Supplementary Material

An Unusual Rearrangement of Pyrazole Nitrene and Coarctate 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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NMR spectra of compounds

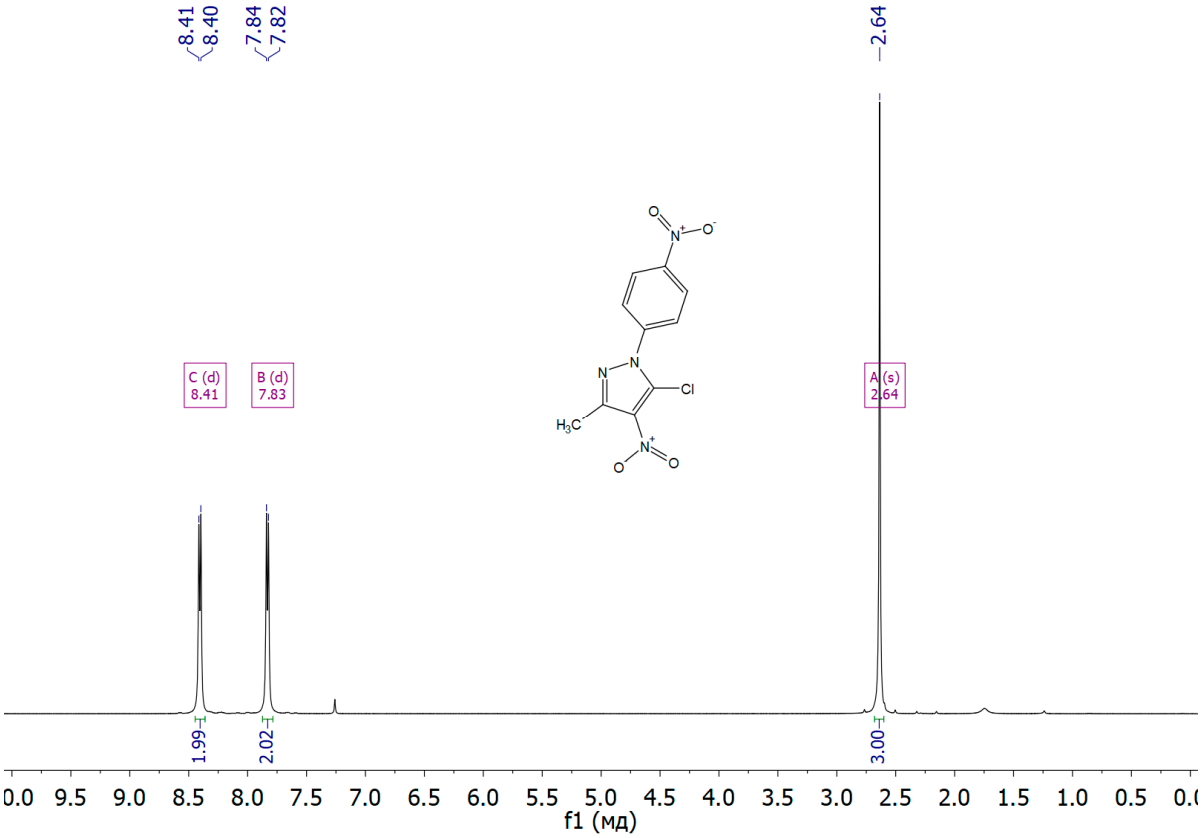


Figure S1. ^{1}H NMR spectrum of **3** ($CDCl_3$, 500 MHz)

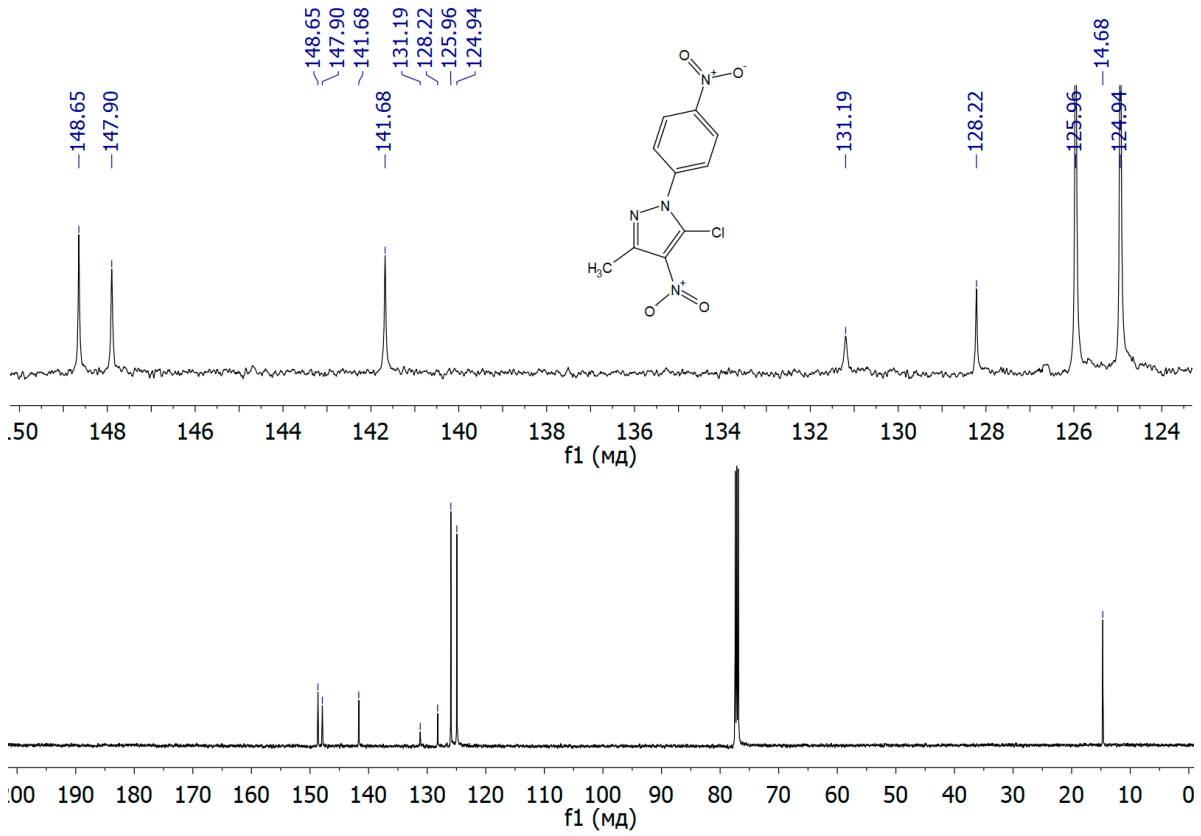


Figure S2. ^{13}C NMR spectrum of **3** ($CDCl_3$, 126 MHz)

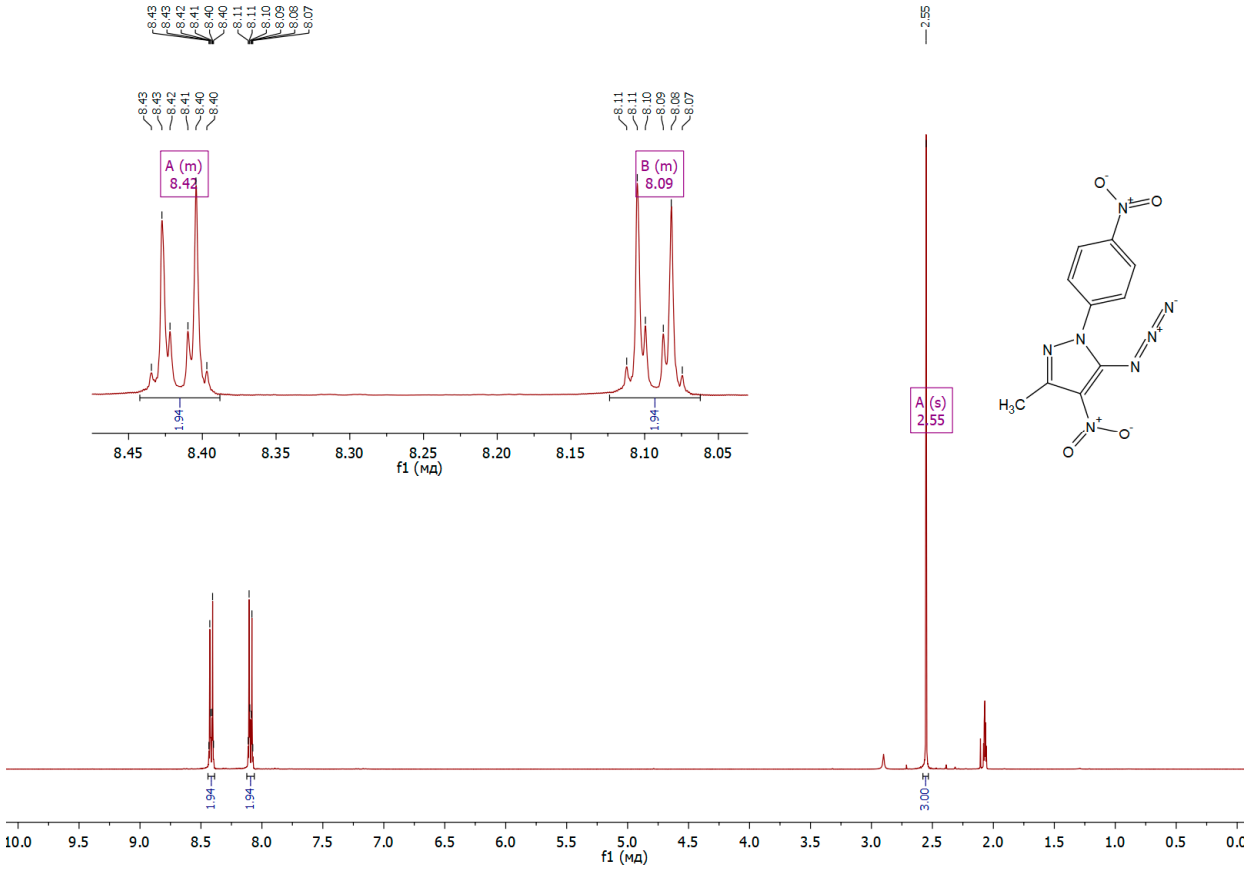


Figure S3.[1]H NMR spectrum of **4** (Acetone-d_6, 500 MHz)

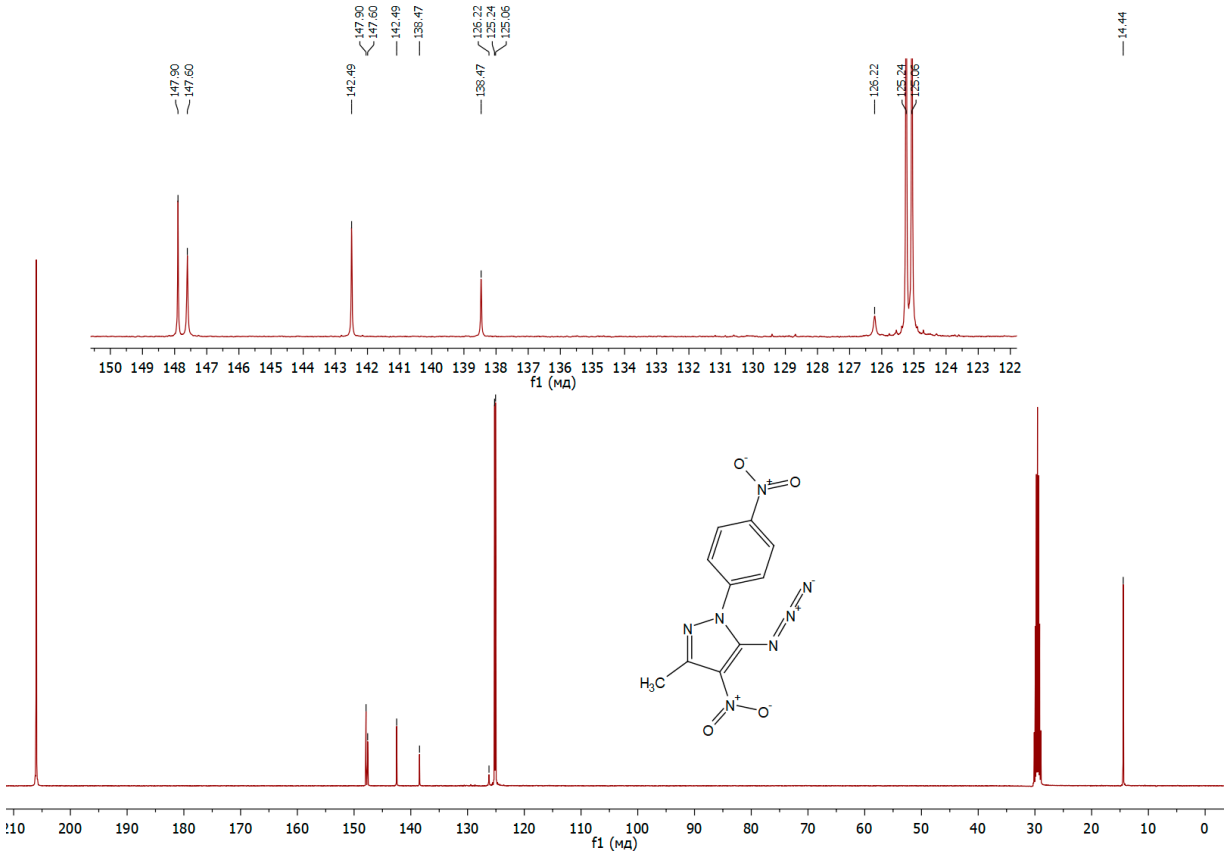


Figure S4.[13]C NMR spectrum of **4** (Acetone-d_6, 101 MHz)

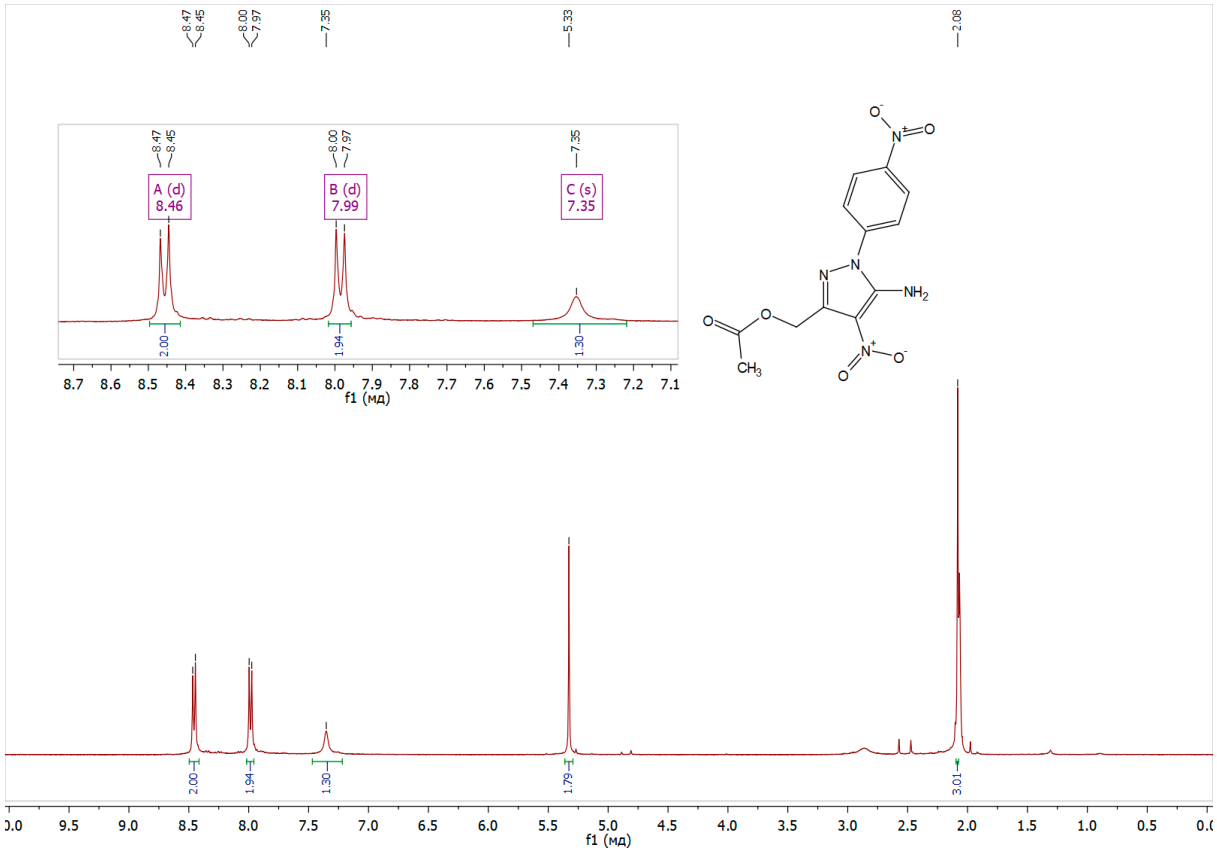


Figure S5.[1]H NMR spectrum of **5a** (Acetone-d_6, 400 MHz)

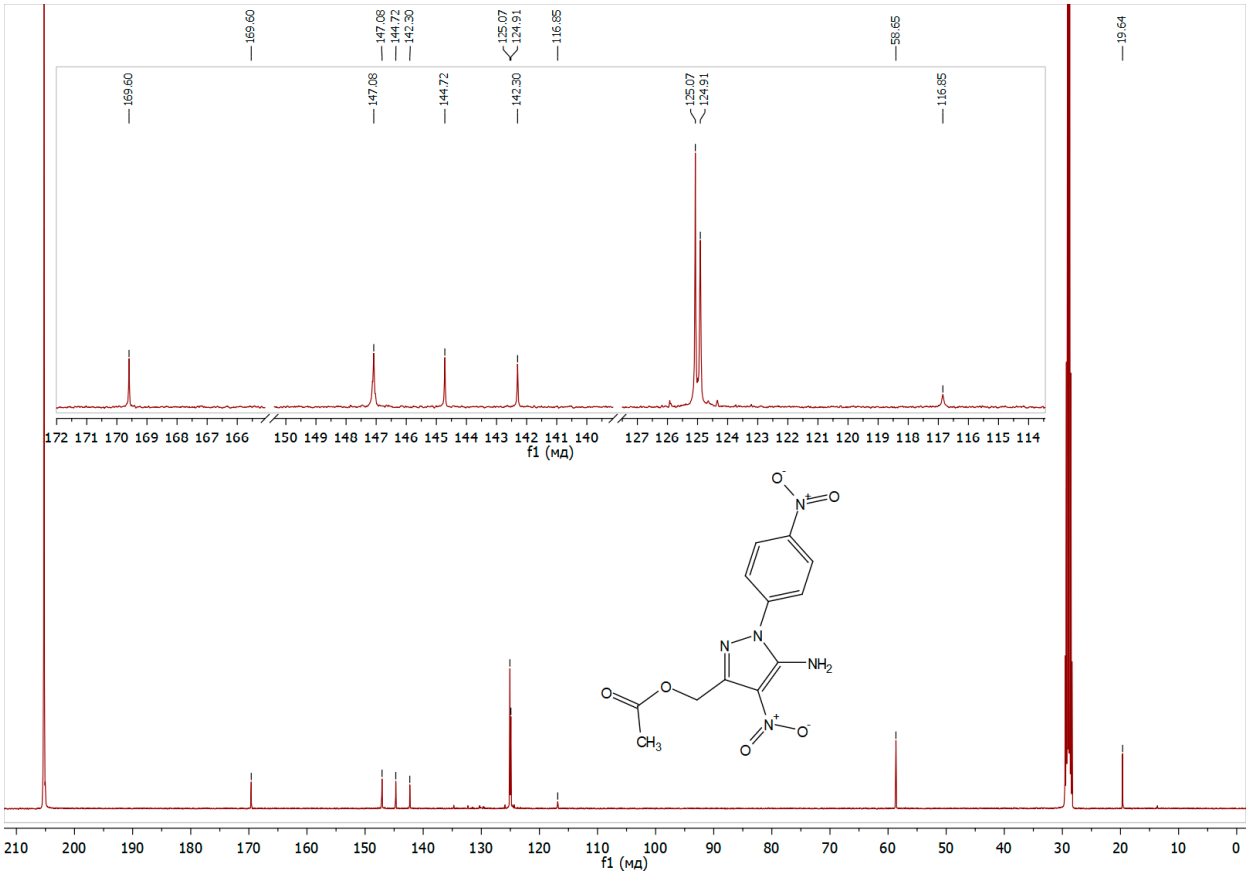


Figure S6.[13]C NMR spectrum of **5a** (Acetone-d_6, 101 MHz)

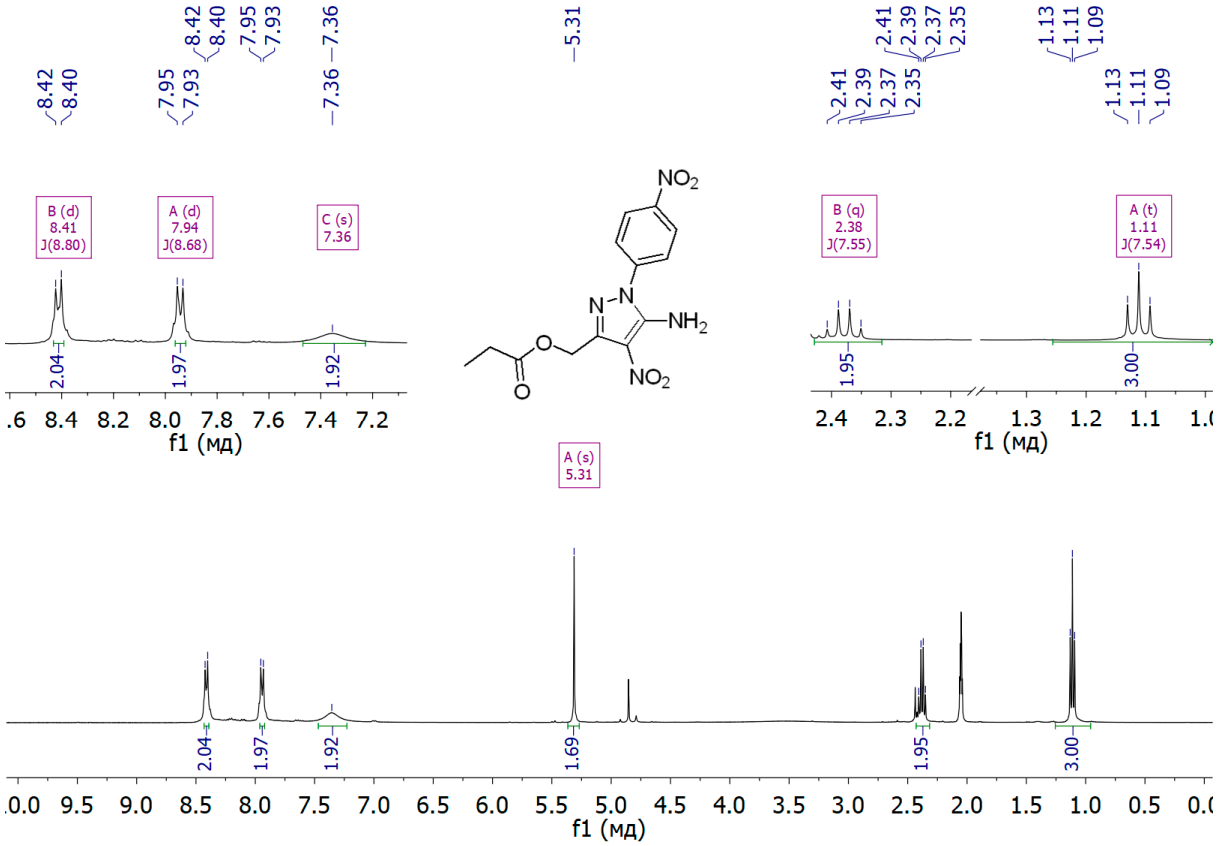


Figure S7. ^{1}H NMR spectrum of **5b** (Acetone-d_6, 400 MHz)

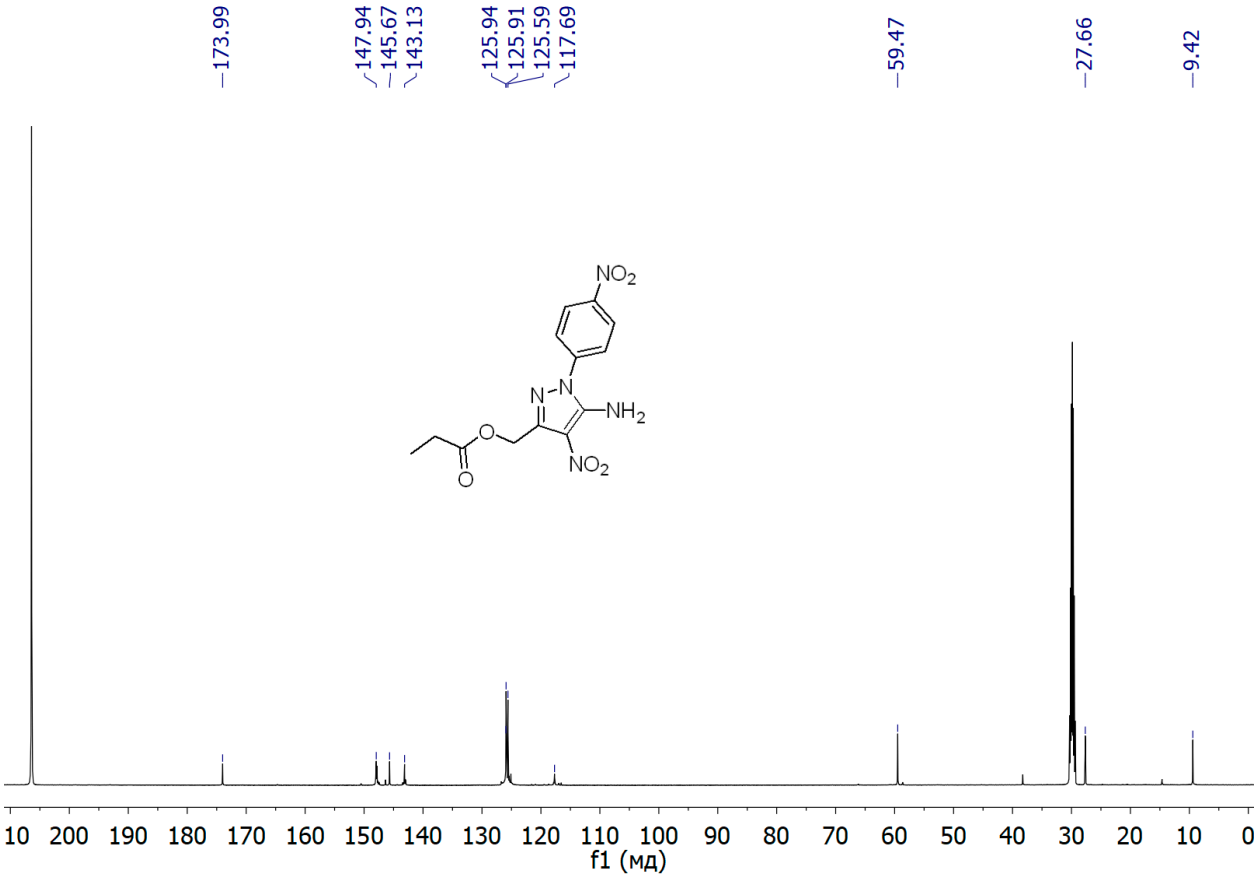


Figure S8. ^{13}C NMR spectrum of **5b** (Acetone-d_6, 101 MHz)

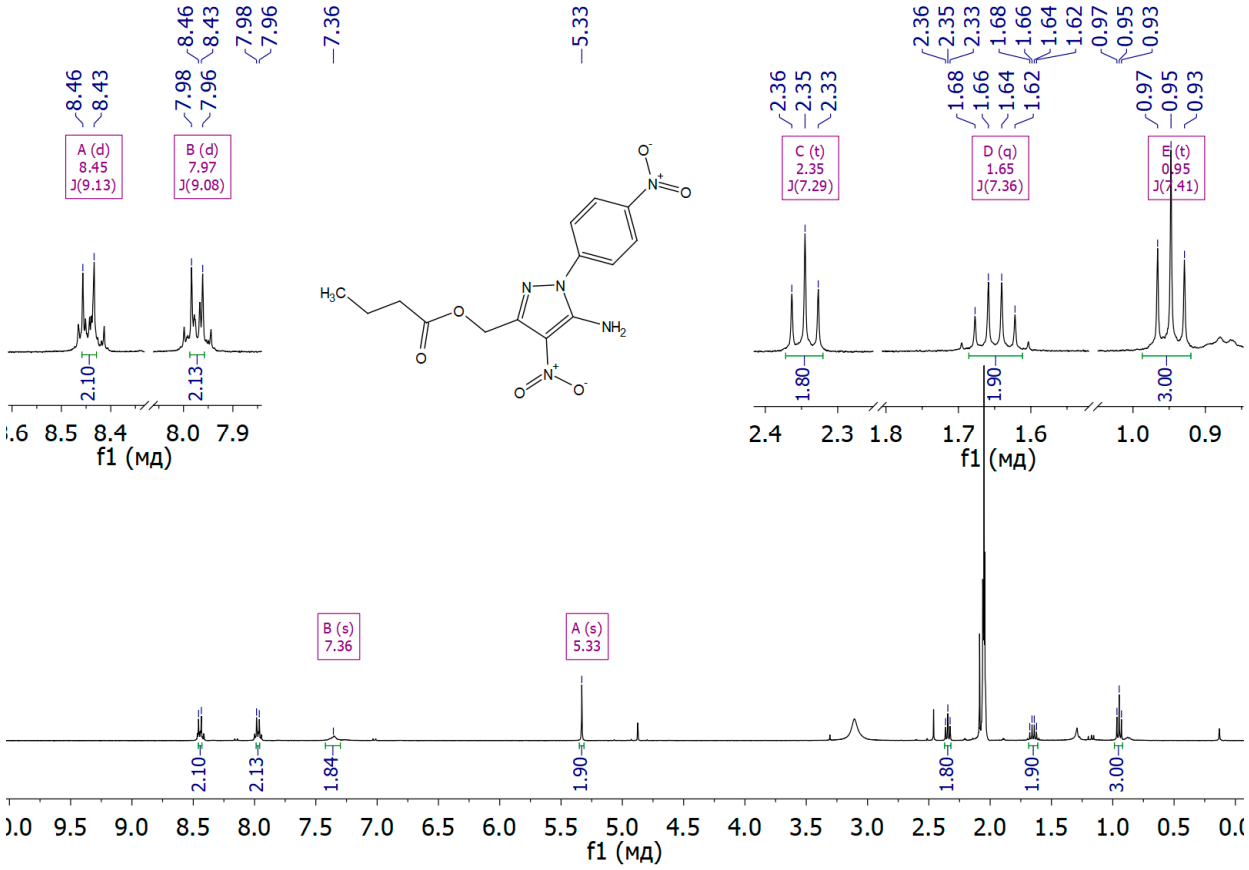


Figure S9.[1]H NMR spectrum of **5c**(Acetone-*d*$_6$, 600 MHz)

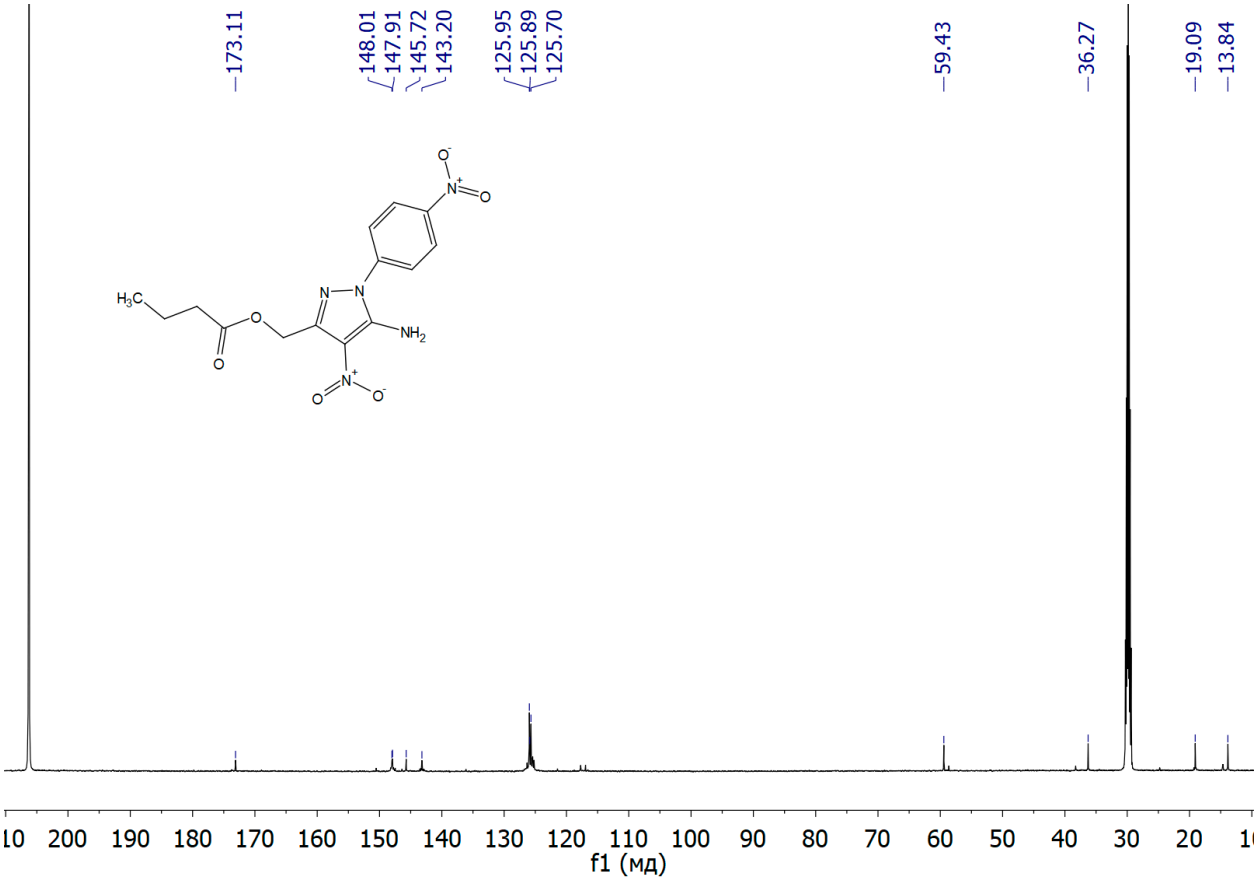


Figure S10.[13]C NMR spectrum of **5c** (Acetone-*d*$_6$, 126 MHz)

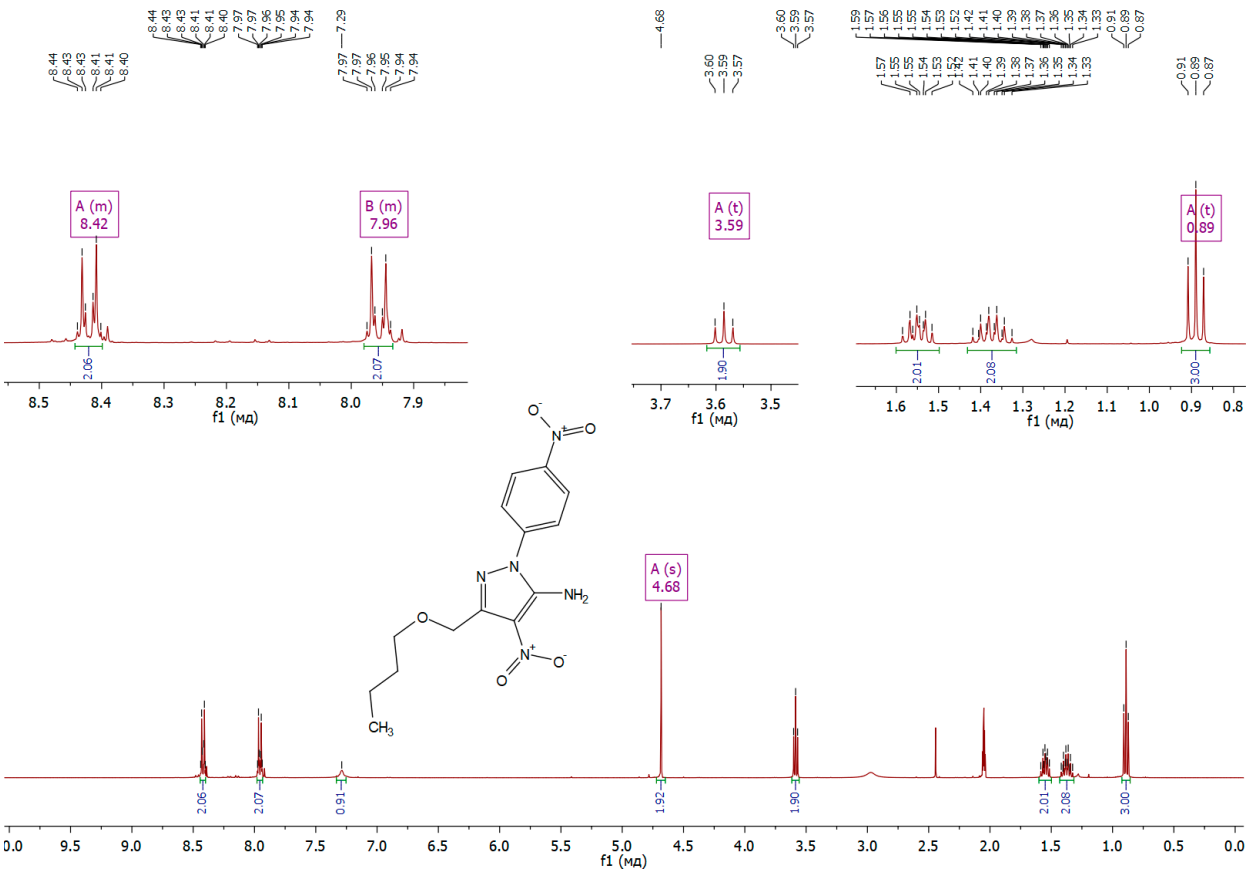


Figure S11.[1]H NMR spectrum of **5d** (Acetone-*d*$_6$, 400 MHz)

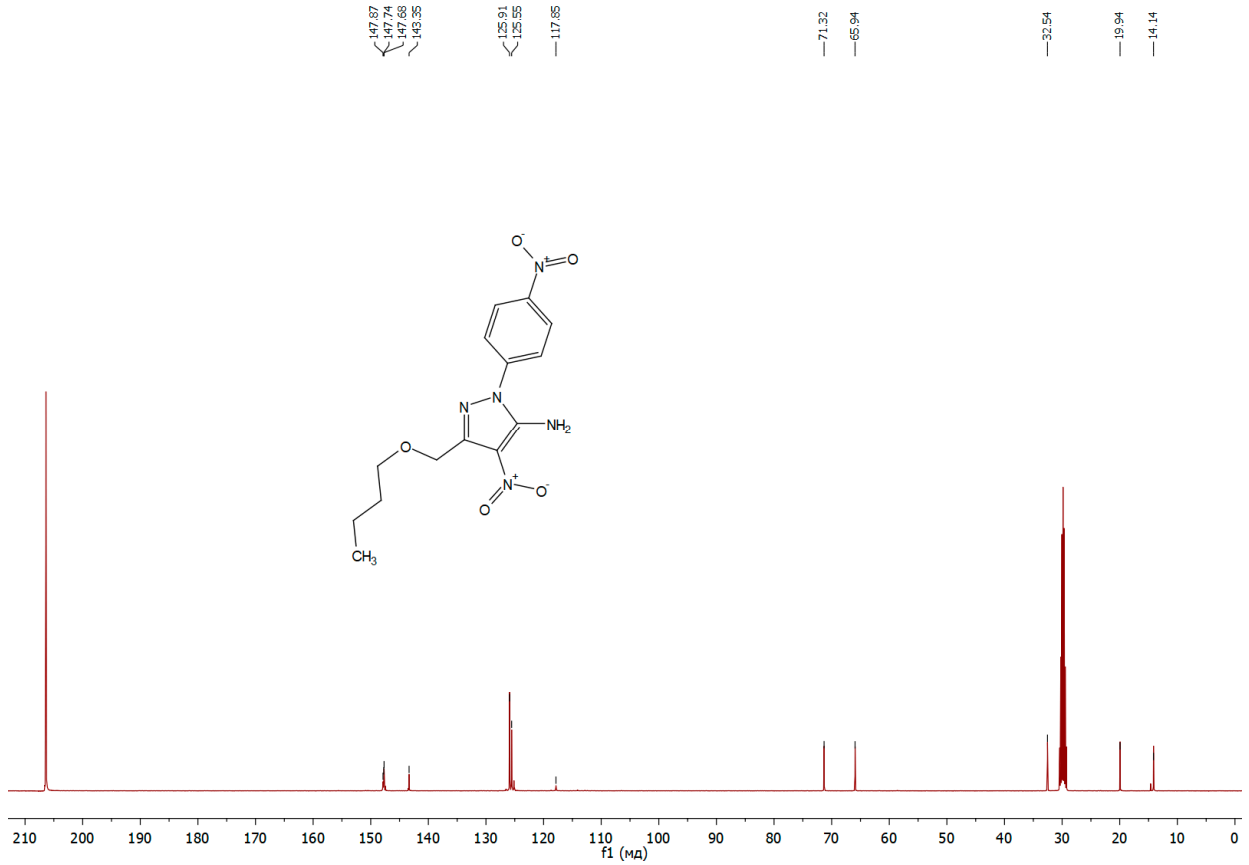


Figure S12.[13]C NMR spectrum of **5d** (Acetone-*d*$_6$, 101 MHz)

The X-ray diffraction data

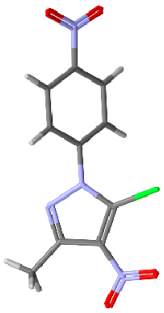


Figure S13. Molecular structure of compound **3**

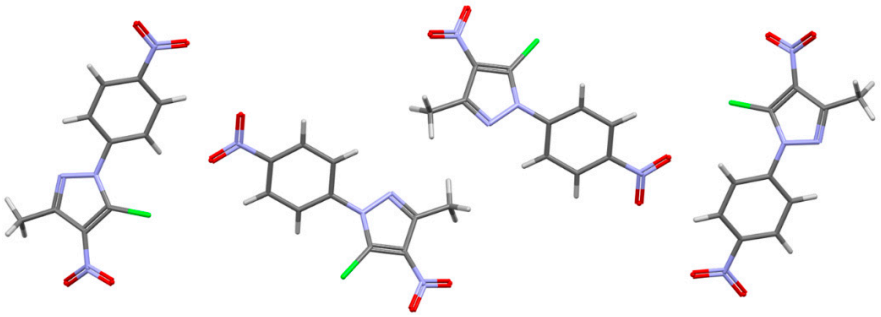
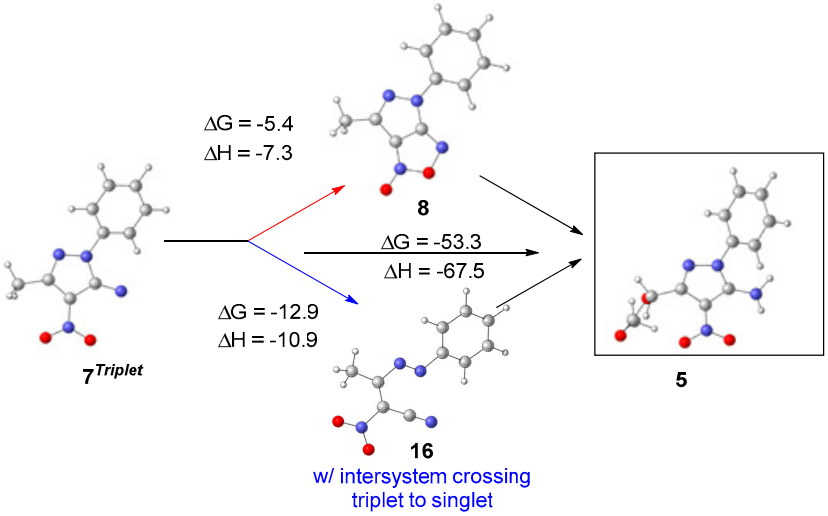


Figure S14. Unit cell of compound **3**(view along *a* axis)

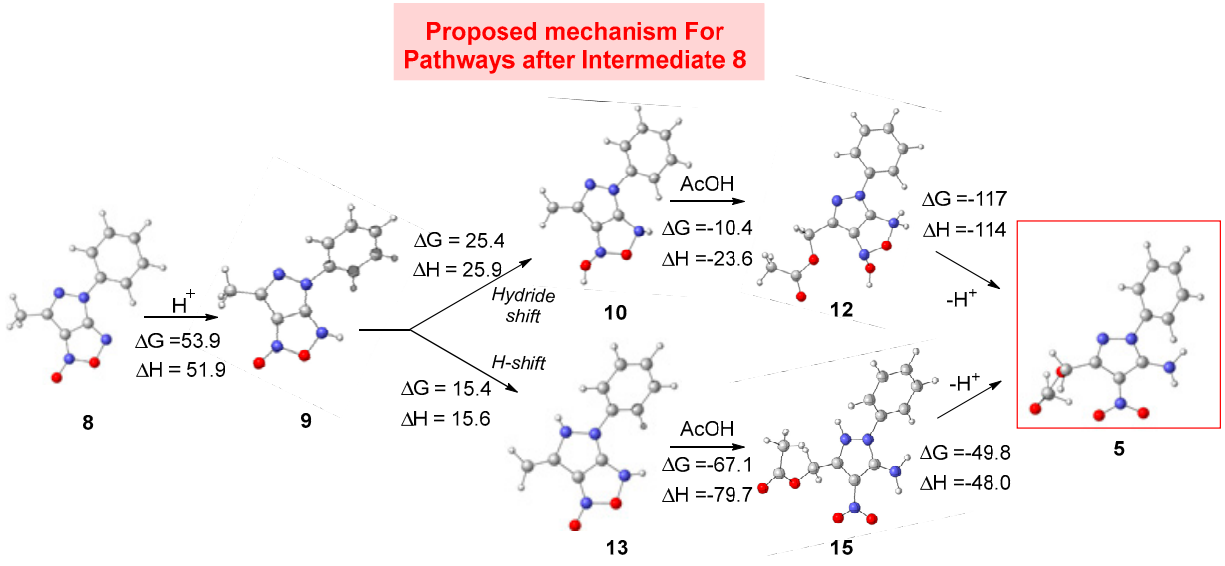
Computational details

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-dimensionalstructureswereproducedwith CYLView.[5]

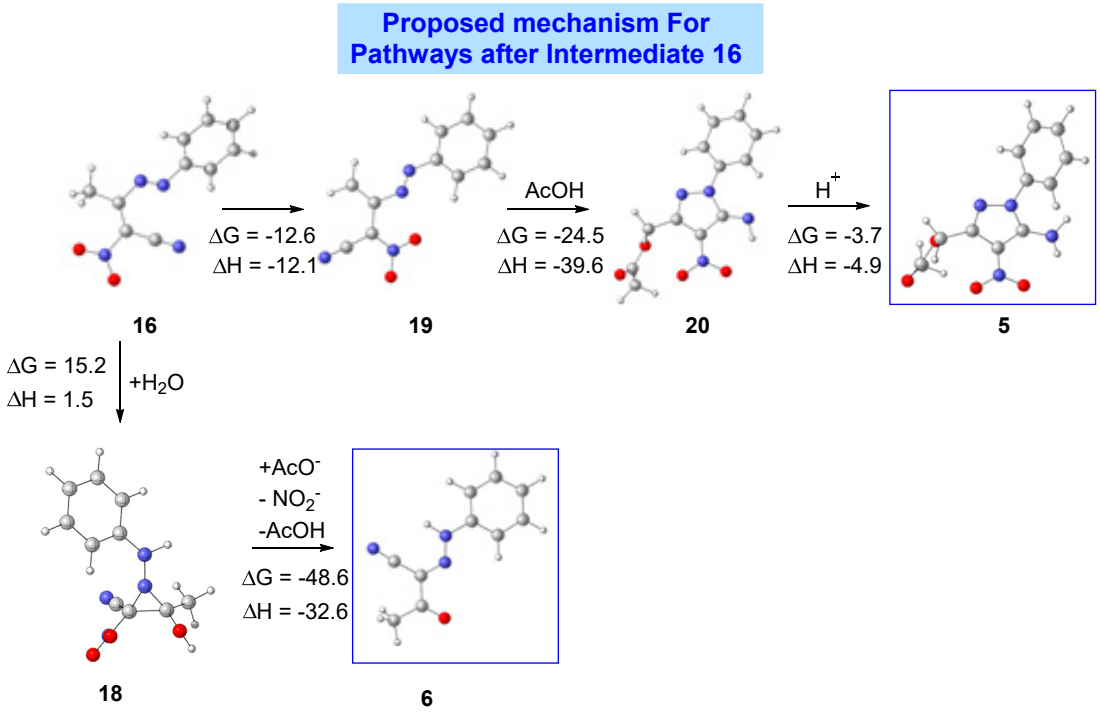


Scheme S1. The mechanistic study of the two possible pathways to lead to the same product **5**. From pyrazole nitrene to intermediate **16**, proceeds with intersystem crossing triplet to singlet.

There are two possible pathways that led to the observed product **5** from pyrazole nitrene.However, intermediate **16** can lead to formation of the byproduct **6**. The following Schemes S2 and S3 outline the full proposed mechanism from intermediates **8** and **16**.

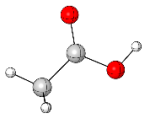


Scheme S2. Pathways from intermediate **8**.



Scheme S3. Pathways from intermediate **16**.

XYZ Coordinates



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G= -228.9720468
symmetry cs

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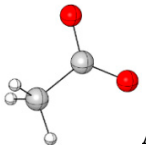

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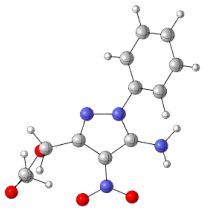

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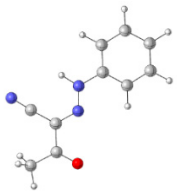

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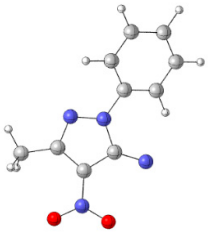

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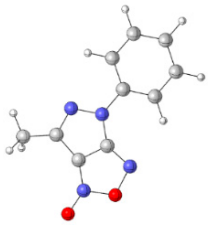

8 – Bicyclic Intermediate ($C_{10}N_4H_8O_2$)

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H= -754.682821
G= -754.735967
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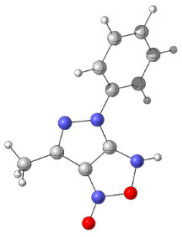

9 – Intermediate ion (+)

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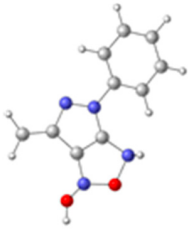
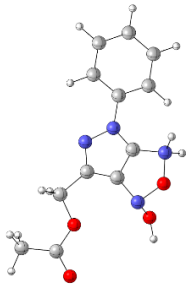
C	-4.030750000	-0.034505000	0.220615000
C	-3.354777000	1.167761000	0.011418000
C	-1.963611000	1.210383000	0.039137000
H	2.672147000	2.916017000	1.325418000
H	3.802244000	2.204573000	0.142429000
H	3.786212000	1.609935000	1.810788000
H	0.530574000	-2.534943000	-1.237025000
H	-1.365246000	-2.081603000	0.753138000
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

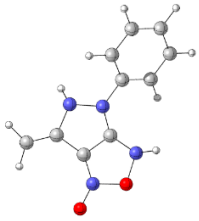
C	-2.295423000	2.776413000	-0.080972000
C	-1.578399000	1.632313000	0.028217000
C	-1.938754000	0.260405000	0.229880000
C	-0.791853000	-0.431532000	0.235316000
N	-0.980710000	-1.808585000	0.297496000
O	-2.406027000	-1.831583000	0.682688000
N	-3.046682000	-0.627823000	0.285049000
O	-3.465451000	-0.773402000	-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



12 – Intermediate ion (+)

Charge = 1
Multiplicity =1
Imaginary Frequency= 0
Zero-point Energies=-984.017563
E=-984.000225
H=-983.999281
G=-984.064255
symmetry c1

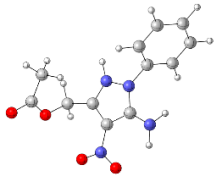
C	-0.827485000	-0.674562000	-0.098112000
C	-0.694948000	0.712151000	-0.279674000
C	0.636848000	0.943983000	-0.211869000
O	-0.395326000	2.834402000	-0.833919000
N	-1.433068000	1.927053000	-0.417993000
O	-1.822442000	2.300863000	0.857106000
N	0.379949000	-1.210054000	0.052003000
N	1.289457000	-0.211251000	-0.016859000
C	2.691764000	-0.469625000	0.062411000
C	3.182032000	-1.667918000	-0.449982000
C	4.550506000	-1.911022000	-0.379222000
C	5.409801000	-0.964720000	0.180202000
C	4.898676000	0.228240000	0.687855000
C	3.529082000	0.479625000	0.642270000
H	-2.650496000	2.796860000	0.733914000
H	2.502833000	-2.386789000	-0.894783000
H	4.946015000	-2.841592000	-0.773057000
H	6.476222000	-1.160475000	0.226132000
H	5.560757000	0.959505000	1.139786000
H	3.127347000	1.384934000	1.089109000
C	-2.080844000	-1.485908000	-0.069246000
H	-2.049122000	-2.200431000	0.758101000
H	-2.209438000	-2.020415000	-1.015714000
O	-3.124220000	-0.527219000	0.111135000
C	-4.421927000	-0.904062000	0.141621000
O	-5.246590000	-0.027675000	0.277549000
C	-4.744776000	-2.360996000	0.009373000
H	-4.400558000	-2.742169000	-0.956783000
H	-4.252596000	-2.937161000	0.798086000
H	-5.823937000	-2.482520000	0.085043000
N	0.904915000	2.350544000	-0.369769000
H	1.165192000	2.841826000	0.502988000
H	1.555268000	2.600303000	-1.133215000



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

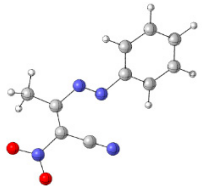
C	2.578090000	2.599780000	0.221118000
C	1.722531000	1.579792000	0.176512000
C	1.964572000	0.152772000	0.099256000
C	0.723704000	-0.505824000	0.087973000
N	0.905146000	-1.833113000	-0.044088000
O	2.282417000	-2.023887000	-0.249025000
N	2.900954000	-0.729491000	-0.152491000
O	4.100981000	-0.702413000	-0.281274000
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



15 – Intermediate ion (+)

Charge = 1
Multiplicity =1
Imaginary Frequency= 0
Zero-point Energies=-984.123698
E= -984.106145
H=-984.105201
G=-984.170620
symmetry c1

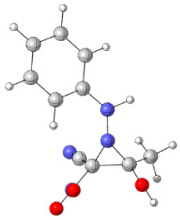
N	0.290765000	0.618360000	0.006193000
N	-0.661404000	-0.251608000	0.078220000
C	1.646455000	0.224816000	-0.001264000
C	-1.915769000	0.112183000	0.045088000
C	-2.960260000	-0.942860000	0.131492000
C	-4.385473000	-0.495693000	-0.018997000
O	-2.649469000	-2.107778000	0.318095000
C	2.610102000	1.222944000	0.149325000
C	3.957904000	0.875494000	0.142049000
C	4.340514000	-0.457137000	-0.007417000
C	3.363968000	-1.443143000	-0.157191000
C	2.011970000	-1.112703000	-0.161499000
C	-2.288689000	1.492740000	-0.073881000
N	-2.527911000	2.630633000	-0.170094000
H	0.084981000	1.616168000	-0.088309000
H	-4.512340000	0.081628000	-0.940655000
H	-5.039365000	-1.367647000	-0.029454000
H	-4.656670000	0.157246000	0.818751000
H	2.304600000	2.258755000	0.272499000
H	4.708592000	1.650925000	0.258741000
H	5.391997000	-0.725898000	-0.009754000
H	3.654522000	-2.481999000	-0.279928000
H	1.250299000	-1.874333000	-0.285177000



16 - Intermediate

Charge = 0
Multiplicity =1
Imaginary Frequency= 0
Zero-point Energies= -754.703640
E= -754.689467
G= -754.688523
H= -754.747241
symmetry c1

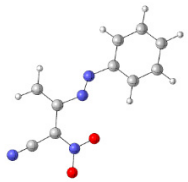
C	-2.020548000	0.126608000	0.241756000
C	-2.641478000	0.875860000	-0.766815000
C	-4.006322000	0.727139000	-0.966339000
C	-4.744451000	-0.157750000	-0.170688000
C	-4.119457000	-0.898245000	0.830668000
C	-2.750339000	-0.755075000	1.041234000
N	-0.632943000	0.178992000	0.530635000
N	0.036299000	0.954497000	-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



18 - Intermediate

Charge = 0
Multiplicity =1
Imaginary Frequency= 0
Zero-point Energies=-831.081693
E=-831.066448
H=-831.065504
G=-831.124547
symmetry c1

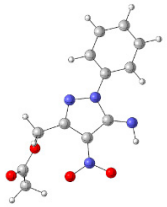
N	0.497811000	1.203618000	-0.141750000
N	-0.572139000	0.458063000	-0.702078000
C	1.740180000	0.521791000	-0.182475000
C	-1.880832000	1.019686000	-0.554513000
C	-1.425318000	-0.173365000	0.294933000
C	-2.127209000	2.341013000	0.118416000
O	-2.660432000	0.736856000	-1.647715000
C	2.897968000	1.272020000	0.057974000
C	4.135500000	0.641672000	0.094218000
C	4.234573000	-0.739218000	-0.096183000
C	3.078904000	-1.477761000	-0.331267000
C	1.828665000	-0.857666000	-0.378340000
N	-1.889172000	-1.537907000	-0.053218000
O	-1.694888000	-1.938946000	-1.177590000
O	-2.481419000	-2.139052000	0.827202000
C	-1.185838000	-0.005191000	1.706064000
N	-0.976587000	0.160999000	2.829761000
H	0.537099000	2.106579000	-0.611696000
H	-1.956462000	3.135238000	-0.614175000
H	-3.167497000	2.385216000	0.450897000
H	-1.473179000	2.493492000	0.977419000
H	-3.576077000	1.007843000	-1.479221000
H	2.818899000	2.344166000	0.219127000
H	5.028272000	1.232540000	0.276583000
H	5.202262000	-1.229368000	-0.062495000
H	3.139679000	-2.550836000	-0.487033000
H	0.941957000	-1.447034000	-0.586539000



19 – Intermediate ion (-)

Charge = -1
Multiplicity =1
Imaginary Frequency= 0
Zero-point Energies= -754.258985
E= -754.245328
G= -754.244384
H= -754.301627
symmetry c1

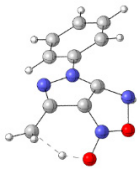
N	0.824295000	-0.886408000	0.436185000
N	-0.101837000	-0.428088000	-0.248210000
C	2.107105000	-0.342231000	0.118610000
C	-1.386336000	-0.995304000	0.040130000
C	-1.535358000	-2.322396000	0.166840000
C	-2.501575000	-0.055154000	-0.040984000
N	-2.396641000	1.224538000	0.405862000
C	-3.763546000	-0.457902000	-0.526306000
O	-3.366005000	2.016247000	0.272027000
O	-1.332621000	1.609421000	0.951027000
N	-4.785499000	-0.841119000	-0.929752000
C	2.274653000	0.911377000	-0.478806000
C	3.561681000	1.375919000	-0.728353000
C	4.672378000	0.597757000	-0.389944000
C	4.496337000	-0.644894000	0.218115000
C	3.211142000	-1.110507000	0.488090000
H	-0.678731000	-2.981282000	0.078667000
H	-2.517453000	-2.762325000	0.307899000
H	1.401751000	1.510268000	-0.718256000
H	3.701510000	2.352474000	-1.182249000
H	5.673838000	0.967684000	-0.589096000
H	5.358004000	-1.246509000	0.490968000
H	3.048971000	-2.068113000	0.974678000



20 – Intermediate ion (-)

Charge = -1
Multiplicity =1
Imaginary Frequency= 0
Zero-point Energies=-983.265217
E=-983.247947
H= -983.247003
G= -983.312672
symmetry c1

N	-1.312489000	-2.470978000	0.380485000
C	-0.635667000	-1.439070000	0.000112000
C	0.756769000	-1.237943000	-0.358605000
N	1.709006000	-2.201453000	-0.400865000
O	2.877844000	-1.914618000	-0.758902000
O	1.409425000	-3.378554000	-0.080507000
C	0.913087000	0.148968000	-0.665795000
C	2.144828000	0.875779000	-1.085308000
O	3.078509000	0.803639000	0.005670000
C	4.356311000	0.510383000	-0.280489000
C	5.136884000	0.202778000	0.959318000
O	4.800737000	0.490950000	-1.410371000
N	-0.216031000	0.780007000	-0.529577000
N	-1.166680000	-0.148155000	-0.153384000
C	-2.469947000	0.307034000	0.122697000
C	-2.679132000	1.673878000	0.360934000
C	-3.962063000	2.146544000	0.617174000
C	-5.051139000	1.274814000	0.647392000
C	-4.836961000	-0.081265000	0.409675000
C	-3.560027000	-0.573296000	0.143865000
H	-0.668047000	-3.258854000	0.421539000
H	1.908258000	1.925436000	-1.274987000
H	2.589052000	0.425750000	-1.974411000
H	4.878602000	0.899254000	1.759306000
H	6.203747000	0.238428000	0.742013000
H	4.862155000	-0.806726000	1.282850000
H	-1.836066000	2.353706000	0.343790000
H	-4.106646000	3.207393000	0.801241000
H	-6.049931000	1.647778000	0.852531000
H	-5.672895000	-0.774995000	0.423508000
H	-3.401593000	-1.626513000	-0.040499000



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

References

(1) Young, T. A.; Silcock, J. J.; Sterling, A. J.; Duarte, F. autodE: Automated Calculation of Reaction Energy Profiles— Application to Organic and Organometallic Reactions. *Angew. Chem. Int. Ed.***2021**, *60* (8), 4266–4274. https://doi.org/10.1002/anie.202011941.

(2) Riniker, S.; Landrum, G. A. Better Informed Distance Geometry: Using What We Know To Improve Conformation Generation. *J. Chem. Inf. Model.***2015**, *55* (12), 2562–2574. https://doi.org/10.1021/acs.jcim.5b00654.

(3) Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016. .

(4) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.***2005**, *7* (18), 3297–3305. https://doi.org/10.1039/B508541A.

(5) *CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org)*.