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Supporting Information

General and Greener Synthesis of Diverse Functional Organic Salts through Schiff Base Chemistry

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Safety Precautions. Although none of organic salts described herein have exploded or detonated in the course of this research, some organic salts containing rich-nitrogen heterocyclic anions should be handled with extreme care using the best safety practices.

1. Materials and Instruments
All aldehydes, ketones, and organic acids, aminoguanidinium bicarbonate were obtained commercially from various chemical companies. Amino-containing cations containing simple dinitropyrazolate salts such as ammonium 3,5-dinitropyazole, hydrazinium 3,5-dinitropyrazole, aminoguanidinium 3,5-dinitropyrazole and guanidinium 3,5-dinitropyrazole was prepared according to the literature procedures [39]. A few of simple aminoguanidinium salts were prepared according to the literature procedures, too. [40-47] Most of simple aminoguanidinium salts with organic anions have been previously reported; these salts were mainly prepared from one-step acid-based neutralization reaction between aminoguanidinium bicarbonate and organic acids.

All compounds were characterized by 1H NMR, 13C NMR, IR spectroscopy, as well as, in most instances, mass spectra and elemental analysis. Some organic salts have also been characterized by single-crystal X-ray diffraction analysis. NMR spectroscopy was performed on a Bruker AVANCE III 600 instrument with Me₄Si as an internal standard. IR spectrum was recorded on a Bruker Tensor 27 spectrophotometer with HTS-XT (KBr pellets). Elemental analysis was performed on an Elementar Vario EL. ESI was recorded on Brucker-MAS2010. To determine the thermal stability of the described compounds, a TA-DSC Q2000 differential scanning calorimeter (heating rate: 10 °C min⁻¹) was used; the flow rate of nitrogen gas, 60 mL min⁻¹; the sample size, about 2.0 mg was used. The crystal structure of organic salts was determined by a Rigaku RAXIS IP diffractometer and SHELXTL crystallographic software package of molecular structure. The single crystals were mounted on a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å). Data were collected by the o scan technique. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atom was determined with theoretical calculations and refined with an isotropic vibration factor. The CIF files were deposited with CCDC 1854699 (compound 4), 1854698 (compound 24), 1854702 (compound 39), 1854701 (compound 46), 1854704 (compound 58), 1854700 (compound 70), 1854703 (compound 72).
2. Optimization condition for the condensation reaction

General procedures for evaluation of amino-containing cations containing simple dinitropyrazolate salts:

In a 50 mL round bottom flask, benzaldehyde (1 mmol) and ethanol (6 mL) were placed. An amino-containing cation containing simple dinitropyrazolate salt (1 mmol) dissolved in ethanol (20 mL) was added dropwise to the flask. The resulting mixture was stirred at different temperatures. The reaction mixture was then cooled to room temperature and the solvent was slowly removed under vacuum. The reaction was monitored by TLC.

Table S1. Evaluation of various primary amine salts for the condensation reaction with benzaldehyde

<table>
<thead>
<tr>
<th>Entry</th>
<th>Simple organic salts</th>
<th>Temperature (°C)</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Product (Yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2a</td>
<td>25</td>
<td>ethanol</td>
<td>12</td>
<td>No Product</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>65</td>
<td>ethanol</td>
<td>12</td>
<td>No Product</td>
</tr>
<tr>
<td>3</td>
<td>2a</td>
<td>78 (refluxing)</td>
<td>ethanol</td>
<td>12</td>
<td>No Product</td>
</tr>
<tr>
<td>4</td>
<td>2b</td>
<td>25</td>
<td>ethanol</td>
<td>12</td>
<td>No Product</td>
</tr>
<tr>
<td>5</td>
<td>2b</td>
<td>65</td>
<td>ethanol</td>
<td>12</td>
<td>No Product</td>
</tr>
<tr>
<td>6</td>
<td>2b</td>
<td>78 (refluxing)</td>
<td>ethanol</td>
<td>12</td>
<td>No Product</td>
</tr>
<tr>
<td>7</td>
<td>2c</td>
<td>25</td>
<td>ethanol</td>
<td>1</td>
<td>3 (95.2%)</td>
</tr>
<tr>
<td>8</td>
<td>2c</td>
<td>65</td>
<td>ethanol</td>
<td>1</td>
<td>3 (96.0%)</td>
</tr>
<tr>
<td>9</td>
<td>2d</td>
<td>25</td>
<td>ethanol</td>
<td>7</td>
<td>4 (82.0%)</td>
</tr>
<tr>
<td>10</td>
<td>2d</td>
<td>65</td>
<td>ethanol</td>
<td>7</td>
<td>4 (92.0%)</td>
</tr>
<tr>
<td>11</td>
<td>2d</td>
<td>65</td>
<td>ethanol</td>
<td>3</td>
<td>4 (80.1%)</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>11</td>
<td>2d</td>
<td>78</td>
<td>ethanol</td>
<td>7</td>
<td>4 (90.1%)</td>
</tr>
<tr>
<td>12</td>
<td>2d</td>
<td>25</td>
<td>water</td>
<td>7</td>
<td>4 (85.2%)</td>
</tr>
<tr>
<td>13</td>
<td>2d</td>
<td>65</td>
<td>water</td>
<td>7</td>
<td>4 (90.1%)</td>
</tr>
</tbody>
</table>

(1E,2E)-1,2-dibenzylidenedrazine (3)

\[
\text{IR (KBr, cm}^{-1}\text{)}: \nu = 449, 498, 692, 752, 857, 956, 1020, 1073, 1172, 1211, 1305, 1323, 1447, 1493, 1575, 1625, 2949, 3001, 3052.\
\]

\(^1\)H NMR (600 MHz, d\text{6-DMSO}) \(\delta = 7.52 (\text{m, } 6\text{H, CH}), 7.89 (\text{m, } 4\text{H, CH}), 8.73 (\text{s, } 2\text{H, CH}) \text{ ppm.}\
\]

\(^13\)C NMR (150 MHz, d\text{6-DMSO}) \(\delta = 128.85 (\text{s}), 129.37 (\text{s}), 131.81 (\text{s}), 134.30 (\text{s}), 161.93 (\text{s}) \text{ ppm.}\

**Elemental analysis:** calcd (%): C 80.74, N 13.45, H 5.81, found: C 81.04, N 13.26, H 5.62.

**Gaussian calculation of aminoguanidinium cation**

FigS1. The Gaussian calculation result of aminoguanidinium cation

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>bond</td>
<td>bond length</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1-N2</td>
<td>1.33\AA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1-N4</td>
<td>1.34\AA</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C1-N7</td>
<td>1.35\AA</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3. General procedures for the condensation reaction of aldehydes and simple aminoguanidinium salts

General Procedure: A solution of simple aminoguanidinium salt (1 mmol) in ethanol was added dropwise to aldehyde in ethanol. The resulting mixture was stirred for 7 h at 65°C. After that, the solvent was slowly removed under vacuum, and the products were obtained upon recrystallization from different solvents.

4. Condensation reactions between various aldehydes and aminoguanidinium 3,5-dinitropyrazolate

3,5-dinitropyrazolate (E)-amino(2-benzylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (4)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the light yellow needle crystal was obtained upon recrystallization from water. (0.294 g, 92%)

IR (KBr, cm⁻¹): ν = 759, 834, 1010, 1318, 1351, 486, 541, 1622, 1670, 3255.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.35 (s, 1H, CH), 7.45 (s, 3H, NH), 7.72 (t, 3H, CH), 7.87 (m, 2H, CH), 8.22(s, 1H, CH), 11.59(s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 98.89 (s), 128.07(s.), 129.13(s), 130.98 (s), 133.85 (s), 147.75(s), 155.57 (s), 156.81 (s) ppm.

MS: m/z: 163.05 (C₈H₁₁N₄⁺, cation); 156.95 (C₃H₇NO₄⁻, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 42.25, N 34.99, H 3.78, found: C 42.82, N 34.52, H 3.96.

(E)-amino(2-(4-methylbenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol -1-ide (6)
Following the general procedure, in a 50 mL round bottom flask, 4-methylbenzaldehyde (0.120 g, 1 mmol) and ethanol (8 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (15 mL) was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white powder was obtained upon recrystallization from water and methanol. (0.264 g, 79%)

IR (KBr, cm⁻¹): v = 518, 750, 836, 953, 1011, 1154, 1275, 1317, 1354, 1443, 1483, 1537, 1653, 1672, 3150, 3451.

¹H NMR (600 MHz, d₆-DMSO): δ = 2.33 (s, 3H, CH), 7.25 (d, 2H, CH), 7.35 (s, 1H, CH), 7.74 (d, 2H, CH), 8.18 (s, 1H, CH), 11.53 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 21.49 (s), 98.87 (s), 128.06 (s), 129.74 (s), 131.15 (s), 140.93 (s), 147.78 (s), 155.52 (s), 156.81 (s) ppm.

MS: m/z: 177.10 (C₉H₁₃N₄⁺, cation); 156.95 (C₃H₄N₄O₄⁻, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 43.11, N 33.52, H 4.22, found: C 43.63, N 33.86, H 4.51.

(E)-(2-(4-acetamidobenzylidene)hydrazinyl)(amino)methaniminium 3,5-dinitropyrazol -1-ide (7)

Following the general procedure, in a 50 mL round bottom flask, N-(4-formylphenyl)acetamide (0.163 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white powder was obtained upon recrystallization from water and methanol. (0.328 g, 87%)

IR (KBr, cm⁻¹): v = 453, 526, 700, 749, 832, 1011, 1063, 1175, 1266, 1281, 1317, 1369, 1412, 1439, 1479, 1538, 1591, 1632, 1674, 2812, 3113, 3365, 3440.

¹H NMR (600 MHz, d₆-DMSO): δ = 2.07 (s, 3H, CH), 7.35 (s, 1H, CH), 7.67 (d, 2H, CH), 7.78 (d, 2H, CH), 8.14 (s, 1H, CH), 10.16 (s, 1H, NH), 11.49 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 24.52 (s), 98.89 (s), 119.20 (s), 128.44 (s), 128.97 (s), 141.86 (s), 147.42 (s), 155.47 (s), 156.81 (s), 169.14 (s) ppm.
MS: m/z: 220.2 (C_{10}H_{4}N_{5}O^{+}, cation); 156.9 (C_{3}H_{7}N_{4}O^{-}, 3,5-dinitropyrazolate anion).

Elemental analysis: calcld (%): C 41.38, N 33.41, H 4.01, found: C 41.92, N 33.05, H 3.84.

(E)-amino(2-(4-(methylsulfonyl)benzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (8)

Following the general procedure, in a 50 mL round bottom flask, 4-(methylsulfonyl) benzaldehyde (0.184 g, 1 mmol) and ethanol (20 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white powder was obtained upon recrystallization from water and methanol. (0.358 g, 90%)

IR (KBr, cm⁻¹): ν = 549, 754, 773, 833, 971, 1013, 1146, 1290, 1321, 1352, 1406, 1438, 1477, 1532, 1593, 1626, 1682, 2924, 3007, 3152, 3351, 3403, 3460.

¹H NMR (600 MHz, d_{6}-DMSO): δ = 3.26 (s, 3H, CH), 7.35 (s, 1H, CH), 7.84 (s, 3H, NH), 7.99 (s, 2H, CH), 8.13 (s, 2H, CH), 8.31 (s, 1H, CH), 11.84 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d_{6}-DMSO): δ = 43.84 (s), 98.93 (s), 127.72 (s), 128.70 (s), 138.65 (s), 142.22 (s), 145.87 (s), 155.66 (s), 156.76 (s) ppm.

MS: m/z: 241.1 (C_{9}H_{13}N_{4}O_{2}S^{+}, cation); 157.0 (C_{3}H_{7}N_{4}O^{-}, 3,5-dinitropyrazolate anion).


(E)-amino(2-(4-fluorobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (9)

Following the general procedure, in a 50 mL round bottom flask, 4-fluorobenzaldehyde (0.124 g, 1 mmol) and water (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in water (15 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow powder was obtained upon recrystallization from water. (0.328 g,
97%)

IR (KBr, cm$^{-1}$): $v = 524, 745, 834, 1008, 1140, 1236, 1319, 1350, 1425, 1486, 1514, 1538, 1621, 1674, 3251, 3351, 3462.$

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.28$ (t, 2H, CH), 7.35 (s, 1H, CH), 7.75 (s, 3H, NH), 7.92 (m, 2H, CH), 8.21 (s, 1H, CH), 11.60 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 98.88$ (s), 116.11 (s), 130.32 (s), 146.56 (s), 155.59 (s), 156.79 (s), 163.04 (s), 164.69 (s) ppm.

MS: m/z: 181.05 (C$_8$H$_{10}$FN$_4$+, cation), 157.00 (C$_3$HN$_4$O$_4$-, 3,5-dinitropyrazolate anion).


(E)-amino(2-(4-chlorobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (10)

Following the general procedure, in a 50 mL round bottom flask, 4-chlorobenzaldehyde (0.141 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the yellow crystal was obtained upon recrystallization from water and methanol. (0.290 g, 79%)

IR (KBr, cm$^{-1}$): $v = 453, 748, 834, 939, 1012, 1085, 1165, 1225, 1280, 1309, 1352, 1441, 1473, 1504, 1538, 1625, 1687, 3151, 3411, 3437.$

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.33$ (s, 1H, CH), 7.53 (d, 2H, CH), 7.70 (s, 3H, NH), 7.89 (d, 2H, CH), 8.19 (s, 1H, CH), 11.59 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 98.87$ (s), 129.23 (s), 129.75 (s), 132.83 (s), 135.53 (s), 146.43 (s), 155.57 (s), 156.83 (s) ppm.

MS: m/z: 197.1 (C$_8$H$_{10}$ClN$_4$+, cation); 157.0 (C$_3$HN$_4$O$_4$-, 3,5-dinitropyrazolate anion).

(E)-amino(2-(4-bromobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (11)

Following the general procedure, in a 50 mL round bottom flask, 4-bromobenzaldehyde (0.185 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the light yellow crystal was obtained upon recrystallization from water and methanol. (0.355 g, 89%)

IR (KBr, cm⁻¹): v = 446, 566, 747, 833, 939, 1012, 1163, 1221, 1270, 1311, 1352, 1404, 1442, 1473, 1503, 1538, 1624, 1680, 3158, 3407, 3441.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.33 (s, 1H, CH), 7.64 (d, 2H, CH), 7.75 (s, 3H, NH), 7.82 (d, 2H, CH), 8.18 (s, 1H, CH), 11.62 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 98.87 (s), 124.38 (s), 129.95 (s), 132.14 (s), 133.16 (s), 146.54 (s), 155.57 (s), 156.82 (s) ppm.

MS: m/z: 241.0 (C₈H₁₀BrN₄⁺, cation); 156.9 (C₃HN₄O₄⁻, 3,5-dinitropyrazolate anion).


(E)-amino(2-(4-cyanobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (12)

Following the general procedure, in a 50 mL round bottom flask, 4-formylbenzonitrile (0.131 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the light yellow powder was obtained upon recrystallization from water and ethanol. (0.299 g, 85%)

IR (KBr, cm⁻¹): v = 455, 556, 752, 941, 945, 1012, 1156, 1224, 1284, 1322, 1354, 1433, 1478, 1538, 1599, 1629, 1662, 1693, 2223, 3381, 3571.
$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.33$ (s, 1H), 7.82 (bs, 3H, NH), 7.91 (d, 2H, NH), 8.05 (d, 2H, NH), 8.25 (s, 1H, CH), 11.76 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 98.88$ (s), 112.81 (s), 119.06 (s), 128.62 (s), 132.99 (s), 138.26 (s), 145.79 (s), 155.63 (s), 156.78 (s) ppm.

MS: m/z: 188.1 (C$_9$H$_{10}$N$_5$+, cation); 157.0 (C$_3$HN$_4$O$_4$-, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 4.74, N 36.51, H 3.21, found: C 4.36, N 36.72, H 3.16.

(E)-amino(2-(4-nitrobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (13)

Following the general procedure, in a 50 mL round bottom flask, 4-nitrobenzaldehyde (0.151 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the yellow crystal was obtained upon recrystallization from water and methanol. (0.329 g, 90%)

IR (KBr, cm$^{-1}$): v = 694, 751, 833, 853, 949, 1016, 1163, 1232, 1279, 1322, 1343, 1442, 1474, 1518, 1541, 1595, 1634, 1690, 3402, 3499.

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.32$ (s, 1H), 7.85 (b, 3H, NH), 8.14 (d, 2H, CH), 8.26 (d, 2H, CH), 8.30 (s, 1H, CH), 11.84 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta=98.86$ (s), 124.23 (s), 129.02 (s), 140.09 (s), 145.34 (s), 148.58 (s), 155.66 (s), 156.78 (s) ppm.

MS: m/z: 208.1 (C$_8$H$_{10}$N$_5$O$_2$+, cation); 156.9 (C$_3$HN$_4$O$_4$-, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 36.17, N 34.51, H 3.04, found: C 36.53, N 34.18, H 3.17.

(E)-amino(2-(4-(trifluoromethyl)benzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (14)

11
Following the general procedure, in a 50 mL round bottom flask, 4-(trifluoromethyl) benzaldehyde (0.174 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the yellow crystal was obtained upon recrystallization from water and methanol. (0.338 g, 87%)

**IR (KBr, cm⁻¹):** ν = 599, 752, 845, 949, 1009, 1068, 1107, 1229, 1270, 1307, 1319, 1474, 1538, 1610, 1637, 1674, 3154, 3339, 3376, 3446.

**¹H NMR (600 MHz, d₆-DMSO):** δ = 7.34 (s, 1H, CH), 7.78 (s, 2H, CH), 8.10 (s, 2H, CH), 8.29 (s, 1H, CH), 11.79 (s, 1H, NH) ppm.

**¹³C NMR (150 MHz, d₆-DMSO):** δ = 98.85 (s), 121.78 (s), 123.58 (s), 125.39 (s), 127.19 (s), 128.64 (s), 130.28 (s), 130.49 (s), 130.70 (s), 130.91 (s), 137.80 (s), 146.07 (s), 155.66 (s), 156.78 (s) ppm.

**MS:** m/z: 231.1 (C₉H₁₀F₃N₄⁺, cation); 156.9 (C₃H₈N₄O₄⁻, 3,5-dinitropyrazolate anion).

**Elemental analysis:** calcd (%): C 37.12, N 28.86, H 2.86, found: C 36.83, N 29.01, H 3.07.

(E)-amino(2-(3-hydroxybenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (15)

Following the general procedure, in a 50 mL round bottom flask, 3-hydroxybenzaldehyde (0.151 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) was dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the yellow powder was obtained upon recrystallization from water. (0.289 g, 86 %)

**IR (KBr, cm⁻¹):** ν = 587, 751, 835, 1013, 1181, 1315, 1351, 1440, 1467, 1537, 1583, 1625, 1682, 3115, 3425, 3449.

**¹H NMR (600 MHz, d₆-DMSO):** δ = 6.88 (d, 1H, CH), 7.25 (m, 3H, CH), 7.35 (s, 1H, CH), 7.70 (s, 3H, NH), 8.13 (s, 1H, CH), 9.66 (s, 1H, OH), 11.50 (s, 1H, NH) ppm.

**¹³C NMR (150 MHz, d₆-DMSO):** δ = 98.89 (s), 114.57 (s), 118.20 (s), 119.19 (s), 130.13 (s), 135.09 (s), 148.08 (s), 155.52 (s), 156.80 (s), 158.09 (s) ppm.
MS: m/z: 179.05 (C$_8$H$_{11}$N$_4$O$^+$, cation); 157.00 (C$_3$H$_{2}$N$_4$O$_4^-$, 3,5-dinitropyrazolate anion).

**Elemental analysis:** calcd (%): C 39.29, N 33.32, H 3.60, found: C 38.62, N 33.55, H 3.68.

(E)-amino (2-(3-methoxybenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol -1-ide (16)

![Chemical Structure](image1)

Following the general procedure, in a 50 mL round bottom flask, 3-methoxybenzaldehyde (0.136 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the white powder was obtained upon recrystallization from water. (0.322 g, 92%)

IR (KBr, cm$^{-1}$): v = 688, 751, 835, 1010, 1036, 1175, 1256, 1289, 1318, 1353, 1438, 1477, 1537, 1597, 1631, 1666, 3245, 3350, 3472.

$^1$H NMR (600 MHz, d$_6$-DMSO): δ = 3.80 (s, 3H, CH), 7.02 (m, 1H, CH), 7.36 (m, 3H, CH), 7.50 (s, 1H, CH), 7.75 (s, 3H, NH), 8.19 (s, 1H, CH), 11.59 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): δ = 55.74 (s), 98.89 (s), 112.25 (s), 117.07 (s), 121.22 (s), 130.21 (s), 135.22 (s), 147.64 (s), 155.56 (s), 156.80 (s), 160.03 (s) ppm.

MS: m/z: 193.10 (C$_9$H$_{13}$N$_4$O$^+$, cation); 156.95 (C$_3$H$_{2}$N$_4$O$_4^-$, 3,5-dinitropyrazolate anion).

**Elemental analysis:** calcd (%): C 41.15, N 31.99, H 4.03, found: C 41.76, N 31.62, H 4.32.

(E)-amino(2-(2,4,6-trimethoxybenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazol -1-ide (17)

![Chemical Structure](image2)

Following the general procedure, in a 50 mL round bottom flask, 2,4,6-trimethoxybenzaldehyde (0.196 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the yellow crystal was obtained upon recrystallization from
Following the general procedure, in a 50 mL round bottom flask, 9-anthraldehyde (0.206 g, 1 mmol) and ethanol (5 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum and washed by dichloromethane, and the yellow powder was obtained upon recrystallization from methanol and water. (0.282 g, 67%)

IR (KBr, cm⁻¹): ν = 553, 610, 666, 708, 738, 784, 834, 875, 902, 973, 1012, 1070, 1157, 1253, 1276, 1315, 1350, 1441, 1473, 1530, 1622, 1682, 3153, 3243, 3401.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.38 (s, 1H, CH), 7.58 (t, 2H, CH), 7.65 (m, 2H, CH), 7.80 (s, 4H, NH), 8.15 (d, 2H, CH), 8.52 (d, 2H, CH), 8.72 (s, 1H, CH), 9.41 (s, 1H, CH), 11.88 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 98.94 (s), 125.20 (s), 125.28 (s), 126.08 (s), 127.77 (s), 129.37 (s), 130.11 (s), 130.24 (s), 131.25 (s), 147.47 (s), 155.63 (s), 156.88 (s) ppm.

Elemental analysis: calcd (%): C 54.28, N 26.66, H 3.84, found: C 54.56, N 26.37, H 4.03.
(E)-amino(2-(naphthalen-2-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (19)

Following the general procedure, in a 50 mL round bottom flask, naphthaldehyde (0.156 g, 1 mmol) and ethanol (20 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow needle crystal was obtained upon recrystallization from water and methanol. (0.311 g, 84%)

IR (KBr, cm⁻¹): v = 529, 638, 727, 783, 885, 1109, 1139, 1301, 1438, 1631, 1682, 2222, 2231, 3045, 3174, 3246, 3363, 3424, 3597.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.40 (s, 1H, CH), 7.59 (m, 2H, CH), 7.65 (t, 1H, CH), 7.83(s, 4H, NH), 7.99 (d, 1H, CH), 8.04 (d, 1H, CH), 8.27 (d, 1H, CH), 8.50 (d, 1H, CH), 9.07 (s, 1H, CH), 11.75 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 98.97 (s), 123.67 (s), 125.89 (s), 126.71 (s), 126.98 (s), 127.83 (s), 129.11 (s), 129.24 (s), 130.93 (s), 131.42 (s), 133.82 (s), 146.54 (s), 155.54 (s), 156.81 (s) ppm.


Amino(2-methylenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (20)

Following the general procedure, in a 50 mL round bottom flask, formaldehyde (0.030 g, 1 mmol) and water (5 mL) were placed. Aminoguanidinium 3, 5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. After that the solvent was slowly removed under vacuum, and the white needle crystal was obtained upon recrystallization from water. (0.210 g, 83%)

IR (KBr, cm⁻¹): v = 446, 534, 584, 695, 751, 837, 987, 1017, 1146, 1174, 1278, 1322, 1359, 1375, 1444, 1471, 1537, 1666.
$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 6.69$ (d, 1H, CH), 7.16 (d, 1H, CH), 7.33 (s, 1H, CH), 7.62 (s, 4H, NH), 11.45 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 98.85$ (s), 139.54 (s), 155.72 (s), 156.80 (s) ppm.

MS: m/z: 87.0 (C$_2$H$_7$N$_4^+$, cation); 157.0 (C$_3$H$_4$O$_4^-$, 3,5-dinitropyrazolate anion).


(E)-amino(2-(cyclopentylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (21)

Following the general procedure, in a 50 mL round bottom flask, cyclopentanecarbaldehyde (0.098 g, 1 mmol) and water (5 mL) were placed. Aminoguanidinium 3, 5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water. (0.197 g, 63%)

IR (KBr, cm$^{-1}$): v = 518, 750, 834, 1010, 1062, 1163, 1278, 1319, 1351, 1439, 1480, 1534, 1634, 1661, 2953, 3360, 3444, 3468.

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 1.58$ (m, 6H, CH), 1.77 (s, 2H, CH), 2.68 (m, 1H, CH), 7.32 (s, 1H, CH), 7.47 (d, 1H, CH), 11.11 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 25.41$ (s), 30.23 (s), 42.36 (s), 98.80 (s), 155.34 (s), 155.89 (s), 156.81 (s) ppm.

MS: m/z: 155.1 (C$_7$H$_{15}$N$_4^+$, cation); 157.0 (C$_3$H$_4$O$_4^-$, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 54.16, N 36.10, H 9.74, found: C 53.72, N 36.45, H 9.83.

(E)-amino(2-(cyclohexylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (22)
Following the general procedure, in a 50 mL round bottom flask, cyclohexanecarboxaldehyde (0.112 g, 1 mmol) and water (5 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and ethanol. (0.235 g, 72%)

IR (KBr, cm⁻¹): v = 525, 711, 751, 833, 949, 1008, 1063, 1165, 1279, 1318, 1349, 1439, 1477, 1536, 1632, 1664, 2926, 3356, 3380, 3429, 3497.

¹H NMR (600 MHz, d₆-DMSO): δ = 1.23 (m, 6H, CH), 1.63 (m, 4H, CH), 2.24 (s, 1H, CH), 7.31 (s, 1H, CH), 7.42 (d, 1H, CH), 11.07 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 25.38 (s), 25.90 (s), 29.78 (s), 40.53 (s), 98.79 (s), 155.40 (s), 156.09 (s), 156.84 (s) ppm.

MS: m/z: 169.1(C₈H₁₇N₄⁺, cation); 157.0 (C₃HN₄O₄⁻, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 40.49, N 34.34, H 5.56, found: C 40.01, N 34.72, H 5.32.

(E)-(2-((1H-pyrrol-2-yl)methylene)hydrazinyl)(amino)methaniminium3,5-dinitropyrazol-1-ide (23)

Following the general procedure, in a 50 mL round bottom flask, 1H-pyrrole-2-carbaldehyde (0.095 g, 1mmol) and water (5 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. After that the solvent was slowly removed under vacuum, and the gray crystal was obtained upon recrystallization from water. (0.278 g, 90%)

IR (KBr, cm⁻¹): v = 448, 580, 641, 673, 745, 835, 881, 954, 999, 1012, 1152, 1315, 1350, 1443, 1476, 1529, 1630, 1686, 3152, 3368, 3413, 3475.

¹H NMR (600 MHz, d₆-DMSO): δ = 6.15 (s, 1H, CH), 6.50 (s, 1H, CH), 7.07 (s, 1H, CH), 7.33 (s, 1H, CH), 7.98 (s, 1H, CH), 11.30 (s, 1H, NH), 11.44 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 98.84 (s), 109.83 (s), 114.09 (s), 122.97 (s), 127.43 (s), 138.82 (s), 155.46 (s), 156.84 (s) ppm.
MS: m/z: 152.0 (C₆H₁₀N₅⁺, cation); 156.9 (C₃H₄N₄O₄⁻, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 34.96, N 40.76, H 3.59, found: C 34.33, N 41.02, H 3.12.

(E)-(2-(1H-imidazol-4-yl)vinyl)amino)(amino)methaniminium 3,5-dinitropyrazol-1-ide (24)

Following the general procedure, in a 50 mL round bottom flask, 1H-imidazole-4-carbaldehyde (0.096 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the brown plate crystal was obtained upon recrystallization from water. (0.276 g, 89%)

IR (KBr, cm⁻¹): v = 453, 586, 749, 835, 1012, 1072, 1089, 1131, 1169, 1281, 1318, 1350, 1439, 1478, 1545, 1652, 1680, 3334, 3480.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.33 (s, 1H, CH), 7.53 (s, 3H, NH), 7.85 (s, 1H, CH), 8.11 (s, 1H, CH), 11.40 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ=98.85 (s), 138.14 (s), 155.50 (s), 156.85 (s) ppm.

MS: m/z: 153.1 (C₆H₁₀N₅⁺, cation); 156.9 (C₃H₄N₄O₄⁻, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 34.96, N 40.76, H 3.59, found: C 35.54, N 40.53, H 3.42.

(E)-amino(2-(thiophen-2-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (25)

Following the general procedure, in a 50 mL round bottom flask, 2-thiophene formaldehyde (0.112 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the yellow acicular crystal was obtained upon recrystallization from water. (0.303 g, 93%)
IR (KBr, cm⁻¹): ν = 430, 516, 570, 750, 833, 950, 1004, 1160, 1284, 1321, 1351, 1431, 1474, 1532, 1632, 1682, 3154, 3405, 3512.

¹H NMR (600 MHz, d⁶-DMSO): δ = 7.14 (t, 1H, CH), 7.34 (s, 1H, CH), 7.53 (d, 1H, CH), 7.59 (s, 3H, NH), 7.72 (d, 1H, CH), 8.41 (s, 1H, CH), 11.51 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d⁶-DMSO): δ = 98.88 (s), 128.38 (s), 130.37 (s), 132.17 (s), 138.01 (s), 143.07 (s), 155.23 (s), 156.83 (s) ppm.

MS: m/z: 169.00 (C₇H₁₀N₃S⁺, cation); 157.00 (C₃H₄N₄O₄⁻, 3,5-dinitropyrazolate anion).


(E)-amino(2-((2-bromothiazol-5-yl)methylene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (26)

Following the general procedure, in a 50 mL round bottom flask, 2-bromothiazole-5-carbaldehyde (0.192 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the gray needle crystal were obtained upon recrystallization from water and methanol. (0.385 mg, 95%)

IR (KBr, cm⁻¹): ν = 441, 535, 589, 714, 751, 836, 937, 1012, 1072, 1148, 1235, 1279, 1322, 1358, 1372, 1395, 1468, 1533, 1651, 1681, 3151, 3444, 3418, 3464.

¹H NMR (600 MHz, d⁶-DMSO): δ = 7.33 (s, 1H, CH), 7.73 (s, 5H, NH), 8.05 (s, 1H, CH), 8.39 (s, 1H, CH), 11.77 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d⁶-DMSO): δ = 98.88 (s), 138.18 (s), 139.21 (s), 139.57 (s), 146.02 (s), 155.30 (s), 156.76 (s) ppm.

MS: m/z: 249.9 (C₅H₇BrN₅S⁺, cation); 157.0 (C₃H₄N₄O₄⁻, 3,5-dinitropyrazolate anion).

(E)-amino(2-((5-methylthiophen-2-yl)methylene)hydrazinyl)methaniminium 3,5-dinitropyrazol -1-ide (27)

Following the general procedure, in a 50 mL round bottom flask, 5-methylthiophene-2-carbaldehyde (0.126 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the light yellow needle crystals were obtained upon recrystallization from water. (0.296 g, 87%)

IR (KBr, cm⁻¹): v = 511, 751, 792, 836, 1014, 1223, 1356, 1440, 1476, 1537, 1648, 1678, 3397, 3504.

¹H NMR (600 MHz, d₆-DMSO): δ = 2.46 (s, 3H, CH), 6.84 (d, 1H, CH), 7.32 (d, 1H, CH), 7.34 (s, 1H, CH), 7.54 (s, 3H, NH), 8.31 (s, 1H, CH), 11.45 (s, 1H, NH) ppm,

¹³C NMR (150 MHz, d₆-DMSO): δ = 15.75 (s), 98.87 (s), 126.88 (s), 132.63 (s), 135.78 (s), 143.21 (s), 144.43 (s), 155.17 (s), 156.82 (s) ppm.

MS: m/z: 183.00 (C₈H₁₂N₃S⁺, cation); 157.00 (C₃H₄N₄O₄, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 38.93, N 28.89, H 3.86, found: C 38.46, N 28.64, H 4.15.

(E)-amino (2-(pyridin-2-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazol -1-ide (28)

Following the general procedure, in a 50 mL round bottom flask, nicotinaldehyde (0.107 g, 1 mmol) and ethanol (6 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the white powder was obtained upon recrystallization from water. (0.295 g, 92%)

IR (KBr, cm⁻¹): v = 750, 774, 838, 1016, 1145, 1322, 1352, 1443, 1487, 1540, 1590, 1624, 1695, 3375.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.34 (s, 1H, CH), 7.42 (t, 1H, CH), 7.87 (t, 1H, CH), 8.20 (s, 1H, CH), 8.26 (d, 1H, CH), 8.60 (d, 1H, CH) ppm.
$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta=98.87$ (s), 121.27 (s), 125.23 (s), 137.19 (s), 147.81 (s), 149.86 (s), 152.79 (s), 155.60 (s), 156.80 (s) ppm.

MS: m/z: 164.05 (C$_7$H$_{10}$N$_5^+$, cation); 157.00 (C$_3$H$_4$O$_4^-$, 3,5-dinitropyrazolate anion).


(E)-amino(2-(quinolin-3-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (29)

Following the general procedure, in a 50 mL round bottom flask, quinoline-3-carbaldehyde (0.157 g, 1 mmol) and water (10 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. The white powder was obtained after filtration. (0.223 g, 60%)

IR (KBr, cm$^{-1}$): v = 750, 833, 1013, 1192, 1325, 1353, 1440, 1483, 1535, 1634, 3006.

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.33$ (s, 1H, CH), 7.67 (t, 1H, CH), 7.82 (t, 1H, CH), 8.02 (d, 1H, CH), 8.07 (d, 1H, CH), 8.39 (s, 1H, CH), 8.67 (s, 1H, CH), 9.54 (s, 1H, CH), 11.75 (s, 1H, NH).

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 98.84$ (s), 127.15 (s), 127.61 (s), 127.90 (s), 129.04 (s), 129.44 (s), 131.09 (s), 136.14 (s), 145.46 (s), 148.45 (s), 149.27 (s), 155.61 (s), 156.87 (s).

MS: m/z: 214.1 (C$_{11}$H$_{12}$N$_5^+$, cation); 157.0 (C$_3$H$_4$O$_4^-$, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 45.29, N33.95, H 3.53, found: C 44.76, N 34.32, H 3.71.

(E)-amino(2-(ferrocene) hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (30)

Following the general procedure, in a 50 mL round bottom flask, ferrocenecarboxaldehyde (0.214 g, 1 mmol) and ethanol (5 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. After that the solvent was slowly removed under vacuum, and the red powder was obtained upon recrystallization from
water and methanol. (0.390 g, 91%).

**IR (KBr, cm⁻¹):** ν = 495, 750, 803, 837, 1009, 1099, 1162, 1317, 1350, 1437, 1474, 1534, 1629, 1678, 3273, 3356, 3442.

**¹H NMR (600 MHz, d₆-DMSO):** δ = 4.22 (s, 5H, CH), 4.45 (s, 2H, CH), 4.76 (s, 2H, CH), 7.32 (s, 1H, CH), 8.01 (s, 1H, CH) ppm.

**¹³C NMR (150 MHz, d₆-DMSO):** δ = 68.34 (s), 69.50 (s), 70.84 (s), 78.39 (s), 98.83 (s), 148.85 (s), 155.09 (s), 156.98 (s) ppm.

**MS:** m/z: 271.1 (C₁₂H₁₅FeN₄⁺, cation); 157.0 (C₃HN₄O₄⁻, 3,5-dinitropyrazolate anion).

**Elemental analysis:** calcd (%): C 42.05, N 26.16, H 3.74. found: C 41.43, N 26.35, H 3.96.
5. Condensation reaction with various ketones

Amino (2-(propan-2-ylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

Following the general procedure, in a 50 mL round bottom flask, Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) was dissolved in acetone (30 mL) and was added to the flask. The resulting mixture was stirred for 7 h at 55 °C. After that the solvent was slowly removed under vacuum, and yellow granular crystal was obtained upon recrystallization from acetone. (0.226 g, 83%)

IR (KBr, cm⁻¹): ν = 635, 749, 832, 1009, 1161, 1353, 1372, 1439, 1479, 1538, 1616, 1684, 3122, 3390.

¹H NMR (600 MHz, d₆-DMSO): δ = 1.89 (s, 3H, CH), 1.98 (s, 3H, CH), 7.32 (s, 1H, CH), 10.09 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 17.83 (s), 25.11 (s), 98.80 (s), 155.68 (s), 155.87 (s), 156.83 (s) ppm.

MS: m/z: 115.1 (C₄H₁₁N₅⁺, cation); 156.9 (C₃H₇N₄O₂⁻, 3,5-dinitropyrazolate anion).


(E)-amino(2-(1-phenylethylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

Following the general procedure, in a 50 mL round bottom flask, acetophenone (0.120 g, 1 mmol) and ethanol (5 mL) were placed. Aminoguanidinium 3, 5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white needle crystal was obtained upon recrystallization from water. (0.201 g, 87%)

IR (KBr, cm⁻¹): ν = 689, 748, 835, 1010, 1136, 1319, 1354, 1439, 1480, 1537, 1605, 1680, 3315.

¹H NMR (600 MHz, d₆-DMSO): δ = 2.30 (s, 3H, CH), 7.31 (s, 1H, CH), 7.43 (d, 3H, CH), 7.96 (t, 2H, CH), 10.43 (s, 1H, NH) ppm.
$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 14.50$ (s), 98.82 (s), 127.20 (s), 128.79 (s), 130.28 (s), 137.21 (s), 152.56 (s), 156.06 (s), 156.90 (s) ppm.

**MS: m/z:** 177.2(C$_9$H$_{10}$N$_4^+$, cation); 156.9 (C$_3$HN$_4$O$_4^-$, 3,5-dinitropyrazolate anion).

**Elemental analysis:** calcd (%): C 43.11, N 33.52, H 4.22, found: C 42.82, N 33.85, H 4.43.
6. Condensation reaction with simple aminoguanidinium salts containing various organic anions

\[ (E)\text{-}\text{amino(2-benzylidenehydrazinyl)methaniminium benzoate (31)} \]

\[
\text{Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Amino(hydrazinyl)methaniminium benzoate (0.196 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65}^\circ \text{C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.236 g, 83\%)}
\]

\(\text{IR (KBr, cm}^{-1}\): v = 453, 515, 674, 696, 719, 756, 851, 956, 1005, 1146, 1389, 1444, 1532, 1592, 1641, 1681, 3056, 3336, 3342, 3456.}

\(\text{\textit{H} NMR (600 MHz, d}_6\text{-DMSO)}\): \(\delta = 7.41\) (m, 6H, CH), 7.87 (d, 2H, CH), 8.01 (d, 2H, CH), 8.23 (s, 1H, CH) ppm.

\(\text{\textit{C} NMR (150 MHz, d}_6\text{-DMSO)}\): \(\delta = 127.75\) (s), 128.04 (s), 129.10 (s), 129.58 (s), 130.39 (s), 130.46 (s), 134.63 (s), 138.19 (s), 145.75 (s), 157.22 (s), 172.06 (s) ppm.

\(\text{Elemental analysis: calculated: } C 63.37, N 19.71, H 5.67, \text{ found: } C 63.12, N 20.04, H 5.83.\)

\[ (E)\text{-}\text{amino(2-benzylidenehydrazinyl)methaniminium 4-methoxybenzoate (32)} \]

\[
\text{Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Amino(hydrazinyl)methaniminium 4-methoxybenzoate (0.226 g, 1 mmol) dissolved in ethanol (50 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65}^\circ \text{C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.236 g, 75\%)}
\]

\(\text{IR (KBr, cm}^{-1}\): v = 446, 510, 613, 690, 754, 789, 848, 947, 1031, 1169, 1252, 1308, 1379, 1510, 1605, 1680.\)
\(^1\text{H NMR (600 MHz, d}_6\text{-DMSO)}: \delta = 3.79 (s, 3H, CH), 6.93 (d, 2H, CH), 7.43 (m, 3H, CH), 7.88 (d, 4H, CH), 7.94 (d, 4H, CH), 8.22 (s, 1H, CH) ppm.

\(^1\text{C NMR (150 MHz, d}_6\text{-DMSO)}: \delta = 55.63 (s), 113.44 (s), 127.74 (s), 129.09 (s), 130.38 (s), 131.43 (s), 134.63 (s), 145.69 (s), 157.21 (s), 161.75 (s), 171.00 (s) ppm.

**Elemental analysis:** calcd (%): C 55.55, N 20.73, H 5.97, found: C 55.23, N 20.94, H 5.83.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-methylbenzoate (33)

![Structure](image)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium 4-methylbenzoate (0.210 g, 1 mmol) dissolved in ethanol (40 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.227 g, 76%)

**IR (KBr, cm\(^{-1}\):** \(v = 448, 514, 611, 692, 760, 844, 948, 1007, 1153, 1230, 1362, 1507, 1624, 1679, 3392, 3454.

\(^1\text{H NMR (600 MHz, d}_6\text{-DMSO)}: \delta = 2.33 (s, 3H, CH), 7.19 (d, 2H, CH), 7.43 (m, 3H, CH), 7.87 (d, 2H, CH), 7.90 (d, 2H, CH), 8.24 (s, 1H, CH) ppm.

\(^1\text{C NMR (150 MHz, d}_6\text{-DMSO)}: \delta = 21.46 (s), 127.73 (s), 128.67 (s), 129.09 (s), 129.69 (s), 130.36 (s), 134.66 (s), 135.24 (s), 140.07 (s), 145.71 (s), 157.26 (s), 172.06 (s) ppm.

**Elemental analysis:** calcd (%): C 64.14, N 18.78, H 6.08, found: C 64.43, N 18.94, H 5.91.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-cyanobenzoate (34)

![Structure](image)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol
(10 mL) were placed. amino(hydrazinyl)methaniminium 4-cyanobenzoate (0.221 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.260 g, 84%)

IR (KBr, cm⁻¹): v = 442, 509, 544, 567, 687, 753, 780, 846, 869, 952, 1179, 1232, 1369, 1545, 1599, 1638, 1691, 2230, 3454.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.44 (m, 3H, CH), 7.86 (dd, 4H, CH), 8.11 (d, 2H, CH), 8.22 (s, 1H, CH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 112.70 (s), 119.41 (s), 127.85 (s), 129.12 (s), 130.18 (s), 130.58 (s), 132.26 (s), 134.36 (s), 142.93 (s), 146.12 (s), 156.82 (s), 170.37 (s) ppm.

Elemental analysis: calcd (%): C 62.13, N 22.64, H 4.89, found: C 61.87, N 22.94, H 5.01.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 3-nitrobenzoate (35)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium 3-nitrobenzoate (0.241 g, 1 mmol) was dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.204 g, 62%)

IR (KBr, cm⁻¹): v = 491, 694, 718, 760, 823, 904, 951, 999, 1075, 1102, 1157, 1226, 1270, 1347, 1373, 1522, 1619, 1684, 3076, 3469.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.44 (m, 3H, CH), 7.68 (t, 1H, CH), 7.90 (m, 2H, CH), 8.24 (s, 1H, CH), 8.28 (d, 1H, CH), 8.39 (d, CH), 8.72 (t, 1H, CH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 123.90 (s), 124.98 (s), 127.87 (s), 129.10 (s), 129.75 (s), 130.59 (s), 134.34 (s), 135.83 (s), 140.55 (s), 146.15 (s), 148.05 (s), 156.81 (s), 169.68 (s) ppm.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-chlorobenzoate (36)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium 4-chlorobenzoate (0.230 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.274 g, 86%)

IR (KBr, cm⁻¹): ν = 514, 691, 759, 839, 954, 1009, 1168, 1231, 1390, 1625, 1678, 3469.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.43 (m, 5H, CH), 7.88 (d, 2H, CH), 7.98 (d, 2H, CH), 8.22 (s, 1H, CH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 127.80 (s), 128.08 (s), 129.10 (s), 130.49 (s), 131.43 (s), 134.48 (s), 135.26 (s), 137.19 (s), 145.90 (s), 156.99 (s), 170.94 (s) ppm.

Elemental analysis: calcld (%): C 56.52, N 17.58, H 4.74, found: C 55.27, N 17.86, H 4.54.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-bromobenzoate (37)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium 4-bromobenzoate (0.274 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.264 g, 73%)

IR (KBr, cm⁻¹): ν = 442, 472, 512, 691, 759, 837, 954, 1007, 1065, 1170, 1231, 1375, 1585, 1625, 1678, 3469.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.44 (d, 3H, CH), 7.57 (d, 2H, CH), 7.90 (dd, 2H, CH), 8.22 (s, 1H, CH) ppm.
\[^{13}\text{C} \text{NMR (150 MHz, d}_6\text{-DMSO)}: \delta = 124.32 \text{ (s), 127.82 (s), 129.11 (s), 130.53 (s), 131.08 (s), 131.73 (s), 134.43 (s), 137.29 (s), 145.95 (s), 156.92 (s), 170.89 (s) ppm.}

**Elemental analysis:** calcd (%): C 49.60, N 15.43, H 4.16, found: C 49.37, N 15.65, H 4.34.

(E)-amino(2-benzylidenehydrazinyl)methaniminium formate (38)

\[
\begin{align*}
\text{HCOO} \\
\text{N} \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{N} \\
\text{N}
\end{align*}
\]

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Amino(hydrazinyl)methaniminium formate (0.120 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white powder was obtained upon recrystallization from water. (0.123 g, 59%)

**IR (KBr, cm\(^{-1}\)):** \(v = 454, 636, 693, 757, 844, 946, 1019, 1071, 1154, 1231, 1347, 1381, 1446, 1592, 1639, 1667, 1699, 3057.

\[^1\text{H} \text{NMR (600 MHz, d}_6\text{-DMSO)}: \delta = 7.41 \text{ (m, 3H, CH), 7.84 (m, 2H, CH), 8.13 (s, 1H, CH), 8.50 (s, 1H, CH) ppm.}

\[^{13}\text{C} \text{NMR (150 MHz, d}_6\text{-DMSO)}: \delta = 127.75 \text{ (s), 129.08 (s), 130.48 (s), 134.44 (s), 145.93 (s), 156.94 (s), 168.63 (s) ppm.}

**Elemental analysis:** calcd (%): C 51.92, N 26.91, H 5.81, found: C 52.23, N 26.64, H 5.67.

(E)-amino(2-benzylidenehydrazinyl)methaniminium acetate (39)

\[
\begin{align*}
\text{CH}_3\text{COO} \\
\text{N} \\
\text{NH}_2 \\
\text{NH}_2 \\
\text{N} \\
\text{N}
\end{align*}
\]

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Amino(hydrazinyl)methaniminium acetate (0.134 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white powder was obtained upon recrystallization from water. (0.184 g, 83%)
IR (KBr, cm⁻¹): ν = 458, 510, 525, 557, 613, 654, 690, 718, 759, 853, 870, 929, 1011, 1072, 1128, 1155, 1168, 1230, 1364, 1413, 1546, 1631, 1690, 3446.

¹H NMR (600 MHz, d₆-DMSO): δ = 1.81 (s, 3H, CH), 7.39 (d, 3H, CH), 7.80 (d, 2H, CH), 8.09 (s, 1H, CH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 24.33 (s), 127.48 (s), 129.01 (s), 129.92 (s), 135.17 (s), 145.16 (s), 157.93 (s), 176.41 (s) ppm.


(E)-amino(2-benzylidenehydrazinyl)methaniminium heptanoate (40)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium heptanoate (0.204 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.248 g, 85%)

IR (KBr, cm⁻¹): ν = 445, 509, 615, 690, 753, 965, 1072, 1122, 1161, 1231, 1319, 1402, 1448, 1470, 1597, 1624, 1692, 1713, 2869, 2914, 2925, 2951, 3483.

¹H NMR (600 MHz, d₆-DMSO): δ = 0.85 (t, 3H, CH), 1.26 (m, 6H, CH), 1.49(m, 2H, CH), 2.09 (t, 2H, CH), 7.40 (d, 3H, CH), 7.81 (d, 2H, CH), 8.11 (s, 1H, CH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 14.36 (s), 22.52 (s), 25.83 (s), 29.11 (s), 31.65 (s), 36.47 (s), 127.55 (s), 129.00 (s), 130.11 (s), 134.87 (s), 145.48 (s), 157.53 (s), 177.92 (s) ppm.


(E)-amino(2-benzylidenehydrazinyl)methaniminium benzenesulfonate (41)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol
(10 mL) were placed. amino(hydrazinyl)methaniminium benzenesulfonate (0.232 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.272 g, 85%)

**IR (KBr, cm⁻¹):** ν = 445, 511, 552, 609, 692, 730, 758, 946, 1015, 1033, 1072, 1127, 1154, 1231, 1446, 1598, 1631, 1679, 3015, 3171, 3329, 3423.

**¹H NMR (600 MHz, d₆-DMSO):** δ = 7.39 (m, 3H, CH), 7.44 (m, 3H, CH), 7.73 (m, 2H, CH), 7.87 (m, 2H, CH), 8.16 (s, 1H, CH), 11.65 (s, 1H, NH) ppm.

**¹³C NMR (150 MHz, d₆-DMSO):** δ = 125.89 (s), 128.06 (s), 128.44 (s), 129.11 (s), 129.62 (s), 130.95 (s), 133.81 (s), 147.42 (s), 155.65 (s) ppm.

**Elemental analysis:** calcd (%): C 52.49, N 17.49, H 5.03, found: C 53.82, N 17.56, H 4.86.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-methylbenzenesulfonate (42)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium benzenesulfonate (0.246 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.281 g, 84%)

**IR (KBr, cm⁻¹):** ν = 568, 634, 686, 759, 815, 947, 1011, 1034, 1126, 1207, 1447, 1490, 1598, 1631, 1688, 3019, 3170.

**¹H NMR (600 MHz, d₆-DMSO):** δ = 2.30 (s, 3H, CH), 7.19 (d, 2H, CH), 7.44 (t, 3H, CH), 7.60 (d, 2H, CH), 7.86 (m, 2H, CH), 8.14 (s, 1H, CH), 11.67 (s, 1H, NH) ppm.

**¹³C NMR (150 MHz, d₆-DMSO):** δ = 21.27 (s), 125.94 (s), 128.08 (s), 128.89 (s), 129.15 (s), 130.98 (s), 133.85 (s), 139.07 (s), 144.80 (s), 147.41 (s), 155.68 (s) ppm.

**Elemental analysis:** calcd (%): C 53.88, N 16.75, H 5.43, found: C 53.45, N 17.06, H 5.62.
(E)-amino(2-benzylidenehydrazinyl)methaniminium 3-aminobenzenesulfonate (43)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium 3-aminobenzenesulfonate (0.247 g, 1 mmol) dissolved in ethanol (55 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow powder was obtained upon recrystallization from water and methanol. (0.265 g, 79%)  
IR (KBr, cm⁻¹): v = 562, 618, 690, 705, 756, 784, 845, 882, 951, 998, 1035, 1073, 1107, 1145, 1165, 1214, 1480, 1563, 1624, 1676, 3175, 3368, 3441.

¹H NMR (600 MHz, d₆-DMSO): δ = 5.24 (s, 2H, CH), 6.57 (d, 1H, CH), 6.85 (d, 1H, CH), 7.00 (t, 2H, CH), 7.44 (s, 3H, CH), 7.86 (s, 4H, NH), 8.13 (s, 1H, CH), 11.73 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 111.66 (s), 113.42 (s), 115.10 (s), 128.07 (s), 128.80 (s), 129.16 (s), 130.98 (s), 133.85 (s), 147.33 (s), 147.78 (s), 148.80 (s), 155.70 (s) ppm.
Elemental analysis: calcd (%): C 50.14, N 20.88, H 5.11, found: C 50.46, N 21.05, H 4.95.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-nitrobenzenesulfonate (44)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium 4-nitrobenzenesulfonate (0.277 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.237 g, 65%)  
IR (KBr, cm⁻¹): v = 472, 555, 640, 694, 746, 764, 846, 955, 1003, 1029, 1122, 1194, 1350, 1448, 1493, 1525, 1561, 1626, 1680, 3241, 3319, 3392.
$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.44$ (s, 3H, CH), 7.86 (s, 2H, CH), 7.92 (d, 2H, CH), 8.16 (s, 1H, CH), 8.23 (d, 2H, CH), 11.48 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 123.95$ (s), 127.44 (s), 128.10 (s), 129.12 (s), 130.98 (s), 133.81 (s), 147.65 (s), 147.99 (s), 153.91 (s), 155.61 (s) ppm.

**Elemental analysis:** calcld (%): C 46.02, N 19.17, H 4.14, found: C 46.42, N 18.89, H 4.35.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-amino-3,5-dinitropyrazol -1-ide (45)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 4-amino-3,5-dinitropyrazolate (0.247 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow powder was obtained upon recrystallization from water and methanol. (0.233 g, 83%)

IR (KBr, cm$^{-1}$): v = 484, 694, 840, 966, 1073, 1145, 1234, 1262, 1324, 1380, 1458, 1552, 1575, 1628, 1682, 3114, 3385, 3482.

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 6.68$ (s, 2H, NH), 7.44 (t, 3H, CH), 7.70 (s, 3H, NH), 7.87 (m, 2H, CH), 8.24 (s, 1H, CH), 11.61 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 128.08$ (s), 129.15 (s), 131.00 (s), 132.32 (s), 133.85 (s), 143.93 (s), 147.78 (s), 155.56 (s) ppm.

**MS:** m/z: 163.1(C$_8$H$_{11}$N$_4$+, cation); 172.0(C$_3$H$_2$N$_2$O$_4$-, 4-amino-3,5-dinitropyrazolate anion).

**Elemental analysis:** calcld (%): C 39.41, N 37.60, H 3.91, found: C 38.92, N 37.92, H 4.16.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 4,5-dicyanoimidazol -1-ide (46)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 4,5-dicyanoimidazolate (0.192 g, 1 mmol) dissolved in ethanol (20 mL) and
was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the colorless bulk crystal was obtained upon recrystallization from water and methanol. (0.252 g, 90%)

IR (KBr, cm\(^{-1}\)): \(\nu = 642, 661, 693, 760, 1008, 1072, 1108, 1141, 1230, 1304, 1447, 1474, 1537, 1629, 1678, 2225, 3359, 3466,\)

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 7.34\) (s, 1H, CH), 7.45 (t, 3H, CH), 7.64 (s, 3H, NH), 7.85 (m, 2H, CH), 8.17 (s, 1H, CH) ppm.

\(^{13}\)C NMR (150 MHz, d\(_6\)-DMSO): \(\delta = 117.25\) (s), 117.94 (s), 128.08 (s), 129.13 (s), 130.99 (s), 133.84 (s), 147.69 (s), 149.13 (s), 155.60 (s) ppm.

MS: \(m/z: 163.1(C_8H_{11}N_4^+, \text{cation}); 117.0 (C_3HN_4O_4^-, 2,4-dicyanoimidazolate anion).\)

Elemental analysis: calcd (%): C 55.71, N 39.98, H 4.32, found: C 55.26, N 40.26, H 4.08.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 2,4-dinitroimidazol -1-ide (47)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 2,4-dinitroimidazolate (0.232 g, 1 mmol) dissolved in ethanol (30 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the light yellow needle crystal was obtained upon recrystallization from water and methanol. (0.275 g, 86%)

IR (KBr, cm\(^{-1}\)): \(\nu = 661, 761, 838, 1228, 1296, 1356, 1436, 1471, 1496, 1515, 1617, 1679, 3259, 3435.\)

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 7.44\) (t, 3H, CH), 7.65 (s, 3H, NH), 7.81 (s, 1H, CH), 7.89 (m, 2H, CH), 8.18 (s, 1H, CH), 11.46 (s, 1H, NH) ppm.

\(^{13}\)C NMR (150 MHz, d\(_6\)-DMSO): \(\delta = 128.07\) (s), 129.12 (s), 130.68 (s), 130.98 (s), 133.83 (s), 147.35 (s), 147.72 (s), 154.53 (s), 155.56 (s) ppm.

MS: \(m/z: 163.1(C_8H_{11}N_4^+, \text{cation}); 157.0 (C_3HN_4O_4^-, 2,4-dinitroimidazolate anion).\)

Elemental analysis: calcd (%): C 41.25, N 34.99, H 3.78, found: C 40.76, N 35.23, H 3.52.
(E)-amino(2-benzylidenehydrazinyl)methaniminium 3,5-dibromo-1,2,4-triazol -1-ide (48)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dibromo-1,2,4-triazolate (0.301 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the colorless crystal was obtained upon recrystallization from water and methanol. (0.317 g, 82%)

IR (KBr, cm\(^{-1}\)): \(v = 465, 512, 694, 761, 954, 992, 1151, 1237, 1421, 1447, 1490, 1627, 1657, 1681, 3062, 3433\).

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 7.45 \text{ (t, 3H, CH)}, 7.85 \text{ (m, 2H, CH)}, 8.20 \text{ (s, 1H, CH)} \) ppm.

\(^{13}\)C NMR (150 MHz, d\(_6\)-DMSO): \(\delta = 128.02 \text{ (s)}, 129.16 \text{ (s)}, 130.91 \text{ (s)}, 133.97 \text{ (s)}, 135.85 \text{ (s)}, 147.36 \text{ (s)}, 155.78 \text{ (s)} \) ppm.

MS: \(m/z: 163.1\text{(C}_8\text{H}_{11}\text{N}_4^+\text{, cation)}; 225.8\text{(C}_3\text{BrN}_3^+, \text{3,5-dibromo-1,2,4-triazolate anion)}.\)

Elemental analysis: calcd (%): C 30.87, N 25.20, H 2.85, found: C 30.32, N 25.54, H 2.46.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 3,5-dinitro-1,2,4-triazol -1-ide (49)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dinitro-1,2,4-triazolate (0.233 g, 1 mmol) dissolved in ethanol (50 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow needle crystal was obtained upon recrystallization from water and methanol. (0.250 g, 78%)

IR (KBr, cm\(^{-1}\)): \(v = 448, 515, 546, 596, 697, 763, 844, 964, 1122, 1146, 1236, 1302, 1352, 1390, 1488, 1549, 1620, 1677, 3143, 3375, 3499\).

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 7.43 \text{ (s, 3H, CH)}, 7.64 \text{ (s, 3H, NH)}, 7.86 \text{ (m, 2H, CH)}, 8.18 \text{ (s, 1H, CH)},\)
11.45 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 128.06$ (s), 129.09 (s), 130.96 (s), 133.81 (s), 147.73 (s), 155.56 (s), 163.34 (s) ppm.

**MS:** m/z: 163.1(C$_8$H$_{11}$N$_4^+$, cation); 158.0(C$_2$N$_3$O$_4^-$, 3,5-dinitro-1,2,4-triazolate anion)

**Elemental analysis:** calcd (%): C 37.39, N 39.24, H 3.45, found: C 36.94, N 39.82, H 3.23.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-chlorotetrazol-1-ide (50)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and water (10 mL) were placed. Aminoguanidinium 5-chlorotetrazolate (0.181 g, 1 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water. (0.234 g, 88%)

**IR (KBr, cm$^{-1}$):** v = 687, 753, 948, 1143, 1230, 1348, 1447, 1626, 1686, 3104.

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.45$ (m, 3H, CH), 7.86 (dd, 2H, CH), 8.19 (s, 1H, CH), 11.60 (s, 1H, NH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 128.10$ (s), 129.15 (s), 131.01 (s), 133.82 (s), 147.69 (s), 150.88 (s), 155.62 (s) ppm.

**MS:** m/z: 163.0 (C$_8$H$_{11}$N$_4^+$, cation); 103.0 (CClN$_4^-$, 5-chlorotetrazolate anion).

**Elemental analysis:** calcd (%): C 40.53, N 42.02, H 4.16, found: C 40.21, N 42.27, H 3.88.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-nitrotetrazol-1-ide (51)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 5-nitrotetrazolate (0.189 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly
removed under vacuum, and the colorless plate crystal was obtained upon recrystallization from water and methanol. (0.244 g, 88%)

IR (KBr, cm⁻¹): ν = 695, 758, 838, 1147, 1319, 1418, 1446, 1536, 1632, 1657, 1682, 3216, 3437.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.44 (t, 3H, CH), 7.64 (s, 3H, NH), 7.87 (m, 2H, CH), 8.18 (s, 1H, CH), 11.45 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 128.09 (s), 129.13 (s), 131.01 (s), 133.81 (s), 147.75 (s), 155.56 (s), 169.17 (s) ppm.

MS: m/z: 163.00 (C₈H₁₁N₄⁺, cation); 114.00 (CN₅O₂⁻, 5-nitrotetrazolate anion).

Elemental analysis: calcd (%): C 38.99, N 45.47, H 4.00, found: C 38.47, N 45.32, H 3.83.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-(trifluoromethyl) tetrazol-1-ide (52)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 5-(trifluoromethyl) tetrazolate (0.212 g, 1 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. After that the solvent was slowly removed under vacuum, and the colorless plate crystal was obtained upon recrystallization from water. (0.240 g, 80%)

IR (KBr, cm⁻¹): ν = 509, 688, 750, 948, 1038, 1127, 1169, 1230, 1449, 1505, 1629, 1682, 3172, 3470.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.44 (t, 3H, CH), 7.85 (m, 1H, CH), 8.19 (s, 1H, CH), 11.54 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 120.40 (s), 122.17 (s), 123.95 (s), 125.73 (s), 128.08 (s), 129.11 (s), 130.99 (s), 133.80 (s), 147.72 (s), 153.64 (s), 153.87 (s), 154.10 (s), 154.32 (s), 155.62 (s) ppm.

MS: m/z: 163.00 (C₈H₁₁N₄⁺, cation); 136.9 (C₂F₃N₄⁺, 5-(trifluoromethyl) tetrazolate anion).

Elemental analysis: calcd (%): C 40.00, N 37.32, H 3.69, found: C 39.67, N 37.54, H 3.84.

(E)-amino(2-benzylidenehydrazinyl)methaniminium(Z)-5-(nitroimino)-4,5-dihydrotetrazol-1-ide (53)
Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and water (10 mL) were placed. Aminoguanidinium 5-nitroimino-tetrazolate (0.204 g, 1 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. And the white powder was obtained after filtration. (0.280 g, 96%)

IR (KBr, cm⁻¹): ν = 454, 509, 669, 691, 753, 1072, 1102, 1147, 1235, 1324, 1431, 1542, 1611, 1691, 3091, 3328, 3471.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.44 (s, 3H, CH), 7.73 (s, 3H, NH), 7.87 (s, 2H, CH), 8.25 (s, 1H, CH), 11.56 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 128.09 (s), 129.15 (s), 131.01 (s), 133.85 (s), 147.83 (s), 155.60 (s), 158.31 (s) ppm.

MS: m/z: 163.1(C₈H₁₁N₄⁺, cation); 129.9(CHN₆O₂⁻, 5-(nitrimino)-tetrazolate);

Elemental analysis: calcd (%): C 36.99, N 47.93, H 4.14, found: C 36.32, N 47.38, H 3.98.

(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-nitro-2H-tetrazol-2-olatate (54)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 5-nitrotetrazolate-2N-oxide (0.205 g, 1 mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow needle crystal was obtained upon recrystallization from water and methanol. (0.264 g, 90%)

IR (KBr, cm⁻¹): ν = 449, 521, 694, 760, 784, 841, 949, 1005, 1099, 1151, 1228, 1316, 1426, 1465, 1550, 1615, 1675, 3098, 3199, 3251, 3327, 3444.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.45 (d, 3H, CH), 7.65 (s, 3H, NH), 7.86 (d, 2H, CH), 8.18 (s, 1H, CH), 11.44 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 128.09 (s), 129.12 (s), 130.99 (s), 133.82 (s), 147.74 (s), 155.57 (s), 157.70 (s) ppm.

MS: m/z: 163.1(C₈H₁₁N₄⁺, cation); 129.9(CHN₆O₂⁻, 5-nitrotetrazolate-2N-oxide).
**Elemental analysis:** calcd (%): C 36.86, N 42.99, H 3.78, found: C 37.46, N 42.67, H 3.59.

*(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-nitrobenzo-1,2,3-triazol -1-ide (55)*

![Chemical structure](image)

Following the general procedure, in a 50 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and water (20 mL) were placed. Aminoguanidinium 5-nitrobenzo-1, 2, 3-triazolate (0.238 g, 1mmol) dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. And the light brown powder was obtained after filtration. (0.183 g, 56%)

**IR (KBr, cm⁻¹):** v = 694, 738, 759, 800, 941, 1056, 1128, 1232, 1307, 1334, 1400, 1448, 1508, 1598, 1629, 1680, 3359.

**1H NMR (600 MHz, d₆-DMSO):** δ = 7.43 (d, 3H, CH), 7.85 (m, 4H, CH) 7.94 (m, 1H, CH), 8.23 (s, 1H, CH), 8.74 (s, 1H, NH) ppm.

**13C NMR (150 MHz, d₆-DMSO):** δ = 114.23 (s), 116.35 (s), 116.47 (s), 127.92 (s), 129.09 (s), 130.62 (s), 134.33 (s), 142.10 (s), 143.86 (s), 147.08 (s), 147.19 (s), 156.42 (s) ppm.

**MS:** m/z: 163.1 ([C₈H₁₁N₄]+); 163.0 ([C₆H₃N₄O₂]⁻).

**Elemental analysis:** calcd (%): C 51.53, N 34.34, H 4.32, found: C 51.81, N 34.01, H 4.08.

*(E)-amino(2-benzylidenehydrazinyl)methaniminium furan-2-carboxylate (56)*

![Chemical structure](image)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium furan-2-carboxylate (0.186 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.195 g, 71%)

**IR (KBr, cm⁻¹):** v = 448, 513, 590, 667, 695, 757, 798, 883, 955, 1002, 1118, 1160, 1186, 1229, 1364, 1393, 1483, 1559, 1622, 1684, 3046, 3429.
$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 6.49$ (m, 1H, CH), 6.85 (d, 1H, CH), 7.42 (m, 3H, CH), 7.65 (s, 1H, CH), 7.87 (m, 2H, CH), 8.19 (s, 1H, CH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 111.51$ (s), 113.27 (s), 127.81 (s), 129.35 (s), 130.66 (s), 134.37 (s), 143.90 (s), 145.98 (s), 152.12 (s), 156.87 (s), 164.87 (s) ppm.

**Elemental analysis:** calcd (%): C 59.93, N 20.43, H 5.14, found: C 60.24, N 20.76, H 4.93.

**(E)-amino(2-benzylidenehydrazinyl)methaniminium thiophene-3-carboxylate (57)**

![Chemical Structure](image)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium thiophene-3-carboxylate (0.202 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.212 g, 73%)

**IR (KBr, cm$^{-1}$):** v = 513, 625, 692, 757, 833, 952, 1009, 1072, 1125, 1151, 1233, 1351, 1417, 1447, 1535, 1598, 1631, 1686, 3436.

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.42$ (s, 5H, CH), 7.85 (d, 2H, CH), 7.92 (s, 1H, CH), 8.20 (s, 1H, CH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 125.48$ (s), 127.72 (s), 129.10 (s), 129.31 (s), 129.39 (s), 130.36 (s), 134.65 (s), 142.76 (s), 145.72 (s), 157.24 (s), 168.79 (s) ppm.

**Elemental analysis calcd (%)**: C 53.78, N 19.30, H 4.86, found: C 54.02, N 18.89, H 4.94.
7. Scalable experiments for the preparation of organic salts containing organic anions

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (1.061 g, 10 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaninium benzenesulfonate (2.461 g, 10 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (2.840 g, 85%)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (1.061 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 4,5-dicyanoimidazolate (1.921 g, 1 mmol) dissolved in ethanol (40 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the colorless bulk crystal were obtained upon recrystallization from water and methanol. (2.465 g, 88%)
8. Condensation reaction for complex pharmaceutical salts

(E)-amino(2-benzylidenehydrazinyl)methaniminium 1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine-3-carboxylate (58)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Amino(hydrazinyl)methaniminium1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine-3-carboxylate (0.306 g, 1 mmol) dissolved in ethanol (60 mL) was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65°C. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.339 g, 86%)

IR (KBr, cm⁻¹): \( \nu = 654, 692, 747, 817, 948, 1130, 1158, 1256, 1346, 1386, 1442, 1583, 1629, 1685, 3356. \)

\(^1\)H NMR (600 MHz, d₆-DMSO): \( \delta = 1.42 \) (t, 3H, CH), 2.70 (s, 3H, CH), 4.62 (m, 2H, CH), 7.27 (t, 1H, CH), 7.34 (t, 2H, CH), 7.56 (d, 1H, CH), 7.69 (d, 2H, CH), 8.02 (s, 1H, CH), 8.59 (d, 1H, CH), 9.11 (s, 1H, CH) ppm.

\(^13\)C NMR (150 MHz, d₆-DMSO): \( \delta = 15.47 \) (s), 25.47 (s), 47.04 (s), 110.49 (s), 119.06 (s), 122.77 (s), 126.80 (s), 128.43 (s), 128.83 (s), 136.11 (s), 137.07 (s), 143.95 (s), 148.79 (s), 149.71 (s), 160.51 (s), 164.78 (s), 166.56 (s), 178.16 (s) ppm.

Elemental analysis: calcd (%): C 60.90, N 21.31, H 5.62, found: C 61.32, N 20.98, H 5.32.

(E)-amino(2-benzylidenehydrazinyl)methaniminium (R)-2-(6-methoxynaphthalen-2-yl)propanoate (59)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. Amino(hydrazinyl)methaniminium (R)-2-(6-methoxynaphthalen-2-yl)propanoate (0.304 g, 1 mmol) dissolved in ethanol (60 mL) was added dropwise to the flask. The resulting mixture was refluxed for 7 h. After that the solvent was slowly removed under vacuum, and the light green solid was obtained upon recrystallization from water and methanol. (0.342 g, 87%)

IR (KBr, cm⁻¹): \( \nu = 472, 515, 614, 697, 707, 762, 813, 853, 891, 926, 1010, 1029, 1063, 1075, 1120, 1162, 1176, \ldots \)
1H NMR (600 MHz, d6-DMSO): $\delta = 1.43$ (d, 3H, CH), 3.69 (m, 1H, CH), 3.86 (s, 3H, CH), 7.14 (d, 1H, CH), 7.27 (s, 1H, CH), 7.40 (s, 2H, CH), 7.47 (d, 1H, CH), 7.71 (s, 1H, CH), 7.73 (d, 1H, CH), 7.79 (t, 3H, CH), 8.06 (s, 1H, CH) ppm.

13C NMR (150 MHz, d6-DMSO): $\delta =$ 19.57 (s), 46.82 (s), 55.59 (s), 106.16 (s), 118.89 (s), 125.79 (s), 126.93 (s), 127.30 (s), 127.62 (s), 128.93 (s), 129.05 (s), 129.49 (s), 130.20 (s), 133.48 (s), 134.76 (s), 138.61 (s), 145.42 (s), 157.35 (s), 178.04 (s) ppm.


(E)-amino(2-benzyldenehydrazinyl)methaniminium2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl) acetate (60)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (0.431 g, 1 mmol) dissolved in ethanol (60 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the light green solid was obtained upon recrystallization from water and methanol. (0.389 g, 75%)

IR (KBr, cm$^{-1}$): $\nu =$ 639, 691, 755, 797, 831, 857, 920, 948, 995, 1036, 1072, 1091, 1157, 1178, 1194, 1214, 1231, 1276, 1286, 1335, 1359, 1370, 1383, 1448, 1459, 1478, 1567, 1597, 1638, 1672.

1H NMR (600 MHz, d6-DMSO): $\delta =$ 2.22 (s, 3H, CH), 3.49 (s, 2H, CH), 3.75 (s, 3H, CH), 6.70 (d, 1H, CH), 6.96 (d, 1H, CH), 7.10 (s, 1H, CH), 7.40 (s, 3H, CH), 7.64 (d, 2H, CH), 7.67 (d, 2H, CH), 7.77 (d, 2H, CH), 8.05 (s, 1H, CH) ppm.

13C NMR (150 MHz, d6-DMSO): $\delta =$ 13.81 (s), 32.79 (s), 55.83 (s), 102.70 (s), 111.45 (s), 114.91 (s), 116.55 (s), 127.51 (s), 129.04 (s), 129.48 (s), 130.07 (s), 130.81 (s), 131.51 (s), 131.90 (s), 134.61 (s), 134.93 (s), 137.89 (s), 145.40 (s), 155.95 (s), 157.61 (s), 168.30 (s), 175.28 (s) ppm.

(E)-amino(2-benzylidenehydrazinyl)methaniminium(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (61)

Following the general procedure, in a 100 mL round bottom flask, benzaldehyde (0.106 g, 1 mmol) and ethanol (10 mL) were placed. amino(hydrazinyl)methaniminium(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (0.306 g, 1 mmol) dissolved in ethanol (60 mL) was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the white crystal was obtained upon recrystallization from water and methanol. (0.296 g, 75%)

IR (KBr, cm⁻¹): v = 512, 692, 758, 791, 952, 1039, 1151, 1168, 1193, 1231, 1449, 1634, 1685, 1732, 3166, 3266, 3335.

¹H NMR (600 MHz, d₆-DMSO): δ = 0.76 (s, 3H, CH), 1.05 (s, 3H, CH), 1.31 (t, 1H, CH), 1.40 (t, 1H, CH), 1.85 (t, 2H, CH), 1.97 (s, 1H, CH), 2.25 (d, 1H, CH), 2.64 (t, 1H, CH), 3.04 (d, 1H, CH), 3.37 (s, 1H, CH), 7.45 (s, 3H, CH), 7.86 (s, 2H, CH), 8.14 (s, 1H, CH), 11.77 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 19.97 (s), 20.41 (s), 24.61 (s), 26.85 (s), 42.58 (s), 42.70 (s), 47.46 (s), 47.65 (s), 58.56 (s), 128.03 (s), 129.16 (s), 130.94 (s), 133.90 (s), 147.27 (s), 155.69 (s), 216.34 (s) ppm.

Elemental analysis: calcd (%): C 54.80, N 14.20, H 6.64, found: C 54.52, N 13.89, H 6.85.
9. Condensation reaction for organic salts containing various polyanions

((2E,2′E)-2,2′-(ethane-1,2-diyldene)bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium)5-nitrotetrazol-1-ide (68)

Following the general procedure, in a 50 mL round bottom flask, glyoxal aqueous solution (0.058 g, 1 mmol) and water (10 mL) were placed. Aminoguanidinium 5- nitrotetrazolate (0.378 g, 2 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. After that the solvent was slowly removed under vacuum, and the white needle crystal was obtained upon recrystallization from water. (0.340 g, 85%)

IR (KBr, cm⁻¹): ν = 500, 842, 944, 1035, 1061, 1143, 1297, 1321, 1448, 1474, 1535, 1614, 1697, 2844, 3127, 3341, 3448.

¹HNMR (600 MHz, d₆-DMSO): δ = 7.81 (s, 2H, CH), 11.82 (s, 2H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 144.71 (s, 2C), 155.34 (s, 2C), 169.13 (s, 2C) ppm.

MS: m/z: 171.1([C₆H₁₂N₈]⁺, cation); 114.0 (CN₅O₂⁻, 5- nitrotetrazolate anion).


((2E,2′E)-2,2′-(ethane-1,2-diyldene)bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium)

(E)-5-(nitroimino)-4,5-dihydrotetrazol-1-ide (Z)-5-(nitroimino)-4,5-dihydrotetrazol-1-ide (69)

Following the general procedure, in a 50 mL round bottom flask, glyoxal aqueous solution (0.058 g, 1 mmol) and water (10 mL) were placed. Aminoguanidinium 5- nitroimino-tetrazolate (0.408 g, 2 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 ºC. Cooled to room temperature, and the white powder was obtained after filtration. (0.344 g, 80%)

IR (KBr, cm⁻¹): ν = 473, 665, 746, 769, 949, 1077, 1144, 1247, 1329, 1439, 1459, 1542, 1602, 1645, 1698, 3094, 3343, 3467.
1H NMR (600 MHz, d$_6$-DMSO): δ = 7.86 (s, 2H, CH), 11.93 (s, 2H, NH) ppm.

13C NMR (150 MHz, d$_6$-DMSO): δ = 144.77 (s, 2C), 155.42 (s, 2C), 158.17 (s, 2C) ppm.

MS: m/z: 171.1 (1/2[C$_4$H$_{12}$N$_8^{2+}$, cation]); 128.9 (CHN$_3$O$_2^-$, 5-nitrimino-tetrazolate anion)


((2E,2'E)-2,2'-(ethane-1,2-diylidene)bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium) 5-nitro-2H-tetrazol-2-olate (70)

Following the general procedure, in a 50 mL round bottom flask, glyoxal aqueous solution (0.058 g, 1mmol) and water (10 mL) were placed. Aminoguanidinium 5-nitrotetrazolate-2N-oxide (0.410 g, 2 mmol) dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow needle crystal was obtained upon recrystallization from water. (0.372 g, 86%)

IR (KBr, cm$^{-1}$): v = 492, 618, 637, 791, 847, 946, 998, 1057, 1079, 1144, 1229, 1322, 1438, 1475, 1539, 1557, 1615, 1694, 2882, 2989, 3117, 3328, 3438, 3551.

1H NMR(600 MHz, d$_6$-DMSO): δ=7.78 (s, 2H, CH), 11.82 (s, 2H, NH) ppm.

13C NMR (150 MHz, d$_6$-DMSO): δ = 144.71 (s, 2C), 155.33 (s, 2C), 157.73 (s, 2C) ppm.

MS: m/z: 171.1 (1/2[C$_4$H$_{12}$N$_8^{2+}$, cation]); 129.9 (CN$_3$O$_3^-$, 5-nitrotetrazolate-2N-oxide anion)

Elemental analysis: calcd (%): C 16.67, N 58.32, H 2.80, found: C 16.15, N 58.73, H 3.10.

((2E,2'E)-2,2'-(ethane-1,2-diylidene)bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium)nitrate (71)

Following the general procedure, in a 50 mL round bottom flask, glyoxal aqueous solution (0.058 g, 1mmol) and methanol (10 mL) were placed. Aminoguanidinium nitrate (0.274 g, 2 mmol) dissolved in water (20 mL) and was
added dropwise to the flask. The resulting mixture was refluxed for 5 h at room temperature. The colorless crystal was obtained after filtration. (0.225 g, 76%)

**IR (KBr, cm⁻¹):** ν = 470, 593, 675, 726, 924, 1051, 1150, 1384, 1460, 1605, 1680, 2913, 3005, 3181, 3323, 3439.

**¹H NMR (600 MHz, d₆-DMSO):** δ = 7.79 (d, 2H, CH) ppm.

**¹³C NMR (150 MHz, d₆-DMSO):** δ = 144.63 (s), 155.32 (s) ppm.

**Elemental analysis:** calcd (%): C 16.67, N 58.32, H 2.80, found: C 16.15, N 58.73, H 3.10.

((2E,2'E)-2,2'-((1,4-phenylenebis(methanylylidene))bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium) 5-nitrotetrazol -1-ide (72)

![Chemical Structure Image]

Following the general procedure, in a 50 mL round bottom flask, terephthalaldehyde (0.134 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 5-nitrotetrazolate (0.378 g, 2 mmol) dissolved in water (30 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C and cooled to room temperature. After filtration, the yellow granular crystal was obtained upon recrystallization from water and DMSO. (0.362 g, 76%)

**IR (KBr, cm⁻¹):** ν = 437, 544, 838, 1147, 1229, 1319, 1418, 1447, 1537, 1626, 1659, 1683, 2923, 3206, 3427.

**¹H NMR (600 MHz, d₆-DMSO):** δ = 7.70 (s, 6H, NH), 7.93 (s, 4H, CH), 8.20 (s, 2H, CH), 11.54 (s, 2H, NH) ppm.

**¹³C NMR (150 MHz, d₆-DMSO):** δ = 128.32 (s, 4C), 135.61 (s, 2C), 147.01 (s, 2C), 155.56 (s, 2C), 169.19 (s, 2C) ppm.

**MS:** m/z: 124.3(1/2[C₁₀H₁₆N₈²⁺, cation]; (CN₅O₂⁻, 5-nitrotetrazolate anion).

**Elemental analysis:** calcd (%): C 30.26, N 52.92, H 3.39, found: C 29.83, N 52.58, H 3.17.

((2E,2'E)-2,2'-((1,4-phenylenebis(methanylylidene))bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium) 5-((trifluoromethyl)tetrazol -1-ide (73)

48
Following the general procedure, in a 50 mL round bottom flask, terephthalaldehyde (0.134 g, 1 mmol) and ethanol (5 mL) were placed. Aminoguanidinium 5-(trifluoromethyl) tetrazolate (0.424 g, 2 mmol) dissolved in water (30 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C and cooled to room temperature. The white powder was obtained after filtration. (0.376 g, 72%)

IR (KBr, cm⁻¹): ν = 690, 748, 879, 948, 1036, 1144, 1180, 1229, 1504, 1632, 1679, 3126, 3467.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.94 (s, 4H, CH), 8.20 (s, 2H, CH), 11.59 (s, 2H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 120.43 (s), 122.21 (s), 123.98 (s), 125.76 (s), 128.33 (s), 135.62 (s), 146.98 (s), 153.59 (s), 153.82 (s), 154.04 (s), 154.27 (s), 155.58 (s) ppm.

MS: m/z: 124.3 (1/2[C₁₀H₁₆N₈]²⁺, cation); 136.9 (C₅F₅N₄ ᵅ⁻, 5-(trifluoromethyl) tetrazolate anion).

Elemental analysis: calcd (%): C 32.19, N 42.90, H 3.09, found: C 32.53, N 42.68, H 3.26.

((2E,2'E)-2,2'(1,4-phenylenebis(methanylylidene))bis(hydrizin-1-yl-2-ylidene))bis(aminomethaniminium) 4, 5-dicyanoimidazol -1-ide (74)

Following the general procedure, in a 50 mL round bottom flask, terephthalaldehyde (0.134 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 4,5-dicyanoimidazolate (0.384 g, 2 mmol) dissolved in water (30 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C and cooled to room temperature, the white powder was obtained after filtration. (0.400 g, 83%)

IR (KBr, cm⁻¹): ν = 423, 523, 640, 664, 831, 867, 969, 1110, 1222, 1295, 1416, 1449, 1491, 1626, 1687, 2222, 3337, 3489.

¹H NMR (600 MHz, d₆-DMSO): δ = 7.33 (s, 2H, CH), 7.93 (s, 4H, CH), 8.19V(s, 2H, CH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 117.25 (s), 118.09 (s), 128.30 (s), 135.64 (s), 146.92 (s), 149.14 (s), 155.63 (s) ppm.

MS: m/z: 124.3 (1/2[C₁₀H₁₆N₈]²⁺, cation); 117.0 (C₅H₄N₄ ᵅ⁻, 4,5-dicyanoimidazolate anion).
Elemental analysis: calcd (%): C 49.79, N 46.45, H 3.76, found: C 49.43, N 46.89, H 3.22.

\((2E,2'E)-2,2'-(1,4-phenylenebis(methanylylidene))bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium)\)
3,5-dibromo-1,2,4-triazol -1-ide (75)

Following the general procedure, in a 50 mL round bottom flask, terephthalaldehyde (0.134 g, 1 mmol) and ethanol (10 mL) were placed. Aminoguanidinium 3,5-dibromo-1,2,4-triazolate (0.602 g, 2 mmol) dissolved in water (30 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C and cooled to room temperature. After filtration, the white powder was obtained upon recrystallization from water and DMSO. (0.522 g, 75%)

IR (KBr, cm\(^{-1}\)): \(v = 432, 825, 945, 998, 1160, 1251, 1429, 1483, 1628, 1682, 3031, 3454\).

\(^1\)H NMR (600 MHz, \textit{d}_6-DMSO): \(\delta = 7.78\) (s, 6H, NH), \(7.93\) (s, 4H, CH), \(8.22\) (s, 2H, CH), ppm.

\(^13\)C NMR (150 MHz, \textit{d}_6-DMSO): \(\delta = 128.25\) (s), \(135.84\) (s), 135.68 (s), 146.59 (s), 155.83 (s) ppm.

MS: \(m/z: 124.3\) (1/2[C\(_{10}\)H\(_{16}\)N\(_{8}\)\(^{2+}\), cation]); 225.8 (C\(_2\)Br\(_2\)N\(_3\); 3,5-dibromo-1,2,4-triazolate anion).

Elemental analysis: calcd (%): C 24.02, N 28.01, H 2.30, found: C 23.54, N 28.37, H 2.52.

\((2E,2'E)-2,2'-(pyridine-2,6-diylbis(methanylylidene))bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium)\)
4,5-dicyanoimidazol -1-ide (76)

Following the general procedure, in a 50 mL round bottom flask, pyridine-2, 6-dicarbaldehyde (0.135 g, 1 mmol) and methanol (20 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.464 g, 2 mmol) dissolved in methanol (20 mL) was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow crystal was obtained upon recrystallization from water and methanol. (0.391 g, 81%)

IR (KBr, cm\(^{-1}\)): \(v = 521, 637, 665, 737, 809, 941, 990, 1105, 1164, 1293, 1343, 1436, 1459, 1562, 1622, 1683, 2221\).
$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.95$ (t, 1H, CH), 8.18 (s, 2H, CH), 8.27 (d, 2H, CH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 116.91$ (s), 117.83 (s), 121.88 (s), 137.72 (s), 147.12 (s), 148.79 (s), 152.80 (s), 155.66 (s) ppm.

**Elemental analysis:** calcd (%): C 47.20, N 49.25, H 3.54, found: C 47.46, N 49.57, H 3.32.
10. Modulation the melting points of organic salts

We measured the melting point of the compound 62, 63, 64 with a melting point apparatus. The melting range of compound 62 is 137.9-138.7 °C, the melting range of compound 63 is 75.3-75.9 °C, the melting range of compound 64 is 95.8-96.5 °C.

(E)-amino(2-butylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (62)

Following the general procedure, in a 50 mL round bottom flask, butyraldehyde (0.072 g, 1 mmol) and water (5 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) was dissolved in water (20 mL) and was added dropwise to the flask. The resulting mixture was stirred for 7 h at room temperature. After that the solvent was slowly removed under vacuum, and the yellow crystal were obtained upon recrystallization from water. (0.240 g, 84%)

IR (KBr, cm⁻¹): v = 750, 835, 944, 1011, 1062, 1162, 1318, 1352, 1440, 1479, 1537, 1633, 1667, 2965, 3151, 3350, 3453.

¹H NMR (600MHz, d₆-DMSO): δ = 0.89 (s, 3H, CH), 1.51 (s, 2H, CH), 2.22 (s, 2H, CH), 7.32 (s, 1H, CH), 7.51 (s, 1H, CH), 11.13 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 13.97 (s), 19.53 (s), 34.17 (s), 98.80 (s), 152.76 (s), 155.33 (s), 156.84 (s) ppm.

MS: m/z: 129.1 (C₅H₁₃N⁺, cation); 156.9 (C₃H₁₄O₄⁻, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 33.57, N 39.15, H 4.93, found: C 33.12, N 39.41, H 5.02.

(E)-amino(2-octylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (63)

Following the general procedure, in a 50 mL round bottom flask, octanal (0.128 g, 1 mmol) and methanol (20 mL) were placed. Aminoguanidinium 3,5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in methanol (20 mL) was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 °C. After that the solvent was slowly removed under vacuum, and the yellow crystal were obtained upon recrystallization from methanol. (0.245 g, 85%)

IR (KBr, cm⁻¹): v = 750, 835, 944, 1011, 1062, 1162, 1318, 1352, 1440, 1479, 1537, 1633, 1667, 2965, 3151, 3350, 3453.

¹H NMR (600MHz, d₆-DMSO): δ = 0.89 (s, 3H, CH), 1.51 (s, 2H, CH), 2.22 (s, 2H, CH), 7.32 (s, 1H, CH), 7.51 (s, 1H, CH), 11.13 (s, 1H, NH) ppm.

¹³C NMR (150 MHz, d₆-DMSO): δ = 13.97 (s), 19.53 (s), 34.17 (s), 98.80 (s), 152.76 (s), 155.33 (s), 156.84 (s) ppm.

MS: m/z: 129.1 (C₅H₁₃N⁺, cation); 156.9 (C₃H₁₄O₄⁻, 3,5-dinitropyrazolate anion).

Elemental analysis: calcd (%): C 33.57, N 39.15, H 4.93, found: C 33.12, N 39.41, H 5.02.
removed under vacuum, and the yellow plate crystal was obtained upon recrystallization from water and methanol.

(0.280 g, 82%)

IR (KBr, cm\(^{-1}\)): \(\nu = 477, 582, 755, 833, 1015, 1162, 1278, 1317, 1355, 1472, 1536, 1625, 1651, 1679, 2930, 3108, 3341, 3423, 3474\).

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 0.82\) (t, 3H, CH), 1.23 (m, 8H, CH), 1.45 (m, 2H, CH), 2.24 (m, 2H, CH), 7.32 (s, 1H, CH), 7.55 (t, 1H, CH), 11.19 (s, 1H, NH) ppm.

\(^13\)C NMR (150 MHz, d\(_6\)-DMSO): \(\delta = 14.23\) (s), 22.49 (s), 25.72 (s), 26.11 (s), 27.84 (s), 28.81 (s), 28.89 (s), 29.01 (s), 29.14 (s), 31.60 (s), 32.26 (s), 98.72 (s), 151.66 (s), 152.84 (s), 155.30 (s), 156.25 (s), 156.70 (s) ppm.

Elemental analysis: calcd (%): C 42.10, N 32.73, H 6.48, found: C 41.82, N 32.86, H 6.21.

(E)-amino(2-dodecylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (64)

Following the general procedure, in a 50 mL round bottom flask, dodecanal (0.184 g, 1 mmol) and methanol (20 mL) were placed. Aminoguanidinium 3, 5-dinitropyrazolate (0.232 g, 1 mmol) dissolved in methanol (20 mL) was added dropwise to the flask. The resulting mixture was stirred for 7 h at 65 \(^\circ\)C. After that the solvent was slowly removed under vacuum, and the yellow plate crystal was obtained upon recrystallization from water and methanol.

(0.347 g, 87%)

IR (KBr, cm\(^{-1}\)): \(\nu = 716, 753, 838, 1018, 1174, 1280, 1323, 1358, 1467, 1532, 1651, 1683, 2850, 2915, 3152, 3407, 3493\).

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 0.83\) (t, 3H, CH), 1.21 (m, 16H, CH), 1.46 (m, 2H, CH), 2.23 (m, 2H, CH), 7.31 (s, 1H, CH), 7.54 (t, 1H, CH), 11.22 (s, 1H, NH) ppm.

\(^13\)C NMR (150 MHz, d\(_6\)-DMSO): \(\delta = 14.30\) (s), 22.56 (s), 29.09 (s), 29.20 (s), 29.26 (s), 29.42 (s), 29.49 (s), 29.51 (s), 26.12 (s), 31.77 (s), 32.27 (s), 98.70 (s), 152.81 (s), 155.35 (s), 156.74 (s) ppm.

Fig S2. TG/DSC curves of (E)-amino(2-butylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (62)

Fig S3. TG/DSC curves of (E)-amino(2-octylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (63)
Fig S4. TG/DSC curves of (E)-amino(2-dodecylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (64)
11. Modulation the fluorescent properties of organic salts

\((E)-\text{amino}(2-(\text{pyren-1-ylmethylene})\text{hydrazinyl})\text{methaniminium 3,5-dibromo-1,2,4-triazolate (65)}\)

Following the general procedure, in a 50 mL round bottom flask, 1-pyrenecarboxaldehyde (0.230 g, 1 mmol) and ethanol (5 mL) were placed. Aminoguanidinium 3, 5-dibromo-1, 2, 4-triazolate (0.301 g, 1 mmol) was dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was refluxed for 7 h. After that the solvent was slowly removed under vacuum, the solid was washed by dichloromethane. After filtration, the yellow powder was obtained upon recrystallization from water and methanol. (0.302 g, 59%)

IR (KBr, cm\(^{-1}\)): \(v = 600, 715, 844, 875, 994, 1121, 1182, 1242, 1421, 1628, 1685, 3040\).

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 7.90\) (s, 4H, NH), 8.10 (t, 1H, CH), 8.21 (d, 1H, CH), 8.25 (d, 1H, CH), 8.34 (m, 4H, CH), 8.59 (d, 1H, CH), 8.87 (d, 1H, CH), 9.34 (s, 1H, CH) ppm.

\(^13\)C NMR (150 MHz, d\(_6\)-DMSO): \(\delta = 122.30\) (s), 124.21 (s), 124.44 (s), 125.01 (s), 125.54 (s), 126.31 (s), 126.64 (s), 127.06 (s), 127.84 (s), 129.00 (s), 129.27 (s), 129.32 (s), 130.54 (s), 131.28 (s), 132.65 (s), 135.87 (s), 145.32 (s), 155.82 (s), ppm.

Elemental analysis: calcd (%): C 46.81, N 19.11, H 2.95, found: C 46.53, N 19.42, H 2.68.

\((E)-\text{amino}(2-(\text{pyren-1-ylmethylene})\text{hydrazinyl})\text{methaniminium 4,5-dicyanoimidazolate (66)}\)

Following the general procedure, in a 50 mL round bottom flask, 1-pyrenecarboxaldehyde (0.230 g, 1 mmol) and ethanol (5 mL) were placed. Aminoguanidinium 4, 5-dicyanoimidazolate (0.192 g, 1 mmol) was dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was refluxed for 7 h. After that the solvent was slowly removed under vacuum, the solid was washed by dichloromethane. After filtration, the yellow powder was obtained upon recrystallization from water and methanol. (0.255 g, 63%)

IR (KBr, cm\(^{-1}\)): \(v = 522, 609, 638, 666, 713, 849, 927, 972, 1050, 1108, 1258, 1294, 1439, 1628, 1685, 2225\). \(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 7.35\) (s, 1H, CH), 7.79 (s, 4H, NH), 8.11 (t, 1H, CH), 8.22 (d, 1H, CH), 8.26 (d,
1H, CH), 8.34 (m, 4H, CH), 8.56 (d, 1H, CH), 8.87 (d, 1H, CH), 9.32 (s, 1H, CH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 117.36$ (s), 117.98 (s), 122.31 (s), 124.20 (s), 124.44 (s), 125.07 (s), 125.54 (s), 126.35 (s), 126.57 (s), 127.09 (s), 127.84 (s), 129.05 (s), 129.30 (s), 129.37 (s), 130.54 (s), 131.28 (s), 132.71 (s), 145.66 (s), 149.25 (s), 155.69 (s) ppm.

**Elemental analysis:** calcd (%): C 68.31, N 27.71, H 3.99, found: C 68.03, N 27.94, H 4.12.

(E)-amino(2-(pyren-1-ylmethylene)hydrazinyl)methaniminium nitrate (67)

Following the general procedure, in a 50 mL round bottom flask, 1-pyrenecarboxaldehyde (0.230 g, 1 mol) and ethanol (5 mL) were placed. Aminoguanidinium nitrate (0.138 g, 1 mmol) was dissolved in ethanol (20 mL) and was added dropwise to the flask. The resulting mixture was refluxed for 7 h. After that the solvent was slowly removed under vacuum, the solid was washed by dichloromethane. After filtration, the yellow powder was obtained upon recrystallization from water and methanol. (0.185 g, 53%)

IR (KBr, cm$^{-1}$): $\nu = 612, 712, 820, 850, 1046, 1092, 1153, 1190, 1260, 1335, 1385, 1467, 1629, 1676, 3192, 3437.$

$^1$H NMR (600 MHz, d$_6$-DMSO): $\delta = 7.81$ (s, 4H, NH), 8.08 (t, 1H, CH), 8.19 (d, 1H, CH), 8.22 (d, 1H, CH), 8.32 (m, 4H, CH), 8.52 (d, 1H, CH), 8.85 (d, 1H, CH), 9.29 (s, 1H, CH) ppm.

$^{13}$C NMR (150 MHz, d$_6$-DMSO): $\delta = 122.26$ (s), 124.18 (s), 124.40 (s), 125.04 (s), 125.52 (s), 126.30 (s), 126.56 (s), 126.62 (s), 127.03 (s), 127.82 (s), 128.98 (s), 129.24 (s), 129.32 (s), 130.51 (s), 131.25 (s), 132.66 (s), 145.54 (s), 155.78 (s) ppm.

**Elemental analysis:** calcd (%): C 61.89, N 20.05, H 4.33, found: C 62.04, N 20.42, H 4.62.
Measurement of the fluorescence of organic salts

**Fig S5.** Fluorescence spectra of organic salts 65-67 in methanol (the concentration is 1 mmol L\(^{-1}\)).

**Fig S6.** Absorption spectrum of organic salts 65-67
**Table S3.** The photophysical properties of as-synthesized organic salts 65-67

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Absorption $I_{\text{max}}$ [nm]</th>
<th>Fluorescence $I_{\text{max}}$ [nm]</th>
<th>$\tau$ [ch]</th>
<th>QY</th>
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<tr>
<td>65</td>
<td>324</td>
<td>415</td>
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<tr>
<td>67</td>
<td>324</td>
<td>415</td>
<td>45.421</td>
<td>0.007</td>
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12. Single-crystal X-ray diffraction diagrams of organic salts

Fig S7. Molecule structure of organic salt 4

Fig S8. Packing diagram of organic salt 4
Fig S9. Molecule structure of organic salt 24

Fig S10. Packing diagram of organic salt 24
Fig S11. Molecule structure of organic salt 38

Fig S12. Packing diagram of organic salt 38
Fig S13. Molecule structure of organic salt 46

Fig S14. Packing diagram of organic salt 46
Fig S15. Molecule structure of organic salt 58

Fig S16. Packing diagram of organic salt 58
Fig S17. Molecule structure of organic salt 70

Fig S18. Packing diagram of organic salt 70
Fig S19. Molecule structure of organic salt 72

Fig S20. Packing diagram of organic salt 72
13. Theoretical calculation for the heats of formation of organic salts and DSC/TG spectrum of organic salts

Computations were performed with the Gaussian 09 program. The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses were carried out by using the B3LYP functional with 6-311+G** basis set, and single energy points were calculated at the MP2/6-311 +G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Based on a Born–Haber energy cycle, the heat of formation of a salt can be simplified by Equation (3):

$$\Delta H^*_{f} \text{(ionic salt, 298K)} = \Delta H^*_{f} \text{(antion, 298K)} + \Delta H^*_{f} \text{(cation, 298K)} - \Delta H_L$$

in which $\Delta H_L$ is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Equation (4)]:

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

in which $n_M$ and $n_X$ depend on the nature of the ions $M^{p+}$ and $X^{q-}$, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy $U_{POT}$ is Equation (5):

$$U_{POT} \left[kJ \text{ mol}^{-1}\right] = \gamma \left(\rho m / Mm\right)^{1/3} + \delta$$

in which $\rho$ [g cm$^{-3}$] is the density, $M$ is the chemical formula mass of the ionic material, and values for $\gamma$ and the coefficients $\gamma$ [kJ mol$^{-1}$] and $\delta$ [kJ mol$^{-1}$] are taken from the literature.
### Table S4

Total energy (E0), zero-point energy (ZPE), thermal correction (H_T), and heat of formation (HOF) form NIST.

<table>
<thead>
<tr>
<th></th>
<th>ZPE</th>
<th>HT</th>
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<th>HOF/ kJ mol(^{-1})</th>
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<tr>
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<td>-79.25155819</td>
<td>-84</td>
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<td>0.003865</td>
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Table S5. Physical properties of as-synthesized organic salts and TNT

<table>
<thead>
<tr>
<th>Comp.</th>
<th>68</th>
<th>69</th>
<th>70</th>
<th>71</th>
<th>TNT</th>
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<tbody>
<tr>
<td>$\rho^b$</td>
<td>1.66</td>
<td>1.69</td>
<td>1.68</td>
<td>1.57</td>
<td>1.65</td>
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<tr>
<td>$T_d^c$</td>
<td>257</td>
<td>282</td>
<td>241</td>
<td>-</td>
<td>295</td>
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<tr>
<td>N$%^d$</td>
<td>62.99</td>
<td>65.10</td>
<td>58.32</td>
<td>47.29</td>
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<td>O+N$%^e$</td>
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<td>79.97</td>
<td>80.53</td>
<td>79.70</td>
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<td>IS$^g$</td>
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<td>15</td>
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<tr>
<td>FS$^h$</td>
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<td>&gt;360</td>
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<td>-</td>
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<tr>
<td>$\Delta H^i$</td>
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<td>536.80</td>
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<tr>
<td>$\Delta H^j$</td>
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<td>1811.56</td>
<td>1811.56</td>
<td>1811.56</td>
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<td>P$^l$</td>
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<td>7981</td>
<td>8840</td>
<td>7441</td>
<td>6881</td>
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</tbody>
</table>

$^a$Density measured from gas pycnometer (g cm$^{-3}$). $^b$Decomposition temperature (ºC). $^c$Nitrogen content. $^d$Oxygen and nitrogen content. $^e$Oxygen balance. $^f$Impact sensitivity (J). $^g$Friction sensitivity (N). $^h$Heat of formation of anion. $^i$Heat of formation of cation. $^j$Heat of formation of salt. $^k$Heat of formation. $^l$Detonation pressure. $^m$Detonation velocity. The detonation properties were calculated by EXPLO5 v6.01. Properties of TNT are taken from reference 40.
Fig S21. TG/DSC curves of ((2E,2'E)-2,2"-(ethane-1,2-diylidene)bis(hydrazin-1-yl-2-ylidene))

bis(aminomethaniminium)5-nitrotetrazol -1-ide (68)

Fig S22. TG/DSC curves of ((2E,2'E)-2,2"-(ethane-1,2-diylidene)bis(hydrazin-1-yl-2-ylidene))bis
(aminomethaniminium) (E)-5-(nitroimino)-4,5-dihydrotetrazol-1-ide(Z)-5-(nitroimino)-4,5-dihydrotetrazolate(69)
Fig S23. TG/DSC curves of $\{(2E,2'E)-2,2'-(\text{ethane-1,2-diylidene})\text{bis(hydrazin-1-yl-2-ylidene})\}\text{bis(aminomethaniminium)}\ 5$-nitro-$2\text{H}$-tetrazol-2-olate (70)

Fig S24. TG/DSC curves of $\{(2E,2'E)-2,2'-(\text{ethane-1,2-diylidene})\text{bis(hydrazin-1-yl-2-ylidene})\}\text{bis(aminomethaniminium)}\ \text{nitrate} \ (71)$
14. Controlled experiment

A solution of (E)-amino(2-benzylidenehydrazinyl)methaniminium chloride in 30 mL water was added to silver(I) 3,4-dicyanopyrazol-1-ide suspension in 60 mL water. After the mixture was stirred at room temperature for 6 h, filter residue was removed by filtration, and washed with methanol. The filtrate was slowly evaporated under vacuum. The goal product is not obtained by IR.
15. Synthesis of simple aminoguanidinium salts with various organic anions

**General procedures:** A commercial available organic acid (1 mmol) was added to a solution of aminoguanidinium bicarbonate (1 mmol) in 30 mL methanol. The reaction mixture was stirred with heating (50 °C) until a transparent solution was formed. If not, more methanol was added to the mixture. Then, methanol was slowly evaporated at ambient pressure and temperature, giving the corresponding product in good yields. Most of as-synthesized simple aminoguanidinium salts with various organic anions have been characterized by IR, 1H and 13C NMR. Since some of these salts have been previously reported, they are been mainly characterized by TLC and melting points.

**Amino(hydrazinyl)methaniminium benzoate**

![Amino(hydrazinyl)methaniminium benzoate](image)

White crystal. (0.182 g, 93%)

**IR (KBr, cm⁻¹):** ν = 408, 572, 710, 841, 919, 1027, 1069, 1121, 1160, 1215, 1391, 1537, 1621, 1667, 3363, 3410.

**1H NMR (600 MHz, d₆-DMSO):** δ = 4.61 (s, 2H, NH), 7.31 (m, 3H, CH), 7.87 (m, 2H, CH), 8.21 (s, 2H, NH) ppm.

**13C NMR (151MHz, d₆-DMSO):** δ = 127.79 (s), 129.40 (s), 129.77 (s), 139.45 (s), 160.24 (s), 171.52 (s) ppm.

**Amino(hydrazinyl)methaniminium 4-methylbenzoate**

![Amino(hydrazinyl)methaniminium 4-methylbenzoate](image)

White crystal. (0.193 g, 92%)

**IR (KBr, cm⁻¹):** ν = 464, 555, 615, 759, 785, 848, 924, 1023, 1129, 1179, 1214, 1392, 1535, 1607, 1661, 3361, 3431.

**1H NMR (600 MHz, d₆-DMSO):** δ = 2.28 (s, 3H, CH), 4.60 (s, 2H, NH), 7.08 (d, 2H, CH), 7.76 (d, 2H, CH), 8.24 (s, 2H, NH) ppm.

**13C NMR (151MHz, d₆-DMSO):** δ = 21.37 (s), 128.39 (s), 129.49 (s), 136.76 (s), 139.08 (s), 160.26 (s), 171.61 (s) ppm.
Amino(hydrazinyl)methaniminium 4-methoxybenzoate

![Structure](image)

White crystal. (0.201 g, 89%)

IR (KBr, cm⁻¹): ν = 505, 538, 614, 636, 698, 782, 849, 950, 1021, 1097, 1136, 1182, 1251, 1294, 1384, 1508, 1529, 1602, 1676, 3304, 3340.

¹H NMR (600 MHz, d_6-DMSO): δ = 3.73 (s, 3H, CH), 4.60 (s, 2H, NH), 6.83 (d, 2H, CH), 7.83 (d, 2H, CH), 8.25 (s, 2H, NH) ppm.

¹³C NMR (151MHz, d_6-DMSO): δ = 55.45 (s), 112.95 (s), 131.05 (s), 131.95 (s), 160.26 (s), 160.78 (s), 171.43 (s) ppm.

Amino(hydrazinyl)methaniminium 4-bromobenzoate

![Structure](image)

White crystal. (0.258 g, 94%)

IR (KBr, cm⁻¹): ν = 460, 476, 619, 624, 683, 711, 762, 841, 918, 1011, 1069, 1105, 1175, 1388, 1555, 1592, 1674, 3023, 3352, 3450.

¹H NMR (600 MHz, d_6-DMSO): δ = 4.60 (s, 2H, NH), 7.47 (d, 2H, CH), 7.78 (d, 2H, CH), 8.12 (s, 2H, NH) ppm.

¹³C NMR (151MHz, d_6-DMSO): δ = 123.50 (s), 130.77 (s), 131.56 (s), 138.71 (s), 160.17 (s), 170.37 (s) ppm.

Amino(hydrazinyl)methaniminium 4-chlorobenzoate

![Structure](image)

White crystal. (0.219 g, 95%)

IR (KBr, cm⁻¹): ν = 469, 528, 672, 660, 685, 765, 843, 920, 1013, 1091, 1391, 1487, 1557, 1593, 1675, 3028, 3352, 3453.

¹H NMR (600 MHz, d_6-DMSO): δ = 4.60 (s, 2H, NH), 7.35 (d, 2H, CH), 7.85 (d, 2H, CH), 8.12 (s, 2H, NH),
10.25 (s, 1H, NH) ppm.

$^{13}$C NMR (151 MHz, $d_6$-DMSO): $\delta = 127.82$ (s), 131.23 (s), 134.58 (s), 138.31 (s), 160.18 (s), 170.25 (s) ppm.

Amino(hydrazinyl)methaniminium 4-cyanobenzoate

Amino(hydrazinyl)methaniminium 4-cyanobenzoate

White crystal. (0.203 g, 92%)

IR (KBr, cm$^{-1}$): $\nu = 499, 548, 621, 708, 759, 786, 845, 868, 974, 1017, 1099, 1290, 1384, 1546, 1584, 1686, 2233, 3361, 3472.$

$^1$H NMR (600 MHz, $d_6$-DMSO): $\delta = 4.61$ (s, 2H, NH), 7.78 (d, 2H, CH), 7.99 (d, 2H, CH), 10.08 (s, 1H, NH) ppm.

$^{13}$C NMR (151 MHz, $d_6$-DMSO): $\delta = 112.19$ (s), 119.48 (s), 130.01 (s), 132.10 (s), 143.82 (s), 160.10 (s), 169.60 (s) ppm.

Amino(hydrazinyl)methaniminium benzenesulfonate

Light red crystal. (0.202 g, 87%)

IR (KBr, cm$^{-1}$): $\nu = 569, 617, 685, 733, 752, 997, 1018, 1035, 1070, 1129, 1181, 1445, 1682, 3326, 3401.$

$^1$H NMR (600 MHz, $d_6$-DMSO): $\delta = 4.67$ (m, 2H, NH), 7.33 (m, 3H, CH), 7.61 (s, 2H, CH) ppm.

$^{13}$C NMR (151 MHz, $d_6$-DMSO): $\delta = 125.85$ (s), 128.31 (s), 129.36 (s), 147.78 (s), 159.28 (s) ppm.

Amino(hydrazinyl)methaniminium 4-methylbenzenesulfonate

White powder. (0.236 g, 96%)

IR (KBr, cm$^{-1}$): $\nu = 516, 573, 629, 687, 815, 955, 1009, 1034, 1126, 1189, 1224, 1453, 1598, 1690, 3182, 3330,
\(^1H\) NMR (600 MHz, \(d_6\)-DMSO): \(\delta = 2.28\) (s, 3H, CH), 4.55 (s, 2H, NH), 7.14 (d, 2H, CH), 7.49 (d, 2H, CH), 8.64 (s, 1H, NH) ppm.

\(^{13}C\) NMR (151MHz, \(d_6\)-DMSO): \(\delta = 21.24\) (s), 125.87 (s), 128.73 (s), 138.73 (s), 145.12 (s), 159.27 (s) ppm.

Amino(hydrazinyl)methaniminium thiophene-3-carboxylate

\[
\begin{array}{c}
\text{H}_2\text{N}^+ \\
\text{H} \quad \text{N} \quad \text{NH}_2^- \\
\text{OOC} \\
\text{S}
\end{array}
\]

White crystal. (0.190g, 94%)

IR (KBr, cm\(^{-1}\)): \(\nu = 408, 525, 569, 760, 832, 869, 929, 1070, 1116, 1218, 1351, 1415, 1512, 1554, 1665, 3357, 3410\).

\(^1H\) NMR (600 MHz, \(d_6\)-DMSO): \(\delta = 4.60\) (s, 2H, NH), 7.29 (m, 1H, CH), 7.32 (m, 1H, CH), 7.72 (m, 1H, CH), 8.14 (s, 2H, NH), 10.29 (s, 1H, NH) ppm.

\(^{13}C\) NMR (151MHz, \(d_6\)-DMSO): \(\delta = 124.97\) (s), 128.28 (s), 129.41 (s), 144.33 (s), 160.19 (s), 168.40 (s) ppm.

Amino(hydrazinyl)methaniminium furan-2-carboxylate

\[
\begin{array}{c}
\text{H}_2\text{N}^+ \\
\text{H} \quad \text{N} \quad \text{NH}_2^- \\
\text{OOC} \\
\text{C}
\end{array}
\]

White crystal. (0.156 g, 84%)

IR (KBr, cm\(^{-1}\)): \(\nu = 446, 531, 613, 711, 753, 795, 884, 926, 990, 1020, 1075, 1137, 1184, 1221, 1363, 1388, 1486, 1556, 1588, 1662, 1698, 2853, 3188, 3362, 3471\).

\(^1H\) NMR (600 MHz, \(d_6\)-DMSO): \(\delta = 4.60\) (s, 2H, NH), 6.39 (m, 1H, CH), 6.65 (d, 1H, CH), 7.54 (m, 1H, CH), 7.98 (s, 4H, NH), 10.01 (s, 1H, NH) ppm.

\(^{13}C\) NMR (151MHz, \(d_6\)-DMSO): \(\delta = 111.25\) (s), 112.29 (s), 143.29 (s), 153.02 (s), 160.10 (s), 164.22 (s) ppm.
Amino(hydrazinyl)methaniminium formate

![Chemical structure]

White crystal. (0.113 g, 94%)

IR (KBr, cm\(^{-1}\)): \(\nu = 511, 569, 767, 809, 1019, 1103, 1220, 1349, 1371, 1592, 1680, 2731, 2815, 3410\).

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 4.54\) (s, 2H, NH), 7.89 (s, 4H, NH), 8.42 (s, 1H, CH) ppm.

\(^{13}\)C NMR (151MHz, d\(_6\)-DMSO): \(\delta = 160.08\) (s), 168.18 (s) ppm.

Amino(hydrazinyl)methaniminium acetate

![Chemical structure]

White crystal. (0.118 g, 88%)

IR (KBr, cm\(^{-1}\)): \(\nu = 521, 652, 720, 812, 932, 1016, 1126, 1345, 1408, 1566, 1671, 3209, 3332, 3456\).

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 1.64\) (s, 3H, CH), 4.48 (s, 2H, NH), 8.03 (s, 2H, NH) ppm.

\(^{13}\)C NMR (151MHz, d\(_6\)-DMSO): \(\delta = 25.47\) (s), 160.16 (s), 176.63 (s) ppm.

Amino(hydrazinyl)methaniminium 4,5-dicyanoimidazol-1-ide

![Chemical structure]

White crystal. (0.173 g, 90%)

IR (KBr, cm\(^{-1}\)): \(\nu = 482, 524, 639, 664, 798, 868, 957, 1107, 1215, 1296, 1438, 1491, 1671, 2226, 3352, 3502\).

\(^1\)H NMR (600 MHz, d\(_6\)-DMSO): \(\delta = 4.66\) (s, 2H, NH), 6.75 (s, 2H, NH), 7.29 (s, 1H, CH), 8.60 (s, 1H, NH) ppm.

\(^{13}\)C NMR (151MHz, d\(_6\)-DMSO): \(\delta = 117.25\) (s), 117.90 (s), 149.23 (s), 159.18 (s) ppm.
Amino(hydrazinyl)methaniminium 1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine -3-carboxylate

Yellow crystal. (0.229 g, 75%)

IR (KBr, cm⁻¹): ν = 717, 749, 809, 967, 984, 1128, 1226, 1254, 1289, 1318, 1352, 1385, 1443, 1500, 1579, 1606, 1630, 1659, 1688, 3250, 3342, 3397.

¹H NMR (600 MHz, D₂O): δ = 1.13 (t, 3H, CH), 2.29 (s, 3H, CH), 4.09 (m, 2H, CH), 6.91 (d, 1H, CH), 8.01 (d, 1H, CH), 8.27 (s, 1H, CH) ppm.

¹³C NMR (151MHz, D₂O): δ = 16.76 (s), 26.58 (s), 48.87 (s), 120.74 (s), 122.05 (s), 123.68 (s), 138.06 (s), 149.55 (s), 150.14 (s), 161.31 (s), 166.17 (s), 174.40 (s), 178.91 (s) ppm.

Amino(hydrazinyl)methaniminium 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate

Light green powder. (0.354 g, 82%)

IR (KBr, cm⁻¹): ν = 854, 1070, 1091, 1219, 1289, 1319, 1327, 1360, 1374, 1395, 1434, 1465, 1477, 1598, 1610, 1621, 1681, 3363.

¹H NMR (600 MHz, d₆-DMSO): δ = 2.19 (s, 3H, CH), 3.46 (s, 2H, CH), 3.74 (s, 3H, CH), 6.68 (d, 1H, CH), 6.93 (d, 1H, CH), 7.06 (s, 1H, CH), 7.62 (m, 4H, CH) ppm.

¹³C NMR (151MHz, d₆-DMSO): δ = 18.49 (s), 37.30 (s), 60.57 (s), 107.38 (s), 116.15 (s), 119.62 (s), 121.23 (s), 134.19 (s), 135.53 (s), 136.20 (s), 136.62 (s), 139.34 (s), 139.63 (s), 142.63 (s), 160.69 (s), 164.86 (s), 173.01 (s), 178.69 (s) ppm.
Amino(hydrazinyl)methaniminium (R)-2-(6-methoxynaphthalen-2-yl)propanoate

Yellow crystal. (0.262 g, 86%)

**IR (KBr, cm⁻¹):** ν = 474, 637, 819, 853, 890, 926, 1030, 1162, 1216, 1263, 1305, 1342, 1360, 1400, 1455, 1482, 1502, 1529, 1565, 1609, 1632, 1673, 3177, 3300, 3409.

**¹H NMR (600 MHz, D₂O):** δ = 1.61 (d, 3H, CH), 3.88 (s, 4H, CH), 7.16 (d, 1H, CH), 7.21 (d, 1H, CH), 7.57 (s, 1H, CH), 7.77 (t, 3H, CH) ppm.

**¹³C NMR (151MHz, D₂O):** δ = 18.54 (s), 48.66 (s), 55.62 (s), 106.61 (s), 118.21 (s), 125.46 (s), 127.08 (s), 129.14 (s), 129.48 (s), 133.14 (s), 139.30 (s), 156.72 (s), 183.70 (s) ppm.
16. Spectral data

(1E,2E)-1,2-dibenzylidenehydrazine (3)

Fig S25. $^{13}$C NMR spectrum of compound 3

Fig S26. $^1$H NMR spectrum of compound 3
Fig S27. IR spectrum of compound 3
Amino(hydrazinyl)methaniminium benzoate

Fig S28. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium benzoate

Fig S29. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium benzoate
Fig S30. IR spectrum of amino(hydrazinyl)methaniminium benzoate
Amino(hydrazinyl)methaniminium 4-methylbenzoate

Fig S31. ^13^C NMR spectrum of amino(hydrazinyl)methaniminium 4-methylbenzoate

Fig S32. ^1^H NMR spectrum of amino(hydrazinyl)methaniminium 4-methylbenzoate
Fig S33. IR spectrum of amino(hydrazinyl)methaniminium 4-methylbenzoate
Amino(hydrazinyl)methaniminium 4-methoxybenzoate

Fig S34. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium 4-methoxybenzoate

Fig S35. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium 4-methoxybenzoate
Fig S36. IR spectrum of amino(hydrazinyl)methaniminium 4-methoxybenzoate
Amino(hydrazinyl)methaniminium 4-bromobenzoate

Fig S37. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium 4-bromobenzoate

Fig S38. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium 4-bromobenzoate
Fig S39. IR spectrum of amino(hydrazinyl)methaniminium 4-bromobenzoate
Amino(hydrazinyl)methaniminium 4-chlorobenzoate

**Fig S40.** $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium 4-chlorobenzoate

**Fig S41.** $^1$H NMR spectrum of amino(hydrazinyl)methaniminium 4-chlorobenzoate
Fig S42. IR spectrum of amino(hydrazinyl)methaniminium 4-chlorobenzoate
Amino(hydrazinyl)methaniminium 4-cyanobenzoate

**Fig S43.** $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium 4-cyanobenzoate

**Fig S44.** $^1$H NMR spectrum of amino(hydrazinyl)methaniminium 4-cyanobenzoate
Fig S45. IR spectrum of amino(hydrazinyl)methaniminium 4-cyanobenzoate
Amino(hydrazinyl)methaniminium benzenesulfonate

Fig S46. $^1$C NMR spectrum of amino(hydrazinyl)methaniminium benzenesulfonate

Fig S47. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium benzenesulfonate
Fig S48. IR spectrum of amino(hydrazinyl)methaniminium benzenesulfonate
Amino(hydrazinyl)methaniminium 4-methylbenzenesulfonate

Fig S49. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium 4-methylbenzenesulfonate

Fig S50. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium 4-methylbenzenesulfonate
Fig S51. IR spectrum of amino(hydrazinyl)methaniminium 4-methylbenzenesulfonate
Amino(hydrazinyl)methaniminium thiophene-3-carboxylate

Fig S52. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium thiophene-3-carboxylate

Fig S53. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium thiophene-3-carboxylate
Fig S54. IR spectrum of amino(hydrazinyl)methaniminium thiophene-3-carboxylate
Amino(hydrazinyl)methaniminium furan-2-carboxylate

Fig S55. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium furan-2-carboxylate

Fig S56. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium furan-2-carboxylate
Fig S57. IR spectrum of amino(hydrazinyl)methaniminium furan-2-carboxylate
Amino(hydrazinyl)methaniminium formate

Fig S58. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium formate

Fig S59. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium formate
Fig S60. IR spectrum of amino(hydrazinyl)methaniminium formate
Amino(hydrazinyl)methaniminium acetate

Fig S61. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium acetate

Fig S62. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium acetate
Fig S63. IR spectrum of amino(hydrazinyl)methaniminium acetate
Amino(hydrazinyl)methaniminium 4,5-dicyanoimidazol-1-ide

Fig S64. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium 4,5-dicyanoimidazol-1-ide

Fig S65. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium 4,5-dicyanoimidazol-1-ide
Fig S66. IR spectrum of amino(hydrazinyl)methaniminium 4,5-dicyanoimidazol-1-ide
Amino(hydrazinyl)methaniminium 1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine -3-carboxylate

Fig S67. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium 1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine -3-carboxylate

Fig S68. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium 1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine -3-carboxylate
Fig S69. IR spectrum of amino(hydrazinyl)methaniminium 1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine -3-carboxylate
Amino(hydrazinyl)methaniminium 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate

**Fig S70.** $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate

**Fig S71.** $^1$H NMR spectrum of amino(hydrazinyl)methaniminium 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate
Fig S72. IR spectrum of amino(hydrazinyl)methaniminium 
2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate
Amino(hydrazinyl)methaniminium (R)-2-(6-methoxynaphthalen-2-yl)propanoate

Fig S73. $^{13}$C NMR spectrum of amino(hydrazinyl)methaniminium (R)-2-(6-methoxynaphthalen-2-yl)propanoate

Fig S74. $^1$H NMR spectrum of amino(hydrazinyl)methaniminium (R)-2-(6-methoxynaphthalen-2-yl)propanoate
Fig S75. IR spectrum of amino(hydrazinyl)methaniminium \((R)-2-(6\text{-methoxynaphthalen}-2\text{-yl})\text{propanoate}\)
(E)-amino(2-benzylidenehydrazinyl)methaniminium 3,5-dinitropyrazolate (4)

Fig S76. $^{13}$C NMR spectrum of compound 4

Fig S77. $^1$H NMR spectrum of compound 4
Fig S78. IR spectrum of compound 4

Fig S79. ESI-MS spectrum of cation of compound 4

m/z: 163.10

Fig S80. ESI-MS spectrum of anion compound 4

m/z: 157.00
(E)-amino(2-(4-methylbenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (6)

Fig S81. $^{13}$C NMR spectrum of compound 6

Fig S82. $^1$H NMR spectrum of compound 6
Fig S83. IR spectrum of compound 6

Fig S84. ESI-MS spectrum of cation of compound 6

Fig S85. ESI-MS spectrum of anion of compound 6
(E)-(2-(4-acetamidobenzylidene)hydrazyl)(amino)methaniminium 3,5-dinitropyrazolate (7)

Fig S86. $^{13}$C NMR spectrum of compound 7

Fig S87. $^1$H NMR spectrum of compound 7
**Fig S88.** IR spectrum of compound 7

**Fig S89.** ESI-MS spectrum of cation of compound 7

**Fig S90.** ESI-MS spectrum of anion of compound 7
(E)-amino(2-(4-(methylsulfonyl)benzylidene)hydrazinyl)methaniminium

3,5-dinitropyrazolate (8)

Fig S91. $^{13}$C NMR spectrum of compound 8

Fig S92. $^1$H NMR spectrum of compound 8
Fig S93. IR spectrum of compound 8

Fig S94. ESI-MS spectrum of cation of compound 8

Fig S95. ESI-MS spectrum of anion of compound 8
(E)-amino(2-(4-fluorobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (9)

Fig S96. $^{13}$C NMR spectrum of compound 9

Fig S97. $^1$H NMR spectrum of compound 9
Fig S98. IR spectrum of compound 9

Fig S99. ESI-MS spectrum of cation of compound 9

Fig S100. ESI-MS spectrum of anion of compound 9
(E)-amino(2-(4-chlorobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (10)

Fig S101. $^{13}$C NMR spectrum of compound 10

Fig S102. $^1$H NMR spectrum of compound 10
Fig S103. IR spectrum of compound 10

Fig S104. ESI-MS spectrum of cation of compound 10

Fig S105. ESI-MS spectrum of anion of compound 10
(E)-amino(2-(4-bromobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (11)

Fig S106. $^{13}$C NMR spectrum of compound 11

Fig S107. $^1$H NMR spectrum of compound 11
Fig S108. IR spectrum of compound 11

Fig S109. ESI-MS spectrum of cation of compound 11

Fig S110. ESI-MS spectrum of anion of compound 11
(E)-amino(2-(4-cyanobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (12)

Fig S11. $^{13}$C NMR spectrum of compound 12

Fig S12. $^1$H NMR spectrum of compound 12
Fig S113. IR spectrum of compound 12

Fig S114. ESI-MS spectrum of cation of compound 12

Fig S115. ESI-MS spectrum of anion of compound 12

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(E)-amino(2-(4-nitrobenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (13)

Fig S116. $^{13}$C NMR spectrum of compound 13

Fig S117. $^1$H NMR spectrum of compound 13
Fig S118. IR spectrum of compound 13

Fig S119. ESI-MS spectrum of cation of compound 13

Fig S120. ESI-MS spectrum of anion of compound 13
(E)-amino(2-(4-(trifluoromethyl)benzylidene)hydrazinyl)methaniminium3,5-dinitropyrazolate (14)

Fig S121. $^{13}$C NMR spectrum of compound 14

Fig S122. $^1$H NMR spectrum of compound 14
**Fig S123.** IR spectrum of compound 14

**Fig S124.** ESI-MS spectrum of cation of compound 14

**Fig S125.** ESI-MS spectrum of anion of compound 14
(E)-amino(2-(3-hydroxybenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (15)

Fig S126. $^{13}$C NMR spectrum of compound 15

Fig S127. $^1$H NMR spectrum of compound 15
Fig S128. IR spectrum of compound 15

Fig S129. ESI-MS spectrum of cation of compound 15

Fig S130. ESI-MS spectrum of anion of compound 15
(E)-amino (2-(3-methoxybenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (16)

Fig S131. $^{13}$C NMR spectrum of compound 16

Fig S132. $^1$H NMR spectrum of compound 16
Fig S133. IR spectrum of compound 16

Fig S134. ESI-MS spectrum of cation of compound 16

Fig S135. ESI-MS spectrum of anion of compound 16
(E)-amino(2-(2,4,6-trimethoxybenzylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (17)

Fig S136. $^1$C NMR spectrum of compound 17

Fig S137. $^1$H NMR spectrum of compound 17
Fig S138. IR spectrum of compound 17

Fig S139. ESI-MS spectrum of cation of compound 17

Fig S140. ESI-MS spectrum of anion of compound 17
(E)-amino(2-(anthracen-9-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (18)

**Fig S141.** $^{13}$C NMR spectrum of compound 18

**Fig S142.** $^1$H NMR spectrum of compound 18
Fig S143. IR spectrum of compound 18
(E)-amino(2-(naphthalen-2-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (19)

![Fig S144. $^{13}$C NMR spectrum of compound 19](image1)

![Fig S145. $^1$H NMR spectrum of compound 19](image2)
Fig S146. IR spectrum of compound 19
Amino(2-methylenehydrazinyImethaniminium 3,5-dinitropyrazolate (20)

Fig S147. $^{13}$C NMR spectrum of compound 20

Fig S148. $^1$H NMR spectrum of compound 20
Fig S149. IR spectrum of compound 20
(E)-amino(2-(cyclopentylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (21)

Fig S150. $^{13}$C NMR spectrum of compound 21

Fig S151. $^1$H NMR spectrum of compound 21
Fig S152. IR spectrum of compound 21

Fig S153. ESI-MS spectrum of cation of compound 21

Fig S154. ESI-MS spectrum of anion of compound 21
(E)-amino(2-(cyclohexylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (22)

Fig S155. $^{13}$C NMR spectrum of compound 22

Fig S156. $^1$H NMR spectrum of compound 22
Fig S157. IR spectrum of compound 22

Fig S158. ESI-MS spectrum of cation of compound 22

Fig S159. ESI-MS spectrum of anion of compound 22
(E)-(2-((1H-pyrrol-2-yl)methylene)hydrazinyl)(amino) methaniminium 3,5-dinitropyrazolate (23)

Fig S160. $^{13}$C NMR spectrum of compound 23

Fig S161. $^1$H NMR spectrum of compound 23
Fig S162. IR spectrum of compound 23

Fig S163. ESI-MS spectrum of cation of compound 23

Fig S164. ESI-MS spectrum of anion of compound 23
(E)-((2-(1H-imidazol-4-yl)vinyl)amino)(amino)methaniminium 3,5-dinitropyrazolate (24)

Fig S165. $^{13}$C NMR spectrum of compound 24

Fig S166. $^1$H NMR spectrum of compound 24
Fig S167. IR spectrum of compound 24

Fig S168. ESI-MS spectrum of cation of compound 24

Fig S169. ESI-MS spectrum of anion of compound 24
(E)-amino(2-(thiophen-2-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (25)

Fig S170. $^{13}$C NMR spectrum of compound 25

Fig S171. $^1$H NMR spectrum of compound 25
Fig S172. IR spectrum of compound 25

Fig S173. ESI-MS spectrum of cation of compound 25

Fig S174. ESI-MS spectrum of anion of compound 25
(E)-amino(2-((2-bromothiazol-5-yl)methylene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (26)

Fig S175. $^{13}$C NMR spectrum of compound 26

Fig S176. $^1$H NMR spectrum of compound 26
**Fig S177.** IR spectrum of compound 26

**Fig S178.** ESI-MS spectrum of cation of compound 26

**Fig S179.** ESI-MS spectrum of anion of compound 26
(E)-amino(2-((5-methylthiophen-2-y1)methylene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (27)

Fig S180. $^{13}$C NMR spectrum of compound 27

Fig S181. $^1$H NMR spectrum of compound 27
Fig S182. IR spectrum of compound 27

Fig S183. ESI-MS spectrum of cation of compound 27

Fig S184. ESI-MS spectrum of anion of compound 27
(E)-amino (2-(pyridin-2-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (28)

Fig S185. $^{13}$C NMR spectrum of compound 28

Fig S186. $^1$H NMR spectrum of compound 28
Fig S187. IR spectrum of compound 28

Fig S188. ESI-MS spectrum of cation of compound 28

Fig S189. ESI-MS spectrum of anion of compound 28
(E)-amino(2-(quinolin-3-ylmethylene)hydrazinyl)methaniminium 3,5-dinitropyrazolate (29)

Fig S190. $^{13}$C NMR spectrum of compound 29

Fig S191. $^1$H NMR spectrum of compound 29
**Fig S192.** IR spectrum of compound 29

**Fig S193.** ESI-MS spectrum of cation of compound 29

**Fig S194.** ESI-MS spectrum of anion of compound 29
(E)-amino(2-(ferrocene) hydrazinyl)methaniminium 3,5-dinitropyrazole-1-ide (30)

**Fig S195.** $^{13}$C NMR spectrum of compound 30

**Fig S196.** $^1$H NMR spectrum of compound 30
Fig S197. IR spectrum of compound 30

Fig S198. ESI-MS spectrum of cation of compound 30

Fig S199. ESI-MS spectrum of anion of compound 30

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Amino (2-(propan-2-ylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

**Fig S200.** $^{13}$C NMR spectrum of compound amino (2-(propan-2-ylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

**Fig S201.** $^1$H NMR spectrum of compound amino (2-(propan-2-ylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

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**Fig S202.** IR spectrum of compound amino (2-(propan-2-ylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

**Fig S203.** ESI-MS spectrum of cation of compound amino (2-(propan-2-ylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

**Fig S204.** ESI-MS spectrum of anion of compound amino (2-(propan-2-ylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate
(E)-amino(2-(1-phenylethylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

Fig S205. $^{13}$C NMR spectrum of compound (E)-amino(2-(1-phenylethylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

Fig S206. $^1$H NMR spectrum of compound (E)-amino(2-(1-phenylethylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate
Fig S207. IR spectrum of compound (E)-amino(2-(1-phenylethylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

Fig S208. ESI-MS spectrum of cation of compound (E)-amino(2-(1-phenylethylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate

Fig S209. ESI-MS spectrum of anion of compound (E)-amino(2-(1-phenylethylidene)hydrazinyl)methaniminium 3,5-dinitropyrazolate
(E)-amino(2-benzylidenehydrazinyl)methaniminium benzoate (31)

**Fig S210.** $^{13}$C NMR spectrum of compound 31

**Fig S211.** $^1$H NMR spectrum of compound 31
Fig S212. IR spectrum of compound 31
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-methoxybenzoate (32)

Fig S213. $^{13}$C NMR spectrum of compound 32

Fig S214. $^1$H NMR spectrum of compound 32
Fig S215. IR spectrum of compound 32
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-methylbenzoate (33)

Fig S216. $^{13}$C NMR spectrum of compound 33

Fig S217. $^1$H NMR spectrum of compound 33
Fig S218. IR spectrum of compound 33
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-cyanobenzoate (34)

Fig S219. $^{13}$C NMR spectrum of compound 34

Fig S220. $^1$H NMR spectrum of compound 34
Fig S221. IR spectrum of compound 34
(E)-amino(2-benzylidenehydrazinyl)methaniminium 3-nitrobenzoate (35)

Fig S222. $^{13}$C NMR spectrum of compound 35

Fig S223. $^1$H NMR spectrum of compound 35
Fig S224. IR spectrum of compound 35
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-chlorobenzoate (36)

**Fig S225.** $^{13}$C NMR spectrum of compound 36

**Fig S226.** $^1$H NMR spectrum of compound 36
Fig S227. IR spectrum of compound 36
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-bromobenzoate (37)

Fig S228. $^{13}$C NMR spectrum of compound 37

Fig S229. $^1$H NMR spectrum of compound 37
Fig S230. IR spectrum of compound 37
(E)-amino(2-benzylidenehydrazinyl) methaniminium formate (38)

Fig S231. $^{13}$C NMR spectrum of compound 38

Fig S232. $^1$H NMR spectrum of compound 38
Fig S233. IR spectrum of compound 38
(E)-amino(2-benzylidenehydrazinyl)methaniminium acetate (39)

Fig S234. $^{13}$C NMR spectrum of compound 39

Fig S235. $^1$H NMR spectrum of compound 39
Fig S236. IR spectrum of compound 39
(E)-amino(2-benzylidenehydrazinyl)methaniminium heptanoate (40)

Fig S237. $^{13}$C NMR spectrum of compound 40

Fig S238. $^1$H NMR spectrum of compound 40
Fig S239. IR spectrum of compound 40
(E)-amino(2-benzylidenehydrazinyl) methaniminium benzenesulfonate (41)

Fig S240. $^{13}$C NMR spectrum of compound 41

Fig S241. $^1$H NMR spectrum of compound 41
Fig S242. IR spectrum of compound 41
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-methylbenzenesulfonate (42)

**Fig S243.** $^{13}$C NMR spectrum of compound 42

**Fig S244.** $^1$H NMR spectrum of compound 42
Fig S245. IR spectrum of compound 42
(E)-amino(2-benzylidenehydrazinyl)methaniminium 3-aminobenzenesulfonate (43)

Fig S246. $^{13}$C NMR spectrum of compound 43

Fig S247. $^1$H NMR spectrum of compound 43
IR spectrum of compound 43
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-nitrobenzenesulfonate (44)

Fig S249. $^{13}$C NMR spectrum of compound 44

Fig S250. $^1$H NMR spectrum of compound 44
Fig S251. IR spectrum of compound 44
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4-amino-3,5-dinitropyrazolate (45)

Fig S252. $^{13}$C NMR spectrum of compound 45

Fig S253. $^1$H NMR spectrum of compound 45
Fig S254. IR spectrum of compound 45

Fig S255. ESI-MS spectrum of cation of compound 45

Fig S256. ESI-MS spectrum of anion of compound 45
(E)-amino(2-benzylidenehydrazinyl)methaniminium 4,5-dicyanoimidazolate (46)

Fig S257. $^{13}$C NMR spectrum of compound 46

Fig S258. $^1$H NMR spectrum of compound 46
Fig S259. IR spectrum of compound 46

Fig S260. ESI-MS spectrum of cation of compound 46

Fig S261. ESI-MS spectrum of anion of compound 46
(E)-amino(2-benzylidenehydrazinyl)methaniminium 2,4-dinitroimidazolate (47)

Fig S262. $^{13}$C NMR spectrum of compound 47

Fig S263. $^1$H NMR spectrum of compound 47
**Fig S264.** IR spectrum of compound 47

**Fig S265.** ESI-MS spectrum of cation of compound 47

**Fig S266.** ESI-MS spectrum of anion of compound 47
(E)-amino(2-benzylidenehydrazinyl) methaniminium 3,5-dibromo-1,2,4-triazolate (48)

**Fig S267.** $^{13}$C NMR spectrum of compound 48

**Fig S268.** $^1$H NMR spectrum of compound 48
Fig S269. IR spectrum of compound 48

Fig S270. ESI-MS spectrum of cation of compound 48

Fig S271. ESI-MS spectrum of anion of compound 48
(E)-amino(2-benzylidenehydrazinyl)methaniminium 3,5-dinitro-1,2,4-triazolate (49)

Fig S272. $^{13}$C NMR spectrum of compound 49

Fig S273. $^1$H NMR spectrum of compound 49
Fig S274. IR spectrum of compound 49

Fig S275. ESI-MS spectrum of cation of compound 49

Fig S276. ESI-MS spectrum of anion of compound 49
(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-chlorotetrazolate (50)

Fig S277. $^{13}$C NMR spectrum of compound 50

Fig S278. $^1$H NMR spectrum of compound 50
Fig S279. IR spectrum of compound 50

Fig S280. ESI-MS spectrum of cation of compound 50

Fig S281. ESI-MS spectrum of anion of compound 50
(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-nitrotetrazolate (51)

Fig S282. $^{13}$C NMR spectrum of compound 51

Fig S283. $^1$H NMR spectrum of compound 51
**Fig S284.** IR spectrum of compound 51

**Fig S285.** ESI-MS spectrum of cation of compound 51

**Fig S286.** ESI-MS spectrum of anion of compound 51
(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-(trifluoromethyl) tetrazolate (52)

Fig S287. $^{13}$C NMR spectrum of compound 52

Fig S288. $^1$H NMR spectrum of compound 52
Fig S289. IR spectrum of compound 52

Fig S290. ESI-MS spectrum of cation of compound 52

Fig S291. ESI-MS spectrum of anion of compound 52
(E)-amino(2-benzylidenehydrazinyl)methaniminium(Z)-5-(nitroimino)-4,5-dihydrotetrazolate (53)

Fig S292. $^{13}$C NMR spectrum of compound 53

Fig S293. $^1$H NMR spectrum of compound 53
Fig S294. IR spectrum of compound 53

Fig S295. ESI-MS spectrum of cation of compound 53

Fig S296. ESI-MS spectrum of anion of compound 53
(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-nitro-2H-tetrazol-2-olate (54)

Fig S297. $^{13}$C NMR spectrum of compound 54

Fig S298. $^1$H NMR spectrum of compound 54
Fig S299. IR spectrum of compound 54

Fig S300. ESI-MS spectrum of cation of compound 54

Fig S301. ESI-MS spectrum of anion of compound 54
(E)-amino(2-benzylidenehydrazinyl)methaniminium 5-nitrobenzo-1,2,3-triazolate (55)

Fig S302. $^{13}$C NMR spectrum of compound 55

Fig S303. $^1$H NMR spectrum of compound 55
Fig S304. IR spectrum of compound 55

Fig S305. ESI-MS spectrum of cation of compound 55

Fig S306. ESI-MS spectrum of anion of compound 55

(E)-amino(2-benzylidenehydrazinyl)methaniminium furan-2-carboxylate (56)

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Fig S307. $^{13}$C NMR spectrum of compound 56

Fig S308. $^1$H NMR spectrum of compound 56
Fig S309. IR spectrum of compound 56
(E)-amino(2-benzylidenehydrazinyl)methaniminium thiophene-3-carboxylate (57)

Fig S310. $^{13}$C NMR spectrum of compound 57

Fig S311. $^1$H NMR spectrum of compound 57
Fig S312. IR spectrum of compound 57
(E)-amino(2-benzylidenehydrazinyl)methaniminium 1-ethyl-7-methyl-4-oxo-1,4-dihydro-1,8-naphthyridine-3-carboxylate (58)

Fig S313. $^{13}$C NMR spectrum of compound 58

Fig S314. $^1$H NMR spectrum of compound 58
Fig S315. IR spectrum of compound 58
(E)-amino(2-benzylidenehydrazinyl)methaniminium (R)-2-(6-methoxynaphthalen-2-yl)propanoate (59)

Fig S31. $^{13}$C NMR spectrum of compound 59

Fig S317. $^1$H NMR spectrum of compound 59
Fig S318. IR spectrum of compound 59
(E)-amino(2-benzylidenehydrazinyl)methaniminium2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl) acetate (60)

Fig S31. $^{13}$C NMR spectrum of compound 60

Fig S32. $^1$H NMR spectrum of compound 60
Fig S321. IR spectrum of compound 60
(E)-amino(2-benzylidenehydrazinyl)methaniminium(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate (61)

Fig S322. $^{13}$C NMR spectrum of compound 61

Fig S323. $^1$H NMR spectrum of compound 61
Fig S324. IR spectrum of compound 61
(E)-amino(2-butylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (62)

Fig S325. $^{13}$C NMR spectrum of compound 62

Fig S326. $^1$H NMR spectrum of compound 62
Fig S327. IR spectrum of compound 62

Fig S328. ESI-MS spectrum of cation of compound

Fig S329. ESI-MS spectrum of anion of compound
(E)-amino(2-octylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (63)

Fig S330. $^{13}$C NMR spectrum of compound 63

Fig S331. $^1$H NMR spectrum of compound 63
Fig S332. IR spectrum of compound 63
(E)-amino(2-dodecylidenehydrazinyl)methaniminium 3,5-dinitropyrazol-1-ide (64)

Fig S333. $^{13}$C NMR spectrum of compound 64

Fig S334. $^1$H NMR spectrum of compound 64
Fig S335. IR spectrum of compound 64
(E)-amino(2-(pyren-1-ylmethylene)hydrazinyl)methaniminium 3,5-dibromo-1,2,4-triazolate (65)

Fig S336. $^1$C NMR spectrum of compound 65

Fig S337. $^1$H NMR spectrum of compound 65
Fig S338. IR spectrum of compound 65
(E)-amino(2-(pyren-1-ylmethylene)hydrazinyl) methaniminium 4,5-dicyanoimidazolate (66)

Fig S339. $^{13}$C NMR spectrum of compound 66

Fig S340. $^1$H NMR spectrum of compound 66
Fig S341. IR spectrum of compound 66
Fig S342. $^{13}$C NMR spectrum of compound 67

Fig S343. $^1$H NMR spectrum of compound 67
Fig S344. IR spectrum of compound 67
((2E,2'E)-2,2'-{ethane-1,2-diylidene)bis(hydrazin-1-yl-2-ylidene)}bis(aminomethaniminium)5-nitrotetrazolate (68)

Fig S345. $^{13}$C NMR spectrum of compound 68

Fig S346. $^1$H NMR spectrum of compound 68
Fig S347. IR spectrum of compound 68

Fig S348. ESI-MS spectrum of cation of compound 68

Fig S349. ESI-MS spectrum of anion of compound 68
(2E,2'E)-2,2'-[(ethane-1,2-diylidene)bis(hydrazin-1-yl-2-yldiene)]bis(aminomethaniminium)(E)-5-(nitroimino)-4,5-dihydropyrazole-1-ide (Z)-5-(nitroimino)-4,5-dihydropyrazolate (69)

Fig S350. $^{13}$C NMR spectrum of compound 69

Fig S351. $^1$H NMR spectrum of compound 69
Fig S352. IR spectrum of compound 69

Fig S353. ESI-MS spectrum of cation of compound 69

Fig S354. ESI-MS spectrum of anion of compound 69
\((2E,2'E)-2,2'-(\text{ethane-1,2-diylidene})\text{bis(hydrizin-1-yl-2-ylidene)})\text{bis(aminomethaniminium)}5\text{-nitro-2H-tetrazol-2-olate}\) (70)

**Fig S355.** $^{13}$C NMR spectrum of compound 70

**Fig S356.** $^1$H NMR spectrum of compound 70
Fig S357. IR spectrum of compound 70

Fig S358. ESI-MS spectrum of cation of compound 70

Fig S359. ESI-MS spectrum of anion of compound 70
((2E,2'E)-2,2'-[(ethane-1,2-diylidene)bis(hydrazin-1-yl-2-ylidene)]bis(aminomethaniminium)nitrate (71)

Fig S360. $^{13}$C NMR spectrum of compound 71

Fig S361. $^1$H NMR spectrum of compound 71
Fig S362. IR spectrum of compound 71
(2E,2’E)-2,2’-(1,4-phenylenebis(methanylylidene))bis(hydrazin-1-yl-2-ylidene)) bis(aminomethaniminium) 5-nitrotetrazolate (72)

Fig S363. $^{13}$C NMR spectrum of compound 72

Fig S364. $^1$H NMR spectrum of compound 72
Fig S365. IR spectrum of compound 72

Fig S366. ESI-MS spectrum of cation of compound 72

Fig S367. ESI-MS spectrum of anion of compound 72

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$((2E,2'E)-2,2'-(1,4-phenylenebis(methanylylidene))bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium)$

5-(trifluoromethyl)tetrazolate (73)

**Fig S368.** $^{13}$C NMR spectrum of compound 73

**Fig S369.** $^1$H NMR spectrum of compound 73
Fig S370. IR spectrum of compound 73

Fig S371. ESI-MS spectrum of cation of compound 73

Fig S372. ESI-MS spectrum of anion of compound 73
((2E,2'E)-2,2'-(1,4-phenylenebis(methanylylidene))bis(hydrazin-1-yl-2-ylidene))bis (aminomethaniminium) 4, 5-dicyanoimidazolate (74)

Fig S373. $^{13}$C NMR spectrum of compound 74

Fig S374. $^1$H NMR spectrum of compound 74
Fig S375. IR spectrum of compound 74

Fig S376. ESI-MS spectrum of cation of compound 74

Fig S377. ESI-MS spectrum of anion of compound 74
(2E,2'E)-2,2'-((1,4-phenylenebis(methanylylidene))bis(hydrazin-1-yl-2-ylidene)) bis(aminomethaniminium) 3,5-dibromo-1,2,4-triazolate (75)

Fig S378. $^{13}$C NMR spectrum of compound 75

Fig S379. $^1$H NMR spectrum of compound 75
Fig S380. IR spectrum of compound 75

Fig S381. ESI-MS spectrum of cation of compound 75

Fig S382. ESI-MS spectrum of anion of compound 75
((2E,2'E)-2,2'-((pyridine-2,6-diylbis(methanylylidene))bis(hydrazin-1-yl-2-ylidene))bis(aminomethaniminium) 4,5-dicyanoimidazol -1-ide (76)

Fig S383. $^{13}$C NMR spectrum of compound 76

Fig S384. $^1$H NMR spectrum of compound 76
Fig S385. IR spectrum of compound 76
References:


