 1424 (w), 1178 (m), 1084 (s), 1027 (s), 1015 (s); 790 (s), 785 (s), 740 (s). Separately, a crystal was obtained from 1:1 MeOH/CH_3CN by slow diffusion of diethyl ether and submitted for single crystal X-ray diffraction analysis.

D. Isolation and recrystallization of 1-(5-tetrazolidyl)methyl-3-methylimidazolium zwitterion **(4)***:* Compound **4** was obtained from the 1-(5-1*H*-tetrazolyl)methyl-3-methylimidazolium chloride salt (**3**) via neutralization reaction using hydroxide-exchanged anion exchange resin as solid-supported base. Yields and reaction times are not optimized.

Conditioning of anion exchange resin (OH$^-$*):* Approximately 5 g of BioRad AG 1-X8 strongly basic anion exchange resin in chloride form was eluted with ~20 bed volumes (~1 L) of 1 N NaOH and each eluted volume was tested for Cl^- anion by using the silver nitrate test[§§]. The column was then washed with 2 bed volumes of D.I. water, filtered, and rinsed dry with ethanol before storing under high vacuum for 48 h.

*Neutralization of **3** by OH*$^-$ *form of anion exchange resin:* The required volume of dry resin needed to convert **3** to the zwitterion **4** (eq. 1) was added to a 125 mL Erlenmeyer flask, washed three times with

[‡‡] Svehla, G. Ed. *Vogel's Qualitative Inorganic Analysis*, ed. G. Svehla, Longman Scientific & Technical, Essex, U.K., 1987, p. 126.

[§§] To each eluted volume, concentrated HNO_3 was added until pH neutral or slightly acidic to neutralize ambient OH^- anions that can interfere with the $AgNO_3$ test. Then, an equal volume of 0.1 M $AgNO_3$ was added to a sample of the elute fraction (1 mL to 1 mL) and observed for precipitation. At the end of 1 L of elution, the precipitation was quite faint, detecting < 10% Cl^- anion from the resin.

25 mL of D.I. water and decanted to remove fines from ruptured resin beads, and then **3** (0.240 g, 1.20 mmol) was added to the flask as a solution in 25 mL of water.

$$\text{Dry Resin required (g)} = (\text{mmol Cl- salt}) \times \left(\frac{1\text{ g dry resin}}{(2.6\text{ meq exchange capacity})}\right) \qquad \textbf{[EQ. 1]}$$

$$= (1.2\text{ mmol}) \times \left(\frac{1\text{ g}}{2.6\text{ meq}}\right) = 0.46\text{ g dry resin needed}$$

$$= 2.30\text{ g dry resin (5 × excess)}$$

The mixture was gently stirred by rotating the flask for 20 min prior to spot checking the solution for Cl^- anion by silver nitrate test (0.1 M $AgNO_3$), the resin was filtered and washed with 3 x 10 mL D.I. water, and the resulting aqueous filtrates combined and evaporated to dryness at room temperature in an open beaker.

Isolation of 1-(5-tetrazolidyl)methyl-3-methylimidazolium **(4)***:* Neutralized fractions were combined and allowed to evaporate at room temperature to remove water. Additional recrystallization of isolated **4** from slow evaporation from hot methanol resulted in the final product. A crystal was submitted for single crystal X-ray diffraction analysis. White solid, 75% yield, mp (DSC) $\boldsymbol{T}_m$ = 124.8 °C; onset for 5% decomposition, $\boldsymbol{T}_{5\%onset}$ = 241.0 °C, ^{1}H-NMR (500 MHz, DMSO-d_6) $\boldsymbol{\delta}$ ppm 9.15 (s, 1H), 7.72 (t, J = 1.50 Hz, 1H), 7.65 (t, J = 1.51 Hz, 1H), 5.52 (s, 2H), 3.84 (s, 3H); ^{13}C-NMR (125 MHz, DMSO-d_6) $\boldsymbol{\delta}$ ppm 155.58, 136.46, 123.23, 122.65, 44.62, 35.61. FT-IR ($\boldsymbol{\nu}_{max}$): 3146 (m), 3094 (s), 3074 (s), 1575 (m), 1560 (m), 1402 (w), 1331 (s), 1193 (w), 1150 (s), 1122 (m), 1080 (w), 862 (s), 815 (s), 780 (s), 751 (s), 698 (s).

E. Preparation of 1-(2-cyanoethyl)-1,2,4-triazole **(6)*:*** Compound **6** was prepared from the 1,2,4-triazole, **5**. Yields and reaction times are unoptimized. The following serves as a general procedure. A sample of 1,2,4-triazole (1.724 g, 25 mmol) was dissolved in toluene (10 mL) and placed into a 50 mL round bottom flask to which a Teflon stirbar was added. Acrylonitrile (1.3562 g, 25 mmol) was added to the flask dropwise as a solution in toluene (2 mL) followed by addition of triethylamine (0.5 mL) directly to the reaction mixture. The reaction mixture was fitted with a condenser and heated to reflux. The reaction mixture was then refluxed for an additional 30 hours. *Caution: Acrylonitrile is a very hazardous irritant and permeator for skin and eyes, so protective clothing and a properly ventilated workspace should be utilized when handling this material. Prolonged exposure should be avoided, as there are possible carcinogenic/tetratogenic/mutagenic effects as well as well as toxicity related to target organs including blood, liver, central nervous system and kidneys. Additionally, explosive mixtures can be formed when vapors are allowed to mix with air, so accumulation of evaporated material is to be avoided. Please refer to Material Safety Data Sheet (MSDS) for further precautionary details (CAS # 107-13-1).*

At the end of the reaction time, **6** separated from the toluene as a second amber liquid phase and was isolated by decanting the toluene from the mixture and washing the residue with additional toluene. Residual solvent was then removed by rotary evaporation. White solid, 93.3% yield, mp (DSC) $\boldsymbol{T}_m$ = 31.4 ^oC ; onset for 5% decomposition, $\boldsymbol{T}_{5\%onset}$ = 120.4 ^oC, ^1H NMR (360 MHz, DMSO-d_6) **δ** ppm 8.62 (s, 1H), 8.07 (s, 1H), 4.51 (d, *J* = 6.38 Hz, 2H), 3.13 (t, *J* = 6.38 Hz, 2H); ^{13}C NMR (90 MHz, DMSO-d_6) **δ** ppm 152.4, 144.9, 118.7, 44.74, 18.86. FT-IR ($\boldsymbol{\nu}_{max}$): 3406 (br m), 3120 (m), 2253 (m), 1508 (s), 1450 (m), 1418 (m), 1274 (s) 1206 (m), 1135 (s), 1040 (m), 1022 (m), 1003 (s), 919 (m), 872 (m), 679 (s).

***F. Preparation of 5-(2-(1,2,4-triazol-1-yl)ethyl)tetrazolate dihydrate as sodium coordination polymer* (7·2H_2O):** Compound **7**·2H_2O was prepared from 1-(2-cyanoethyl)-1,2,4-triazole (**6**). Yields and reaction times are not optimized. The following serves as a general procedure. In an Ace Glass high-pressure glass vial with a Teflon screw-cap, 1-(2-cyanoethyl)-1,2,4-triazole (1.195 g, 9.8 mmol) was combined with sodium azide (0.6437 g, 9.8 mmol) in glacial acetic acid (0.6 mL, 10 mmol). A Teflon magnetic stir bar was added, the vial sealed, and the mixture stirred on an oil bath at 60-70 ^oC for 24 h. At the end of the reaction period, the vial was set on a rotary evaporator at 70-80 ^oC for 4 h to remove residual acetic acid followed by dissolving the white solids with dry ethanol. Single crystals were obtained from slow evaporation of ethanol from the crude reaction mixture, and the final product, **7**·2H_2O, was obtained from removal of residual solvent by high vacuum. White solid, 48.5% yield, mp (DSC) $\boldsymbol{T}_m$ = at decomposition temperature; onset for 5% decomposition, $\boldsymbol{T}_{5\%onset}$ = 313.7 ^oC, ^1H NMR (360 MHz, DMSO-d_6) **δ** ppm 8.42 (s, 1H), 7.92 (s, 1H), 4.47 (t, *J* = 7.62 Hz, 2H), 3.15 (t, *J* = 7.59 Hz, 2H); ^{13}C NMR (90 MHz, DMSO-d_6) **δ** ppm 157.889, 151.547, 144.329, 48.809, 26.953. FT-IR ($\boldsymbol{\nu}_{max}$): 3322 (s), 3219 (s), 3144 (s), 1687 (m), 1571 (s), 1516 (s), 1468 (m), 1435 (m), 1380 (s), 1277 (s), 1205 (s), 1139 (s), 1104 (w), 1043 (w), 1014 (s), 970 (w), 923 (w), 858 (m), 673 (m).

***G. Preparation of 1-(2-(5-tetrazolidyl)ethyl)-3-(5-1H-tetrazolyl)methylimidazolium zwitterion* (10):** Azolium zwitterion, **10**, was achieved by reacting **9** (3.037 g, 20 mmol) with sodium azide (2.880 g, 44 mmol) in 10 mL of glacial acetic acid in a heated oil bath (60-70 ^oC) for 48 h. The mixture resulted in a suspended white solid in amber liquid, and the solid product was washed several times with dry ethanol. Final drying at high vacuum resulted in the final product. White solid, 78% yield, mp (DSC) $\boldsymbol{T}_m$ = 49.4 ^oC; onset of 5% decomposition, $\boldsymbol{T}_{5\%onset}$ = 237.5 ^oC, ^1H NMR (500 MHz, DMSO- d_6) **δ** ppm 9.27 (s, 1H), 7.75 (dd, *J* = 10.47 Hz, 2H), 5.55 (s, 2H), 4.64 (t, *J* = 6.95 Hz, 2H), 3.50 (t, *J* = 6.97 Hz, 2H); ^{13}C (500 MHz, DMSO- d_6) **δ** ppm: 155.953, 154.151, 137.013, 123.361, 122.885, 46.868, 45.196, 24.732. FTIR ($\boldsymbol{\nu}_{max}$): 3143 (m), 3113 (m), 3043 (m), 2344 (br m), 1945 (br m), 1567 (s), 1459

(m), 1434 (m), 1234 (m), 1211 (m), 1170 (s), 1099 (s), 1045 (m), 950 (m), 872 (m), 860 (m), 802 (s), 761 (s), 744 (s), 690 (s), 665 (s).

***H. Preparation of 1-(2-(5-1H-tetrazolyl)ethyl)-3-(5-1H-tetrazolyl)methylimidazolium bis(trifluoromethanesulfonyl)amide* (11):** The synthesis of **11** was carried out in the hood by reacting 123 mg (0.5 mmol) of zwitterion **10** and 140 mg (0.5 mmol) of hydrogen bis(trifluoromethanesulfonyl)amide ($HNTf_2$) in 10 mL of 1:1 methanol:water at RT for about 72 h in a 20 mL borosilicate glass vial. The mixture was kept at ambient conditions in order to allow the volatile solvent to evaporate and then water was removed by air stream. The product **11** was kept under high vacuum to afford a clear, viscous oil. Colorless oil, 80% yield, glass transition temperature (DSC) $\boldsymbol{T}_g/\boldsymbol{T}_m$ = 10.5 ^oC, 50.8 ^oC; onset for 5% decomposition, $\boldsymbol{T}_{5\%onset}$ = 245.6 ^oC, ^1H NMR (500 MHz, DMSO- d_6) $\boldsymbol{\delta}$ ppm 9.35 (s, 1H), 7.87 (dt, J = 24.61 Hz, 2H), 5.91 (s, 2H), 4.71 (t, J = 6.81 Hz, 2H), 3.54 (t, J = 6.82 Hz, 2H); ^{13}C NMR (500 MHz, DMSO- d_6) $\boldsymbol{\delta}$ ppm: 138.05, 123.83, 123.40, 121.40, 121.23, 118.67, 467.84, 43.07, 24,37. FTIR ($\boldsymbol{\nu}_{max}$): 3531 (w), 3245 (w), 3153 (m), 3090 (m), 1562 (s), 1442 (m), 1345 (s), 1183 (s), 1134 (s), 1054 (s), 791 (m), 741 (s).

***I. Preparation of 1,3-dimethylimidazolium 1-(2-(5-tetrazolidyl)ethyl)-3-(5-tetrazolidyl)methyl-imidazolium* (12):** The synthesis of **12** was carried out in the hood by reacting 123 mg (0.5 mmol) of zwitterion **10** and 70 mg (0.5 mmol) of 1,3-dimethylimidazolium-2-carboxylate in 10 mL of a 1:1 solution of methanol:water (and 2 drops of DMSO) at RT for about 72 h in a 20 mL borosilicate glass vial. The mixture was kept at ambient conditions in order to allow the volatile solvent to evaporate and then water was removed by air stream. The compound was kept under high vacuum to afford a clear, viscous oil. Colorless oil, 78% yield. The NMR spectrum revealed the presence of 33% 1,3-dimethylimidazolium-2-carboxylate, which was removed by slow dissolution in hot acetone (6 x 2 mL). Yield of **12** after purification, 52%, glass transition temperature/mp (DSC) $\boldsymbol{T}_g/\boldsymbol{T}_m$ = -24.4 ^oC, 44.9 ^oC; onset of 5% decomposition, $\boldsymbol{T}_{5\%onset}$ = 224.4 ^oC, ^1H NMR (500 MHz, DMSO- d_6) $\boldsymbol{\delta}$ ppm 9.21 (d, J = 78.05 Hz, 2H), 7.69 (dt, J = 15.80, 15.54, 1.47 Hz, 4H), 5.51 (s, 2H), 4.52 (t, J = 7.23 Hz, 2H), 3.84 (s, 1H), 3.21 (t, J = 7.24 Hz, 2H); ^{13}C NMR (500 MHz, DMSO- d_6) $\boldsymbol{\delta}$ ppm: 157.28, 156.11, 137.54, 136.70, 123.93, 122.93, 122.90, 48.66, 45.18, 36.15, 26.93. FTIR ($\boldsymbol{\nu}_{max}$): 3372 (w), 3149 (w), 3096 (m), 2956 (w), 2858 (w) 2602 (w), 2338 (w), 1727 (w), 1701 (w), 1656 (m), 1567 (s), 1516 (w), 1439 (m), 1397 (m), 1326 (m), 1229 (m), 1170 (s), 1111 (w), 1083 (w), 1051 (w), 1019 (w), 990 (w), 836 (w), 742 (s), 693 (w), 662 (w).

^{1}H AND ^{13}C SPECTRA OF REPORTED MAJOR PRODUCTS

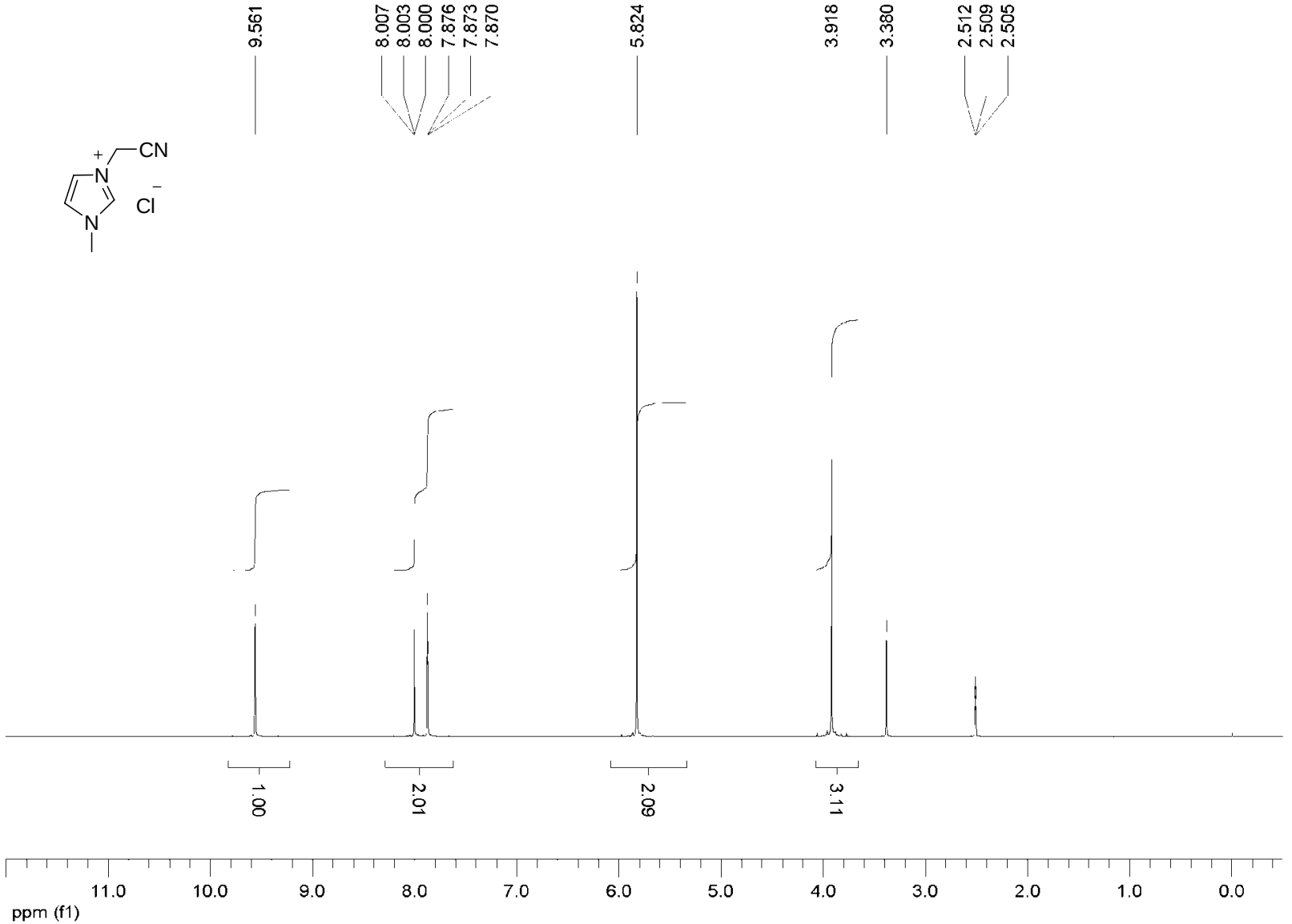

Figure S1. ^{1}H spectrum of 1-cyanomethyl-3-methylimidazolium chloride (**1**)

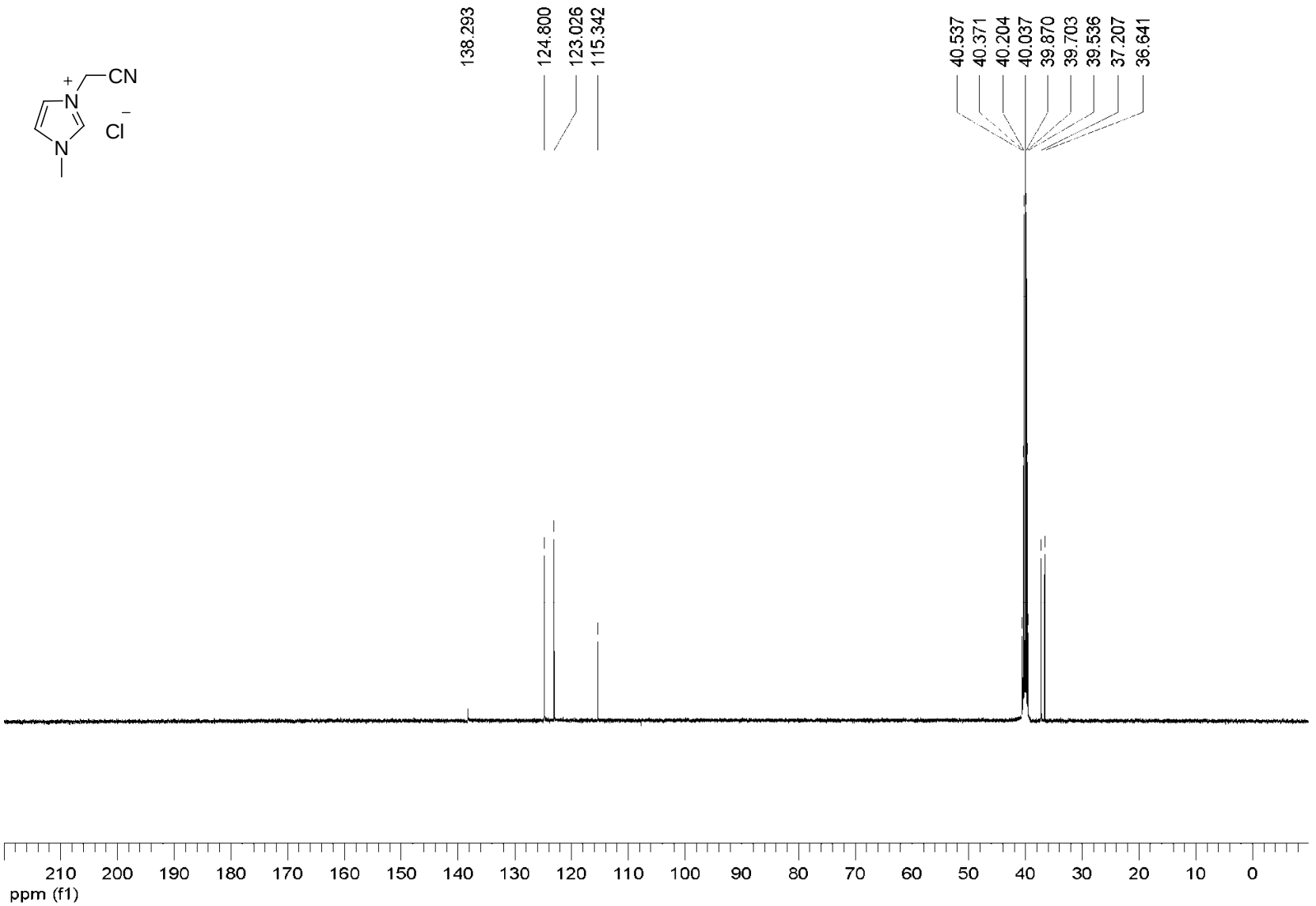

Figure S2. ^{13}C spectrum of 1-cyanomethyl-3-methylimidazolium chloride (**1**)

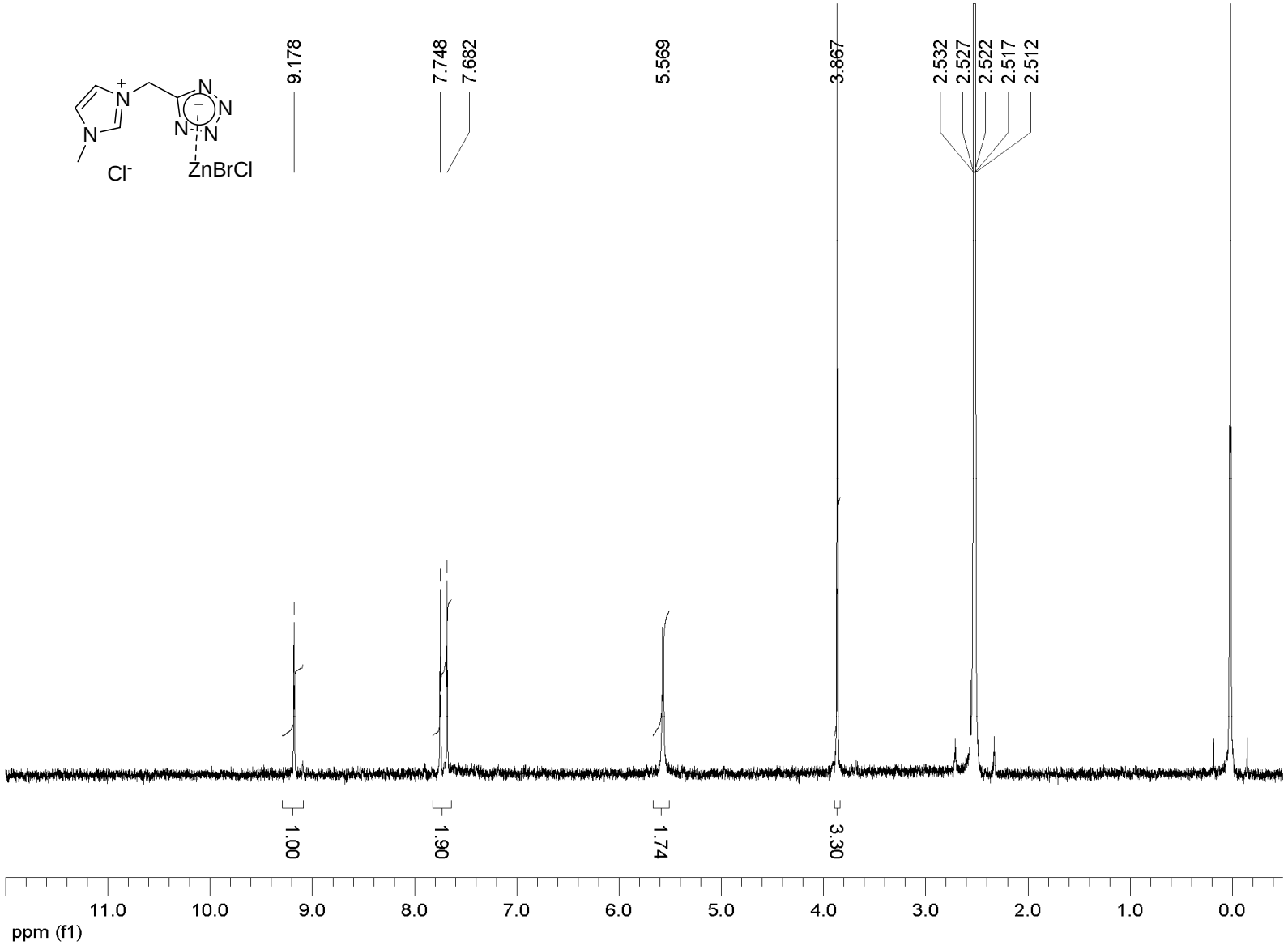

Figure S3. ^{1}H spectrum of 1-(5-tetrazolidyl)methyl-3-methylimidazolium (ZnBrCl) (**2**)

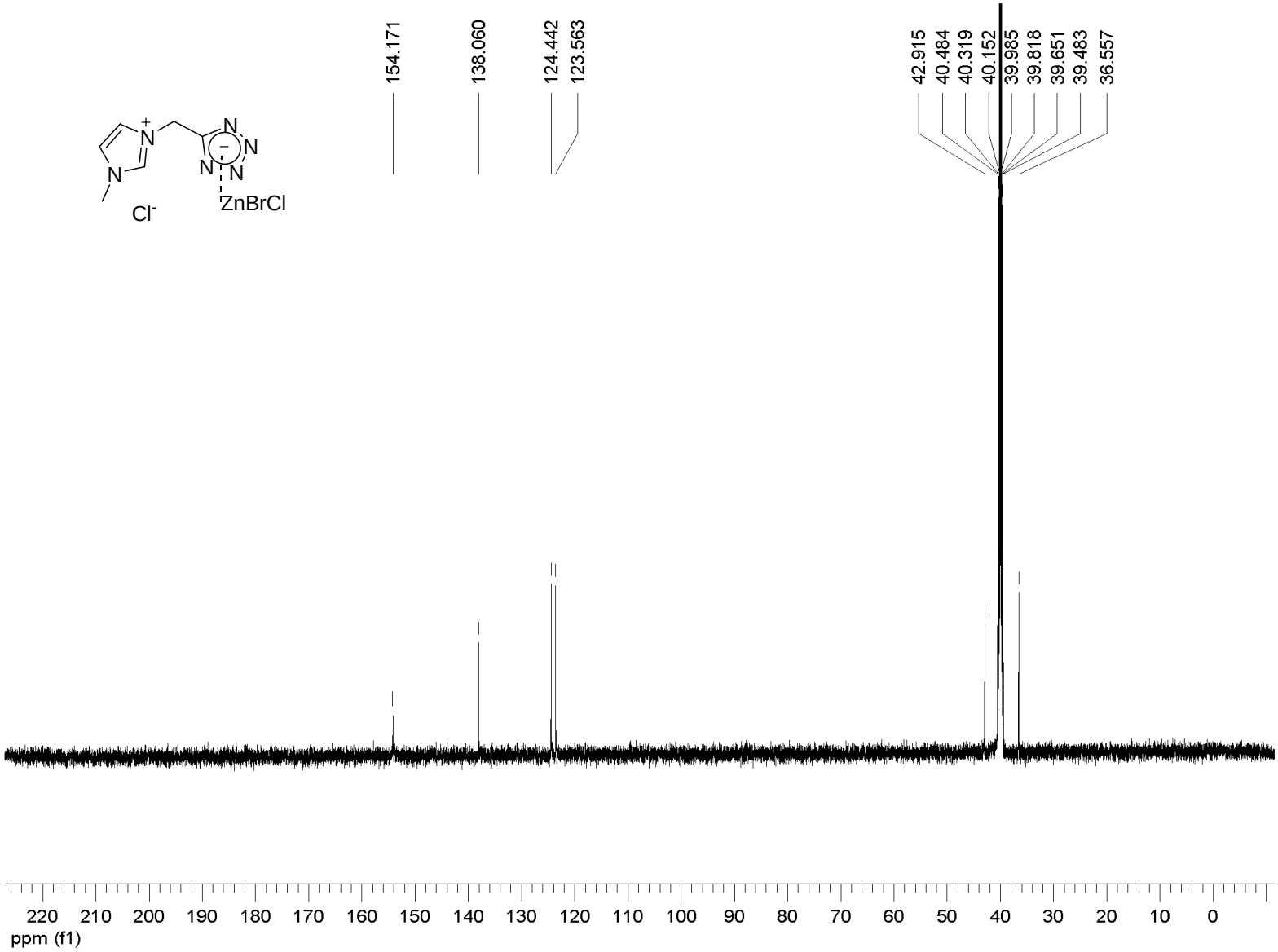

Figure S4. ^{13}C spectrum of 1-(5-tetrazolidyl)methyl-3-methylimidazolium (ZnBrCl) (**2**)

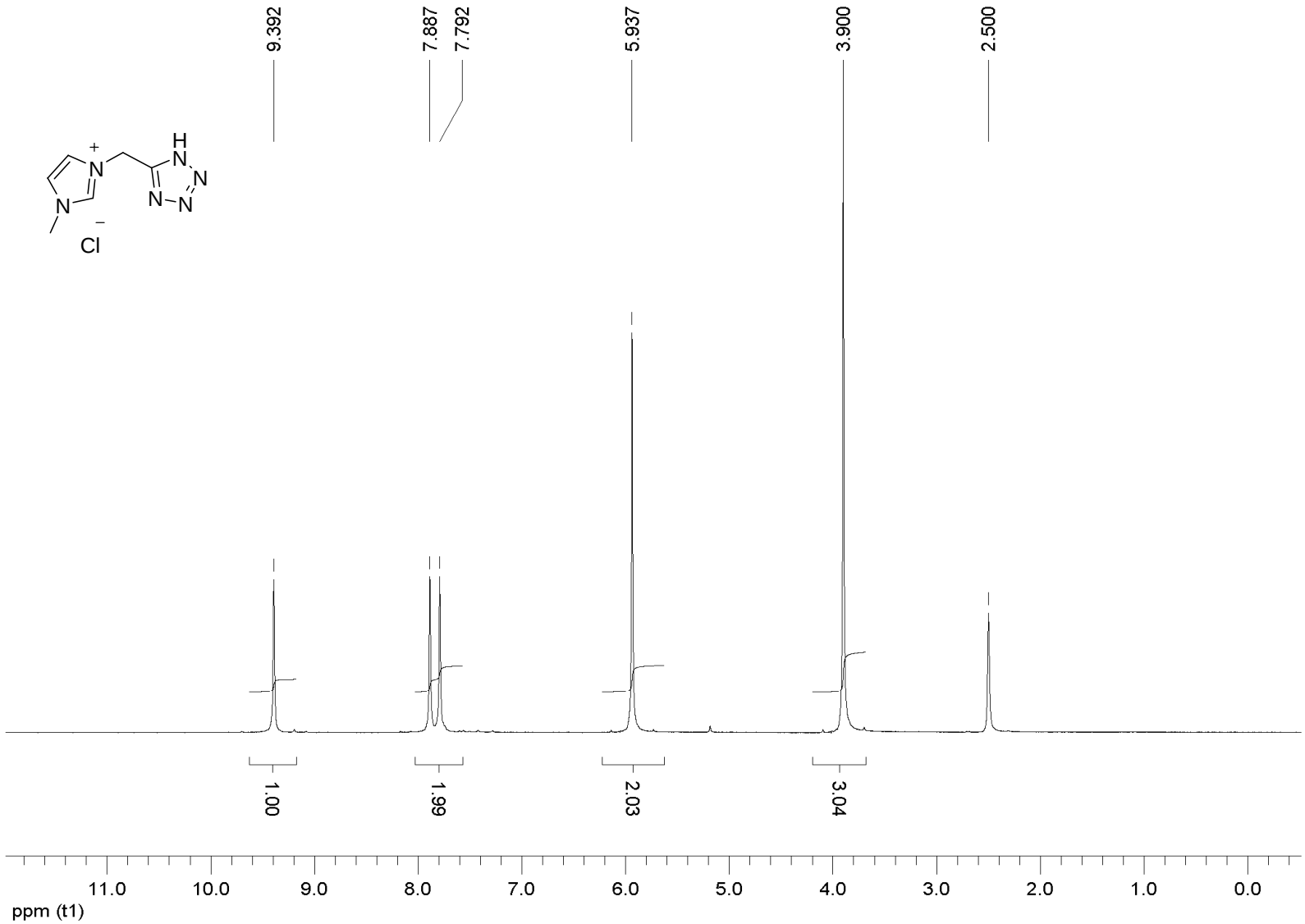

Figure S5. ^{1}H spectrum of 1-(5-1*H*-tetrazolyl)methyl-3-methylimidazolium chloride (**3**)

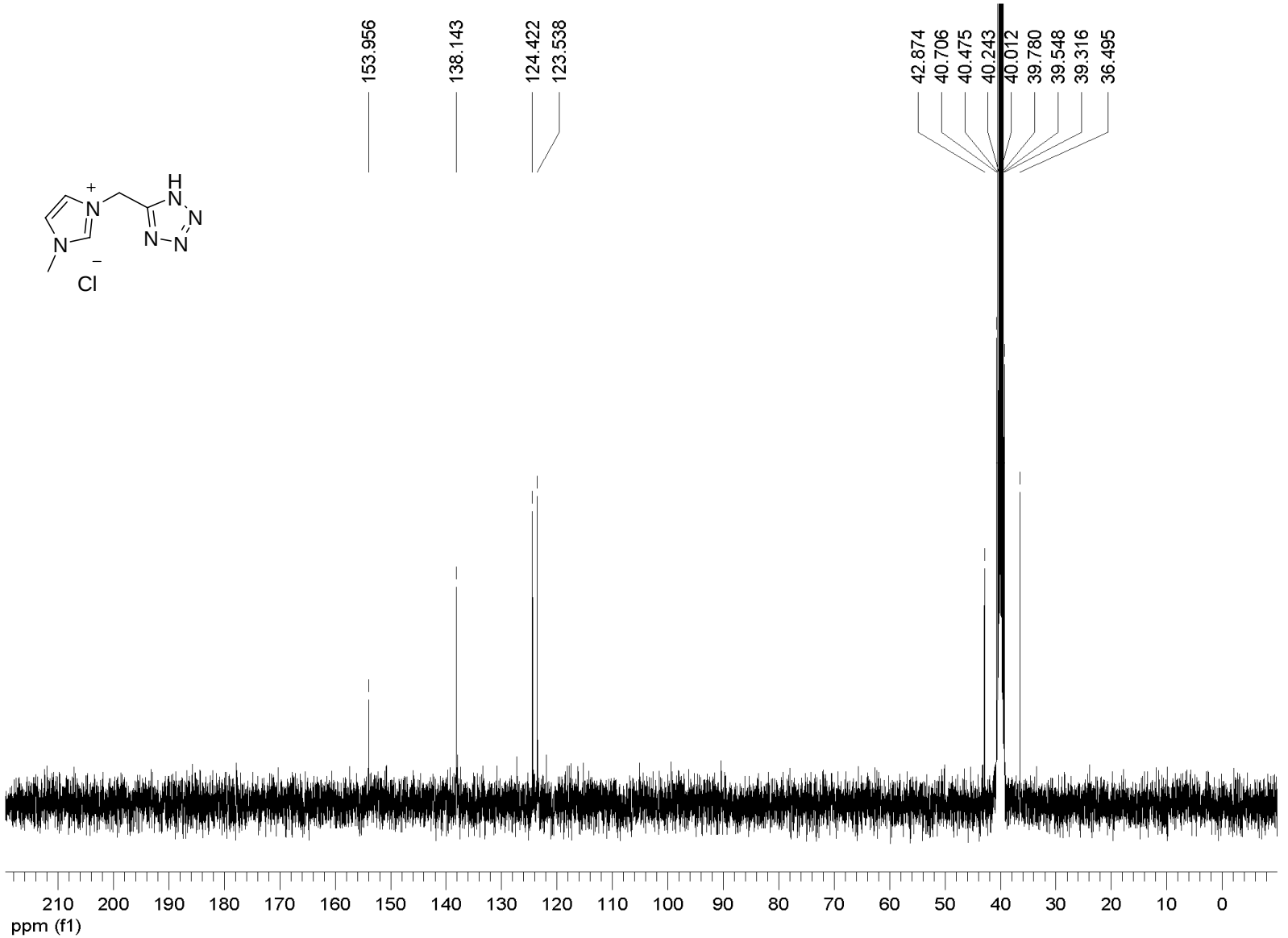

Figure S6. ^{13}C spectrum of 1-(5-1*H*-tetrazolyl)methyl-3-methylimidazolium chloride (**3**)

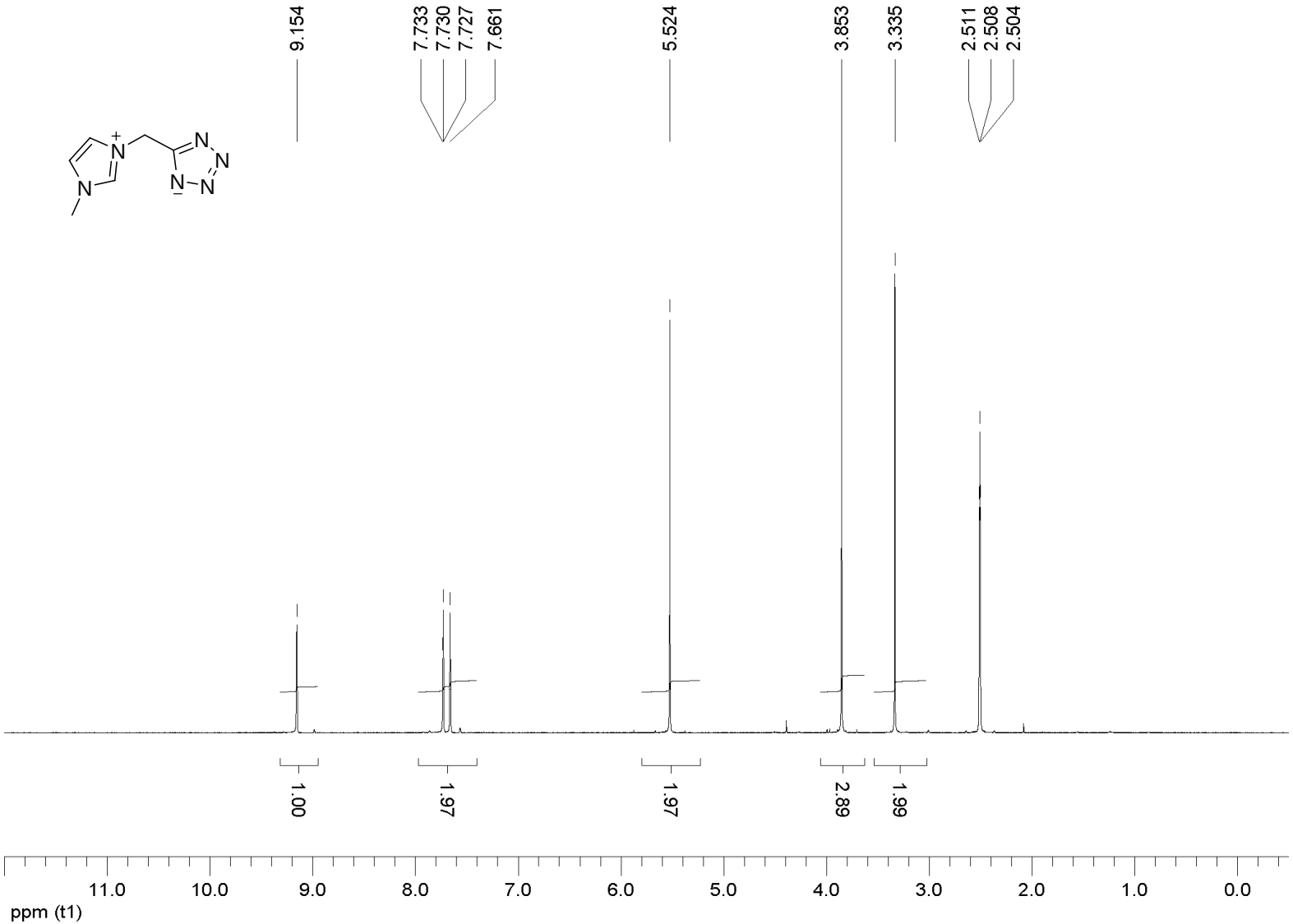

Figure S7. ^{1}H spectrum of 1-(5-tetrazolidyl)methyl-3-methylimidazolium zwitterion (**4**)

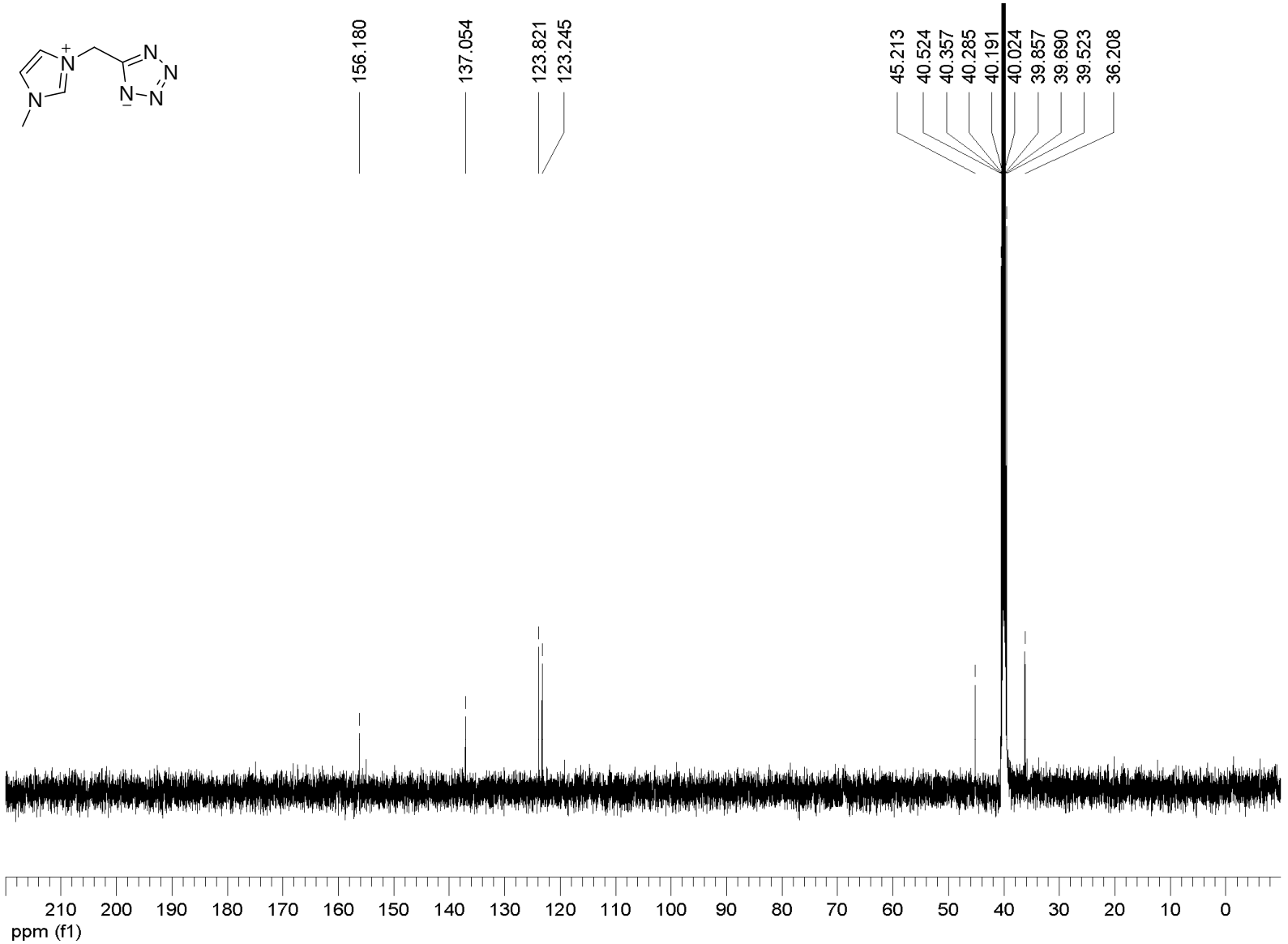

Figure S8. ^{13}C spectrum of 1-(5-tetrazolidyl)methyl-3-methylimidazolium zwitterion (**4**)

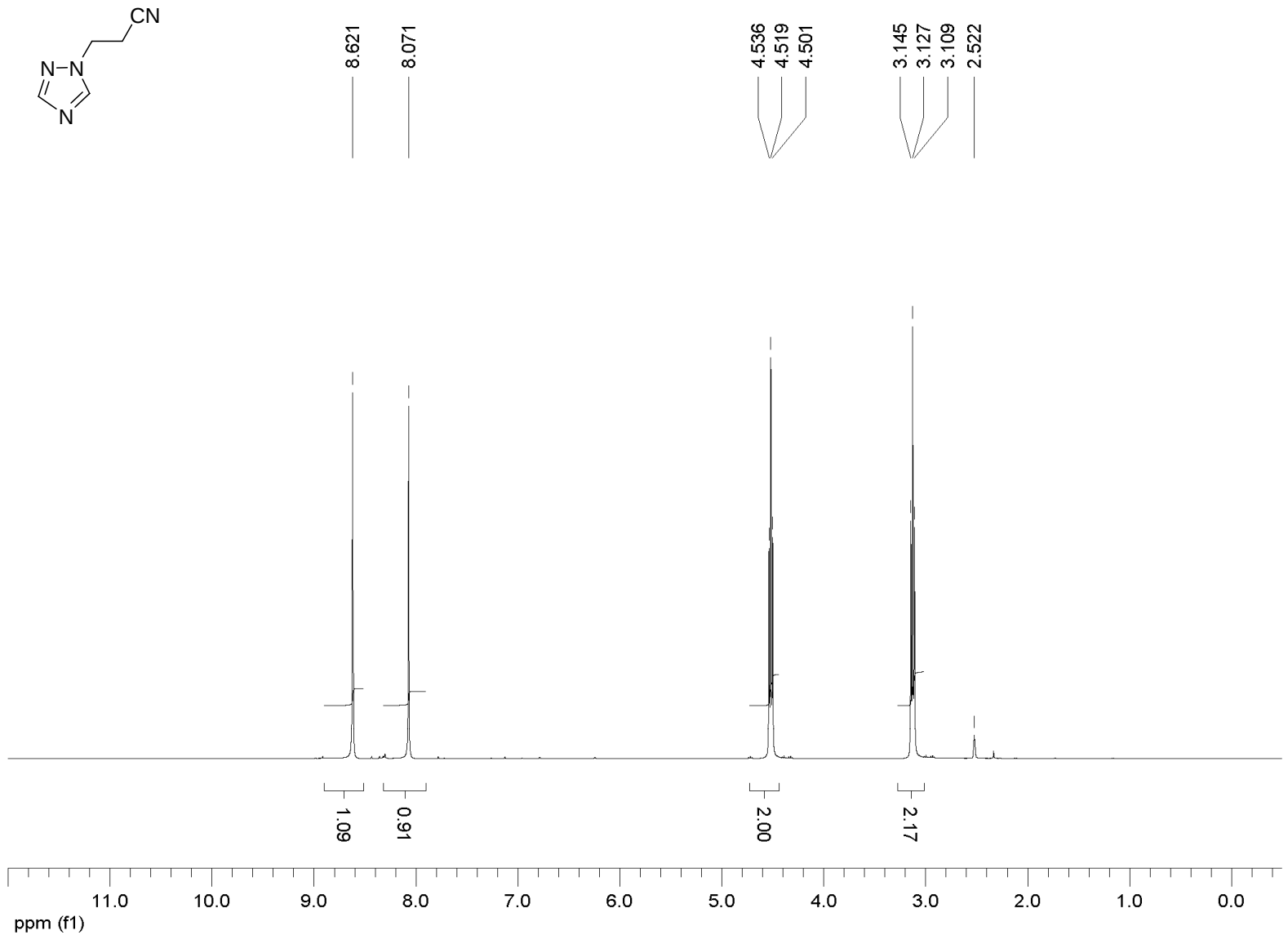

Figure S9. ^{1}H spectrum of 1-(2-cyanoethyl)-1,2,4-triazole (**6**)

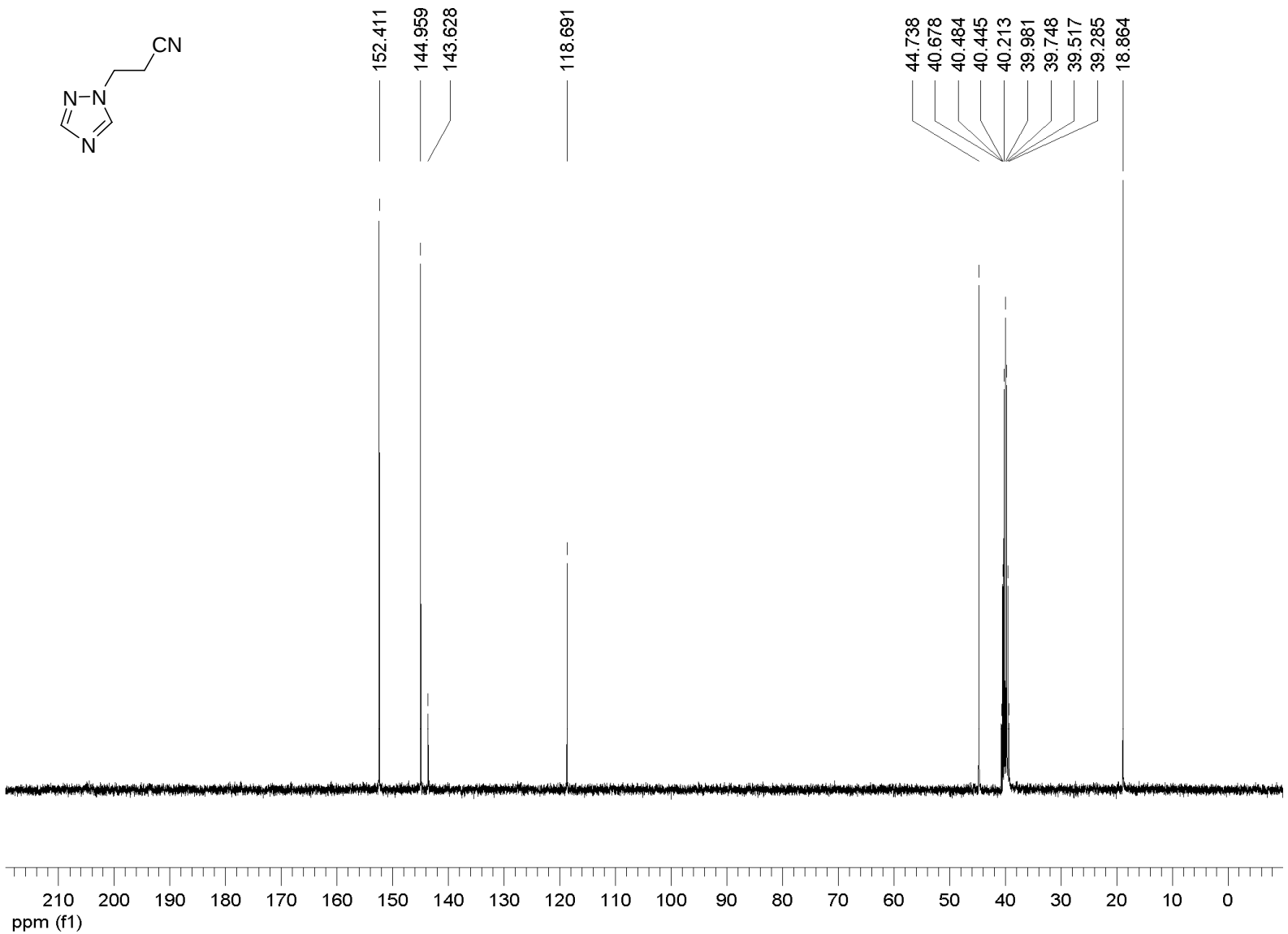

Figure S10. ^{13}C spectrum of 1-(2-cyanoethyl)-1,2,4-triazole (**6**)

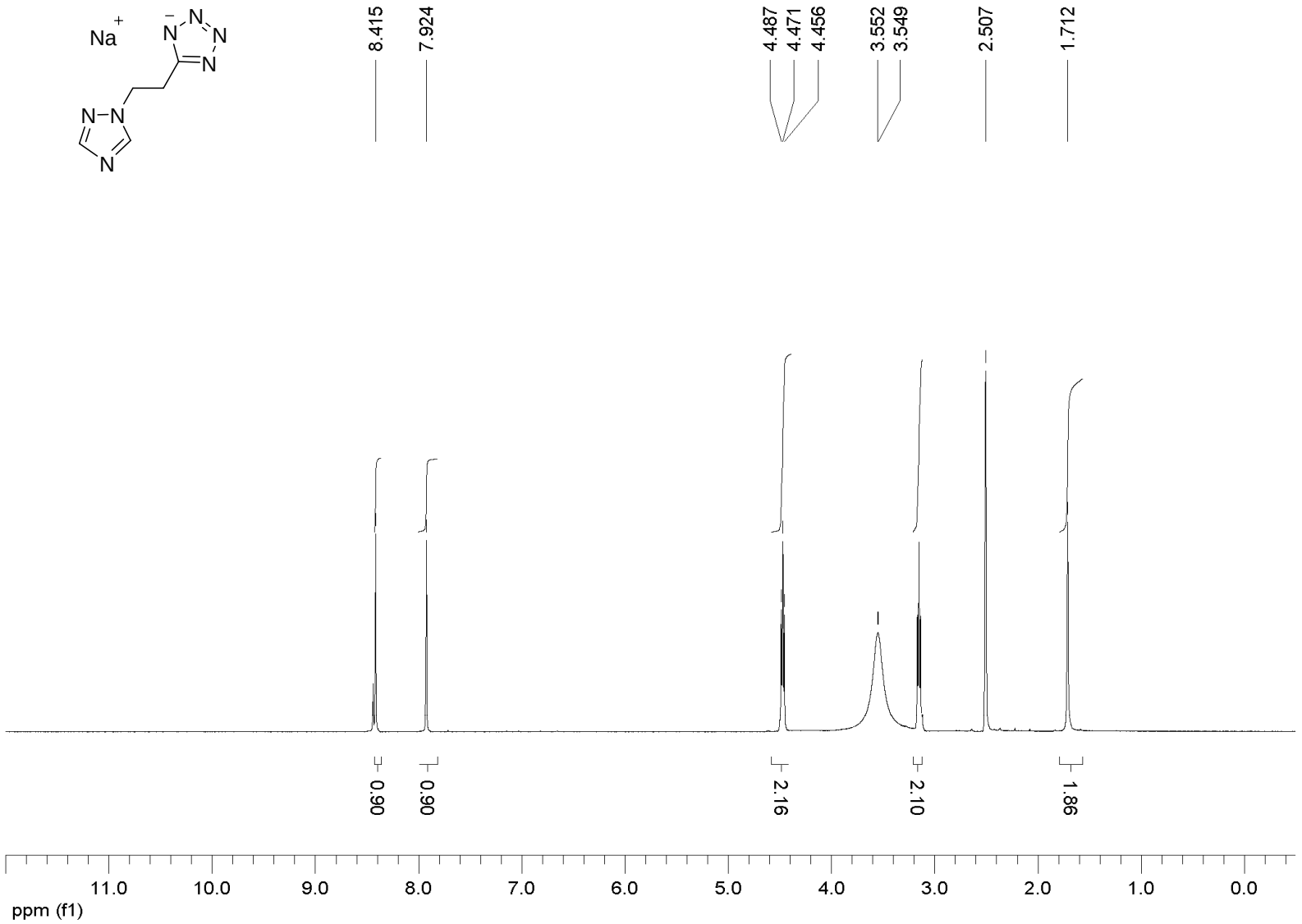

Figure S11. ^{1}H spectrum of sodium 5-(2-(1,2,4-triazol-1-yl)ethyl)tetrazolate dihydrate (**7**·$2H_2O$)

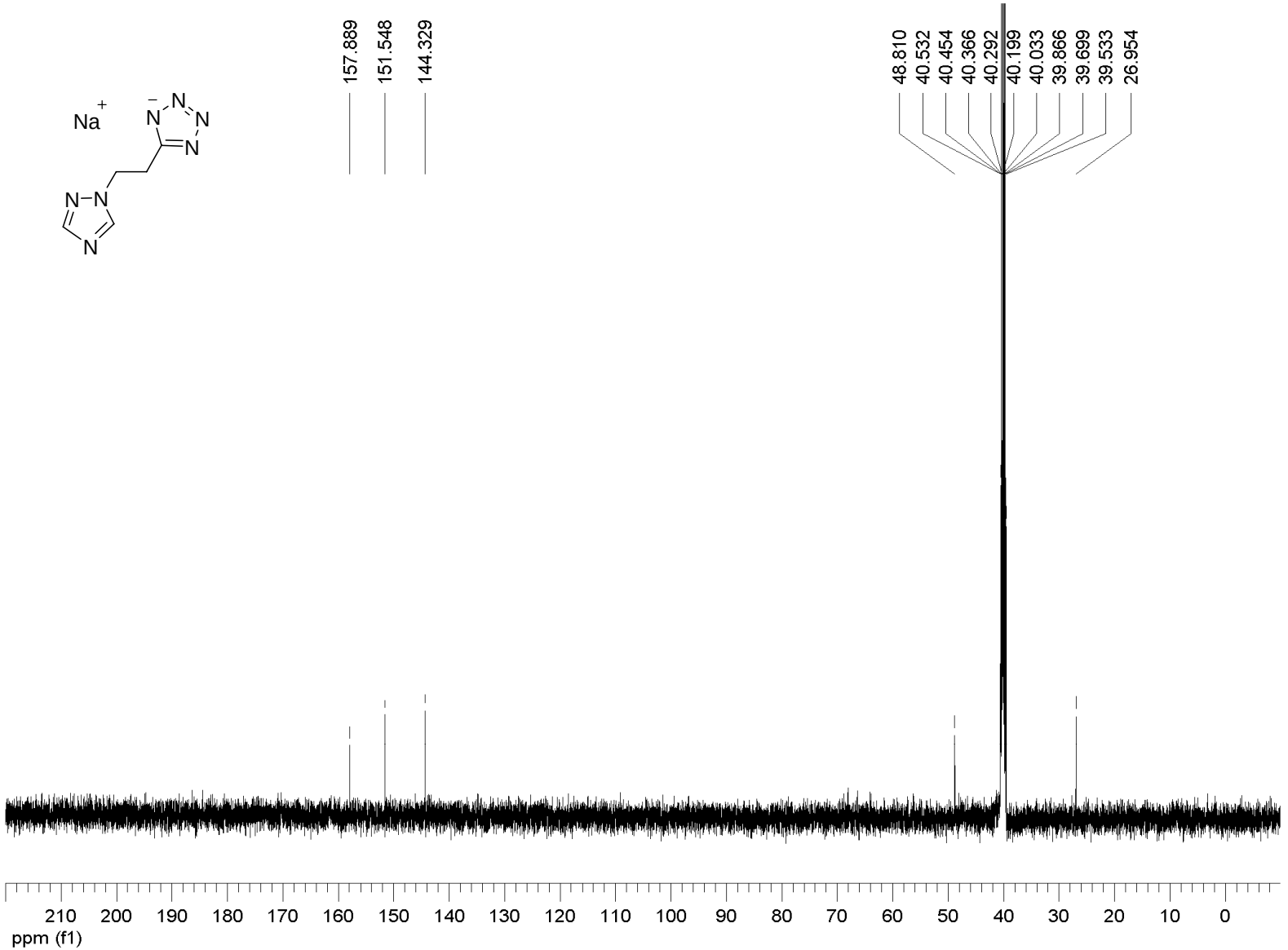

Figure S12. ^{13}C spectrum of sodium 5-(2-(1,2,4-triazol-1-yl)ethyl)tetrazolate dihydrate (**7**·$2H_2O$)

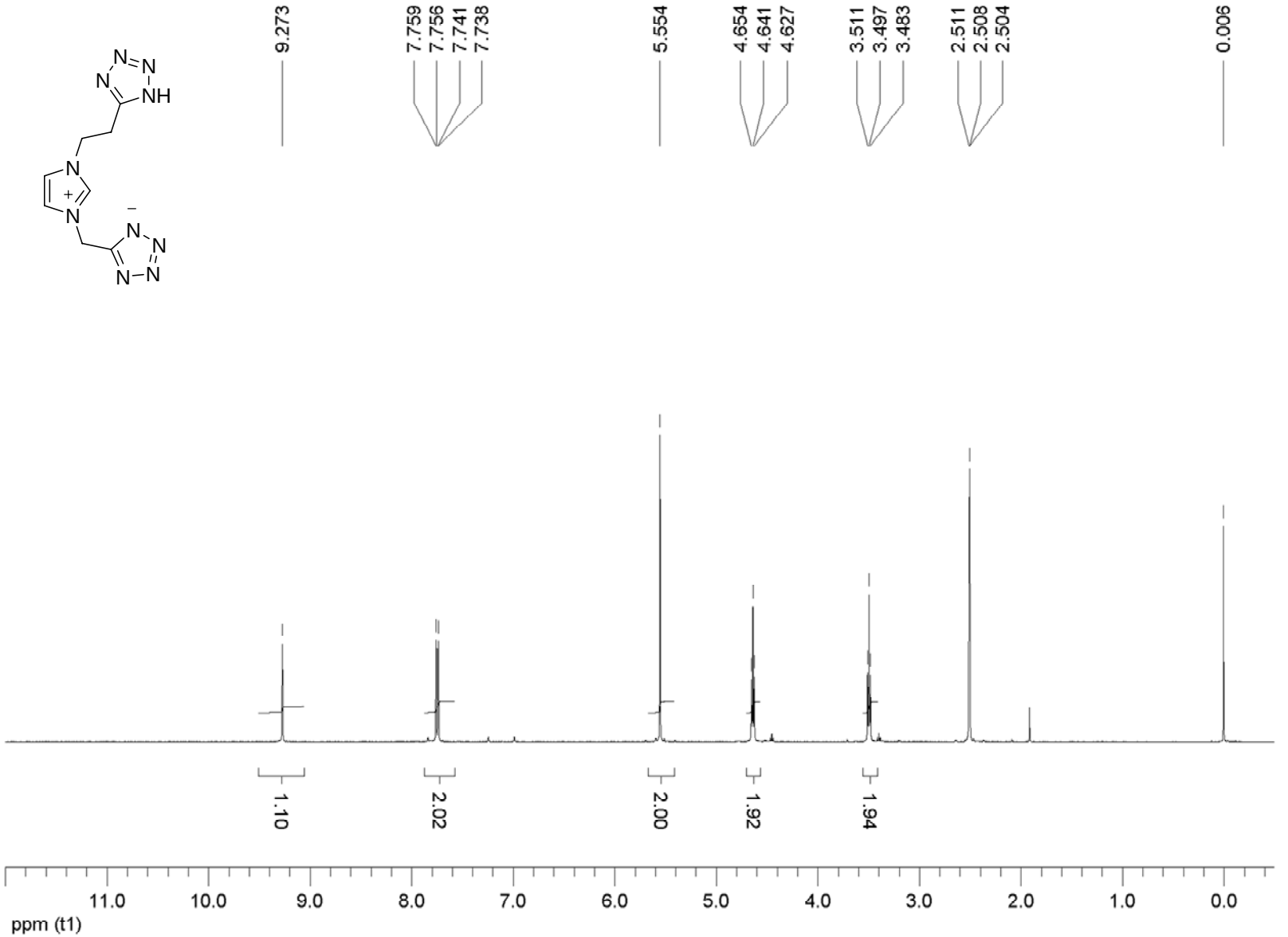

Figure S13. ^{1}H spectrum of 1-(2-(5-tetrazolidyl)ethyl)-3-(5-1*H*-tetrazolyl)imidazolium zwitterion (**10**)

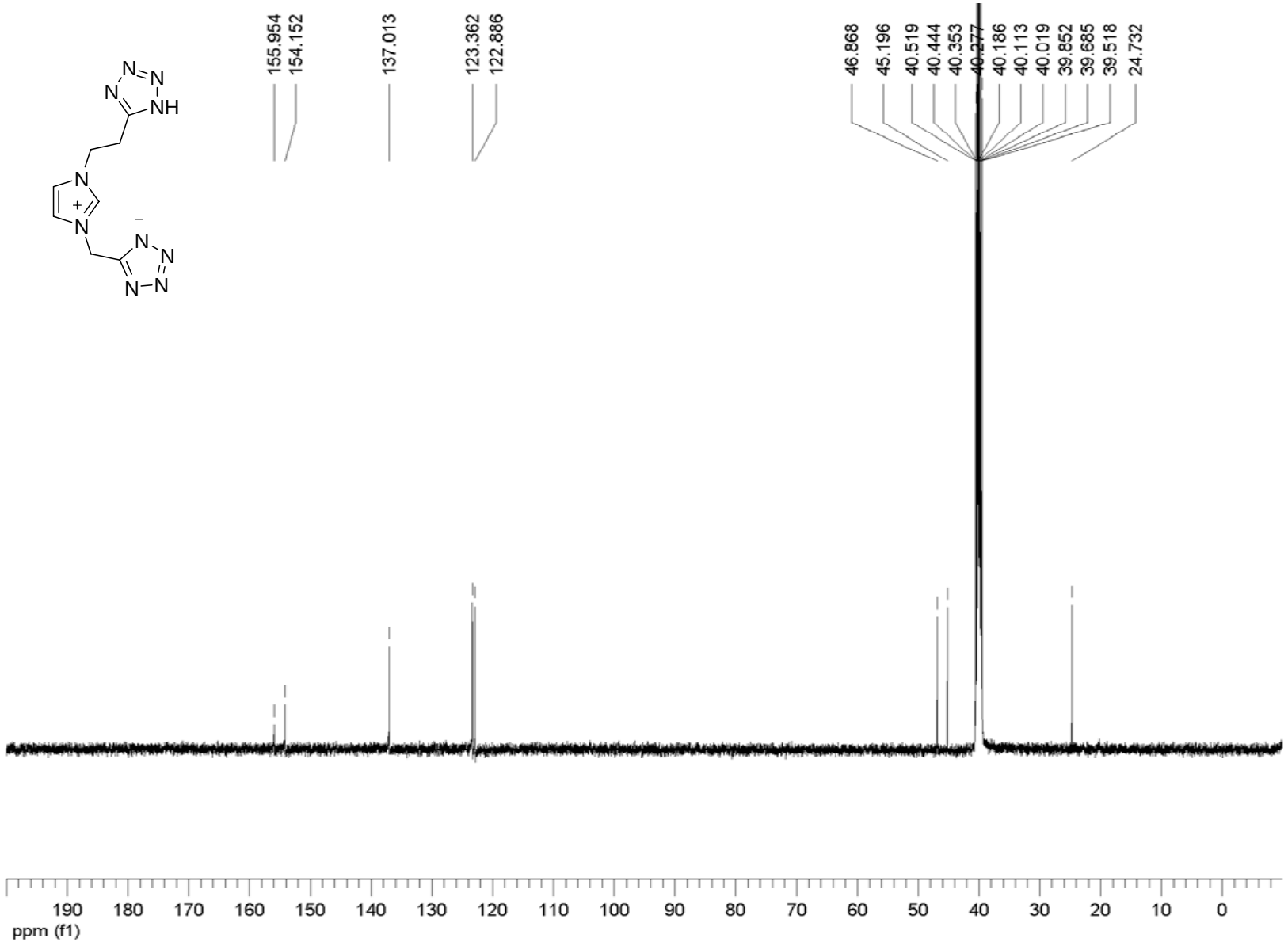

Figure S14. ^{13}C spectrum of 1-(2-(5-tetrazolidyl)ethyl)-3-(5-1*H*-tetrazolyl)imidazolium zwitterion (**10**)

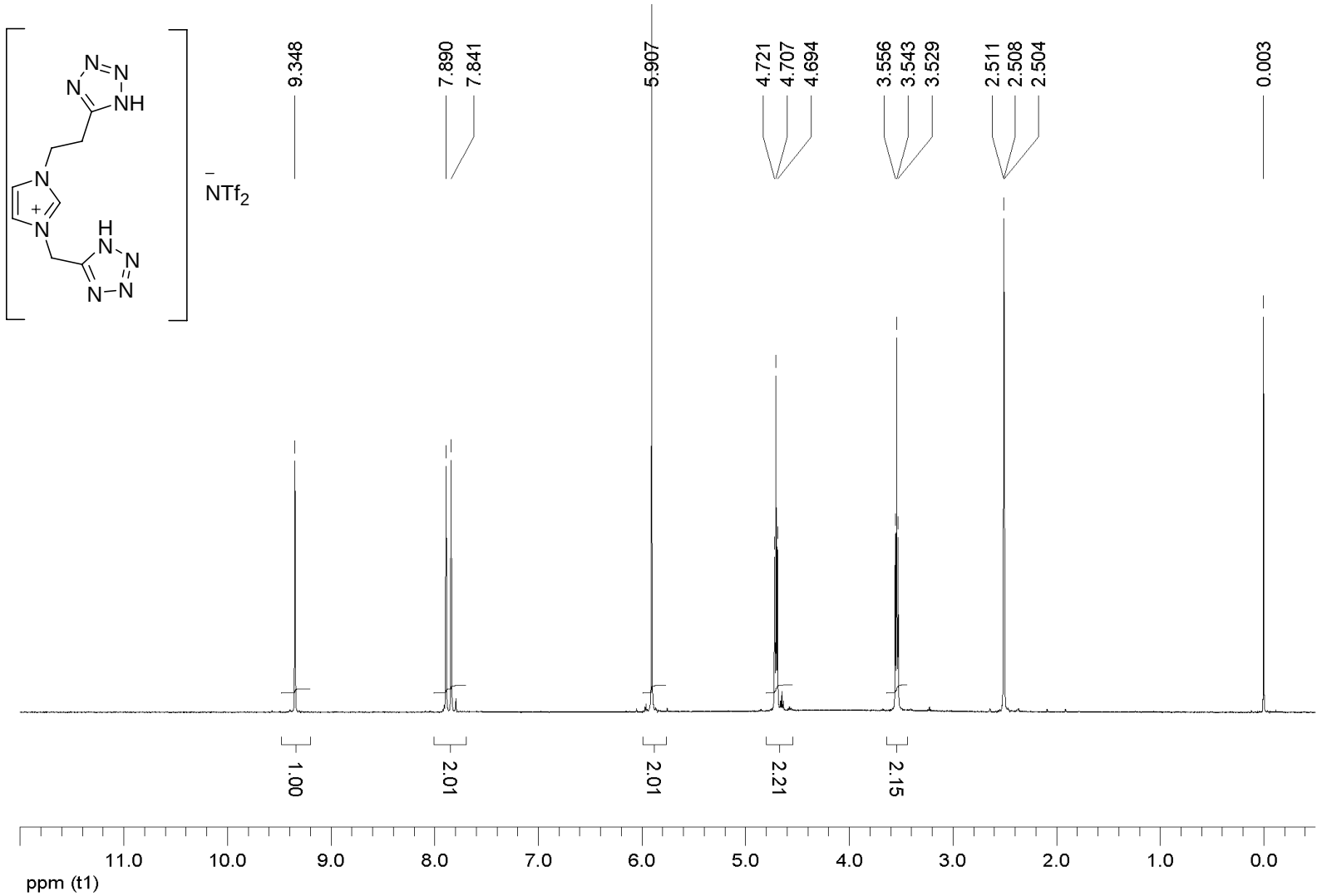

Figure S15. ^{1}H spectrum of 1-(2-(5-1*H*-tetrazolyl)ethyl)-3-(5-1*H*-tetrazolyl)methylimidazolium bis(trifluoromethanesulfonyl)amide (**11**)

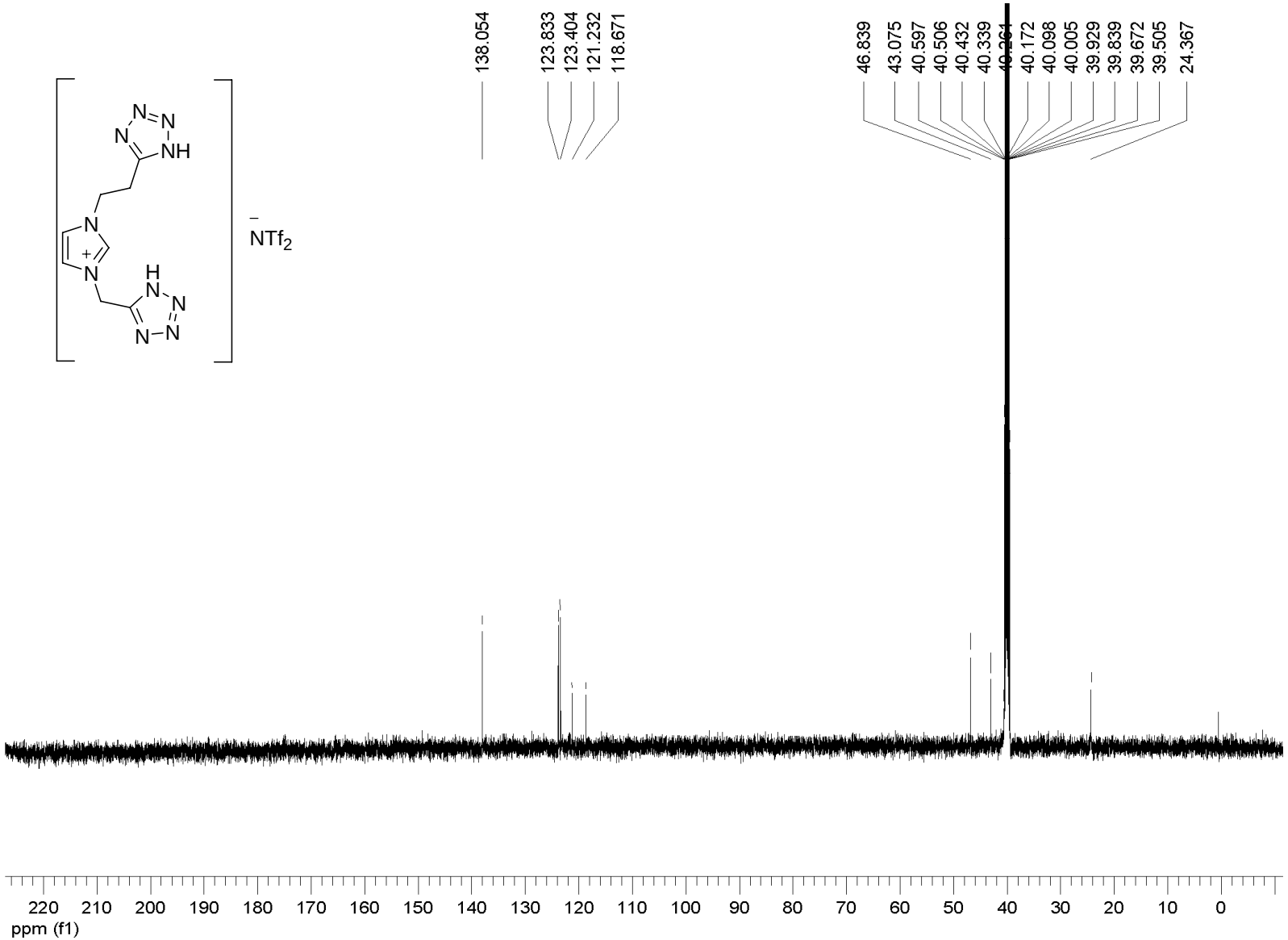

Figure S16. ^{13}C spectrum of 1-(2-(5-1*H*-tetrazolyl)ethyl)-3-(5-1*H*-tetrazolyl)methylimidazolium bis(trifluoromethanesulfonyl)amide (**11**)

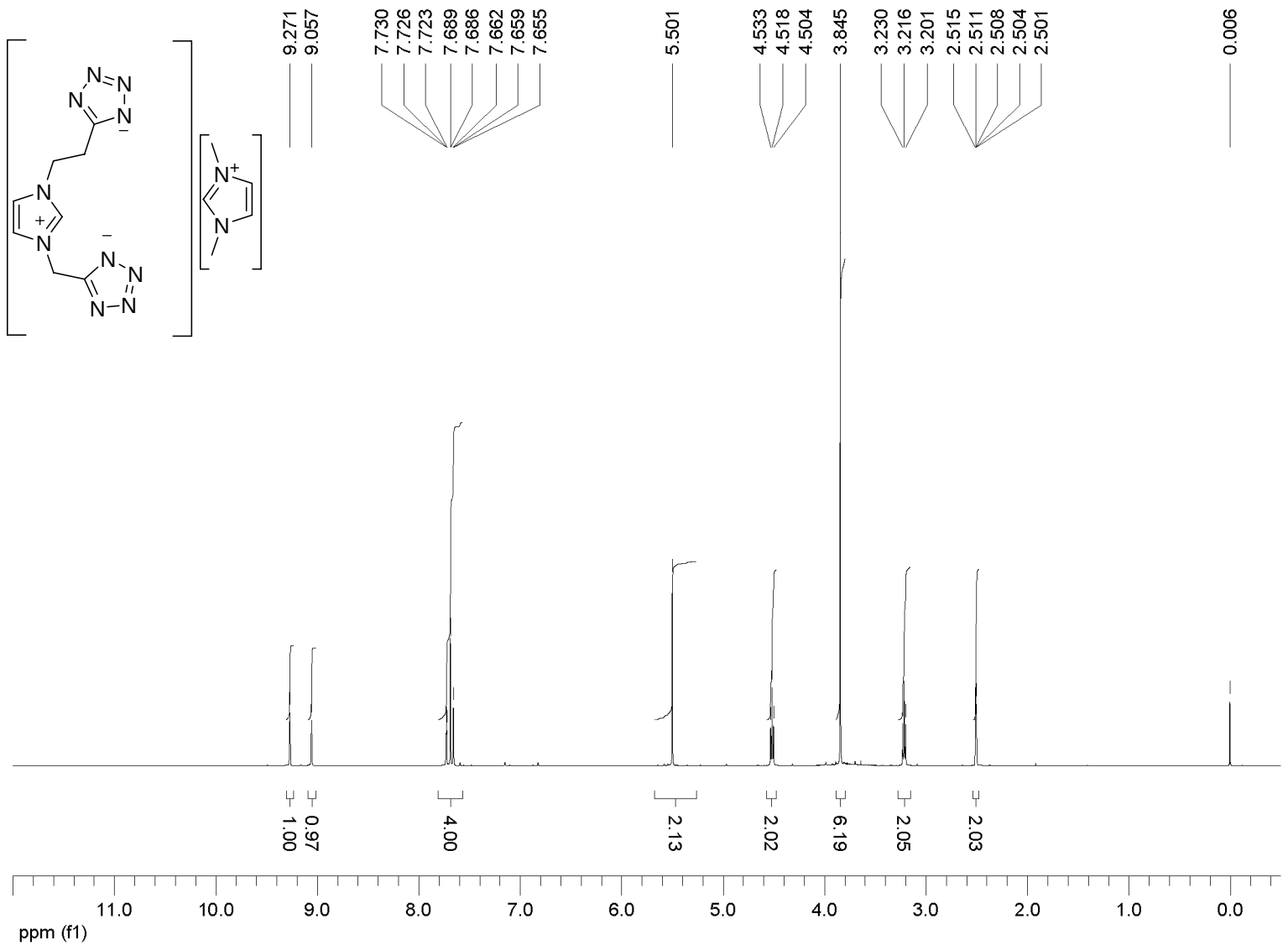

Figure S17. ^{1}H spectrum of 1,3-dimethylimidazolium 1-(2-(5-tetrazolidyl)ethyl)-3-(5-tetrazolidyl)methylimidazolium (**12**)

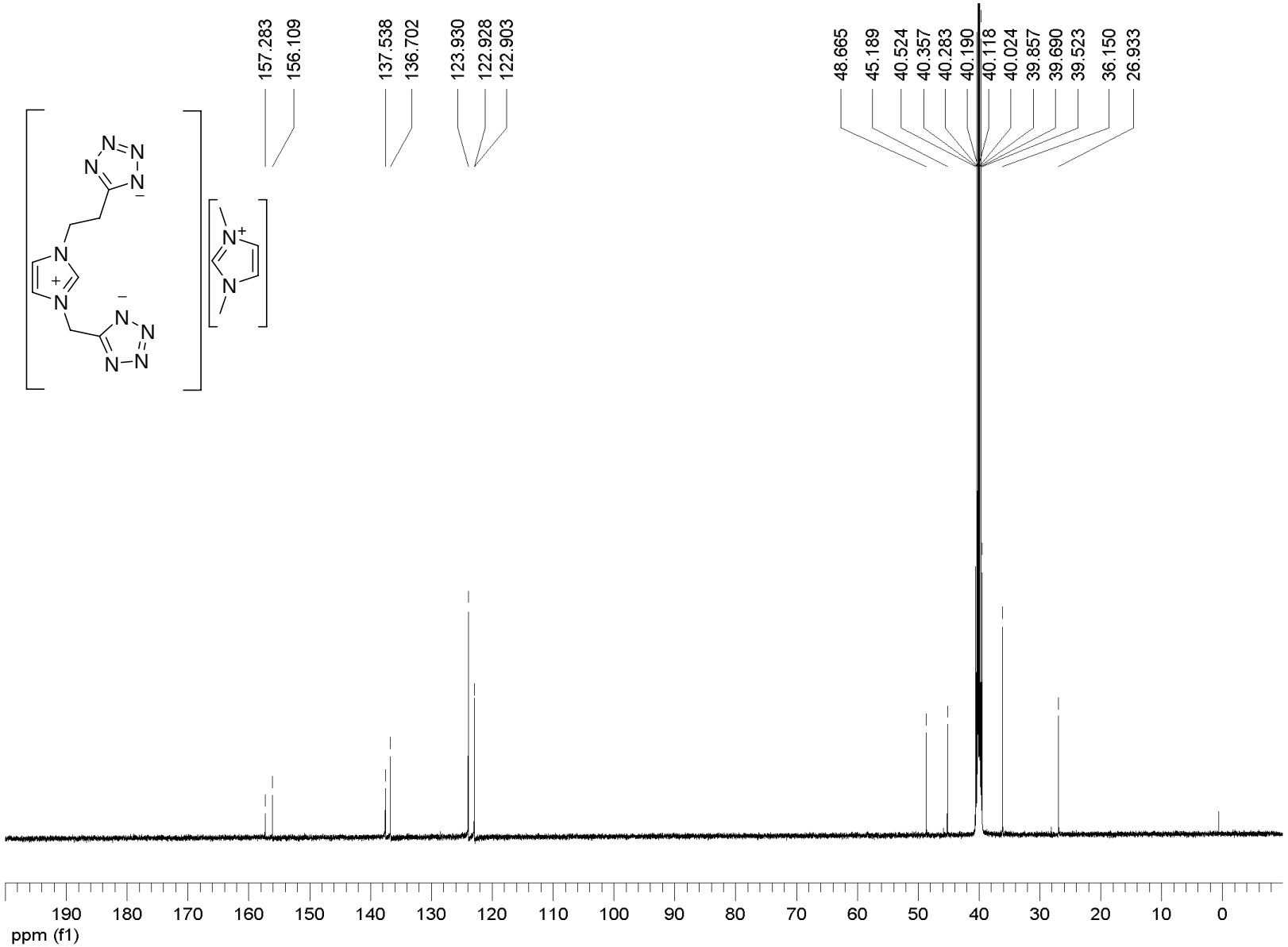

Figure S18. ^{13}C spectrum of 1,3-dimethylimidazolium 1-(2-(5-tetrazolidyl)ethyl)-3-(5-tetrazolidyl)methylimidazolium (**12**)

FT-IR SPECTRA OF REPORTED MAJOR PRODUCTS

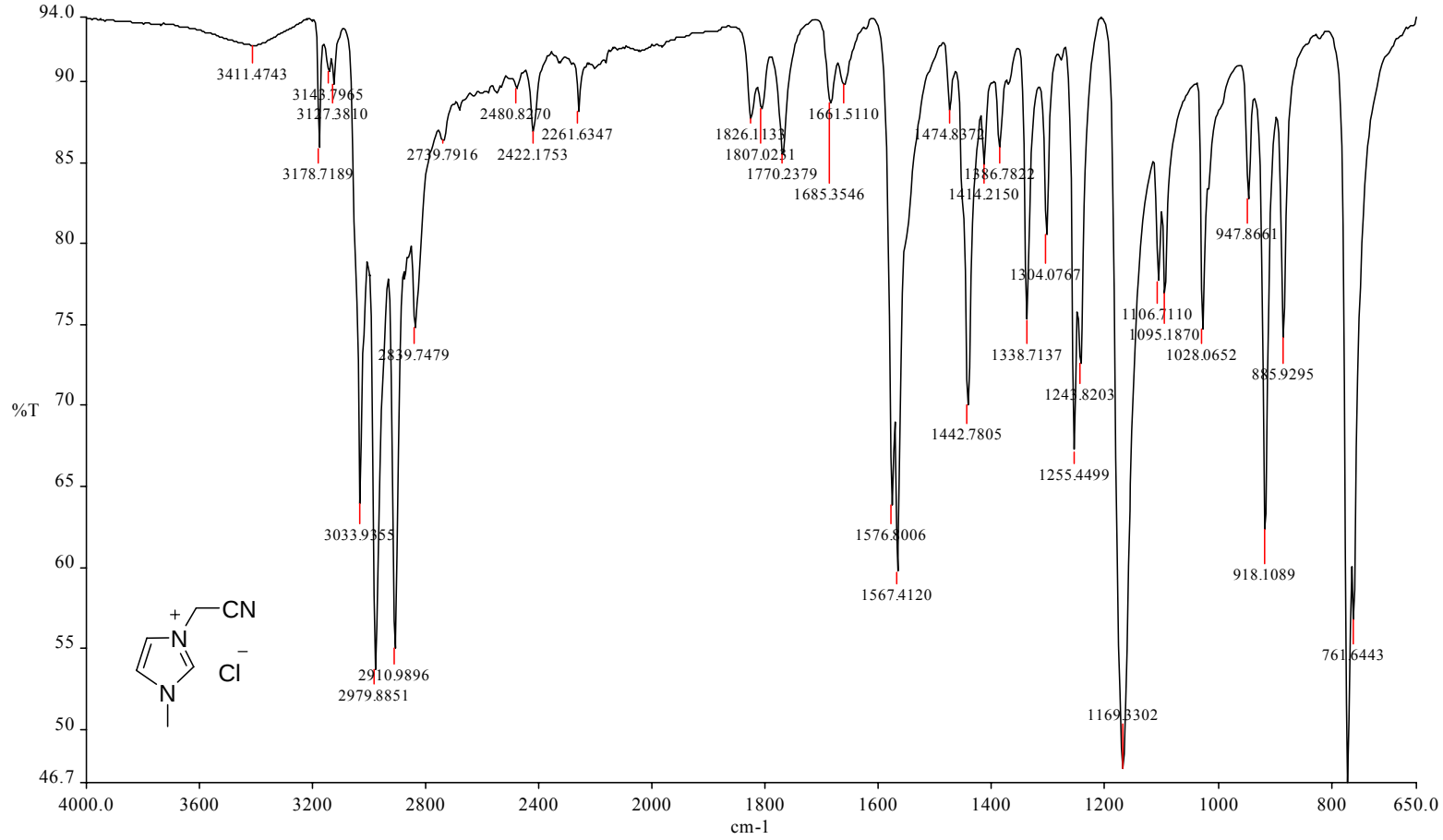

Figure S19. FT-IR spectrum of 1-cyanomethyl-3-methylimidazolium chloride (**1**)

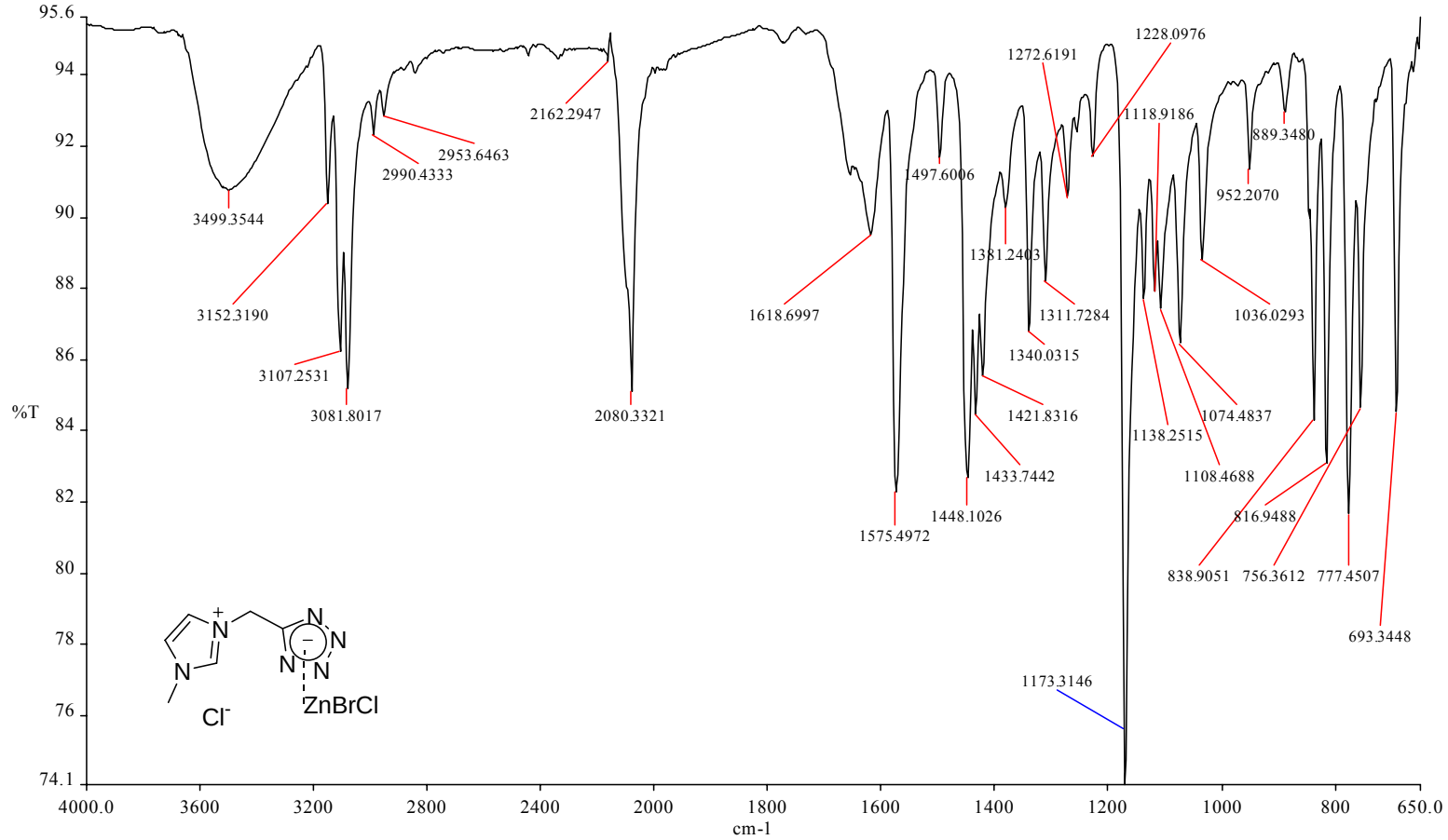

Figure S20. FT-IR spectrum of 1-(5-tetrazolidyl)methyl-3-methylimidazolium•(ZnBrCl) (**2**)

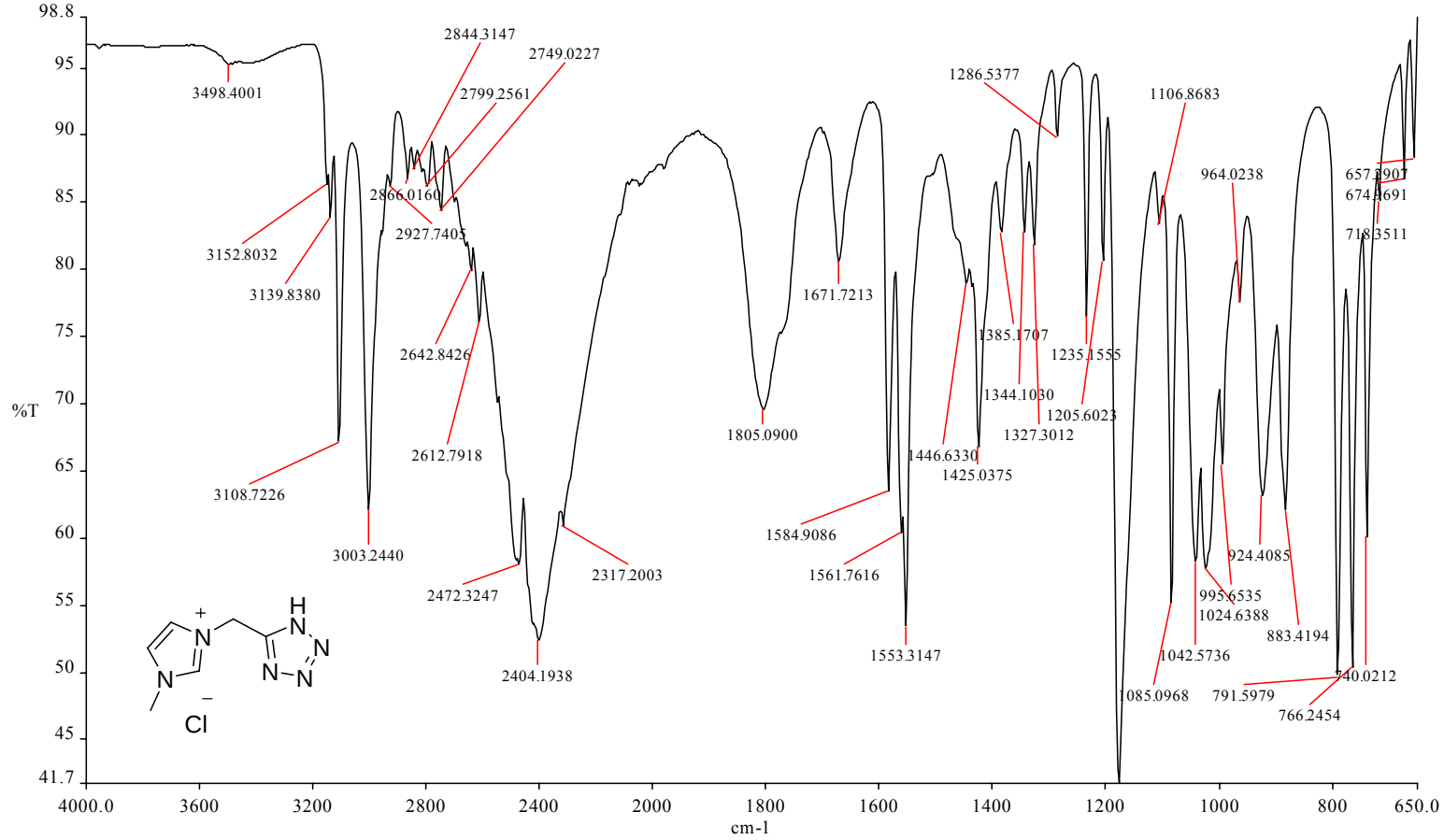

Figure S21. FT-IR spectrum of 1-(5-1*H*-tetrazolyl)methyl-3-methylimidazolium chloride (**3**)

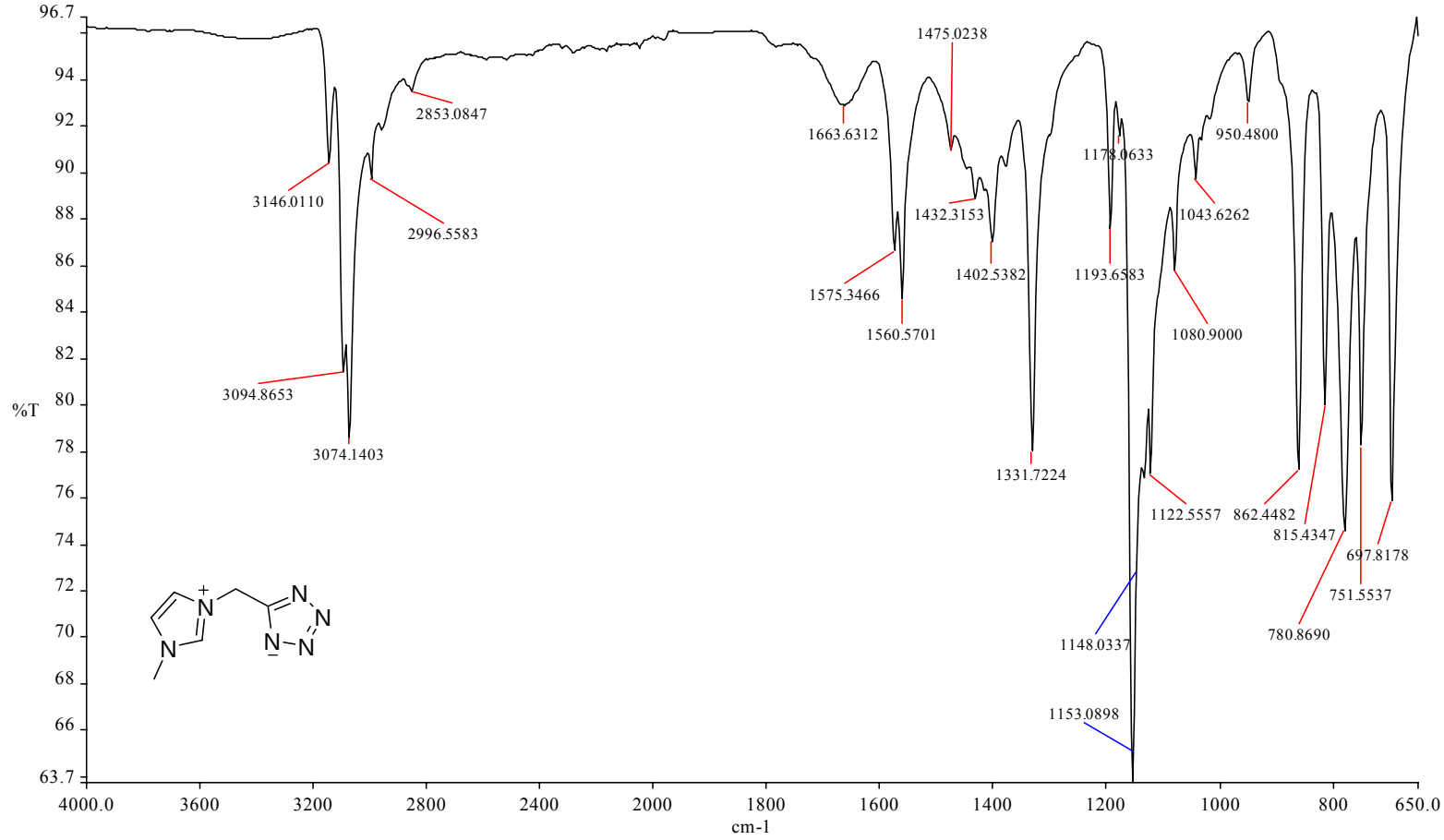

Figure S22. FT-IR spectrum of 1-(5-tetrazolidyl)methyl-3-methylimidazolium zwitterion (**4**)

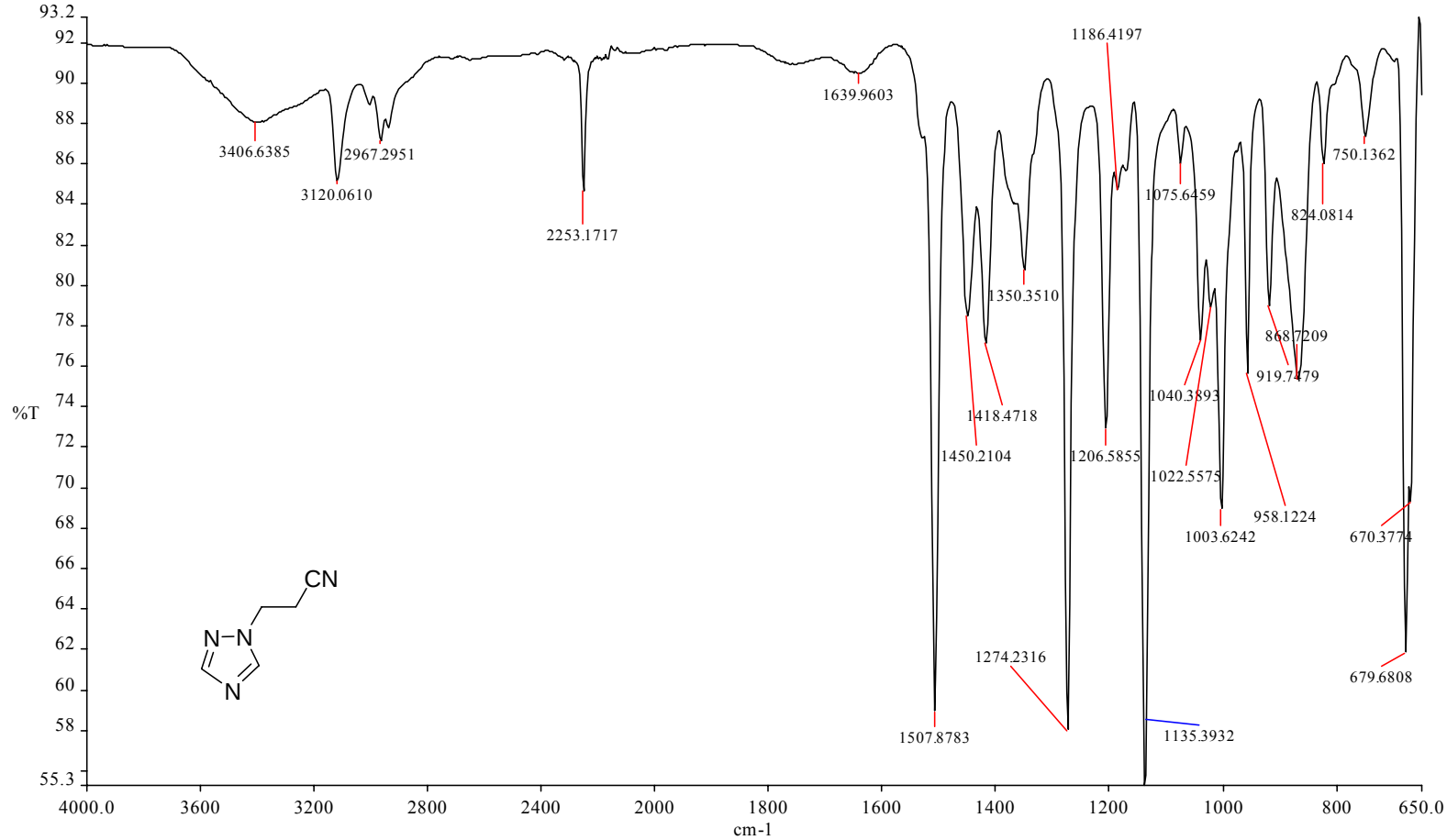

Figure S23. FT-IR spectrum of 1-(2-cyanoethyl)-1,2,4-triazole (**6**)

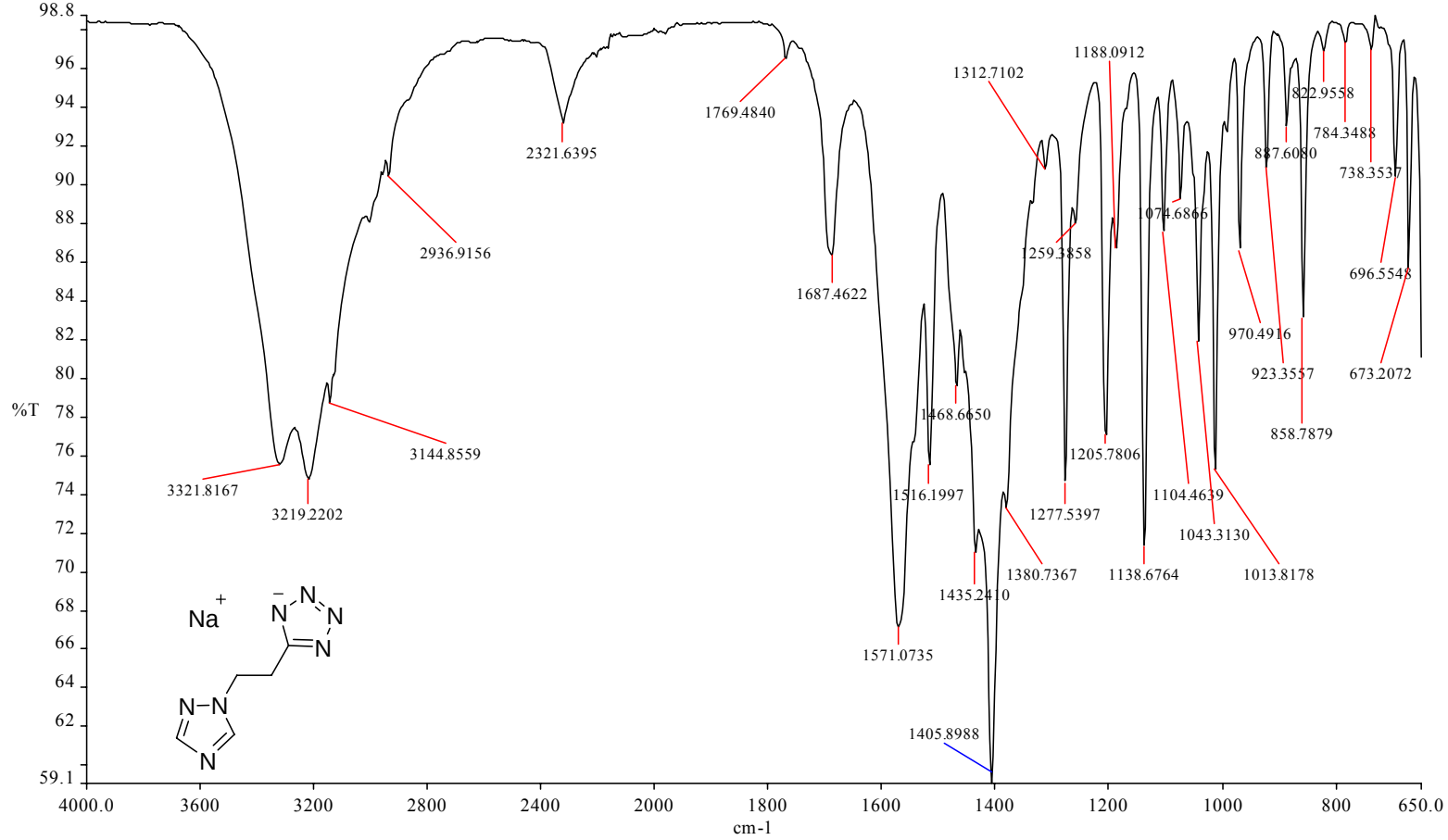

Figure S24. FT-IR spectrum of sodium 5-(2-(1,2,4-triazol-1-yl)ethyl)tetrazolate dihydrate (**7**·2H_2O)

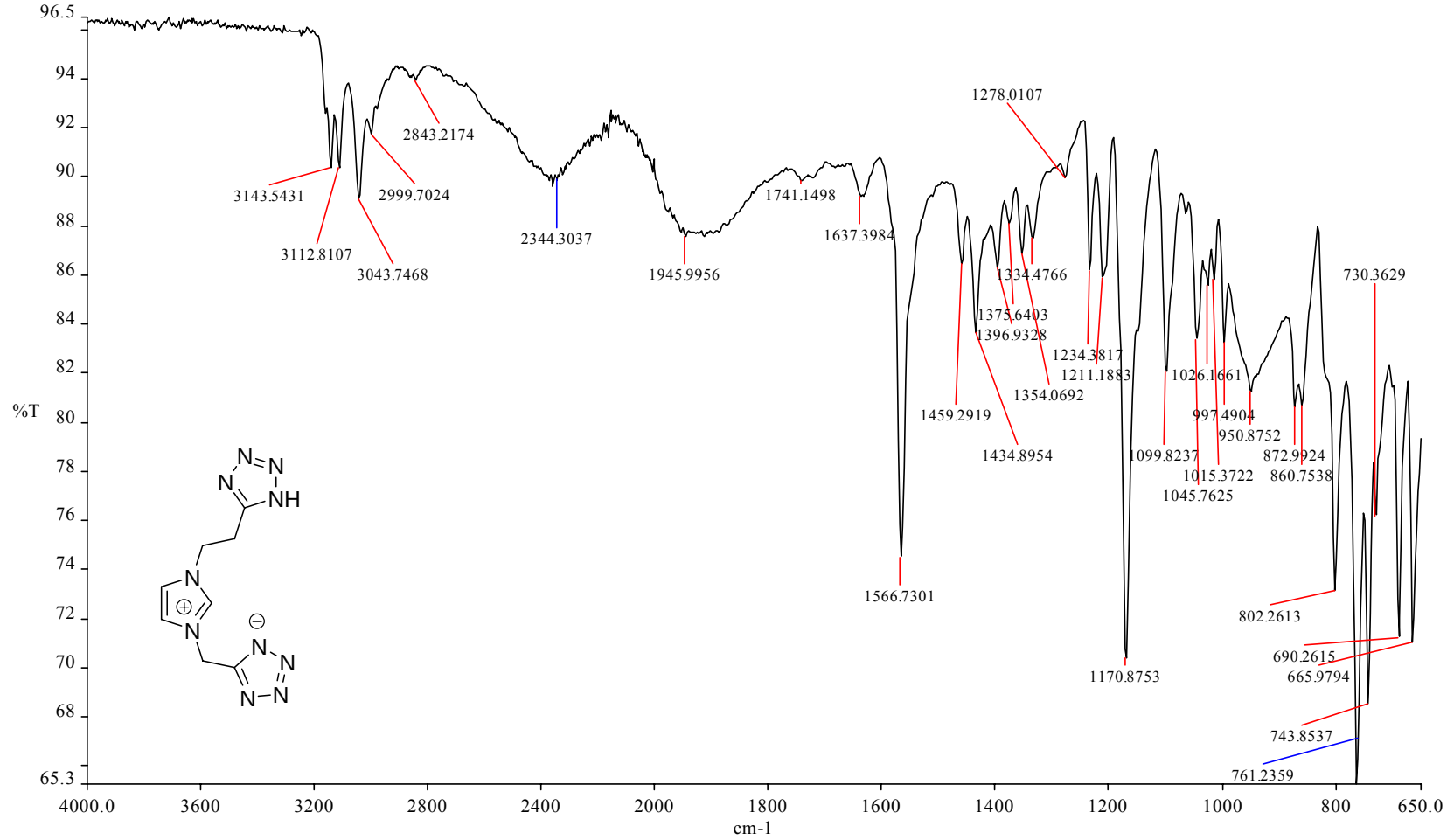

Figure S25. FT-IR spectrum of 1-(2-(5-tetrazolidyl)ethyl)-3-(5-1*H*-tetrazolyl)methylimidazolium zwitterion (**10**)

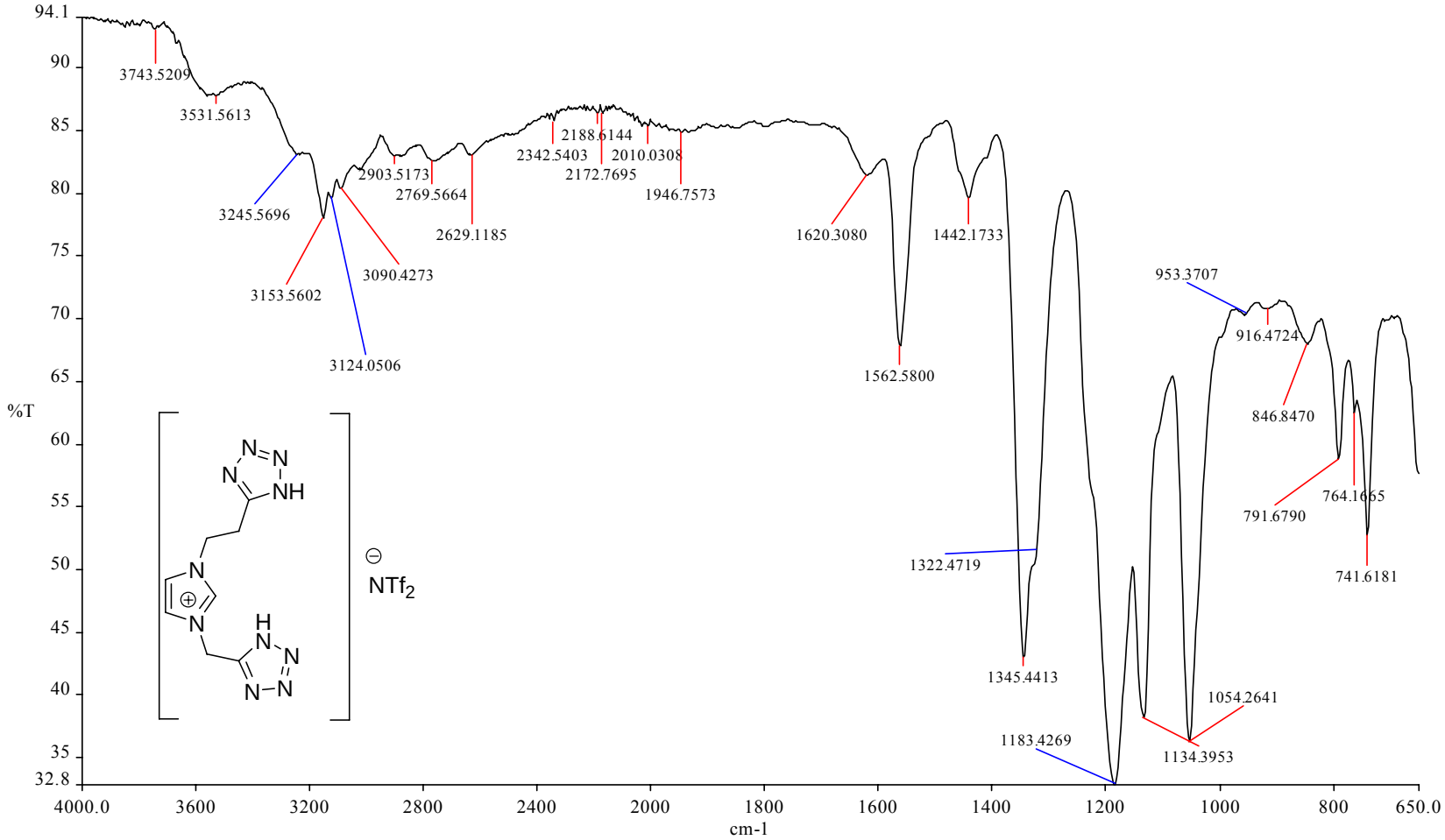

Figure S26. FT-IR spectrum of ***1***-(2-(5-1*H*-tetrazolyl)ethyl)-3-(5-1*H*-tetrazolyl)methylimidazolium bis(trifluoromethanesulfonyl)amide (**11**).

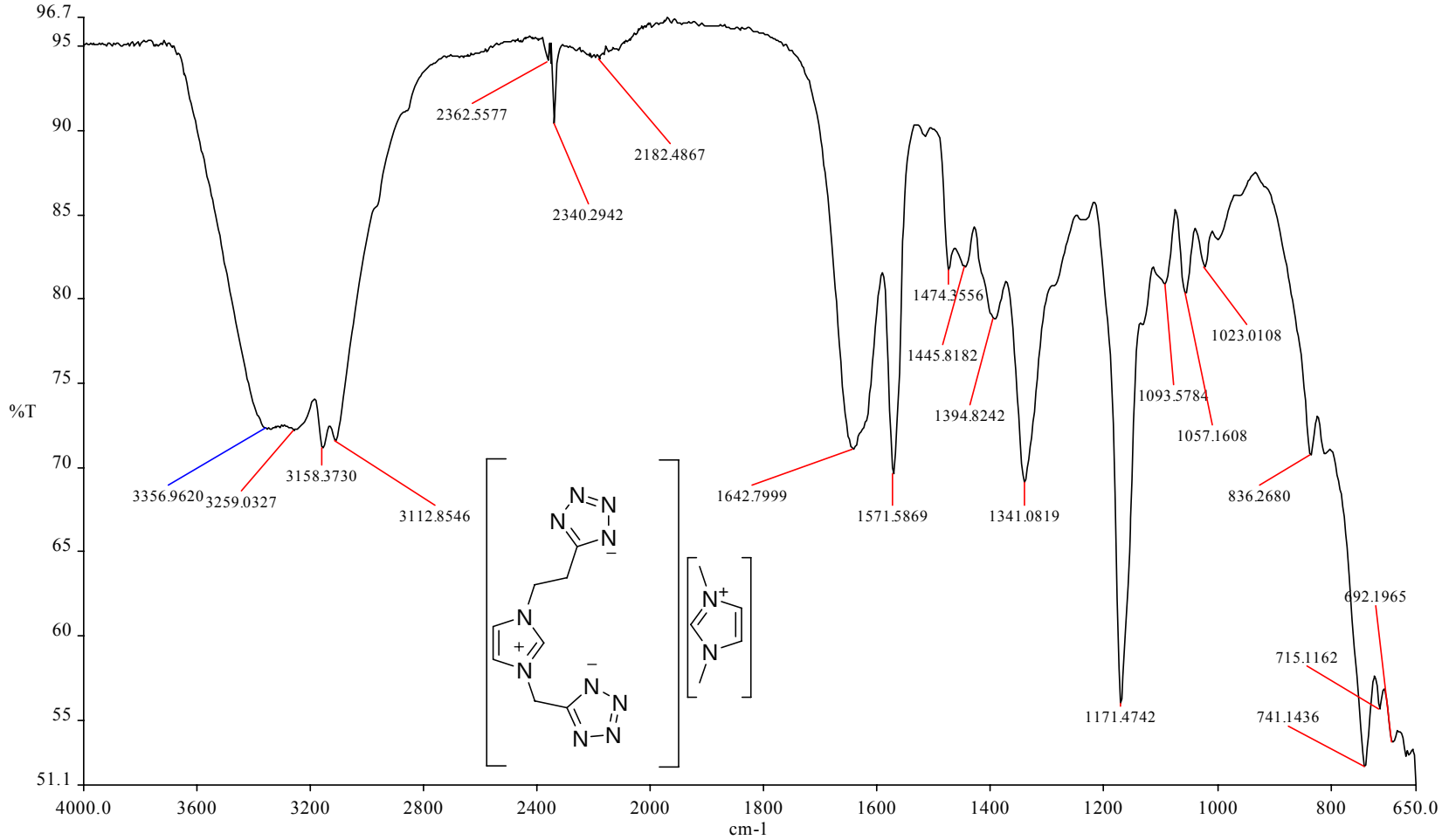

Figure S27. FT-IR spectrum of 1,3-dimethylimidazolium 1-(2-(5-tetrazolidyl)ethyl)-3-(5-tetrazolidyl)methylimidazolium (**12**).

NMR OPTIMIZATION DATA

TIME OPTIMIZATION OF ZN-ASSISTED "CLICK" REACTION (CONVERSION OF 1 INTO 2)

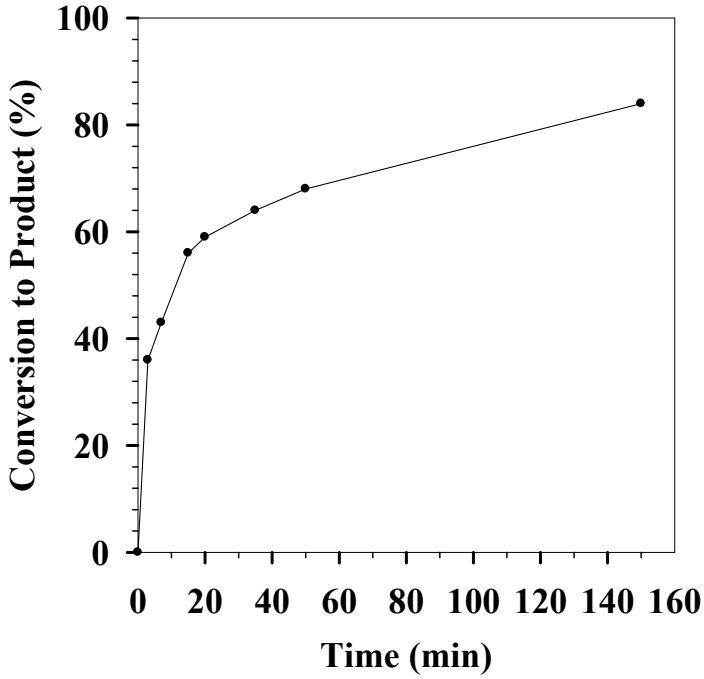

Figure S28. Optimization of 1-cyanomethyl-3-methylimidazolium chloride (**1**) conversion to Zn-coordination product (**2**) by Zn-assisted addition of sodium azide to nitrile (**1**).

Table S1. Kinetic Data Collected for reaction of 1-cyanomethyl-3-methylimidazolium chloride (**1**) with sodium azide and zinc bromide in water at room temperature.

Time (min)	Concentration of 1 (g/mL)	Remaining 1 (%)	Conversion to Product (%)
0	0.151	100	0
3	0.096	64	36
7	0.086	57	43
15	0.066	44	56
20	0.063	41	59
35	0.055	36	64
50	0.049	32	68
150	0.024	16	84

THERMAL DATA (DSC/TGA)

Table S2. Thermal Data of Reported Major products

Compound	$T_{5\%onset}$ (^{o}C)	T_{onset} (^{o}C)	T_g/T_m (^{o}C)
1-(2-(5-tetrazolidyl)ethyl)-3-(5-1*H*-tetrazolyl)-methylimidazolium, (10)	**237.5**	**247.4**	**49.4**
1-(2-(5-1*H*-tetrazolyl)ethyl)-3-(5-1*H*-tetrazolyl)-methylimidazolium bis(trifluoromethanesulfonyl)amide, (11)	**245.6**	**345.0**	**10.5**
1,3-dimethylimidazolium 1-(2-(5-tetrazolidyl)ethyl)-3-(5-tetrazolidyl)methylimidazolium, (12)	**224.4**	**235.7**	**-24.4**

STRUCTURES SOLVED BY X-RAY DIFFRACTION ANALYSIS

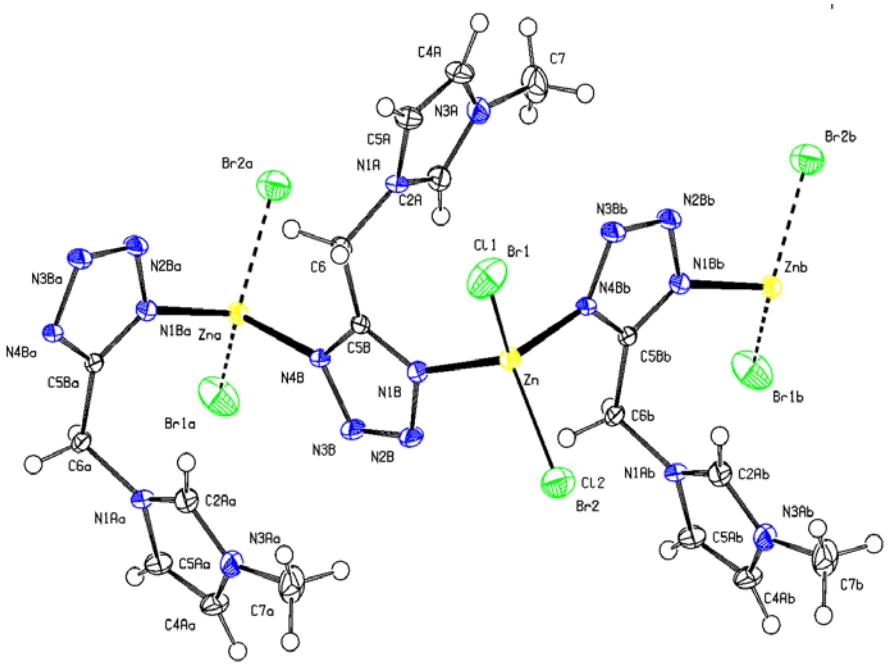

Figure S29. *catena*-poly[(bromochlorozinc)-μ-[1-(5-tetrazolato)methyl-3-methylimidazolium]-N^1:N^4], **2** (50 % probability thermal ellipsoid plot).

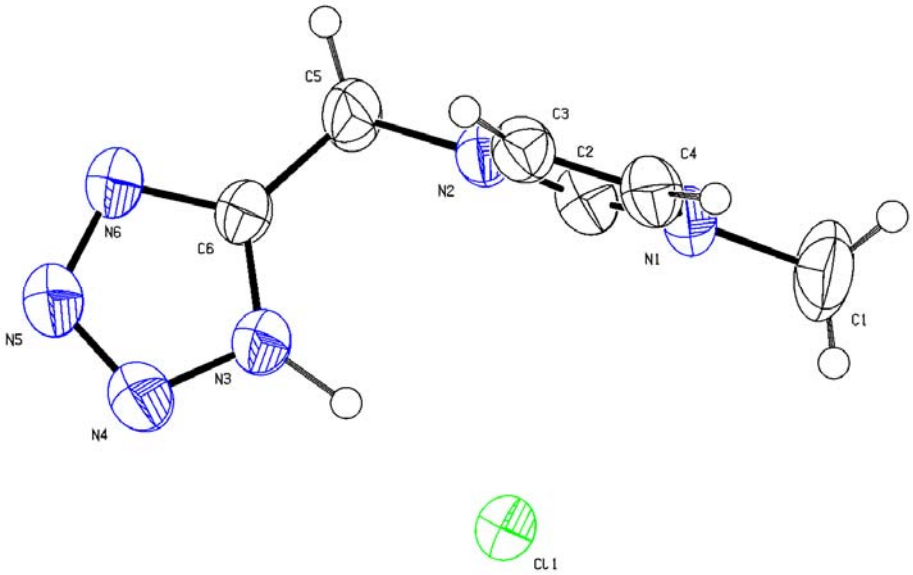

Figure S30. 1-(5-1*H*-tetrazolyl)methyl-3-methylimidazolium chloride, **3** (50 % probability thermal ellipsoid plot).

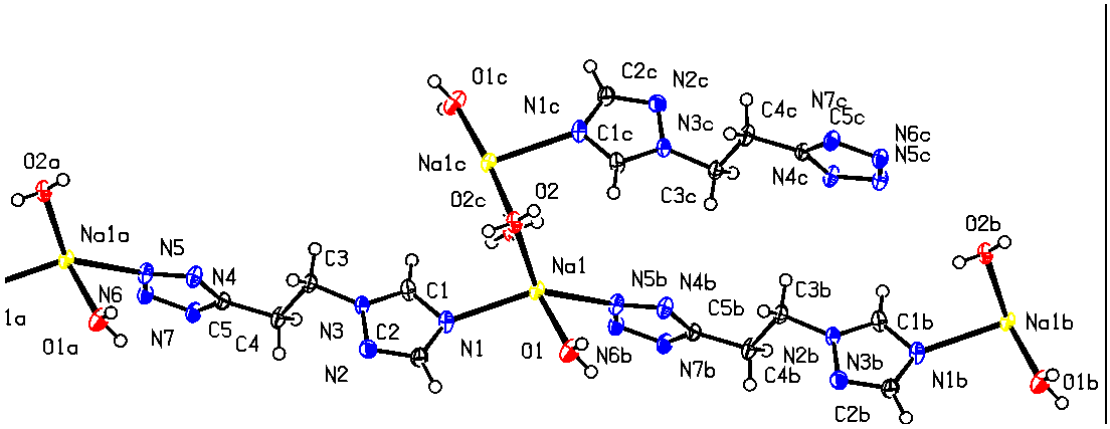

Figure S32. Sodium 5-(2-(1,2,4-triazol-1-yl)ethyl)tetrazolate·dihydrate, **7**·2H_2O (50 % probability thermal ellipsoid plot).

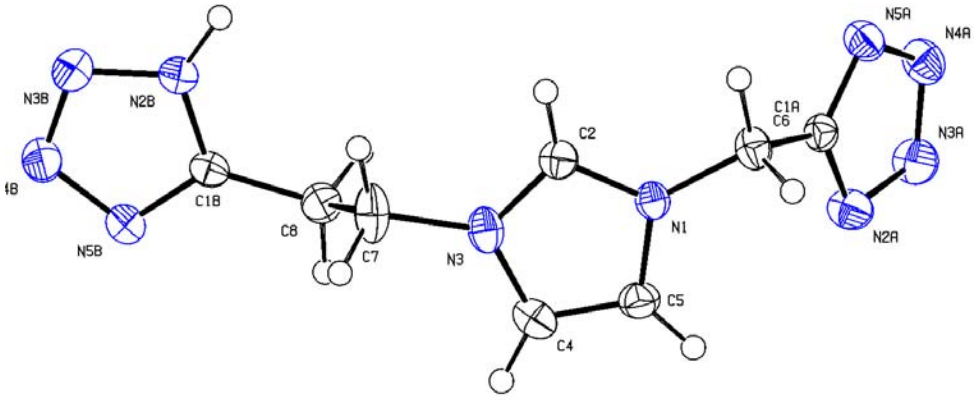

Figure S33. 1-(2-(5-tetrazolidyl)ethyl)-3-(5-1*H*-tetrazolyl)methylimidazolium, **10** (50 % probability thermal ellipsoid plot).

Table S3. Crystal data summary for compounds **2**, **3**, **7**·2H_2O, and **10**.

Compound	Compound Formula	FW (g·mol^{-1})	Crystal System	Unit Cell Parameters			V (Å^3)	T (K)	Space Group	Z	# Refl. Reported	R (wR^2)
				a (Å)	b (Å)	c (Å)						
				α (°)	β (°)	γ (°)						
2	$C_6H_9N_6Cl$	200.64	Monoclinic	29.128(5)	5.2371(9)	12.583(2)	1867.7(5)	173	C2/c	8	2210	0.0421 (0.1189)
				90	103.339(3)	90						
3	$C_6H_8Br_{0.80}Cl_{1.20}N_6Zn$	336.02	Monoclinic	6.5163(4)	9.5129(6)	17.9703(12)	1103.32(12)	173	P2(1)/n	4	2581	0.0461 (0.1395)
				90	97.924(1)	90						
7·2H_2O	$C_5H_{10}N_7NaO_2$	223.19	Triclinic	7.0435(8)	8.2860(9)	8.5121(10)	478.86(9)	178	P-1	2	2182	0.0332 (0.0832)
				91.350(2)	91.457(2)	105.267(2)						
10	$C_8H_{10}N_{10}$	246.26	Monoclinic	6.1144(9)	25.233(4)	7.1186(11)	1062.2(3)	173	P2(1)/c	4	1509	0.0330 (0.0842)
				90	104.739(2)	90						