Electronic Supplementary Information

Efficient synthesis of N-methyltetranitropyrrole – Stable, insensitive and high energy melt-castable material

Vikranth Thaltiri,[a,b] *Kurumurthy Chavva,*[b] *B. Sathish Kumar*[a] *and Pradeepta K. Panda*[a,b] *

[a]*School of Chemistry, University of Hyderabad, Hyderabad – 500046, India.*

[b]*Advance Centre of Research in High Energy Materials, University of Hyderabad, Hyderabad – 500046, India.*

**Email:* *pradeepta.panda@uohyd.ac.in ; pkpsc@uohyd.ernet.in*

Contents

1. General Experimental

NMR spectra were recorded on a Bruker Avance-400 and 500 MHz FT NMR spectrometers using the solvent resonance as internal standard (^{1}H NMR, CD_3CN at 1.94 & 2.13 ppm, DMSO D_6 at 2.50 & 3.33 ppm; ^{13}C NMR, CD_3CN at 1.32 & 118.26 ppm, DMSO D_6 at 39.52 ppm). Mass spectral determinations were carried out by Shimadzu-LCMS-2010 and Waters Xevo G-2XS QTOF spectrometer by ESI techniques. IR spectra were recorded on a Bruker Tensor II FT-IR spectrometer. Elemental (C, H, N) analysis were carried out using FLASH EA 1112 analyzer. Decomposition temperature was determined by DSC-TGA on SDT Q600 V20.9 Build 20 instrument. Powder X-ray diffraction was recorded on Bruker D8 Advance diffractometer (Bruker-AXS, Karlsruhe, Germany) using Cu-Kα X-radiation (λ = 1.5406 Å) at 40 kV and 30 mA power. X-ray diffraction patterns were collected over the 2θ range 5–50° at a scan rate of 3.9°/min. Crystallographic data for **1, 3a, 3b and 6** were collected on BRUKER APEX-II CCD microfocus diffractometer. Mo α (λ = 0.71073 Å) radiation was used to collect X-ray reflections on the single crystal. Data reduction was performed using Bruker SAINT[S1] software. Intensities for absorption were corrected using SADABS 2014/5,[S2] refined using SHELXL-2014/7[S3] with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. All C−H atoms were fixed geometrically using HFIX command in SHELX-TL. A check of the final CIF file using PLATON[S4] did not show any missed symmetry.

Crystallographic data (including the structure factor files) for structures **1, 3a, 3b and 6** in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication number **CCDC** 1885801, 1885802, 1885803 and 1885804, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

2. Crystal Structure Data

Table S1. Crystal data and structure refinement for Compound **1**.

Identification code	**1**	
Empirical formula	$C_5 H_3 N_5 O_8$	
Formula weight	261.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 11.3262(5) Å	α = 90°.
	b = 10.6080(4) Å	β = 90°.
	c = 15.3741(7) Å	γ = 90°.
Volume	1847.17(14) Å^3	
Z	8	
Density (calculated)	1.878 Mg/m^3	
Absorption coefficient	0.181 mm^{-1}	
F(000)	1056	
Crystal size	0.24 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.650 to 27.535°.	
Index ranges	-14<=h<=14, -13<=k<=13, -20<=l<=17	
Reflections collected	20200	
Independent reflections	2110 [R(int) = 0.0252]	
Completeness to theta = 25.242°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6656	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2110 / 0 / 164	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0843	
R indices (all data)	R1 = 0.0333, wR2 = 0.0862	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.349 and -0.263 e.Å^{-3}	

Table S2. Crystal data and structure refinement for Compound **3a**.

Identification code	**3a**	
Empirical formula	$C_4 H_3 N_3 O_4$	
Formula weight	157.09	
Temperature	301(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.5935(11) Å	α = 90°.
	b = 7.7118(14) Å	β = 90°.
	c = 11.559(2) Å	γ = 90°.
Volume	587.75(19) $Å^3$	
Z	4	
Density (calculated)	1.775 Mg/m^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	320	
Crystal size	0.18 x 0.14 x 0.08 mm^3	
Theta range for data collection	3.557 to 25.651°.	
Index ranges	-8<=h<=7, -9<=k<=9, -14<=l<=14	
Reflections collected	6178	
Independent reflections	1091 [R(int) = 0.0203]	
Completeness to theta = 25.242°	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6581	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1091 / 0 / 104	
Goodness-of-fit on F^2	1.102	
Final R indices [I>2sigma(I)]	R1 = 0.0246, wR2 = 0.0656	
R indices (all data)	R1 = 0.0251, wR2 = 0.0661	
Absolute structure parameter	0.5	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.163 and -0.128 e.$Å^{-3}$	

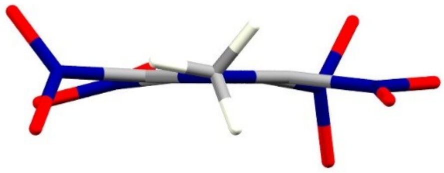
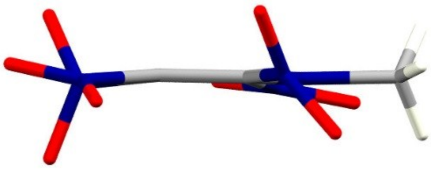
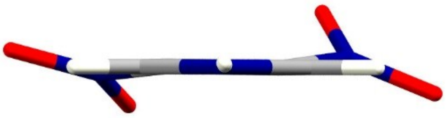
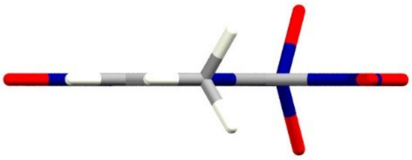
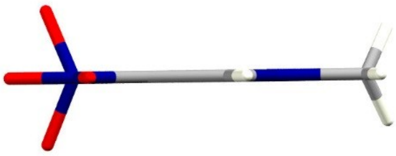
Table S3. Crystal data and structure refinement for Compound **3b**.

Identification code	**3b**	
Empirical formula	$C_4 H_3 N_3 O_4$	
Formula weight	157.09	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 9.0328(6) Å	α = 90°.
	b = 10.8978(9) Å	β = 90°.
	c = 12.4228(10) Å	γ = 90°.
Volume	1222.87(16) Å^3	
Z	8	
Density (calculated)	1.707 Mg/m^3	
Absorption coefficient	0.155 mm^{-1}	
F(000)	640	
Crystal size	0.24 x 0.20 x 0.16 mm^3	
Theta range for data collection	3.357 to 30.550°.	
Index ranges	-9<=h<=12, -15<=k<=15, -16<=l<=17	
Reflections collected	10229	
Independent reflections	1849 [R(int) = 0.0601]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6068	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1849 / 0 / 101	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1429	
R indices (all data)	R1 = 0.0533, wR2 = 0.1499	
Extinction coefficient	0.081(17)	
Largest diff. peak and hole	0.444 and -0.271 e.Å^{-3}	

Table S4. Crystal data and structure refinement for Compound **6**.

Identification code	**6**	
Empirical formula	$C_5 H_4 N_4 O_6$	
Formula weight	216.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n m a	
Unit cell dimensions	a = 15.7046(10) Å	α = 90°.
	b = 19.0277(10) Å	β = 90°.
	c = 8.4560(5) Å	γ = 90°.
Volume	2526.8(3) Å^3	
Z	12	
Density (calculated)	1.704 Mg/m^3	
Absorption coefficient	0.158 mm^{-1}	
F(000)	1320	
Crystal size	0.16 x 0.12 x 0.08 mm^3	
Theta range for data collection	2.594 to 27.536°.	
Index ranges	-20<=h<=20, -24<=k<=23, -10<=l<=10	
Reflections collected	30783	
Independent reflections	2938 [R(int) = 0.0341]	
Completeness to theta = 25.242°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6119	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2938 / 0 / 231	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0885	
R indices (all data)	R1 = 0.0376, wR2 = 0.0899	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.351 and -0.232 e.Å^{-3}	

Table S5: Representation of X-ray structures of compounds with capped stick model in two different side views:

1		
3a		
3b		
6		

Color code: grey = Carbon, white = Hydrogen, blue = Nitrogen and red = Oxygen.

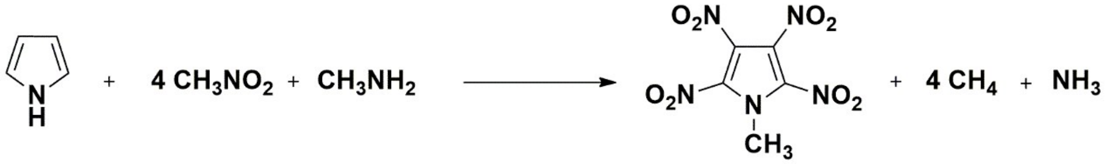
3. Computational study and isodesmic reaction

Theoretical calculation was performed using Gaussian 09 program provided by CMSD facility of University of Hyderabad.[S5] The geometric optimization of the structures and frequency analyses were carried out using B3LYP functional with 6-31G+(d, p) basis set. The optimized geometry was a minimum on the potential-energy surface and no imaginary frequencies were found. The method of isodesmic reaction has been employed to calculate HOF from total energies obtained from DFT calculations. Crystal packing density was predicted by the molecular packing calculations using CVFF force field in the polymorph module of Material Studio Suite.[S6] Based on the predicted densities and HOFs, using Explo5 *version* 6.03,[S7] the detonation velocity (*D*) and detonation pressure (*P*) for the energetic materials are calculated.

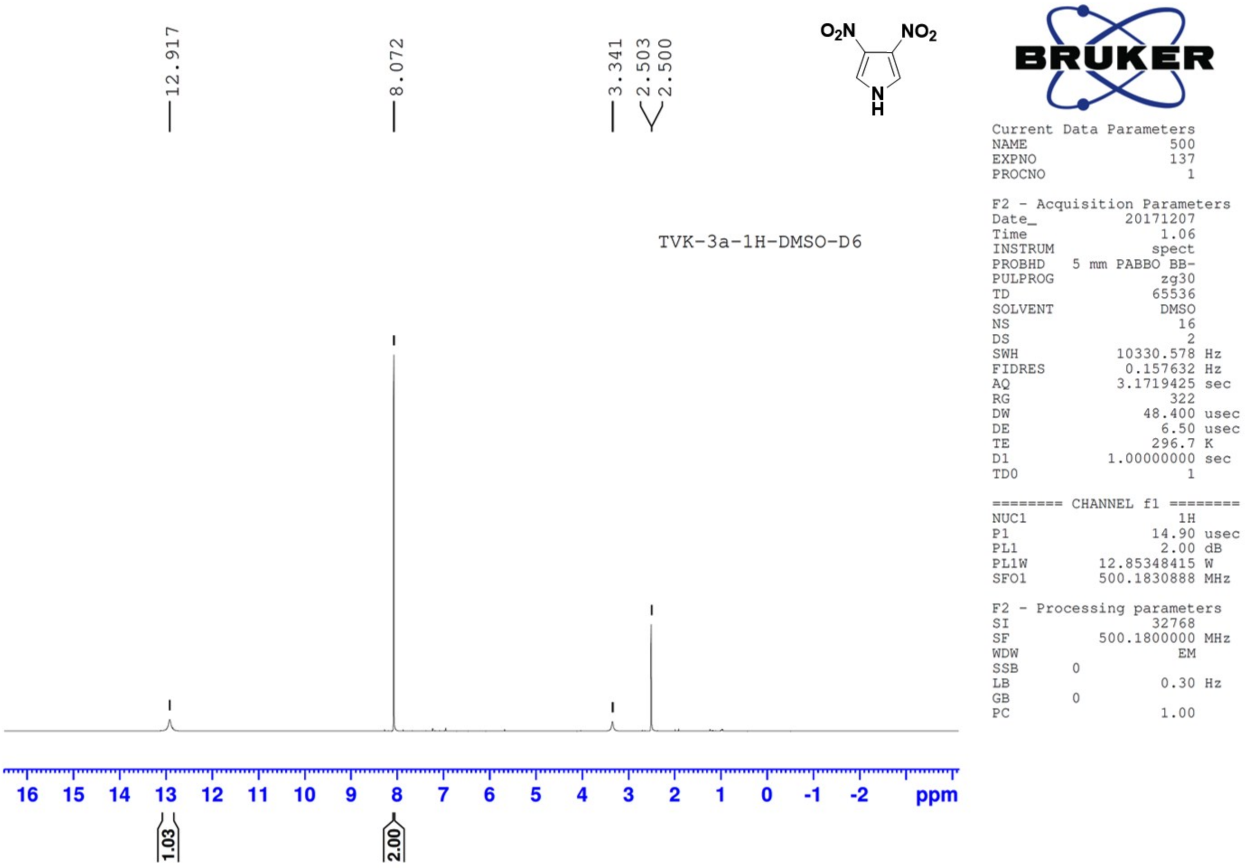
Table S5. Theoretical energetic properties of **1**.

Compound	**OB** ^{a} **(%)**	ρ^{b} **(g cm^{-3})**	$D_v{}^{c}$ **(m s^{-1})**	P^{d} **(GPa)**	$\Delta H_f{}^{e}$ **(kJ mol^{-1})**
1	-21.44	1.90	8851	36.13	99.7
‘a’ Oxygen balance, ‘b’ Calculated density, ‘c’ Detonation velocity (calculated with Explo5 *version* 6.03), ‘d’ Detonation pressure (calculated with Explo5 *version* 6.03), ‘e’ Heat of formation.					

Isodesmic reaction for compound 1

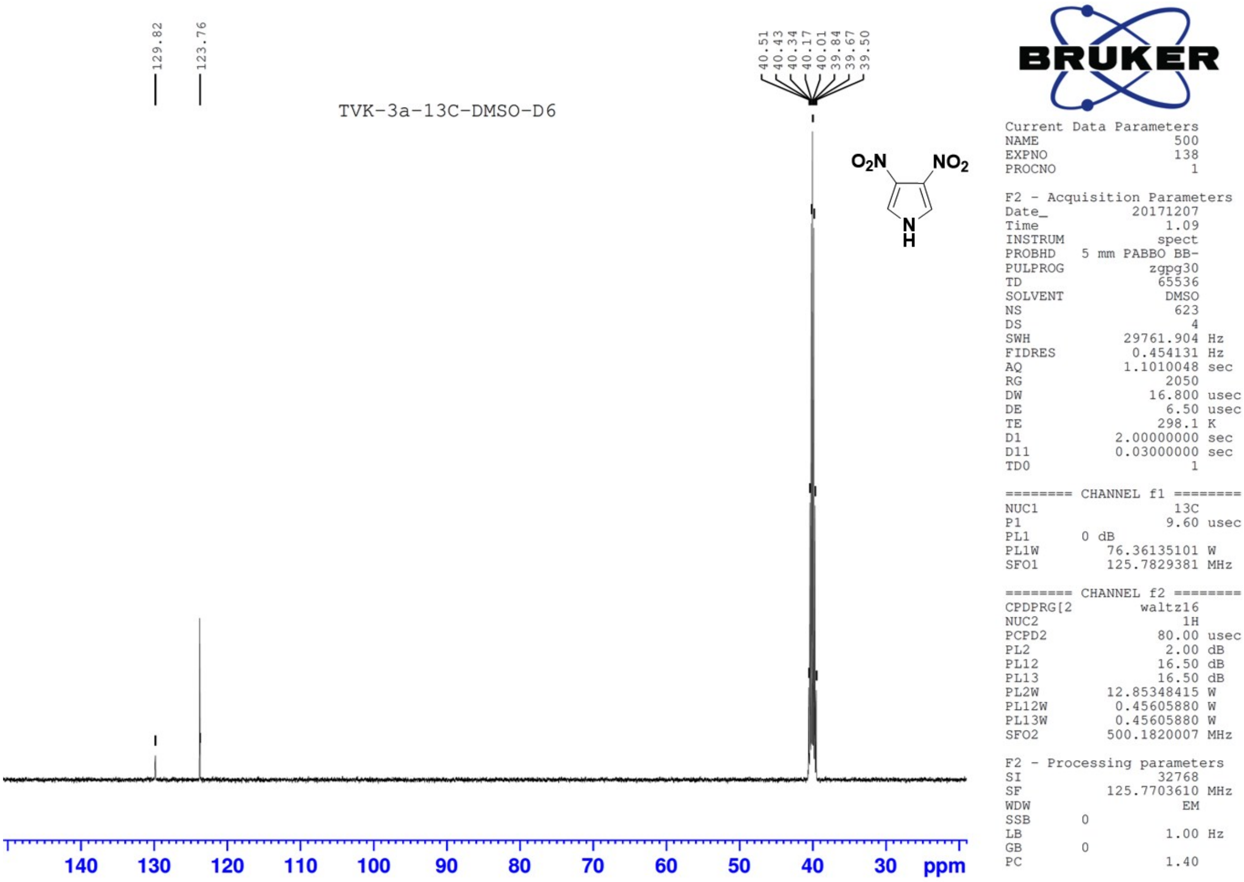


4. NMR spectra, Elemental analysis, LCMS, HRMS and IR data of compounds:



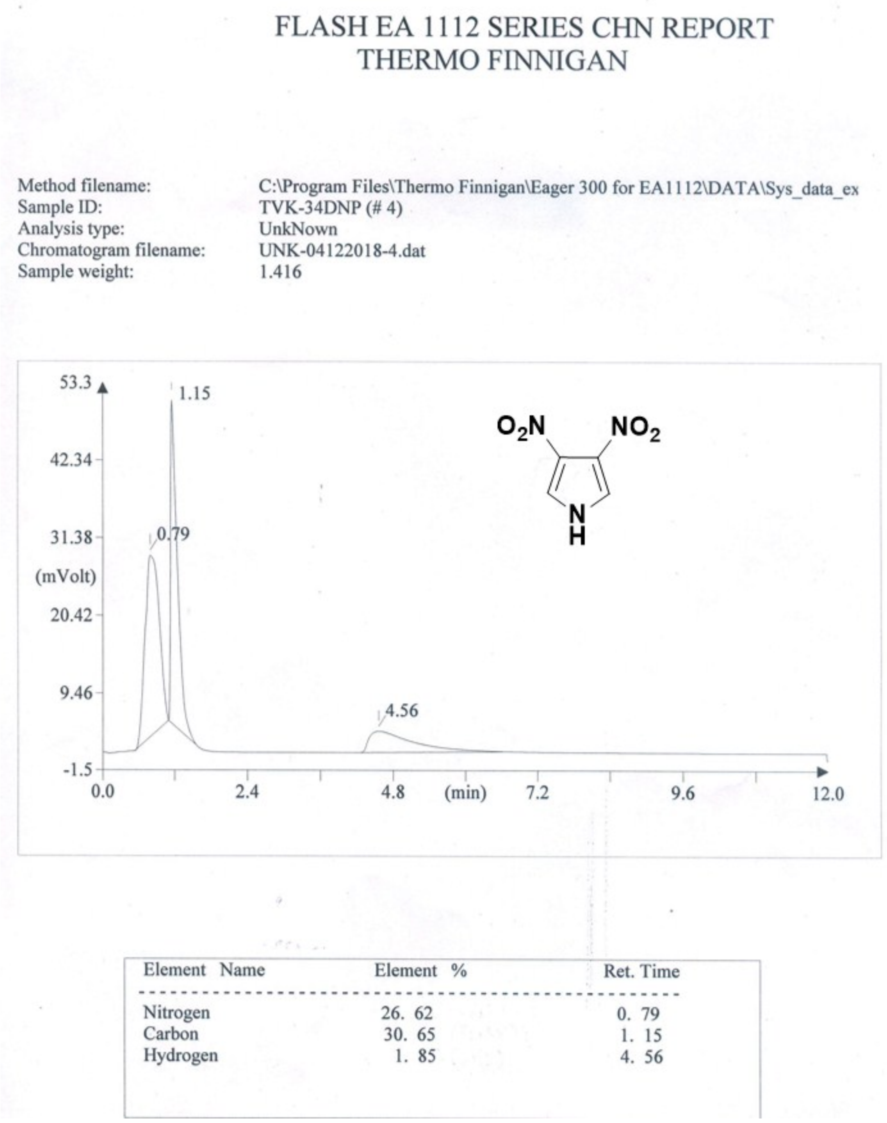
```
Current Data Parameters
NAME                  500
EXPNO                 137
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171207
Time                 1.06
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                    322
DW                 48.400 usec
DE                   6.50 usec
TE                  296.7 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.90 usec
PL1                  2.00 dB
PL1W          12.85348415 W
SFO1          500.1830888 MHz

F2 - Processing parameters
SI                  32768
SF            500.1800000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

Figure S1: ^{1}H NMR spectrum of **3a** in dimethyl sulfoxide-d_6.



```
Current Data Parameters
NAME                500
EXPNO               138
PROCNO                1

F2 - Acquisition Parameters
Date_          20171207
Time               1.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                  623
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG                 2050
DW               16.800 usec
DE                 6.50 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.60 usec
PL1       0 dB
PL1W        76.36135101 W
SFO1        125.7829381 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                2.00 dB
PL12              16.50 dB
PL13              16.50 dB
PL2W        12.85348415 W
PL12W        0.45605880 W
PL13W        0.45605880 W
SFO2        500.1820007 MHz

F2 - Processing parameters
SI                32768
SF          125.7703610 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S2: ^{13}C NMR spectrum of **3a** in dimethyl sulfoxide-d_6.



FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	TVK-34DNP (# 4)
Analysis type:	UnkNown
Chromatogram filename:	UNK-04122018-4.dat
Sample weight:	1.416

Element Name	Element %	Ret. Time
Nitrogen	26. 62	0. 79
Carbon	30. 65	1. 15
Hydrogen	1. 85	4. 56

Figure S3: Elemental analysis of **3a**.

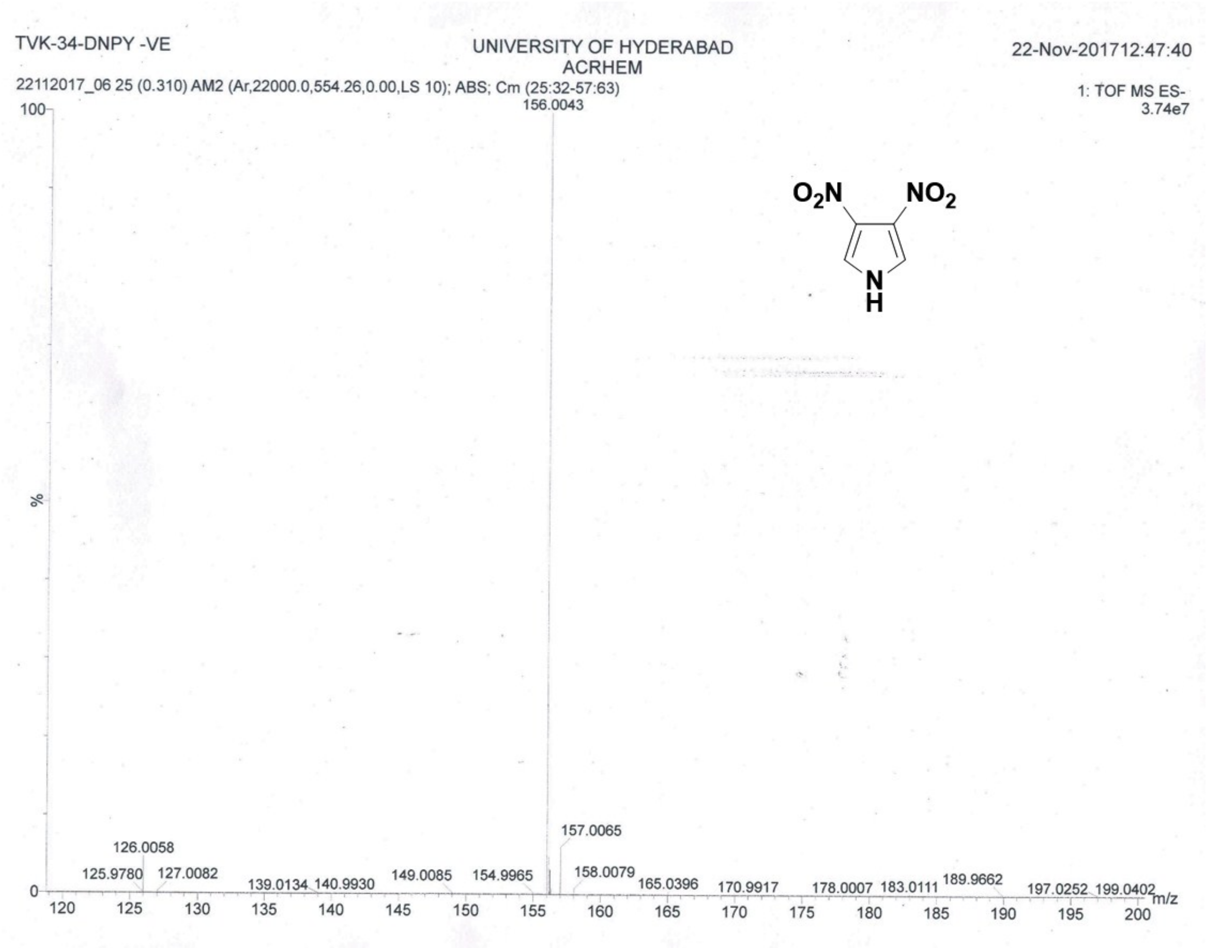


Figure S4: HRMS of **3a**.

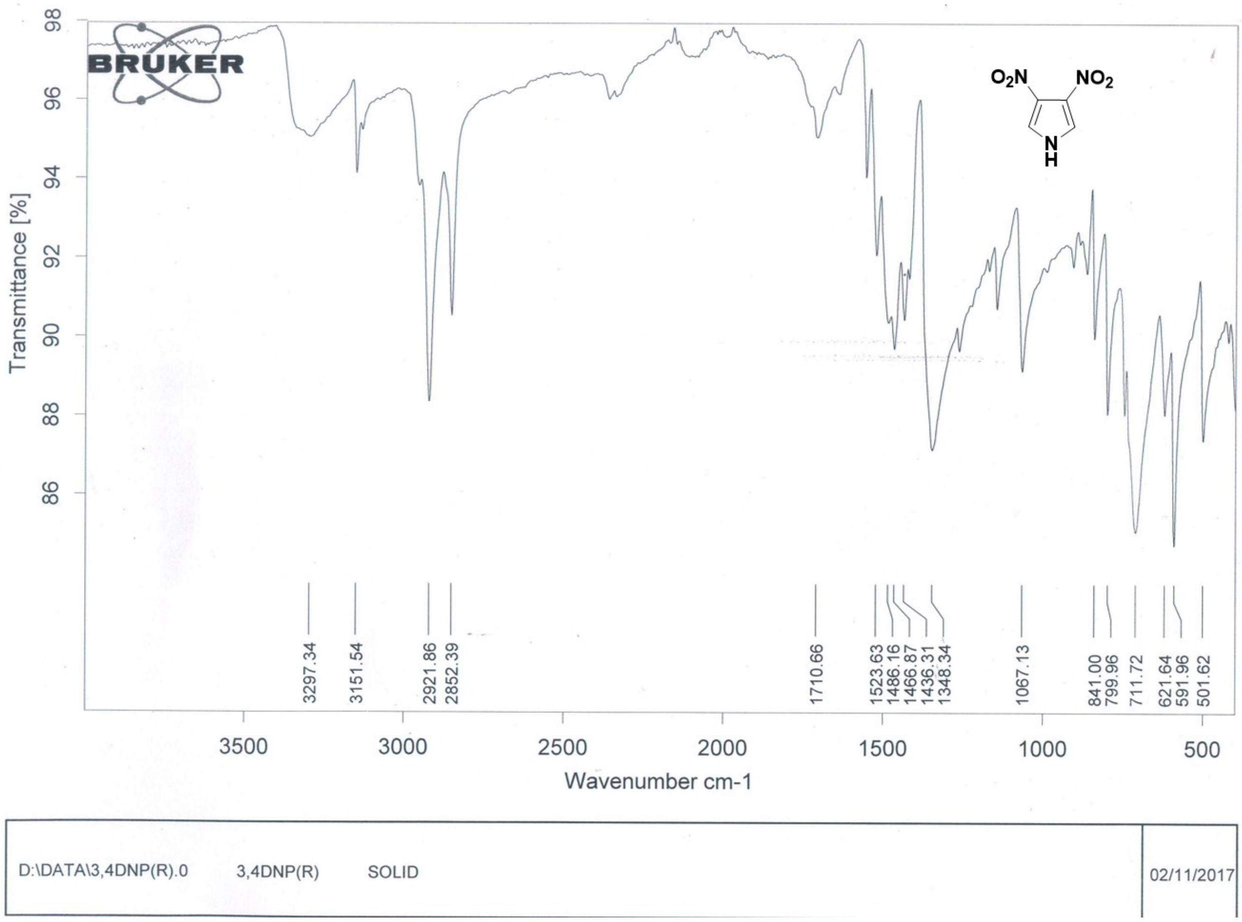
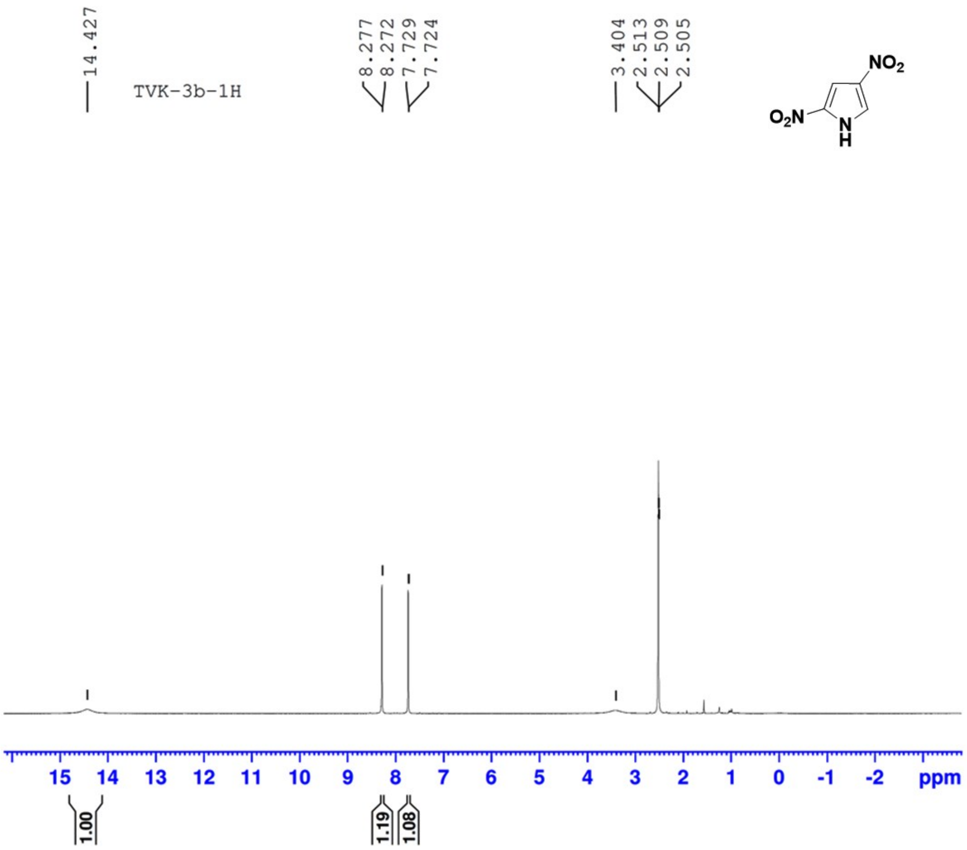
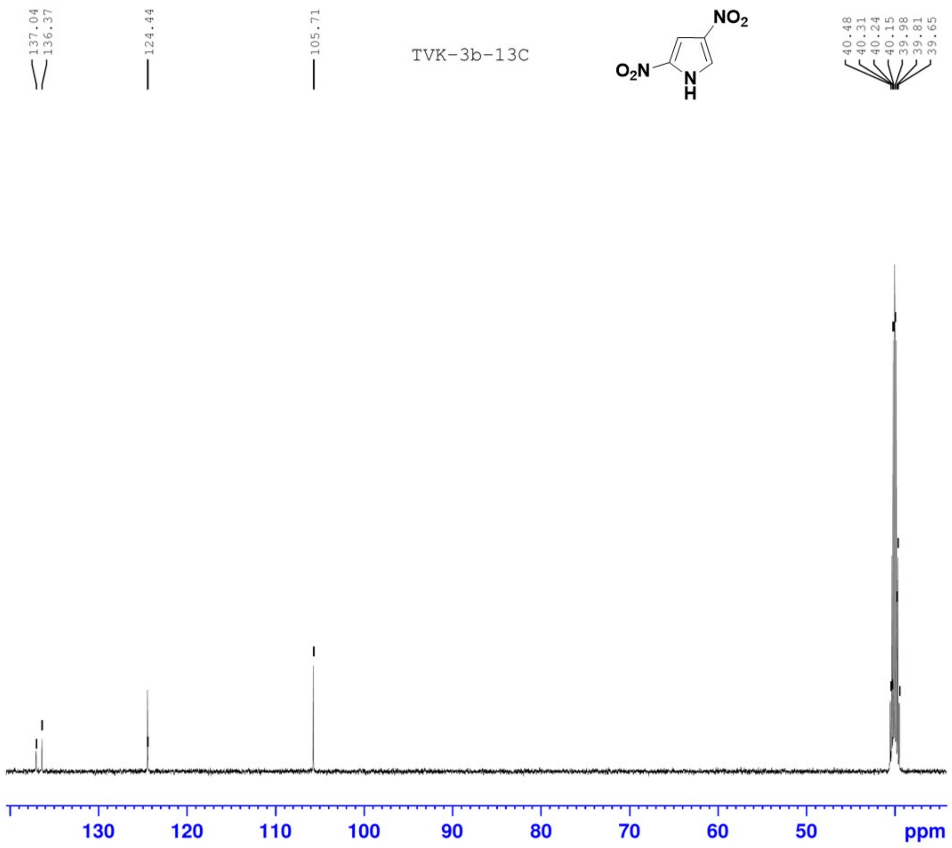


Figure S5: IR spectrum of **3a**.



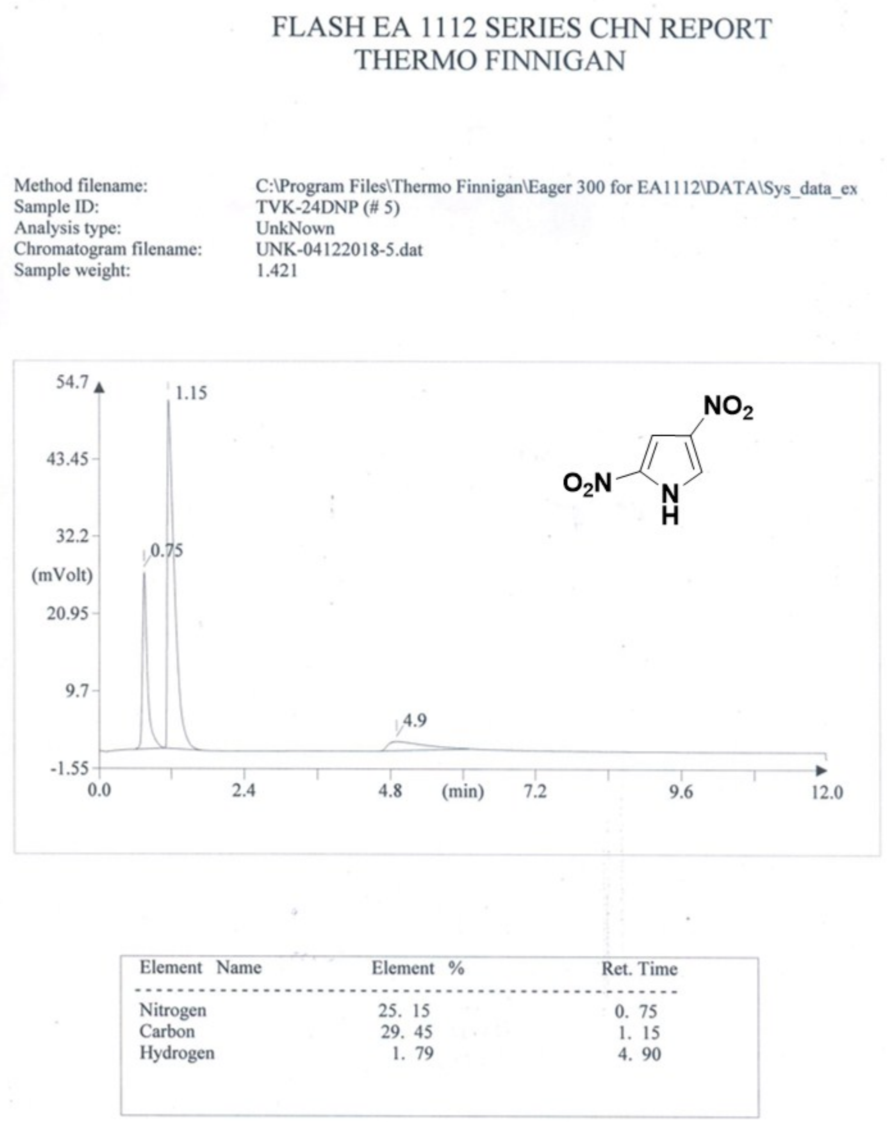
```
Current Data Parameters
NAME                 400
EXPNO                 73
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171103
Time                5.45
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9845889 sec
RG                   512
DW                60.800 usec
DE                  6.50 usec
TE                 295.3 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.90 usec
PL1                 1.50 dB
PL1W         15.18650627 W
SFO1         400.0934707 MHz

F2 - Processing parameters
SI                 32768
SF           400.0910000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

Figure S6: ^{1}H NMR spectrum of **3b** in dimethyl sulfoxide-d_6.



```
Current Data Parameters
NAME                600
EXPNO                17
PROCNO                1

F2 - Acquisition Parameters
Date_          20171208
Time              17.34 h
INSTRUM           spect
PROBHD   Z125331_0034 (
PULPROG         zgpg30
TD                65536
SOLVENT            DMSO
NS                  619
DS                    4
SWH           29761.904 Hz
FIDRES         0.908261 Hz
AQ            1.1010048 sec
RG                18.03
DW               16.800 usec
DE                 6.50 usec
TE                299.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.8304669 MHz
NUC1                13C
P1                12.00 usec
PLW1       172.66999817 W
SFO2        500.3710015 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        12.18000031 W
PLW12        0.12180000 W
PLW13        0.06126500 W

F2 - Processing parameters
SI                32768
SF          125.8178851 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

Figure S7: ^{13}C NMR spectrum of **3b** in dimethyl sulfoxide-d_6.



FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	TVK-24DNP (# 5)
Analysis type:	UnkNown
Chromatogram filename:	UNK-04122018-5.dat
Sample weight:	1.421

Element Name	Element %	Ret. Time
Nitrogen	25. 15	0. 75
Carbon	29. 45	1. 15
Hydrogen	1. 79	4. 90

Figure S8: Elemental analysis of **3b**.

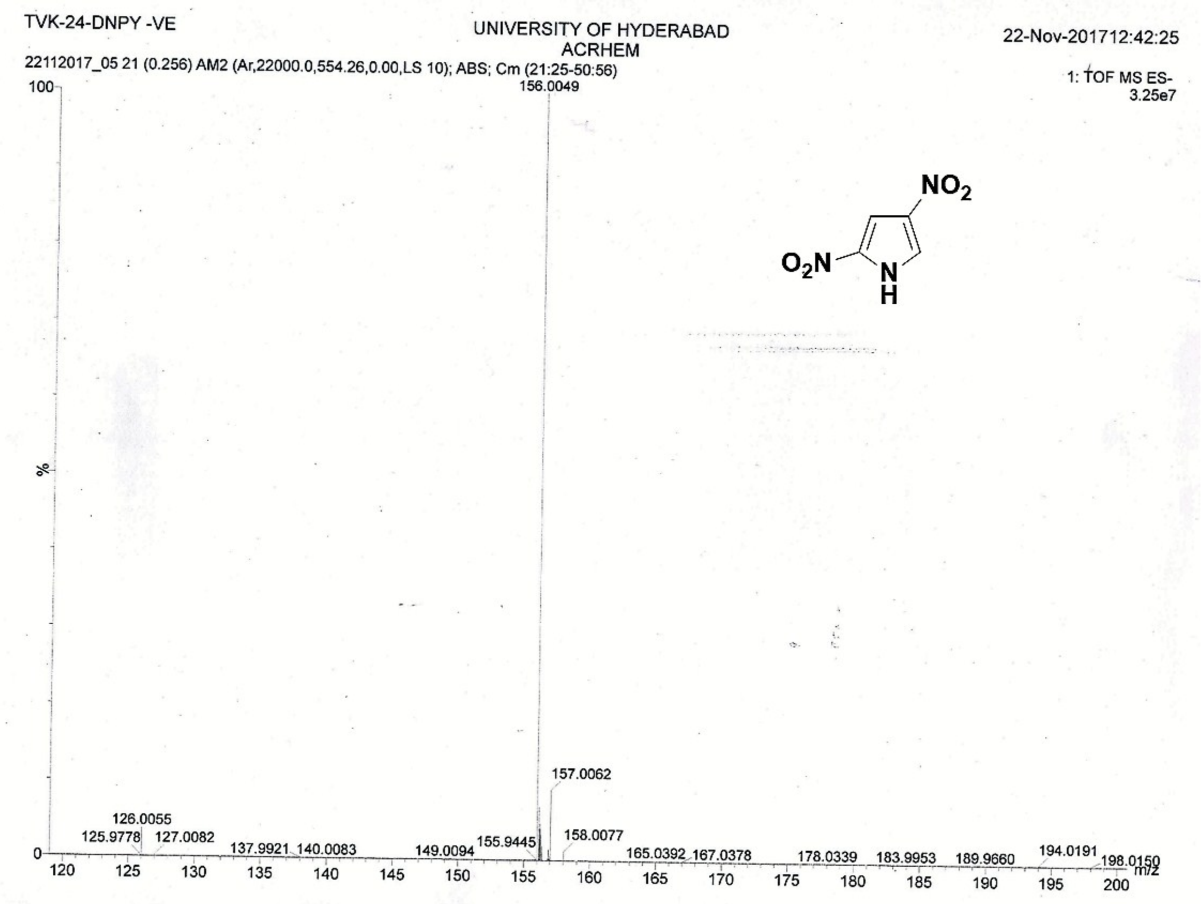


Figure S9: HRMS of **3b**.

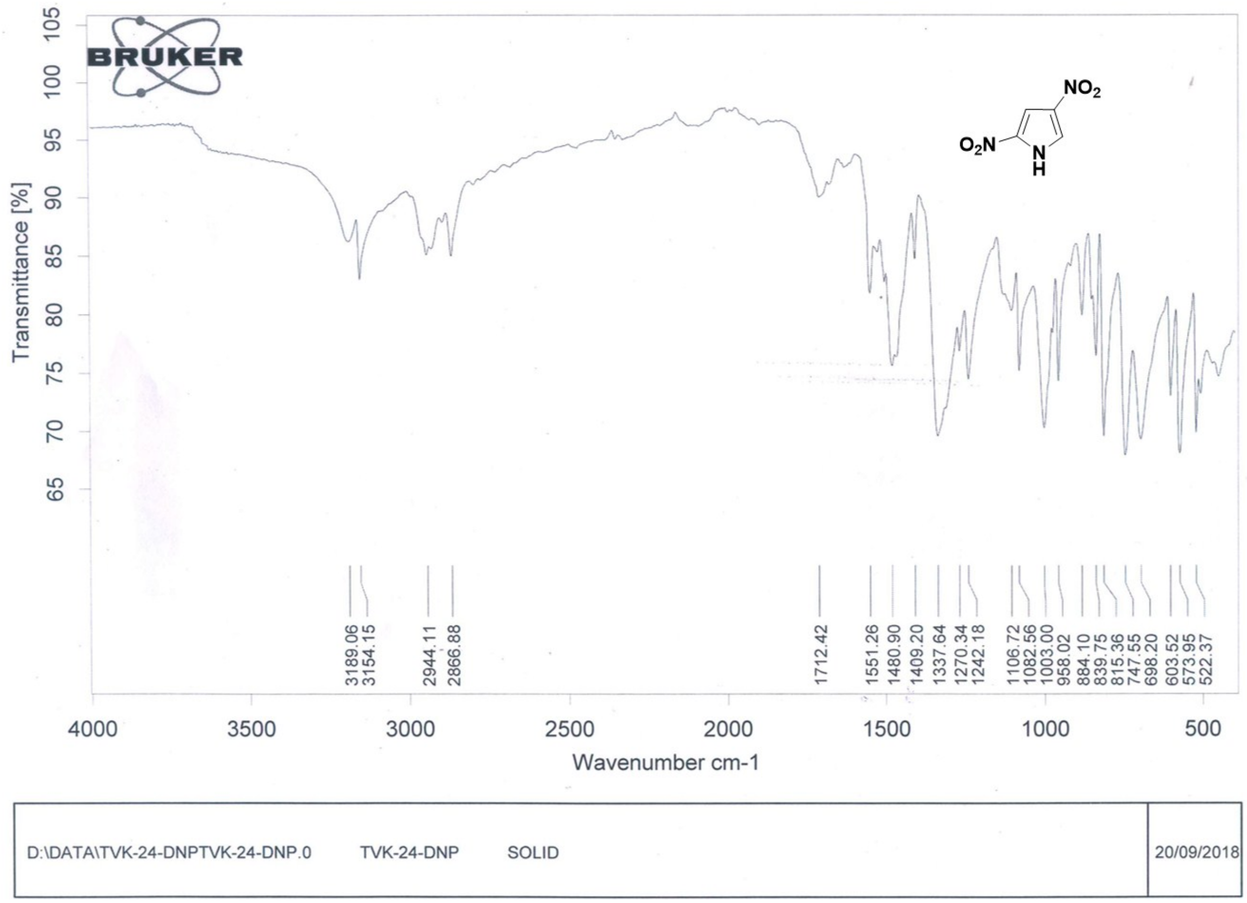
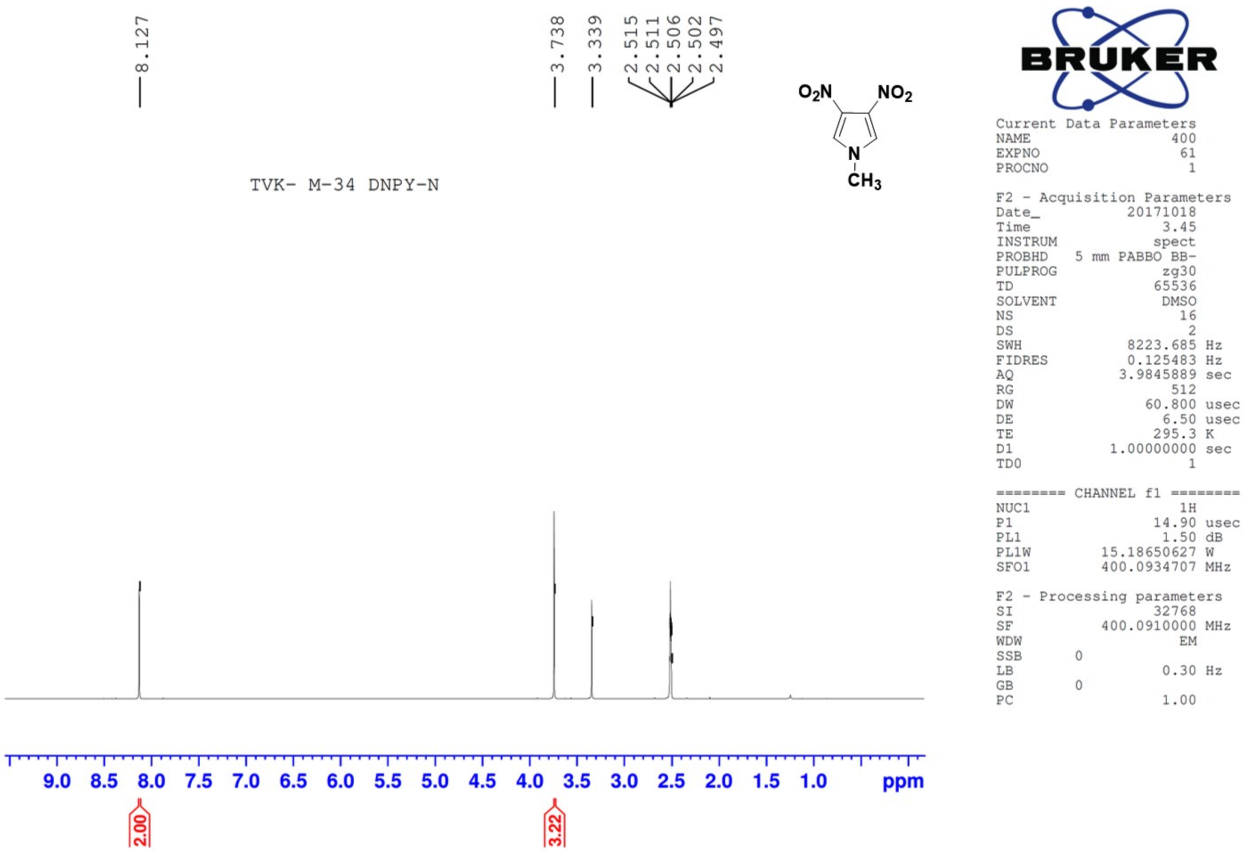
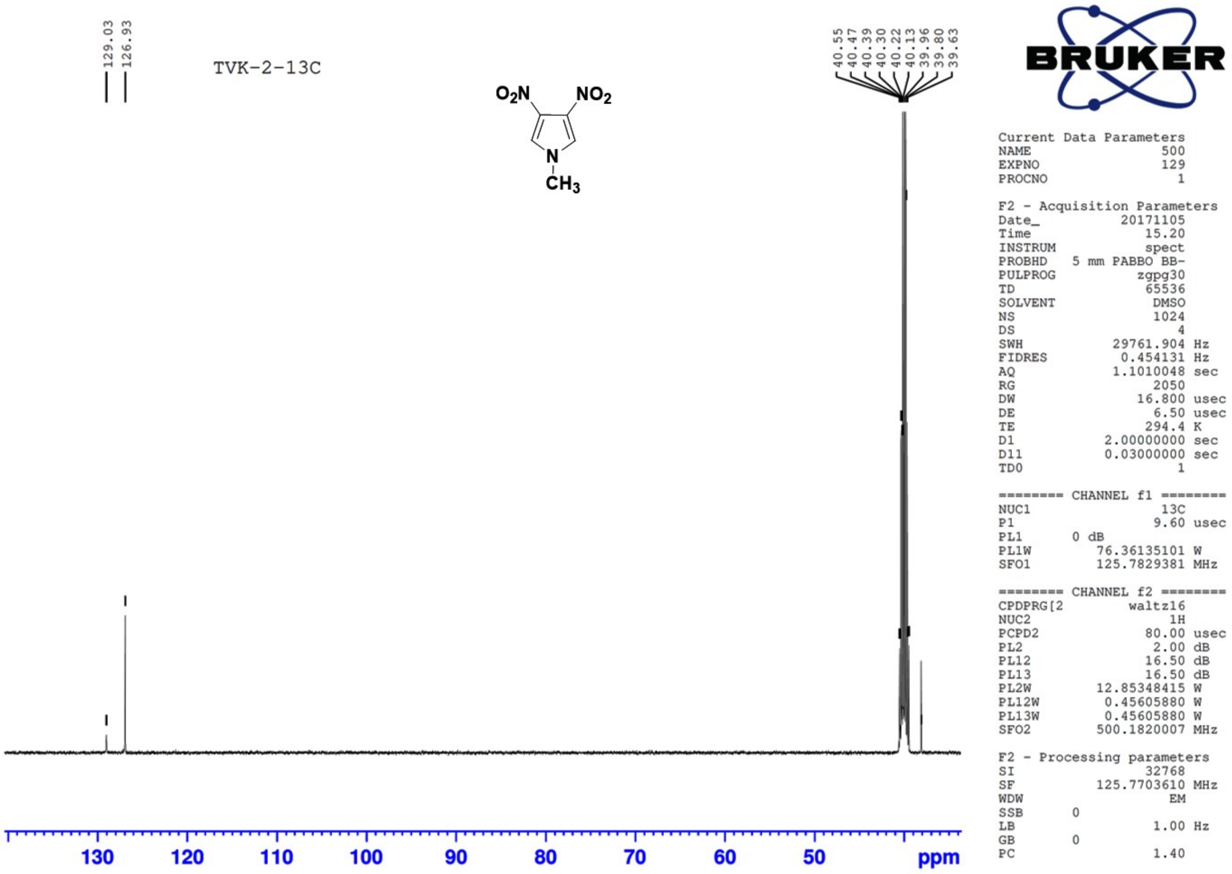


Figure S10: IR spectrum of **3b**.



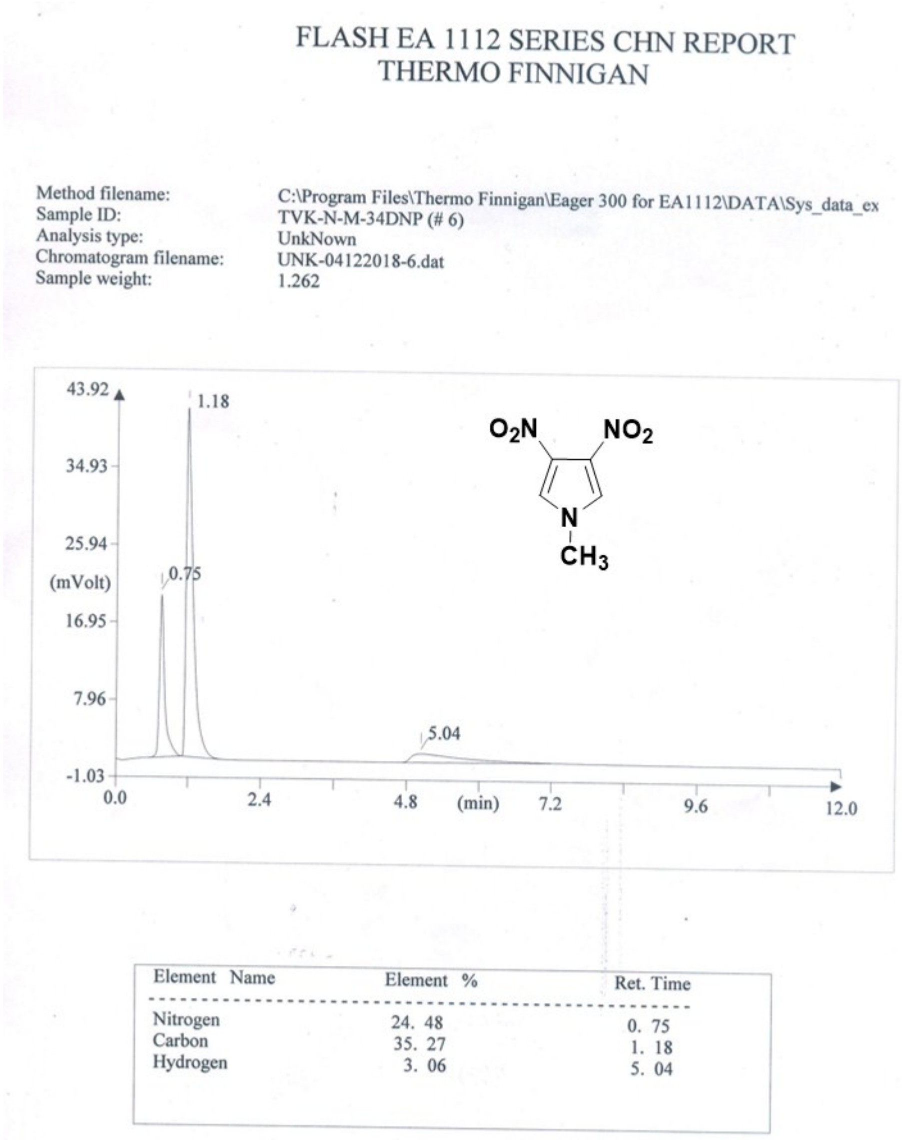
```
Current Data Parameters
NAME                  400
EXPNO                  61
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171018
Time                 3.45
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9845889 sec
RG                    512
DW                 60.800 usec
DE                   6.50 usec
TE                  295.3 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.90 usec
PL1                  1.50 dB
PL1W          15.18650627 W
SFO1          400.0934707 MHz

F2 - Processing parameters
SI                  32768
SF            400.0910000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

Figure S11: ^{1}H NMR spectrum of **2** in dimethyl sulfoxide-d_6.



```
Current Data Parameters
NAME                    500
EXPNO                   129
PROCNO                    1

F2 - Acquisition Parameters
Date_              20171105
Time                  15.20
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT                DMSO
NS                     1024
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010048 sec
RG                     2050
DW                   16.800 usec
DE                     6.50 usec
TE                    294.4 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.60 usec
PL1         0 dB
PL1W            76.36135101 W
SFO1            125.7829381 MHz

======== CHANNEL f2 ========
CPDPRG[2            waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    2.00 dB
PL12                  16.50 dB
PL13                  16.50 dB
PL2W            12.85348415 W
PL12W            0.45605880 W
PL13W            0.45605880 W
SFO2            500.1820007 MHz

F2 - Processing parameters
SI                    32768
SF              125.7703610 MHz
WDW                      EM
SSB         0
LB                     1.00 Hz
GB          0
PC                     1.40
```

Figure S12: ^{13}C NMR spectrum of **2** in dimethyl sulfoxide-d_6.



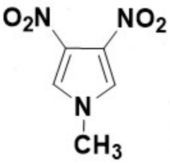
FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: TVK-N-M-34DNP (# 6)
Analysis type: UnkNown
Chromatogram filename: UNK-04122018-6.dat
Sample weight: 1.262

Element Name	Element %	Ret. Time
Nitrogen	24. 48	0. 75
Carbon	35. 27	1. 18
Hydrogen	3. 06	5. 04

Figure S13: Elemental analysis of **2**.

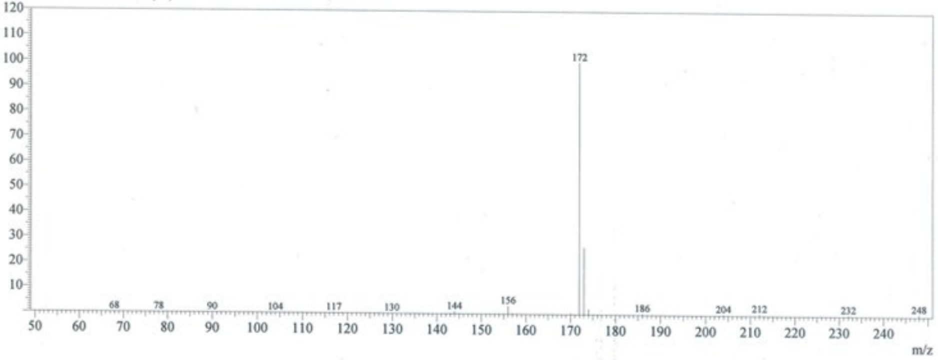
LCMS-2010A DATA REPORT
SHIMADZU



User : Admin
Sample : TVK-M-34-DNPY
Inj. Volume : 5.000
Data Name : E:\Data\TVK-M-34-DNPY-APCI-POS1.qld
Method Name : C:\LCMSsolution\User\Method\esi.qlm

MS Spectrum

Line#:1 R.Time:0.823(Scan#:50) Positive
MassPeaks:96 BasePeak:171.95(12272129)
RawMode:Single 0.823(50)
BG Mode:Peak Start 0.527(32)



MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name
1	0.823	0.527	1.243	413198023	17472604	23.64		100.00	
				413198023	17472604			100.00	

Base m/z	Base Int.
171.95	12272129

Figure S14: LCMS of **2**.

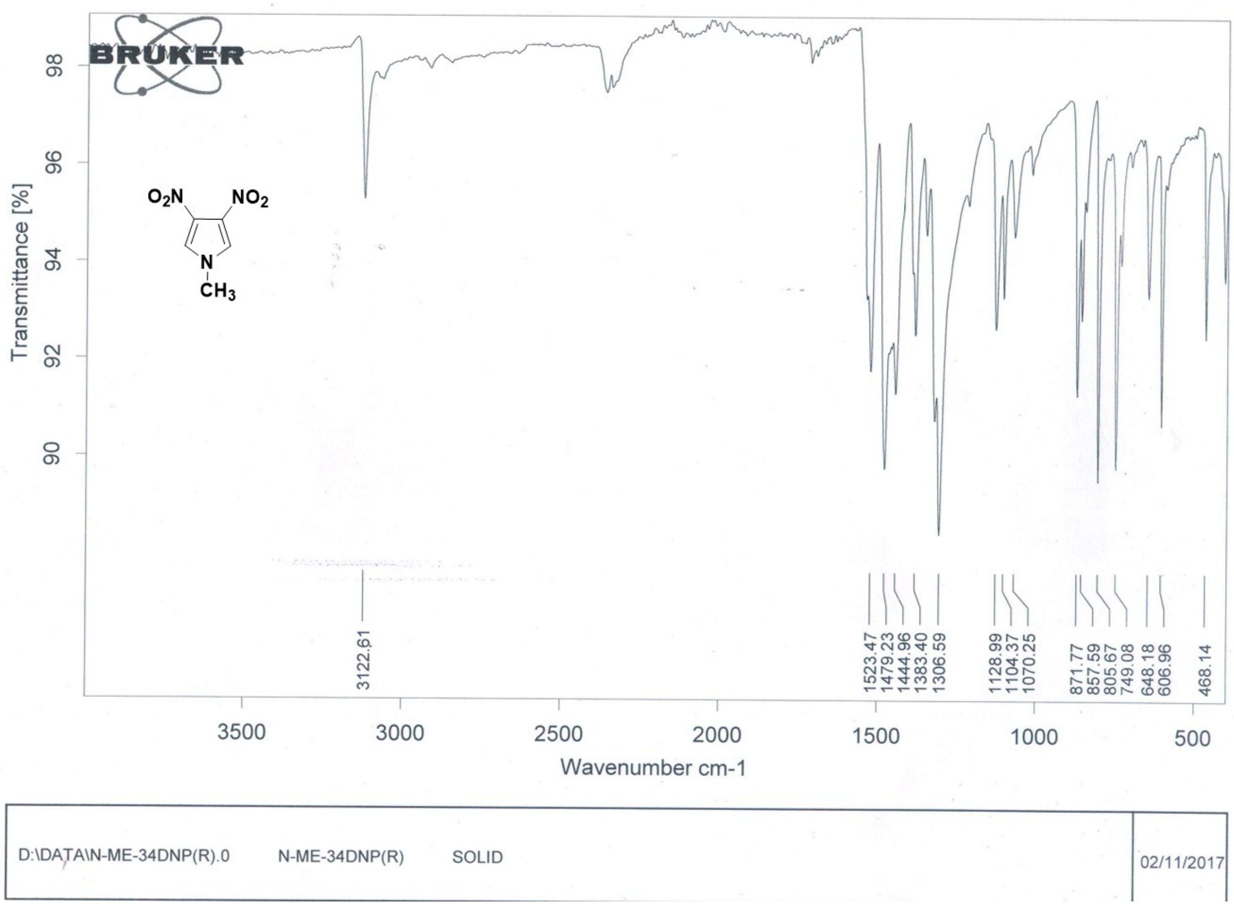
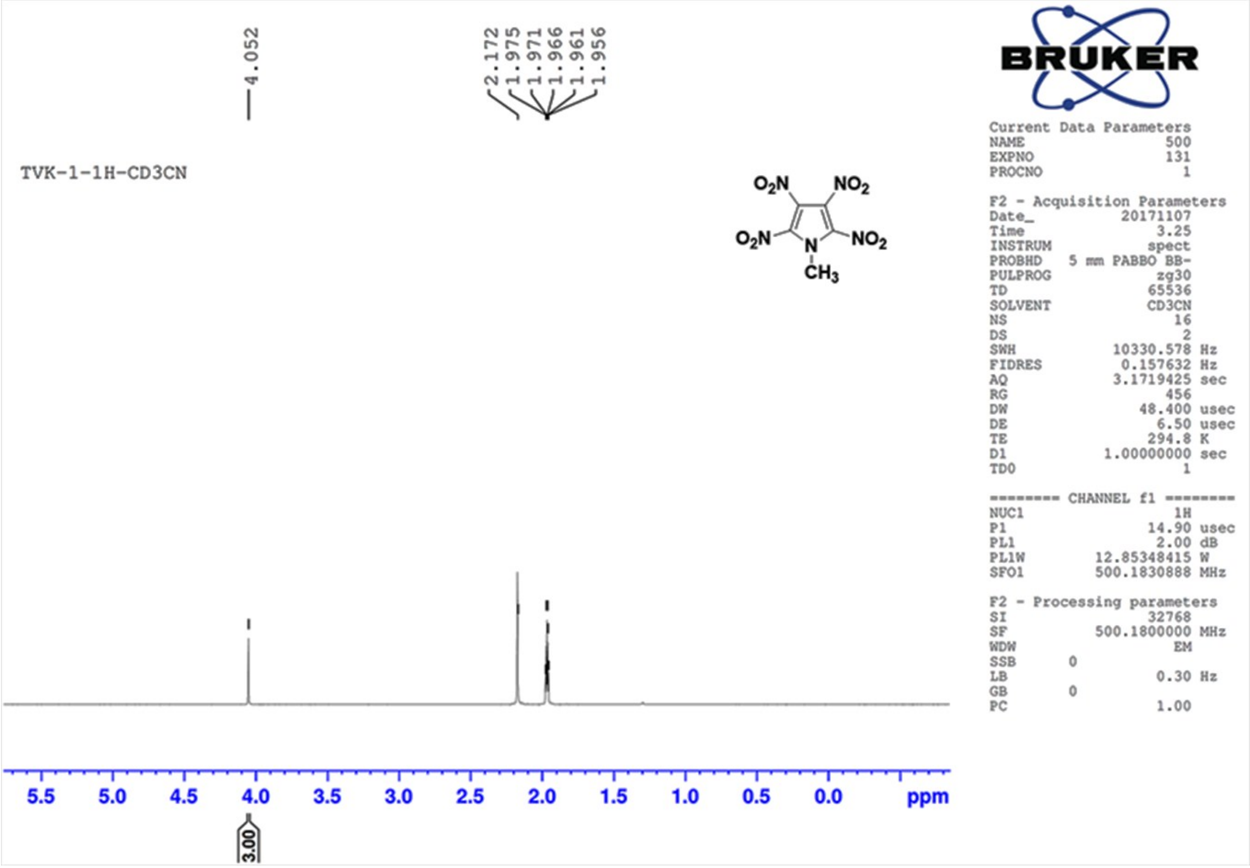
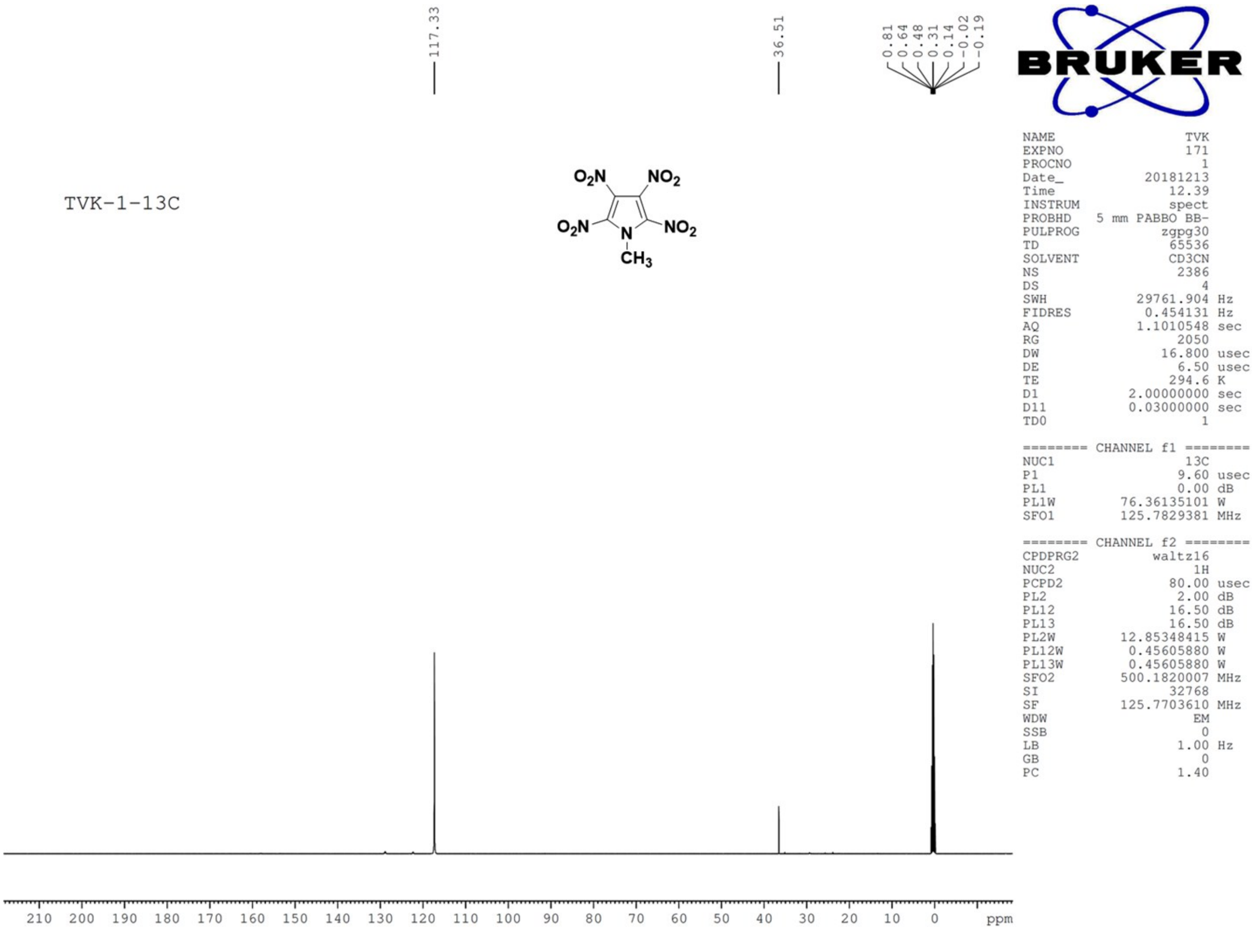


Figure S15: IR spectrum of **2**.



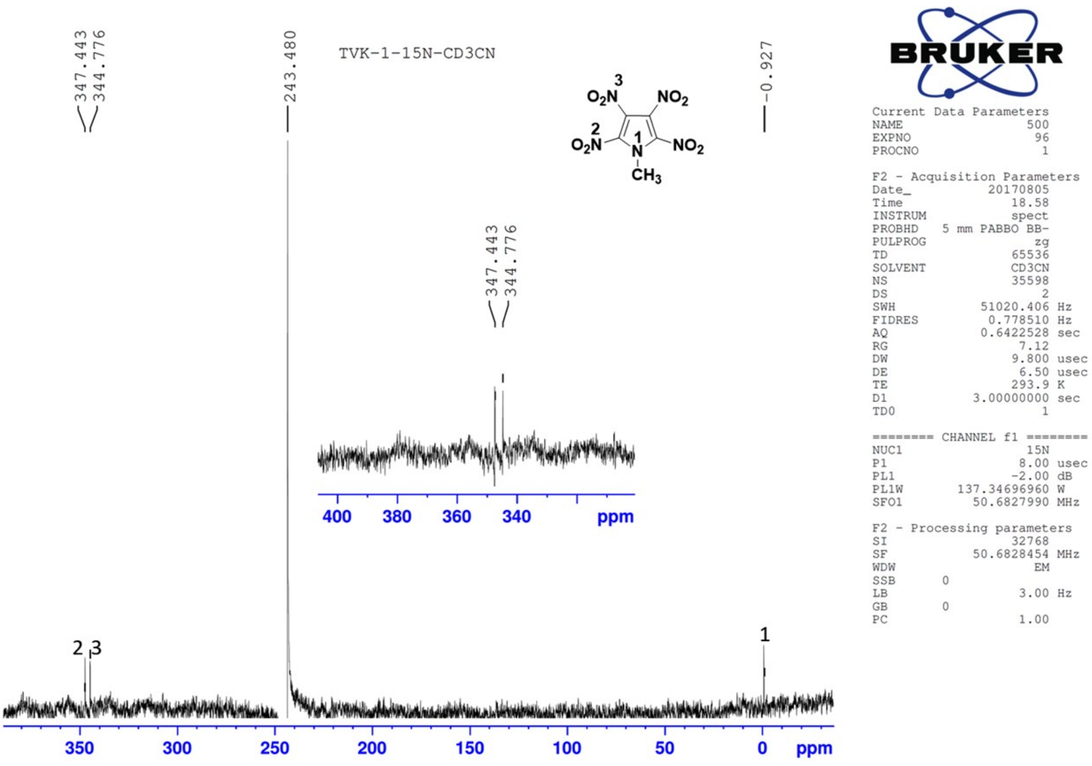
```
Current Data Parameters
NAME                  500
EXPNO                 131
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171107
Time                 3.25
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CD3CN
NS                     16
DS                      2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719425 sec
RG                    456
DW                 48.400 usec
DE                   6.50 usec
TE                  294.8 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.90 usec
PL1                  2.00 dB
PL1W          12.85348415 W
SFO1          500.1830888 MHz

F2 - Processing parameters
SI                  32768
SF            500.1800000 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```

Figure S16: ^{1}H NMR spectrum of **1** in acetonitrile-d_3.



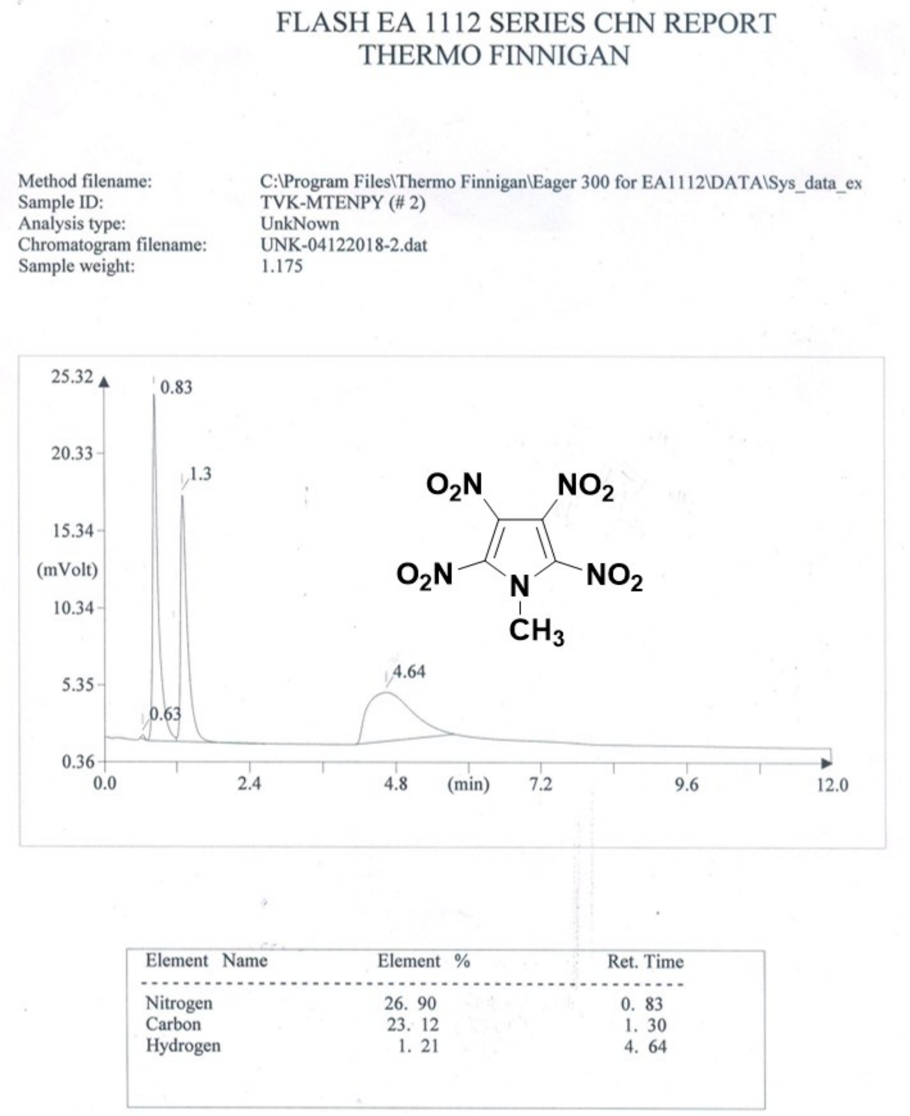
```
NAME               TVK
EXPNO              171
PROCNO               1
Date_         20181213
Time             12.39
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CD3CN
NS                2386
DS                   4
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ           1.1010548 sec
RG                2050
DW              16.800 usec
DE                6.50 usec
TE               294.6 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.60 usec
PL1               0.00 dB
PL1W       76.36135101 W
SFO1       125.7829381 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2               2.00 dB
PL12             16.50 dB
PL13             16.50 dB
PL2W       12.85348415 W
PL12W       0.45605880 W
PL13W       0.45605880 W
SFO2       500.1820007 MHz
SI               32768
SF         125.7703610 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

Figure S17: ^{13}C NMR spectrum of **1** in acetonitrile-*d*$_3$.



```
Current Data Parameters
NAME                 500
EXPNO                 96
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170805
Time               18.58
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG               zg
TD                 65536
SOLVENT            CD3CN
NS                 35598
DS                     2
SWH            51020.406 Hz
FIDRES          0.778510 Hz
AQ             0.6422528 sec
RG                  7.12
DW                 9.800 usec
DE                  6.50 usec
TE                 293.9 K
D1            3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 15N
P1                  8.00 usec
PL1                -2.00 dB
PL1W        137.34696960 W
SFO1         50.6827990 MHz

F2 - Processing parameters
SI                 32768
SF            50.6828454 MHz
WDW                   EM
SSB      0
LB                  3.00 Hz
GB       0
PC                  1.00
```

Figure S18: ^{15}N NMR spectrum of **1** in acetonitrile-d_3.

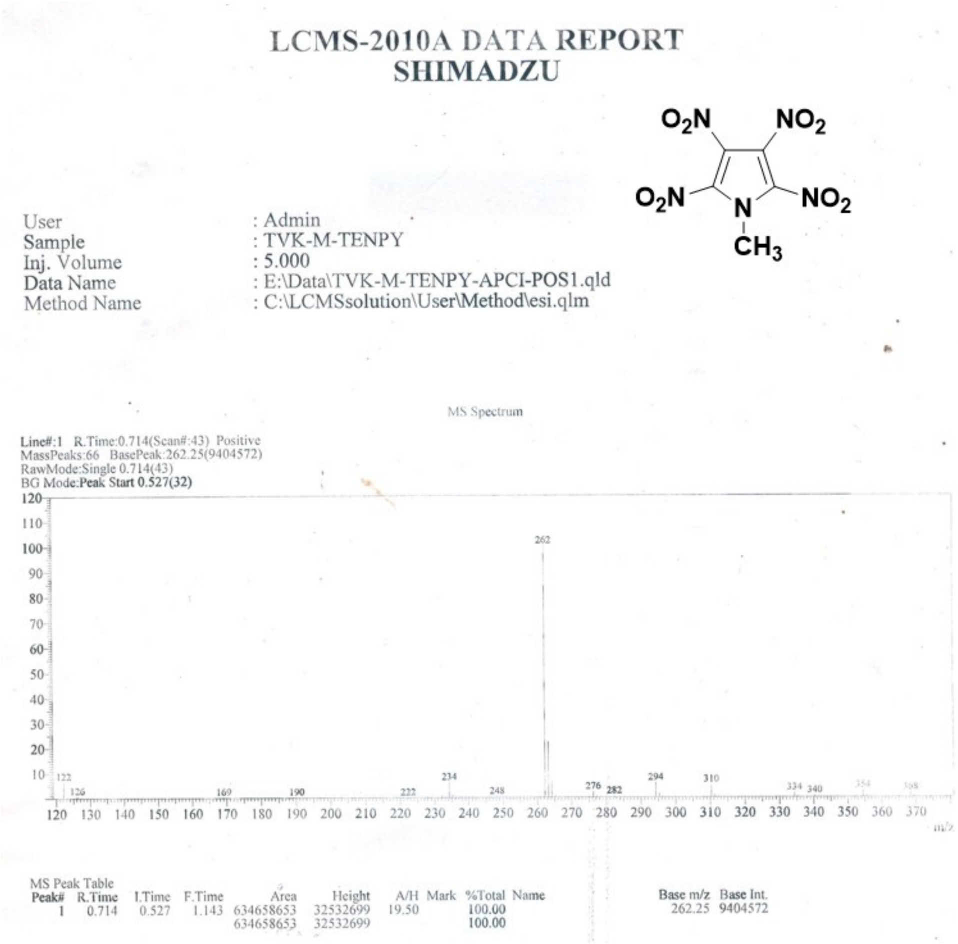


FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	TVK-MTENPY (# 2)
Analysis type:	UnkNown
Chromatogram filename:	UNK-04122018-2.dat
Sample weight:	1.175

Element Name	Element %	Ret. Time
Nitrogen	26. 90	0. 83
Carbon	23. 12	1. 30
Hydrogen	1. 21	4. 64

Figure S19: Elemental analysis of **1**.



LCMS-2010A DATA REPORT
SHIMADZU

User : Admin
Sample : TVK-M-TENPY
Inj. Volume : 5.000
Data Name : E:\Data\TVK-M-TENPY-APCI-POS1.qld
Method Name : C:\LCMSsolution\User\Method\esi.qlm

MS Spectrum

Line#:1 R.Time:0.714(Scan#:43) Positive
MassPeaks:66 BasePeak:262.25(9404572)
RawMode:Single 0.714(43)
BG Mode:Peak Start 0.527(32)

MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name
1	0.714	0.527	1.143	634658653	32532699	19.50		100.00	
				634658653	32532699			100.00	

Base m/z	Base Int.
262.25	9404572

Figure S20: LCMS of **1**.

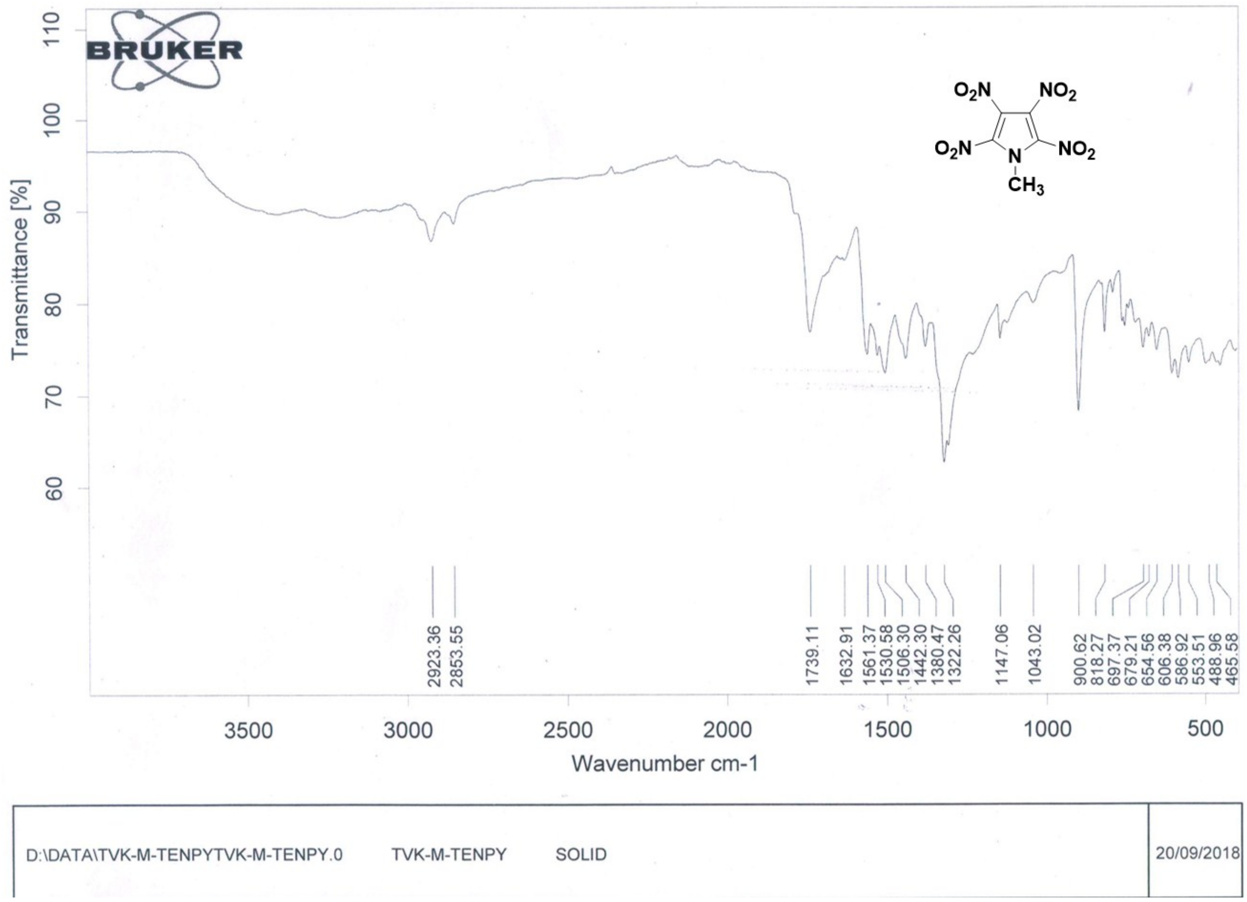
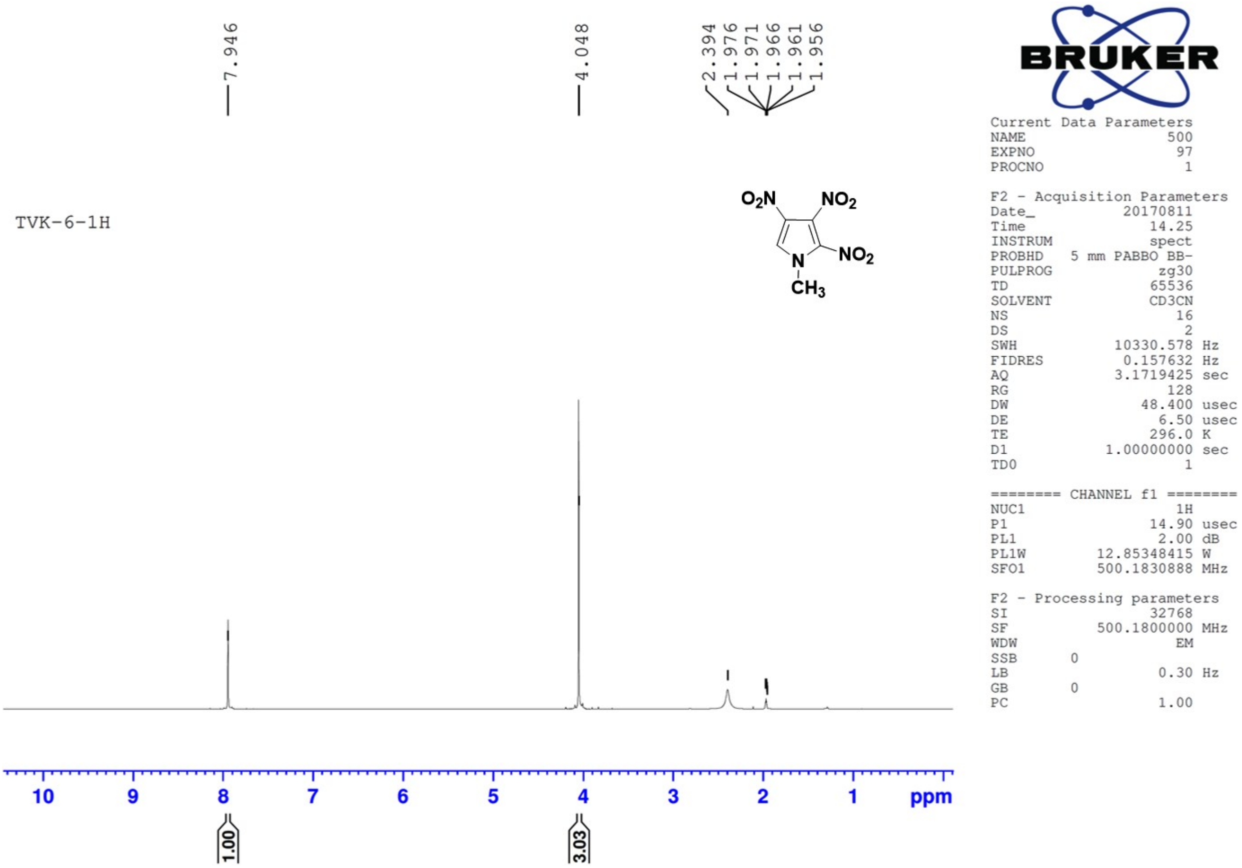
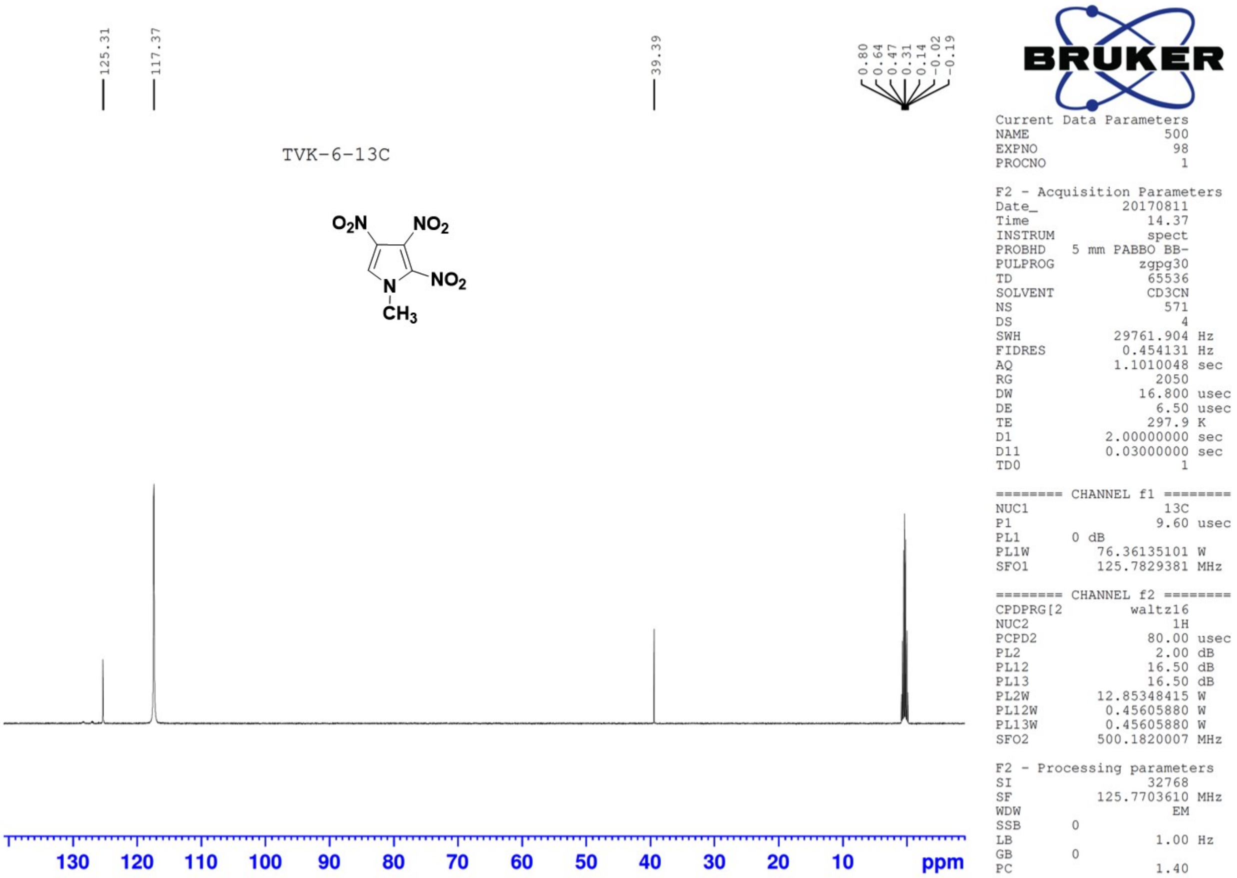


Figure S21: IR Spectrum of **1**.



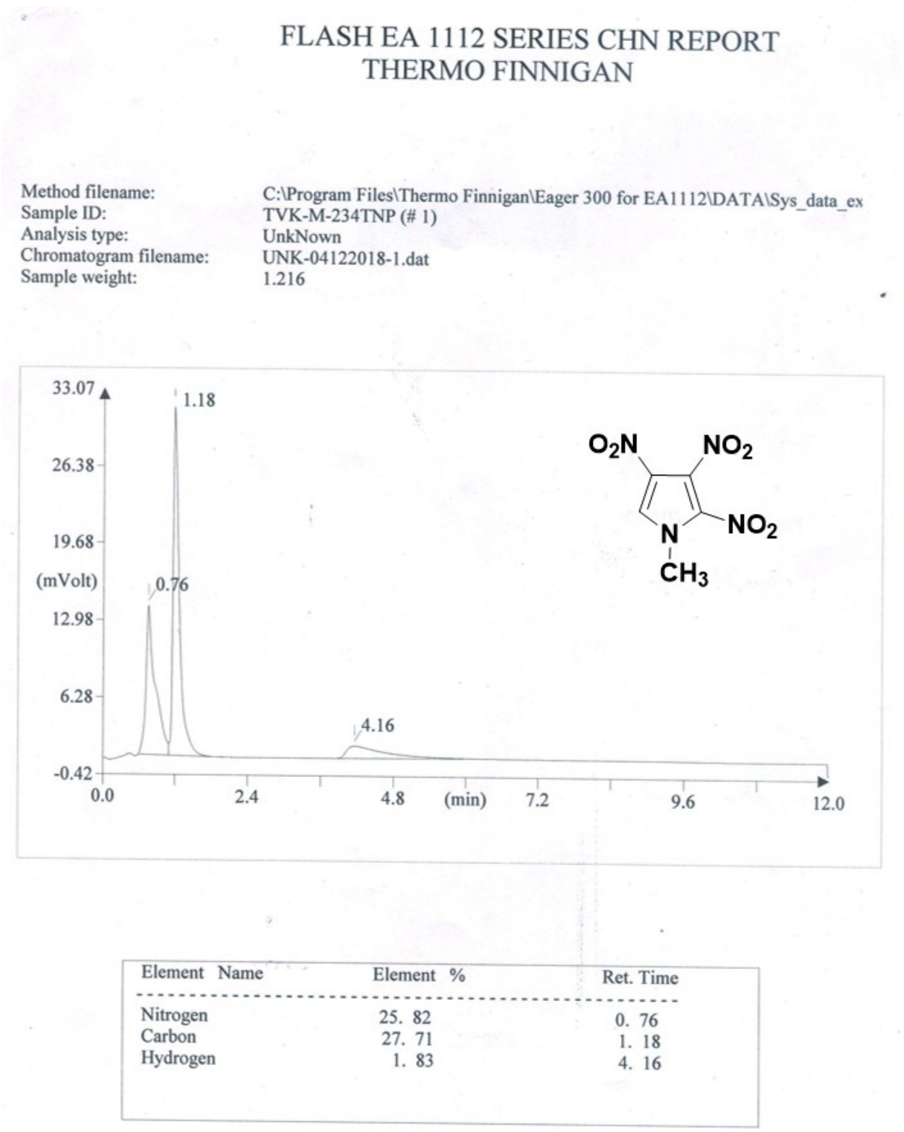
```
Current Data Parameters
NAME                    500
EXPNO                    97
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170811
Time                  14.25
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CD3CN
NS                       16
DS                        2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1719425 sec
RG                      128
DW                   48.400 usec
DE                     6.50 usec
TE                    296.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    14.90 usec
PL1                    2.00 dB
PL1W            12.85348415 W
SFO1           500.1830888 MHz

F2 - Processing parameters
SI                    32768
SF             500.1800000 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

Figure S22: ^{1}H NMR spectrum of **6** in acetonitrile-d_3.



```
Current Data Parameters
NAME                  500
EXPNO                  98
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170811
Time                14.37
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CD3CN
NS                    571
DS                      4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG                   2050
DW               16.800 usec
DE                 6.50 usec
TE                297.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.60 usec
PL1      0 dB
PL1W        76.36135101 W
SFO1        125.7829381 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  2.00 dB
PL12                16.50 dB
PL13                16.50 dB
PL2W        12.85348415 W
PL12W        0.45605880 W
PL13W        0.45605880 W
SFO2        500.1820007 MHz

F2 - Processing parameters
SI                  32768
SF          125.7703610 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

Figure S23: ^{13}C NMR spectrum of **6** in acetonitrile-d_3.

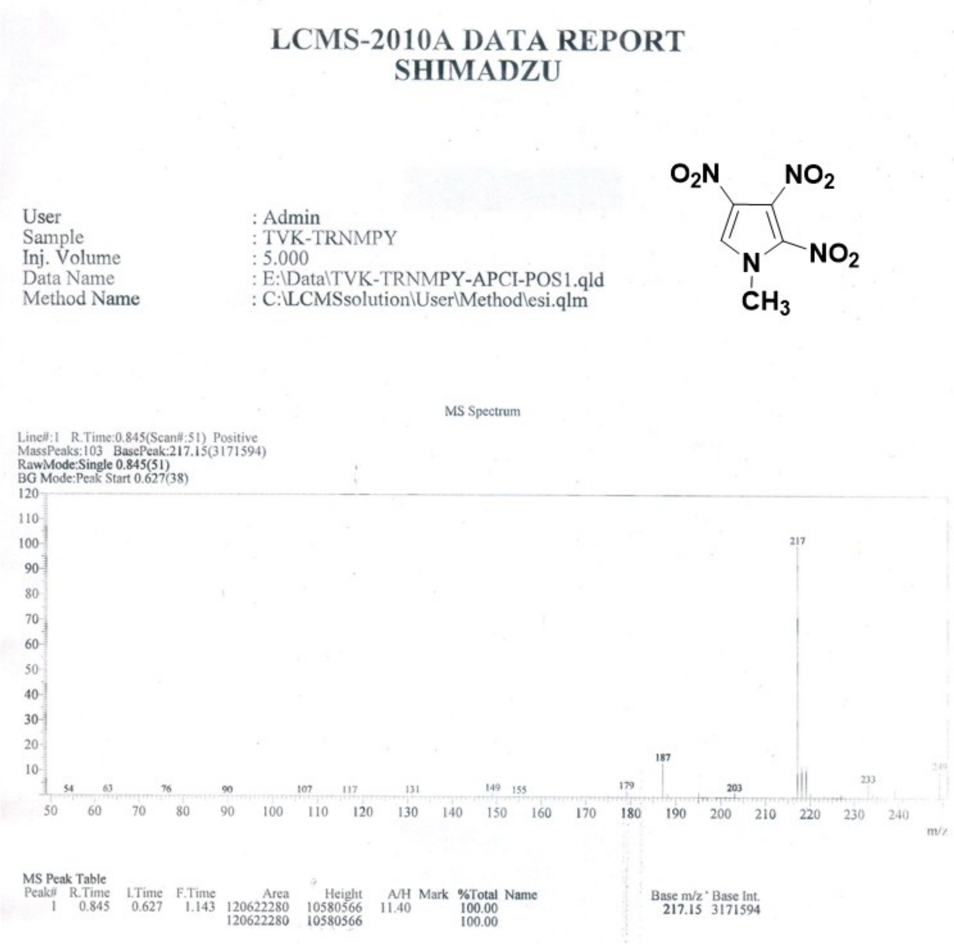


FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: TVK-M-234TNP (# 1)
Analysis type: UnkNown
Chromatogram filename: UNK-04122018-1.dat
Sample weight: 1.216

Element Name	Element %	Ret. Time
Nitrogen	25. 82	0. 76
Carbon	27. 71	1. 18
Hydrogen	1. 83	4. 16

Figure S24: Elemental analysis of **6**.



LCMS-2010A DATA REPORT
SHIMADZU

User	: Admin
Sample	: TVK-TRNMPY
Inj. Volume	: 5.000
Data Name	: E:\Data\TVK-TRNMPY-APCI-POS1.qld
Method Name	: C:\LCMSsolution\User\Method\esi.qlm

MS Spectrum

Line#:1 R.Time:0.845(Scan#:51) Positive
MassPeaks:103 BasePeak:217.15(3171594)
RawMode:Single 0.845(51)
BG Mode:Peak Start 0.627(38)

MS Peak Table

Peak#	R.Time	I.Time	F.Time	Area	Height	A/H	Mark	%Total	Name
1	0.845	0.627	1.143	120622280	10580566	11.40		100.00	
				120622280	10580566			100.00	

Base m/z	Base Int.
217.15	3171594

Figure S25: LCMS of **6**.

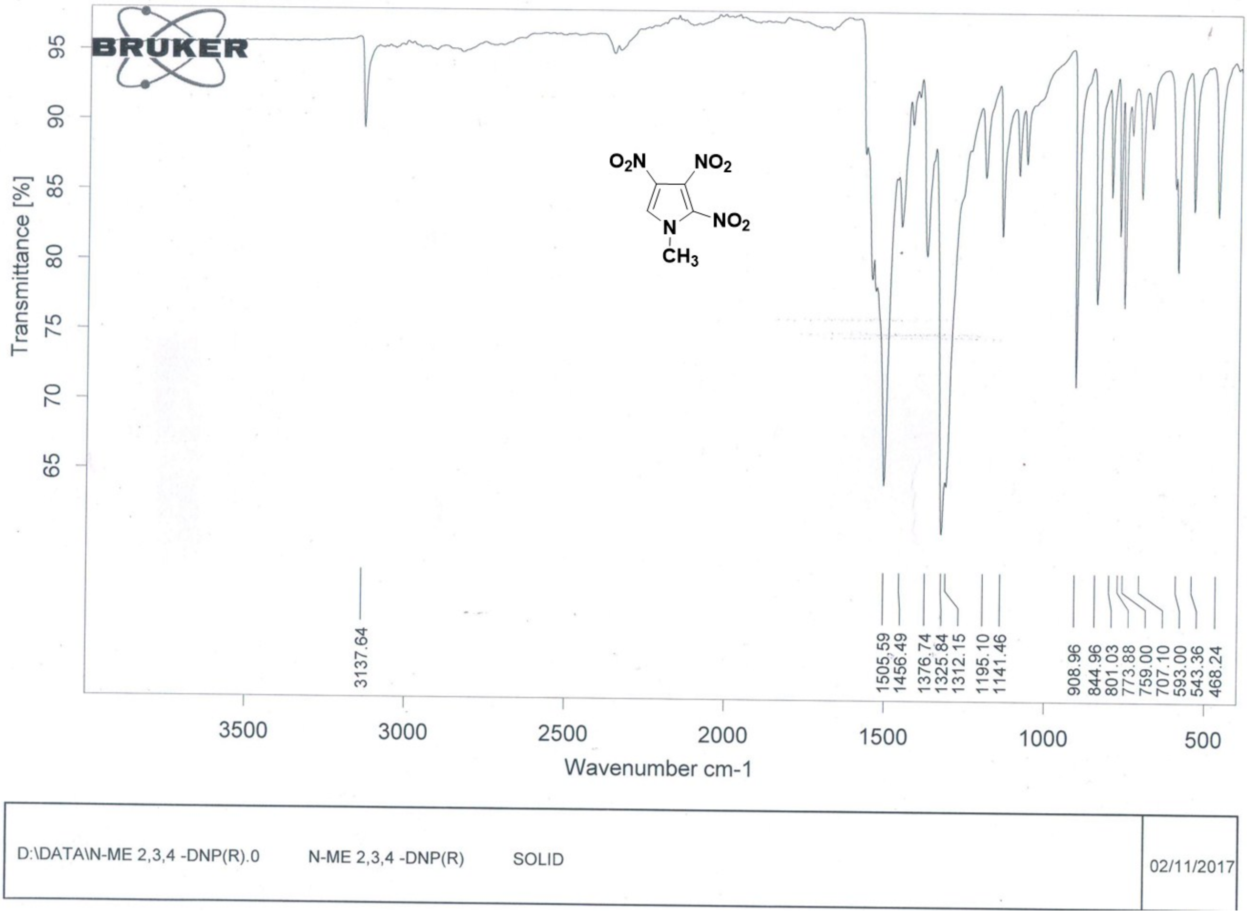
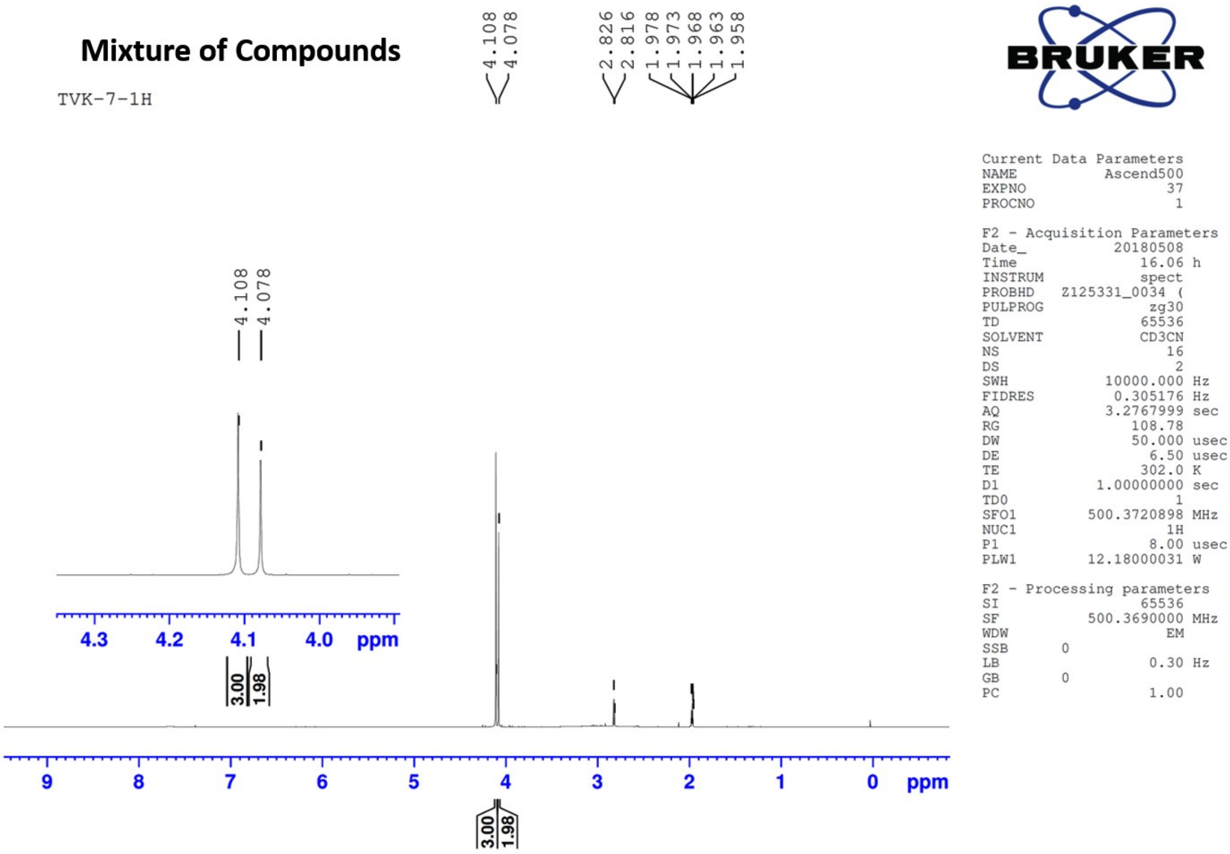
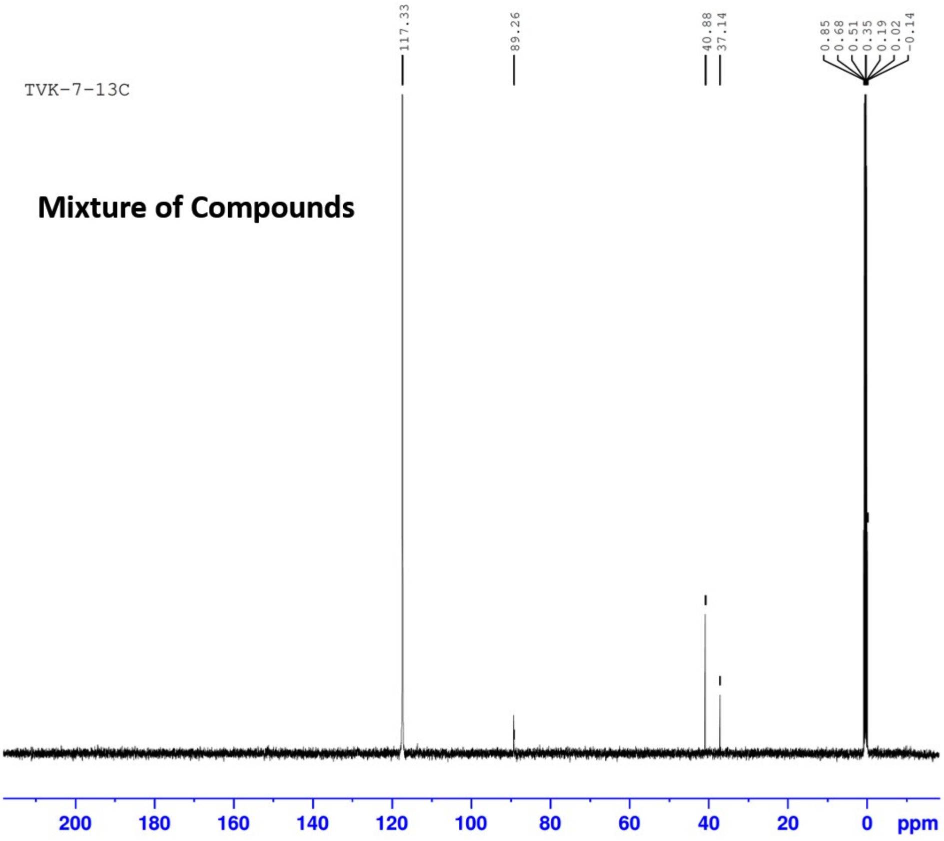


Figure S26: IR Spectrum of **6**.



```
Current Data Parameters
NAME           Ascend500
EXPNO                 37
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180508
Time               16.06 h
INSTRUM            spect
PROBHD   Z125331_0034 (
PULPROG             zg30
TD                 65536
SOLVENT             CD3CN
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES         0.305176 Hz
AQ            3.2767999 sec
RG               108.78
DW               50.000 usec
DE                 6.50 usec
TE                302.0 K
D1           1.00000000 sec
TD0                    1
SFO1        500.3720898 MHz
NUC1                  1H
P1                 8.00 usec
PLW1        12.18000031 W

F2 - Processing parameters
SI                 65536
SF          500.3690000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

Figure S27: ^{1}H NMR spectrum of **7** in acetonitrile-d_3.



```
Current Data Parameters
NAME             Ascend500
EXPNO                   33
PROCNO                   1

F2 - Acquisition Parameters
Date_             20180213
Time                 16.45 h
INSTRUM              spect
PROBHD   Z125331_0034 (
PULPROG            zgpg30
TD                  65536
SOLVENT             CD3CN
NS                    575
DS                      4
SWH             29761.904 Hz
FIDRES           0.908261 Hz
AQ              1.1010048 sec
RG                  15.92
DW                 16.800 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1
SFO1          125.8304669 MHz
NUC1                  13C
P1                  12.00 usec
PLW1         172.66999817 W
SFO2          500.3710015 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          12.18000031 W
PLW12          0.12180000 W
PLW13          0.06126500 W

F2 - Processing parameters
SI                  32768
SF            125.8178851 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

Figure S28: ^{13}C NMR spectrum of **7** in acetonitrile-d_3.

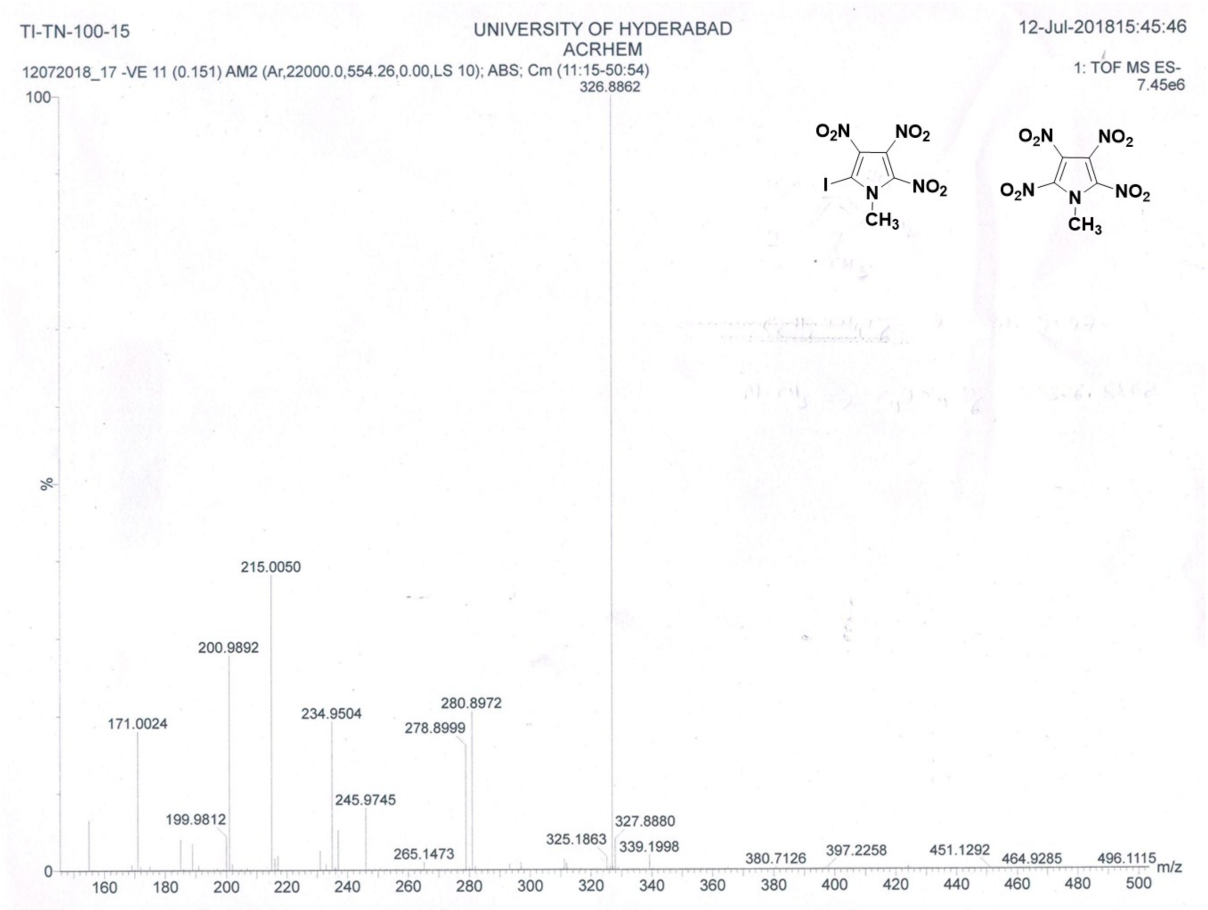
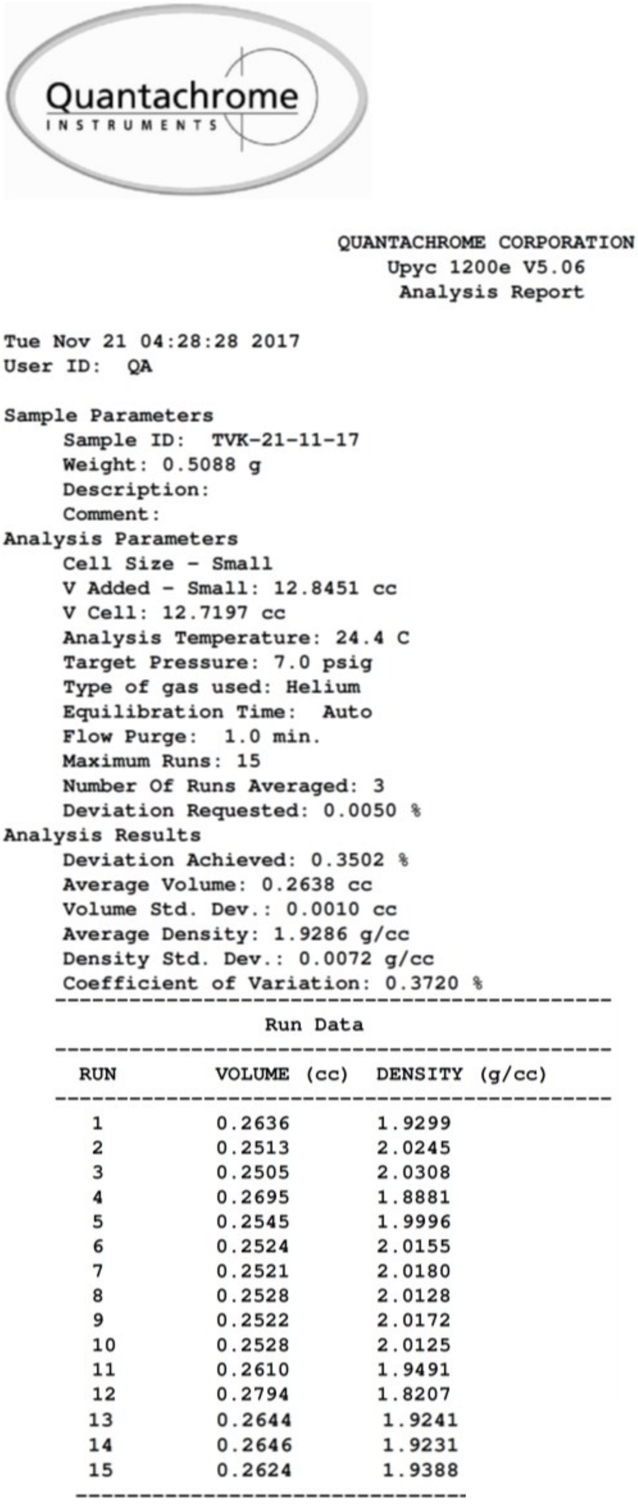


Figure S29: HRMS spectrum of **7**.

5. Density by Gas Pycnometer for Compound 1



```
                       QUANTACHROME CORPORATION
                          Upyc 1200e V5.06
                           Analysis Report

Tue Nov 21 04:28:28 2017
User ID:  QA

Sample Parameters
     Sample ID:  TVK-21-11-17
     Weight: 0.5088 g
     Description:
     Comment:
Analysis Parameters
     Cell Size - Small
     V Added - Small: 12.8451 cc
     V Cell: 12.7197 cc
     Analysis Temperature: 24.4 C
     Target Pressure: 7.0 psig
     Type of gas used: Helium
     Equilibration Time:  Auto
     Flow Purge:  1.0 min.
     Maximum Runs: 15
     Number Of Runs Averaged: 3
     Deviation Requested: 0.0050 %
Analysis Results
     Deviation Achieved: 0.3502 %
     Average Volume: 0.2638 cc
     Volume Std. Dev.: 0.0010 cc
     Average Density: 1.9286 g/cc
     Density Std. Dev.: 0.0072 g/cc
     Coefficient of Variation: 0.3720 %
    ---------------------------------------------
                     Run Data
    ---------------------------------------------
      RUN        VOLUME (cc)  DENSITY (g/cc)
    ---------------------------------------------
       1         0.2636       1.9299
       2         0.2513       2.0245
       3         0.2505       2.0308
       4         0.2695       1.8881
       5         0.2545       1.9996
       6         0.2524       2.0155
       7         0.2521       2.0180
       8         0.2528       2.0128
       9         0.2522       2.0172
      10         0.2528       2.0125
      11         0.2610       1.9491
      12         0.2794       1.8207
      13         0.2644        1.9241
      14         0.2646        1.9231
      15         0.2624        1.9388
      -------------------------------
```

Figure S30: Density measured for **1** by gas pycnometer at 25 °C.

6. DSC-TGA of Compound 1

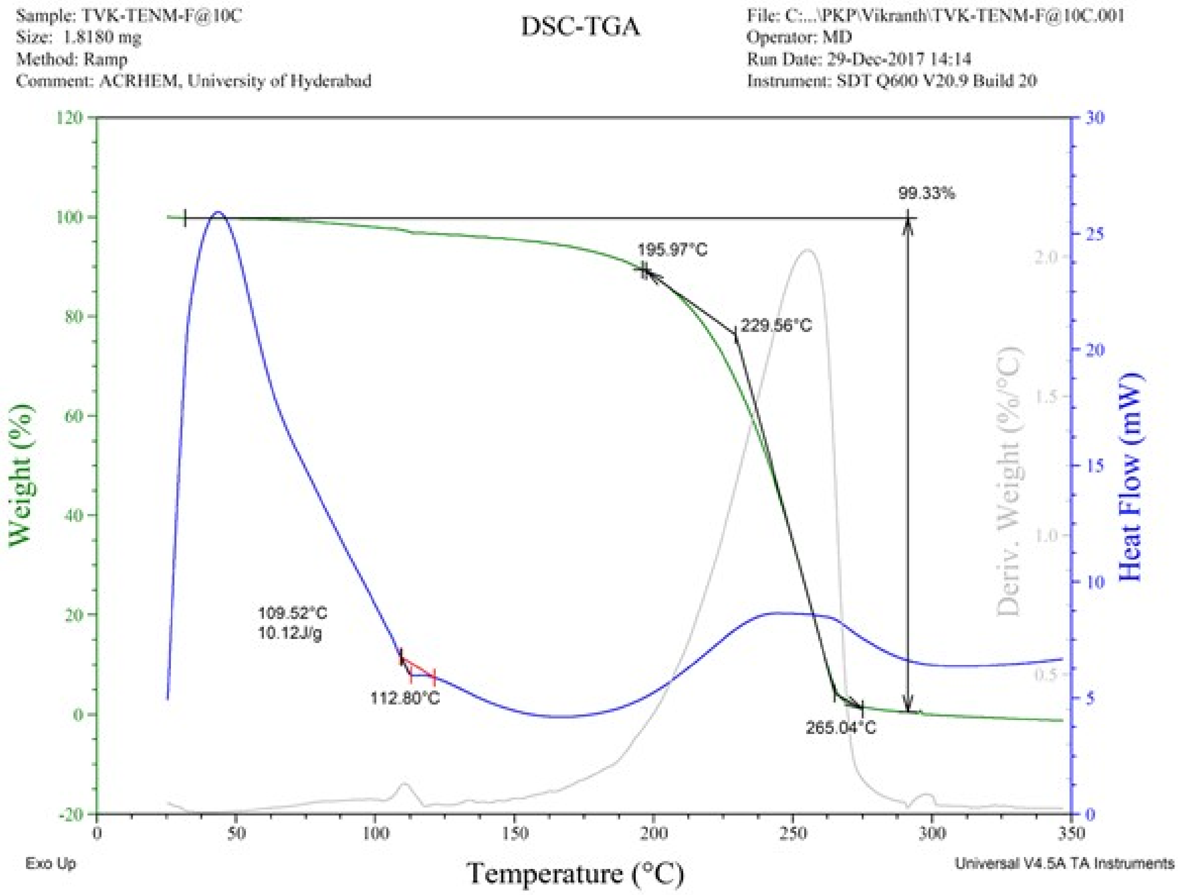
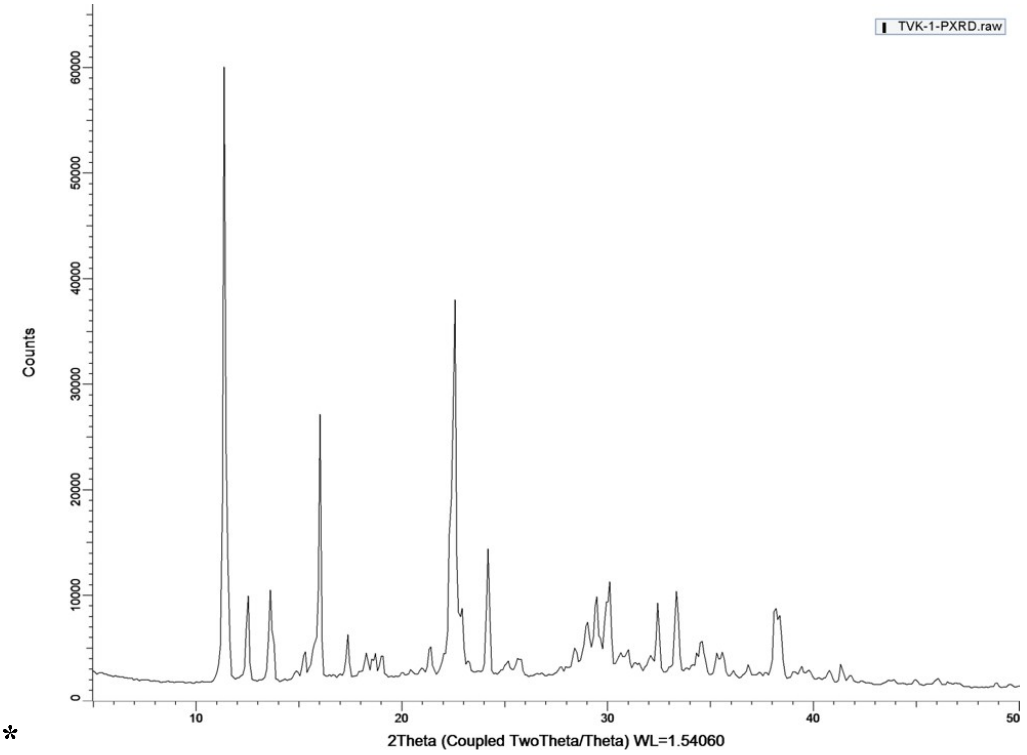


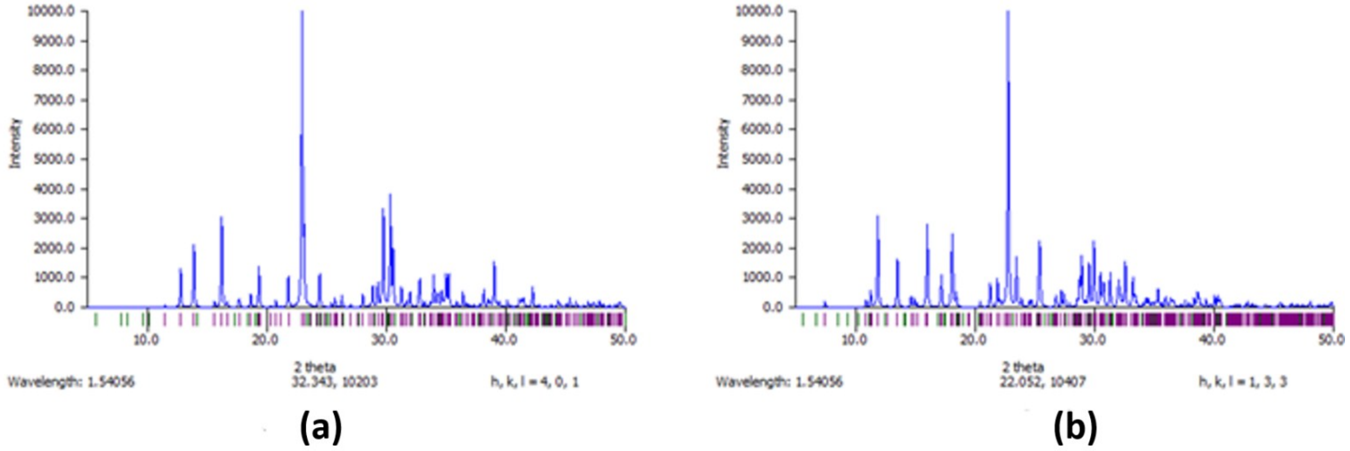
Figure S31: Thermal behavior of Compound **1**

7. Powder X-ray diffraction spectra of Compound 1



*

Figure S32: Powder X-ray diffraction of bulk sample of Compound **1**.



(a) Simulated PXRD pattern of compound **1** from crystal data recorded at 100 K (this work).

(b) Simulated PXRD pattern of compound **1** at 297 K from crystal data reported by Cromer *et al.*[S8]

8. References

S1. SAINT version 8.34A, Bruker AXS, 2014.

S2. G. M. Sheldrick, SADABS 2014/5, *Program for Empirical Absorption Correction of Area Detector Data,* University of Göttingen, Germany, 2014.

S3. SHELXL -version 2014/7; *Program for the Solution and Refinement of Crystal Structures,* University of Göttingen, Germany, 2014.

S4. (a) A. L. Spek, *PLATON*, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2002. (b) A. L. Spek, *J. Appl. Cryst.* 2003, ***36***, 7.

S5. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

S6. M. D. Segall, P. J. D, Lindan, M. J. al. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, *J. Phys.: Condens. Matter.*, 2002, **14**, 2717.

S7. EXPLO5 version 6.02, M. Suceska, 2014.

S8. D. T. Cromer, M. D. Coburn, R. R. Ryan and H. J. Wasserman, *Acta Cryst. C*, 1986, **42**, 1428.