Supplementary Material

An unusual rearrangement of pyrazole nitrene and ring opening/recyclization cascade: formal CH-acetoxylation and azide/amine conversion without external oxidants and reductants

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Experimental details, copies of NMR spectra, X-ray crystallographic data, computational details

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Experimental section

IR spectra were recorded as emulsion in vaseline oil (sample concentration 0.25%) on a Tensor 37 Vertex 70 RAM II spectrometer (Bruker Optik GmbH, Germany) in the range 400–4000 cm^{-1}; given are the most intense absorption bands. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 400 spectrometer (Bruker BioSpin, Rheinstetten, Germany) operating at 400 MHz (for ^{1}H NMR) and 101 MHz (for ^{13}C NMR) and on Brucker spectrometers AVANCE*III*-500 (Bruker BioSpin, Rheinstetten, Germany) operating at 500.1 MHz for ^{1}Hat 303 K and 126 MHz (for ^{13}C NMR). Chemical shifts were measured in δ (ppm) with reference to the solvent (δ = 7.27 ppm and 77.00 ppm for $CDCl_3$, δ = 2.06 ppm and 28.94 ppm for $(CD_3)_2CO$ for ^{1}H and ^{13}C NMR, respectively). Electrospray ionization (ESI) mass spectra were obtained on an Amazon X mass spectrometer from Bruker Daltonics (Bremen, Germany) with an ion trap. The measurements were carried out in the mode of recording negative ions in the m/z range from 100 to 2000. Elemental analysis was performed on a CHNS-O Elemental Analyser EuroEA3028-HT-OM (EuroVector S.p.A., Milan, Italy) with an accuracy ±0.4% for C, H, Cl and N. The melting point was determined in glass capillaries on a Stuart SMP 10 instrument (Keison Products, Chelmsford, UK). The progress of reactions and the purity of product were monitored by TLC on Sorbfil UV-254 plates (Sorbpolimer, Krasnodar, Russia); the chromatograms were developed under UV light.

5-Chloro-3-methyl-4-nitro-1-(4-nitrophenyl)-1*H*-pyrazole (3). Acetic anhydride (6 mL) was added to 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole **2** (0.44 g, 2.3 mmol), reaction mixture was cooled to 0 °C and then fuming nitric acid (97–99%, 4 mL) was added dropwise. Reaction mixture was stirred at room temperature for 4 h, then poured over crushed ice. The obtained precipitate was filtered off, washed with cold water (100 mL) and dried under vacuum (0.06 mm Hg) at 40 °C to constant weight. Crude product was recrystallized from acetone to give target compound. Yellow powder, yield 0.55 g (85%), m.p.: 148–150 °C. IR (*ν*, cm^{-1}): 1346 (NO_2 symm), 1530 (NO_2 asymm). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 2.64 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.7, 147.9, 141.7, 131.2, 128.2, 126.0, 125.0, 14.7. Anal. calcd (%) for $C_{10}H_7ClN_4O_4$: C, 42.50; H, 2.50; Cl, 12.54; N, 19.82. Found: C, 42.54; H, 2.48; Cl, 12.53; N, 19.85.

5-Azido-3-methyl-4-nitro-1-(4-nitrophenyl)-1*H*-pyrazole (4). To a solution of 5-chloro-3-methyl-4-nitro-1-(4-nitrophenyl)-1*H*-pyrazole **3** (0.50 g, 1.8 mmol) in acetone (5 mL) at room temperature was added a solution of sodium azide (0.15 g, 2.3 mmol) in 1 mL of water. The reaction mixture was stirred for 1 h (the reaction was monitored by thin layer chromatography, eluent: toluene – ethylacetate (2:1, v/v)). After completion of the reaction, the solvent was removed under reduced pressure, washed with cold water and dried in vacuum (0.06 mm Hg) at 40 °C to constant weight. Light brown powder, yield 0.45 g (86%), m.p.: 104–106 °C. IR (ν, cm^{-1}): 1349 (NO_2 symm), 1557 (NO_2 asymm), 2151 (N_3). ^{1}H NMR (500 MHz, Acetone-d_6): δ = 8.40–8.43 (m, 2H), 8.07–8.11 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ = 147.9, 147.6, 142.5, 138.5, 126.2, 125.2, 125.1, 14.4. Anal. calcd (%) for $C_{10}H_7N_7O_4$: C, 41.53; H, 2.44; N, 33.90. Found: C, 41.58; H, 2.47; N, 33.87.

Synthesis of compounds 5a-d (general method). 5-Azido-3-methyl-4-nitro-1-(4-nitrophenyl)-1*H*-pyrazole **4** (0.1 g, 0.34 mmol) was heated in 3 mL of acid/butanol at 118 °C for 5 h (for acetic acid) or 10 h (for propionic, butyric acids and butanol). Then solvent was removed under reduced pressure. In case of propionic, butyric acids and butanol crude product was purified by column chromatography on silica gel (eluent: toluene – ethylacetate (10:1, v/v)) to give the target compound (the side-product **6** was isolated in trace amount).

5-Amino-4-nitro-1-(4-nitrophenyl)-1*H*-pyrazol-3-yl)methyl acetate (5a). Gray pearlescent solid (0.08 g) was obtained in 78% yield. M.p.: 198–199 °C. IR (ν, cm^{-1}): 1346 (NO_2 symm), 1599 (NO_2 asymm), 1637 (CO), 1721 (C=O), 3408 (NH_2). ^{1}H NMR (400 MHz, Acetone-d_6): δ = 8.46 (d, *J* = 9.0 Hz, 2H), 7.99 (d, *J* = 9.0 Hz, 2H), 7.35 (br.s, 2H), 5.33 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ = 169.6, 147.1, 144.7, 142.3, 125.1, 124.9, 116.9, 58.7, 19.6. Anal. calcd (%) for $C_{12}H_{11}N_5O_6$: C, 44.87; H, 3.45; N, 21.80. Found: C, 44.83; H, 3.52; N, 21.85. ESI, m/z for $C_{12}H_{11}N_5O_6$: 319.99 $[M-H]^-$.

(5-Amino-4-nitro-1-(4-nitrophenyl)-1*H*-pyrazol-3-yl)methyl propionate (5b). Orange oil, yield 0.085 g (73%). IR (ν, cm^{-1}): 1347 (NO_2 symm), 1598 (NO_2 asymm), 1635 (CO), 1738 (C=O), 3430 (NH_2). ^1H NMR (400 MHz, Acetone-d_6): δ = 8.38–8.42 (m, 2H), 7.91–7.97 (m, 2H), 7.36 (br.s, 2H), 5.31 (s, 2H), 2.38 (q, *J* = 7.6 Hz, 2H), 1.11 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ = 173.9, 147.9, 145.7, 143.1, 125.9(4), 125.9(1), 125.6, 117.7, 59.5, 27.7, 9.4. Anal. calcd (%) for $C_{13}H_{13}N_5O_6$: C, 46.57; H, 3.91; N, 20.89. Found: C, 46.72; H, 4.02; N, 20.92. ESI, m/z for $C_{13}H_{13}N_5O_6$: 334.04 $[M-H]^-$.

(5-Amino-4-nitro-1-(4-nitrophenyl)-1*H*-pyrazol-3-yl)methyl butyrate (5c). Orange oil, yield 0.096 g (80%). IR (ν, cm^{-1}): 1347 (NO_2 symm), 1598 (NO_2 asymm), 1634 (CO), 1734 (C=O), 3434 (NH_2). ^1H NMR (600 MHz, Acetone-d_6): δ = 8.42–8.48 (m, 2H), 7.95–8.01 (m, 2H), 7.36 (br.s, 2H), 5.33 (s, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.65 (q, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, Acetone-d_6): δ = 173.1, 148.0, 147.9, 145.7, 143.2, 125.9(5), 125.8(9), 125.7, 59.4, 36.3, 19.1, 13.8. Anal. calcd (%) for $C_{14}H_{15}N_5O_6$: C, 48.14; H, 4.33; N, 20.05. Found: C, 48.20; H, 4.37; N, 20.01. ESI, m/z for $C_{14}H_{15}N_5O_6$: 348.05 $[M-H]^-$.

3-(Butoxymethyl)-4-nitro-1-(4-nitrophenyl)-1*H*-pyrazol-5-amine (5d). Orange oil, yield 0.075 g (68%). IR (ν, cm^{-1}): 1346 (NO_2 symm), 1598 (NO_2 asymm), 1634 (CO), 1702 (C=O), 3430 (NH_2). ^1H NMR (400 MHz, Acetone-d_6): δ = 8.41–8.45 (m, 2H), 7.94–7.99 (m, 2H), 7.29 (br.s, 2H), 4.68 (s, 2H), 3.59 (t, *J* = 6.5 Hz, 2H), 1.62–1.53 (m, 2H), 1.48–1.32 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6): δ = 147.9, 147.7(4), 147.6(8), 143.4, 125.9, 125.6, 117.9, 71.3, 65.9, 32.5, 19.9, 14.1. Anal. calcd (%) for $C_{14}H_{17}N_5O_5$: C, 50.15; H, 5.11; N, 20.89. Found: C, 50.23; H, 5.17; N, 20.82. ESI,) m/z for $C_{14}H_{17}N_5O_5$: 334.08 $[M-H]^-$.

NMR spectra of compounds

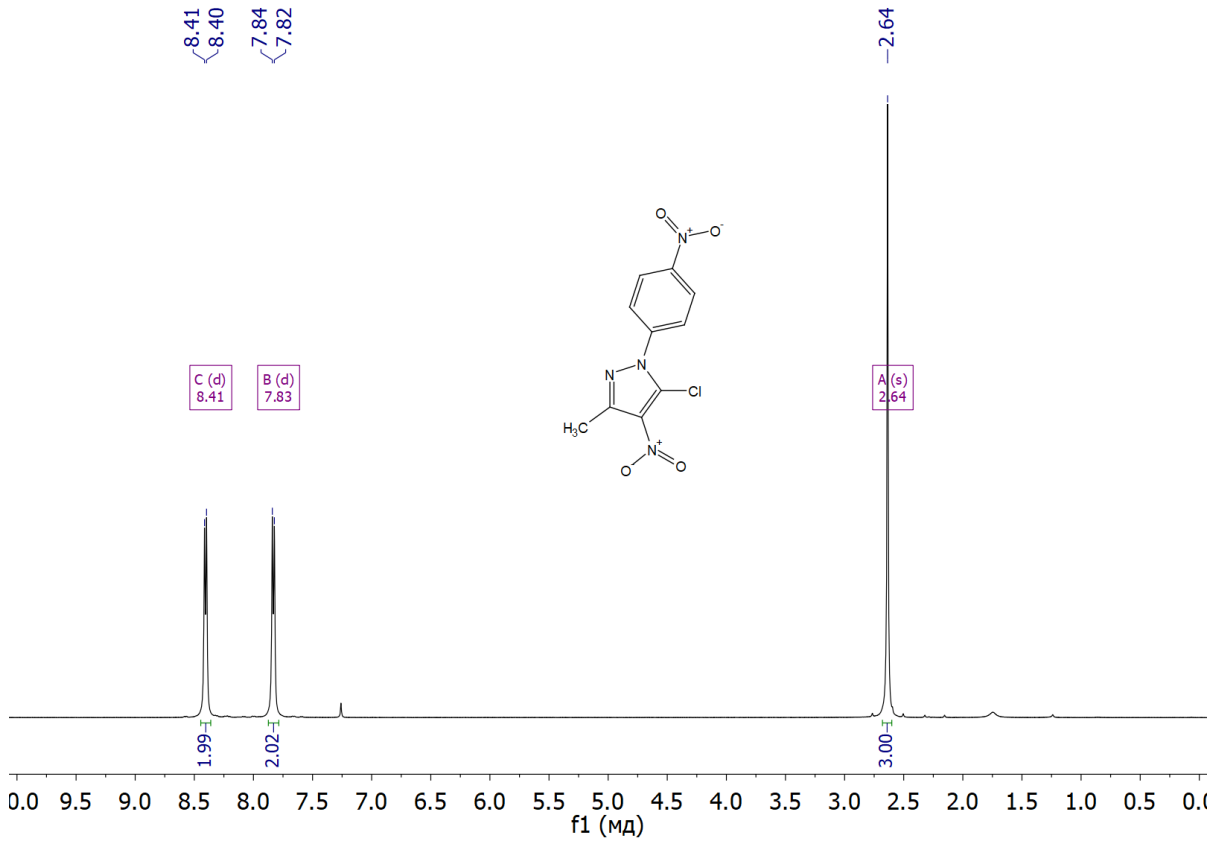


Figure S1: ^{1}H NMR spectrum of **3** ($CDCl_3$, 500 MHz)

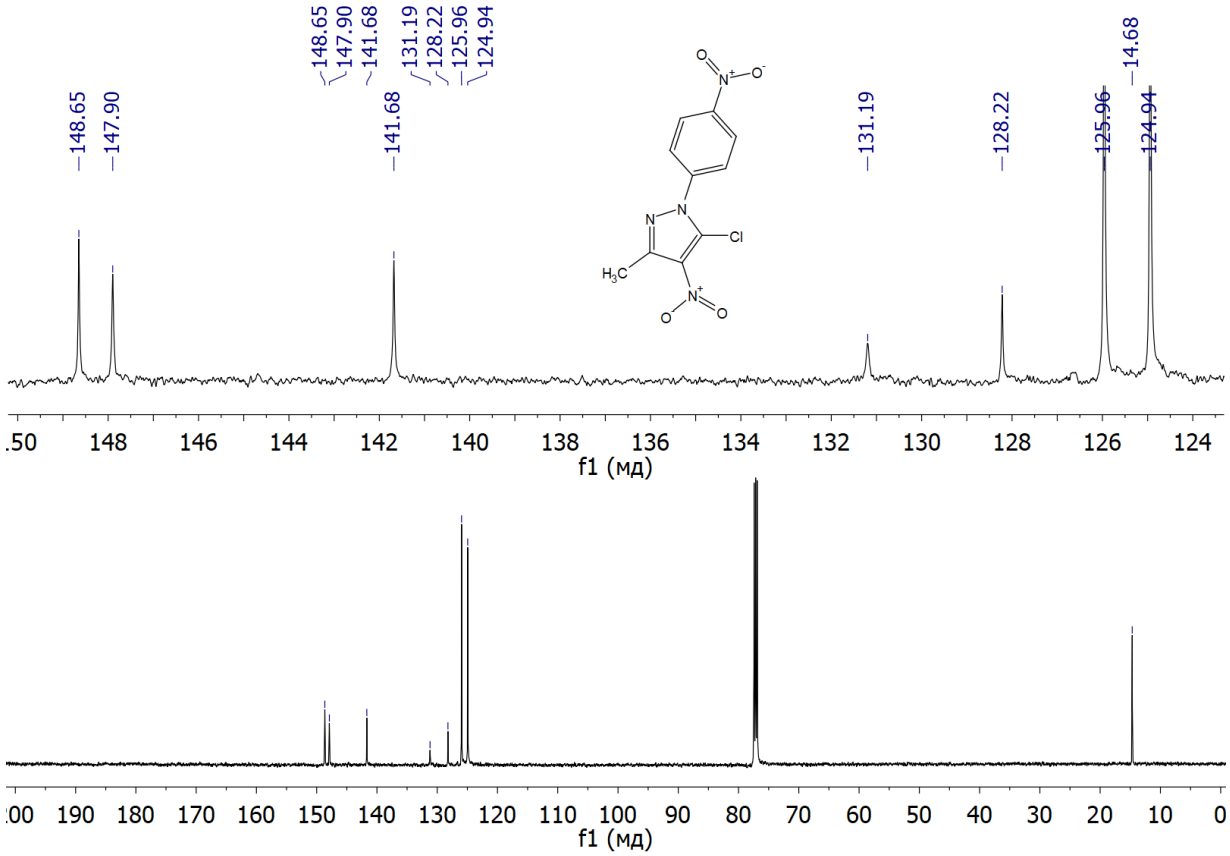


Figure S2: ^{13}C NMR spectrum of **3** ($CDCl_3$, 126 MHz)

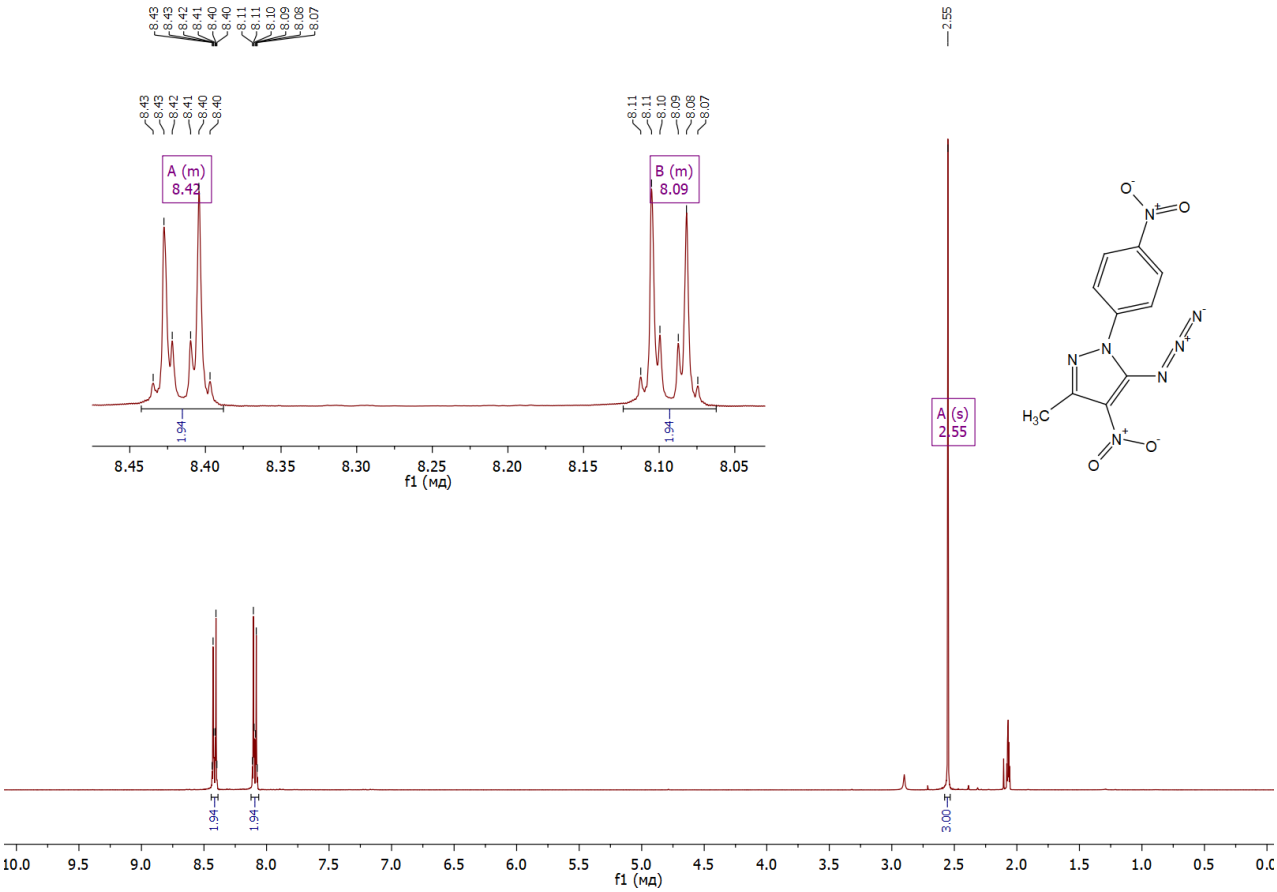


Figure S3: ^{1}H NMR spectrum of **4** (Acetone-d_6, 500 MHz)

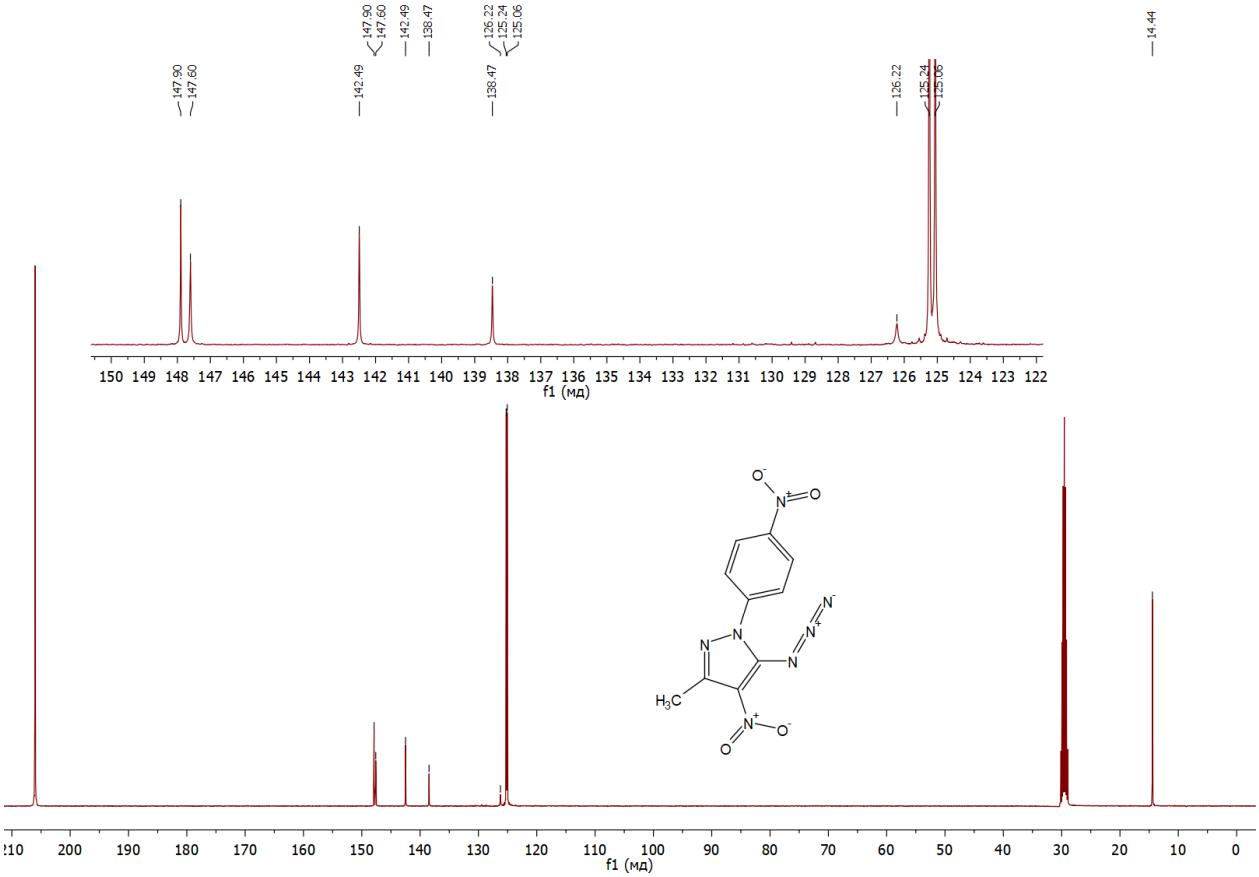


Figure S4: ^{13}C NMR spectrum of **4** (Acetone-d_6, 101 MHz)

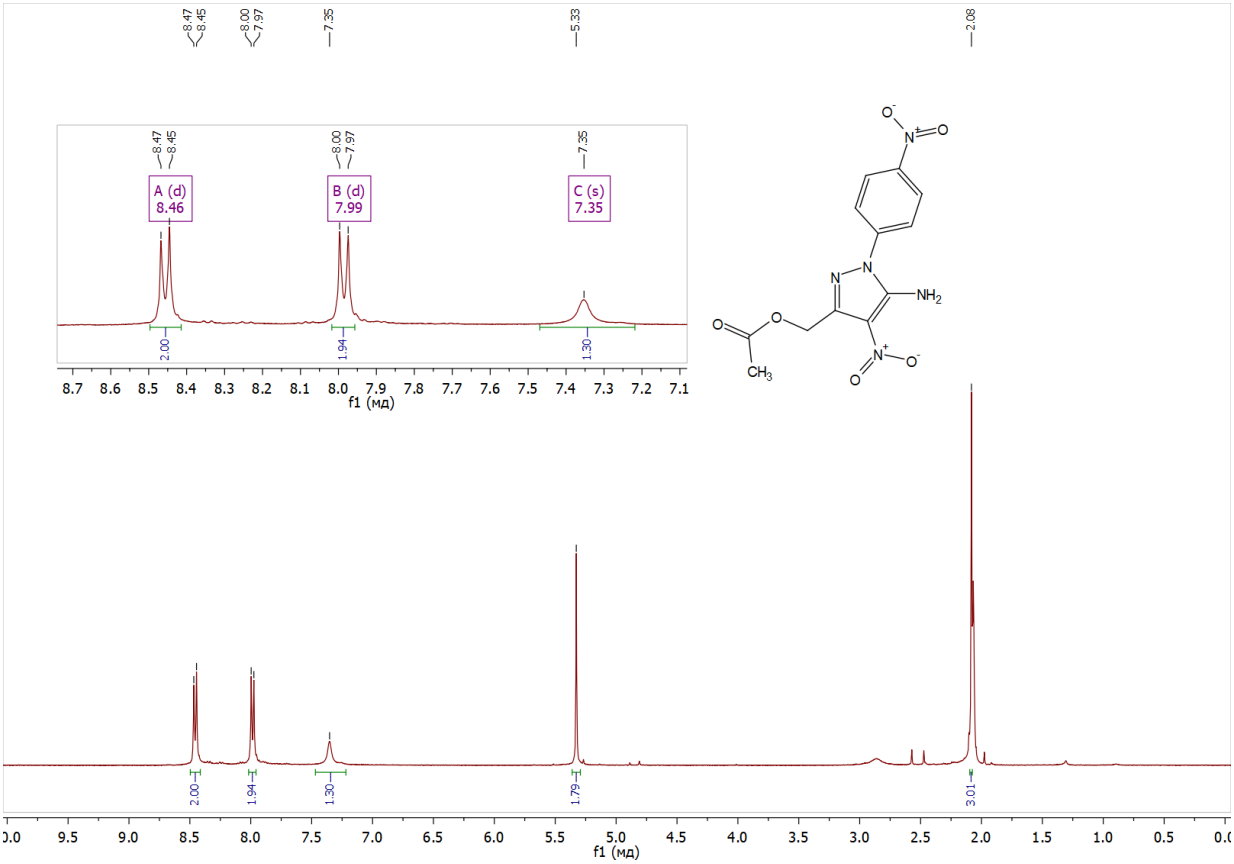


Figure S5: ^{1}H NMR spectrum of **5a** (Acetone-d_6, 400 MHz)

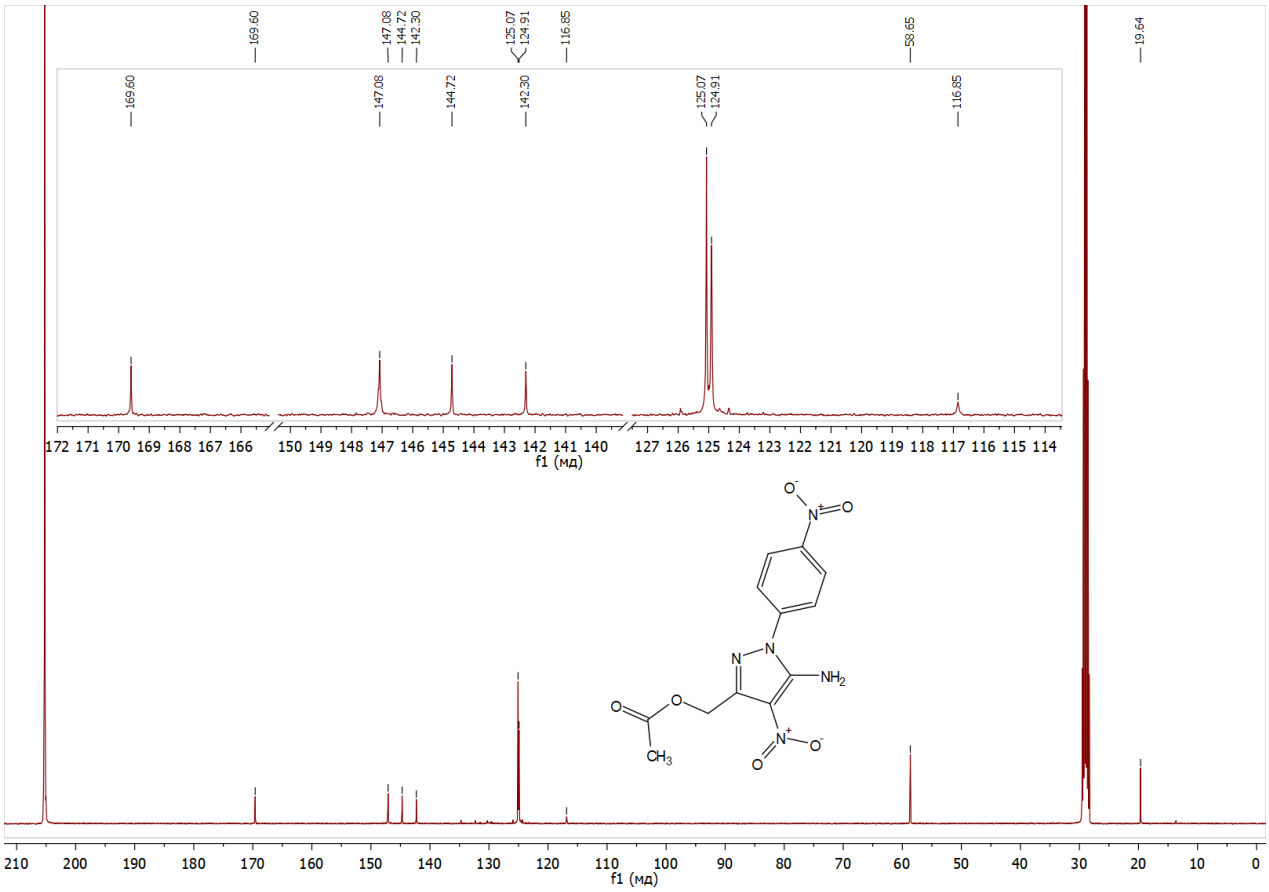


Figure S6: ^{13}C NMR spectrum of **5a** (Acetone-d_6, 101 MHz)

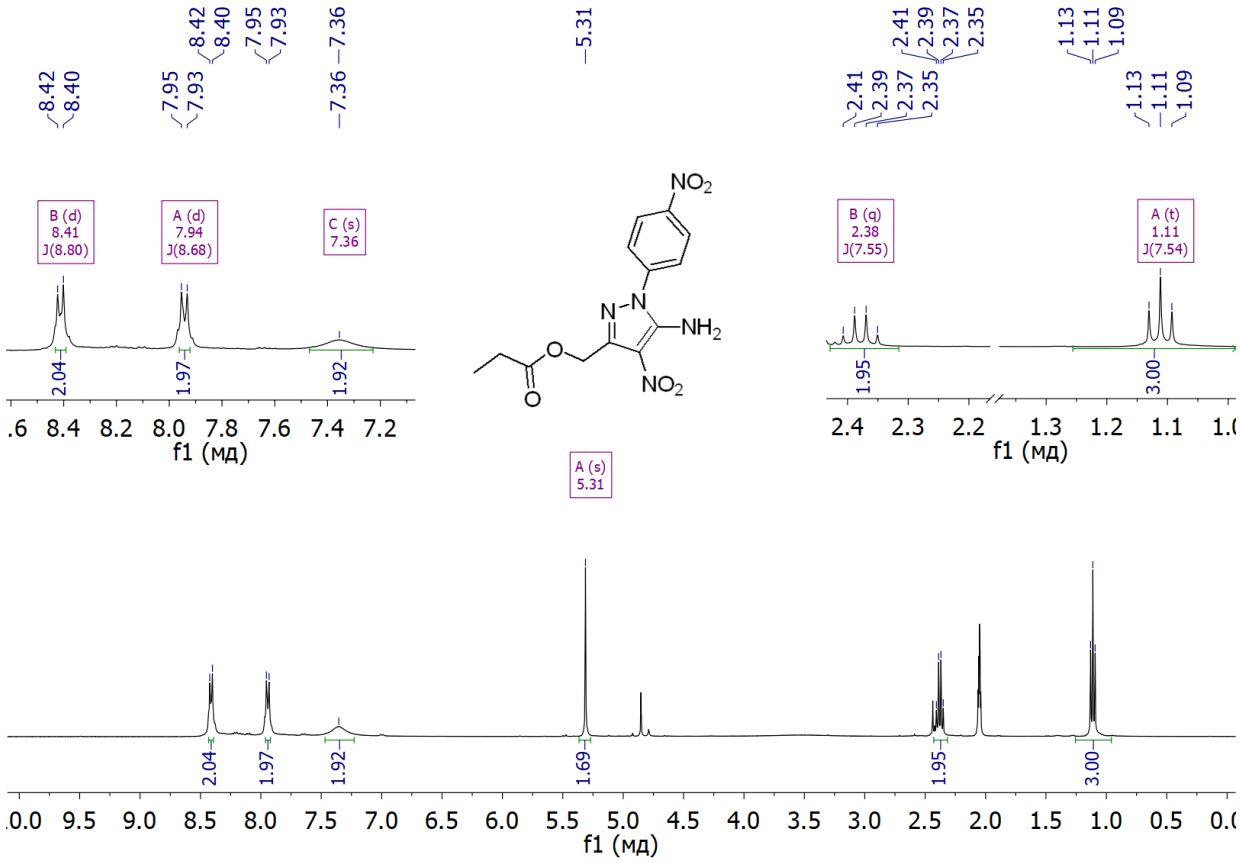


Figure S7: [1]H NMR spectrum of **5b** (Acetone-*d*6, 400 MHz)

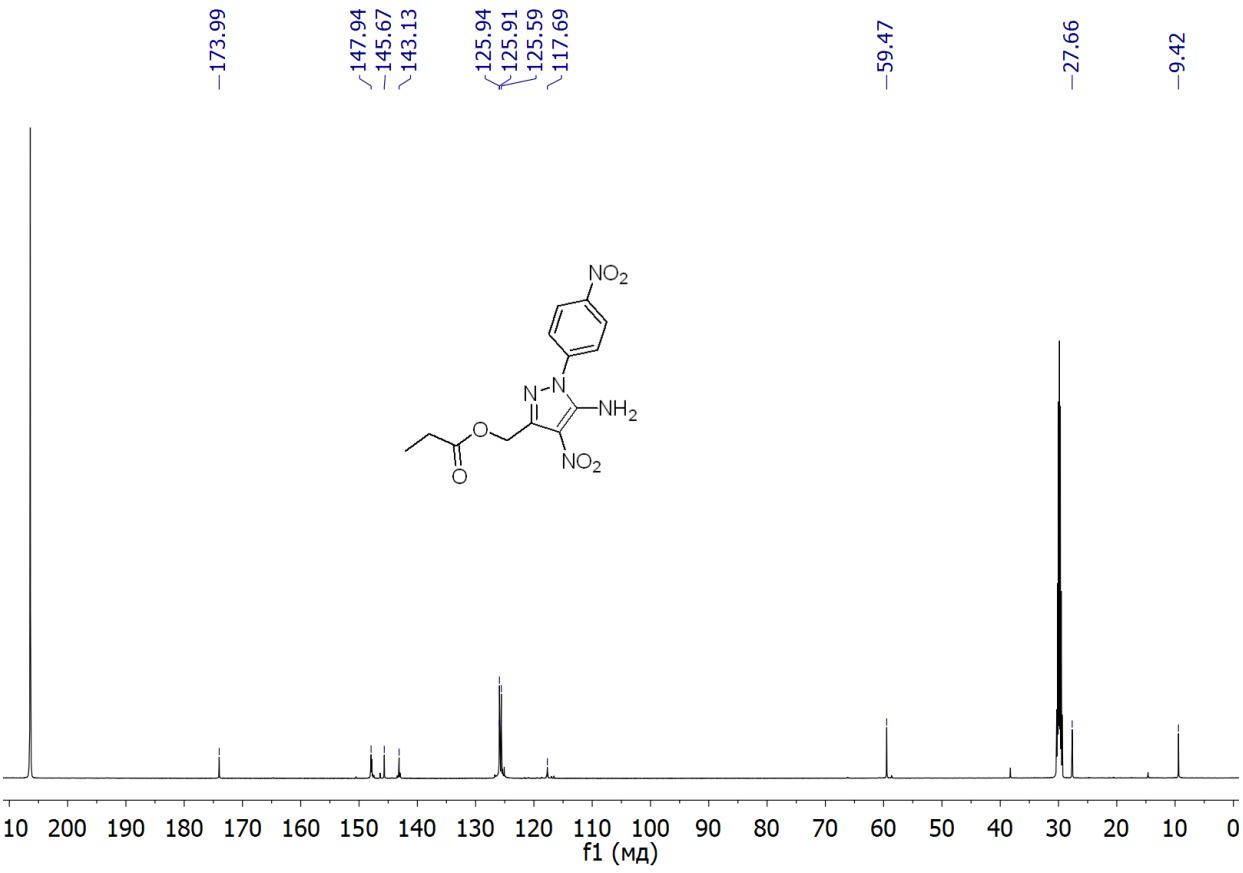


Figure S8: [13]C NMR spectrum of **5b** (Acetone-*d*6, 101 MHz)

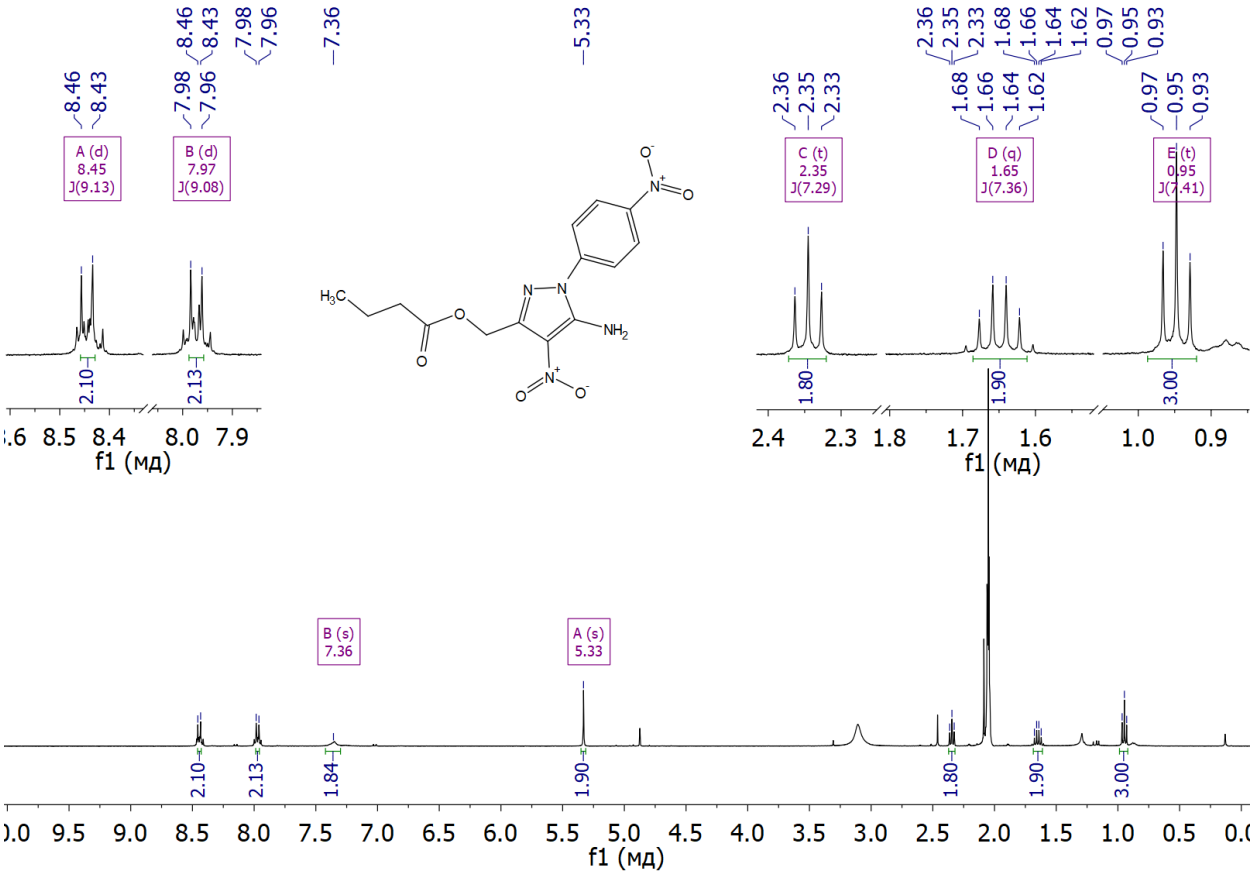


Figure S9: ^{1}H NMR spectrum of **5c**(Acetone-d_6, 600 MHz)

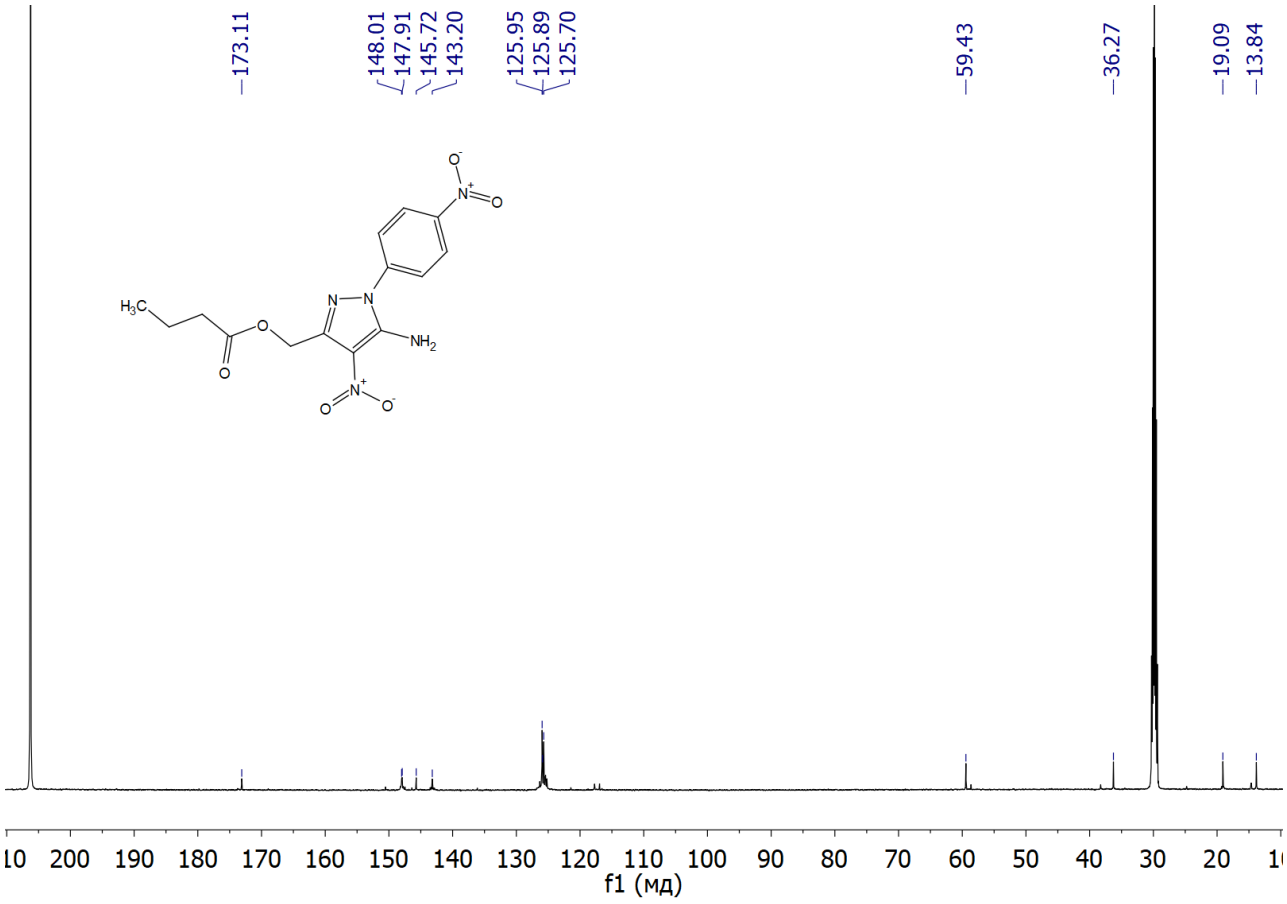


Figure S10: ^{13}C NMR spectrum of **5c** (Acetone-d_6, 126 MHz)

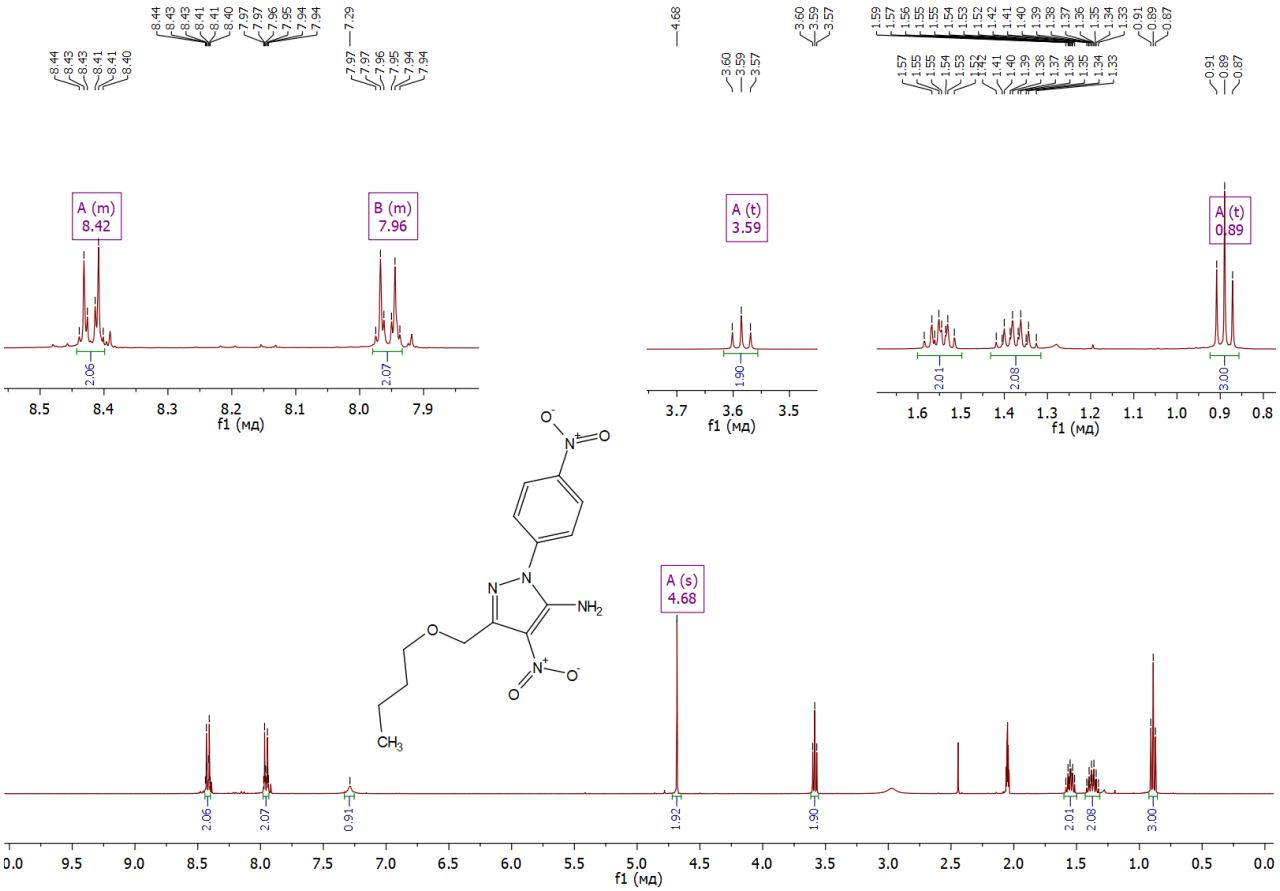


Figure S11: ^{1}H NMR spectrum of **5d** (Acetone-d_6, 400 MHz)

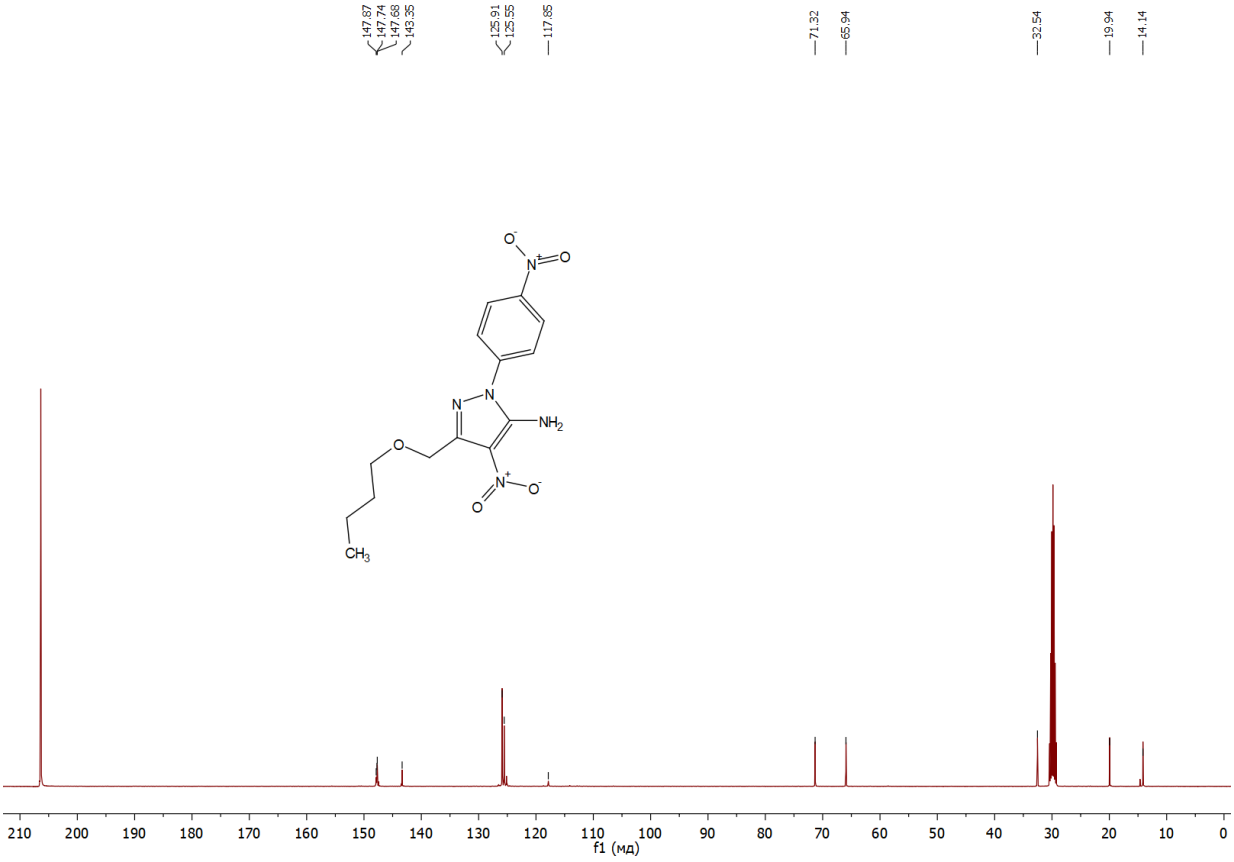


Figure S12: ^{13}C NMR spectrum of **5d** (Acetone-d_6, 101 MHz)

The X-ray diffraction data

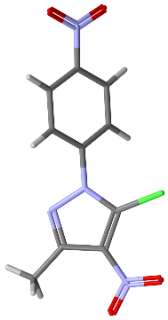


Figure S13: molecular structure of compound **3**

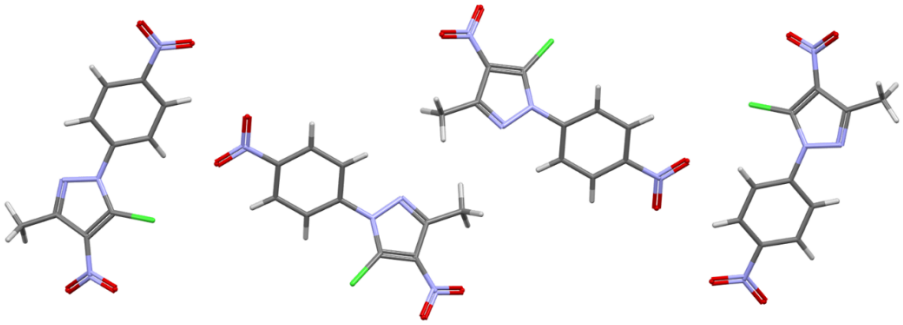
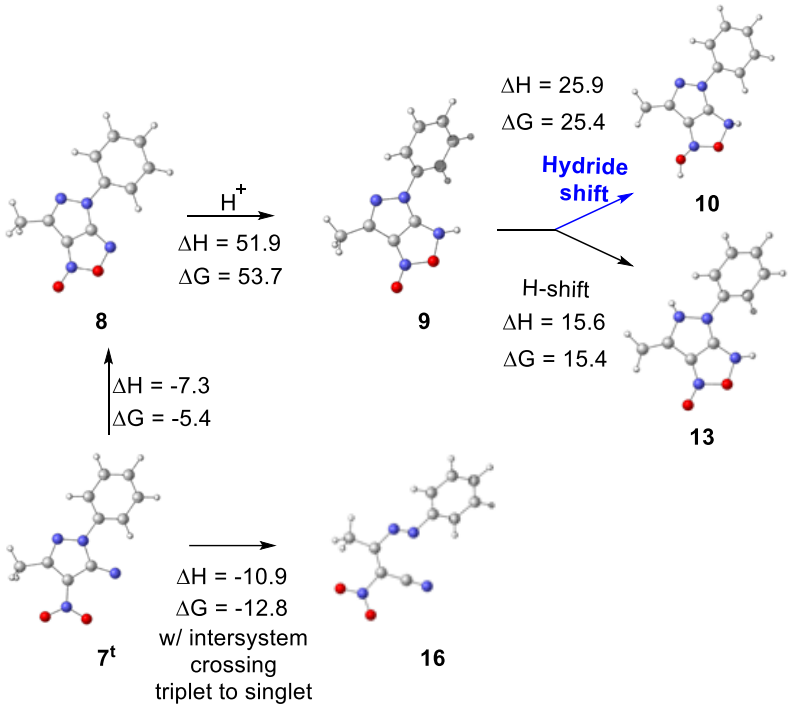


Figure S14: unit cell of compound **3**(view along *a* axis)

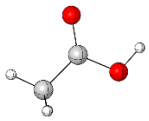
Computational details

Computational Methods. Initial transition state calculations were performed in autodE v. 1.3.5.[1] Low energy conformers were located with the ETKDGv3 algorithm[2] implemented in RDKit v. 2022.09.5 and optimized using XTB then with Gaussian16 (G16, Revision C.01). [3] Single point energies were performed at the PBEO/D3BJ level in combination with the def2-TZVP[4] basis set. All structures were fully optimized with G16 at the (U)M06-2X/ 6-31+G(d,p)/UF level of theory. The implicit SMD solvation model was used to simulate acetic acid. Harmonic frequencies were used to verify geometry minima (no imaginary frequency), or saddle points (one imaginary frequency). Three-dimensional structures were produced with CYLView.[5]



Scheme S1: Formation of the intermediate 6 is more favorable than the formation of 8, the pathway leading to the major product.

XYZ Coordinates



Acetic acid
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Multiplicity =1
Imaginary Frequency= 0
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E=-228.940403
H=-228.939459
G= -228.9720468
symmetry cs

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O	-0.198918000	1.343956000	0.000000000
O	1.241110000	-0.368992000	0.000000000
H	-2.040494000	-0.453759000	0.000000000
H	-0.930515000	-1.546984000	0.883285000
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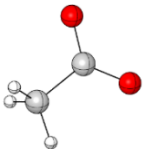

Acetic acid ion (-)

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Multiplicity =1

Imaginary Frequency= 0

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H=-228.476005

G=-228.506304

symmetry cs

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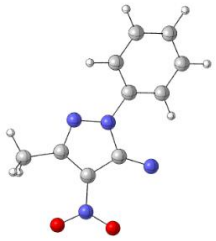

7 - Pyrazole nitrene Triplet

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Multiplicity =3

Imaginary Frequency= 0

Zero-point Energies= -754.685293

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H=-754.671187

G=-754.727307

symmetry c1

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C	0.618392000	-0.791112000	-0.095694000
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N	3.127206000	-0.733279000	-0.113547000
O	3.152934000	-1.947739000	-0.277814000
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H	-4.467365000	1.821566000	-0.951575000
H	-5.572923000	-0.218143000	-0.061771000
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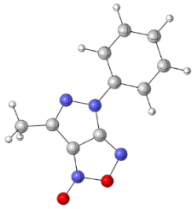

8 – Bicyclic Intermediate ($C_{10}N_4H_8O_2$)

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Multiplicity =1

Imaginary Frequency= 0

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E= -754.683765

H= -754.682821

G= -754.735967

symmetry c1

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C	-2.325631000	0.555310000	0.162520000
C	-1.038228000	0.882497000	0.631965000
N	-1.038857000	1.873703000	1.489444000
O	-2.382752000	2.205639000	1.581042000
N	-3.157238000	1.384920000	0.758798000
O	-4.370971000	1.574028000	0.746084000
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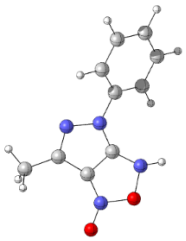
N	-0.175392000	0.029346000	0.014467000
C	1.229286000	-0.056755000	0.129061000
C	1.886763000	0.773424000	1.039227000

C	3.272989000	0.693619000	1.149246000
C	3.997460000	-0.203457000	0.366663000
C	3.323267000	-1.027173000	-0.534822000
C	1.938806000	-0.962093000	-0.662062000
H	-3.735977000	-0.570397000	-2.194603000
H	-3.927775000	-1.721108000	-0.865057000
H	-2.729063000	-2.040402000	-2.145043000
H	1.331471000	1.473211000	1.655749000
H	3.783660000	1.339940000	1.856371000
H	5.077351000	-0.260519000	0.458075000
H	3.876732000	-1.730021000	-1.150079000
H	1.413498000	-1.599299000	-1.363293000



9 – Intermediate ion (+)

Zero-point Energies= -755.076982

E= -755.064470

H= -755.063526

G= -755.116161

Charge = 1

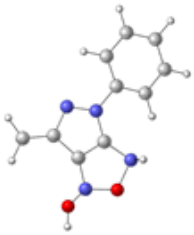
Multiplicity =1

Imaginary Frequency= 0

symmetry c1

C	3.159455000	1.995846000	1.002161000
C	2.131331000	0.993331000	0.635918000
C	2.307939000	-0.354066000	0.149287000
C	1.026269000	-0.875494000	-0.035864000
N	1.098478000	-2.150651000	-0.474141000
O	2.455244000	-2.393073000	-0.712683000
N	3.178081000	-1.264320000	-0.289806000
O	4.366225000	-1.329671000	-0.367301000
N	0.845138000	1.201529000	0.721491000
N	0.156147000	0.056201000	0.312269000
C	-1.271886000	0.028893000	0.289336000
C	-1.924399000	-1.180343000	0.515697000
C	-3.315974000	-1.205000000	0.470725000
C	-4.030750000	-0.034505000	0.220615000
C	-3.354777000	1.167761000	0.011418000
C	-1.963611000	1.210383000	0.039137000
H	2.672147000	2.916017000	1.325418000
H	3.802244000	2.204573000	0.142429000
H	3.786212000	1.609935000	1.810788000

H	0.530574000	-2.534943000	-1.237025000
H	-1.365246000	-2.081603000	0.753138000
H	-3.838382000	-2.139239000	0.648713000
H	-5.115502000	-0.057769000	0.194517000
H	-3.910380000	2.079763000	-0.181171000
H	-1.424578000	2.136344000	-0.128465000



10 – intermediate ion (+)

Charge = 1

Multiplicity =1

Imaginary Frequency= 0

Zero-point Energies=-755.035747

E= -755.023233

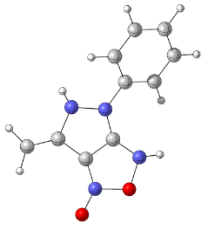
H= -755.022289

G= -755.075621

symmetry c1

C	-2.295423000	2.776413000	-0.080972000
C	-1.578399000	1.632313000	0.028217000
C	-1.938754000	0.260405000	0.229880000
C	-0.791853000	-0.431532000	0.235316000
N	-0.980710000	-1.808585000	0.297496000
O	-2.406027000	-1.831583000	0.682688000
N	-3.046682000	-0.627823000	0.285049000
O	-3.465451000	-0.773402000	-1.048554000
N	-0.186100000	1.683442000	-0.067807000
N	0.248260000	0.474640000	0.036423000
C	1.643214000	0.166399000	-0.013268000
C	2.566026000	1.181430000	0.238910000
C	3.917396000	0.868534000	0.172644000
C	4.327303000	-0.429778000	-0.140330000
C	3.385086000	-1.426550000	-0.390171000
C	2.025944000	-1.136865000	-0.326962000
H	-3.379698000	2.757262000	-0.026009000
H	-1.781776000	3.722505000	-0.227153000
H	-0.538461000	-2.246264000	1.112946000
H	-4.400027000	-1.031306000	-0.983285000
H	2.230447000	2.181202000	0.489951000
H	4.652907000	1.640555000	0.371241000
H	5.385897000	-0.663869000	-0.188978000
H	3.703226000	-2.432210000	-0.642855000

H	1.292697000	-1.904333000	-0.556649000



13 – intermediate ion (+)

Charge = 1

Multiplicity =1

Imaginary Frequency= 0

Zero-point Energies=-755.052196

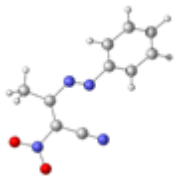
E=-755.039688

H=-755.038743

G=-755.091591

symmetry c1

C	2.578090000	2.599780000	0.221118000
C	1.722531000	1.579792000	0.176512000
C	1.964572000	0.152772000	0.099256000
C	0.723704000	-0.505824000	0.087973000
N	0.905146000	-1.833113000	-0.044088000
O	2.282417000	-2.023887000	-0.249025000
N	2.900954000	-0.729491000	-0.152491000
O	4.100981000	-0.702413000	-0.281274000
N	0.279945000	1.681983000	0.171943000
N	-0.257038000	0.358157000	0.168076000
C	-1.660753000	0.147199000	0.072294000
C	-2.185034000	-1.057254000	0.540506000
C	-3.554836000	-1.274019000	0.425588000
C	-4.379122000	-0.294539000	-0.128111000
C	-3.833799000	0.910359000	-0.570352000
C	-2.464539000	1.144245000	-0.476557000
H	3.643792000	2.402992000	0.231117000
H	2.224066000	3.623960000	0.254641000
H	0.360982000	-2.418232000	-0.686674000
H	-1.550952000	-1.800947000	1.014955000
H	-3.977432000	-2.206081000	0.785898000
H	-5.447192000	-0.468361000	-0.208729000
H	-4.473904000	1.674508000	-0.999002000
H	-2.027615000	2.070220000	-0.833461000
H	-0.086861000	2.174535000	0.990206000



16 - Intermediate

Charge = 0

Multiplicity =1

Imaginary Frequency= 0

Zero-point Energies= -754.703640

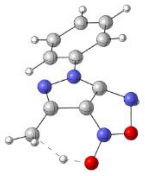
E= -754.689467

H= -754.688523

G= -754.747241

symmetry c1

C	-2.020548000	0.126608000	0.241756000
C	-2.641478000	0.875860000	-0.766815000
C	-4.006322000	0.727139000	-0.966339000
C	-4.744451000	-0.157750000	-0.170688000
C	-4.119457000	-0.898245000	0.830668000
C	-2.750339000	-0.755075000	1.041234000
N	-0.632943000	0.178992000	0.530635000
N	0.036299000	0.954497000	-0.173785000
C	1.421851000	0.962594000	0.061096000
C	2.093878000	-0.209744000	-0.091201000
C	1.459481000	-1.448781000	-0.419552000
C	1.978655000	2.314575000	0.349011000
N	3.539461000	-0.302576000	0.006080000
O	4.031335000	-1.413406000	-0.111898000
O	4.178541000	0.717518000	0.201310000
N	0.946580000	-2.443951000	-0.710554000
H	-2.057798000	1.558151000	-1.375697000
H	-4.503140000	1.299286000	-1.743492000
H	-5.812029000	-0.266423000	-0.336968000
H	-4.694161000	-1.584124000	1.444415000
H	-2.232168000	-1.319118000	1.811079000
H	1.153946000	3.021635000	0.444418000
H	2.649916000	2.636298000	-0.452738000
H	2.563030000	2.289573000	1.272043000



9 →10 Transition State

Charge = 0

Multiplicity =1

Imaginary Frequency= 1 (-1312.0817)

Zero-point Energies= -754.703640

E= -754.689467

H= -754.688523

G= -754.747241

symmetry c1

C	2.778990000	2.136566000	-0.052553000
C	1.706526000	1.353440000	-0.486523000
C	1.885215000	-0.084263000	-0.649572000
C	0.622456000	-0.671832000	-0.523928000
N	0.771602000	-1.958670000	-0.002568000
O	2.125891000	-1.907422000	0.619794000
N	2.715590000	-0.770881000	0.097188000
O	3.698583000	-0.228227000	0.703669000
N	0.378828000	1.571344000	-0.430801000
N	-0.226961000	0.347158000	-0.392653000
C	-1.624608000	0.223661000	-0.175258000
C	-2.311350000	1.261372000	0.456460000
C	-3.667445000	1.089759000	0.704189000
C	-4.311334000	-0.094020000	0.334725000
C	-3.606835000	-1.115746000	-0.302825000
C	-2.252152000	-0.959648000	-0.574824000
H	3.385910000	0.890148000	0.769340000
H	2.567940000	3.074540000	0.449784000
H	3.731527000	2.058138000	-0.575637000
H	0.135895000	-2.187853000	0.769196000
H	-1.785886000	2.164245000	0.744685000
H	-4.223898000	1.880648000	1.194582000
H	-5.370489000	-0.215370000	0.534618000
H	-4.115731000	-2.021551000	-0.612700000
H	-1.711254000	-1.716147000	-1.139083000

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