

Supplementary Material

Dearomatization of 3,5-dinitropyridines – atom-efficient approach to fused 3-nitropyrrolidines

Maxim A. Bastrakov,^{*a} Anna Yu. Kucherova,^a Alexey K. Fedorenko,^a Alexey M. Starosotnikov,^a Ivan V. Fedyanin,^b Igor L. Dalinger,^a Svyatoslav A. Shevelev^a

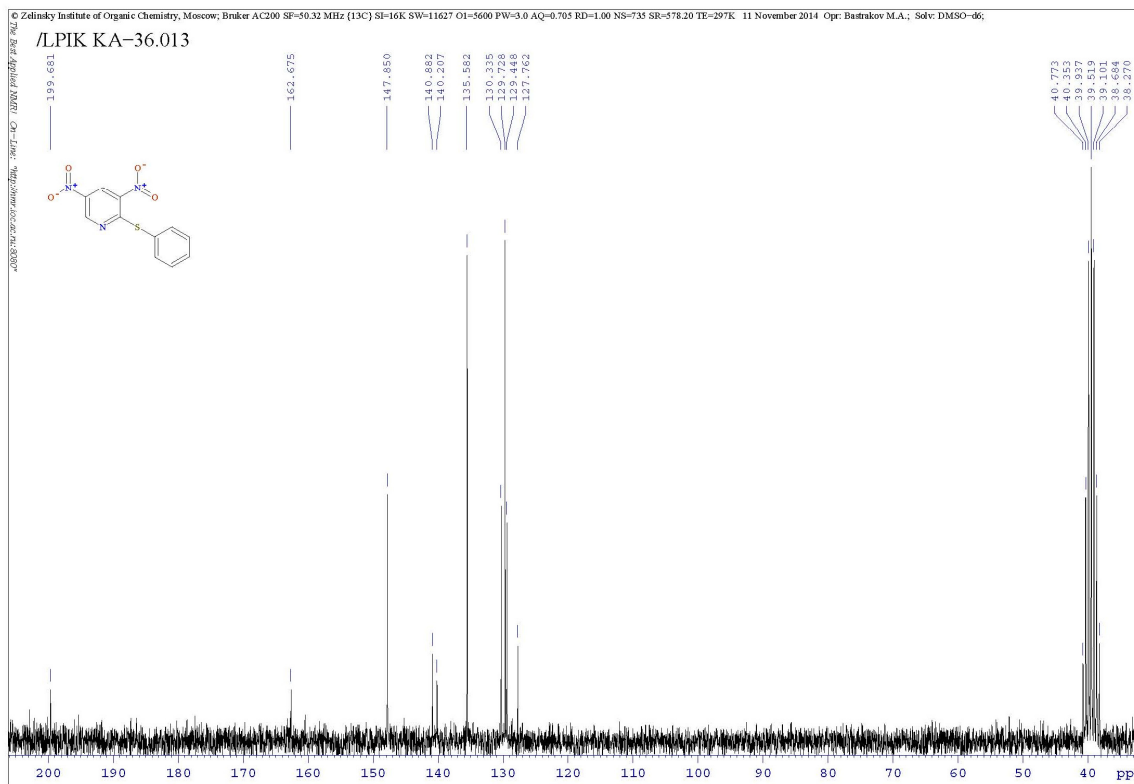
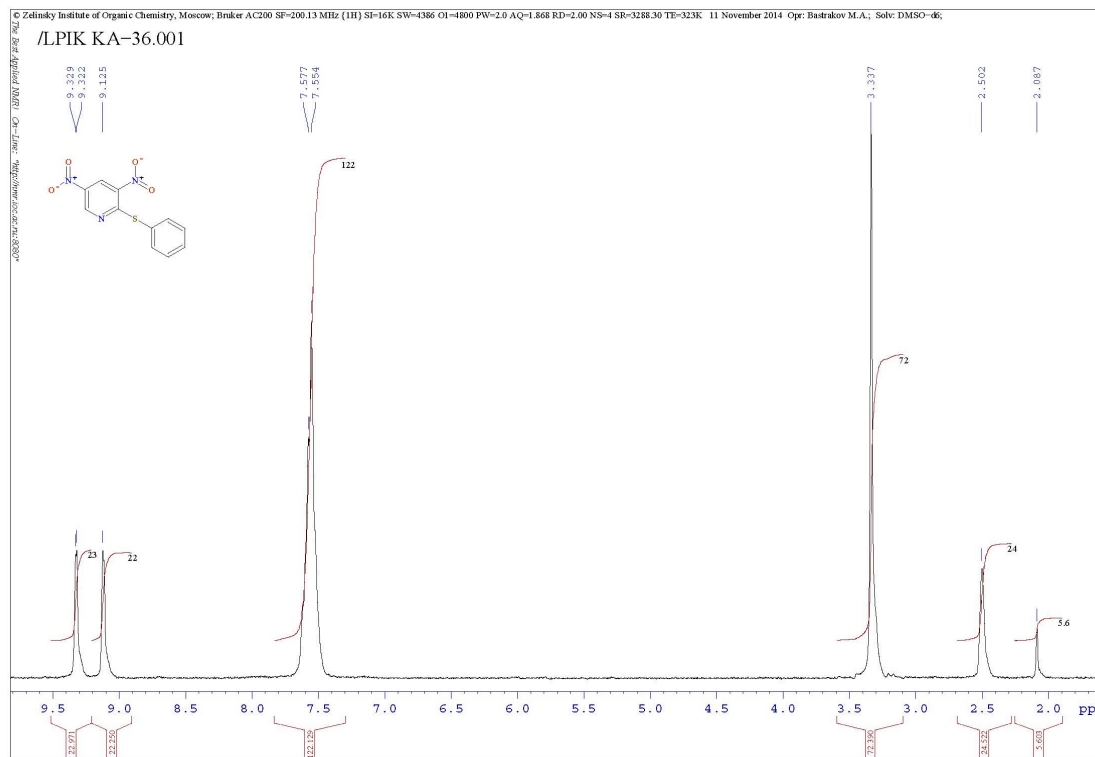
^a*N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, Moscow, 119991, Russian Federation*

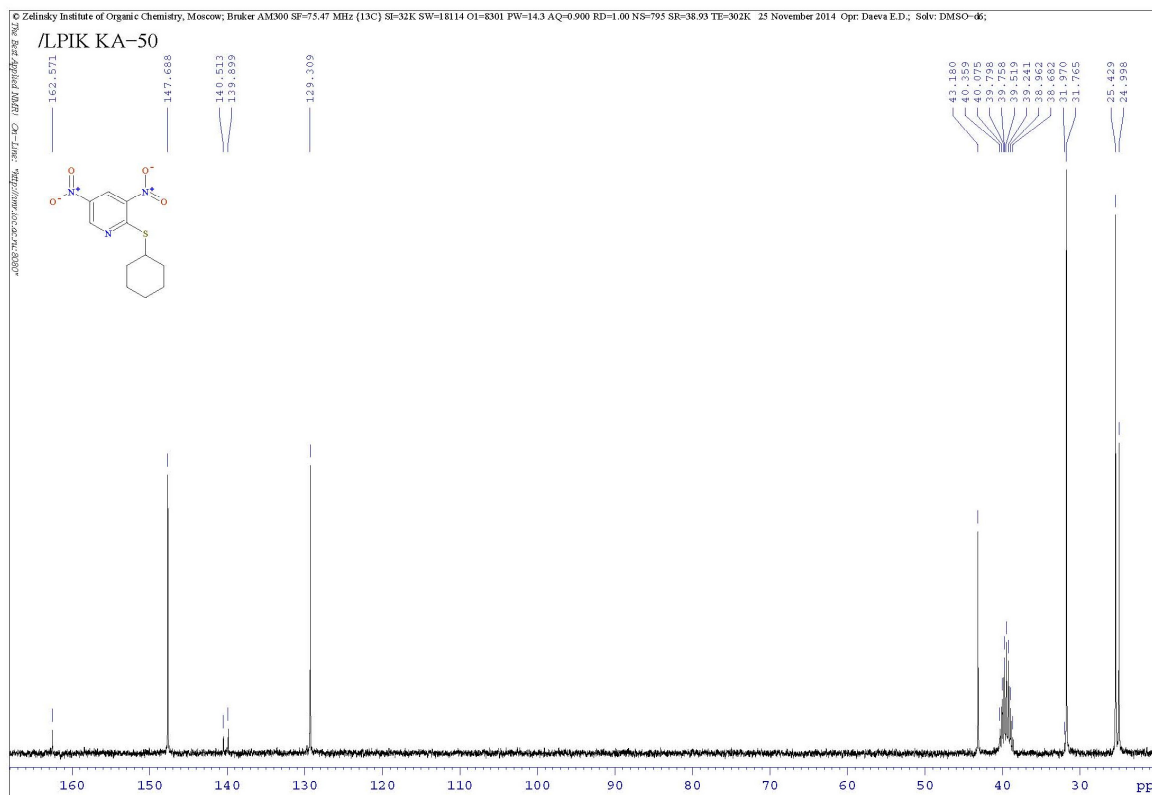
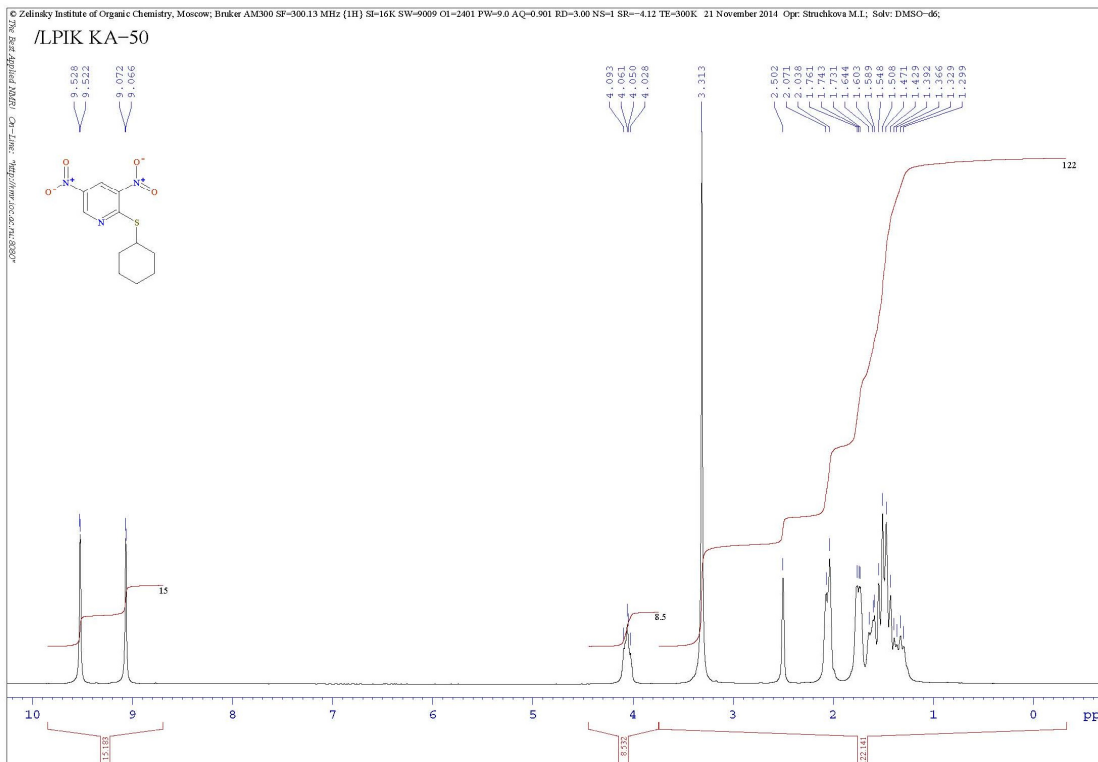
^b*A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova st. 28, Moscow, 11991, Russian Federation*
Email: b_max82@mail.ru

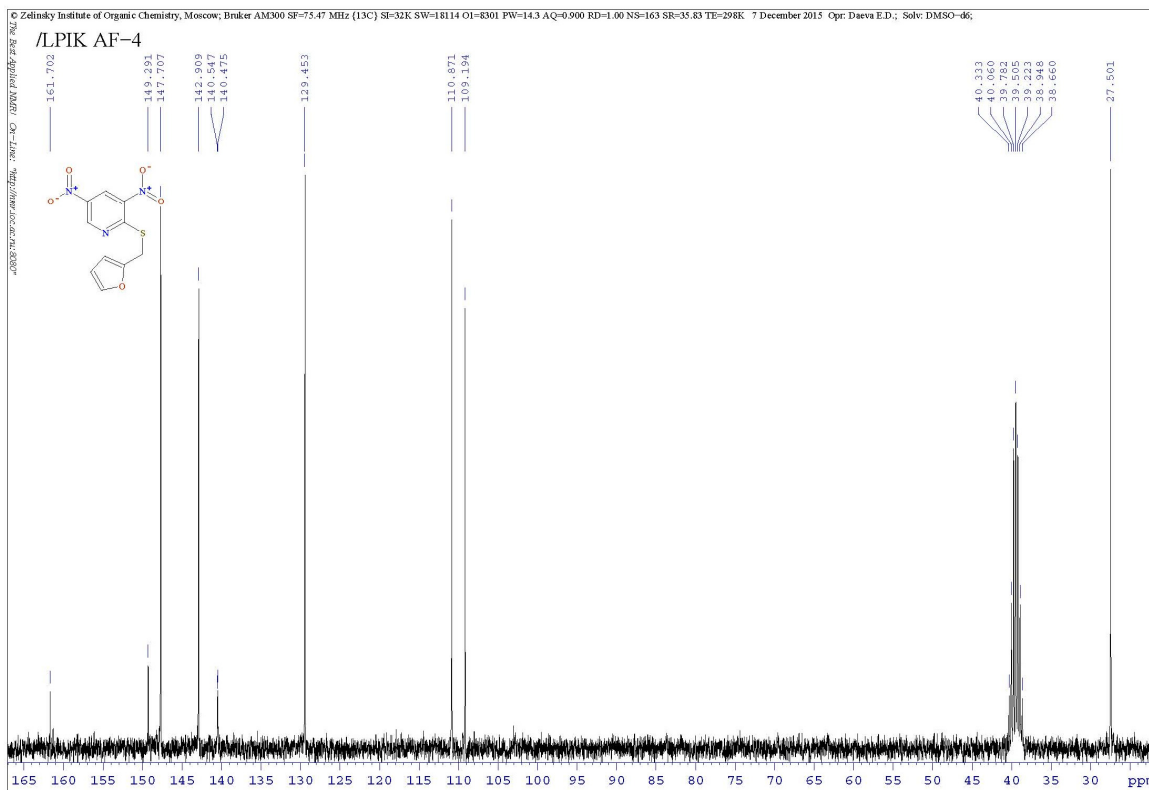
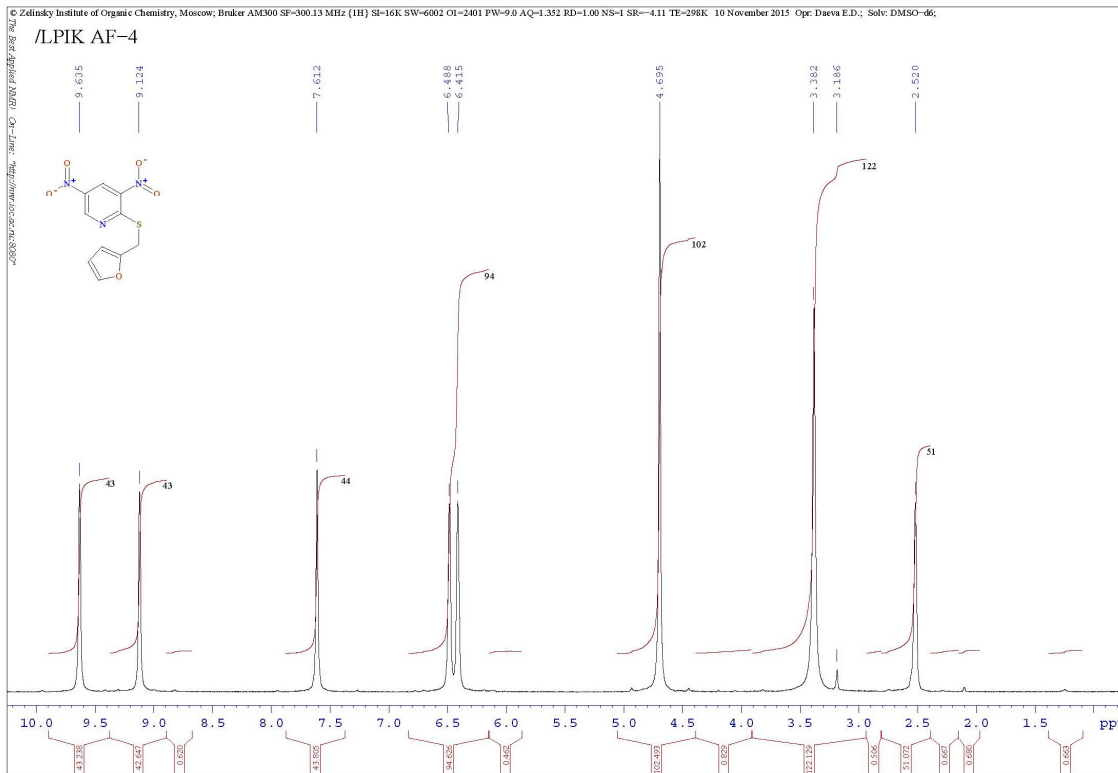
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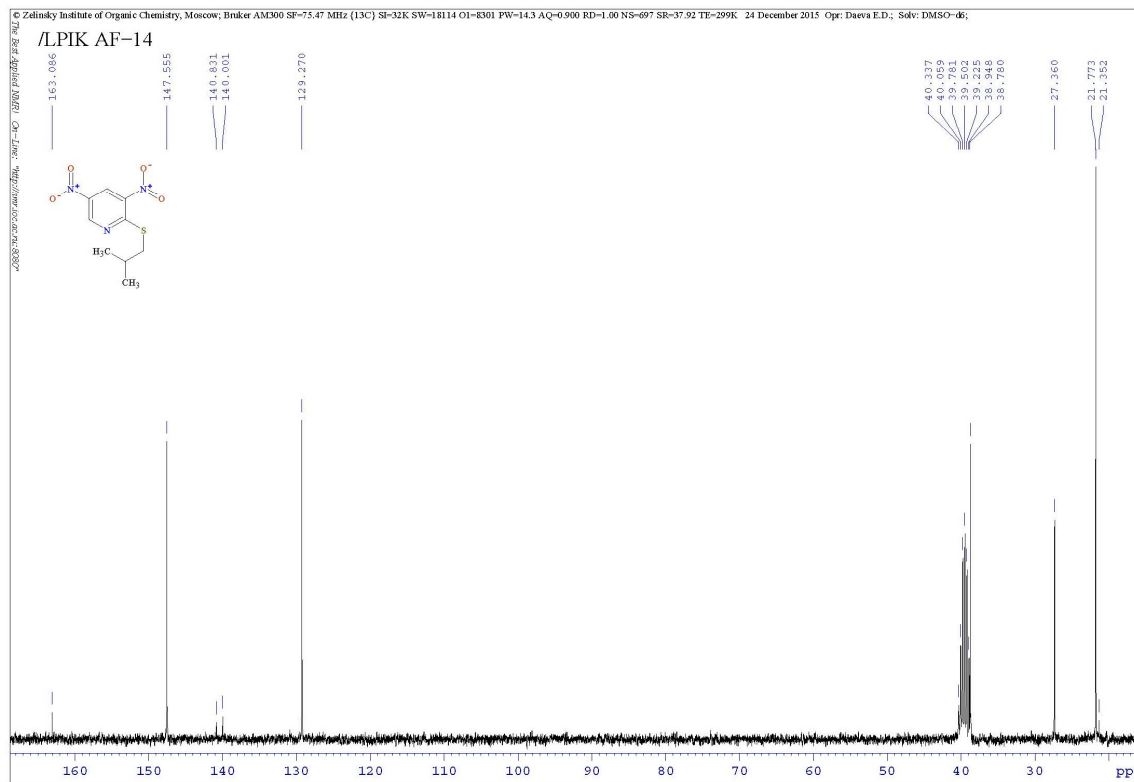
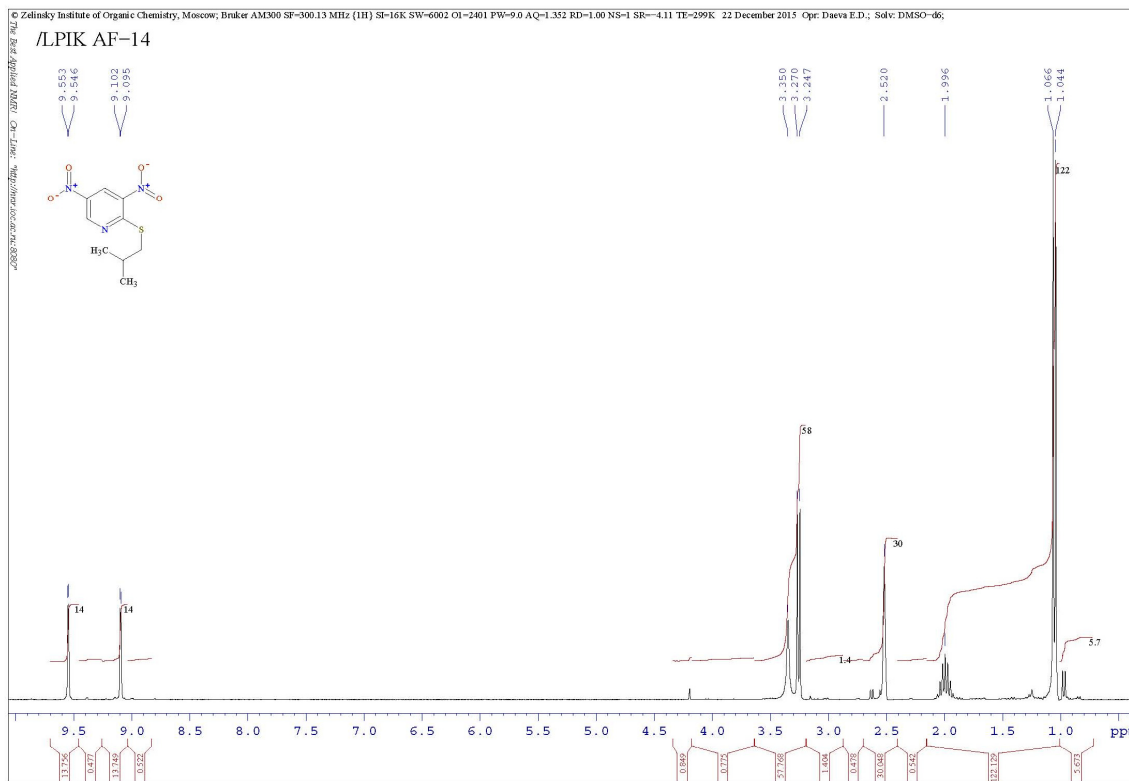
¹ H-NMR of compound 6a	S3
¹³ C-NMR of compound 6a	S3
¹ H-NMR of compound 6b	S4
¹³ C-NMR of compound 6b	S4
¹ H-NMR of compound 6c	S5
¹³ C-NMR of compound 6c	S5
¹ H-NMR of compound 6d	S6
¹³ C-NMR of compound 6d	S6
¹ H-NMR of compound 6e	S7
¹³ C-NMR of compound 6e	S7
¹ H-NMR of compound 7a	S8
¹³ C-NMR of compound 7a	S8
¹ H-NMR of compound 7b	S9
¹³ C-NMR of compound 7b	S9
¹ H-NMR of compound 7c	S10
¹³ C-NMR of compound 7c	S10
¹ H-NMR of compound 7d	S11
¹³ C-NMR of compound 7d	S11
¹ H-NMR of compound 7e	S12
¹³ C-NMR of compound 7e	S12
HRMS of compound 7a	S13

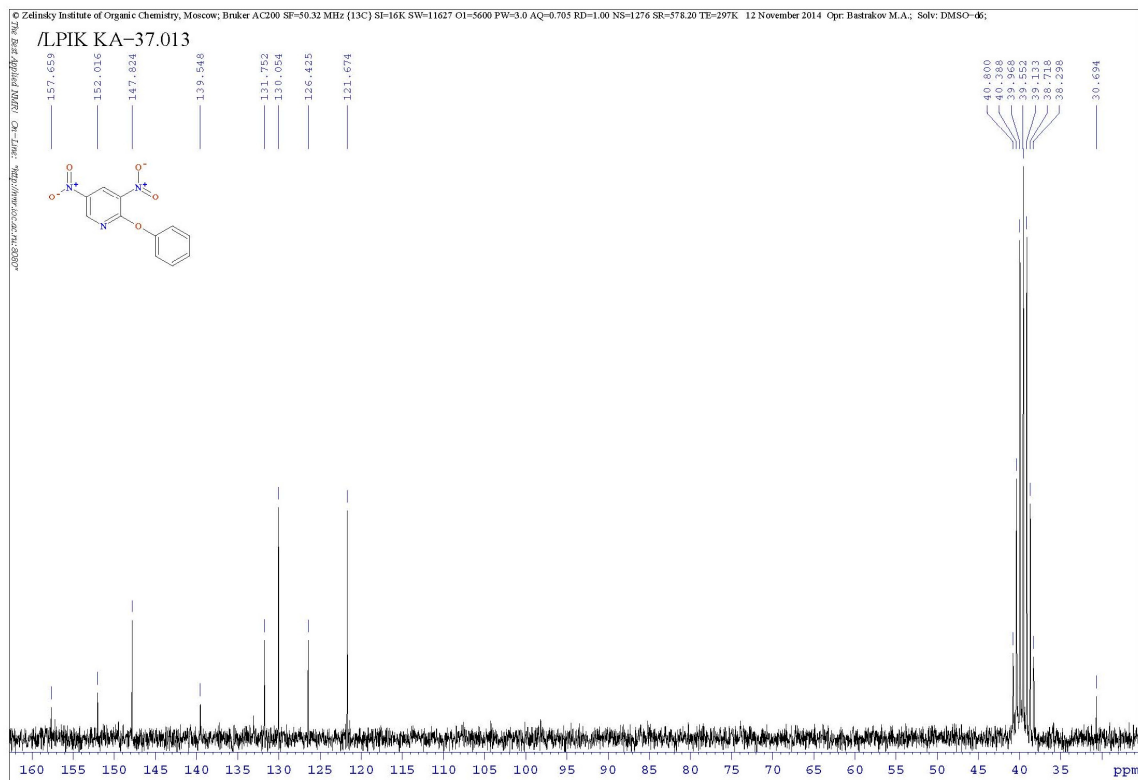
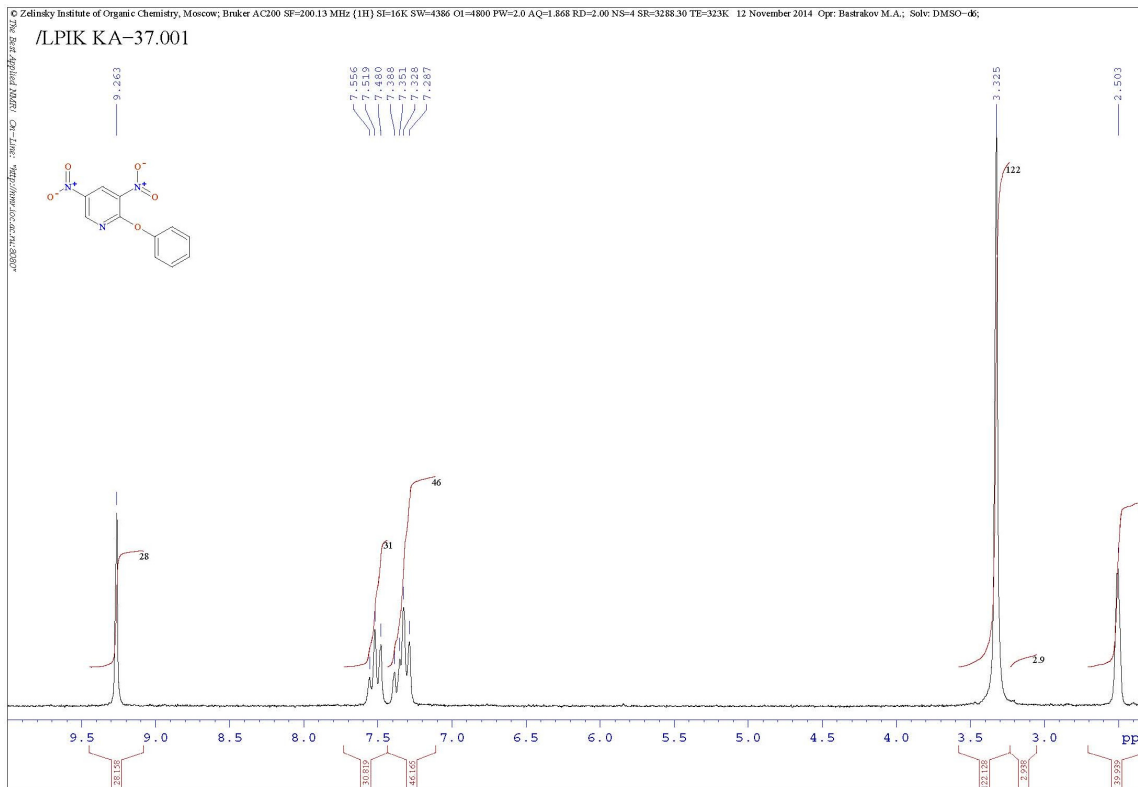
HRMS of compound 7b	S14
HRMS of compound 7c	S15
HRMS of compound 7d	S16
HRMS of compound 7e	S17
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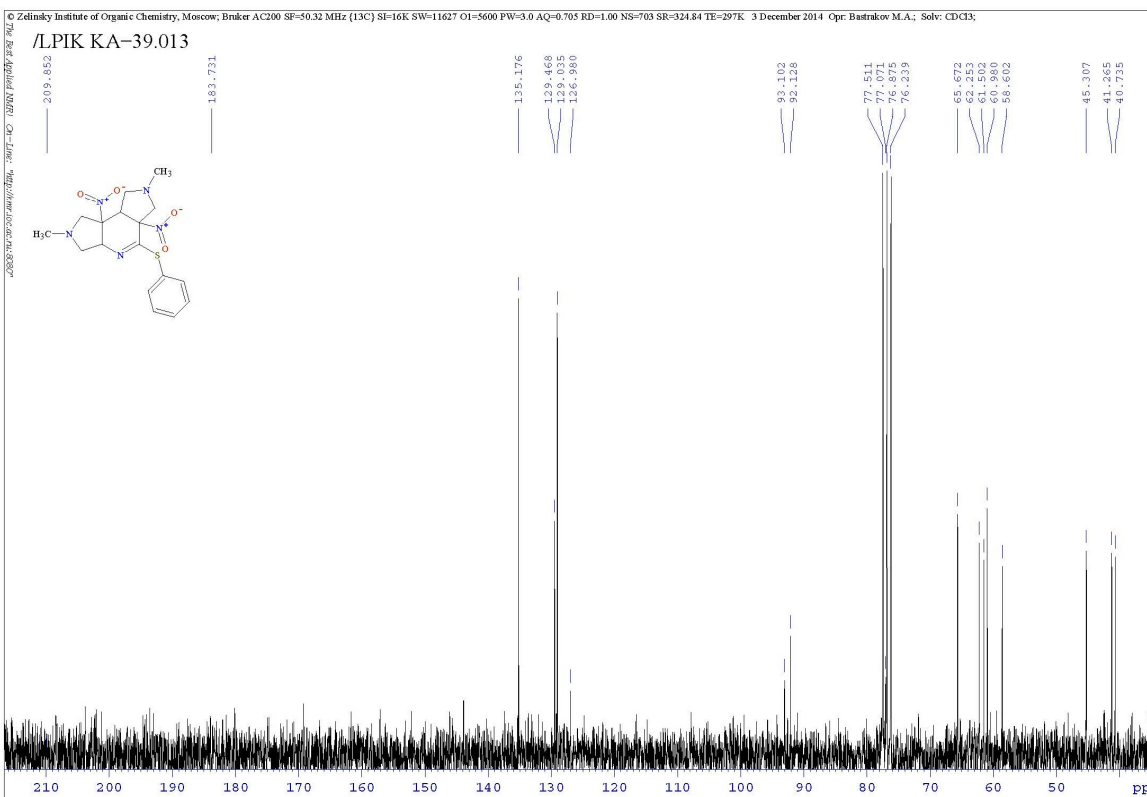
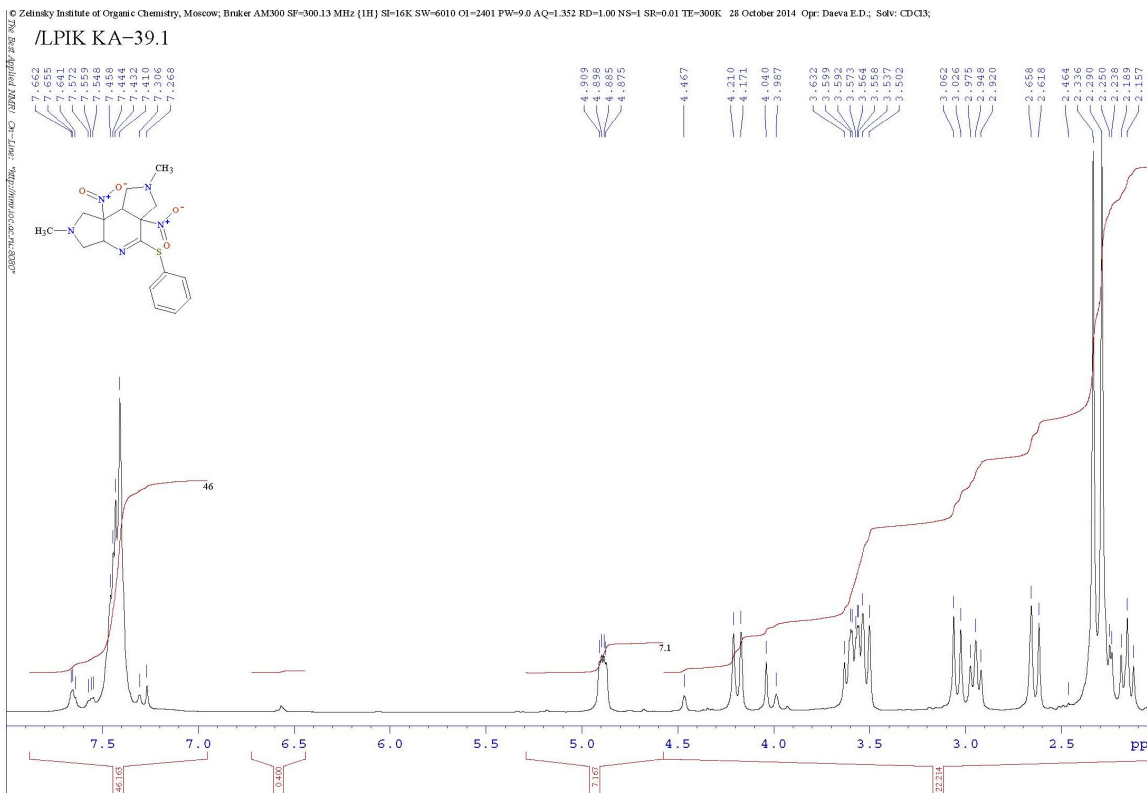


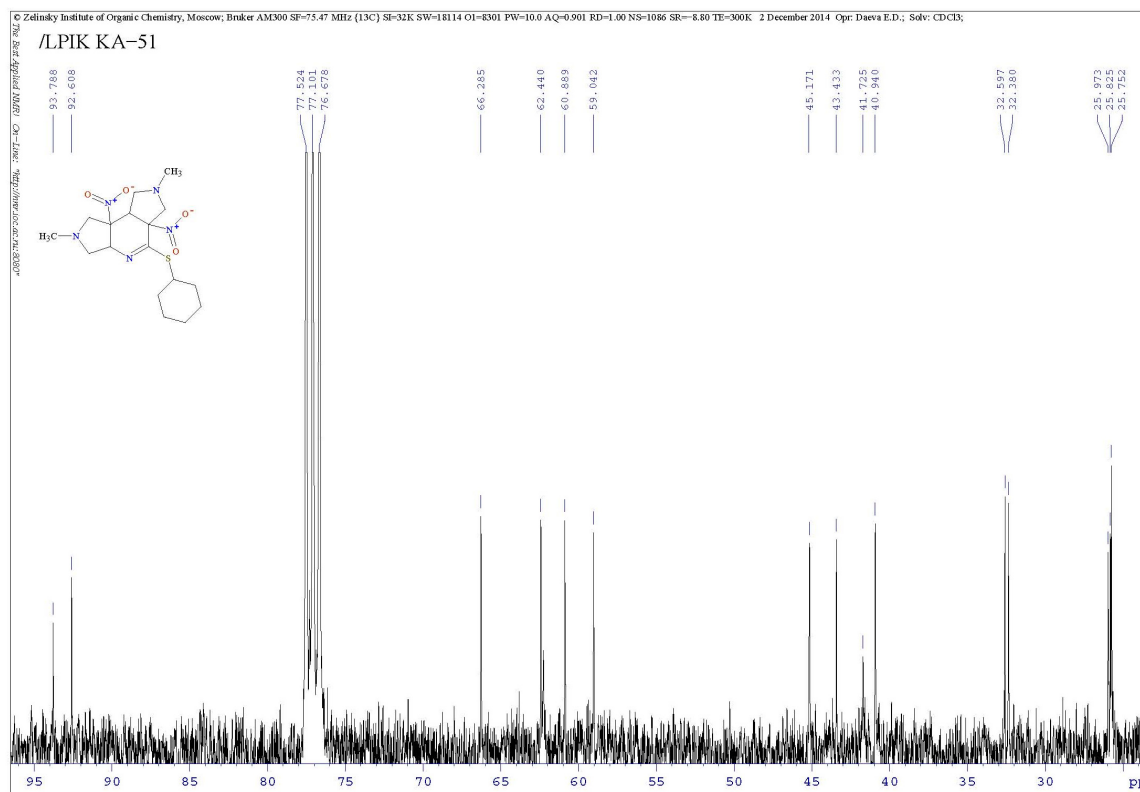
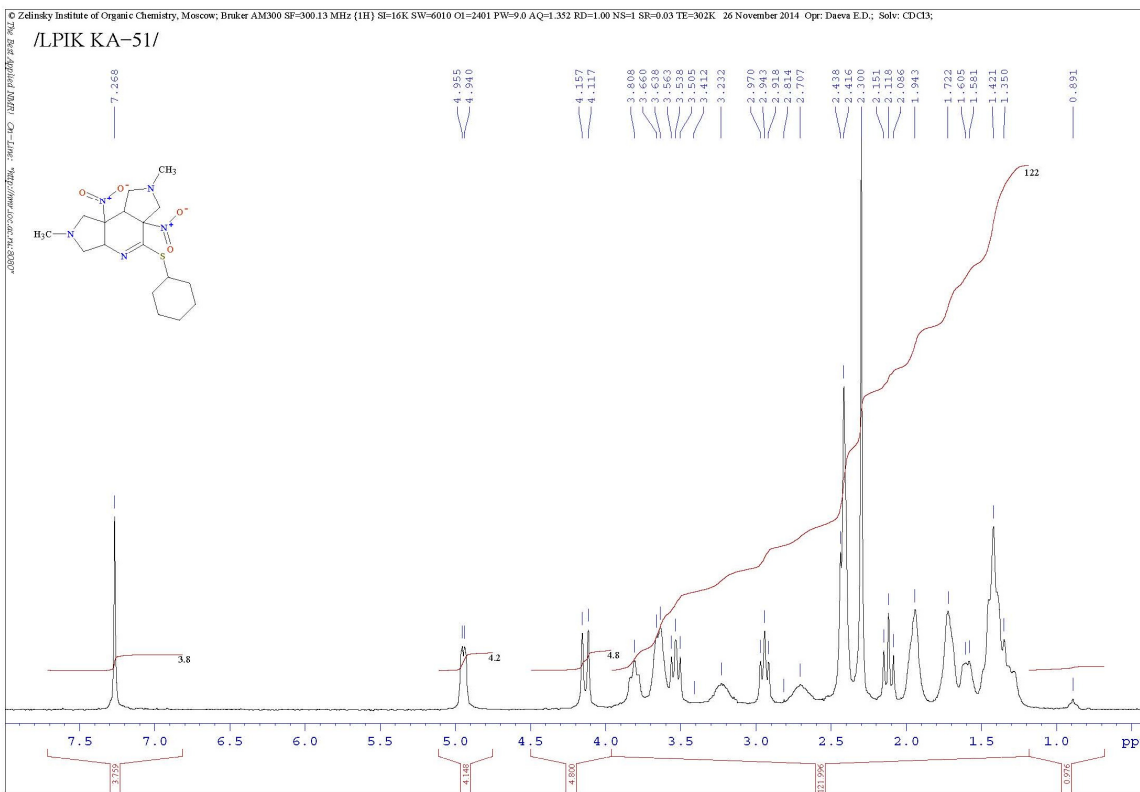


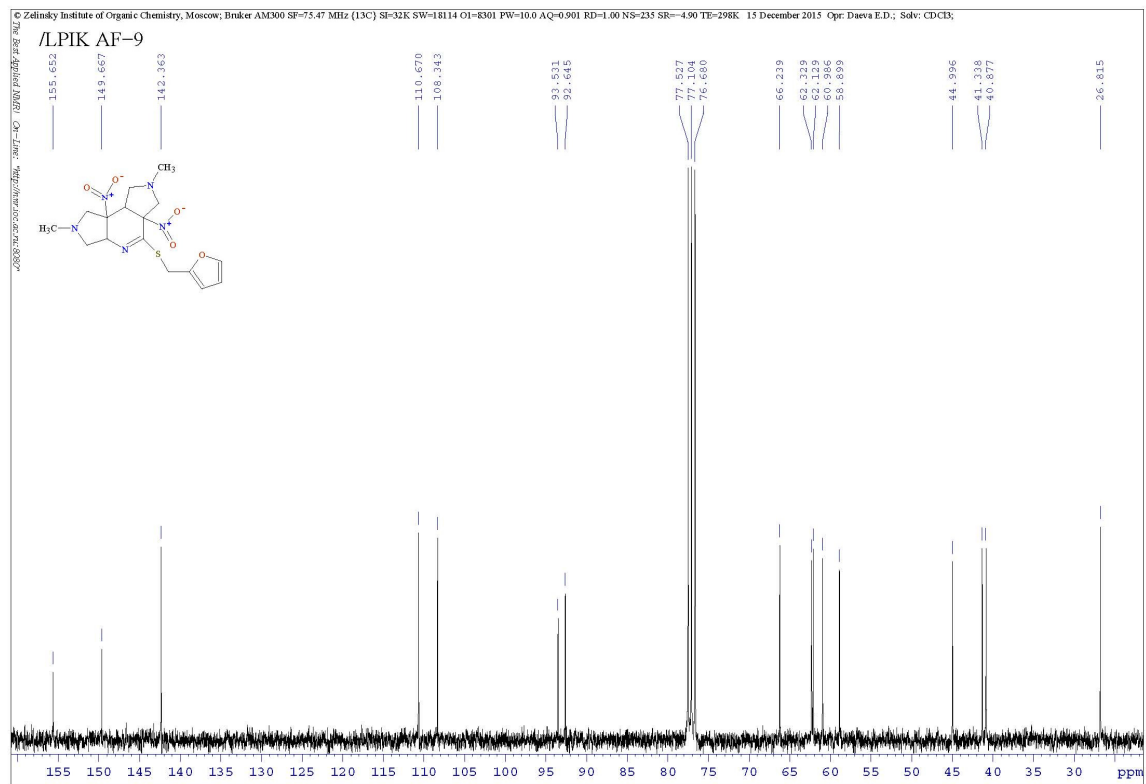
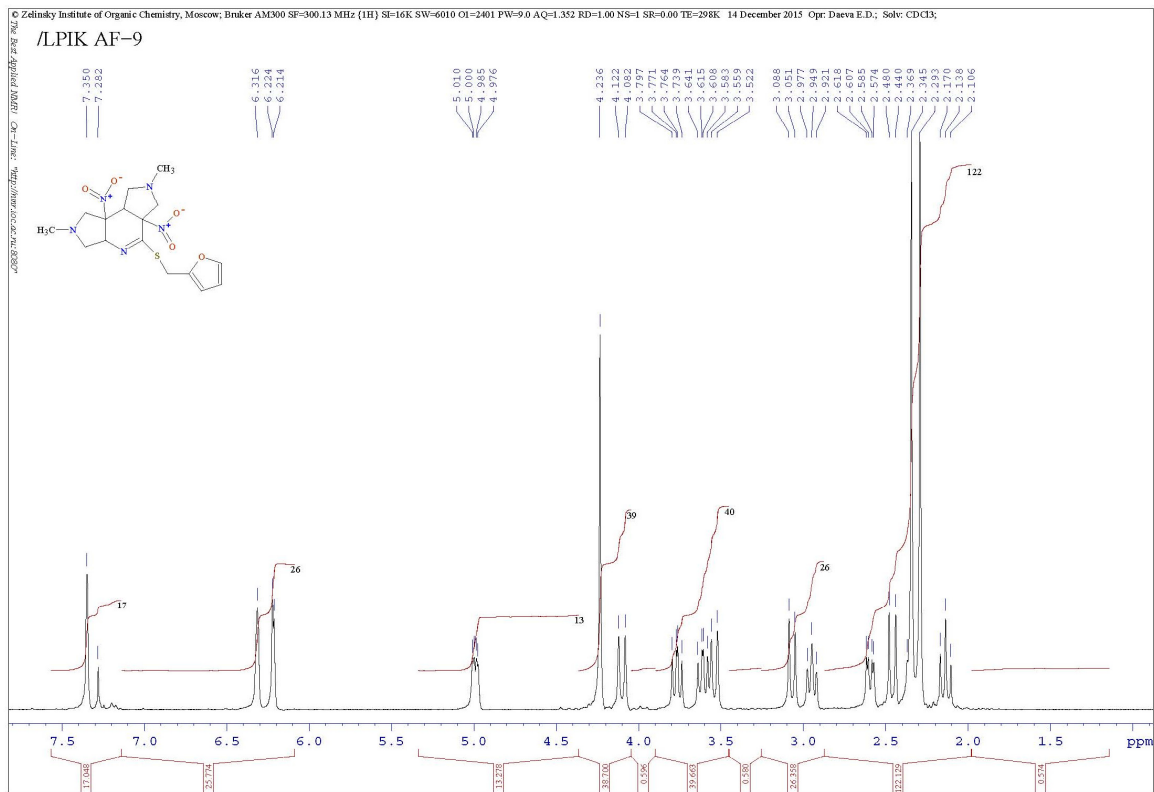


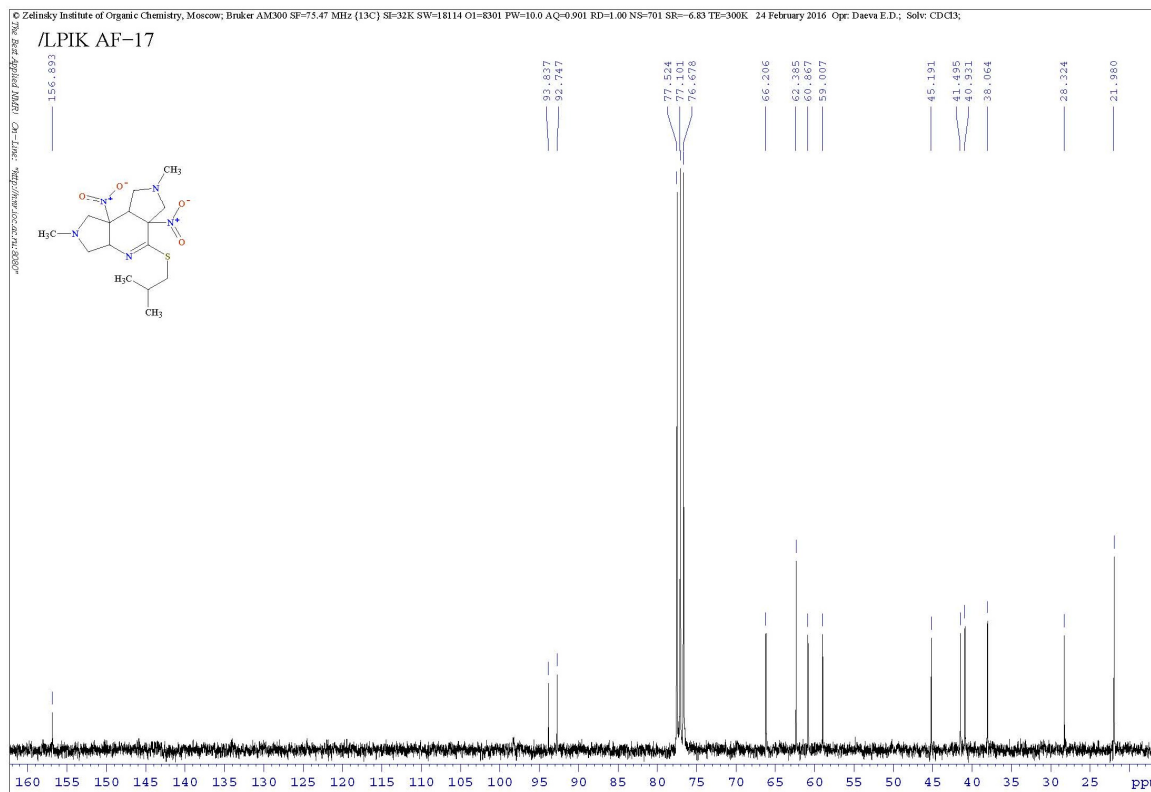
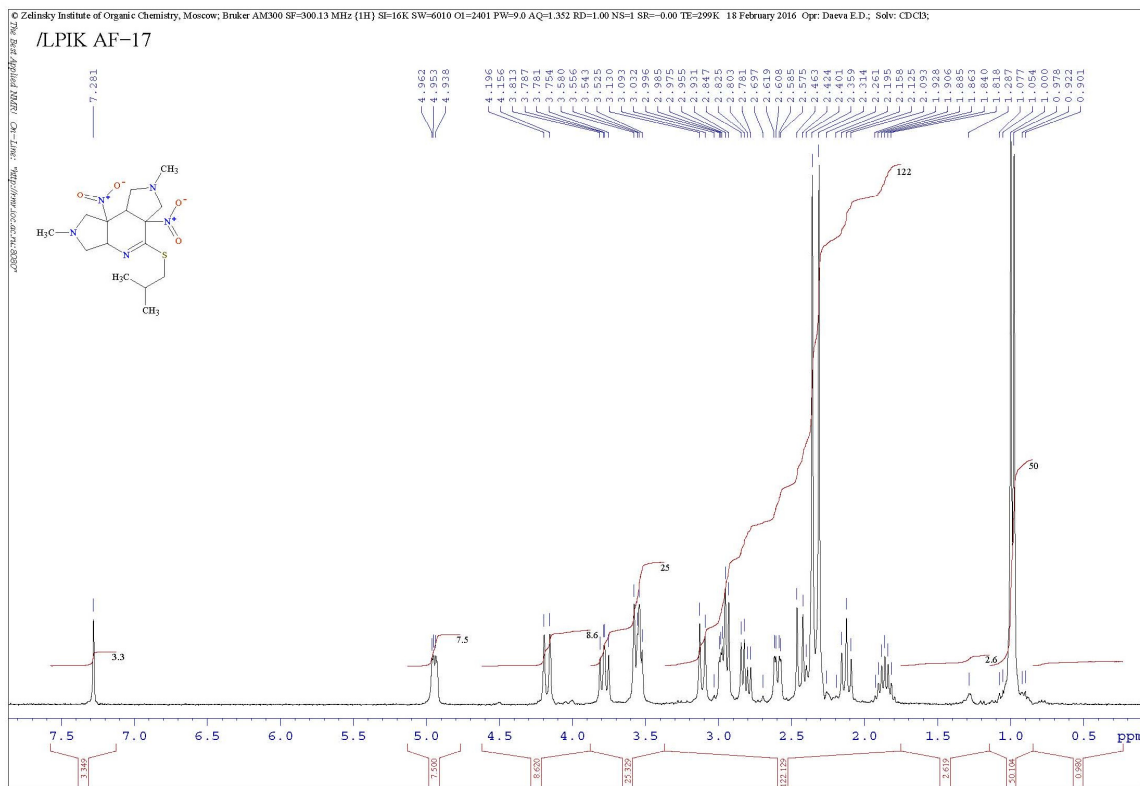


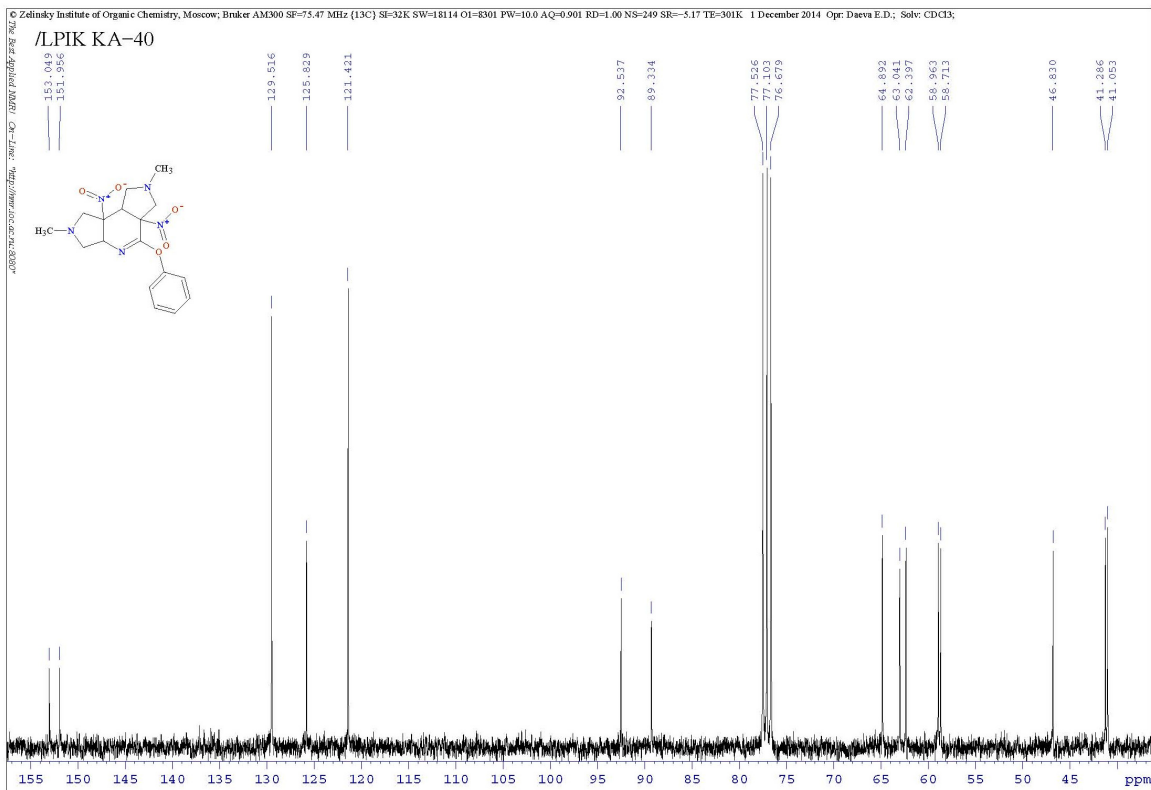
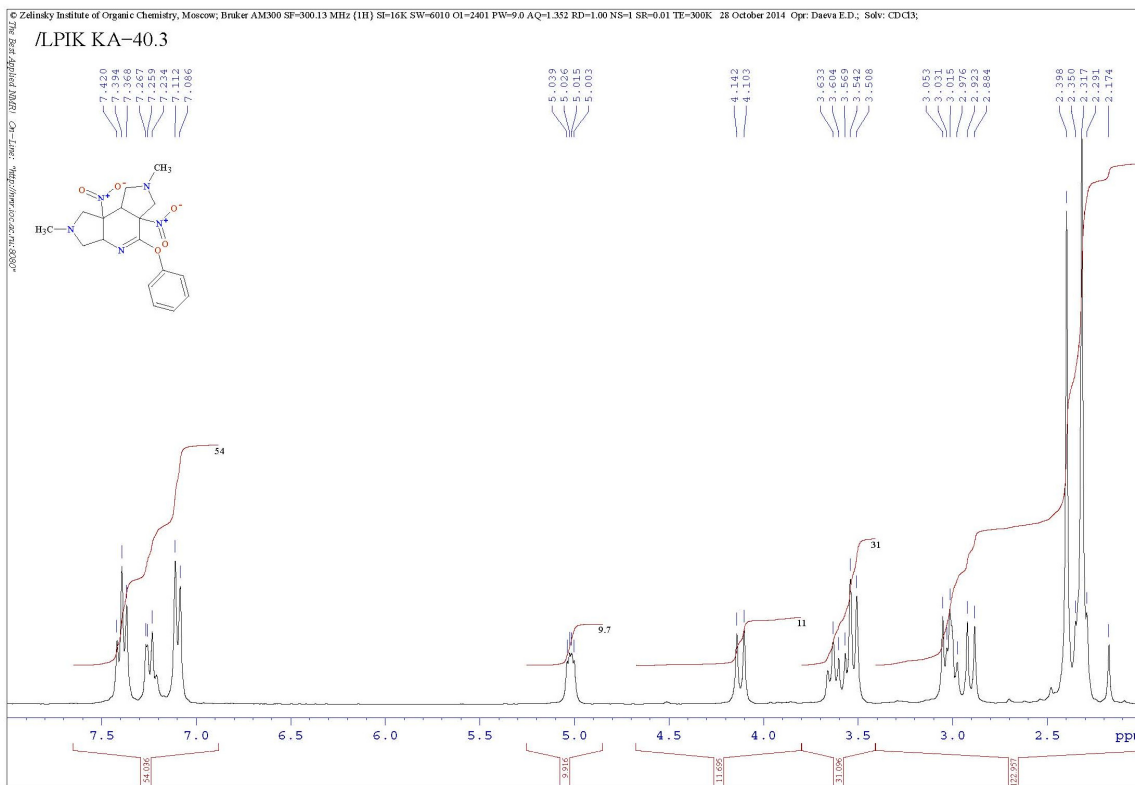












Display Report

Analysis Info

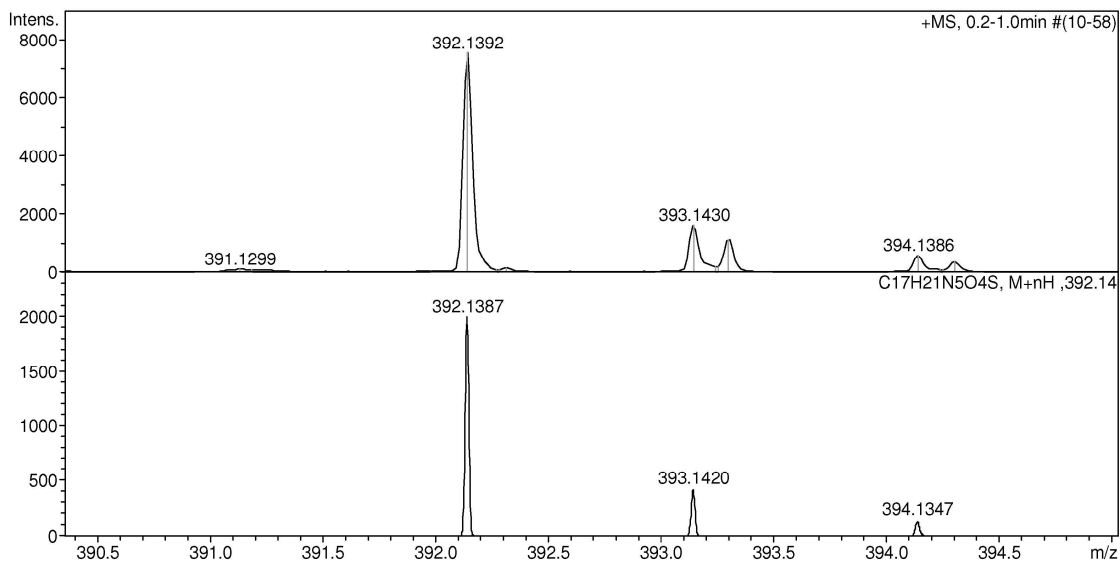
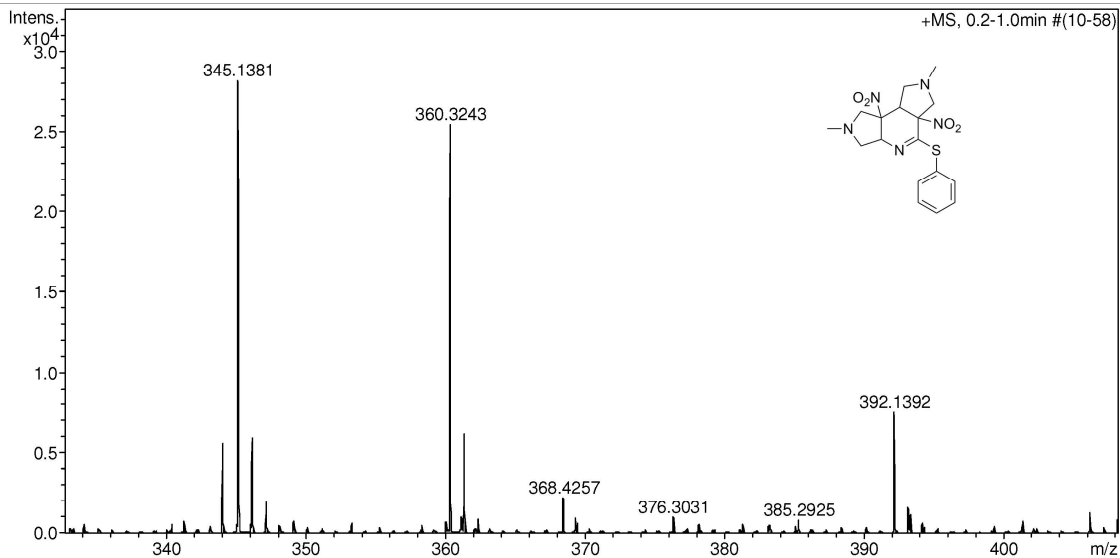
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Method tune_low.m
Sample Name /LPIK KA-39
Comment C17H21N5O4S mw 391 calibrant added

Acquisition Date 11.12.2014 13:18:04

Operator BDAL@DE
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Display Report

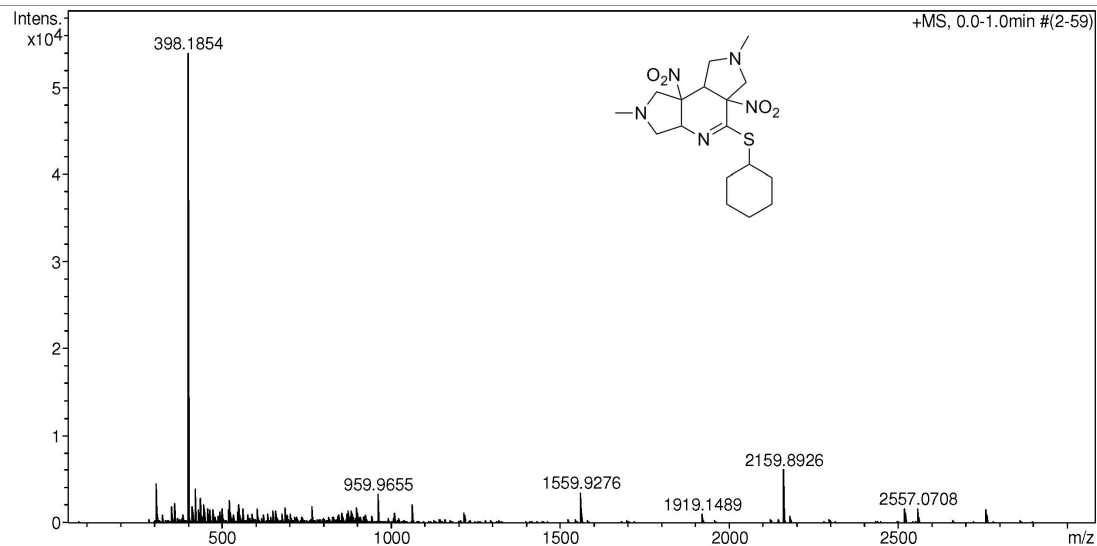
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 Method tune_wide.m
 Sample Name /LPIK KA-51
 Comment CH3CN 100 %, dil. 200, calibrant added

Acquisition Date 28.11.2014 17:39:40
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Display Report

Analysis Info

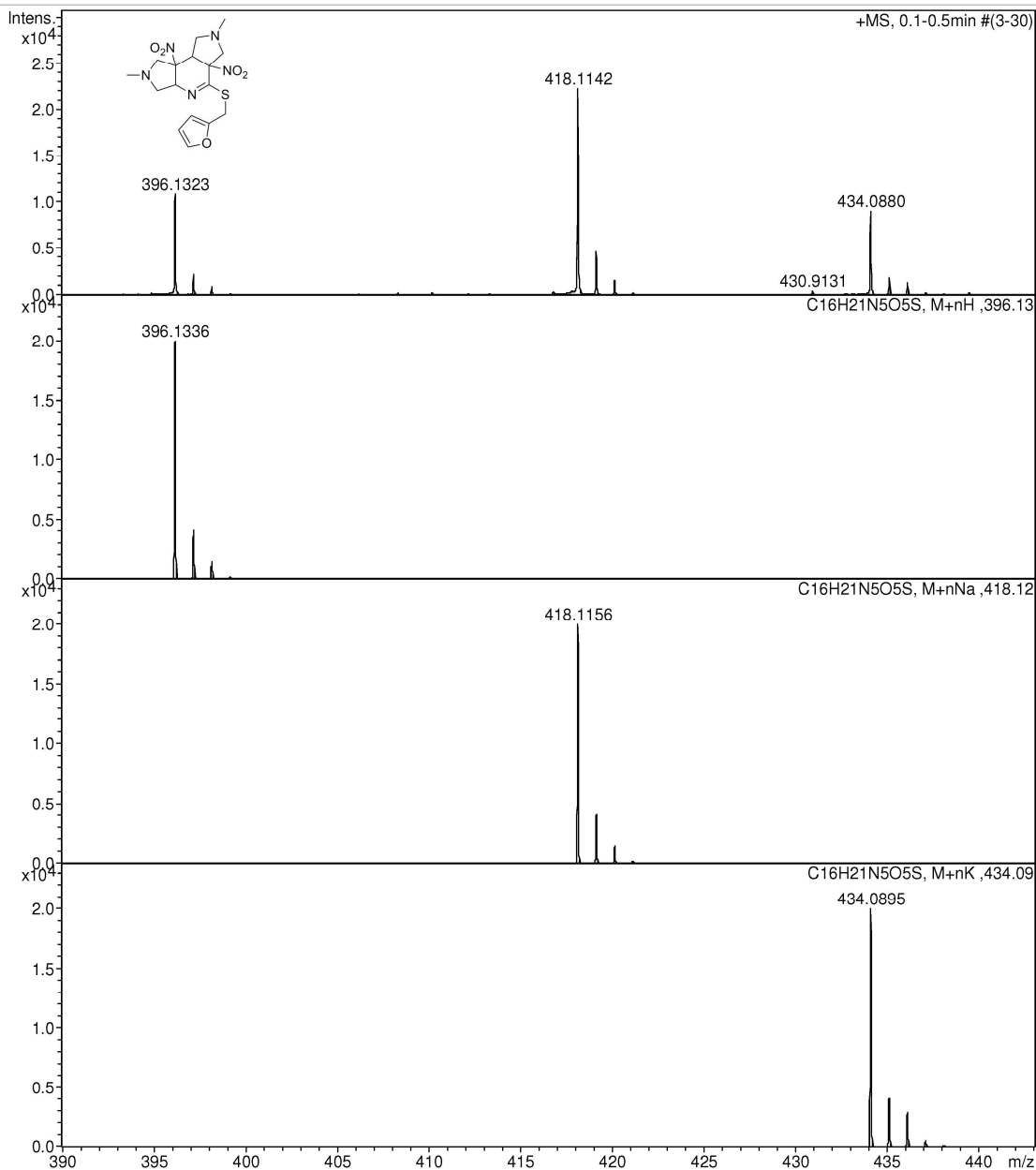
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Method tune_low.m
Sample Name /LPIK AF-9
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Acquisition Date 02.06.2016 17:27:25

Operator BDAL@DE
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Display Report

Analysis Info

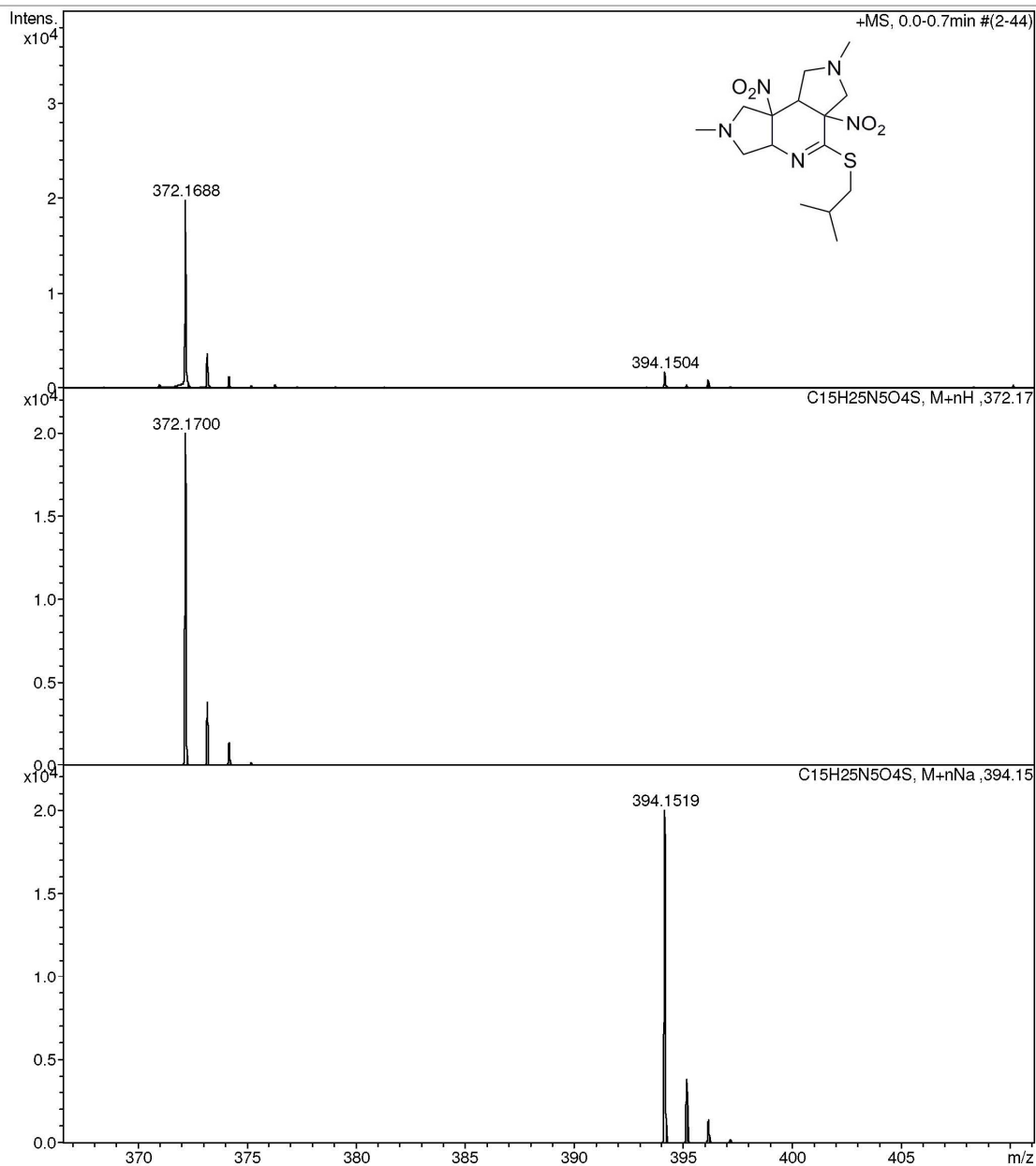
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Method tune_low.m
Sample Name /LPIK AF-19
Comment C15H25N5O4S mH 372.170 clb added

Acquisition Date 02.06.2016 17:35:52

Operator BDAL@DE
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Display Report

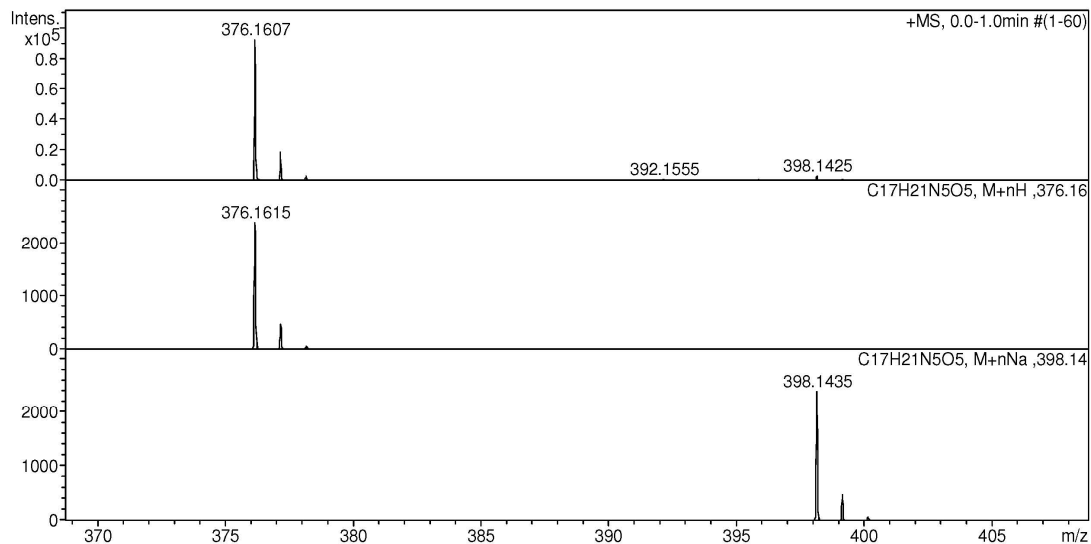
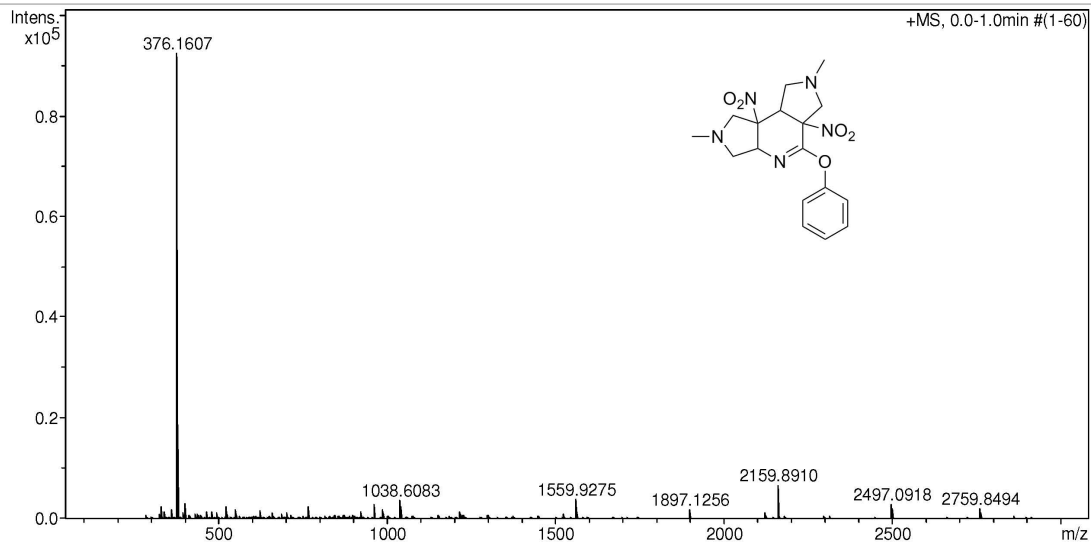
Analysis Info

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Sample Name /LPIK KA-40
Comment CH3CN 100 %, dil. 200, calibrant added

Acquisition Date 28.11.2014 17:33:40
Operator BDAL@DE
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ka39

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: ka39

Bond precision:	C-C = 0.0022 Å	Wavelength=1.54178	
Cell:	a=23.2992 (5)	b=9.9484 (2)	c=16.2653 (3)
	alpha=90	beta=106.144 (1)	gamma=90
Temperature:	120 K		
	Calculated	Reported	
Volume	3621.46 (13)	3621.46 (13)	
Space group	C 2/c	C 2/c	
Hall group	-C 2yc	-C 2yc	
Moiety formula	C17 H21 N5 O4 S	C17 H21 N5 O4 S	
Sum formula	C17 H21 N5 O4 S	C17 H21 N5 O4 S	
Mr	391.45	391.45	
Dx, g cm ⁻³	1.436	1.436	
Z	8	8	
Mu (mm ⁻¹)	1.898	1.898	
F000	1648.0	1648.0	
F000'	1655.61		
h,k,lmax	27,11,19	27,11,19	
Nref	3225	3196	
Tmin,Tmax	0.572,0.610	0.749,0.864	
Tmin'	0.519		

Correction method= # Reported T Limits: Tmin=0.749 Tmax=0.864
AbsCorr = MULTI-SCAN

Data completeness= 0.991 Theta(max)= 66.918

R(reflections)= 0.0318 (3054) wR2(reflections)= 0.0816 (3196)

S = 1.062 Npar= 246

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.597 30 Report

Alert level G

PLAT793_ALERT_4_G The Model has Chirality at C3 (Centro SPGR) S Verify
 PLAT793_ALERT_4_G The Model has Chirality at C4 (Centro SPGR) S Verify
 PLAT793_ALERT_4_G The Model has Chirality at C5 (Centro SPGR) S Verify
 PLAT793_ALERT_4_G The Model has Chirality at C6 (Centro SPGR) S Verify
 PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still 82 % Note
 PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 1 Note
 PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 10 Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain
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 2 ALERT type 3 Indicator that the structure quality may be low
 4 ALERT type 4 Improvement, methodology, query or suggestion
 0 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

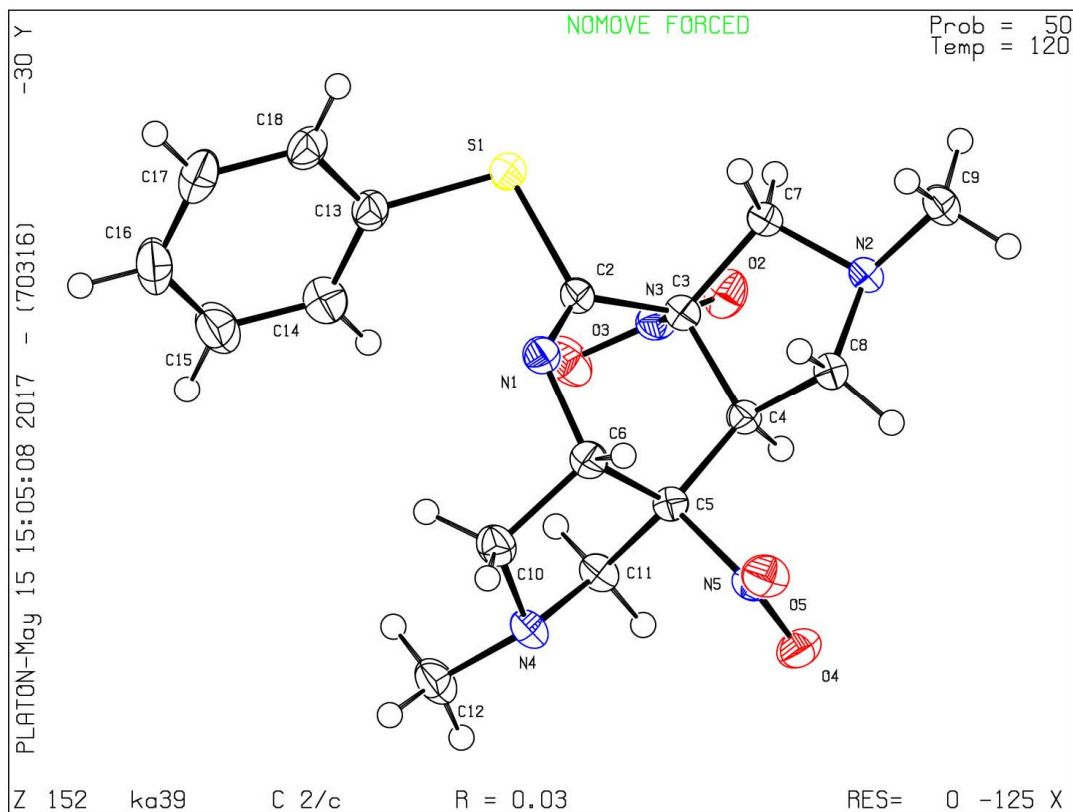
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/03/2017; check.def file version of 24/03/2017

PLATON May 15 15:05:08 2017 - (70316)



Alert level C

PLAT029_ALERT_3_C _diffn_measured_fraction_theta_full value Low .	0.971	Note
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600		94 Report

Alert level G

PLAT142_ALERT_4_G s.u. on b - Axis Small or Missing	0.00010	Ang.
PLAT143_ALERT_4_G s.u. on c - Axis Small or Missing	0.00010	Ang.
PLAT793_ALERT_4_G The Model has Chirality at C3 (Centro SPGR)		S Verify
PLAT793_ALERT_4_G The Model has Chirality at C4 (Centro SPGR)		S Verify
PLAT793_ALERT_4_G The Model has Chirality at C5 (Centro SPGR)		S Verify
PLAT793_ALERT_4_G The Model has Chirality at C6 (Centro SPGR)		S Verify
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still	87	% Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600	10	Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.	12	Note

-
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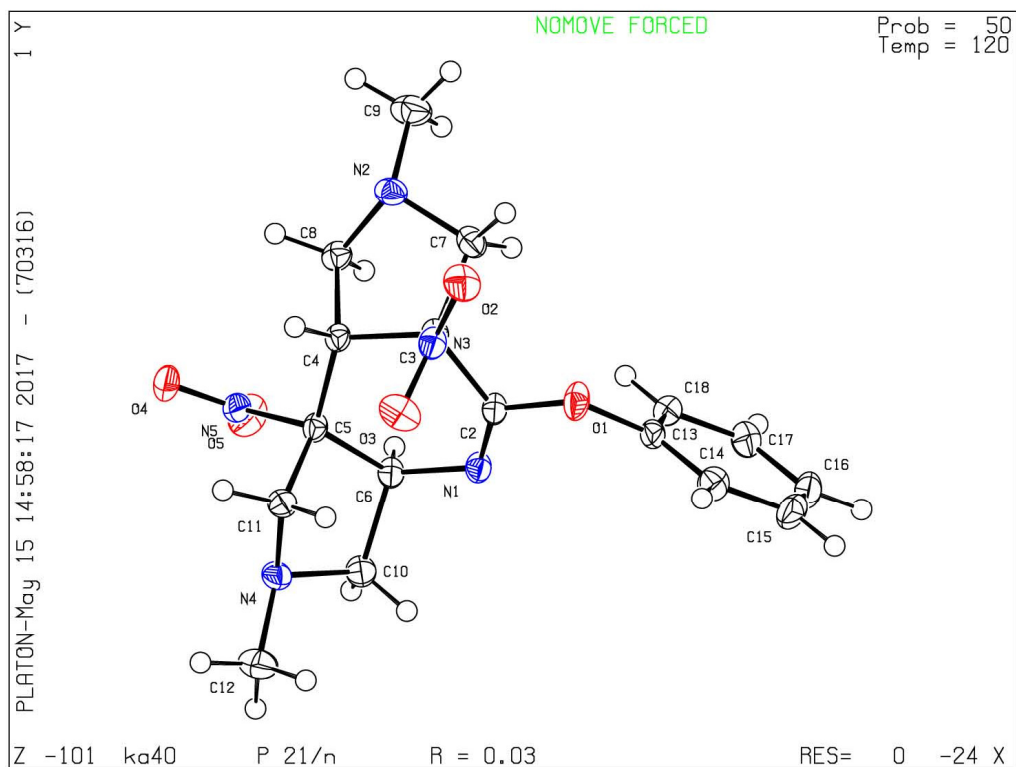
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

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PLATON version of 27/03/2017; check.def file version of 24/03/2017

Datablock ka40 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) ka51

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: ka51

Bond precision:	C-C = 0.0017 A	Wavelength=0.71073	
Cell:	a=13.0403(5)	b=13.3193(5)	c=11.8357(5)
	alpha=90	beta=108.653(1)	gamma=90
Temperature:	120 K		
	Calculated	Reported	
Volume	1947.74(13)	1947.73(13)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C17 H27 N5 O4 S	C17 H27 N5 O4 S	
Sum formula	C17 H27 N5 O4 S	C17 H27 N5 O4 S	
Mr	397.50	397.49	
Dx, g cm ⁻³	1.355	1.356	
Z	4	4	
Mu (mm ⁻¹)	0.200	0.200	
F000	848.0	848.0	
F000'	848.84		
h, k, lmax	18, 18, 16	18, 18, 16	
Nref	5681	5681	
Tmin, Tmax	0.913, 0.929	0.796, 0.862	
Tmin'	0.908		

Correction method= # Reported T Limits: Tmin=0.796 Tmax=0.862
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 29.991

R(reflections)= 0.0369(4665) wR2(reflections)= 0.0998(5681)

S = 1.042 Npar= 246

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT230_ALERT_2_C	Hirshfeld Test Diff for	O4	--	N5	..	5.4 s.u.
PLAT230_ALERT_2_C	Hirshfeld Test Diff for	N5	--	C5	..	6.6 s.u.

Alert level G

PLAT793_ALERT_4_G	The Model has Chirality at C3	(Centro SPGR)	R	Verify
PLAT793_ALERT_4_G	The Model has Chirality at C4	(Centro SPGR)	R	Verify
PLAT793_ALERT_4_G	The Model has Chirality at C5	(Centro SPGR)	R	Verify
PLAT793_ALERT_4_G	The Model has Chirality at C6	(Centro SPGR)	R	Verify
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min)		1	Note
PLAT960_ALERT_3_G	Number of Intensities with I < - 2*sig(I) ...		10	Check
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.		13	Note

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Datablock ka51 - ellipsoid plot

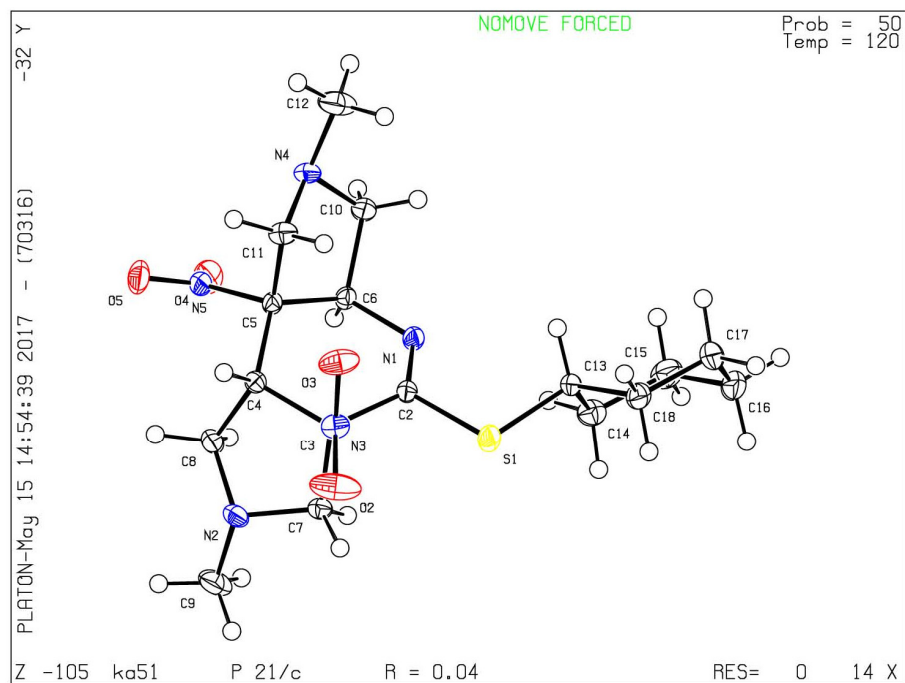


Table S1. Crystallographic data for compounds **7a**, **7b** and **7e**

	7e	7a	7b
Formula	C ₁₇ H ₂₁ N ₅ O ₅	C ₁₇ H ₂₁ N ₅ O ₄ S	C ₁₇ H ₂₇ N ₅ O ₄ S
Formula weight	375.39	391.45	397.50
T, K		120	
Crystal system		Monoclinic	
Space group	P2 ₁ /n	C2/c	P2 ₁ /c
Z / Z'	4 / 1	8 / 1	4 / 1
a, Å	12.64650(10)	23.2992(5)	13.0403(5)
b, Å	11.06250(10)	9.9484(2)	13.3193(5)
c, Å	14.03670(10)	16.2653(3)	11.8357(5)
β, °	113.1430(10)	106.1440(10)	108.6530(10)
V, Å ³	1805.73(3)	3621.46(13)	1947.73(13)
d _{calc} , g cm ⁻³	1.381	1.436	1.356
Radiation type	CuKα	CuKα	MoKα
μ, cm ⁻¹	8.7	18.98	2
2θ _{max} , °	134	134	60
Refls. collected /independent	18589/3175	45770/3196	25510/5681
Observed refls. [I>2σ(I)]	2935	3054	4665
R ₁	0.0326	0.0318	0.0369
wR ₂	0.0829	0.0816	0.0998
GOF	1.055	1.062	1.042
Residual density, eÅ ⁻³ (d _{max} /d _{min})	0.259/-0.226	0.492/-0.371	0.383/-0.242