10.1071/CH14233_AC

Australian Journal of Chemistry 2014, 67(7), 1129-1133

Supplementary Material

# The synthesis and structural characterization of peralkylated triguanide superbases

Vjekoslav Štrukil,[A] Edislav Lekšić,[B] Ernest Meštrović[B] and Mirjana Eckert-Maksić[A,C]

[A]Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia.

[B]Pliva TAPI, Prilaz Baruna Filipovića 29, 10000 Zagreb, Croatia.

[C]Corresponding author. Email: mmaksic@emma.irb.hr

## General comments

Solvents and commercially available chemicals (supplied by Aldrich and Kemika) were purified by standard methods[1] or used as purchased. Toluene, acetonitrile (predried using 3 Å mol. sieves) and dichloromethane were dried over calcium hydride by heating under reflux, distilled and kept over 3 Å or 4 Å molecular sieves (sodium in the case of toluene) under an argon atmosphere. Chloroform was predried with calcium chloride, dried over calcium sulphate and kept over 4 Å molecular sieves. Methanol was absolutized according to the Lund-Bjerrum method using activated magnesium turnings to yield a "cake", followed by refluxing and distillation. Dry methanol was kept over 3 Å mol. sieves under an argon atmosphere. TBD and DBN were used as received and handled under argon. DIPEA was freshly distilled over 4 Å molecular sieves and kept under an argon atmosphere over 4 Å mol. sieves in a dark bottle. The monosubstituted guanidines **3a–b** were synthesized from benzotriazole-1-carboxamidinium tosylate and the corresponding amine according to the literature procedure.[2] Deprotonation of the guanidinium tosylate salts was accomplished with freshly prepared sodium methoxide solution and afforded neutral guanidines **3a–b** in quantitative yield. All the $^{1}$H and $^{13}$C NMR spectra were recorded on Bruker Avance (300 and 600 MHz) spectrometers with tetramethylsilane as an

internal standard. The chemical shifts are given in ppm. IR spectra were recorded using an ABB Bomem MB102 spectrophotometer (CsI optics, DTGS detector, KBr pellets technique). High resolution mass spectra were obtained with Waters Micromass Q-ToF micro and 4800 Plus Maldi TOF/ TOF Analyzer instruments. HPLC analyses were performed on a Varian ProStar Instrument supplied with a UV/Vis detector using a Restek UltraIBD C18 (reversed phase) 5 μm × 250 mm × 4.6 mm column operated at room temperature and a flow rate of 1 mL $min^{-1}$; gradient of 2 % acetic acid (solvent A) and methanol (solvent B): 95 % A + 5 % B, 0–5 min; 85 % A + 15 % B, 5–45min, 35 % A + 65 % B, 45–55min, 5 % A + 95 % B, after 55 min.

Details of data collection and crystal structure refinement are given in Table SM3. Selected bond distances and valence angles are listed in Table SM4. Data collection was performed on Oxford Diffraction Xcalibur CCD diffractometer with graphite-monochromated Cu *Kα* radiation at 296 K using *ω*-scans at crystal to detector distance of 45 mm. Programs CrysAlis CCD and CrysAlis RED[3] were used for data collection, cell refinement and data reduction. The structures was solved by direct methods. Refinement procedure by full-matrix least squares methods based on $F^2$ values against all reflections included anisotropic displacement parameters for all non-H atoms. The positions of hydrogen atoms, bonded to carbon and nitrogen atoms, were geometrically optimized applying the riding model. Calculations were performed with SHELXS97[4] and SHELXL97[4] (both operating under WinGX[5] program package). The molecular graphics were done with PLATON98[6] and Mercury.[7] Supplementary crystallographic data set for the structure $C_{18}H_{32}Cl_1N_7$ is available through the Cambridge Structural Data base with the deposition number CCDC-995347. Copy of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**The synthesis of Vilsmeier salt 2**

Tetramethylurea **1** (240 µL, 0.233 g, 2.0 mmol) was dissolved in dry toluene (3.0 mL) under an argon atmosphere in a three-necked round bottom flask, equipped with a condenser and a dropping funnel, immersed in an ice bath. Then oxalyl chloride (280 µL, 0.410 g, 3.23 mmol) was carefully added via a syringe. The flask was immersed in an oil bath and the light green reaction mixture was gently heated with stirring for 2 hours at 60–65°C, resulting in the precipitation of colourless crystalline product. The mixture was allowed to cool to room temperature and the solvent was distilled off under reduced pressure using the apparatus shown in Figure SM1. After the solvent was removed, dry acetonitrile (2.0 mL) was added under vacuum using a syringe and the solution was cooled in an ice bath.

**Figure SM1.** The apparatus for toluene distillation under an argon atmosphere. Inset: a close-up view of the Vilsmeier salt **2** after removing toluene.

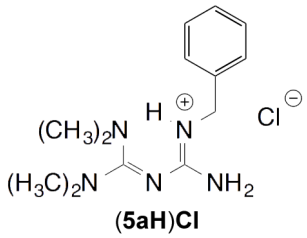
**Triguanide synthesis**

To a cold solution of Vilsmeier salt **2** (ice bath) in dry acetonitrile (2.0 mL), an acetonitrile solution of monosubstituted guanidine **3a–b** (0.5 mmol in 2.0 mL) was added via a syringe under vacuum. The apparatus was next filled with argon to prevent the hydrolysis of the Vilsmeier salt **2**. Finally, potassium fluoride (813 mg, 14.0 mmol) was added in one portion and the mixture was stirred at 60°C for 20 hours. Then *N*,*N*-diisopropylethylamine (345 µL, 0.258 g, 2.0 mmol) was added and the reaction mixture refluxed for another 24 hours.

**Reaction mixture work up**

The solvent was removed in vacuuo, and the red-brown oil was dissolved in saturated aqueous sodium carbonate solution (5 mL) and then extracted with diethylether (3×5 mL). The aqueous layer was again evaporated to dryness, the remaining solid was suspended in dry dichloromethane and the precipitated $Na_2CO_3$ was filtered off. Dichloromethane was removed in vacuuo to afford a red-brown oil from which the product was precipitated out by trituration with ethylacetate. The crude product was separated by filtration and dried in air.

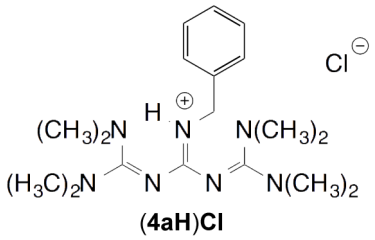
**$N^4$-Benzyl-$N^1$,$N^1$,$N^2$,$N^2$-tetramethylbiguanidium chloride ((5aH)Cl)**



**(5aH)Cl**

The title biguanide salt (0.038 g) was isolated as a white solid from the reaction of *N*-benzylguanidine and Vilsmeier salt in a 1:2 ratio by employing the above described work up procedure. mp 192–194 ºC. $\nu_{max}$ (KBr)/cm$^{-1}$ 3450, 3285, 3155, 2931, 1639, 1603, 1535, 1427, 1400, 1165, 727. $\delta_H$ (300 MHz, DMSO) 2.78 (s, 12H, C*H*$_3$), 4.38 (s, 2H, C*H*$_2$), 7.15–7.50 (overlapped signals, 7H, ArH + $NH_2$), 8.10–8.60 (brs, 1H, N*H*). $\delta_C$(75 MHz, DMSO) 39.6, 44.2, 127.0, 127.3, 128.3, 138.8, 158.6, 163.7. HRMS-MALDI calc. for $C_{13}H_{22}N_5$ ($MH^+$): 248.1870. Found: 248.1863.

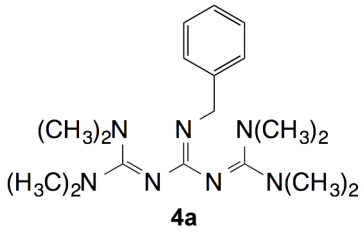
**$N^4$-Benzyl-$N^1$,$N^1$,$N^2$,$N^2$,$N^6$,$N^6$,$N^7$,$N^7$-octamethyltriguanidium chloride ((4aH)Cl)**



**(4aH)Cl**

The title triguanide salt was precipitated out using ethylacetate from 0.198 g of oil remaining after the extraction work up (0.133 g, 69 %). Recrystallisation of the crude product from ethylacetate–ethanol mixture (1:1) afforded single crystals of triguanide chloride (**4aH)Cl** suitable for X-ray analysis. mp 189–192 ºC. $\nu_{max}$ (KBr)/cm$^{-1}$ 3221, 2921, 1561, 1515, 1473, 1399, 1355, 1304, 1230, 1160, 1110, 1064, 1029, 734. $\delta_H$ (600 MHz, DMSO) 2.79 (s, 24H, C*H*$_3$), 4.41 (d, *J* 4.2, 2H, C*H*$_2$), 7.23–7.40 (m, 5H, ArH), 8.21 (poorly resolved triplet, 1H, N*H*). $\delta_C$(150 MHz, DMSO) 39.5, 45.3, 126.9, 127.8, 128.2, 139.3, 161.0. HRMS-MALDI calc. for $C_{18}H_{32}N_7$ ($MH^+$): 346.2714. Found: 346.2712.

**$N^4$-Benzyl-$N^1$,$N^1$,$N^2$,$N^2$,$N^6$,$N^6$,$N^7$,$N^7$-octamethyltriguanide (4a)**

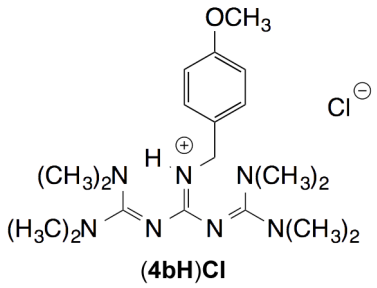


**4a**

The triguanide chloride salt (**4aH**)**Cl** (100.0 mg, 0.26 mmol) was added in one portion to a freshly prepared sodium methoxide solution (6.2 mg Na in 5 mL of dry methanol) with stirring at room temperature under an argon atmosphere. The reaction mixture was stirred for 2 hours, then methanol was evaporated and the residue suspended in dry dichloromethane. The precipitated white solid was filtered over a sintered funnel and the filtrate evaporated to afford neutral triguanide **3** as a viscous pale yellow oil (90.1 mg, 99 %).

$\delta_H$ (300 MHz, DMSO) 2.72 (d, *J* 7.6 Hz, 24H, C$H_3$), 4.28 (s, 2H, C$H_2$), 7.10–7.40 (m, 5H, ArH). $\delta_C$(75 MHz, DMSO) 39.1, 50.7, 125.6, 127.6, 127.7, 142.9, 160.2.

**$N^4$-(4-Methoxybenzyl)-$N^1$,$N^1$,$N^2$,$N^2$,$N^6$,$N^6$,$N^7$,$N^7$-octamethyltriguanidium chloride ((4bH)Cl)**



**(4bH)Cl**

The red-brown oil (0.226 g) remaining after work up was dissolved in chloroform (1.0 mL) and this solution was passed through a short silica column using choroform as an eluent. Evaporation of the solvent afforded dark-yellow oil identified as the triguanide salt (**4bH**)**Cl** (0.128 g, 62 %). $\delta_H$ (600 MHz, DMSO) 2.70–2.86 (br s, 24H, C$H_3$), 3.72 (s, 3H, OC$H_3$), 4.34 (d, *J* 5.8 Hz, 2H, C$H_2$), 6.88 (d, *J* 8.5 Hz, 2H, ArH), 7.27 (d, *J* 8.5 Hz, 2H, ArH), 8.04 (t, *J* 5.8 Hz, 1H, N*H*). $\delta_C$(150 MHz, DMSO) 39.5, 44.8, 55.0, 113.6, 129.1, 131.1, 158.3, 161.0. HRMS-MALDI calc. for $C_{19}H_{34}N_7O$ ($MH^+$): 376.2819. Found: 376.2837.

**Transesterification of vegetable oil**

Purified vegetable oil (a mixture of sunflower, soybean and rapeseed oil), purchased from a supermarket, was used. According to Karl-Fischer titration analysis, the water content in the oil was found to be 0.0618% (wt%). Methanol was of *pro analysis* grade and was not dried before use (the specified max. water content 0.05 %). A screw-capped vial was charged with vegetable oil (4.0 g, 13.6 mmol) followed by a solution of the triguanide catalyst **4a** (0.5, 1.0 or 2.0 mol%) in methanol (1.0 g, 1.27 mL, 31.2 mmol). The mixture was vigorously stirred at 70 ºC for 1 hour and then cooled down to room temperature to allow the two layers separate. The layer containing the fatty acid methyl esters was removed and excess methanol evaporated in vacuuo. The crude mixture was analysed by $^{1}$H NMR spectroscopy to calculate the conversion percentage based on the ratio of the methoxy group signal at 3.68 ppm and the α-methylene group of the fatty acid esters at 2.30 ppm.[8]

## NMR spectra

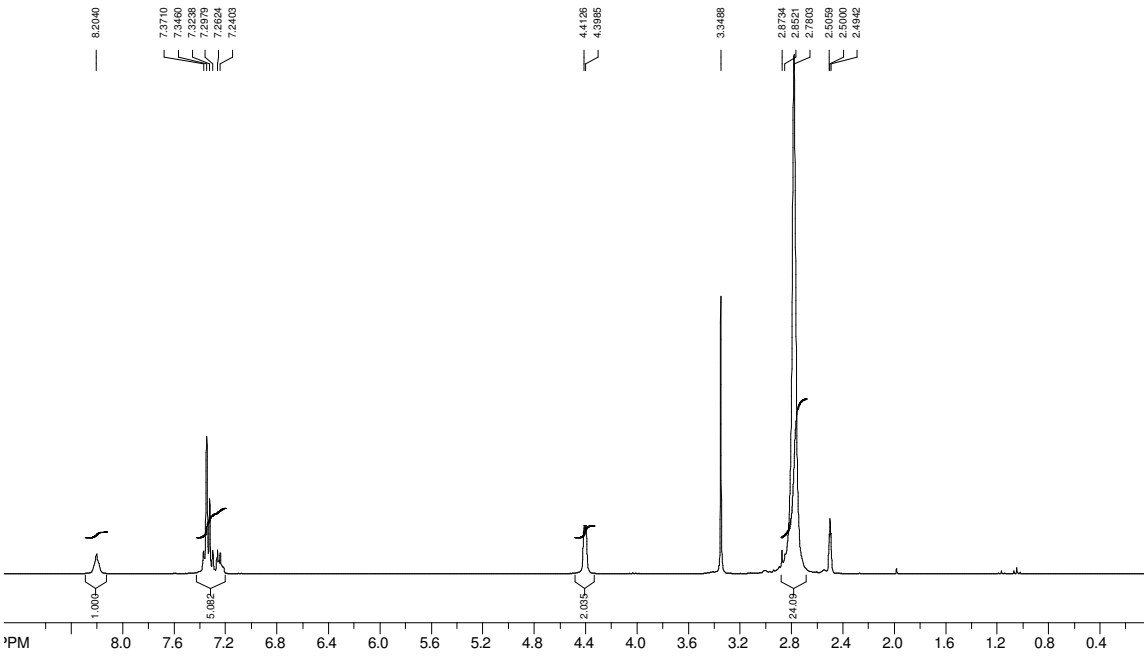



**Figure SM2.** $^{1}$H NMR spectrum (DMSO, 600 MHz) of triguanide salt (**4aH**)**Cl**.

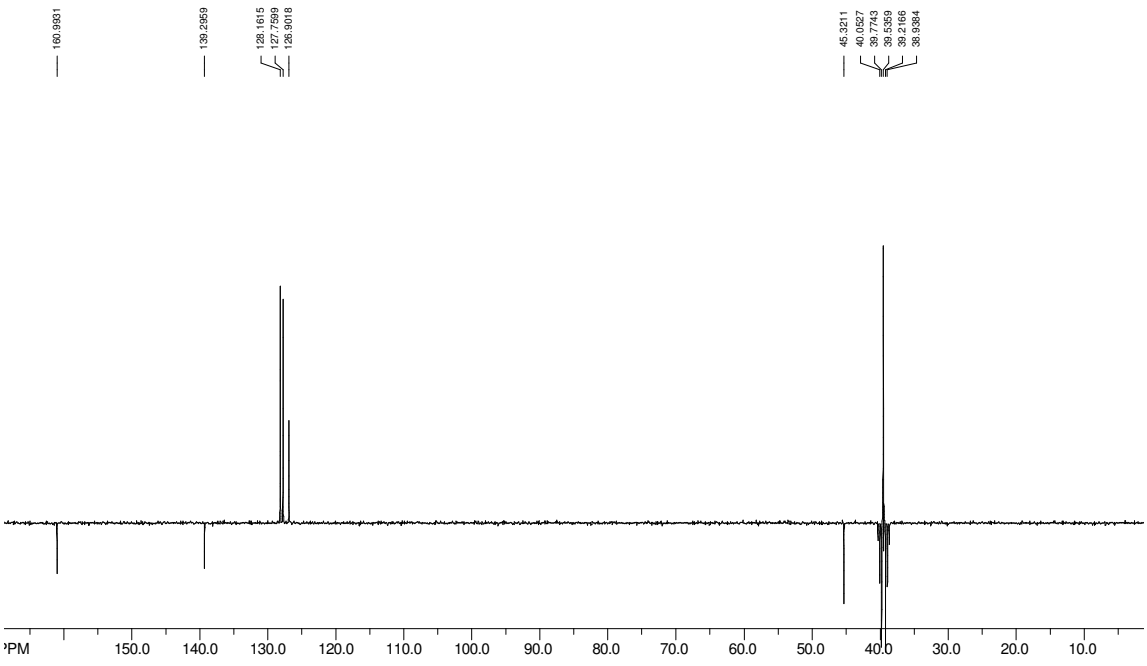



**Figure SM3.** $^{13}$C NMR spectrum (DMSO, 150 MHz) of triguanide salt (**4aH**)**Cl**.

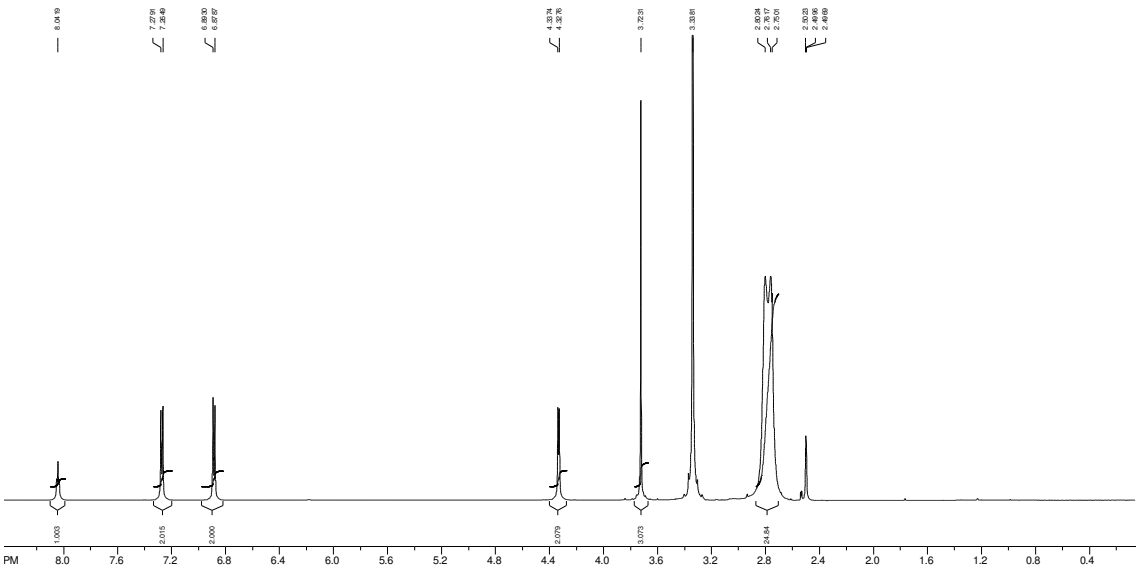


**Figure SM4.** $^{1}$H NMR spectrum (DMSO, 600 MHz) of triguanide salt (**4bH**)**Cl**.

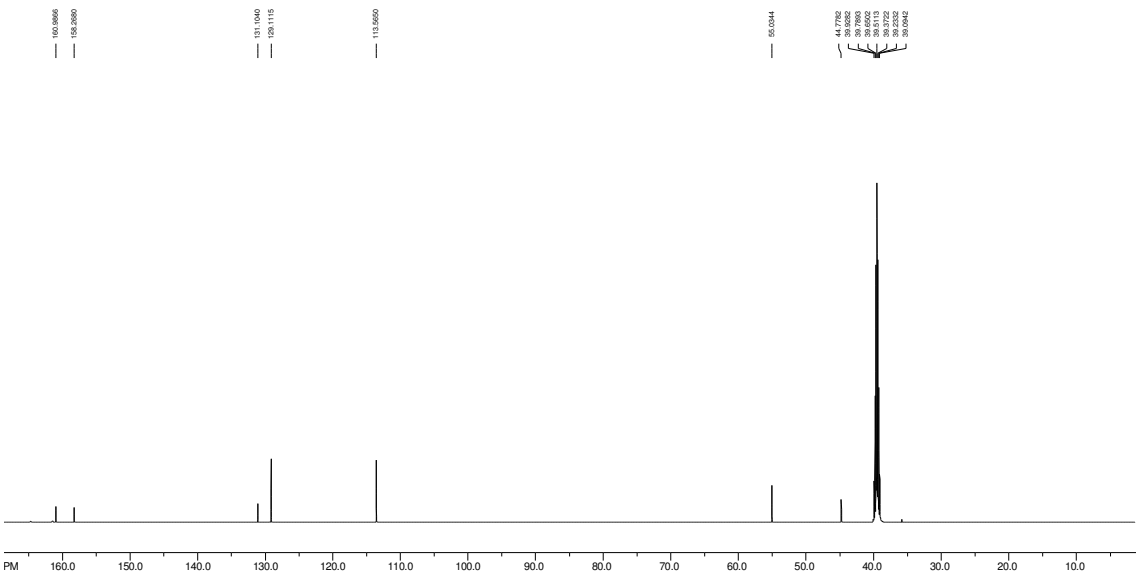


**Figure SM5.** $^{13}$C NMR spectrum (DMSO, 150 MHz) of triguanide salt (**4bH**)**Cl**.

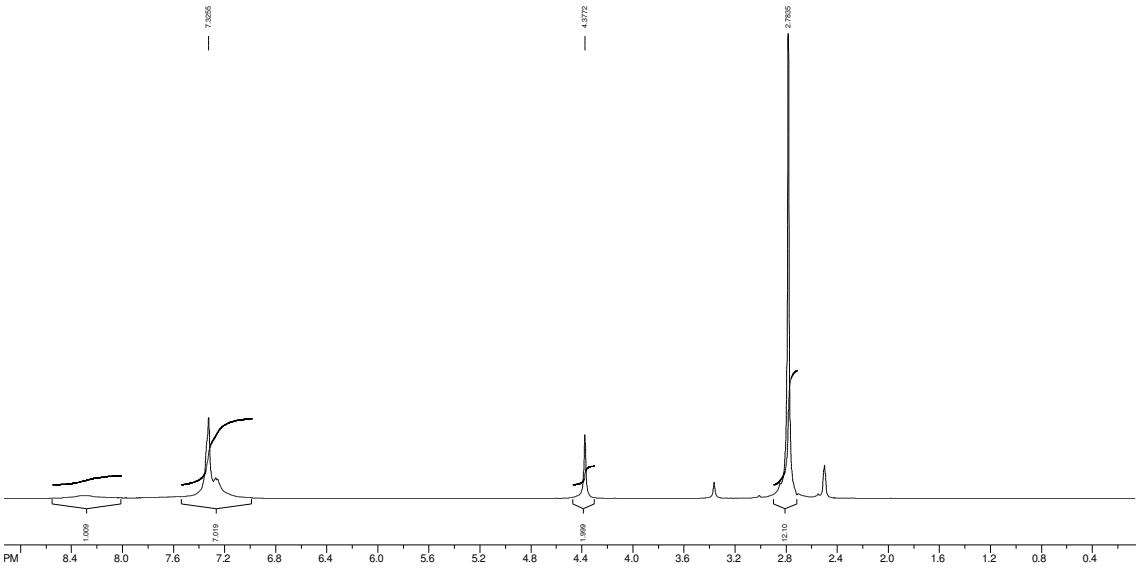



**Figure SM6.** [1]H NMR spectrum (DMSO, 600 MHz) of biguanide salt (**5aH**)**Cl**.

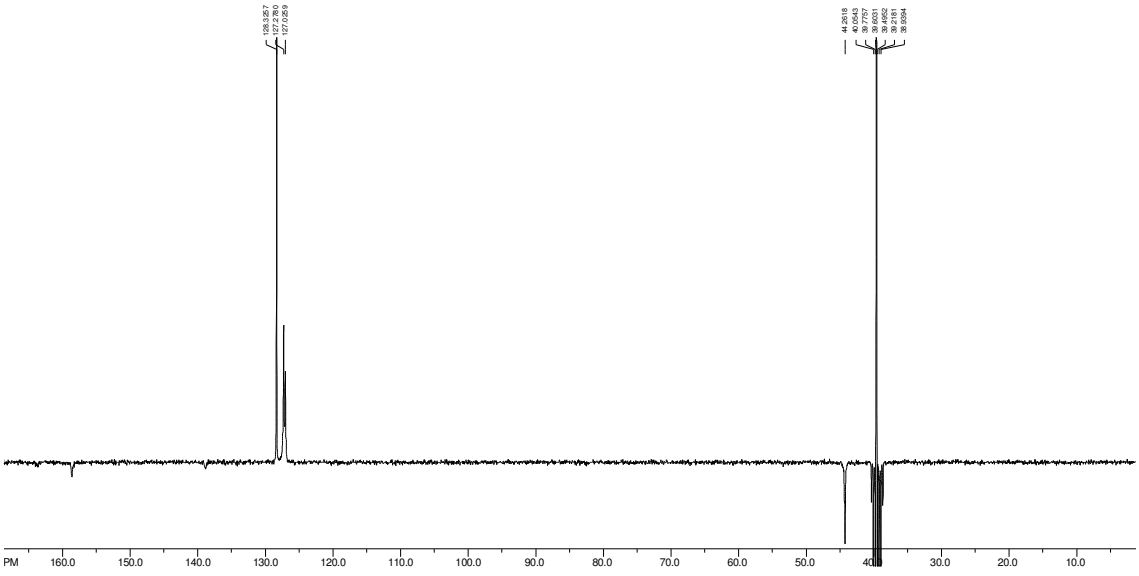



**Figure SM7.** [13]C NMR spectrum (DMSO, 150 MHz) of biguanide salt (**5aH**)**Cl**.

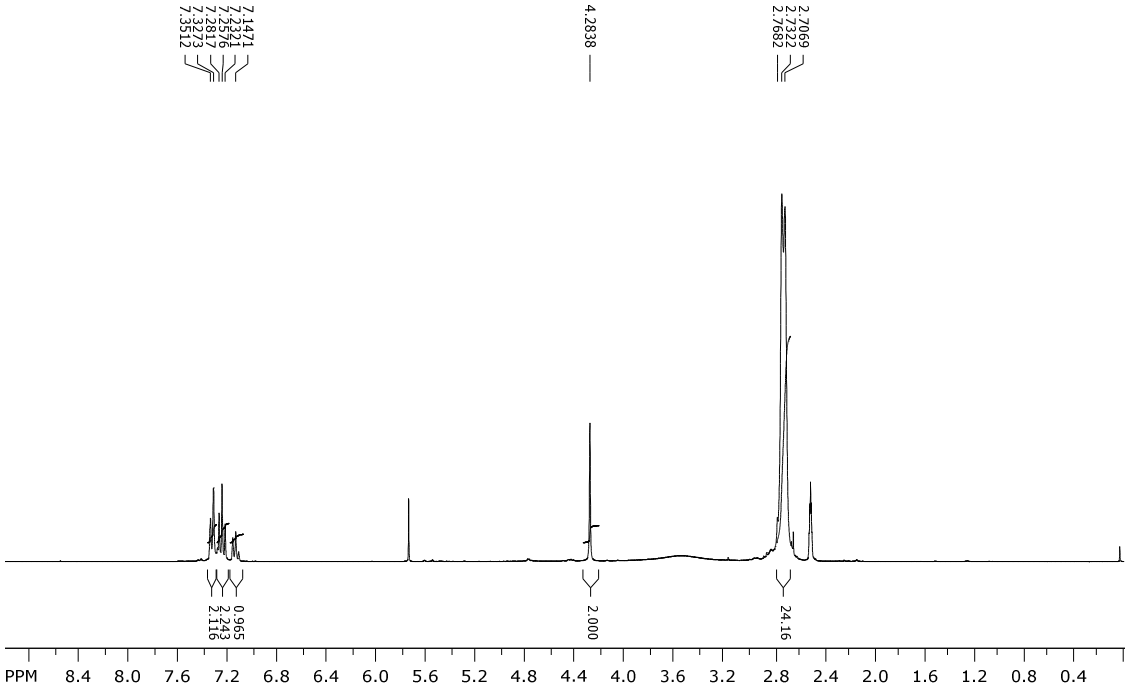



**Figure SM8.** [1]H NMR spectrum (DMSO, 600 MHz) of triguanide **4a**.

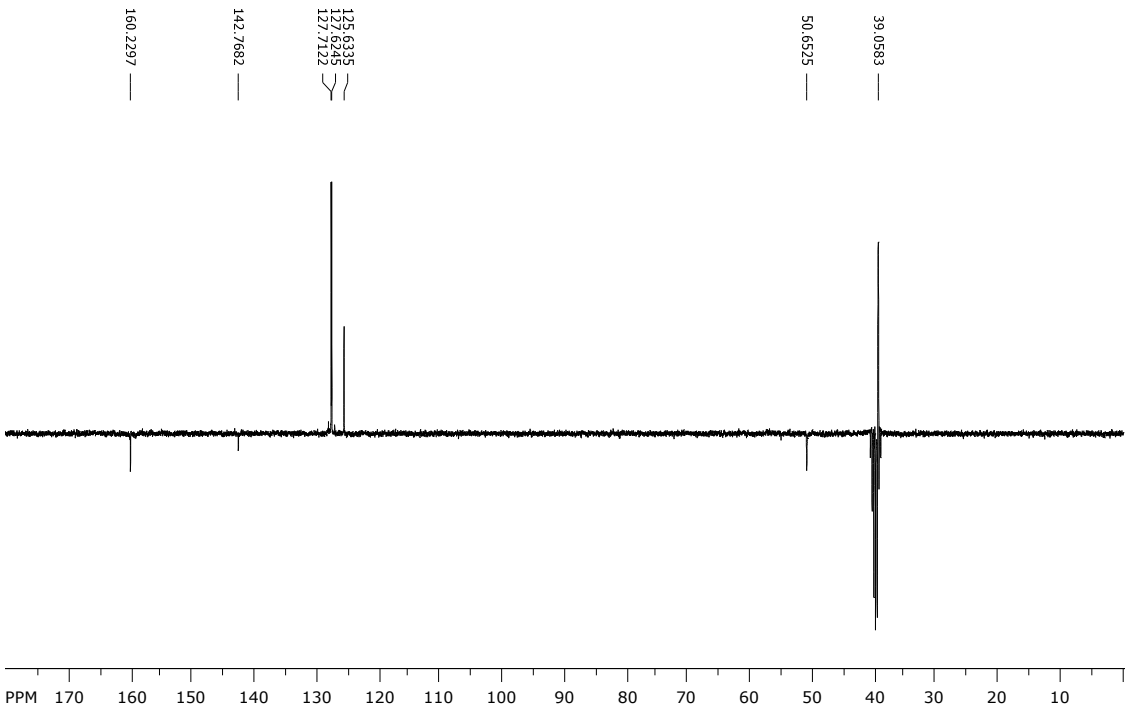



**Figure SM9.** [13]C NMR spectrum (DMSO, 150 MHz) of triguanide **4a**.

## HPLC traces

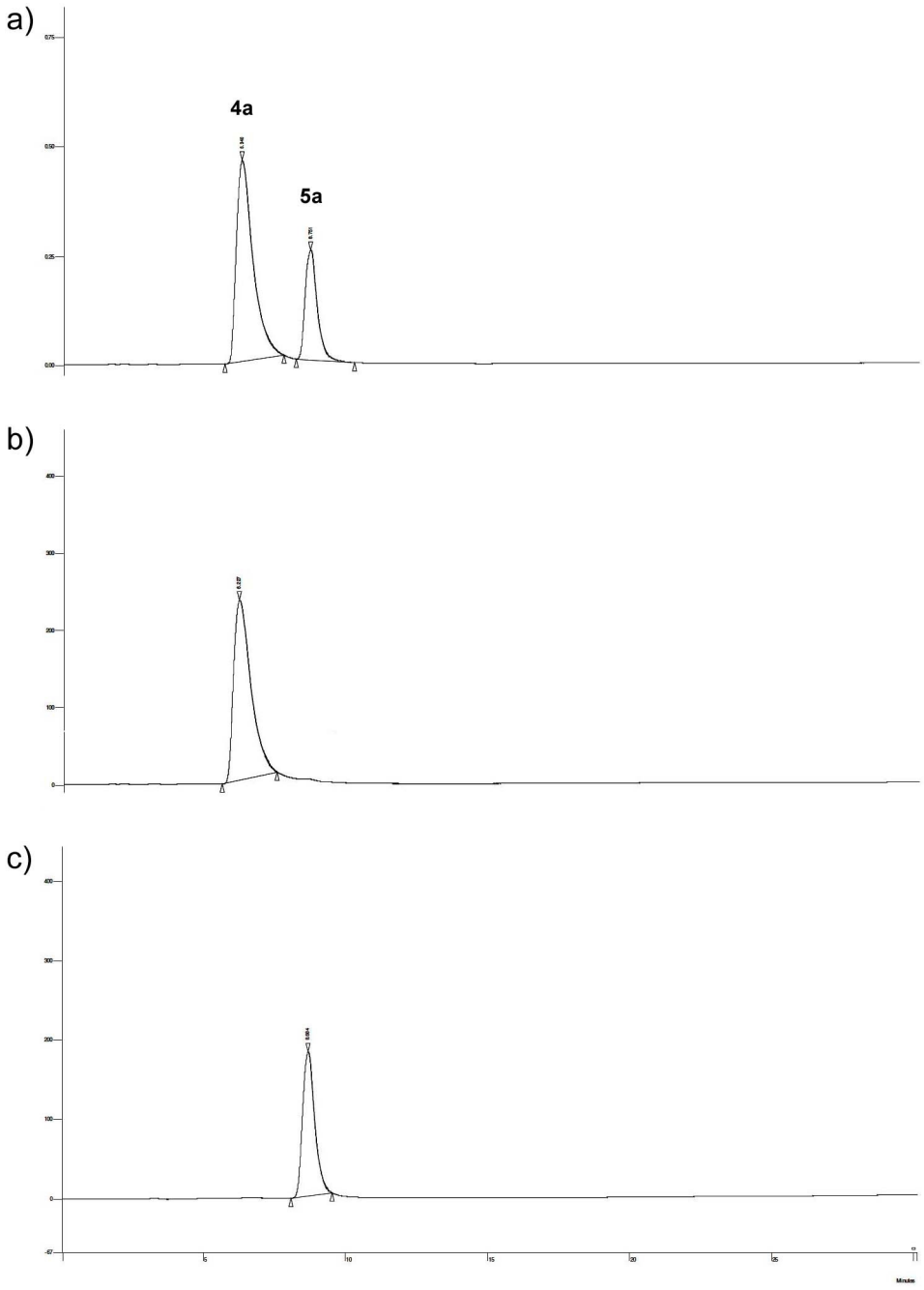



**Figure SM10.** HPLC chromatograms of a) the reaction mixture with the ratio of guanidine **3a** : Vilsmeier salt **2** = 1: 2, b) triguanide salt (**4aH**)**Cl**, c) biguanide salt (**5aH**)**Cl**. Eluted with 2% acetic acid:methanol (95:5) mixture, detector wavelenght 254 nm.

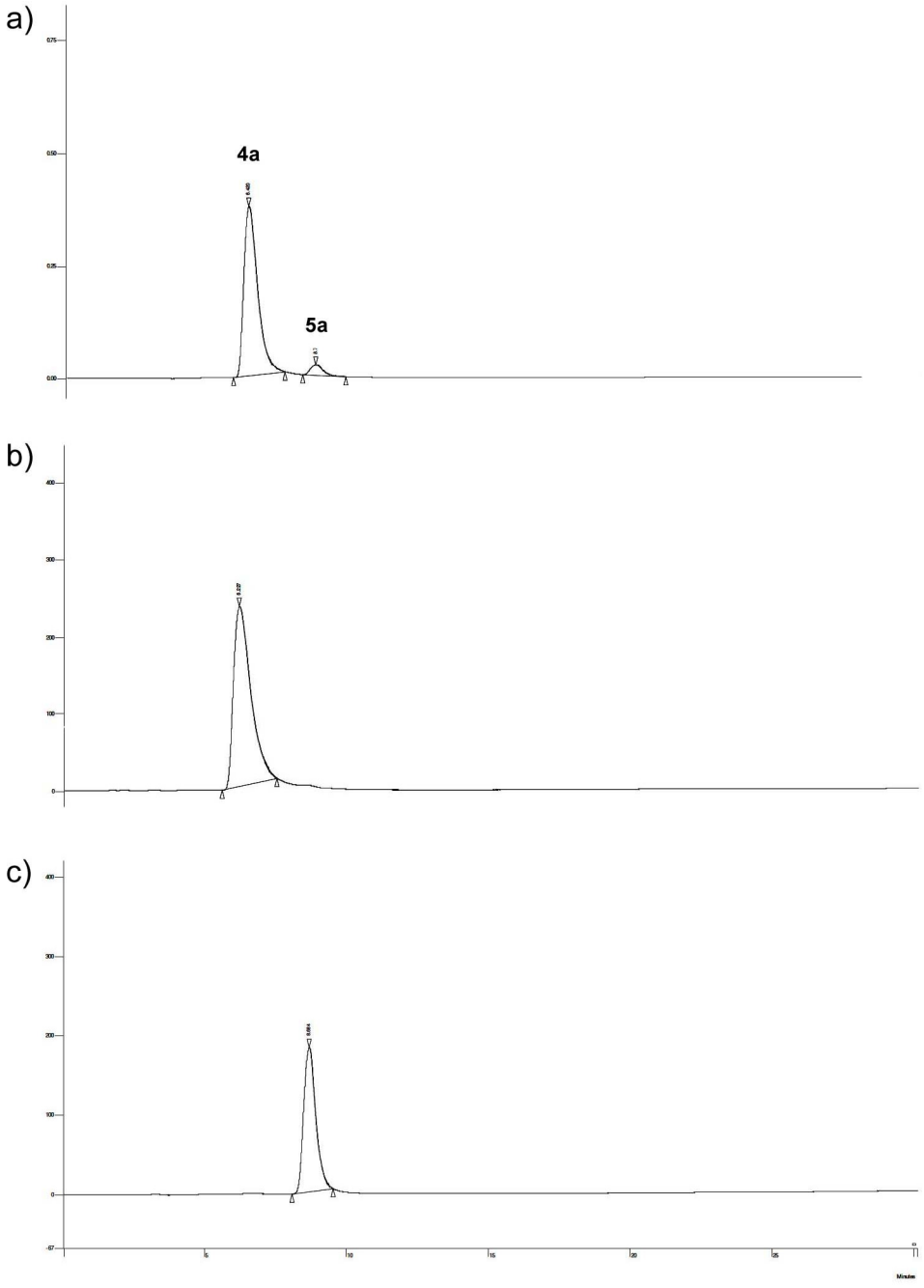



**Figure SM11.** HPLC chromatograms of a) the reaction mixture with the ratio of guanidine **3a** : Vilsmeier salt **2** = 1: 4, b) triguanide salt (**4aH**)**Cl**, c) biguanide salt (**5aH**)**Cl**. Eluted with 2% acetic acid:methanol (95:5) mixture, detector wavelenght 254 nm.

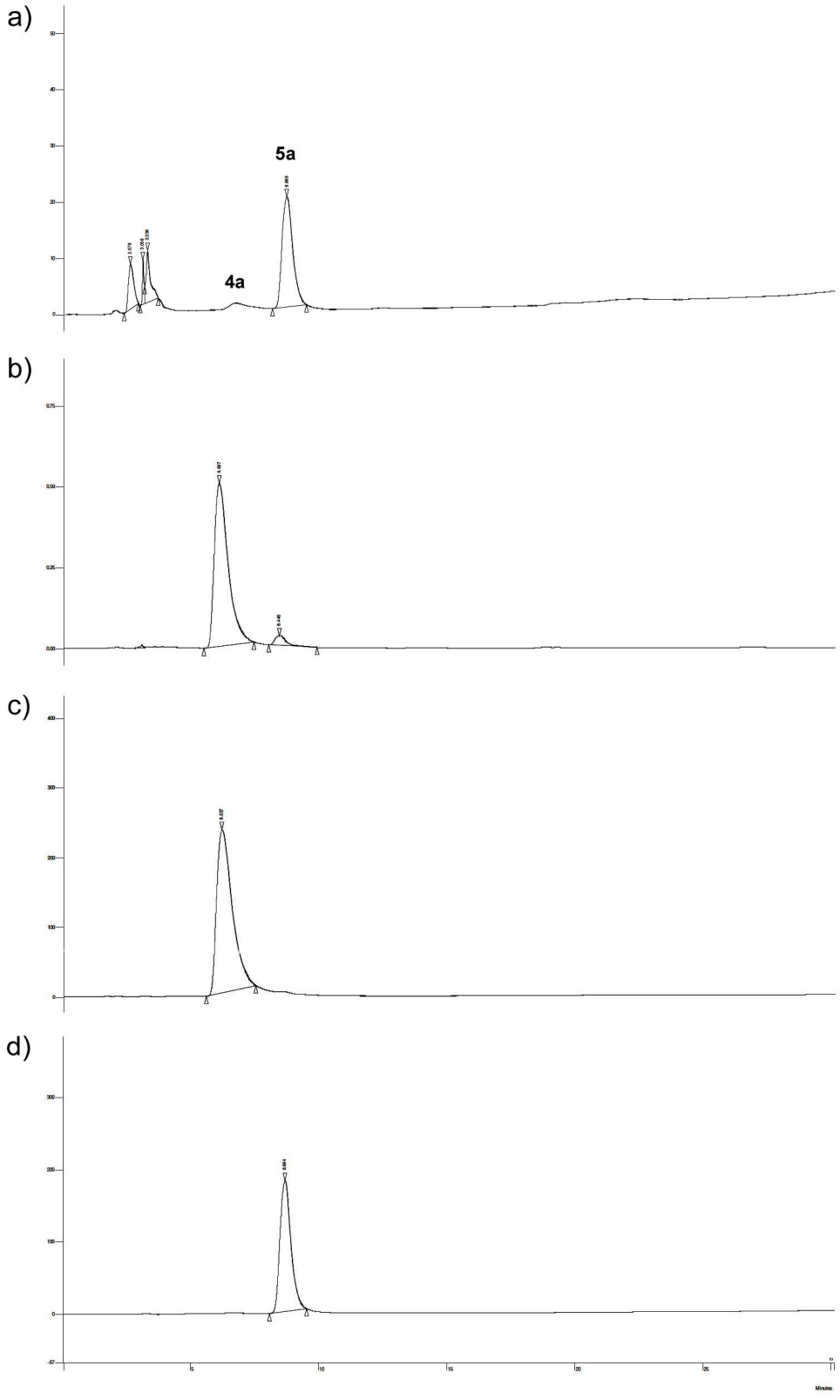



**Figure SM12.** HPLC chromatograms of a) the reaction mixture with the ratio of guanidine **3a** : Vilsmeier salt **2** = 1: 4 using KF as a base after 20 h, b) the mixture under a) after the addition of DIPEA and reflux for 20 h, c) triguanide salt (**4aH**)**Cl**, d) biguanide salt (**5aH**)**Cl**. Eluted with 2% acetic acid:methanol (95:5) mixture, detector wavelenght 254 nm.

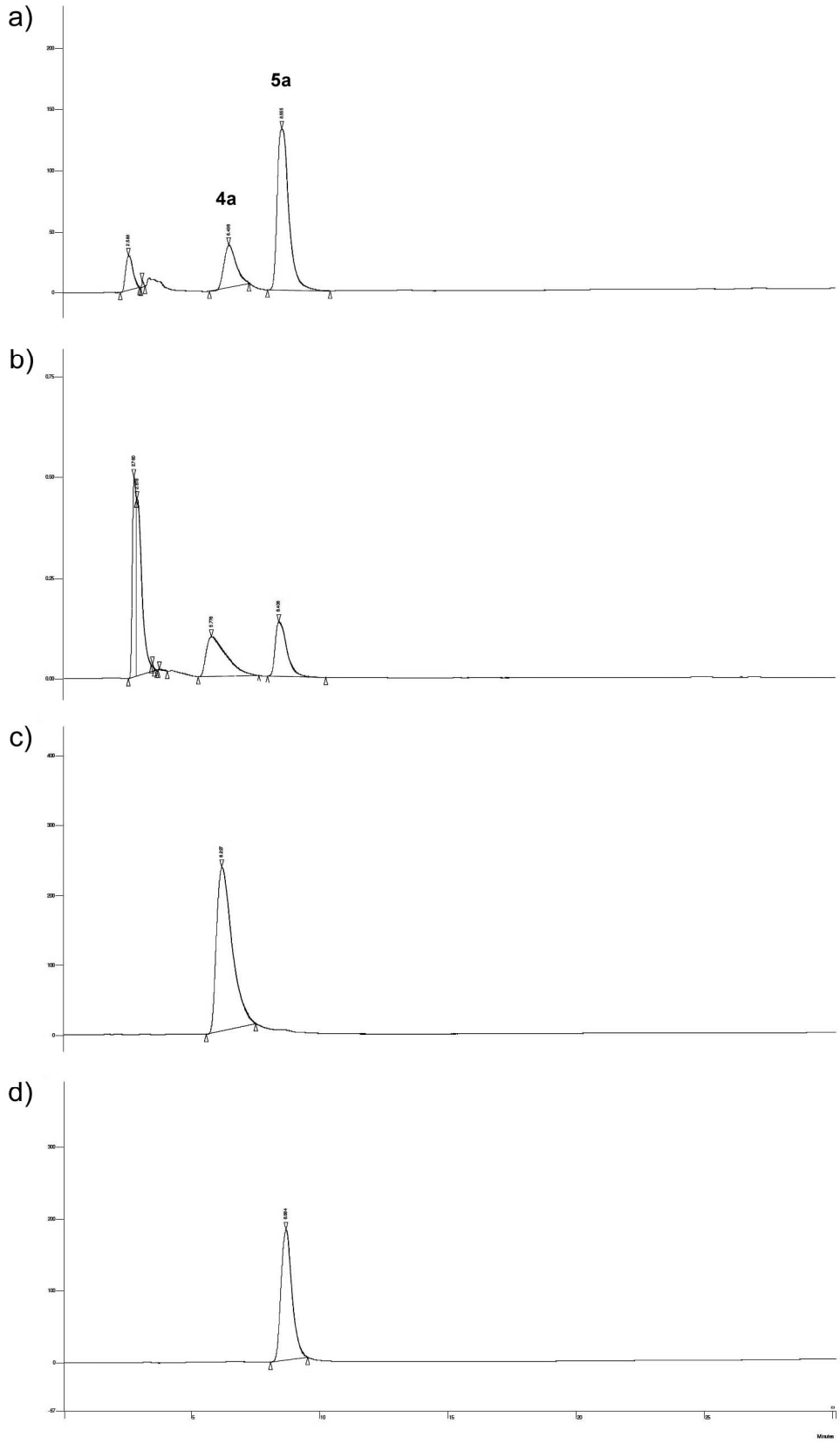



**Figure SM13.** HPLC chromatograms of a) the reaction mixture with the ratio of guanidine **3a** : Vilsmeier salt **2** = 1: 4 in dichloromethane using DIPEA as a base after 2 h at 0 ºC, b) the mixture under a) after 20 h stirring at room temp., c) triguanide salt (**4aH**)**Cl**, d) biguanide salt (**5aH**)**Cl**. Eluted with 2% acetic acid:methanol (95:5) mixture, detector wavelenght 254 nm.

## Gas phase and solution basicity calculations

All computational work was done using *Gaussian* 03 package.[9] The geometries were optimized at the B3LYP/6-31G(d) level of theory and were verified to be minima by the vibrational analysis at the same level of theory. The electronic energies and Gibbs energy corrections ($E_{Gibbs}$) were calculated by the B3LYP/6-311+G(d,p) and B3LYP/6-31G(d) methods, respectively. Zero point vibrational energies were used unscaled. Solvation energies ($\Delta G(X)_{AN}$) of the neutral (X = B) and protonated (X = $BH^+$) species were calculated using the IEF-PCM/HF/6-31G(d) approach with Klamt radii optimized for COSMO-RS.[10]

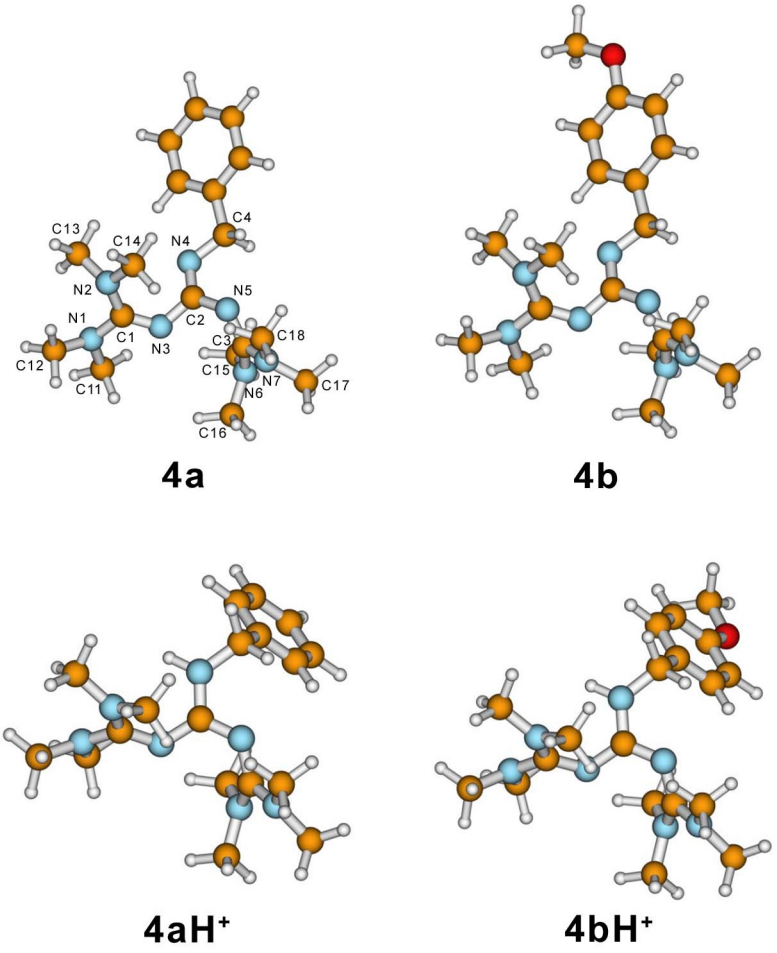



**Figure SM14.** Optimized geometries of neutral and protonated triguanides **4a–b** calculated at the B3LYP/6-31G(d) level of theory.

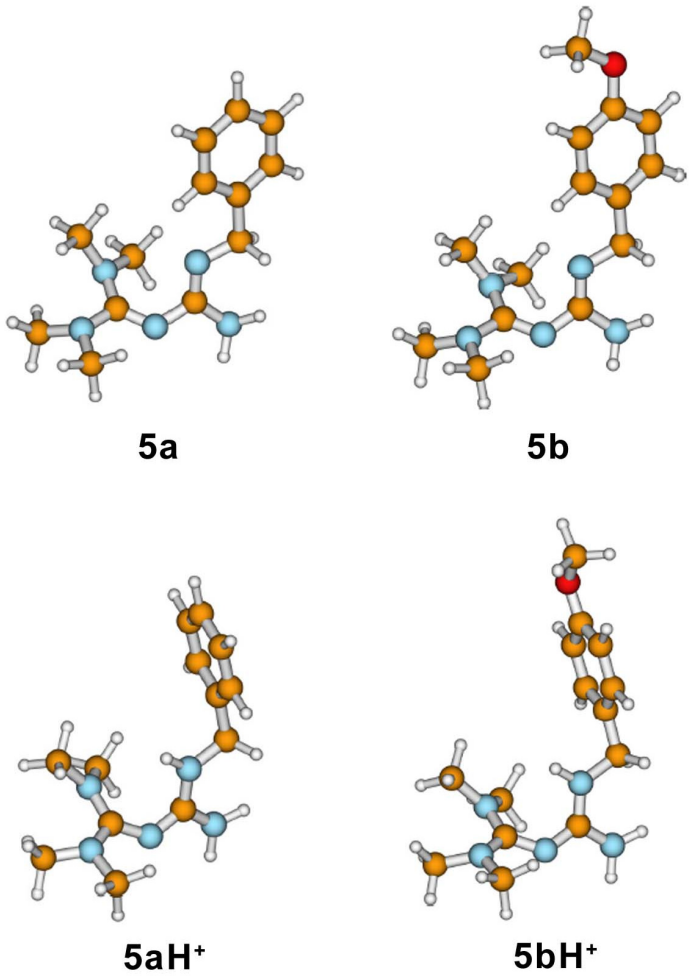



**Figure SM15.** Optimized geometries of neutral and protonated biguanides **5a–b** calculated at the B3LYP/6-31G(d) level of theory.

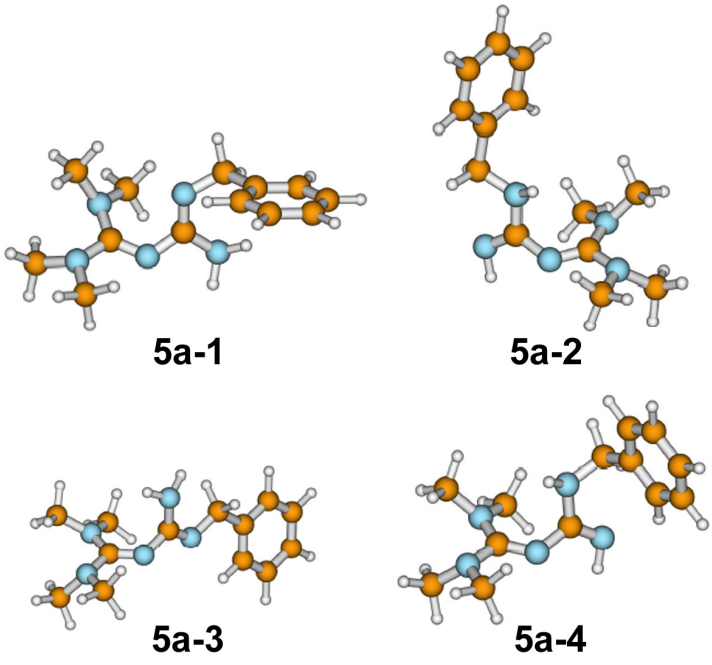



**Figure SM16.** Optimized geometries of biguanide **5a** tautomers calculated at the B3LYP/6-31G(d) level of theory.

**Table SM1.** Electornic energies, zero-point vibrational, enthalpy and Gibbs energy corrections for triguanides **4a–b** and biguanides **5a–b** calculated with B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) method.

| Molecule | $E_{el}$ / a.u. | $E_{ZPV}$ / a.u. | $E_{rel}$ / kcal mol$^{-1}$ | $E_{Gibbs}$ / a.u. | $E_{enth}$ / a.u. |
|---|---|---|---|---|---|
| **4a** | –1088.09260 | 0.48918 | 0.00 | 0.42668 | 0.51874 |
| **4aH$^+$** | –1088.53763 | 0.50483 | –269.44 | 0.44384 | 0.53449 |
| **4b** | –1202.64792 | 0.52211 | 0.00 | 0.45715 | 0.55419 |
| **4bH$^+$** | –1203.09519 | 0.53745 | –271.04 | 0.47293 | 0.56974 |
| **5a** | –781.98445 | 0.33774 | 0.00 | 0.28837 | 0.35793 |
| **5aH$^+$** | –782.41135 | 0.35198 | –258.95 | 0.30200 | 0.37278 |
| **5b** | –896.53997 | 0.37051 | 0.00 | 0.31798 | 0.39331 |
| **5bH$^+$** | –896.97000 | 0.38463 | –260.98 | 0.33110 | 0.40803 |
| **5a-1** | –781.98338 | 0.33831 | 1.03 | 0.28959 | 0.35838 |
| **5a-2** | –781.98228 | 0.33815 | 1.62 | 0.28782 | 0.35845 |
| **5a-3** | –781.97512 | 0.33688 | 5.31 | 0.28701 | 0.35745 |
| **5a-4** | –781.98243 | 0.33868 | 1.85 | 0.28962 | 0.35876 |

**Table SM2.** Selected bond lenghts and dihedral angles for **4a–b** and their protonated forms **4aH$^+$–4bH$^+$** calculated with B3LYP/6-31G(d) method. For numeration, see Figure SM14.

| **Parameter** | **4a** | **4aH$^+$** | **4b** | **4bH$^+$** |
|---|---|---|---|---|
| *Bond* | | *d* / Å | | *d* / Å |
| C1–N1 | 1.387 | 1.363 | 1.389 | 1.364 |
| C1–N2 | 1.397 | 1.374 | 1.393 | 1.374 |
| C1–N3 | 1.298 | 1.326 | 1.298 | 1.325 |
| C2–N3 | 1.402 | 1.357 | 1.403 | 1.358 |
| C2–N4 | 1.292 | 1.358 | 1.290 | 1.356 |
| C2–N5 | 1.396 | 1.334 | 1.394 | 1.335 |
| C3–N5 | 1.295 | 1.335 | 1.294 | 1.334 |
| C3–N6 | 1.394 | 1.364 | 1.396 | 1.364 |
| C3–N7 | 1.388 | 1.359 | 1.388 | 1.359 |
| C4–N4 | 1.454 | 1.473 | 1.453 | 1.477 |
| N1–C11 | 1.453 | 1.461 | 1.453 | 1.460 |
| N1–C12 | 1.458 | 1.466 | 1.458 | 1.466 |
| N2–C13 | 1.460 | 1.464 | 1.460 | 1.464 |
| N2–C14 | 1.454 | 1.459 | 1.454 | 1.459 |
| N6–C15 | 1.456 | 1.460 | 1.455 | 1.460 |
| N6–C16 | 1.459 | 1.464 | 1.460 | 1.464 |
| N7–C17 | 1.459 | 1.466 | 1.459 | 1.465 |
| N7–C18 | 1.454 | 1.462 | 1.455 | 1.462 |
| | | | | |
| *Dihedral angle* | | *θ* / ° | | *θ* / ° |
| N1–C1–N3–C2 | 154.2 | 146.0 | 154.0 | 146.6 |
| C2–N5–C3–N6 | 29.5 | 49.1 | 29.0 | 48.7 |

Cartesian coordinates:

**4a**

| | | | |
|---|---|---|---|
| N | -1.111430 | 1.039670 | -0.179173 |
| N | -2.766647 | -1.416061 | -1.199474 |
| N | -1.024845 | -1.237863 | 0.451960 |
| N | -2.995364 | -2.344699 | 0.932418 |
| N | -1.158851 | 3.343247 | -0.389319 |
| N | 0.911706 | -0.127438 | -0.337698 |
| N | 0.226681 | 2.443146 | 1.254568 |
| C | -1.535524 | 4.511564 | 0.397939 |
| H | -2.630317 | 4.575624 | 0.502185 |
| H | -1.186807 | 5.433897 | -0.083673 |
| H | -1.097269 | 4.443166 | 1.392961 |

| | | | |
|---|---|---|---|
| C | -3.761371 | -3.497195 | 0.470405 |
| H | -3.851558 | -3.470347 | -0.614834 |
| H | -4.764993 | -3.498807 | 0.913945 |
| H | -3.261903 | -4.436313 | 0.755743 |
| C | -4.093210 | -0.815626 | -1.301697 |
| H | -4.659907 | -1.005637 | -0.389669 |
| H | -4.639242 | -1.239742 | -2.153933 |
| H | -4.014712 | 0.273063 | -1.440929 |
| C | -2.200781 | -1.612885 | 0.061711 |
| C | 3.126720 | -1.213211 | -0.287546 |
| C | -0.344719 | -0.127010 | -0.045120 |
| C | -2.593342 | -2.416629 | 2.328388 |
| H | -1.811735 | -3.172599 | 2.496355 |
| H | -3.468909 | -2.676363 | 2.934485 |
| H | -2.203304 | -1.450849 | 2.649508 |
| C | -0.668070 | 2.194282 | 0.216165 |
| C | 1.617618 | -1.393504 | -0.251880 |
| H | 1.332299 | -2.045491 | -1.098306 |
| H | 1.333391 | -1.962851 | 0.647451 |
| C | -1.874935 | 3.212254 | -1.646289 |
| H | -1.402793 | 2.444375 | -2.259248 |
| H | -1.837544 | 4.171918 | -2.175272 |
| H | -2.930887 | 2.936487 | -1.499630 |
| C | 3.963371 | -2.237201 | 0.176024 |
| H | 3.520747 | -3.140809 | 0.592210 |
| C | 5.929423 | -0.955202 | -0.408099 |
| H | 7.011005 | -0.854173 | -0.452966 |
| C | 5.351781 | -2.113644 | 0.116383 |
| H | 5.982768 | -2.919048 | 0.485018 |
| C | 0.440179 | 1.452990 | 2.297548 |
| H | -0.459239 | 0.847360 | 2.422699 |
| H | 0.645814 | 1.976981 | 3.240117 |
| H | 1.280520 | 0.786051 | 2.068113 |
| C | -1.900728 | -1.143413 | -2.336880 |
| H | -1.660092 | -0.077354 | -2.436563 |
| H | -2.409837 | -1.481185 | -3.247963 |
| H | -0.969163 | -1.703830 | -2.233290 |
| C | 1.378890 | 3.309865 | 1.024795 |
| H | 1.188984 | 3.966663 | 0.175516 |
| H | 2.272097 | 2.705873 | 0.807226 |
| H | 1.579722 | 3.924688 | 1.911939 |
| C | 3.715591 | -0.055793 | -0.809780 |
| H | 3.063762 | 0.738277 | -1.158568 |
| C | 5.104965 | 0.072316 | -0.869607 |
| H | 5.545212 | 0.979209 | -1.278354 |

**4aH$^+$**

| | | | |
|---|---|---|---|
| N | -1.344004 | -0.166646 | 0.353242 |
| N | 0.173554 | 2.333243 | 1.304362 |
| N | 0.334002 | 1.107916 | -0.727468 |

| | | | |
|---|---|---|---|
| N | -0.013499 | 3.391044 | -0.767133 |
| N | -2.957961 | -1.549513 | 1.267250 |
| N | 0.283070 | -1.161567 | -1.025363 |
| N | -2.844612 | -1.365079 | -1.058356 |
| C | -4.409678 | -1.740016 | 1.337479 |
| H | -4.810589 | -1.134260 | 2.158882 |
| H | -4.668046 | -2.788192 | 1.524327 |
| H | -4.880614 | -1.413141 | 0.411188 |
| C | 0.522925 | 4.678317 | -0.316478 |
| H | 1.105108 | 4.546689 | 0.595131 |
| H | -0.272542 | 5.410042 | -0.136560 |
| H | 1.185368 | 5.074326 | -1.094451 |
| C | -0.671388 | 3.261929 | 2.056652 |
| H | -1.309985 | 3.828245 | 1.379872 |
| H | -0.073790 | 3.956538 | 2.658012 |
| H | -1.314486 | 2.683898 | 2.731379 |
| C | 0.127050 | 2.242301 | -0.055462 |
| C | 2.760408 | -1.446047 | -0.801731 |
| C | -0.256085 | -0.056027 | -0.450372 |
| C | -0.340483 | 3.333551 | -2.190806 |
| H | 0.568128 | 3.325293 | -2.805966 |
| H | -0.935336 | 4.214570 | -2.450583 |
| H | -0.916275 | 2.435772 | -2.408413 |
| C | -2.338267 | -1.024428 | 0.172583 |
| C | 1.580213 | -1.202737 | -1.723145 |
| H | 1.686522 | -0.254531 | -2.251220 |
| H | 1.506482 | -2.001343 | -2.468653 |
| C | -2.283477 | -1.521995 | 2.562536 |
| H | -1.207185 | -1.623504 | 2.426348 |
| H | -2.647519 | -2.360354 | 3.164241 |
| H | -2.485693 | -0.587730 | 3.102608 |
| C | 3.557388 | -0.380357 | -0.363766 |
| H | 3.338996 | 0.626442 | -0.710234 |
| C | 4.925668 | -1.902472 | 0.926737 |
| H | 5.767416 | -2.080043 | 1.589863 |
| C | 4.634429 | -0.607000 | 0.495775 |
| H | 5.252868 | 0.225836 | 0.819070 |
| C | -2.671416 | -0.494920 | -2.216649 |
| H | -2.503769 | 0.530124 | -1.883916 |
| H | -3.587265 | -0.521385 | -2.816526 |
| H | -1.830030 | -0.809686 | -2.846856 |
| C | 0.808328 | 1.295333 | 2.111254 |
| H | 0.073592 | 0.564314 | 2.466057 |
| H | 1.285620 | 1.771966 | 2.973774 |
| H | 1.575102 | 0.782180 | 1.529125 |
| C | -3.398407 | -2.687800 | -1.352045 |
| H | -3.268110 | -3.350396 | -0.496303 |
| H | -2.863587 | -3.117134 | -2.208547 |
| H | -4.463637 | -2.637091 | -1.606948 |
| C | 3.067420 | -2.743330 | -0.371077 |

| | | | |
|---|---|---|---|
| H | 2.473747 | -3.585216 | -0.723545 |
| C | 4.140719 | -2.971941 | 0.490212 |
| H | 4.372195 | -3.983996 | 0.809982 |
| H | -0.098610 | -2.048175 | -0.727062 |

**4b**

| | | | |
|---|---|---|---|
| N | -1.724068 | 1.029758 | -0.190338 |
| N | -3.301617 | -1.446181 | -1.275007 |
| N | -1.635117 | -1.245557 | 0.450033 |
| N | -3.610164 | -2.377274 | 0.846111 |
| N | -1.794436 | 3.332271 | -0.407285 |
| N | 0.319646 | -0.109858 | -0.255373 |
| N | -0.472797 | 2.454298 | 1.300054 |
| C | -2.225821 | 4.494633 | 0.360556 |
| H | -3.325170 | 4.541800 | 0.413229 |
| H | -1.869207 | 5.422282 | -0.104827 |
| H | -1.833910 | 4.433196 | 1.375245 |
| C | -4.338643 | -3.540911 | 0.352185 |
| H | -4.388497 | -3.511932 | -0.735589 |
| H | -5.358003 | -3.560345 | 0.757714 |
| H | -3.834847 | -4.472759 | 0.653468 |
| C | -4.629334 | -0.860863 | -1.434179 |
| H | -5.234985 | -1.064247 | -0.550505 |
| H | -5.130005 | -1.285973 | -2.313333 |
| H | -4.558194 | 0.229656 | -1.562922 |
| C | -2.788213 | -1.635466 | 0.009606 |
| C | 2.546333 | -1.161276 | -0.122815 |
| C | -0.948028 | -0.126511 | -0.018762 |
| C | -3.264011 | -2.446073 | 2.257244 |
| H | -2.476081 | -3.188064 | 2.455126 |
| H | -4.158724 | -2.723570 | 2.826336 |
| H | -2.905062 | -1.474385 | 2.596398 |
| C | -1.315758 | 2.190827 | 0.222368 |
| C | 1.040313 | -1.365597 | -0.136893 |
| H | 0.787985 | -2.028418 | -0.985330 |
| H | 0.733581 | -1.930263 | 0.758349 |
| C | -2.451429 | 3.188731 | -1.694806 |
| H | -1.939633 | 2.428624 | -2.285210 |
| H | -2.406555 | 4.148664 | -2.222752 |
| H | -3.508088 | 2.895262 | -1.595120 |
| C | 3.392732 | -2.184809 | 0.331341 |
| H | 2.959730 | -3.111283 | 0.705042 |
| C | 5.353749 | -0.855828 | -0.150933 |
| C | 4.774882 | -2.042948 | 0.319651 |
| H | 5.428131 | -2.834318 | 0.675231 |
| C | -0.292838 | 1.468345 | 2.353387 |
| H | -1.188629 | 0.850555 | 2.438593 |
| H | -0.137251 | 1.996253 | 3.303349 |
| H | 0.566069 | 0.812773 | 2.163302 |
| C | -2.390566 | -1.163177 | -2.373959 |

| | | | |
|---|---|---|---|
| H | -2.154932 | -0.094977 | -2.461053 |
| H | -2.858099 | -1.502915 | -3.306320 |
| H | -1.459612 | -1.716158 | -2.232185 |
| C | 0.676453 | 3.336290 | 1.120705 |
| H | 0.517084 | 3.987843 | 0.261117 |
| H | 1.587076 | 2.744043 | 0.946975 |
| H | 0.827718 | 3.956512 | 2.013952 |
| C | 3.138344 | 0.013974 | -0.586147 |
| H | 2.490893 | 0.812958 | -0.931996 |
| C | 4.528394 | 0.177122 | -0.604171 |
| H | 4.948732 | 1.107219 | -0.971475 |
| O | 6.724322 | -0.808588 | -0.120501 |
| C | 7.357501 | 0.368502 | -0.585586 |
| H | 8.430770 | 0.196888 | -0.478134 |
| H | 7.127370 | 0.564696 | -1.642020 |
| H | 7.071284 | 1.247099 | 0.009224 |

**4bH$^+$**

| | | | |
|---|---|---|---|
| N | -1.725906 | -0.517914 | 0.405830 |
| N | -0.943121 | 2.286564 | 1.367755 |
| N | -0.667683 | 1.252812 | -0.757418 |
| N | -1.695920 | 3.314203 | -0.586100 |
| N | -2.731409 | -2.354947 | 1.387745 |
| N | -0.055397 | -0.909054 | -1.203599 |
| N | -2.955476 | -2.072129 | -0.919832 |
| C | -4.045471 | -2.969249 | 1.599670 |
| H | -4.500616 | -2.539199 | 2.499833 |
| H | -3.964425 | -4.053020 | 1.738663 |
| H | -4.701903 | -2.763320 | 0.754918 |
| C | -1.533315 | 4.683647 | -0.090834 |
| H | -0.831738 | 4.702524 | 0.742679 |
| H | -2.487777 | 5.117304 | 0.228033 |
| H | -1.126818 | 5.303130 | -0.898266 |
| C | -1.941330 | 2.860635 | 2.271352 |
| H | -2.798410 | 3.228355 | 1.708339 |
| H | -1.522447 | 3.678279 | 2.868995 |
| H | -2.291031 | 2.075700 | 2.953054 |
| C | -1.125771 | 2.238362 | 0.016598 |
| C | 2.405545 | -0.435587 | -1.297483 |
| C | -0.831203 | -0.047051 | -0.501021 |
| C | -2.166099 | 3.218387 | -1.966680 |
| H | -1.390981 | 3.543000 | -2.672322 |
| H | -3.043142 | 3.862202 | -2.085523 |
| H | -2.440023 | 2.191001 | -2.199564 |
| C | -2.431903 | -1.630545 | 0.271330 |
| C | 1.093974 | -0.526143 | -2.047715 |
| H | 0.839249 | 0.429363 | -2.507900 |
| H | 1.156725 | -1.278451 | -2.840923 |
| C | -1.945943 | -2.162751 | 2.603940 |
| H | -0.910404 | -1.938335 | 2.349520 |

| | | | |
|---|---|---|---|
| H | -1.976763 | -3.086668 | 3.189504 |
| H | -2.345162 | -1.344154 | 3.217185 |
| C | 2.867928 | 0.792310 | -0.794891 |
| H | 2.288510 | 1.694276 | -0.974196 |
| C | 4.832894 | -0.278299 | 0.130955 |
| C | 4.061081 | 0.874853 | -0.089970 |
| H | 4.430186 | 1.822875 | 0.288507 |
| C | -3.185423 | -1.159122 | -2.034218 |
| H | -3.281211 | -0.139174 | -1.660147 |
| H | -4.121191 | -1.437923 | -2.530274 |
| H | -2.372942 | -1.195956 | -2.770795 |
| C | 0.074875 | 1.472086 | 2.024544 |
| H | -0.348358 | 0.532751 | 2.396962 |
| H | 0.481529 | 2.041232 | 2.866915 |
| H | 0.886851 | 1.251067 | 1.330402 |
| C | -3.128513 | -3.491052 | -1.233897 |
| H | -2.709622 | -4.107196 | -0.438248 |
| H | -2.597287 | -3.718663 | -2.166615 |
| H | -4.184451 | -3.752581 | -1.371372 |
| C | 3.188544 | -1.572196 | -1.079762 |
| H | 2.869325 | -2.533434 | -1.479275 |
| C | 4.391002 | -1.509465 | -0.372147 |
| H | 4.975384 | -2.411306 | -0.231794 |
| H | -0.108095 | -1.879311 | -0.926273 |
| O | 5.981463 | -0.092169 | 0.829177 |
| C | 6.834852 | -1.209535 | 1.051462 |
| H | 7.689005 | -0.823563 | 1.609069 |
| H | 6.333580 | -1.984876 | 1.644676 |
| H | 7.182789 | -1.641036 | 0.104755 |

**5a**

| | | | |
|---|---|---|---|
| C | 0.543307 | 0.222328 | 0.101157 |
| N | 0.918160 | 1.502540 | 0.485683 |
| N | 1.478061 | -0.731051 | 0.502136 |
| N | -0.530811 | -0.027960 | -0.571794 |
| C | 0.038366 | 2.411934 | 0.799205 |
| N | -1.193002 | 2.210613 | 1.410410 |
| N | 0.362592 | 3.736274 | 0.580127 |
| C | 0.001226 | 4.789092 | 1.520929 |
| H | 0.898086 | 5.165577 | 2.035496 |
| H | -0.472970 | 5.634055 | 1.005119 |
| H | -0.687916 | 4.397041 | 2.268181 |
| C | 1.498545 | 4.047047 | -0.273875 |
| H | 2.445045 | 4.052966 | 0.286762 |
| H | 1.576080 | 3.301970 | -1.064943 |
| H | 1.348644 | 5.039189 | -0.715748 |
| C | -2.395577 | 2.813444 | 0.842300 |
| H | -3.067257 | 3.157646 | 1.639240 |
| H | -2.129166 | 3.663648 | 0.213681 |
| H | -2.929914 | 2.077496 | 0.224049 |

| | | | |
|---|---|---|---|
| C | -1.447166 | 0.990812 | 2.160797 |
| H | -1.898412 | 0.211934 | 1.533979 |
| H | -0.510697 | 0.609123 | 2.572376 |
| H | -2.125623 | 1.226916 | 2.990499 |
| C | -0.770993 | -1.399610 | -0.973373 |
| H | 0.046197 | -1.775402 | -1.623639 |
| H | -0.788488 | -2.085444 | -0.106913 |
| C | -2.074157 | -1.559200 | -1.740952 |
| C | -2.660363 | -2.824955 | -1.868345 |
| C | -2.692976 | -0.468239 | -2.359890 |
| C | -3.835240 | -3.000439 | -2.599614 |
| H | -2.193953 | -3.682418 | -1.385573 |
| C | -3.869993 | -0.640180 | -3.091654 |
| H | -2.239186 | 0.510791 | -2.248138 |
| C | -4.445693 | -1.905595 | -3.215711 |
| H | -4.277287 | -3.990348 | -2.683535 |
| H | -4.339377 | 0.218616 | -3.566131 |
| H | -5.363178 | -2.038358 | -3.783511 |
| H | 2.373592 | -0.330582 | 0.750767 |
| H | 1.550126 | -1.561567 | -0.071464 |

**5aH$^+$**

| | | | |
|---|---|---|---|
| C | -0.775861 | 1.759301 | -0.198495 |
| N | -2.002767 | 1.237227 | -0.157569 |
| N | -0.690606 | 3.104645 | -0.118661 |
| N | 0.363413 | 1.056511 | -0.346898 |
| C | -2.294631 | -0.022546 | 0.184243 |
| N | -1.676059 | -0.688982 | 1.207199 |
| N | -3.304901 | -0.633336 | -0.476655 |
| C | -4.249841 | -1.548155 | 0.174724 |
| H | -5.265111 | -1.172756 | 0.008522 |
| H | -4.183082 | -2.560368 | -0.237778 |
| H | -4.071767 | -1.579888 | 1.248863 |
| C | -3.758241 | -0.100319 | -1.764941 |
| H | -4.541818 | 0.653505 | -1.624748 |
| H | -2.925152 | 0.354130 | -2.298605 |
| H | -4.159324 | -0.926621 | -2.358528 |
| C | -1.518020 | -2.145878 | 1.239381 |
| H | -2.133532 | -2.610291 | 2.018176 |
| H | -1.777638 | -2.574702 | 0.271531 |
| H | -0.467859 | -2.377649 | 1.451697 |
| C | -1.060601 | 0.026581 | 2.325475 |
| H | 0.033673 | 0.024088 | 2.252165 |
| H | -1.418110 | 1.056273 | 2.353259 |
| H | -1.347719 | -0.466712 | 3.260015 |
| C | 1.723878 | 1.620050 | -0.465436 |
| H | 1.801314 | 2.191493 | -1.400112 |
| H | 1.887828 | 2.308625 | 0.371913 |
| C | 2.748698 | 0.510020 | -0.441557 |
| C | 3.305471 | 0.085584 | 0.772032 |

| | | | |
|---|---|---|---|
| C | 3.126667 | -0.127213 | -1.630505 |
| C | 4.227298 | -0.961180 | 0.796472 |
| H | 3.031339 | 0.587383 | 1.697668 |
| C | 4.046991 | -1.175817 | -1.605885 |
| H | 2.711818 | 0.206197 | -2.579290 |
| C | 4.597076 | -1.593860 | -0.392508 |
| H | 4.663891 | -1.275319 | 1.739979 |
| H | 4.341813 | -1.657676 | -2.533381 |
| H | 5.320177 | -2.403946 | -0.374507 |
| H | -1.562498 | 3.614633 | -0.093391 |
| H | 0.141701 | 3.608451 | -0.385795 |
| H | 0.279261 | 0.055763 | -0.457867 |

**5a-1**

| | | | |
|---|---|---|---|
| C | -0.745371 | 1.637694 | -0.427649 |
| N | -1.864166 | 2.088887 | -1.115858 |
| N | -1.094099 | 0.930666 | 0.721964 |
| N | 0.465716 | 1.886873 | -0.816185 |
| C | -1.868342 | 2.217333 | -2.412998 |
| N | -1.194787 | 1.425990 | -3.339223 |
| N | -2.676311 | 3.187118 | -2.969391 |
| C | -3.391854 | 2.983341 | -4.221848 |
| H | -4.474833 | 2.925566 | -4.036496 |
| H | -3.212108 | 3.811312 | -4.920103 |
| H | -3.067466 | 2.051471 | -4.683970 |
| C | -3.229805 | 4.221498 | -2.109578 |
| H | -4.185159 | 3.912884 | -1.659948 |
| H | -2.529605 | 4.440350 | -1.304293 |
| H | -3.401300 | 5.125410 | -2.706058 |
| C | -0.331340 | 2.064858 | -4.329028 |
| H | -0.350148 | 1.502050 | -5.270794 |
| H | -0.668119 | 3.084171 | -4.521303 |
| H | 0.702565 | 2.105402 | -3.956798 |
| C | -0.769065 | 0.084761 | -2.970654 |
| H | 0.243874 | 0.076341 | -2.549944 |
| H | -1.456813 | -0.328872 | -2.230252 |
| H | -0.795188 | -0.547819 | -3.867098 |
| C | 1.548902 | 1.401946 | 0.031432 |
| H | 1.419544 | 0.340682 | 0.307564 |
| H | 2.469661 | 1.446870 | -0.566944 |
| C | 1.779483 | 2.207293 | 1.308747 |
| C | 1.593905 | 3.597189 | 1.321250 |
| C | 2.216065 | 1.581179 | 2.483743 |
| C | 1.845974 | 4.338759 | 2.474918 |
| H | 1.240579 | 4.084109 | 0.417137 |
| C | 2.469464 | 2.321581 | 3.641538 |
| H | 2.363340 | 0.502444 | 2.490974 |
| C | 2.285966 | 3.704432 | 3.639998 |
| H | 1.697958 | 5.416018 | 2.466463 |
| H | 2.805330 | 1.816015 | 4.543654 |

| | | | |
|---|---|---|---|
| H | 2.479915 | 4.283551 | 4.539178 |
| H | -2.062784 | 1.065924 | 0.982725 |
| H | -0.457460 | 1.021079 | 1.504709 |

**5a-2**

| | | | |
|---|---|---|---|
| C | -1.937388 | -0.961297 | -1.932300 |
| N | -1.830138 | 0.102869 | -1.030081 |
| N | -2.413966 | -0.879411 | -3.124184 |
| N | -1.408415 | -2.174587 | -1.481103 |
| C | -2.264337 | 0.068098 | 0.191649 |
| N | -3.249392 | -0.764447 | 0.716516 |
| N | -1.741788 | 0.979156 | 1.104334 |
| C | -0.555891 | 1.725824 | 0.707332 |
| H | -0.798267 | 2.562932 | 0.036315 |
| H | -0.075093 | 2.122903 | 1.608442 |
| H | 0.138512 | 1.068238 | 0.184276 |
| C | -2.628032 | 1.719876 | 1.998891 |
| H | -2.852795 | 2.717517 | 1.589831 |
| H | -3.567293 | 1.183204 | 2.126970 |
| H | -2.156599 | 1.852570 | 2.980026 |
| C | -3.056216 | -1.436326 | 1.995828 |
| H | -2.839343 | -2.504101 | 1.838010 |
| H | -2.218301 | -0.987909 | 2.529725 |
| H | -3.957004 | -1.360596 | 2.619574 |
| C | -4.241348 | -1.387717 | -0.145723 |
| H | -5.194041 | -1.440864 | 0.396671 |
| H | -4.383830 | -0.791206 | -1.046758 |
| H | -3.950047 | -2.402502 | -0.448112 |
| C | -1.131329 | -3.224050 | -2.463715 |
| H | -2.064546 | -3.408859 | -3.004730 |
| H | -0.406397 | -2.886415 | -3.219547 |
| C | -0.634404 | -4.483143 | -1.785639 |
| C | 0.619205 | -5.018691 | -2.101151 |
| C | -1.422332 | -5.142125 | -0.830177 |
| C | 1.076763 | -6.186453 | -1.485251 |
| H | 1.241894 | -4.517215 | -2.838785 |
| C | -0.969029 | -6.305749 | -0.211057 |
| H | -2.397485 | -4.734226 | -0.575996 |
| C | 0.283818 | -6.832827 | -0.537528 |
| H | 2.052970 | -6.587528 | -1.745512 |
| H | -1.594409 | -6.806196 | 0.524149 |
| H | 0.636690 | -7.741178 | -0.056202 |
| H | -2.786395 | 0.062943 | -3.256492 |
| H | -0.675651 | -2.057439 | -0.791162 |

**5a-3**

| | | | |
|---|---|---|---|
| C | -0.356367 | 1.544673 | 0.736773 |
| N | -1.625466 | 1.623187 | 0.159171 |
| N | 0.373004 | 0.423588 | 0.342873 |
| N | 0.107212 | 2.513124 | 1.443004 |

| | | | |
|---|---|---|---|
| C | -2.646396 | 0.921852 | 0.525058 |
| N | -3.725421 | 0.809566 | -0.354639 |
| N | -2.814882 | 0.242724 | 1.727435 |
| C | -2.131932 | 0.656680 | 2.943782 |
| H | -2.828462 | 0.572311 | 3.788621 |
| H | -1.256989 | 0.025479 | 3.163792 |
| H | -1.795889 | 1.689220 | 2.856362 |
| C | -3.463024 | -1.058854 | 1.793716 |
| H | -4.315537 | -1.051857 | 2.488134 |
| H | -3.817328 | -1.347747 | 0.803991 |
| H | -2.751122 | -1.819351 | 2.149335 |
| C | -5.073393 | 1.095699 | 0.135878 |
| H | -5.809040 | 0.504415 | -0.421390 |
| H | -5.154933 | 0.850041 | 1.194243 |
| H | -5.322442 | 2.161409 | 0.010486 |
| C | -3.507095 | 1.266913 | -1.722177 |
| H | -3.511977 | 2.363717 | -1.799793 |
| H | -2.541444 | 0.911250 | -2.082373 |
| H | -4.304557 | 0.861441 | -2.354812 |
| C | 1.483122 | 2.430446 | 1.886037 |
| H | 1.658551 | 1.541496 | 2.525987 |
| H | 2.169185 | 2.309113 | 1.026844 |
| C | 1.916388 | 3.657514 | 2.674369 |
| C | 3.151059 | 3.656445 | 3.336901 |
| C | 1.119982 | 4.804170 | 2.738943 |
| C | 3.584321 | 4.776083 | 4.045905 |
| H | 3.780327 | 2.768110 | 3.298055 |
| C | 1.551170 | 5.927073 | 3.449650 |
| H | 0.162977 | 4.793155 | 2.228779 |
| C | 2.783037 | 5.919267 | 4.104663 |
| H | 4.545114 | 4.755959 | 4.554770 |
| H | 0.919886 | 6.811730 | 3.490845 |
| H | 3.116948 | 6.793649 | 4.657688 |
| H | -0.153792 | -0.355889 | -0.024221 |
| H | 1.173501 | 0.167737 | 0.904424 |

**5a-4**

| | | | |
|---|---|---|---|
| C | -0.273147 | 1.013378 | -0.107185 |
| N | -1.397463 | 0.343475 | -0.597205 |
| N | 0.024074 | 2.238503 | -0.372226 |
| N | 0.578429 | 0.230781 | 0.676251 |
| C | -2.247288 | -0.303029 | 0.139910 |
| N | -2.491501 | -0.130164 | 1.498267 |
| N | -3.055495 | -1.258198 | -0.470354 |
| C | -4.493529 | -1.278766 | -0.210443 |
| H | -5.041114 | -0.737631 | -0.998059 |
| H | -4.862628 | -2.311030 | -0.186860 |
| H | -4.711595 | -0.802916 | 0.744889 |
| C | -2.703839 | -1.668171 | -1.823687 |
| H | -3.022663 | -0.931876 | -2.575830 |

| | | | |
|---|---|---|---|
| H | -1.623333 | -1.785349 | -1.907031 |
| H | -3.192704 | -2.625579 | -2.036042 |
| C | -2.670139 | -1.275318 | 2.382630 |
| H | -3.550012 | -1.143773 | 3.026841 |
| H | -2.794909 | -2.185066 | 1.795285 |
| H | -1.789507 | -1.395288 | 3.032075 |
| C | -2.123662 | 1.102500 | 2.178861 |
| H | -1.141760 | 1.028216 | 2.664403 |
| H | -2.091071 | 1.927801 | 1.468059 |
| H | -2.881607 | 1.322366 | 2.941498 |
| C | 1.944325 | 0.682944 | 0.966328 |
| H | 1.890467 | 1.769869 | 1.053574 |
| H | 2.232702 | 0.274974 | 1.942918 |
| C | 2.971142 | 0.276898 | -0.075794 |
| C | 3.855963 | -0.779688 | 0.171174 |
| C | 3.037041 | 0.937052 | -1.313213 |
| C | 4.786162 | -1.177203 | -0.792280 |
| H | 3.821345 | -1.293283 | 1.130577 |
| C | 3.964019 | 0.540351 | -2.276315 |
| H | 2.351845 | 1.757865 | -1.504206 |
| C | 4.840942 | -0.517672 | -2.020157 |
| H | 5.467643 | -1.997771 | -0.581663 |
| H | 4.007040 | 1.062089 | -3.229265 |
| H | 5.564959 | -0.821840 | -2.771847 |
| H | -0.743748 | 2.644532 | -0.909171 |
| H | 0.504351 | -0.757938 | 0.468394 |

**5b**

| | | | |
|---|---|---|---|
| C | -0.491970 | 2.029485 | -0.827126 |
| N | -1.551074 | 1.961055 | -1.722885 |
| N | -0.681864 | 3.034735 | 0.119753 |
| N | 0.546077 | 1.264331 | -0.901716 |
| C | -1.941130 | 0.829939 | -2.238861 |
| N | -1.908240 | -0.422803 | -1.635834 |
| N | -2.522434 | 0.848751 | -3.491187 |
| C | -3.657536 | 0.001023 | -3.832665 |
| H | -4.566834 | 0.609535 | -3.949823 |
| H | -3.483233 | -0.531812 | -4.776478 |
| H | -3.826751 | -0.726493 | -3.039480 |
| C | -2.385962 | 2.043105 | -4.310092 |
| H | -3.173643 | 2.780551 | -4.095441 |
| H | -1.420717 | 2.510140 | -4.117560 |
| H | -2.453821 | 1.758625 | -5.366837 |
| C | -1.304832 | -1.550019 | -2.341609 |
| H | -1.856853 | -2.474745 | -2.130056 |
| H | -1.316393 | -1.370761 | -3.417244 |
| H | -0.260728 | -1.680207 | -2.021559 |
| C | -1.834145 | -0.533123 | -0.187061 |
| H | -0.797649 | -0.595428 | 0.166449 |
| H | -2.308714 | 0.335579 | 0.273637 |

| | | | |
|---|---|---|---|
| H | -2.376718 | -1.435656 | 0.122040 |
| C | 1.618740 | 1.487319 | 0.048295 |
| H | 2.015776 | 2.520750 | -0.033731 |
| H | 1.266416 | 1.396556 | 1.092084 |
| C | 2.779962 | 0.528317 | -0.156382 |
| C | 3.722513 | 0.330907 | 0.864026 |
| C | 2.968507 | -0.149346 | -1.360259 |
| C | 4.815026 | -0.508764 | 0.687839 |
| H | 3.597331 | 0.841991 | 1.817315 |
| C | 4.061581 | -1.000936 | -1.556429 |
| H | 2.237708 | -0.008313 | -2.149734 |
| C | 4.992320 | -1.182401 | -0.529200 |
| H | 5.542118 | -0.665026 | 1.479107 |
| H | 4.172611 | -1.511634 | -2.506862 |
| H | -1.385777 | 3.709367 | -0.151475 |
| H | 0.154233 | 3.453519 | 0.506461 |
| O | 6.096917 | -1.989935 | -0.605922 |
| C | 6.321767 | -2.695518 | -1.812560 |
| H | 6.457406 | -2.013598 | -2.663344 |
| H | 7.239660 | -3.267465 | -1.660983 |
| H | 5.498486 | -3.387215 | -2.038609 |

**5bH$^+$**

| | | | |
|---|---|---|---|
| C | 0.756378 | 1.990679 | 0.429826 |
| N | 1.855358 | 1.651272 | 1.107841 |
| N | 0.866952 | 3.047111 | -0.404754 |
| N | -0.442111 | 1.389809 | 0.542820 |
| C | 2.090115 | 0.445892 | 1.636654 |
| N | 1.770022 | -0.728815 | 1.010931 |
| N | 2.742777 | 0.396868 | 2.821200 |
| C | 3.730155 | -0.637931 | 3.149214 |
| H | 4.673036 | -0.146424 | 3.411792 |
| H | 3.409376 | -1.247935 | 4.000314 |
| H | 3.910654 | -1.280518 | 2.288432 |
| C | 2.804478 | 1.591359 | 3.668420 |
| H | 3.681843 | 2.201751 | 3.424129 |
| H | 1.908509 | 2.195016 | 3.533744 |
| H | 2.871354 | 1.271698 | 4.712263 |
| C | 1.451746 | -1.964569 | 1.731828 |
| H | 2.224413 | -2.730216 | 1.597670 |
| H | 1.328564 | -1.759977 | 2.795265 |
| H | 0.506992 | -2.361868 | 1.342652 |
| C | 1.655909 | -0.815027 | -0.445138 |
| H | 0.608853 | -0.887135 | -0.763257 |
| H | 2.114924 | 0.058404 | -0.908948 |
| H | 2.185776 | -1.710114 | -0.787904 |
| C | -1.687599 | 1.778563 | -0.155855 |
| H | -2.033812 | 2.746377 | 0.230580 |
| H | -1.455978 | 1.899607 | -1.221023 |
| C | -2.748259 | 0.724717 | 0.036622 |

| | | | |
|---|---|---|---|
| C | -2.797658 | -0.403448 | -0.800792 |
| C | -3.687763 | 0.830769 | 1.065790 |
| C | -3.751073 | -1.391272 | -0.610831 |
| H | -2.092114 | -0.497901 | -1.623932 |
| C | -4.656173 | -0.153634 | 1.270233 |
| H | -3.678826 | 1.701013 | 1.718602 |
| C | -4.691785 | -1.275017 | 0.429064 |
| H | -3.804908 | -2.258157 | -1.261311 |
| H | -5.376342 | -0.033893 | 2.070831 |
| H | 1.752730 | 3.533209 | -0.405856 |
| H | 0.059856 | 3.540109 | -0.756145 |
| H | -0.520692 | 0.632894 | 1.207650 |
| O | -5.582201 | -2.288279 | 0.526975 |
| C | -6.594864 | -2.221726 | 1.528625 |
| H | -7.190798 | -3.126343 | 1.405366 |
| H | -6.159089 | -2.205945 | 2.535172 |
| H | -7.233736 | -1.341344 | 1.389616 |

## The crystal and molecular structure of triguanide chloride salt (4aH)Cl

**Table SM3.** Crystallographic data for (**4aH**)**Cl**.

| Formula | $C_{18}H_{32}Cl_1N_7$ |
|---|---|
| Molecular weight | 381.95 |
| Crystal system, space group | Orthorhombic, *P*bca |
| Colour, crystal dimensions ($mm^3$) | colourless prism, $0.2 \times 0.2 \times 0.1$ |
| Unit cell dimensions *a*, *b*, *c* (Å) | 15.9304(4), 14.0589(3), 19.0244(4) |
| *α, β, γ* (°) | 90.0, 90.0, 90.0 |
| Volume, *V* ($Å^3$) | 4260.78(17) |
| *Z* | 8 |
| $D_{calc}$ ($g\ cm^{-3}$) | 1.191 |
| Radiation, Co *Kα*, *λ* (Å) | 1.54184 |
| *θ* range | 4.65 – 72.47 |
| Temperature, (K) | 296(2) |
| Reflections collected | 17247 |
| Independent reflections | 4221 |
| Observed reflections | 3536 |
| Absorption coefficient, *μ*, ($mm^{-1}$) | 1.707 |
| Refinement on $F^2$ | |
| $R(F^2(2\sigma F^2))$[A] | 0.0427 |
| *wR* ($F^2$ all reflections)[B] | 0.1322 |
| Goodness-of-fit, *S* | 1.044 |
| Residual electron density, e $Å^{-3}$ | 0.272, –0.151 |

[A] $R = \sum||F_o|-|F_c||/\sum F_o$.
[B] $w = 1/[\sigma(F_o^2)+(0.0823P)^2+0.4379P]$ where $P = (F_o^2+2F_c^2)/3$.

**Table SM4.** Selected bond lenghts (Å) and valence angles (°) for (**4aH**)**Cl**.

| *Bond lenght* / Å | | *Angle* / ° | |
|---|---|---|---|
| C1–N1 | 1.3510(2) | C1–N1–C11 | 119.15(1) |
| C1–N2 | 1.3584(2) | C1–N1–C12 | 122.79(2) |
| C1–N3 | 1.3204(2) | C11–N1–C12 | 113.48(2) |
| C2–N3 | 1.3520(2) | C1–N2–C13 | 122.56(2) |
| C2–N4 | 1.3386(2) | C1–N2–C14 | 122.01(2) |
| C2–N5 | 1.3318(2) | C13–N2–C14 | 114.97(2) |
| C3–N5 | 1.3397(2) | N1–C1–N2 | 117.32(1) |
| C3–N6 | 1.3464(2) | N1–C1–N3 | 118.00(1) |
| C3–N7 | 1.3381(2) | N2–C1–N3 | 124.52(2) |
| C4–N4 | 1.4511(2) | C1–N3–C2 | 126.27(1) |
| N1–C11 | 1.4546(2) | N3–C2–N4 | 122.32(1) |
| N1–C12 | 1.4647(2) | N3–C2–N5 | 120.16(1) |
| N2–C13 | 1.4649(2) | N4–C2–N5 | 117.50(1) |
| N2–C14 | 1.4442(3) | C2–N4–C4 | 123.28(1) |
| N6–C15 | 1.4512(3) | C2–N5–C3 | 120.59(1) |
| N6–C16 | 1.4586(3) | N5–C3–N6 | 121.69(2) |
| N7–C17 | 1.4673(2) | N5–C3–N7 | 118.66(2) |
| N7–C18 | 1.4568(2) | N6–C3–N7 | 119.19(1) |
| | | C3–N6–C15 | 119.75(1) |
| | | C3–N6–C16 | 123.10(2) |
| | | C15–N6–C16 | 113.45(2) |
| | | C3–N7–C17 | 123.98(2) |
| | | C3–N7–C18 | 120.20(2) |
| | | C17–N7–C18 | 114.91(2) |

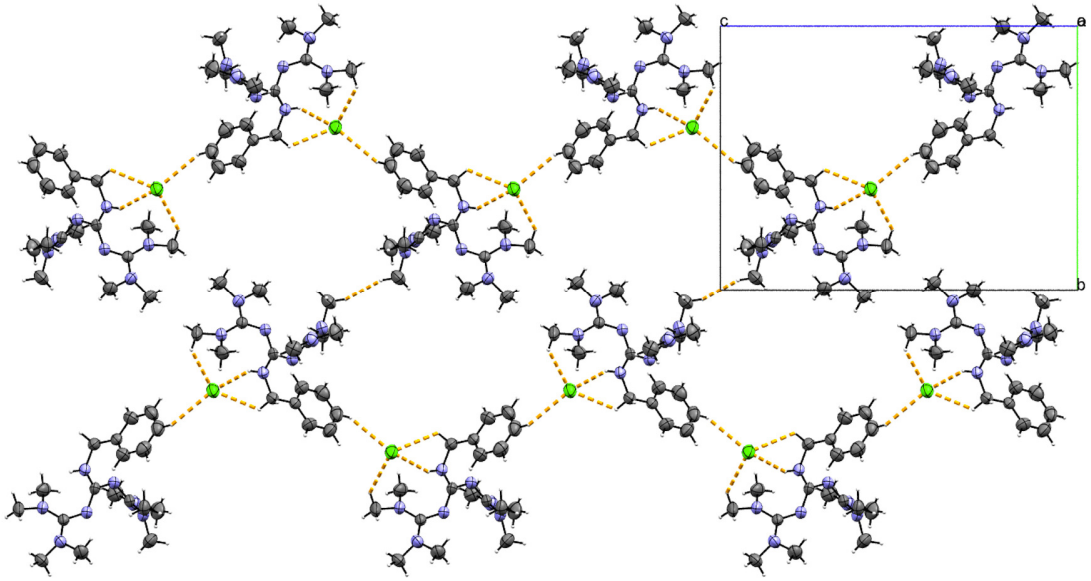



**Figure SM17.** An array of triguanide cations bridged by chloride anions in the crystal structure of (**4aH**)**Cl**. The interactions between ions are displayed as yellow dashed lines. View along the *a* axis.

## References

[1] A. I. Vogel, A. R. Tatchell, B. S. Furnis, A. J. Hannaford, P. W. G. Smith, *Vogel's textbook of practical organic chemistry* **1989** (5th edition, 1989, Longman Scientific & Technical, London)

[2] A. R. Katritzky, R. L. Parris, S. M. Allin, *Synth. Commun.* **1995**, *25*, 1173.

[3] CrysAlis Software system, Version 1.171.33.32, Xcalibur CCD system, Oxford Diffraction Ltd. 2009, Abingdon, UK

[4] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.

[5] L. J. Farrugia, *J. Appl. Crystallogr*. **1999**, *32*, 837.

[6] L. J. Spek, *J.Appl. Cryst.* **2003**, *36*, 7.

[7] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. J. van de Streek, *Appl. Cryst.* **2006**, *39*, 453.

[8] U. Schuchardt, R. M. Vargas, G. Gelbard, *J. Mol. Catal. A: Chem.* **1995**, *99*, 65.

[9] *Gaussian 03*. Revision C.02. Frisch MJ. Trucks GW. Schlegel HB. Scuseria GE. Robb MA. Cheeseman JR. Montgomery Jr JA. Vreven T. Kudin KN. Burant JC. Millam JM. Iyengar SS. Tomasi J. Barone V. Mennucci B. Cossi M. Scalmani G. Rega N. Petersson GA. Nakatsuji H. Hada M. Ehara M. Toyota K. Fukuda R.

Hasegawa J. Ishida M. Nakajima T. Honda Y. Kitao O. Nakai H. Klene M. Li X. Knox JE. Hratchian HP. Cross JB. Bakken V. Adamo C. Jaramillo J. Gomperts R. Stratmann RE. Yazyev O. Austin AJ. Cammi R. Pomelli C. Ochterski JW. Ayala PY. Morokuma K. Voth GA. Salvador P. Dannenberg JJ. Zakrzewski V G. Dapprich S. Daniels AD. Strain MC. Farkas O. Malick DK. Rabuck AD. Raghavachari K. Foresman JB. Ortiz JV. Cui Q. Baboul AG. Clifford S. Cioslowski J. Stefanov BB. Liu G. Liashenko A. Piskorz P. Komaromi I. Martin RL. Fox DJ. Keith T. Al-Laham MA. Peng CY. Nanayakkara A. Challacombe M. Gill PMW. Johnson B. Chen W. Wong MW. Gonzalez C. Pople JA (2004) Gaussian Inc Wallingford CT

[10] A. Klamt, V. Jonas, T. Buerger, J. C. W. Lohrenz, *J. Phys. Chem.* **1998**, *102*, 5074.