Supporting Information for

Empowering Strategies of Electrochemical N-N Bond Forming Reactions: Direct Access to Previously Neglected 1,2,3-Triazole 1-Oxides

Kseniia Titenkova, a,b Alexander D. Shuvaev, a,b Fedor E. Teslenko, a,b Egor S. Zhilin, a Leonid L. Fershtat a*

a N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences 119991, Leninsky Prosp., 47, Moscow (Russia). * E-mail: fershtat@bk.ru
b Department of Chemistry, Moscow State University, 119991 Leninskie Gory 1-3, Moscow

Table of Contents

S1. Optimization Studies .......................................................................................................................... 2
S2. Experimental Section .......................................................................................................................... 3
  S2.1 General Remarks ................................................................................................................................... 3
  S2.2 Synthesis of Oximinohydrazones ........................................................................................................ 3
  S2.3. Electrochemical Synthesis of 1,2,3-Triazole 1-Oxides .................................................................. 13
  S2.4 NO release assay ................................................................................................................................... 23
S3. Computational Details ...................................................................................................................... 24
S4. CV curves ......................................................................................................................................... 26
S5. DSC data .......................................................................................................................................... 33
S6. X-ray crystallographic data and refinement details ............................................................................ 38
S7. References ....................................................................................................................................... 47
S8. Copies of NMR Spectra ..................................................................................................................... 47
S1. Optimization Studies

Optimization of electrochemical oxidation of a model substrate 1a is presented in Table S1. The found optimal conditions which were used for the synthesis of the entire series of 1,2,3-triazole 1-oxides were as follows: C/Pt electrodes, LiClO$_4$ as an electrolyte, 5 mA current, no mediator and MeOH as a solvent (entry 1). Addition of TEMPO or N-hydroxyphthalimide (NHPI) as mediator resulted in a decrease of a yield of compound 2a (entries 2,3), while utilization of ferrocene or hydroquinone completely suppressed oxidation (entries 4,5). Replacement of MeOH with MeCN slightly decreased the yield of 2a to 89% (entry 6). At the same time, conducting electrochemical oxidation in MeOH using "Bu$_4$NBF$_4$ as an electrolyte resulted in more substantial yield decrease (entry 7). Utilization of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) as one of the widely used reaction media for a variety of electrochemical transformations provided 2a only in trace amounts (entry 8). Nature of electrodes was also crucial for the successful implementation of electrochemical oxidation: replacement of C/Pt electrodes with glassy carbon/Pt or C/C those resulted in a yield decrease (entries 9,12), while more harsh oxidation conditions derived from stainless steel/Pt or Pt/Pt pairs were useless (entries 10,11). Finally, variation of current from 5 mA to 3 mA or 7 mA slightly decreased the yield of 2a (entries 13,14).

Table S1. Optimization of electrochemical oxidation of oximinohydrazone 1a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Electrodes (+)/(-)</th>
<th>Electrolyte</th>
<th>Current</th>
<th>Mediator</th>
<th>Yield of 2a, a %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeOH</td>
<td>C/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>C/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>TEMPO</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td>MeOH</td>
<td>C/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>NHPI</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>MeOH</td>
<td>C/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>FeCp$_2$</td>
<td>traces$^b$</td>
</tr>
<tr>
<td>5</td>
<td>MeOH</td>
<td>C/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>hydroquinone</td>
<td>traces$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>MeCN</td>
<td>C/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>-</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>MeOH</td>
<td>C/Pt</td>
<td>$^a$Bu$_4$NBF$_4$</td>
<td>5 mA</td>
<td>-</td>
<td>74</td>
</tr>
<tr>
<td>8</td>
<td>HFIP</td>
<td>C/Pt</td>
<td>$^a$Bu$_4$NBF$_4$</td>
<td>5 mA</td>
<td>-</td>
<td>traces$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>MeOH</td>
<td>glassy carbon/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>-</td>
<td>81</td>
</tr>
<tr>
<td>10</td>
<td>MeOH</td>
<td>stainless steel/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>-</td>
<td>traces$^b$</td>
</tr>
<tr>
<td>11</td>
<td>MeOH</td>
<td>Pt/Pt</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>-</td>
<td>traces$^b$</td>
</tr>
<tr>
<td>12</td>
<td>MeOH</td>
<td>C/C</td>
<td>LiClO$_4$</td>
<td>5 mA</td>
<td>-</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>MeOH</td>
<td>C/Pt</td>
<td>LiClO$_4$</td>
<td>3 mA</td>
<td>-</td>
<td>86</td>
</tr>
<tr>
<td>14</td>
<td>MeOH</td>
<td>C/Pt</td>
<td>LiClO$_4$</td>
<td>7 mA</td>
<td>-</td>
<td>88</td>
</tr>
</tbody>
</table>

$^a$ Isolated yields.

$^b$ Compound 2a was detected by TLC.

$^c$ Decomposition of starting oximinohydrazone 1a was observed.
S2. Experimental Section

S2.1 General Remarks

All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM-300 (300.13 and 75.47 MHz, respectively) spectrometer and referenced to residual solvent peak. The chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, J, are reported in Hertz. The IR spectra were recorded on a Bruker “Alpha” spectrometer in the range 400-4000 cm$^{-1}$ (resolution 2 cm$^{-1}$). Elemental analyses were performed by the CHN Analyzer Perkin-Elmer 2400. High resolution mass spectra were recorded on a Bruker microTOF spectrometer with electrospray ionization (ESI). All measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range m/z: 50-3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for all analyzed solutions in MeCN (flow rate: 3 μL min$^{-1}$). Nitrogen was used as nebulizer gas (0.4 bar) and dry gas (4.0 L min$^{-1}$); interface temperature was set at 180 °C. All spectra were processed by using Bruker DataAnalysis 4.0 software package. The melting points were determined on Stuart SMP20 apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F$^{254}$ aluminum sheets. The visualization of the TLC plates was accomplished with a UV light. Column chromatography was performed on silica gel 60 A (0.060-0.200 mm, Acros Organics). Thermal analysis was performed using STA 449 F3 (Netzsch) apparatus. Samples of 0.5-1.0 mg mass were poured in alumina pans covered with pierced lids and heated up to 600 °C with a constant rate of 5 K min$^{-1}$. All solvents were purified and dried using standard methods prior to use. All standard reagents were purchased from Aldrich or Acros Organics and used without further purification.

S2.2 Synthesis of Oximinohydrazones

General synthesis of starting oximes 1a-q was accomplished according to the following scheme:

\[
\begin{align*}
\text{N}_{2}X & \quad \rightarrow \quad \text{MeO} + \text{CO}_{2}\text{Me} \\
\text{R} & \quad \rightarrow \quad \text{N} + \text{CO}_{2}\text{Me} \\
\text{NH}_{2}\text{OH} & \quad \rightarrow \quad \text{N} + \text{CO}_{2}\text{Me}
\end{align*}
\]

Corresponding diazonium salt (10 mmol) was added in small portions to a magnetically stirred solution of methyl 4-morpholineacrylate (10 mmol, 1.71 g) in MeCN (10 mL) at 20 °C and left stirred overnight. After the reaction was completed (TLC monitoring), the reaction mixture was diluted with water (20 mL), precipitate formed was filtered off and dried in air. The obtained crude aldehyde was used without further purification for the second step. NH$_2$OH·HCl (15 mmol, 1.04 g) was added to a magnetically stirred suspension of the corresponding crude aldehyde in a mixture of AcONa (25 mmol, 2.05 g) in EtOH (15 mL) at 20 °C and the reaction mixture was left stirring overnight. After the reaction was completed (TLC monitoring), the
reaction mixture was diluted with water (30 mL), precipitate formed was filtered off and dried in air. Crude residue was purified via recrystallization from EtOH to afford pure oxime 1a-q.

**Methyl 3-(hydroxyimino)-2-(2-(p-tolyl)hydrazinylidene)propanoate (1a).**

![Chemical structure of 1a](image)

Yield 1.93 g (82%). Orange powder. M.p. 165-167°C (EtOH).

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 2.29$ (s, 3H), 3.78 (s, 3H), 7.16-7.23 (m, 4H), 8.30 (s, 1H), 12.03 (s, 1H), 12.65 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 20.9, 52.4, 115.2, 122.3, 130.5, 133.4, 140.5, 145.0, 164.7.$

Calcd for C$_{11}$H$_{13}$N$_3$O$_3$ (%): C, 56.16; H, 5.57; N, 17.86. Found (%): C, 56.03; H, 5.69; N, 17.62.

**Methyl 3-(hydroxyimino)-2-(2-phenylhydrazinylidene)propanoate (1b).**

![Chemical structure of 1b](image)

Yield 1.86 g (84%). Pale yellow powder. M.p. 164-166°C (EtOH).

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 3.79$ (s, 3H), 7.10 (t, $J = 7.2$ Hz, 1H), 7.28 (d, $J = 7.7$ Hz, 2H), 7.41 (t, $J = 7.7$ Hz, 2H), 8.30 (s, 1H), 12.10 (br s, 1H), 12.65 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 52.5, 115.2, 122.9, 124.2, 130.1, 142.8, 145.0, 164.6.$

Calcd for C$_{10}$H$_{11}$N$_3$O$_3$ (%): C, 54.30; H, 5.01; N, 19.00. Found (%): C, 54.47; H, 4.93; N, 18.81.

**Methyl 3-(hydroxyimino)-2-(2-(3-methylphenyl)hydrazinylidene)propanoate (1c).**

![Chemical structure of 1c](image)

Yield 1.62 g (69%). Pale yellow powder. M.p. 183-184°C (EtOH).

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 2.33$ (s, 3H), 3.79 (s, 3H), 6.92 (d, $J = 7.7$ Hz, 1H), 7.03-7.11 (m, 2H), 7.28 (t, $J = 7.7$ Hz, 1H), 8.30 (s, 1H), 12.11 (br s, 1H), 12.66 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 21.6, 52.5, 112.5, 115.6, 122.8, 125.0, 129.9, 139.6, 142.7, 145.0, 164.7.$

Calcd for C$_{11}$H$_{13}$N$_3$O$_3$ (%): C, 56.16; H, 5.57; N, 17.86. Found (%): C, 56.37; H, 5.44; N, 17.70.
Methyl 3-(hydroxyimino)-2-(2-mesitylhydrazinylidene)propanoate (1d).

 Yield 2.05 g (78%). Yellow powder. M.p. 150-152°C (EtOH).

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 2.23$ (s, 3H), 2.30 (s, 6H), 3.74 (s, 3H), 6.92 (s, 2H), 8.31 (s, 1H), 11.94 (br. s, 1H), 12.45 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 19.4, 20.8, 52.3, 121.5, 128.7, 130.3, 134.3, 136.8, 144.9, 165.0.$

Calcd for C$_{13}$H$_{17}$N$_3$O$_3$ (%): C, 59.30; H, 6.51; N, 15.96. Found (%): C, 59.46; H, 6.42; N, 16.09.

Methyl 3-(hydroxyimino)-2-(2-(2-chlorophenyl)hydrazinylidene)propanoate (1e).

 Yield 1.79 g (70%). Pale yellow powder. M.p. 156-157°C (EtOH).

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 3.81$ (s, 3H), 7.11 (t, $J = 7.7$ Hz, 1H), 7.43 (t, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.2$ Hz, 1H), 8.32 (s, 1H), 12.30 (br s, 1H), 12.97 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 52.7, 114.0, 114.6, 123.6, 124.1, 131.7, 134.6, 144.3, 144.7, 164.4.$

Calcd for C$_{10}$H$_{10}$ClN$_3$O$_3$ (%): C, 46.98; H, 3.94; N, 16.44. Found (%): C, 47.12; H, 3.81; N, 16.20.

Methyl 3-(hydroxyimino)-2-(2-(3-chlorophenyl)hydrazinylidene)propanoate (1f).

 Yield 1.89 g (74%). Pale yellow powder. M.p. 144-145°C (dec.) (EtOH).

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 3.79$ (s, 3H), 7.10-7.17 (m, 3H), 7.32 (s, 1H), 7.39 (t, $J = 7.7$ Hz, 1H), 8.27 (s, 1H), 12.16 (br s, 1H), 12.59 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 52.6, 114.0, 114.6, 123.6, 124.1, 131.7, 134.6, 144.3, 144.7, 164.4.$

Calcd for C$_{10}$H$_{10}$ClN$_3$O$_3$ (%): C, 46.98; H, 3.94; N, 16.44. Found (%): C, 46.84; H, 4.07; N, 16.31.

Methyl 3-(hydroxyimino)-2-(2-(4-chlorophenyl)hydrazinylidene)propanoate (1g).

 Yield 2.15 g (84%). Pale yellow powder. M.p. 138-139°C (dec.) (EtOH).
$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 3.79$ (s, 3H), 7.28 (d, $J = 8.7$ Hz, 2H), 7.45 (d, $J = 8.7$ Hz, 2H), 8.28 (s, 1H), 12.15 (br s, 1H), 12.61 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 52.6$, 116.8, 123.6, 127.7, 130.0, 141.8, 144.9, 164.5.

Calcd for C$_{10}$H$_{10}$ClN$_3$O$_3$ (%): C, 46.98; H, 3.94; N, 16.44. Found (%): C, 46.79; H, 4.03; N, 16.62.

**Methyl 3-(hydroxyimino)-2-(2-(3,5-dichlorophenyl)hydrazinylidene)propanoate (1h).**

\[
\text{NOH} \\
\text{Cl} \\
\text{NH} \\
\text{CO}_2\text{Me}
\]

Yield 1.89 g (65%). Pale yellow powder. M.p. 182-183°C (EtOH).

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 3.81$ (s, 3H), 7.27 (s, 3H), 8.26 (s, 1H), 12.18 (s, 1H), 12.49 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 52.8$, 113.6, 122.7, 125.3, 135.4, 144.4, 145.3, 164.2.


**Methyl 3-(hydroxyimino)-2-(2-(3-chloro-4-fluorophenyl)hydrazinylidene)propanoate (1i).**

\[
\text{NOH} \\
\text{Cl} \\
\text{NH} \\
\text{CO}_2\text{Me}
\]

Yield 2.38 g (87%). Pale pink solid. M.p. 191-192°C (dec.) (EtOH).

IR (KBr): 3247, 3089, 3002, 2956, 2905, 2849, 1701, 1607, 1569, 1506, 1440, 1336, 1294, 1261, 1211, 1114, 1049, 996, 902, 811, 771 cm$^{-1}$.

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 3.79$ (s, 3H), 7.20-7.22 (m, 1H), 7.41-7.47 (m, 3H), 8.26 (s, 1H), 12.13 (br s, 1H), 12.55 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 52.6$, 115.5 (d, $J = 7.2$ Hz), 116.4, 118.3 (d, $J = 22.5$ Hz), 120.9 (d, $J = 19.0$ Hz), 124.0 (d, $J = 1.7$ Hz), 140.2 (d, $J = 2.7$ Hz), 144.7, 154.0 (d, $J = 242.6$ Hz), 164.4.

HRMS (ESI): $m/z$ calcd for C$_{10}$H$_{10}$ClF$_3$N$_3$O$_3$: 274.0389; found: 274.0382 [M+H]$^+$.  

**Methyl 2-(2-(4-fluorophenyl)hydrazinylidene)-3-(hydroxyimino)propanoate (1j).**

\[
\text{NOH} \\
\text{F} \\
\text{NH} \\
\text{CO}_2\text{Me}
\]

Yield 1.92 g (80%). Light yellow powder. M.p. 192-193°C (dec.) (EtOH).

IR (KBr): 3247, 3089, 3002, 2956, 2905, 2849, 1701, 1607, 1569, 1506, 1440, 1336, 1294, 1261, 1211, 1114, 1049, 996, 956, 902, 811, 771 cm$^{-1}$.  

CO$_2$Me

NH

NOH

Cl

Cl
$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 3.78$ (s, 3H), 7.21-7.32 (m, 4H), 8.29 (s, 1H), 12.13 (br s, 1H), 12.64 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 52.5$, 116.6 (d, $J = 5.4$ Hz), 116.8 (d, $J = 9.4$ Hz), 122.9, 139.3 (d, $J = 2.3$ Hz), 144.9, 159.1 (d, $J = 240.1$ Hz), 164.6.


**Methyl 3-(hydroxyimino)-2-(2-(4-bromophenyl)hydrazinylidene)propanoate (1k).**

Yield 2.35 g (78%). Yellow powder. M.p. 199-200°C (EtOH).

IR (KBr): 3268, 3027, 3000, 2951, 1695, 1592, 1559, 1474, 1434, 1335, 1239, 1187, 1106, 1067, 989, 938, 826, 810, 776 cm$^{-1}$.

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 3.79$ (s, 3H), 7.23 (d, 2H, $J = 8.7$ Hz), 7.57 (d, 2H, $J = 8.7$ Hz), 8.28 (s, 1H), 12.18 (s, 1H), 12.64 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 52.6$, 115.7, 117.1, 123.6, 132.8, 142.2, 144.9, 164.5.

HRMS (ESI): m/z calcd for C$_{10}$H$_{11}$BrN$_3$O$_3$: 299.9978; found: 299.9979 [M+H]$^+$.

**Methyl 3-(hydroxyimino)-2-(2-(4-methoxyphenyl)hydrazinylidene)propanoate (1l).**

Yield 2.13 g (85%). Yellow powder. M.p. 200-201°C (EtOH).

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 3.76$ (s, 3H), 3.77 (s, 3H), 7.00 (d, 2H, $J = 9.0$ Hz), 7.24 (d, 2H, $J = 9.0$ Hz), 8.30 (s, 1H), 11.96 (s, 1H), 12.68 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 52.6$, 115.7, 117.1, 123.6, 132.8, 142.2, 144.9, 164.5.

Calcd for C$_{11}$H$_{13}$N$_3$O$_4$ (%): C, 52.59; H, 5.22; N, 16.73. Found (%): C, 52.76; H, 5.09; N, 16.55.

**Methyl 3-(hydroxyimino)-2-(2-(4-ethoxyphenyl)hydrazinylidene)propanoate (1m).**

Yield 2.34 g (88%). Orange powder. M.p. 188-189°C (EtOH).

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 1.32$ (t, $J = 6.9$ Hz, 3H), 3.77 (s, 3H), 4.01 (q, $J = 6.9$ Hz, 2H), 6.97 (d, $J = 8.7$ Hz, 2H), 7.21 (d, $J = 8.7$ Hz, 2H), 8.29 (s, 1H), 12.00 (s, 1H), 12.68 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 15.1$, 52.3, 63.7, 115.9, 116.6, 121.6, 136.2, 145.1, 155.8, 164.8.
Calcd for C\textsubscript{12}H\textsubscript{15}N\textsubscript{3}O\textsubscript{4} (%): C, 54.33; H, 5.70; N, 15.84. Found (%): C, 54.21; H, 5.79; N, 15.68.

**Methyl 3-(hydroxyimino)-2-(2-(2-nitrophenyl)hydrazinylidene)propanoate (1n).**

\[
\begin{align*}
\text{NOH} & \quad \text{CO}_2\text{Me} \\
\text{NH} & \quad \text{NO}_2
\end{align*}
\]

Yield 2.02 g (76%). Yellow powder. M.p. 188-189°C (EtOH).

\textsuperscript{1}H NMR (300 MHz, DMSO-d\textsubscript{6}): \(\delta = 3.89 \text{ (s, 3H)}, 7.18 \text{ (t, } J = 7.8 \text{ Hz, 1H)}, 7.77 \text{ (t, } J = 7.8 \text{ Hz, 1H)}, 7.96\text{-7.98 (m, 2H)}, 8.21 \text{ (d, } J = 8.3 \text{ Hz, 1H)}, 11.71 \text{ (s, 1H)}, 13.63 \text{ (s, 1H)}.\)

\textsuperscript{13}C NMR (75.5 MHz, DMSO-d\textsubscript{6}): \(\delta = 53.1, 116.4, 122.2, 126.2, 129.6, 133.7, 136.9, 139.4, 145.4, 162.1.\)

Calcd for C\textsubscript{10}H\textsubscript{10}N\textsubscript{4}O\textsubscript{5} (%): C, 45.12; H, 3.79; N, 21.05. Found (%): C, 44.95; H, 3.92; N, 20.89.

**Methyl 3-(hydroxyimino)-2-(2-(2-nitrophenyl)hydrazinylidene)propanoate (1o).**

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{NH} \\
\text{N} & \quad \text{CO}_2\text{Me}
\end{align*}
\]

Yield 2.16 g (81%). Yellow powder. M.p. 177-178°C (dec.) (EtOH).

\textsuperscript{1}H NMR (300 MHz, DMSO-d\textsubscript{6}): \(\delta = 3.82 \text{ (s, 3H)}, 7.66 \text{ (br s, 2H)}, 7.90 \text{ (br s, 1H)}, 8.06 \text{ (s, 1H)}, 8.29 \text{ (s, 1H)}, 12.24 \text{ (s, 1H)}, 12.70 \text{ (s, 1H)}.\)

\textsuperscript{13}C NMR (75.5 MHz, DMSO-d\textsubscript{6}): \(\delta = 52.7, 109.3, 118.0, 121.3, 125.0, 131.4, 144.1, 144.5, 149.1, 164.2.\)

Calcd for C\textsubscript{10}H\textsubscript{10}N\textsubscript{4}O\textsubscript{5} (%): C, 45.12; H, 3.79; N, 21.05. Found (%): C, 45.31; H, 3.65; N, 20.82.

**Methyl 3-(hydroxyimino)-2-(2-(2-nitrophenyl)hydrazinylidene)propanoate (1p).**

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{NH} \\
\text{N} & \quad \text{CO}_2\text{Me}
\end{align*}
\]

Yield 1.94 g (73%). Orange powder. M.p. 170-171°C (dec.) (EtOH).

\textsuperscript{1}H NMR (300 MHz, DMSO-d\textsubscript{6}): \(\delta = 3.81 \text{ (s, 3H)}, 7.39 \text{ (d, } J = 8.9 \text{ Hz, 2H)}, 8.24\text{-8.27 (m, 3H)}, 12.37 \text{ (s, 1H)}, 12.68 \text{ (s, 1H)}.\)

\textsuperscript{13}C NMR (75.5 MHz, DMSO-d\textsubscript{6}): \(\delta = 52.8, 115.0, 126.3, 126.7, 142.7, 144.5, 148.3, 164.1.\)

Calcd for C\textsubscript{10}H\textsubscript{10}N\textsubscript{4}O\textsubscript{5} (%): C, 45.12; H, 3.79; N, 21.05. Found (%): C, 45.25; H, 3.68; N, 20.94.
2-(2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)hydrazinylidene)-3-(hydroxyimino)propanoate (1q).

Yield 2.22 g (67%). Orange solid. M.p. 99-101°C.

IR (KBr): 3447, 3206, 3146, 3038, 2908, 1710, 1639, 1590, 1545, 1491, 1435, 1334, 1296, 1240, 1190, 1102, 984, 906, 769 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆): δ = 2.53 (s, 3H), 3.04 (s, 3H), 3.76 (s, 3H), 7.33-7.41 (m, 3H), 7.50-7.55 (m, 2H), 8.28 (s, 1H), 12.05 (s, 1H), 12.07 (s, 1H).

¹³C NMR (75.5 MHz, DMSO-d₆): δ = 11.4, 36.7, 52.4, 114.6, 122.3, 124.1, 127.1, 129.7, 134.9, 143.4, 144.9, 159.0, 164.6.


2-(2-Phenylhydrazinylidene)propanal oxime (1aa).

This compound was synthesized according to a previously reported procedure.¹ All characterization data were consistent with those reported.

2-Phenyl-2-(2-phenylhydrazinylidene)acetaldehyde oxime (1ab).

Phenylhydrazine (3 mL, 30 mmol) was added to a solution of 2-phenyl-2-(2-phenylhydrazinylidene)acetaldehyde (7.17 g, 30 mmol) in EtOH (50 mL). The reaction mixture was refluxed for 48 h, then poured into H₂O (150 mL) and the resulted mixture was left to stand for 2 weeks. The precipitate formed was filtered off, washed with water (2x30 mL) and dried in air.

Yield 1.79 g (25%). Light yellow solid. M.p. 138-140°C.

IR (KBr): 3331, 3217, 3051, 1599, 1539, 1477, 1441, 1296, 1260, 1010, 909, 892, 754 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆): δ = 6.90-6.96 (m, 1H), 7.21-7.25 (m, 2H), 7.30-7.44 (m, 5H), 7.75 (d, J = 7.1 Hz, 2H), 8.50 (s, 1H), 11.92 (s, 1H), 12.06 (s, 1H).

¹³C NMR (75.5 MHz, DMSO-d₆): δ = 113.8, 121.6, 126.3, 128.0, 128.9, 129.9, 131.7, 137.9, 144.6, 145.2.
HRMS (ESI): m/z calcd for C_{14}H_{14}N_{3}O: 240.1131; found: 240.1136 [M+H]^+.

2-(4-Nitrophenyl)-2-(2-(p-tolyl)hydrazinylidene)acetaldehyde oxime (1ac).

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{N} \quad \text{NOH} \\
\text{N} & \quad \text{NH} \\
\text{NH} & \quad \text{NH}
\end{align*}
\]

Yield 0.72 g (48%). Dark red solid. M.p. 152-154°C (dec.).

$^1$H NMR (300 MHz, DMSO-$d_6$): $\delta = 2.27$ (s, 3H), 7.15-7.21 (m, 4H), 7.99-8.02 (m, 2H), 8.19-8.22 (m, 2H), 8.58 (s, 1H), 12.15 (s, 1H), 12.26 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-$d_6$): $\delta = 20.8, 114.4, 124.1, 126.5, 128.8, 130.4, 131.7, 141.6, 144.2, 144.7, 146.4$.

HRMS (ESI): m/z calcd for C_{15}H_{15}N_{4}O_{3}: 299.1139; found: 299.1145 [M+H]^+.

2-Nitro-2-(2-(p-tolyl)hydrazinylidene)acetaldehyde oxime (1ad).

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{N} \quad \text{NOH} \\
\text{N} & \quad \text{NH} \\
\text{NH} & \quad \text{NH}
\end{align*}
\]

This compound was synthesized according to a previously reported procedure. All characterization data were consistent with those reported.

2-Nitro-2-(2-(4-nitrophenyl)hydrazinylidene)acetaldehyde oxime (1ae).

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{N} \quad \text{NOH} \\
\text{N} & \quad \text{NH} \\
\text{NH} & \quad \text{NH}
\end{align*}
\]

This compound was synthesized according to a previously reported procedure. All characterization data were consistent with those reported.

2-Phenyl-2-(2-phenylhydrazinylidene)acetaldehyde oxime (1af).
Et$_3$N (2.1 mL, 15 mmol) was added to a magnetically stirred solution of 2-oxo-$N$-(m-tolyl)propanehydrazonoyl chloride (1.13 g, 5 mmol) in MeOH (35 mL) at 0°C. Then $p$-toluidine (0.54 g, 5 mmol) was added in one portion. The reaction was left stirring for 1 h at 0-5°C and for 24 h at 20°C. Hydroxylamine hydrochloride (0.35 g, 5 mmol) was added to the resulted mixture and then stirred for 24 h. Then the reaction mixture was poured into H$_2$O (100 mL), the precipitate formed was filtered off and recrystallized from EtOH to afford pure oxime 1af.

Yield 0.87 g (25%). Beige solid. M.p. 136-138°C (EtOH).

$^1$H NMR (300 MHz, DMSO-d$_6$): δ = 2.11 (s, 3H), 2.19 (s, 3H), 2.24 (s, 3H), 6.51 (d, $J = 8.3$ Hz, 2H), 6.58 (d, $J = 7.4$ Hz, 2H), 6.91-6.97 (m, 4H), 7.07 (t, $J = 7.8$ Hz, 1H), 7.32 (s, 1H), 8.79 (s, 1H), 11.19 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): δ = 10.9, 20.6, 21.8, 110.6, 113.7, 116.4, 120.4, 128.1, 129.2, 129.5, 136.3, 138.5, 140.8, 145.5, 151.5.

HRMS (ESI): $m/z$ calcd for C$_{17}$H$_{21}$N$_4$O: 297.1710; found: 297.1706 [M+H]$^+$.

$N$-(4-Chlorophenyl)-2-(hydroxyimino)-$N'$-($p$-tolyl)propanehydrazonamide (1ag).

Et$_3$N (2.1 mL, 15 mmol) was added to a magnetically stirred solution of 2-oxo-$N$-($p$-tolyl)propanehydrazonoyl chloride (1.13 g, 5 mmol) in MeOH (35 mL) at 0°C. Then $p$-chloroaniline (0.64 g, 5 mmol) was added in one portion. The reaction was left stirring for 1 h at 0-5°C and for 24 h at 20°C. Hydroxylamine hydrochloride (0.35 g, 5 mmol) was added to the resulted mixture and then stirred for 24 h. Then the reaction mixture was poured into H$_2$O (100 mL), the precipitate formed was filtered off and recrystallized from EtOH to afford pure oxime 1ag.

Yield 1.30 g (59%). White solid. M.p. 172-174°C (EtOH).

$^1$H NMR (300 MHz, DMSO-d$_6$): δ = 2.14 (s, 3H), 2.23 (s, 3H), 6.58 (d, $J = 8.4$ Hz, 2H), 7.01-7.11 (m, 4H), 7.18 (d, $J = 8.4$ Hz, 2H), 7.61 (s, 1H), 9.02 (s, 1H), 11.19 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): δ = 10.2, 20.2, 112.9, 116.9, 122.1, 127.8, 128.2, 129.2, 134.5, 142.3, 142.7, 151.0.

HRMS (ESI): $m/z$ calcd for C$_{16}$H$_{18}$ClN$_4$O: 317.1164; found: 317.1157 [M+H]$^+$.
1,2-Diphenyl-2-(2-phenylhydrazinylidene)ethan-1-one oxime (1ah).

This compound was synthesized according to a previously reported procedure. All characterization data were consistent with those reported.

5,5-Dimethyl-2-(2-(p-tolyl)hydrazinylidene)cyclohexane-1,3-dione dioxime (1ai).

This compound was synthesized according to a previously reported procedure. All characterization data were consistent with those reported.

2-(Hydroxyimino)-5,5-dimethyl-3-(2-phenylhydrazinylidene)cyclohexan-1-one (1aj).

This compound was synthesized according to a previously reported procedure. All characterization data were consistent with those reported.

3-(Hydroxyimino)-4-(2-phenylhydrazinylidene)dihydrofuran-2(3H)-one (1ak).

This compound was synthesized according to a previously reported procedure. All characterization data were consistent with those reported.

4-(Hydroxyimino)-3-(2-(p-tolyl)hydrazinylidene)dihydrofuran-2(3H)-one (1al).

This compound was synthesized according to a previously reported procedure.

Yield 0.91 g (78%). Light yellow solid. M.p. 183-185°C.

$^1$H NMR (300 MHz, DMSO-d$_6$): δ = 2.30 (s, 3H), 5.05 (s, 2H), 7.23 (s, 4H), 11.64 (s, 1H), 12.27 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): δ = 20.9, 64.8, 115.4, 120.7, 130.6, 134.2, 139.9, 152.4, 166.2.
HRMS (ESI): \( m/z \) calcd for \( \text{C}_{15}\text{H}_{12}\text{N}_{3}\text{O}_{3} \): 234.0873; found: 234.0871 [M+H]+.

### S2.3. Electrochemical Synthesis of 1,2,3-Triazole 1-Oxides

General procedure for the synthesis of 1,2,3-triazole 1-oxides 2.

The electrolysis was performed in an undivided cell (50 mL vial) with graphite employed as anode and platinum as a cathode. Corresponding oxime (1 mmol) was dissolved in a solution of LiClO₄ in MeOH (0.1 M, 40 mL) and oxidized under constant current conditions \((j = 2.08 \text{ mA cm}^{-1})\) for 2.2-3.7 F/mol (TLC monitoring). After that, the reaction mixture was concentrated under reduced pressure, the crude residue was extracted with DCM (3x30 mL) and combined organic extracts were evaporated to afford target 1,2,3-triazole 1-oxide. To regenerate LiClO₄, the residue obtained after extraction with DCM was stirred in an additional amount of DCM (10 mL) at 30 °C for 1 h and filtered. The precipitate was recrystallized from 95% EtOH to furnish the regeneration of LiClO₄, which was used in further experiments.

**4-(Methoxycarbonyl)-2-(p-tolyl)-2H-1,2,3-triazole 1-oxide (2a)** was synthesized according to the general procedure in 2.2 F/mol.

Yield 221 mg (95%). Pale yellow powder. M.p. 104-105°C (MeOH).

IR (KBr): 3116, 1745, 1524, 1476, 1416, 1356, 1270, 1188, 1133, 996, 929, 825, 751 cm⁻¹.

\(^1\)H NMR (300 MHz, DMSO-d₆): \( \delta = 2.41 \text{ (s, 3H)}, 3.90 \text{ (s, 3H)}, 7.43 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, 7.71 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, 8.56 \text{ (s, 1H)}.\)

\(^13\)C NMR (75.5 MHz, DMSO-d₆): \( \delta = 21.3, 53.0, 118.2, 124.7, 130.2, 131.9, 136.8, 140.8, 159.8.\)

HRMS (ESI): \( m/z \) calcd for \( \text{C}_{11}\text{H}_{12}\text{N}_{3}\text{O}_{3} \): 234.0873; found: 234.0867 [M+H]+.

**4-(Methoxycarbonyl)-2-phenyl-2H-1,2,3-triazole 1-oxide (2b)** was synthesized according to the general procedure in 2.2 F/mol.

Yield 218 mg (96%). Pale yellow powder. M.p. 93-94°C (MeOH).
IR (KBr): 3112, 1747, 1482, 1417, 1347, 1251, 1192, 1128, 992, 815, 746 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta = 3.91\) (s, 3H), 7.60-7.68 (m, 3H), 7.84-7.88 (m, 2H), 8.58 (s, 1H).

\(^13\)C NMR (75.5 MHz, DMSO-\(d_6\)): \(\delta = 53.1, 118.3, 124.8, 129.8, 130.8, 134.3, 137.0, 159.8\).

HRMS (ESI): \(m/z\) calcd for C\(_{10}\)H\(_{10}\)N\(_3\)O\(_3\): 220.0716; found: 220.0711 [M+H\(^+\)].

**4-(Methoxycarbonyl)-2-(3-methylphenyl)-2\(H\)-1,2,3-triazole 1-oxide (2c)** was synthesized according to the general procedure in 2.3 F/mol.

Yield 219 mg (94%). Light brown powder. M.p. 89-90°C (MeOH).

IR (KBr): 3085, 1753, 1612, 1435, 1353, 1265, 1213, 1135, 1012, 753 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta = 2.42\) (s, 3H), 3.91 (s, 3H), 7.43 (d, \(J = 7.4\) Hz, 1H), 7.52 (t, \(J = 8.1\) Hz, 1H), 7.65 (s, 2H), 8.58 (s, 1H).

\(^13\)C NMR (75.5 MHz, DMSO-\(d_6\)): \(\delta = 21.2, 53.1, 118.3, 121.8, 125.0, 129.5, 131.4, 134.2, 136.9, 139.6, 159.8\).

HRMS (ESI): \(m/z\) [M+H\(^+\)] calcd for C\(_{11}\)H\(_{12}\)N\(_3\)O\(_3\): 234.0873; found: 234.0869.

**2-Mesityl-4-(methoxycarbonyl)-2\(H\)-1,2,3-triazole 1-oxide (2d)** was synthesized according to the general procedure in 2.3 F/mol.

Yield 240 mg (92%). Light yellow powder. M.p. 126-127°C (MeOH).

IR (KBr): 3107, 2954, 1741, 1522, 1482, 1422, 1191, 1144, 1088, 998, 931, 817, 756 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta = 1.95\) (s, 6H), 2.35 (s, 3H), 3.90 (s, 3H), 7.13 (s, 2H), 8.60 (s, 1H).

\(^13\)C NMR (75.5 MHz, DMSO-\(d_6\)): \(\delta = 17.2, 21.2, 53.0, 117.3, 129.5, 139.6, 159.8\).

HRMS (ESI): \(m/z\) [M+H\(^+\)] calcd for C\(_{13}\)H\(_{16}\)N\(_3\)O\(_3\): 262.1186; found: 262.1185.

**2-(2-Chlorophenyl)-4-(methoxycarbonyl)-2\(H\)-1,2,3-triazole 1-oxide (2e)** was synthesized according to the general procedure in 2.3 F/mol.

Yield 225 mg (89%). Light yellow solid. M.p. 120-121°C (MeOH).

IR (KBr): 3100, 2954, 1741, 1522, 1482, 1422, 1191, 1144, 1088, 998, 931, 817, 756 cm\(^{-1}\).
\[ \Delta H NMR (300 \text{ MHz}, \text{DMSO-}d_6): \delta = 3.92 \text{ (s, 3H), 7.62-7.67 (m, 1H), 7.73-7.79 (m, 1H), 7.81-7.86 (m, 1H),} \]
\[ 8.64 \text{ (s, 1H).} \]

\[ ^{13}\text{C NMR (75.5 MHz, DMSO-}d_6): \delta = 53.2, 117.1, 129.1, 130.9, 131.4, 131.5, 132.6, 134.4, 138.1, 159.7. \]

HRMS (ESI): \text{m/z calcd for C}_{10}\text{H}_{8}\text{ClN}_{3}\text{O}_{3}: 254.0327; \text{found: 254.0325 \text{[M+H]}^+.} \]

\text{2-(3-Chlorophenyl)-4-(methoxycarbonyl)-2H-1,2,3-triazole 1-oxide (2f) was synthesized according to the general procedure in 2.2 F/mol.}

\[
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{N} \quad \text{N}
\end{array}
\]

Yield 230 mg (91%). Light yellow solid. M.p. 112-113°C (MeOH).

IR (KBr): 3113, 1743, 1591, 1499, 1431, 1351, 1263, 1189, 1131, 991, 928, 868, 821, 777 cm\(^{-1}\).

\[ \Delta H NMR (300 \text{ MHz, DMSO-}d_6): \delta = 3.92 \text{ (s, 3H), 7.65-7.72 (m, 2H), 7.83-7.87 (m, 1H),} \]
\[ 8.02 \text{ (br s, 1H), 8.63 \text{ (s, 1H).} \}

\[ ^{13}\text{C NMR (75.5 MHz, DMSO-}d_6): \delta = 53.2, 118.5, 123.2, 124.3, 130.6, 131.5, 133.8, 135.2, 137.4, 159.7. \]

HRMS (ESI): \text{m/z calcd for C}_{10}\text{H}_{8}\text{ClN}_{3}\text{O}_{3}: 254.0327; \text{found: 254.0328 \text{[M+H]}^+.} \]

\text{2-(4-Chlorophenyl)-4-(methoxycarbonyl)-2H-1,2,3-triazole 1-oxide (2g) was synthesized according to the general procedure in 2.3 F/mol.}

\[
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{N} \quad \text{N}
\end{array}
\]

Yield 235 mg (93%). Pale yellow solid. M.p. 114-115°C (MeOH).

IR (KBr): 3122, 1751, 1488, 1243, 1191, 1092, 998, 830, 765 cm\(^{-1}\).

\[ \Delta H NMR (300 \text{ MHz, DMSO-}d_6): \delta = 3.91 \text{ (s, 3H), 7.71 (d, } J = 9.1 \text{ Hz, 2H), 7.91 (d, } J = 9.1 \text{ Hz, 2H), 8.61 (s,} \]
\[ 1.1 \text{H).} \]

\[ ^{13}\text{C NMR (75.5 MHz, DMSO-}d_6): \delta = 53.1, 118.4, 126.3, 129.8, 133.0, 135.2, 137.2, 159.7. \]

HRMS (ESI): \text{m/z calcd for C}_{10}\text{H}_{8}\text{ClN}_{3}\text{O}_{3}: 254.0327; \text{found: 254.0326 \text{[M+H]}^+.} \]

\text{2-(3,5-Dichlorophenyl)-4-(methoxycarbonyl)-2H-1,2,3-triazole 1-oxide (2h) was synthesized according to the general procedure in 2.3 F/mol.}

\[
\begin{array}{c}
\text{MeO}_2\text{C} \\
\text{N} \quad \text{N}
\end{array}
\]

Yield 235 mg (93%). Pale yellow solid. M.p. 112-113°C (MeOH).

IR (KBr): 3113, 1743, 1591, 1499, 1431, 1351, 1263, 1189, 1131, 991, 928, 868, 821, 777 cm\(^{-1}\).
Yield 270 mg (94%). Pale yellow solid. M.p. 171-172°C (CH₂Cl₂).

IR (KBr): 3106, 1753, 1585, 1528, 1487, 1436, 1346, 1271, 1187, 1144, 1004, 934, 858, 792, 740 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆): δ = 3.92 (s, 3H), 7.93 (t, J = 1.9 Hz, 1H), 8.01 (d, J = 1.9 Hz, 2H), 8.68 (s, 1H).

¹³C NMR (75.5 MHz, DMSO-d₆): δ = 53.2, 118.5, 123.0, 130.2, 135.7, 137.8, 159.5.

Calcd for C₁₀H₇ClN₃O₃ (%): C, 41.69; H, 2.45; N, 14.59. Found (%): C, 41.82; H, 2.33; N, 14.37.

2-(3-Chloro-4-fluorophenyl)-4-(methoxycarbonyl)-2H-1,2,3-triazole 1-oxide (2i) was synthesized according to the general procedure in 2.3 F/mol.

Yield 253 mg (93%). Pale yellow solid. M.p. 174-175°C (MeOH).

IR (KBr): 3140, 3104, 1734, 1500, 1411, 1364, 1273, 1191, 1122, 1068, 992, 928, 822, 760 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆): δ = 3.92 (s, 3H), 7.72 (t, J = 9.0 Hz, 1H), 7.87-7.93 (m, 1H), 8.19 (dd, J = 4.1, 2.5 Hz, 1H), 8.64 (s, 1H).

¹³C NMR (75.5 MHz, DMSO-d₆): δ = 52.5, 115.4 (d, J = 7.2 Hz), 116.6, 118.4 (d, J = 22.5 Hz), 120.7 (d, J = 19.0 Hz), 124.2 (d, J = 1.7 Hz), 140.3 (d, J = 2.7 Hz), 144.5, 154.3 (d, J = 242.6 Hz), 159.6.

Calcd for C₁₀H₇ClFN₃O₃ (%): C, 44.22; H, 2.60; N, 15.47. Found (%): C, 44.38; H, 2.47; N, 15.29.

2-(4-Fluorophenyl)-4-(methoxycarbonyl)-2H-1,2,3-triazole 1-oxide (2j) was synthesized according to the general procedure in 2.3 F/mol.

Yield 218 mg (92%). Pale grey solid. M.p. 86-87°C (MeOH).

IR (KBr): 3155, 1735, 1495, 1417, 1362, 1266, 1127, 996, 935, 839, 755 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆): δ = 3.91 (s, 3H), 7.49 (t, J = 8.9 Hz, 2H), 7.88-7.93 (m, 2H), 8.59 (s, 1H).

¹³C NMR (75.5 MHz, DMSO-d₆): δ = 53.1, 116.9 (d, J = 23.7 Hz), 118.2, 127.7 (d, J = 9.3 Hz), 130.5 (d, J = 3.3 Hz), 137.0, 159.8, 163.0 (d, J = 248.8 Hz).

¹⁹F NMR (282.4 MHz, DMSO-d₆): δ = -109.7.

2-(4-Bromophenyl)-4-(methoxycarbonyl)-2H-1,2,3-triazole 1-oxide (2k) was synthesized according to the general procedure in 2.3 F/mol.

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{N} \quad \text{N} \quad \text{O}^- \\
& \quad \text{Br} \\
\end{align*}
\]

Yield 259 mg (87%). Pale grey solid. M.p. 114-115°C (CH\textsubscript{2}Cl\textsubscript{2}).

IR (KBr): 3131, 3097, 1742, 1484, 1414, 1354, 1248, 1186, 1125, 1067, 996, 931, 825, 766 cm\textsuperscript{-1}.

\(^1\)H NMR (300 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 3.91 (s, 3H), 7.85 (br s, 4H), 8.60 (s, 1H).

\(^{13}\)C NMR (75.5 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 53.1, 118.4, 123.8, 126.5, 132.8, 133.5, 137.2, 159.7.

HRMS (ESI): \(m/z\) calcd for C\textsubscript{10}H\textsubscript{9}BrN\textsubscript{3}O\textsubscript{3}: 297.9822; found: 297.9821; calcd for C\textsubscript{10}H\textsubscript{8}BrN\textsubscript{3}O\textsubscript{3}: 299.9802; found: 299.9805 [M+H]\textsuperscript{+}.

4-(Methoxycarbonyl)-2-(4-methoxyphenyl)-2H-1,2,3-triazole 1-oxide (2l) was synthesized according to the general procedure in 2.3 F/mol.

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{N} \quad \text{N} \quad \text{O}^- \\
& \quad \text{OMe} \\
\end{align*}
\]

Yield 229 mg (92%). Pale grey solid. M.p. 124-125°C (CH\textsubscript{2}Cl\textsubscript{2}).

IR (KBr): 3140, 1758, 1590, 1506, 1438, 1358, 1258, 1188, 1134, 996, 935, 830, 769 cm\textsuperscript{-1}.

\(^1\)H NMR (300 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 3.85 (s, 3H), 3.90 (s, 3H), 7.15 (d, \(J = 9.1\) Hz, 2H), 7.73 (d, \(J = 9.1\) Hz, 2H), 8.53 (s, 1H).

\(^{13}\)C NMR (75.5 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ = 53.0, 56.2, 114.9, 117.9, 126.9, 127.1, 153.8, 159.9, 161.0.

HRMS (ESI): \(m/z\) calcd for C\textsubscript{11}H\textsubscript{12}N\textsubscript{3}O\textsubscript{4}: 250.0822; found: 250.0828 [M+H]\textsuperscript{+}.

2-(4-Ethoxyphenyl)-4-(methoxycarbonyl)-2H-1,2,3-triazole 1-oxide (2m) was synthesized according to the general procedure in 2.3 F/mol.

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{N} \quad \text{N} \quad \text{O}^- \\
& \quad \text{OEt} \\
\end{align*}
\]

Yield 246 mg (92%). Pale grey solid. M.p. 115-116°C (dec.).

IR (KBr): 3141, 3093, 1753, 1505, 1438, 1363, 1257, 1169, 1120, 1045, 1000, 930, 840, 757 cm\textsuperscript{-1}.
$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 1.37$ (t, $J = 7.0$ Hz, 3H), 3.90 (s, 3H), 4.13 (q, $J = 7.0$ Hz, 2H), 7.13 (d, $J = 9.2$ Hz, 2H), 7.71 (d, $J = 9.2$ Hz, 2H), 8.53 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 14.9$, 53.0, 64.2, 115.2, 117.9, 126.8, 126.9, 136.5, 159.9, 160.2.

HRMS (ESI): $m/z$ calcd for C$_{12}$H$_{14}$N$_3$O$_4$: 264.0979; found: 264.0978 [M+H]$^+$.  

2-(2-Nitrophenyl)-4-(methoxycarbonyl)-2$H$-1,2,3-triazole 1-oxide (2n) was synthesized according to the general procedure in 3.7 F/mol.  

Yield 232 mg (88%). Orange powder. M.p. 145°C; $T_d$ 212°C.

IR (KBr): 3144, 3096, 1745, 1609, 1537, 1473, 1428, 1353, 1260, 1191, 1133, 995, 930, 856, 817, 788, 740 cm$^{-1}$.  

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 3.70$ (s, 3H), 7.95-8.01 (m, 2H), 8.06-8.11 (m, 1H), 8.34-8.37 (m, 1H), 8.70 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 53.2$, 117.8, 125.6, 126.1, 130.3, 133.7, 135.9, 138.6, 144.4, 159.5.

HRMS (ESI): $m/z$ calcd for C$_{10}$H$_9$N$_4$O$_5$: 265.0567; found: 265.0568 [M+H]$^+$.  

2-(3-Nitrophenyl)-4-(methoxycarbonyl)-2$H$-1,2,3-triazole 1-oxide (2o) was synthesized according to the general procedure in 2.5 F/mol.  

Yield 230 mg (87%). Pale grey solid. M.p. 151°C (dec.)

IR (KBr): 3115, 1751, 1537, 1484, 1423, 1350, 1263, 1186, 1141, 1103, 1005, 937, 892, 816, 771, 724 cm$^{-1}$.  

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 3.93$ (s, 3H), 7.94 (t, $J = 8.2$ Hz, 1H), 8.35 (d, $J = 8.2$ Hz, 1H), 8.45 (d, $J = 8.2$ Hz, 1H), 8.70 (s, 1H), 8.80 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 53.2$, 117.8, 119.1, 125.1, 130.3, 131.5, 134.8, 137.7, 148.2, 159.6.

HRMS (ESI): $m/z$ calcd for C$_{10}$H$_9$N$_4$O$_5$: 265.0567; found: 265.0570 [M+H]$^+$.  

\[
\begin{align*}
\text{MeO}_2\text{C} & \quad \text{N} \quad \text{ MeO}_2\text{C} \\
\text{O}_2\text{N} & \quad \text{N} \quad \text{O}_2\text{N} \\
\end{align*}
\]
2-(4-Nitrophenyl)-4-(methoxycarbonyl)-2\(H\)-1,2,3-triazole 1-oxide (2p) was synthesized according to the general procedure in 2.5 F/mol.

\[
\begin{align*}
\text{MeO}_2C
\end{align*}
\]

Yield 240 mg (91%). Orange powder. M.p. 163°C; T\(\text{d}\) 242°C.

IR (KBr): 3106, 1751, 1596, 1524, 1437, 1347, 1251, 1185, 1111, 997, 853, 772, 747 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta = 3.93\) (s, 3H), 8.26 (d, \(J = 9.2\) Hz, 2H), 8.47 (d, \(J = 9.2\) Hz, 2H), 8.70 (s, 1H).

\(^{13}\)C NMR (75.5 MHz, DMSO-d\(_6\)): \(\delta = 53.2, 118.9, 124.3, 125.2, 138.0, 138.8, 147.6, 159.6\).

HRMS (ESI): \(m/z\) calcd for C\(_{10}\)H\(_{9}\)N\(\text{O}_4\): 265.0567; found: 265.0572 [M+H]\(^+\).

2-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1\(H\)-pyrazol-4-yl)-4-(methoxycarbonyl)-2\(H\)-1,2,3-triazole 1-oxide (2q) was synthesized according to the general procedure in 2.1 F/mol.

\[
\begin{align*}
\text{MeO}_2C
\end{align*}
\]

Yield 145 mg (44%). Dark orange solid. M.p. 186°C (dec.)

IR (KBr): 3468, 3104, 2926, 2853, 1737, 1670, 1492, 1420, 1276, 1218, 1127, 992, 929, 754 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta = 2.25\) (s, 3H), 3.35 (s, 3H), 3.90 (s, 3H), 7.39-7.49 (m, 3H), 7.58 (t, \(J = 7.6\) Hz, 2H), 8.53 (s, 1H).

\(^{13}\)C NMR (75.5 MHz, DMSO-d\(_6\)): \(\delta = 10.9, 34.9, 53.1, 100.3, 116.6, 126.7, 128.7, 129.9, 134.1, 137.8, 152.9, 159.3, 159.8\).

HRMS (ESI): \(m/z\) calcd for C\(_{15}\)H\(_{16}\)N\(\text{O}_4\): 330.1197; found: 330.1196 [M+H]\(^+\).

4-Methyl-2-phenyl-2\(H\)-1,2,3-triazole 1-oxide (2aa) was synthesized according to the general procedure in 2.1 F/mol.

\[
\begin{align*}
\text{MeO}_2C
\end{align*}
\]

Yield 140 mg (80%). M.p. 62-63°C (CH\(_2\)Cl\(_2\)).

IR (KBr): 3454, 3102, 1738, 1605, 1525, 1494, 1435, 1351, 1178, 1108, 943, 854 cm\(^{-1}\).

\(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta = 2.28\) (s, 3H), 7.48-7.60 (m, 3H), 7.81-7.84 (m, 2H), 7.88 (s, 1H).

\(^{13}\)C NMR (75.5 MHz, DMSO-d\(_6\)): \(\delta = 12.4, 117.1, 123.6, 129.4, 129.6, 135.1, 143.2\).

Calcd for C\(9\)H\(9\)N\(3\)O (%): C, 61.70; H, 5.18; N, 23.99. Found (%): C, 61.52; H, 5.31; N, 23.73.
2,4-Diphenyl-2H-1,2,3-triazole 1-oxide (2ab) was synthesized according to the general procedure in 2.1 F/mol. Yield 218 mg (92%). White solid. M.p. 88-89°C (CH₂Cl₂).

¹H NMR (300 MHz, DMSO-d₆): δ = 7.48-7.65 (m, 6H), 7.90-7.94 (m, 4H), 8.67 (s, 1H).

¹³C NMR (75.5 MHz, DMSO-d₆): δ = 115.1, 124.1, 125.9, 129.2, 129.5, 129.7, 129.8, 130.2, 135.0, 145.1.


4-(4-Nitrophenyl)-2-(p-tolyl)-2H-1,2,3-triazole 1-oxide (2ac) was synthesized according to the general procedure in 2.6 F/mol.

Yield 104 mg (35%). Beige solid. M.p. 142-143°C (CH₂Cl₂).

¹H NMR (300 MHz, DMSO-d₆): δ = 2.41 (s, 3H), 7.43 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 9.1 Hz, 2H), 8.36 (d, J = 7.9 Hz, 2H), 8.79 (s, 1H).

¹³C NMR (75.5 MHz, DMSO-d₆): δ = 21.3, 115.7, 124.2, 124.8, 126.9, 130.1, 132.3, 135.4, 140.1, 142.7, 148.2.


4-Nitro-2-(p-tolyl)-2H-1,2,3-triazole 1-oxide (2ad) was synthesized according to the general procedure in 2.6 F/mol.

Yield 158 mg (72%). Beige solid. M.p. 126-127°C (CH₂Cl₂).

IR (KBr): 3152, 1566, 1519, 1489, 1436, 1365, 1329, 1194, 1136, 982, 831, 755 cm⁻¹.

¹H NMR (300 MHz, DMSO-d₆): δ = 7.47 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 9.12 (s, 1H).

¹³C NMR (75.5 MHz, DMSO-d₆): δ = 21.4, 113.6, 125.2, 130.3, 131.1, 141.7, 149.1.

HRMS (ESI): m/z calcd for C₉H₉N₄O₃: 221.0669; found: 221.0677 [M+H]⁺.
**4-Nitro-2-(4-nitrophenyl)-2H-1,2,3-triazole 1-oxide (2ae)** was synthesized according to the general procedure in 2.6 F/mol.

![Chemical structure of 2ae](attachment:image.png)

Yield 171 mg (68%). M.p. 132°C; Td 237 °C.

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 8.23$ (d, $J = 9.2$ Hz, 2H), 8.49 (d, $J = 9.2$ Hz, 2H), 9.26 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 114.3$, 125.3, 125.4, 138.1, 148.2, 150.0.

All characterization data were consistent with those previously reported.

**5-Methyl-2-(m-tolyl)-4-(p-tolylamino)-2H-1,2,3-triazole 1-oxide (2af)** was synthesized according to the general procedure in 2.1 F/mol.

![Chemical structure of 2af](attachment:image.png)

Yield 226 mg (77%). Light grey solid. M.p. 130-132°C (CH$_2$Cl$_2$).

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 2.24$ (s, 6H), 2.39 (s, 3H), 7.10 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 1H), 7.40-7.46 (m, 3H), 7.62-7.65 (m, 2H), 8.60 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 7.8$, 20.8, 21.5, 115.0, 117.2, 120.0, 123.1, 128.8, 129.3, 129.5, 129.8, 136.3, 139.0, 139.4, 145.6.

HRMS (ESI): $m/z$ calcd for C$_{17}$H$_{19}$N$_4$O: 295.1553; found: 295.1554 [M+H]$^+$.  

**5-Methyl-2-(m-tolyl)-4-(p-tolylamino)-2H-1,2,3-triazole 1-oxide (2ag)** was synthesized according to the general procedure in 2.1 F/mol.

![Chemical structure of 2ag](attachment:image.png)

Yield 286 mg (91%). Grey solid. M.p. 100-101°C (CH$_2$Cl$_2$).

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 2.23$ (s, 3H), 2.37 (s, 3H), 7.31-7.36 (m, 4H), 7.56 (d, $J = 8.6$ Hz, 2H), 7.70 (d, $J = 8.1$ Hz, 2H), 8.87 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 7.8$, 21.2, 115.0, 118.4, 123.0, 124.1, 129.2, 129.9, 133.8, 138.0, 141.0, 144.9.

HRMS (ESI): $m/z$ calcd for C$_{16}$H$_{15}$ClN$_4$O: 315.1007; found: 315.0998 [M+H]$^+$.  


**2,4,5-Triphenyl-2H-1,2,3-triazole 1-oxide (2ah)** was synthesized according to the general procedure in 2.1 F/mol.

![Triphenyl-2H-1,2,3-triazole 1-oxide](image)

Yield 282 mg (90%). M.p. 143°C (dec.)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.41-7.52$ (m, 7H), 7.56-7.64 (m, 4H), 7.69-7.73 (m, 2H), 8.09-8.12 (m, 2H).

All characterization data were consistent with those previously reported.$^3$

**4-(Hydroximino)-6,6-dimethyl-2-(p-tolyl)-4,5,6,7-tetrahydro-2H-benzo[d][1,2,3]triazole 1-oxide (2ai)** was synthesized according to the general procedure in 2.1 F/mol.

![4-(Hydroximino)-6,6-dimethyl-2-(p-tolyl)-4,5,6,7-tetrahydro-2H-benzo[d][1,2,3]triazole 1-oxide](image)

Yield 266 mg (93%). Beige solid. M.p. 190°C (dec.)

IR (KBr): 3395, 3225, 2956, 2871, 1709, 1632, 1508, 1445, 1368, 1292, 1209, 1110, 986, 945, 815 cm$^{-1}$.

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 1.05$ (s, 6H), 2.39 (s, 3H), 2.57 (s, 2H), 2.60 (s, 2H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 8.2$ Hz, 2H), 11.63 (s, 1H).

$^{13}$C NMR (75.5 MHz, DMSO-d$_6$): $\delta = 21.2, 28.3, 32.0, 36.5, 123.8, 126.1, 130.0, 132.9, 138.3, 139.6, 145.6$.

HRMS (ESI): $m/z$ calcd for C$_{15}$H$_{19}$N$_4$O$_2$: 287.1503; found: 287.1496 [M+H]$^+$.

**5,5-Dimethyl-7-oxo-2-phenyl-4,5,6,7-tetrahydro-2H-benzo[d][1,2,3]triazole 1-oxide (2aj)** was synthesized according to the general procedure in 2.1 F/mol.

![5,5-Dimethyl-7-oxo-2-phenyl-4,5,6,7-tetrahydro-2H-benzo[d][1,2,3]triazole 1-oxide](image)

Yield 244 mg (95%). Beige solid. M.p. 130-131°C (CH$_2$Cl$_2$).

$^1$H NMR (300 MHz, DMSO-d$_6$): $\delta = 1.11$ (s, 6H), 2.52 (s, 2H), 2.84 (s, 2H), 7.55-7.66 (m, 3H), 7.83-7.86 (m, 2H).

HRMS (ESI): $m/z$ calcd for C$_{14}$H$_{16}$N$_3$O$_2$: 258.1237; found: 258.1232 [M+H]$^+$.

All characterization data were consistent with those previously reported.$^8$

**6-Oxo-2-phenyl-2,6-dihydro-4H-furo[3,4-d][1,2,3]triazole 1-oxide (2ak)** was synthesized according to the general procedure in 2.1 F/mol.
Yield 111 mg (51%). Beige solid. M.p. 177°C (dec.)
IR (KBr): 2924, 1773, 1497, 1453, 1284, 1092, 1031, 1012, 970, 764 cm⁻¹.
¹H NMR (300 MHz, DMSO-d₆): δ = 5.52 (s, 2H), 7.60-7.70 (m, 3H), 7.83 (d, J = 8.1 Hz, 2H).
¹³C NMR (75.5 MHz, DMSO-d₆): δ = 66.0, 117.4, 124.7, 130.0, 131.0, 134.6, 157.2, 157.3.

5-(Hydroxymethyl)-4-(methoxycarbonyl)-2-(p-tolyl)-1,2,3-triazole 1-oxide (2al) was synthesized according to the general procedure in 2.1 F/mol.

Yield 150 mg (57%). Yellow solid. M.p. 194°C (dec.)
IR (KBr): 3437, 2925, 2854, 1734, 1637, 1517, 1444, 1360, 1296, 1175, 1072, 1023, 821 cm⁻¹.
¹H NMR (300 MHz, DMSO-d₆): δ = 2.41 (s, 3H), 3.93 (s, 3H), 4.67 (d, J = 5.7 Hz, 2H), 5.38 (t, J = 5.7 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H).
¹³C NMR (75.5 MHz, DMSO-d₆): δ = 21.3, 51.2, 53.0, 124.6, 129.5, 130.3, 131.9, 135.0, 140.8, 160.3.
Calcd for C₁₂H₁₃N₃O₄ (%): C, 54.75; H, 4.98; N, 15.96. Found (%): C, 54.58; H, 5.11; N, 15.68.

S2.4 NO release assay
The test molecule (0.1 mmol) was dissolved in DMSO (50 mL). 20 µL aliquot of the resulted solution was diluted with phosphate buffer solution (180 µL, pH 7.4, containing 2 µmol L-cysteine). The final concentration of the 1,2,3-triazole 1-oxide derivative was 2·10⁻⁴ M. The mixture was incubated at 37 °C for 1 h. 50 µL aliquot of the Griess reagent (prepared by mixing sulfanilamide (4 g), N-naphthylethylenediamine dihydrochloride (0.2 g) and 85% H₃PO₄ (10 mL) in distilled and deionized water (final volume 100 mL)) was added and incubated for 10 min at 37 °C. UV absorbance at 540 nm was measured using a Multiskan GO Microplate Photometer and calibrated using a standard curve prepared from standard solutions of NaNO₂ to give the nitrite concentration. All measurements were made in triplicate. No significant NO release was measured at the absence of L-cysteine.
S3. Computational Details

DFT calculations were performed within Gaussian09 package\textsuperscript{9} using B3LYP/6-311++(d,p) basis set. Solvation effects were taken into account using PCM model (solvent – MeOH, $\varepsilon=32.613$). Stationary points were located by the Hessian matrix calculations by the absence of the imaginary frequencies.

Standard oxidation potentials were calculated according to the following equation:

$$E^0 = -\Delta r G^0/nF - 4.44,$$

where $E^0$ – standard potential, $\Delta r G^0$ – standard Gibbs free energy of reduction, $n$ – number of electrons, $F$ – Faraday constant, 4.44 – absolute oxidation potential of the hydrogen electrode.

Hirshfeld atomic charges\textsuperscript{10} were calculated using MultiWFN software.\textsuperscript{11} Oxidized motif was determined by the difference between atomic charges for neutral molecule and oxidized molecule.

<table>
<thead>
<tr>
<th></th>
<th>Hirshfeld charge for neutral molecule</th>
<th>Hirshfeld charge for oxidized molecule</th>
<th>$\Delta q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CON}^\text{N-H}^\text{p-Tol}$</td>
<td>0.050217</td>
<td>0.118442</td>
<td>0.068225</td>
</tr>
<tr>
<td>$\text{CO}_2\text{Me}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CON}^\text{N-H}^\text{Ph}$</td>
<td>0.00053</td>
<td>0.080933</td>
<td>0.080402</td>
</tr>
<tr>
<td></td>
<td>-0.03963</td>
<td>-0.02324</td>
<td>0.016397</td>
</tr>
<tr>
<td></td>
<td>0.03481</td>
<td>0.086551</td>
<td>0.051741</td>
</tr>
<tr>
<td></td>
<td>0.113815</td>
<td>0.136797</td>
<td>0.022982</td>
</tr>
<tr>
<td></td>
<td>-0.05652</td>
<td>-0.02721</td>
<td>0.029313</td>
</tr>
<tr>
<td></td>
<td>0.008537</td>
<td>0.093195</td>
<td>0.084658</td>
</tr>
<tr>
<td></td>
<td>0.106679</td>
<td>0.136539</td>
<td>0.02986</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>C</td>
<td>0.037661</td>
<td>0.109241</td>
<td>0.071579</td>
</tr>
<tr>
<td>N (double bonded)</td>
<td>-0.10479</td>
<td>-0.06011</td>
<td>0.044679</td>
</tr>
<tr>
<td>N (NH)</td>
<td>-0.02898</td>
<td>0.087697</td>
<td>0.116679</td>
</tr>
<tr>
<td>H</td>
<td>0.126254</td>
<td>0.164015</td>
<td>0.037761</td>
</tr>
<tr>
<td>C</td>
<td>0.070452</td>
<td>0.134284</td>
<td>0.063831</td>
</tr>
<tr>
<td>N (double bonded)</td>
<td>-0.09449</td>
<td>-0.07506</td>
<td>0.019433</td>
</tr>
<tr>
<td>N (NH, hydrazone)</td>
<td>-0.02648</td>
<td>0.066887</td>
<td>0.093368</td>
</tr>
<tr>
<td>H (hydrazone)</td>
<td>0.114228</td>
<td>0.160401</td>
<td>0.046173</td>
</tr>
<tr>
<td>N (NH, amide)</td>
<td>-0.10576</td>
<td>-0.02253</td>
<td>0.083229</td>
</tr>
<tr>
<td>H (amide)</td>
<td>0.107206</td>
<td>0.155722</td>
<td>0.048516</td>
</tr>
</tbody>
</table>
S4. CV curves

- Potential, V (vs Ag/AgCl)
- Current, µA

Graphs 1b, 2b, and blank showing CV curves.
S5. DSC data

Compound 2n reveals two endotherm prior to exothermic effect of thermolysis. The first endotherm (peak at 71°C) may correspond to the elimination of a solvent or phase transition of material. The second endotherm (onset 145°C) is apparently caused by melting of material. The latter peak is followed by the exothermic reaction of thermolysis, the overall heat effect is rather high, showing energetic potential of analyzed compound.

2o reveals thermal decomposition as a series of exothermic events. The initial dip of DSC curve is apparently melting of a starting compound (151°C)
Compound 2p melts at 163°C with subsequent decomposition (the extrapolated onset is 242°C, heat effect is 900 J g⁻¹).

Compound 2q reveals thermal decomposition, the extrapolated onset is 186°C at selected conditions.
Compound 2ae reveals a series of endothermic and exothermic events, the first of which corresponds to melting of the synthesized polymorph of the molecule. After melting, under further heating, compound decomposes with large heat release (1510 J g\(^{-1}\)).

![DSC graph with peaks at 132 °C and 237 °C.](image)

Compound 2ah reveals first endothermic event followed by exothermic one. Based only on DSC data one cannot firmly conclude is it melting or endothermic first stage of thermolysis. The net heat release is not large.

![DSC graph with peaks at 143 °C and 297 J/g.](image)

Compound 2ai decomposes after 190°C under selected heating program, large heat release signifies the energetic character of material. Weak thermal effects around 60°C and 114°C are also observed.
Compound 2ak melts at 177°C with subsequent thermal decomposition.

Compound 2al shows thermal decomposition with extrapolated onset of 194°C and large heat release (1920 J g⁻¹).
Onset*: 194 °C
Area: 1917 J/g
X-ray diffraction data were collected at 100K on a Bruker Quest D8 diffractometer equipped with a Photon-III area-detector (shutterless φ- and ω-scan technique), using graphite-monochromatized Mo Kα-radiation. The intensity data were integrated by the SAINT program\textsuperscript{12} and were corrected for absorption and decay using SADABS.\textsuperscript{13} The structure was solved by direct methods using SHELXT\textsuperscript{14} and refined on $F^2$ using SHELXL-2018.\textsuperscript{15} Positions of all atoms were found from the electron density-difference map. Atoms were refined with individual anisotropic (non-hydrogen atoms) or isotropic (hydrogen atoms) displacement parameters. The SHELXTL program suite\textsuperscript{12} was used for molecular graphics. The CCDC 2258313 contains all additional supporting information.

**Table S2.** Crystal data and structure refinement for 2ah.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C20 H15 N3 O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>313.35</td>
</tr>
<tr>
<td>Temperature</td>
<td>100.00 K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbca</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 19.9852(4) Å, b = 7.55810(10) Å, c = 20.2911(4) Å</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>3064.97(10) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.358 g/cm$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.086 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>1312</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.432 x 0.403 x 0.118 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.251 to 31.498°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-29&lt;=h&lt;=29, -10&lt;=k&lt;=11, -29&lt;=l&lt;=29</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>60450</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5095 [R(int) = 0.0562]</td>
</tr>
<tr>
<td>Observed reflections</td>
<td>3933</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.8%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7463 and 0.6962</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5095 / 1 / 221</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.026</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0497, wR2 = 0.1196</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0687, wR2 = 0.1353</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.413 and -0.282 e.Å$^{-3}$</td>
</tr>
</tbody>
</table>
Table S3. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 x 10^3$) for 2ah. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)</td>
<td>7607(1)</td>
<td>7405(1)</td>
<td>7258(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>N(2)</td>
<td>7600(1)</td>
<td>7022(2)</td>
<td>6598(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>N(3)</td>
<td>6974(1)</td>
<td>6771(1)</td>
<td>6376(1)</td>
<td>20(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>6576(1)</td>
<td>6958(2)</td>
<td>6902(1)</td>
<td>17(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>6961(1)</td>
<td>7343(2)</td>
<td>7468(1)</td>
<td>18(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>6803(1)</td>
<td>7527(2)</td>
<td>8170(1)</td>
<td>18(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>6336(1)</td>
<td>6404(2)</td>
<td>8465(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>6209(1)</td>
<td>6530(2)</td>
<td>9137(1)</td>
<td>31(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>6545(1)</td>
<td>7749(2)</td>
<td>9522(1)</td>
<td>35(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>7012(1)</td>
<td>8861(2)</td>
<td>9232(1)</td>
<td>32(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>7140(1)</td>
<td>8759(2)</td>
<td>8561(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>5846(1)</td>
<td>6823(2)</td>
<td>6822(1)</td>
<td>18(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>5580(1)</td>
<td>5836(2)</td>
<td>6301(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>4892(1)</td>
<td>5751(2)</td>
<td>6206(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>4461(1)</td>
<td>6641(2)</td>
<td>6630(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>4722(1)</td>
<td>7615(2)</td>
<td>7151(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>C(17)</td>
<td>5410(1)</td>
<td>7713(2)</td>
<td>7247(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(18)</td>
<td>8180(1)</td>
<td>6938(2)</td>
<td>6192(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(19)</td>
<td>8770(1)</td>
<td>6215(2)</td>
<td>6436(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>C(20)</td>
<td>9324(1)</td>
<td>6122(2)</td>
<td>6022(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>9284(1)</td>
<td>6730(2)</td>
<td>5377(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(22)</td>
<td>8688(1)</td>
<td>7423(2)</td>
<td>5140(1)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(23)</td>
<td>8131(1)</td>
<td>7546(2)</td>
<td>5548(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>8142(1)</td>
<td>7724(2)</td>
<td>7569(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>O(1A)</td>
<td>6843(4)</td>
<td>6507(13)</td>
<td>5778(2)</td>
<td>24(1)</td>
</tr>
</tbody>
</table>
Table S4. Bond lengths [Å] and angles [°] for 2ah.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-N(2)</td>
<td>1.3715(14)</td>
</tr>
<tr>
<td>N(1)-C(5)</td>
<td>1.3603(15)</td>
</tr>
<tr>
<td>N(1)-O(1)</td>
<td>1.2635(13)</td>
</tr>
<tr>
<td>N(2)-N(3)</td>
<td>1.3427(14)</td>
</tr>
<tr>
<td>N(2)-C(18)</td>
<td>1.4234(15)</td>
</tr>
<tr>
<td>N(3)-C(4)</td>
<td>1.3379(16)</td>
</tr>
<tr>
<td>N(3)-O(1A)</td>
<td>1.257(3)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.4108(16)</td>
</tr>
<tr>
<td>C(4)-C(12)</td>
<td>1.4735(16)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.4662(17)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.3968(17)</td>
</tr>
<tr>
<td>C(6)-C(11)</td>
<td>1.3961(18)</td>
</tr>
<tr>
<td>C(7)-H(7)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.3901(19)</td>
</tr>
<tr>
<td>C(8)-H(8)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.383(2)</td>
</tr>
<tr>
<td>C(9)-H(9)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(9)-C(10)</td>
<td>1.386(2)</td>
</tr>
<tr>
<td>C(10)-H(10)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(10)-C(11)</td>
<td>1.3879(19)</td>
</tr>
<tr>
<td>C(11)-H(11)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(12)-C(13)</td>
<td>1.3989(17)</td>
</tr>
<tr>
<td>C(12)-C(17)</td>
<td>1.3967(17)</td>
</tr>
<tr>
<td>C(13)-H(13)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(13)-C(14)</td>
<td>1.3898(18)</td>
</tr>
<tr>
<td>C(14)-H(14)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(14)-C(15)</td>
<td>1.3913(19)</td>
</tr>
<tr>
<td>C(15)-H(15)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(15)-C(16)</td>
<td>1.3901(19)</td>
</tr>
<tr>
<td>C(16)-H(16)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(16)-C(17)</td>
<td>1.3917(17)</td>
</tr>
<tr>
<td>C(17)-H(17)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(18)-C(19)</td>
<td>1.3902(17)</td>
</tr>
<tr>
<td>C(18)-C(23)</td>
<td>1.3896(17)</td>
</tr>
<tr>
<td>C(19)-H(19)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(19)-C(20)</td>
<td>1.3911(18)</td>
</tr>
<tr>
<td>C(20)-H(20)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(20)-C(21)</td>
<td>1.389(2)</td>
</tr>
<tr>
<td>C(21)-H(21)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(21)-C(22)</td>
<td>1.3884(19)</td>
</tr>
<tr>
<td>Bond</td>
<td>Length (Å)</td>
</tr>
<tr>
<td>----------------------</td>
<td>------------</td>
</tr>
<tr>
<td>C(22)-H(22)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(22)-C(23)</td>
<td>1.3896(18)</td>
</tr>
<tr>
<td>C(23)-H(23)</td>
<td>0.9500</td>
</tr>
<tr>
<td>C(5)-N(1)-N(2)</td>
<td>106.70(9)</td>
</tr>
<tr>
<td>O(1)-N(1)-N(2)</td>
<td>122.52(10)</td>
</tr>
<tr>
<td>O(1)-N(1)-C(5)</td>
<td>130.78(11)</td>
</tr>
<tr>
<td>N(1)-N(2)-C(18)</td>
<td>124.45(10)</td>
</tr>
<tr>
<td>N(3)-N(2)-N(1)</td>
<td>111.52(9)</td>
</tr>
<tr>
<td>N(3)-N(2)-C(18)</td>
<td>124.01(10)</td>
</tr>
<tr>
<td>C(4)-N(3)-N(2)</td>
<td>105.74(10)</td>
</tr>
<tr>
<td>O(1A)-N(3)-N(2)</td>
<td>122.7(4)</td>
</tr>
<tr>
<td>O(1A)-N(3)-C(4)</td>
<td>131.5(4)</td>
</tr>
<tr>
<td>N(3)-C(4)-C(5)</td>
<td>110.30(10)</td>
</tr>
<tr>
<td>N(3)-C(4)-C(12)</td>
<td>119.54(11)</td>
</tr>
<tr>
<td>C(5)-C(4)-C(12)</td>
<td>130.12(11)</td>
</tr>
<tr>
<td>N(1)-C(5)-C(4)</td>
<td>105.71(10)</td>
</tr>
<tr>
<td>N(1)-C(5)-C(6)</td>
<td>120.28(10)</td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)</td>
<td>133.82(11)</td>
</tr>
<tr>
<td>C(7)-C(6)-C(5)</td>
<td>120.16(11)</td>
</tr>
<tr>
<td>C(11)-C(6)-C(5)</td>
<td>120.81(11)</td>
</tr>
<tr>
<td>C(11)-C(6)-C(7)</td>
<td>118.95(12)</td>
</tr>
<tr>
<td>C(6)-C(7)-H(7)</td>
<td>120.0</td>
</tr>
<tr>
<td>C(8)-C(7)-C(6)</td>
<td>120.05(13)</td>
</tr>
<tr>
<td>C(8)-C(7)-H(7)</td>
<td>120.0</td>
</tr>
<tr>
<td>C(7)-C(8)-H(8)</td>
<td>119.6</td>
</tr>
<tr>
<td>C(9)-C(8)-C(7)</td>
<td>120.74(14)</td>
</tr>
<tr>
<td>C(9)-C(8)-H(8)</td>
<td>119.6</td>
</tr>
<tr>
<td>C(8)-C(9)-H(9)</td>
<td>120.3</td>
</tr>
<tr>
<td>C(8)-C(9)-C(10)</td>
<td>119.40(13)</td>
</tr>
<tr>
<td>C(10)-C(9)-H(9)</td>
<td>120.3</td>
</tr>
<tr>
<td>C(9)-C(10)-H(10)</td>
<td>119.8</td>
</tr>
<tr>
<td>C(9)-C(10)-C(11)</td>
<td>120.47(14)</td>
</tr>
<tr>
<td>C(11)-C(10)-H(10)</td>
<td>119.8</td>
</tr>
<tr>
<td>C(6)-C(11)-H(11)</td>
<td>119.8</td>
</tr>
<tr>
<td>C(10)-C(11)-C(6)</td>
<td>120.38(13)</td>
</tr>
<tr>
<td>C(10)-C(11)-H(11)</td>
<td>119.8</td>
</tr>
<tr>
<td>C(13)-C(12)-C(4)</td>
<td>119.77(11)</td>
</tr>
<tr>
<td>C(17)-C(12)-C(4)</td>
<td>121.03(11)</td>
</tr>
<tr>
<td>C(17)-C(12)-C(13)</td>
<td>119.16(11)</td>
</tr>
<tr>
<td>C(12)-C(13)-H(13)</td>
<td>119.9</td>
</tr>
<tr>
<td>C(14)-C(13)-C(12)</td>
<td>120.30(12)</td>
</tr>
</tbody>
</table>
C(14)-C(13)-H(13)  119.9
C(13)-C(14)-H(14)  119.8
C(13)-C(14)-C(15)  120.32(12)
C(15)-C(14)-H(14)  119.8
C(14)-C(15)-H(15)  120.2
C(16)-C(15)-C(14)  119.61(11)
C(16)-C(15)-H(15)  120.2
C(15)-C(16)-H(16)  119.8
C(15)-C(16)-C(17)  120.35(12)
C(17)-C(16)-H(16)  119.8
C(12)-C(17)-H(17)  119.9
C(16)-C(17)-C(12)  120.26(12)
C(16)-C(17)-H(17)  119.9
C(19)-C(18)-N(2)   120.17(11)
C(23)-C(18)-N(2)   118.14(11)
C(23)-C(18)-C(19)  121.67(12)
C(18)-C(19)-H(19)  120.7
C(18)-C(19)-C(20)  118.66(12)
C(20)-C(19)-H(19)  120.7
C(19)-C(20)-H(20)  119.8
C(21)-C(20)-C(19)  120.49(12)
C(21)-C(20)-H(20)  119.8
C(20)-C(21)-H(21)  120.0
C(22)-C(21)-C(20)  119.92(12)
C(22)-C(21)-H(21)  120.0
C(21)-C(22)-H(22)  119.7
C(21)-C(22)-C(23)  120.50(12)
C(23)-C(22)-H(22)  119.7
C(18)-C(23)-C(22)  118.75(12)
C(18)-C(23)-H(23)  120.6
C(22)-C(23)-H(23)  120.6

---------------------------------------------------------------
**Table S5.** Anisotropic displacement parameters (Å² x 10³) for 2ah. The anisotropic displacement factor exponent takes the form: -2π² [ h² a*² U₁₁ + ... + 2 h k a* b* U₁₂ ]

<table>
<thead>
<tr>
<th></th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₂₃</th>
<th>U₁₃</th>
<th>U₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)</td>
<td>15(1)</td>
<td>22(1)</td>
<td>19(1)</td>
<td>0(1)</td>
<td>-2(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>N(2)</td>
<td>14(1)</td>
<td>30(1)</td>
<td>19(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>N(3)</td>
<td>14(1)</td>
<td>24(1)</td>
<td>22(1)</td>
<td>0(1)</td>
<td>-2(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>15(1)</td>
<td>17(1)</td>
<td>21(1)</td>
<td>0(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>15(1)</td>
<td>17(1)</td>
<td>21(1)</td>
<td>1(1)</td>
<td>0(1)</td>
<td>-2(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>16(1)</td>
<td>18(1)</td>
<td>20(1)</td>
<td>2(1)</td>
<td>-1(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>19(1)</td>
<td>24(1)</td>
<td>26(1)</td>
<td>6(1)</td>
<td>0(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>22(1)</td>
<td>42(1)</td>
<td>29(1)</td>
<td>15(1)</td>
<td>4(1)</td>
<td>6(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>29(1)</td>
<td>55(1)</td>
<td>20(1)</td>
<td>3(1)</td>
<td>1(1)</td>
<td>15(1)</td>
</tr>
<tr>
<td>C(10)</td>
<td>30(1)</td>
<td>40(1)</td>
<td>26(1)</td>
<td>-9(1)</td>
<td>-5(1)</td>
<td>7(1)</td>
</tr>
<tr>
<td>C(11)</td>
<td>22(1)</td>
<td>24(1)</td>
<td>25(1)</td>
<td>-2(1)</td>
<td>-2(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(12)</td>
<td>15(1)</td>
<td>16(1)</td>
<td>22(1)</td>
<td>1(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>18(1)</td>
<td>21(1)</td>
<td>26(1)</td>
<td>-3(1)</td>
<td>-2(1)</td>
<td>0(1)</td>
</tr>
<tr>
<td>C(14)</td>
<td>20(1)</td>
<td>26(1)</td>
<td>28(1)</td>
<td>-2(1)</td>
<td>-6(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>C(15)</td>
<td>15(1)</td>
<td>26(1)</td>
<td>28(1)</td>
<td>6(1)</td>
<td>-2(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(16)</td>
<td>17(1)</td>
<td>21(1)</td>
<td>25(1)</td>
<td>4(1)</td>
<td>2(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(17)</td>
<td>18(1)</td>
<td>18(1)</td>
<td>21(1)</td>
<td>2(1)</td>
<td>-1(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(18)</td>
<td>16(1)</td>
<td>20(1)</td>
<td>22(1)</td>
<td>-2(1)</td>
<td>2(1)</td>
<td>-1(1)</td>
</tr>
<tr>
<td>C(19)</td>
<td>18(1)</td>
<td>21(1)</td>
<td>25(1)</td>
<td>2(1)</td>
<td>-1(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(20)</td>
<td>18(1)</td>
<td>24(1)</td>
<td>32(1)</td>
<td>-1(1)</td>
<td>1(1)</td>
<td>3(1)</td>
</tr>
<tr>
<td>C(21)</td>
<td>21(1)</td>
<td>26(1)</td>
<td>29(1)</td>
<td>-5(1)</td>
<td>6(1)</td>
<td>1(1)</td>
</tr>
<tr>
<td>C(22)</td>
<td>26(1)</td>
<td>29(1)</td>
<td>21(1)</td>
<td>-1(1)</td>
<td>3(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(23)</td>
<td>20(1)</td>
<td>28(1)</td>
<td>21(1)</td>
<td>-1(1)</td>
<td>-1(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>13(1)</td>
<td>35(1)</td>
<td>24(1)</td>
<td>-3(1)</td>
<td>-4(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>O(1A)</td>
<td>13(1)</td>
<td>35(1)</td>
<td>24(1)</td>
<td>-3(1)</td>
<td>-4(1)</td>
<td>-3(1)</td>
</tr>
</tbody>
</table>
**Table S6.** Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 2ah.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(7)</td>
<td>6104</td>
<td>5555</td>
<td>8206</td>
<td>28</td>
</tr>
<tr>
<td>H(8)</td>
<td>5887</td>
<td>5769</td>
<td>9333</td>
<td>37</td>
</tr>
<tr>
<td>H(9)</td>
<td>6458</td>
<td>7824</td>
<td>9981</td>
<td>42</td>
</tr>
<tr>
<td>H(10)</td>
<td>7245</td>
<td>9699</td>
<td>9495</td>
<td>38</td>
</tr>
<tr>
<td>H(11)</td>
<td>7459</td>
<td>9532</td>
<td>8367</td>
<td>29</td>
</tr>
<tr>
<td>H(13)</td>
<td>5872</td>
<td>5222</td>
<td>6010</td>
<td>26</td>
</tr>
<tr>
<td>H(14)</td>
<td>4716</td>
<td>5082</td>
<td>5850</td>
<td>29</td>
</tr>
<tr>
<td>H(15)</td>
<td>3991</td>
<td>6583</td>
<td>6563</td>
<td>28</td>
</tr>
<tr>
<td>H(16)</td>
<td>4429</td>
<td>8218</td>
<td>7443</td>
<td>25</td>
</tr>
<tr>
<td>H(17)</td>
<td>5585</td>
<td>8388</td>
<td>7602</td>
<td>23</td>
</tr>
<tr>
<td>H(19)</td>
<td>8794</td>
<td>5792</td>
<td>6876</td>
<td>26</td>
</tr>
<tr>
<td>H(20)</td>
<td>9731</td>
<td>5639</td>
<td>6181</td>
<td>30</td>
</tr>
<tr>
<td>H(21)</td>
<td>9666</td>
<td>6673</td>
<td>5098</td>
<td>30</td>
</tr>
<tr>
<td>H(22)</td>
<td>8660</td>
<td>7816</td>
<td>4696</td>
<td>30</td>
</tr>
<tr>
<td>H(23)</td>
<td>7724</td>
<td>8037</td>
<td>5389</td>
<td>27</td>
</tr>
<tr>
<td>Pair</td>
<td>Torsion Angle [°]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------------------</td>
<td>-------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-N(2)-N(3)-C(4)</td>
<td>-1.24(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-N(2)-N(3)-O(1A)</td>
<td>175.7(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-N(2)-C(18)-C(19)</td>
<td>38.48(18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-N(2)-C(18)-C(23)</td>
<td>-143.43(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-C(5)-C(6)-C(7)</td>
<td>-135.94(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1)-C(5)-C(6)-C(11)</td>
<td>40.82(17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-N(1)-C(5)-C(4)</td>
<td>-1.55(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-N(1)-C(5)-C(6)</td>
<td>174.14(10)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-N(3)-C(4)-C(5)</td>
<td>0.21(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-N(3)-C(4)-C(12)</td>
<td>177.86(10)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-C(18)-C(19)-C(20)</td>
<td>178.75(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2)-C(18)-C(23)-C(22)</td>
<td>-178.07(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-N(2)-C(18)-C(19)</td>
<td>-142.98(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-N(2)-C(18)-C(23)</td>
<td>35.11(18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-C(4)-C(5)-N(1)</td>
<td>0.86(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-C(4)-C(5)-C(6)</td>
<td>-173.97(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-C(4)-C(12)-C(13)</td>
<td>25.82(17)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(3)-C(4)-C(12)-C(17)</td>
<td>-152.02(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)-C(7)</td>
<td>38.3(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)-C(5)-C(6)-C(11)</td>
<td>-144.93(14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)-C(12)-C(13)-C(14)</td>
<td>-177.66(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(4)-C(12)-C(17)-C(16)</td>
<td>177.93(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)-N(1)-N(2)-N(3)</td>
<td>1.80(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)-N(1)-N(2)-C(18)</td>
<td>-179.51(11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)-C(4)-C(12)-C(13)</td>
<td>-157.06(13)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)-C(4)-C(12)-C(17)</td>
<td>25.10(19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)-C(6)-C(7)-C(8)</td>
<td>177.14(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(5)-C(6)-C(11)-C(10)</td>
<td>-176.67(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(6)-C(7)-C(8)-C(9)</td>
<td>-0.5(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(6)-C(11)-C(10)</td>
<td>0.13(19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(7)-C(8)-C(9)-C(10)</td>
<td>0.3(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(8)-C(9)-C(10)-C(11)</td>
<td>0.2(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(9)-C(10)-C(11)-C(6)</td>
<td>-0.4(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(11)-C(6)-C(7)-C(8)</td>
<td>0.32(19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(12)-C(4)-C(5)-N(1)</td>
<td>-176.47(12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(12)-C(4)-C(5)-C(6)</td>
<td>8.7(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(12)-C(13)-C(14)-C(15)</td>
<td>-0.2(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(13)-C(12)-C(17)-C(16)</td>
<td>0.08(18)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(13)-C(14)-C(15)-C(16)</td>
<td>-0.1(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(14)-C(15)-C(16)-C(17)</td>
<td>0.44(19)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table S8. Hydrogen bonds for Zab [Å and °].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C(23)-H(23)..O(1A)</td>
<td>0.95</td>
<td>2.25</td>
<td>2.732(9)</td>
<td>110.5</td>
</tr>
</tbody>
</table>
S7. References

4. Latvijas PSR Zinatnu Akademijas Vestis, 1959, # 7, p. 81,83, 84

S8. Copies of NMR Spectra
$^{1}$H NMR
DMSO-$d_6$
1a
$^{13}$C NMR
DMSO-d$_6$
$1^b$ H NMR
DMSO-d$_6$
NOH

\[
\begin{align*}
\text{CO}_2\text{Me} & \\
& \\
\text{N} & \\
\text{N} & \\
& \\
\text{NH} & \\
& \\
\text{NH} & \\
& \\
\text{N} & \\
\end{align*}
\]

1b

$^{13}$C NMR
DMSO-$d_6$
$^1$H NMR
DMSO-$d_6$
$^1$C NMR
DMSO-$d_6$
$^{1}$H NMR
DMSO-$d_6$

**1d**

Structure of compound 1d with chemical shifts and assignments.
$^{1}$H NMR
DMSO-d$_6$
$^{13}$C NMR
DMSO-\textit{d$_6$}
1f

$^1$H NMR
DMSO-d$_6$
$^{1}$H NMR
DMSO-$d_6$
\[ f_1 (\text{мд}) \]

- 164.48
- 144.85
- 141.76
- 139.95
- 127.73
- 123.55
- 116.75
- 52.56

\[ \text{N} \]
\[ \text{H} \]
\[ \text{N} \]
\[ \text{NH} \]
\[ \text{NOH} \]
\[ \text{Cl} \]

\[ 1g \]
\[ ^{13}\text{C NMR} \]
\[ \text{DMSO-d}_6 \]
$1h$

$^1H$ NMR
DMSO-$d_6$
\[
\text{HO} - N - C = O - O - CH_3
\]

1h

$^{13}$C NMR
DMSO-$d_6$
$^{1}H$ NMR
DMSO-$d_6$
1j

$^1$H NMR
DMSO-d$_6$
$^{13}$C NMR
DMSO-$d_6$
$1k$  
$^1$H NMR  
DMSO-$d_6$
$^{1}H$ NMR
DMSO-d$_6$
$^1$H NMR
DMSO-$d_6$
$1m$

$^{13}$C NMR
DMSO-$d_6$
$^{1}$H NMR
DMSO-$d_6$
$^{1}$H NMR
DMSO-$d_6$
\[ f_1 (\text{мд}) \]

\[ 52.71 \]

\[ 109.26 \]

\[ 117.99 \]

\[ 121.25 \]

\[ 125.02 \]

\[ 131.40 \]

\[ 144.10 \]

\[ 144.52 \]

\[ 149.10 \]

\[ 164.24 \]

\[ N \]

\[ H \]

\[ N \]

\[ CO_2Me \]

\[ NOH \]

\[ NO_2 \]

\[ 10 \]

\[ 13 \]

\[ C \]

\[ N \]

\[ Me \]

\[ DMSO-d_6 \]

\[ ^{13}\text{C NMR} \]
1p
\(^1\)H NMR
DMSO-d\(_6\)
\[ f_1 (\text{мд}) \]

\[ 13^\text{C} \text{ NMR} \]

DMSO-\(d_6\)
1q

$^1$H NMR

DMSO-d$_6$
1q

$^{13}$C NMR
DMSO-$d_6$
1ab
$^1$H NMR
DMSO-d$_6$
1ab

$^{13}$C NMR
DMSO-$d_6$
$^{1}$H NMR
DMSO-$d_6$
$^{13}$C NMR
DMSO-$d_6$
1af

$^1$H NMR

DMSO-$d_6$
1af
$^{13}$C NMR
DMSO-$d_6$
1ag

$^1$H NMR
DMSO-d$_6$
$^{13}$C NMR
DMSO-$d_6$
$^{1}$H NMR
DMSO-$_{d_6}$
$^{13}$C NMR
DMSO-$d_6$
$2a$

$^1$H NMR

DMSO-$d_6$
2a

$^{13}$C NMR
DMSO-$d_6$
**2b**

$^1$H NMR

DMSO-$d_6$
2b

$^1$H NMR
DMSO-$d_6$
$2c$

$^1$H NMR
DMSO-$d_6$
\[ f_1 (\text{\textmd{mD}}) \]

\[ \begin{align*}
2c \\
^{13}\text{C NMR} \\
\text{DMSO-d}_6
\end{align*} \]
$^{1}$H NMR
DMSO-$d_6$
$\text{2d}$

$^{13}$C NMR
DMSO-d$_6$
$^{1}$H NMR
DMSO-$d_6$
$^{13}$C NMR
DMSO-$d_6$
$^{1}$H NMR
DMSO-d$_6$
$^{13}$C NMR
DMSO-d$_6$
2g

$^1$H NMR
DMSO-d$_6$
$^{13}$C NMR
DMSO-$d_6$
2h

$^1$H NMR
DMSO-d$_6$
$^1\text{H NMR}$

DMSO-$d_6$
$2j$

$^1$H NMR

DMSO-$d_6$
2j

$^{13}$C NMR
DMSO-$d_6$
\[ N - O - F \]

**2j**

\[^{19}\text{F NMR)}\]

DMSO-\( d_6 \)
$2k$

$^{13}$C NMR
DMSO-$d_6$
$^{1}H$ NMR
DMSO-$d_6$
$^1\text{H NMR}$

DMSO-$d_6$
2m

$^1$H NMR

DMSO-$d_6$
$f_1 \text{ (мД)}$

2m

$^{13}$C NMR

DMSO-$d_6$
$2n$

$^1$H NMR
DMSO-$d_6$
\[ \text{\textsuperscript{13}C NMR} \]

DMSO-\textit{d}_6
$^{1}H$ NMR
DMSO-$d_6$
$^{13}$C NMR
DMSO-$d_6$
2q

$^1$H NMR
DMSO-$d_6$
$^1$H C NMR
DMSO-$d_6$
2aa
$^1$H NMR
DMSO-$d_6$
2aa

$^{13}$C NMR
DMSO-d$_6$
2ab
$^1$H NMR
DMSO-$d_6$
2ab
$^{13}$C NMR
DMSO-$d_6$
2ac
$^1$H NMR
DMSO-d$_6$
$\text{O}_2\text{N}$

$\text{O}_2\text{N}$

$\text{N}^+\text{N}^-$

$\text{C}_3\text{H}_2\text{O}^-$

$\text{N}^+\text{O}^-$

$\text{C}_2\text{H}_6\text{O}^-$

$\text{CH}_3$

$\text{2ac}$

$\text{C}^{13}\text{NMR}$

$\text{DMSO-d}_6$
$^{1}$H NMR
DMSO-$d_6$
2ad
$^{13}$C NMR
DMSO-d$_6$
\( f_1 (\text{мд}) \)

\( 1^\text{H} \text{NMR} \)

DMSO-\( d_6 \)

2ae
$\text{2ae}$

$^{13}\text{C NMR}$

DMSO-$d_6$
2af

$^1$H NMR
DMSO-$d_6$
2af

$^{13}$C NMR
DMSO-$d_6$
2ag

$^{13}$C NMR
DMSO-$d_6$
$f_1 (\text{мД})$

N
N
$\text{CH}_3$

Cl

$^1\text{C NMR}$

DMSO-$d_6$

$2\text{ag}$
2ah
$^1$H NMR
CDCl$_3$
2ai

$^1$H NMR
DMSO-$d_6$
$^{1}H$ NMR
DMSO-$d_6$
2ak
$^1$H NMR
DMSO-$d_6$
$^{13}$C NMR
DMSO-$d_6$
2al
$^1$H NMR
DMSO-$d_6$
$^\text{13}$C NMR
DMSO-$\text{d}_6$