Supporting Information

Versatile Polyiodopyrazoles: Synthesis and Biocidal Promise

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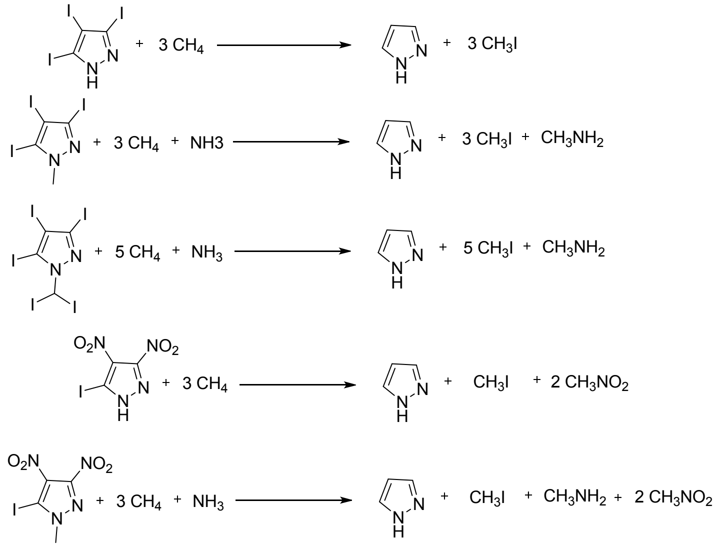
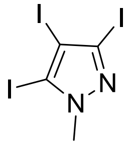
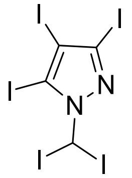
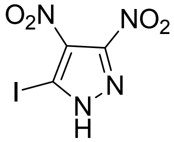
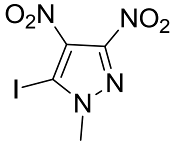
Computational data

The heats of formation of all compounds were calculated by using Gaussian 03 program suite, using isodesmic reactions.[1] For these iodine-containing compounds, the (15s, 11p, 6d) basis of Stromberg et al. was augmented with other p shell and the five valence sp exponents optimized resulting in a [5211111111,411111111,3111] contraction scheme in conjunction with 6-31+G** for first row and second row elements. Single-point energy (SPE) refinement on the optimized geometries was performed with the use of MP2/6-311++G** level. Corresponding iodine sets were constructed in MP2 method by using all electron calculations and quasi relativistic energy-adjusted spin-orbit-averaged seven-valence-electron effective core potentials (ECPs).



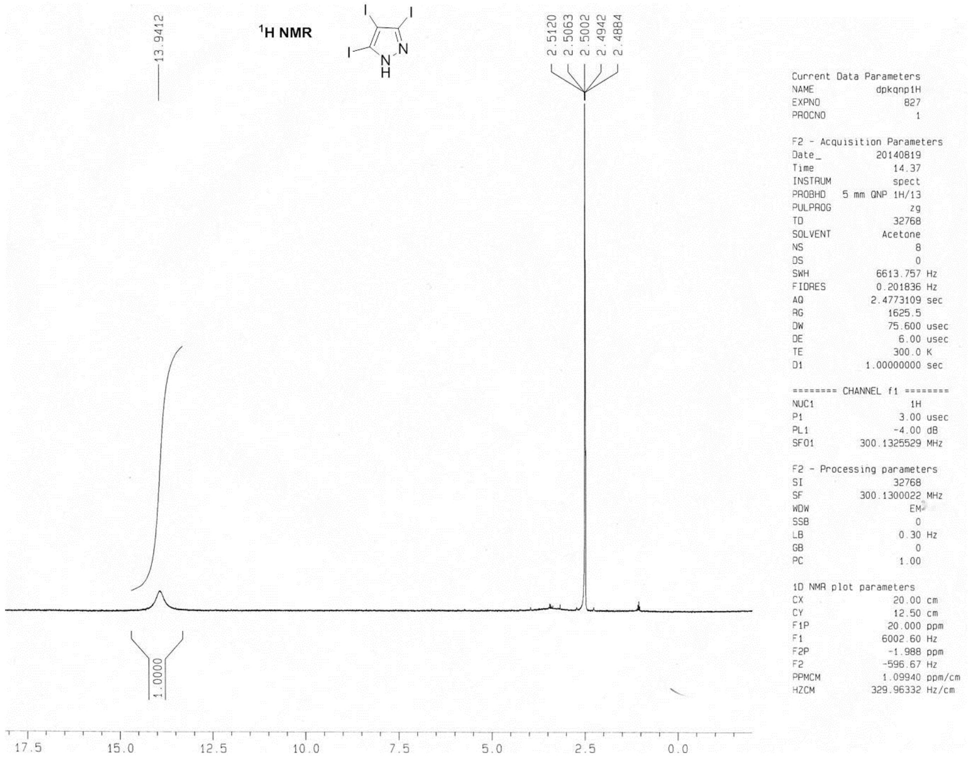
Scheme S1: Isodesmic reactions

Table 1: Ab initio computational values

Compound	E_0 [a]	ZPE[b]	H_T[c]	HOF[d]
	-296.9575337	0.067812	0.078829	307.2263233
	-318.3735761	0.046414	0.06037	453.1315633
	-644.5217199	0.064547	0.075771	621.6506743
	-683.6173645	0.09219	0.10517	644.8263596

[a] Total energy calculated by B3LYP/6-31+G**//MP2/6-311++G** method (Hartree/Particle); [b] zero point correction (Hartree/Particle); [c] thermal correction to enthalpy (Hartree/Particle); [d] heat of formation (kJ/mol).

NMR Spectra



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F2               -596.67 Hz
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HZCM           329.96332 Hz/cm
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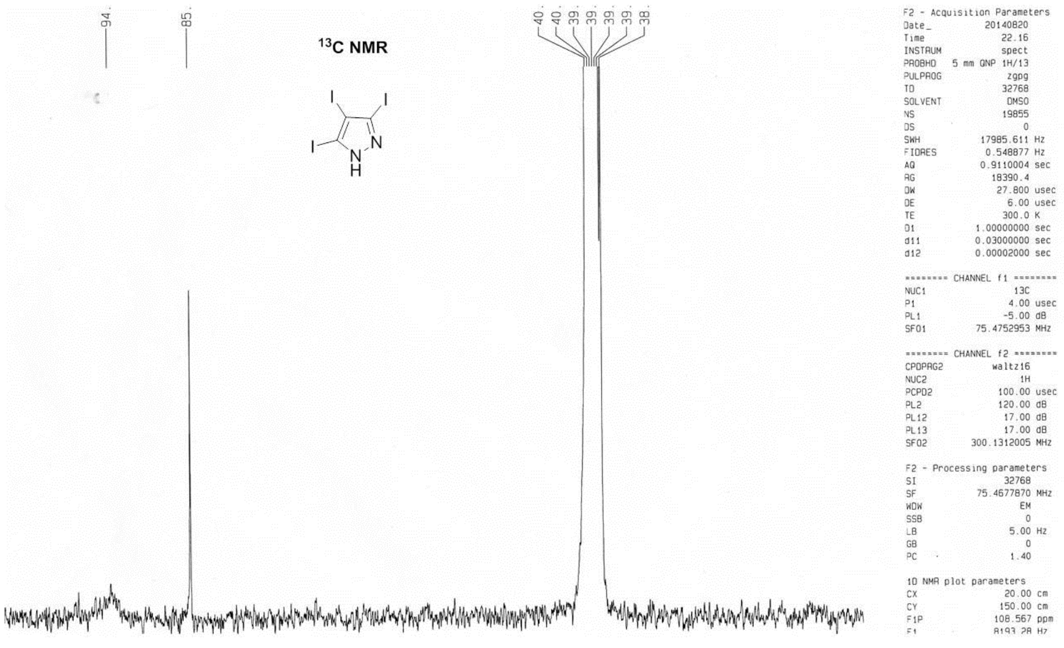

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SFO1          75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                  1H
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PL12               17.00 dB
PL13               17.00 dB
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F2 - Processing parameters
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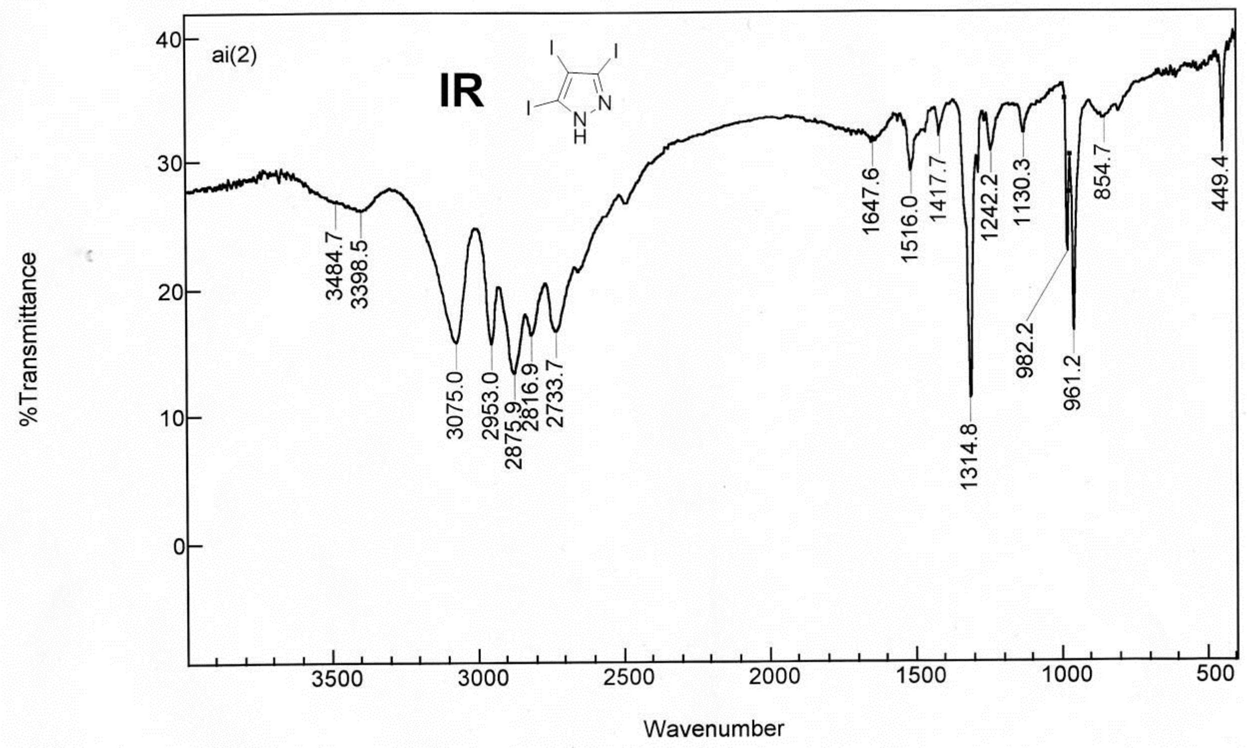
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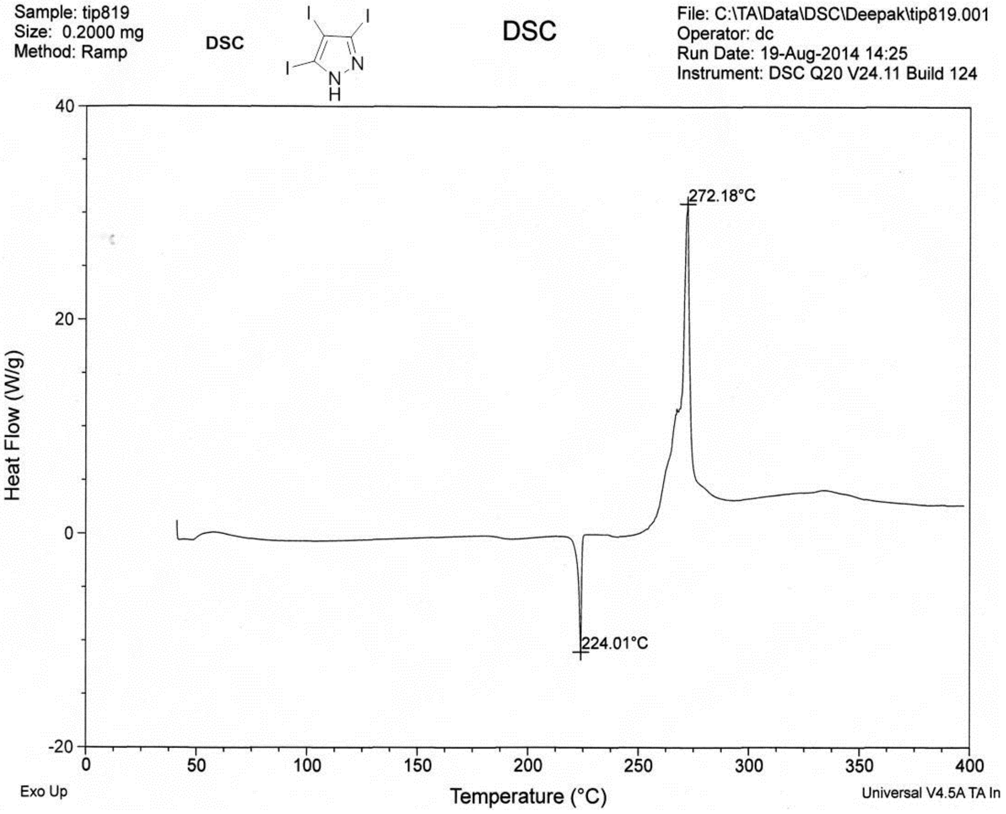
Wavenumber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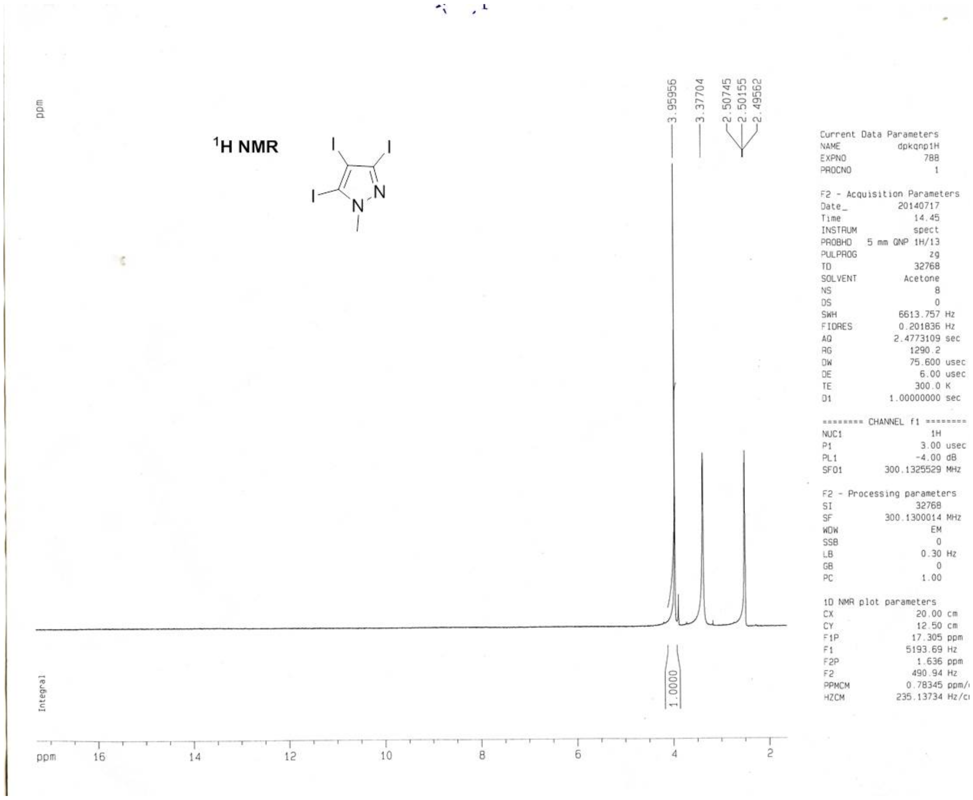

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FIDRES        0.201836 Hz
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RG              1290.2
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TE               300.0 K
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======== CHANNEL f1 ========
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PL1              -4.00 dB
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1D NMR plot parameters
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F1P             17.305 ppm
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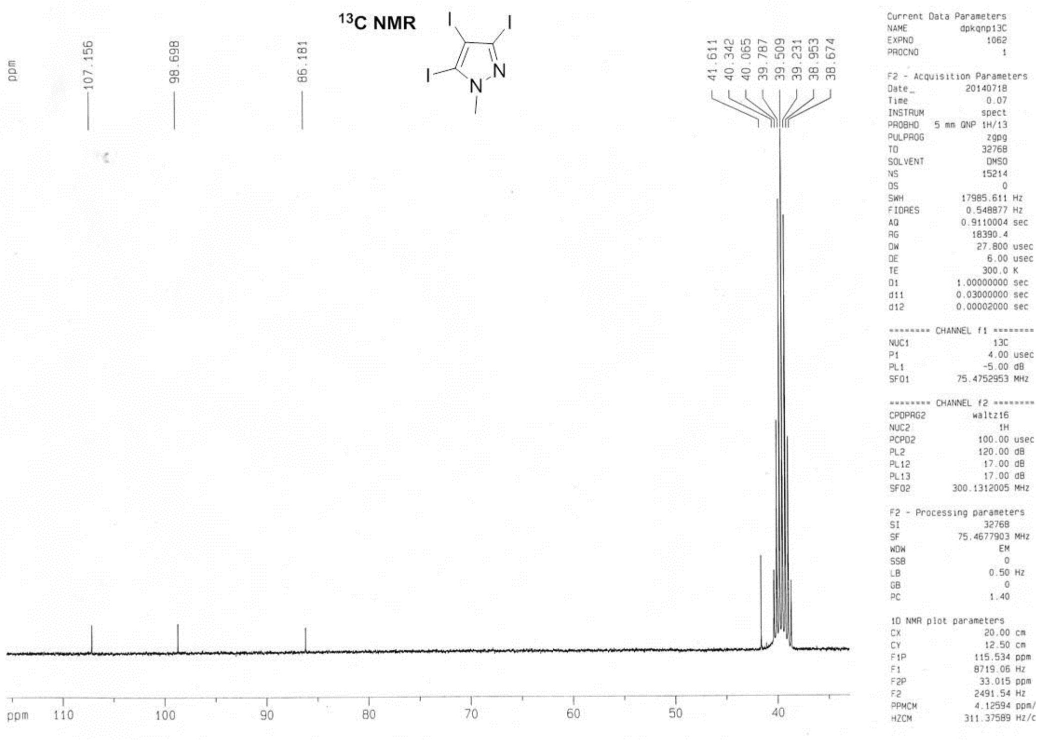

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TD               32768
SOLVENT           DMSO
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FIDRES        0.548877 Hz
AQ           0.9110004 sec
RG             18390.4
DW              27.800 usec
DE                6.00 usec
TE               300.0 K
D1          1.00000000 sec
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d12         0.00002000 sec

======== CHANNEL f1 ========
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P1                4.00 usec
PL1              -5.00 dB
SFO1        75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2           100.00 usec
PL2             120.00 dB
PL12             17.00 dB
PL13             17.00 dB
SFO2       300.1312005 MHz

F2 - Processing parameters
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SF          75.4677903 MHz
WDW                 EM
SSB                  0
LB                0.50 Hz
GB                   0
PC                1.40

1D NMR plot parameters
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CY               12.50 cm
F1P            115.534 ppm
F1             8719.06 Hz
F2P             33.015 ppm
F2             2491.54 Hz
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HZCM         311.37589 Hz/c
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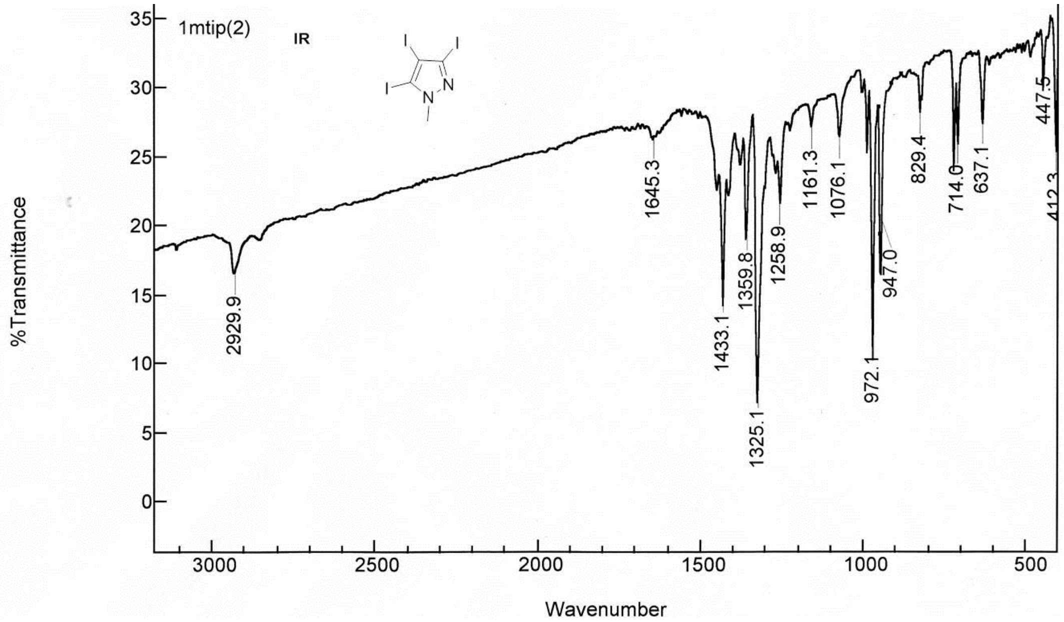
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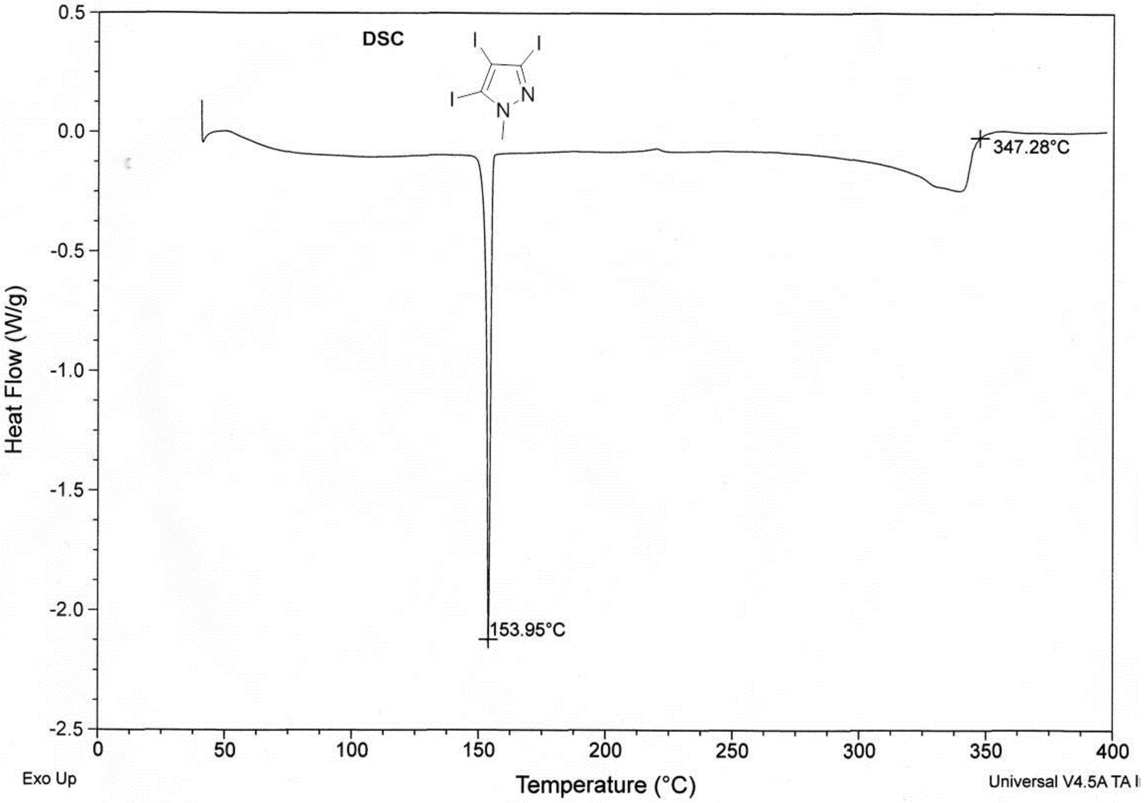
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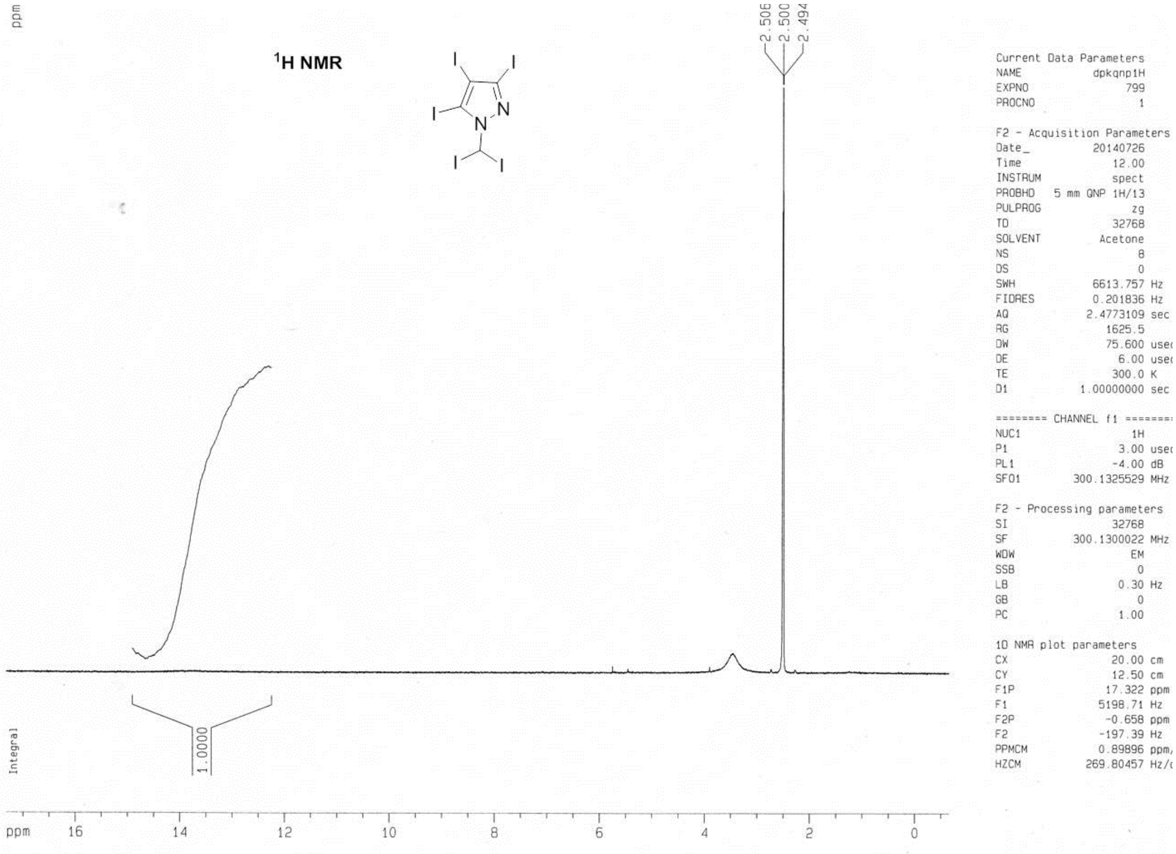

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TD                 32768
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FIDRES          0.201836 Hz
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RG                1625.5
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DE                  6.00 use
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 =======
NUC1                  1H
P1                  3.00 use
PL1                -4.00 dB
SFO1       300.1325529 MHz

F2 - Processing parameters
SI                 32768
SF         300.1300022 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P               17.322 ppm
F1               5198.71 Hz
F2P               -0.658 ppm
F2               -197.39 Hz
PPMCM            0.89896 ppm/
HZCM           269.80457 Hz/
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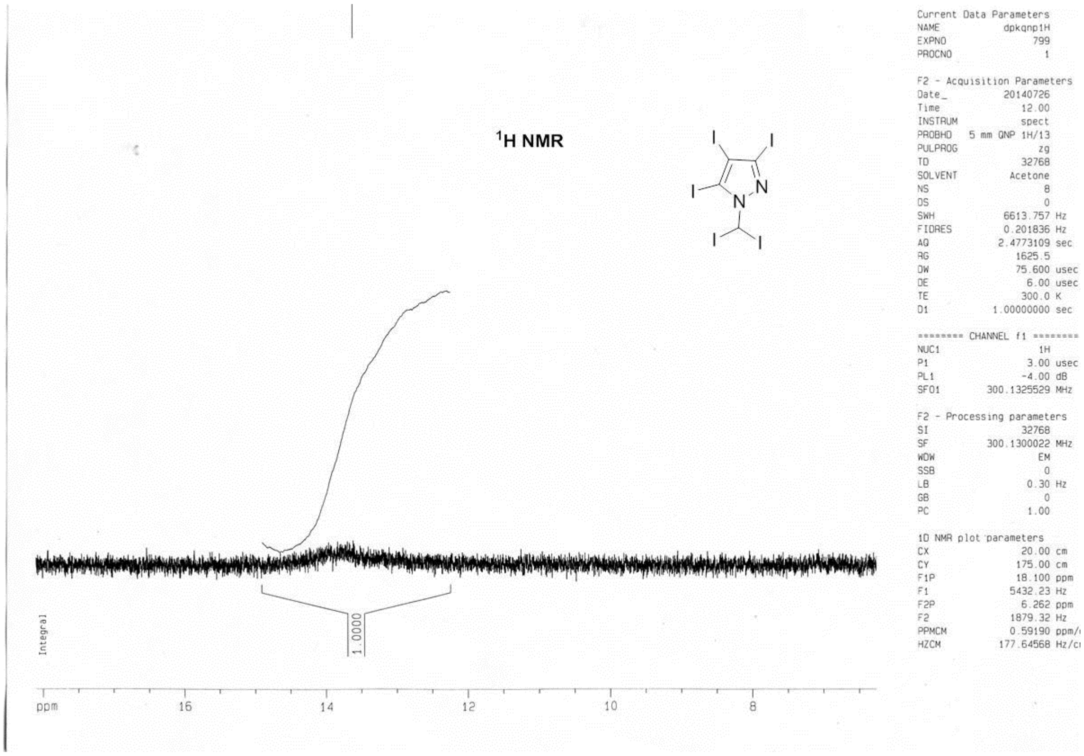

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PROCNO                 1

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PULPROG               zg
TD                 32768
SOLVENT          Acetone
NS                     8
DS                     0
SWH             6613.757 Hz
FIDRES          0.201836 Hz
AQ             2.4773109 sec
RG                1625.5
DW                75.600 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  3.00 usec
PL1                -4.00 dB
SFO1       300.1325529 MHz

F2 - Processing parameters
SI                 32768
SF         300.1300022 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                175.00 cm
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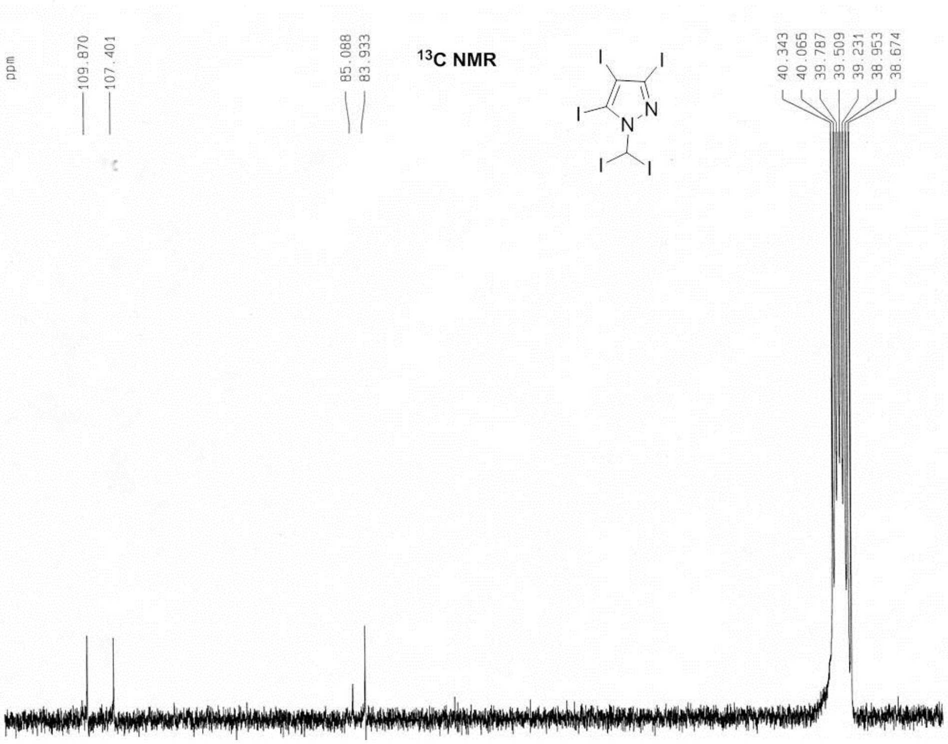

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SOLVENT             DMSO
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DS                     0
SWH            17985.611 Hz
FIDRES          0.548877 Hz
AQ             0.9110004 sec
RG               18390.4
DW                27.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
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======== CHANNEL f1 ========
NUC1                 13C
P1                  4.00 usec
PL1                -5.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
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PL12               17.00 dB
PL13               17.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
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1D NMR plot parameters
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F1               8877.20 Hz
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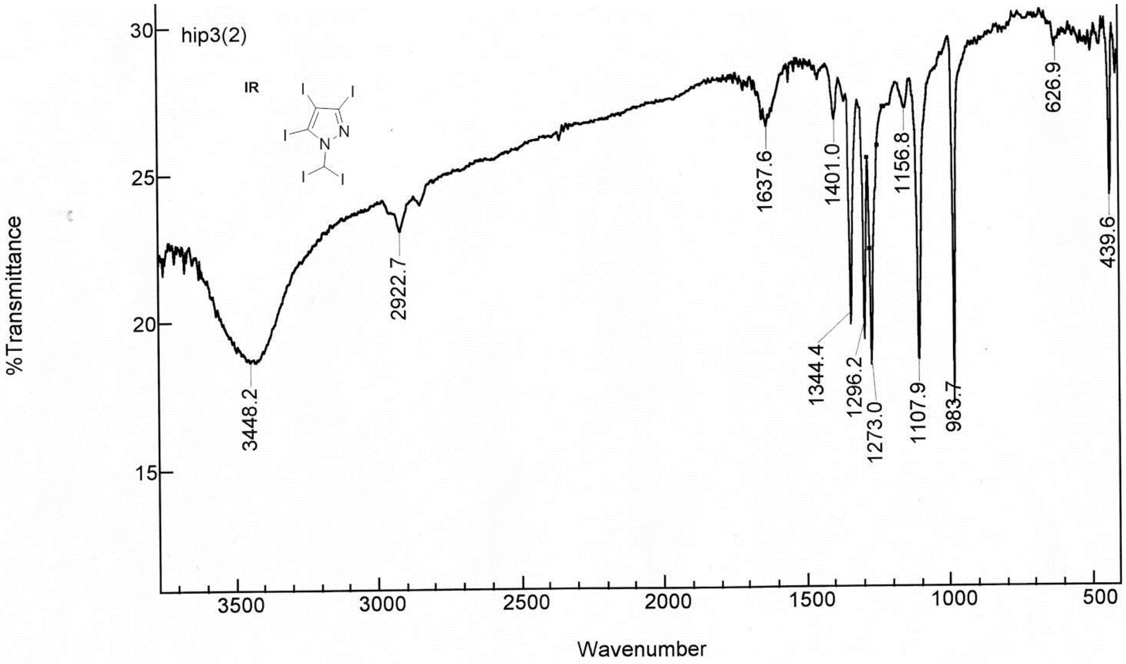

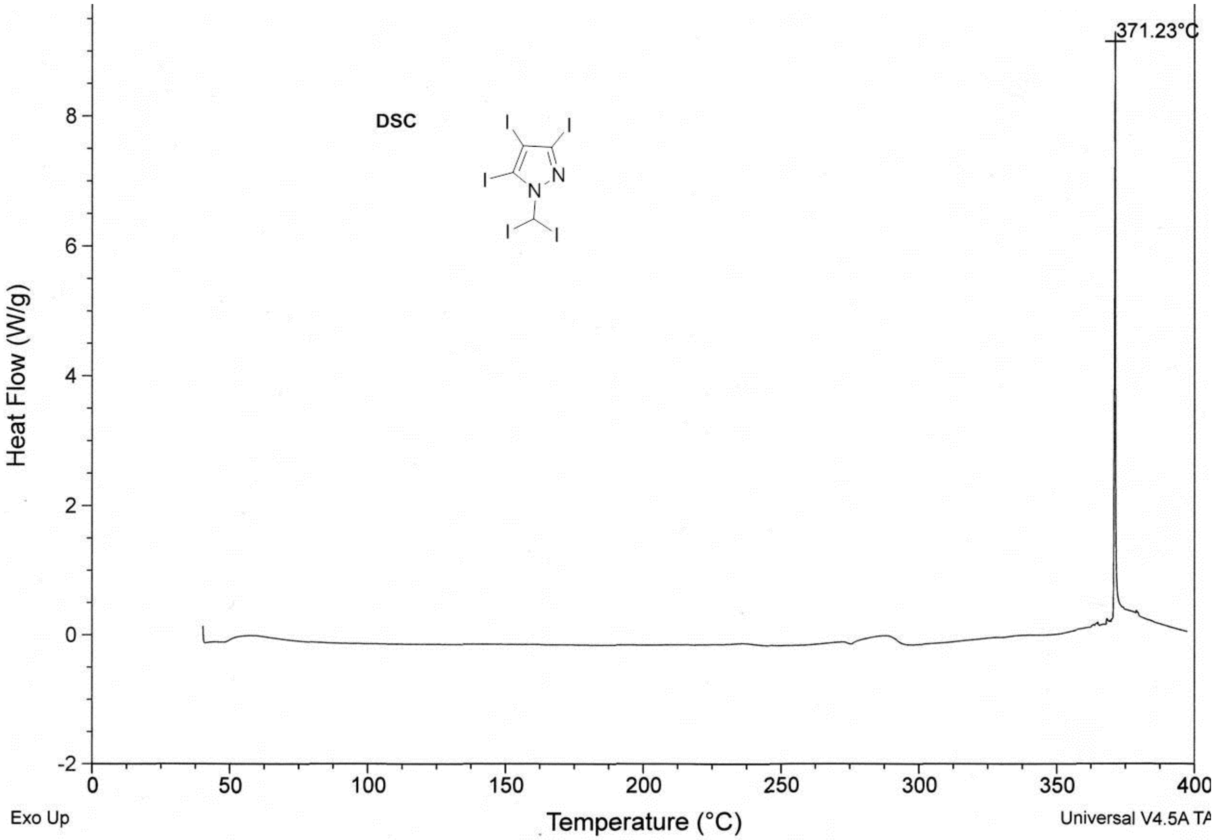

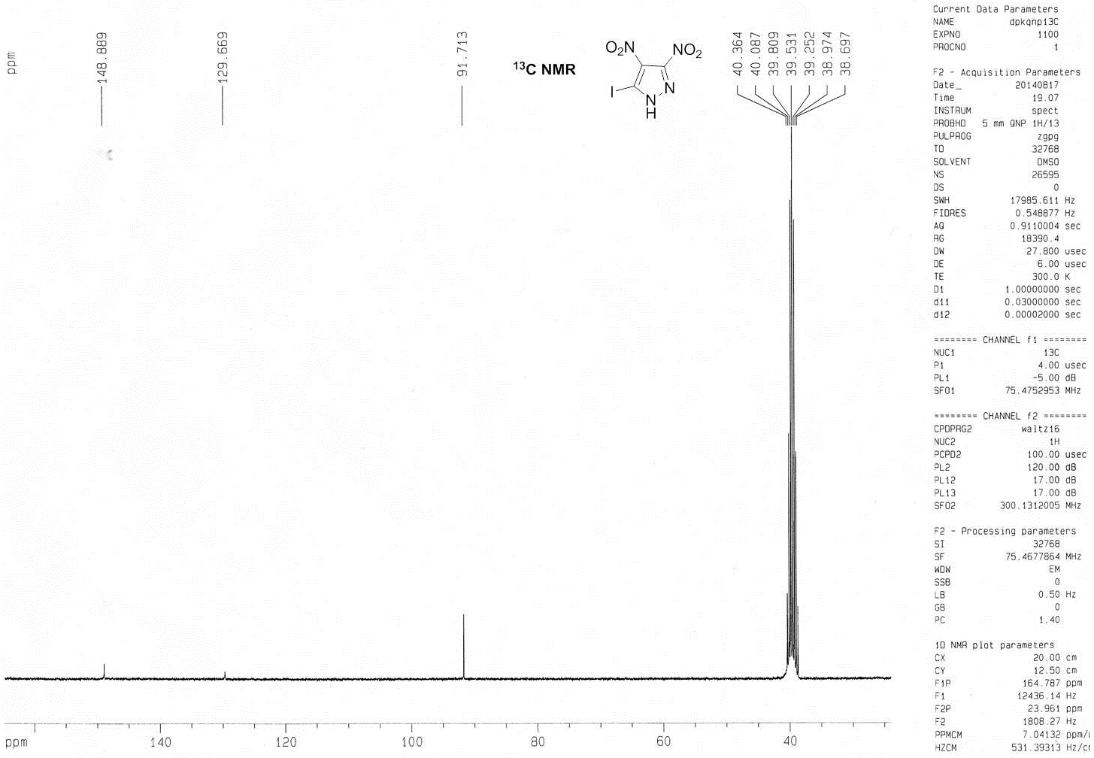

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FIDRES         0.548877 Hz
AQ            0.9110004 sec
RG              18390.4
DW               27.800 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
d11          0.03000000 sec
d12          0.00002000 sec

======== CHANNEL f1 ========
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PL1               -5.00 dB
SF01         75.4752953 MHz

======== CHANNEL f2 ========
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NUC2                 1H
PCPD2            100.00 usec
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PL12              17.00 dB
PL13              17.00 dB
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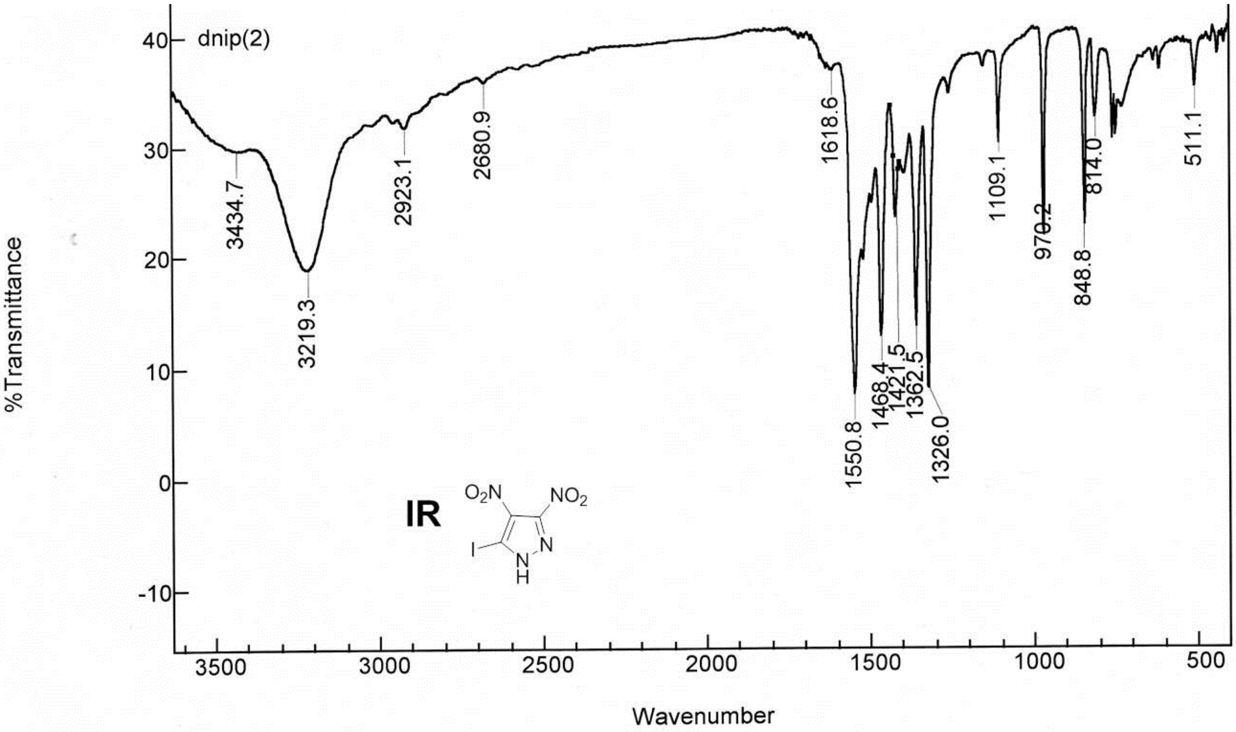
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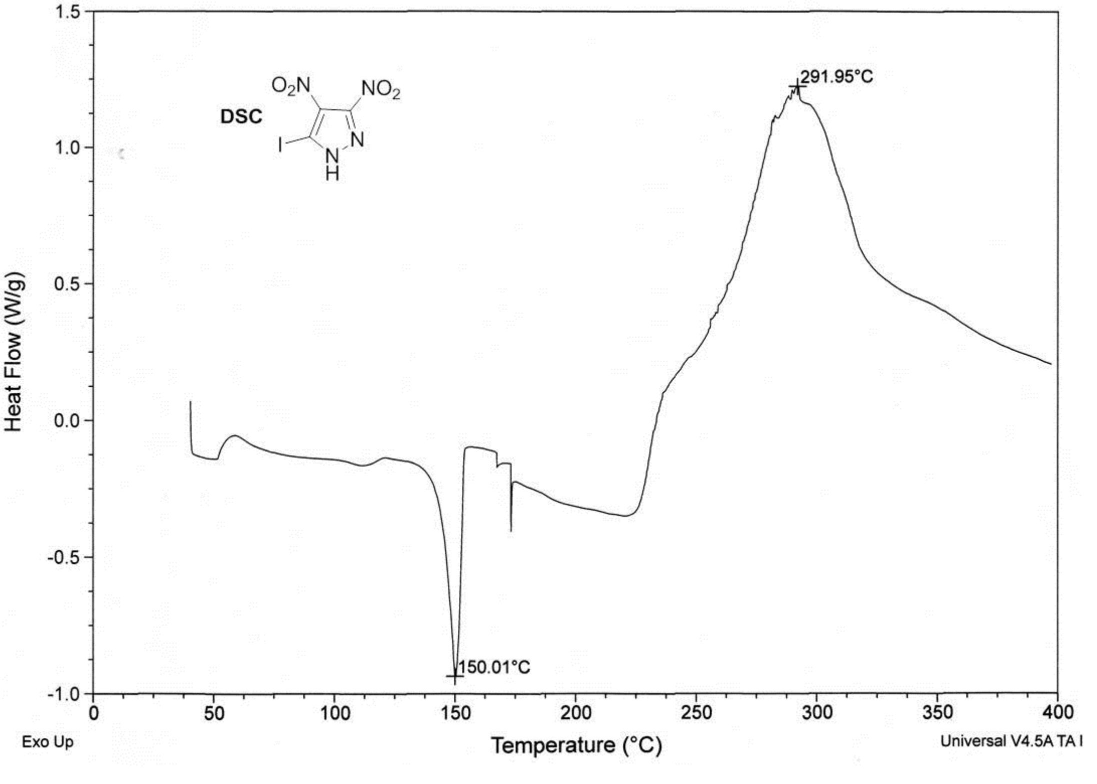
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-1.0
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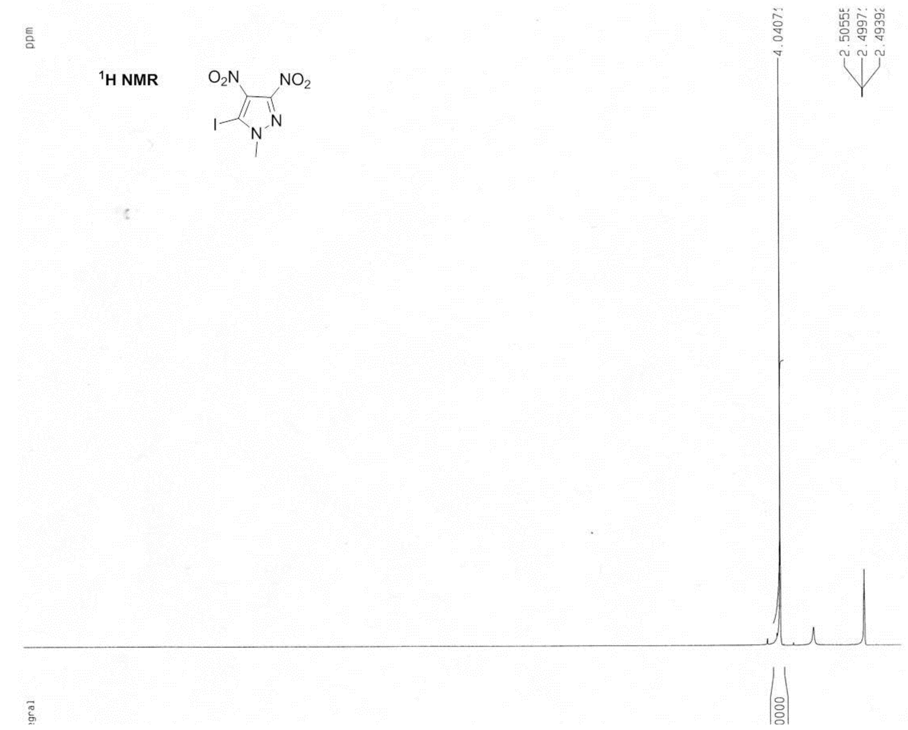
400
Exo Up
Temperature (°C)
Universal V4.5A TA I



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TD                 32768
SOLVENT          Acetone
NS                     8
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FIDRES          0.201836 Hz
AQ             2.4773109 sec
RG                 574.7
DW                75.600 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
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P1                  3.00 usec
PL1                -4.00 dB
SFO1         300.1325529 MHz

F2 - Processing parameters
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WDW                   EM
SSB                    0
LB                  0.30 Hz
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PC                  1.00

1D NMR plot parameters
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CY                 12.50 cm
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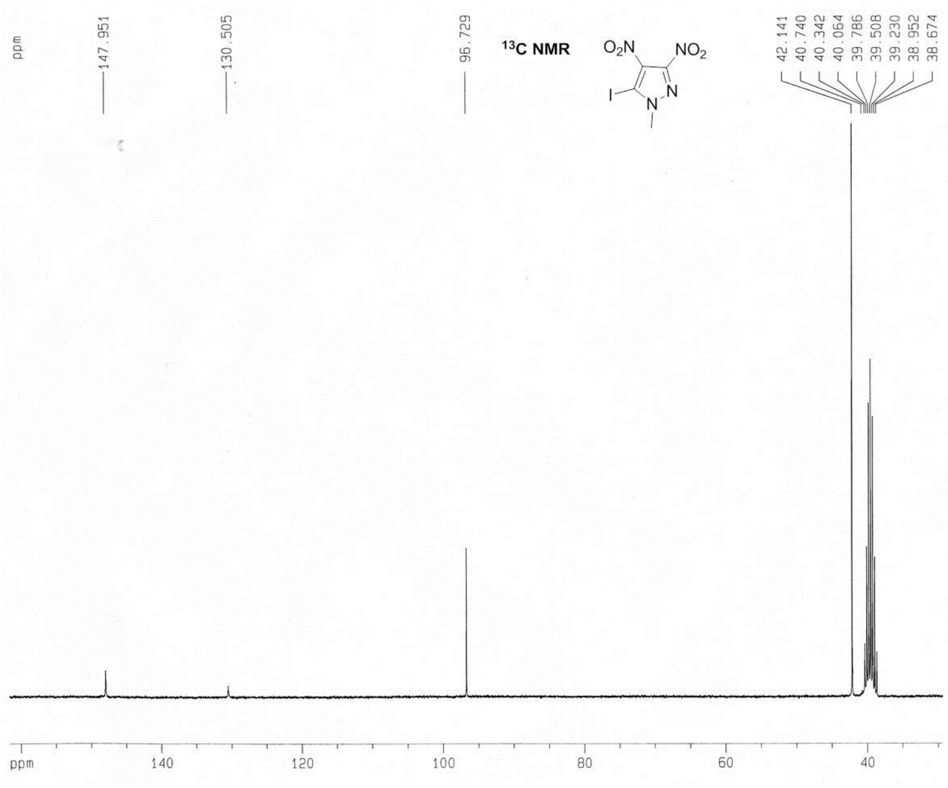

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TD                 32768
SOLVENT             DMSO
NS                 10284
DS                     0
SWH            17985.611 Hz
FIDRES          0.548877 Hz
AQ             0.9110004 sec
RG               18390.4
DW                27.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  4.00 usec
PL1                -5.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2               120.00 dB
PL12               17.00 dB
PL13               17.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
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SF            75.4677886 MHz
WDW                   EM
SSB                    0
LB                  0.50 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P              161.633 ppm
F1              12198.09 Hz
F2P               29.331 ppm
F2               2213.51 Hz
PPMCM            6.61513 ppm/
HZCM           499.22888 Hz/c
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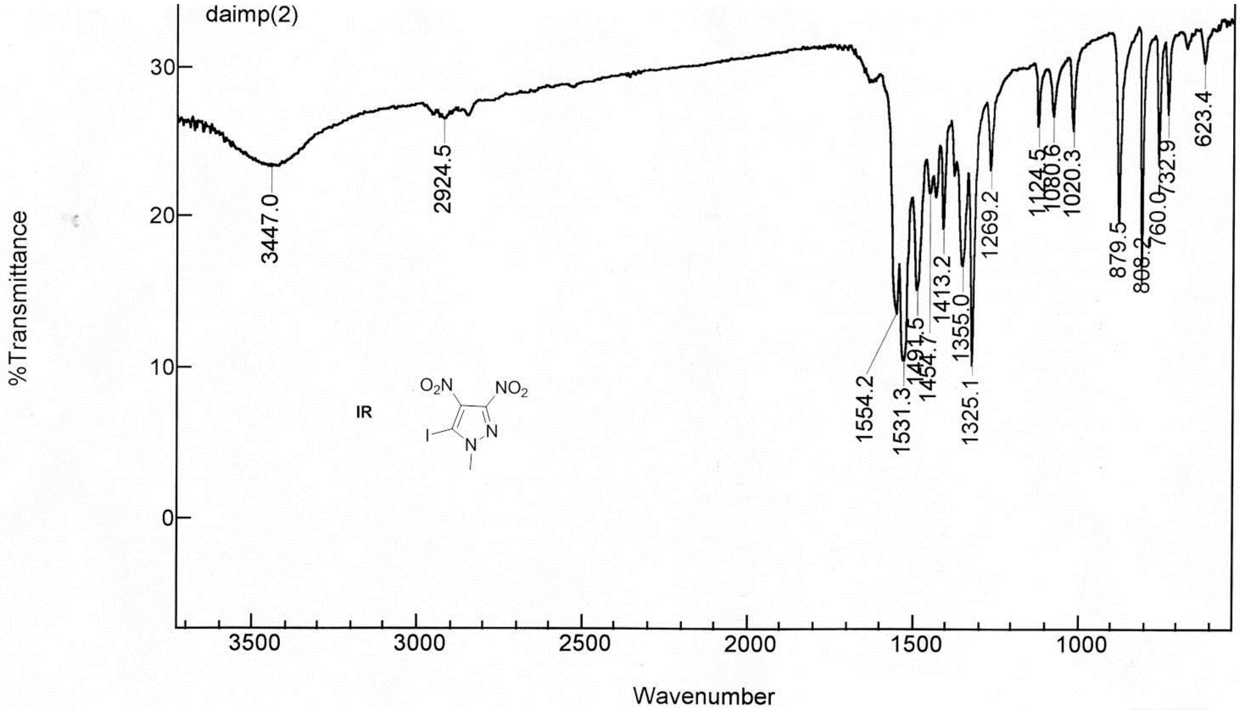
daimp(2)
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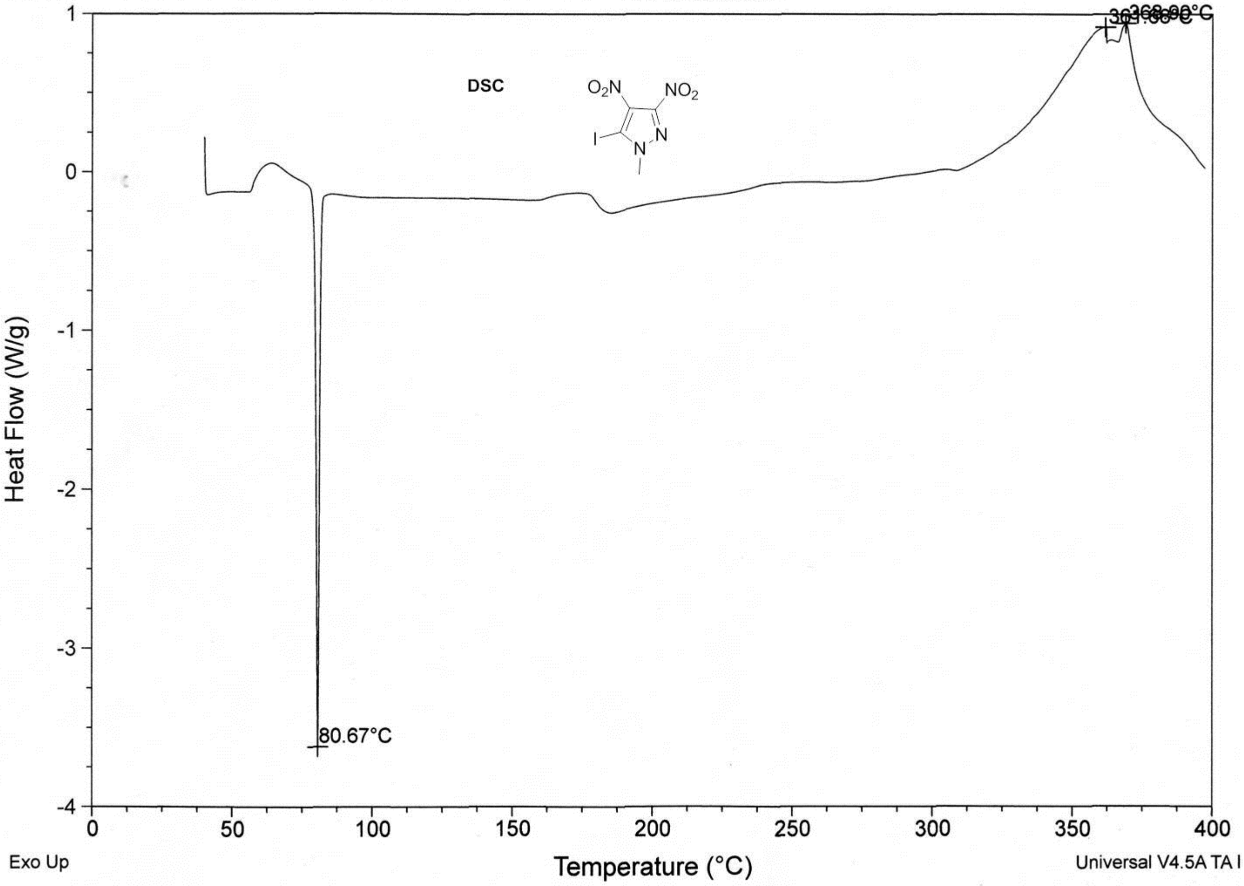
Wavenumber
3447.0
2924.5
1554.2
1531.3
1491.5
1454.7
1413.2
1355.0
1325.1
1269.2
1124.5
1080.6
1020.3
879.5
808.2
760.0
732.9
623.4
IR
O_2N
NO_2
I
N
N


Heat Flow (W/g)
1
0
-1
-2
-3
-4
0
50
100
150
200
250
300
350
400
Temperature (°C)
Exo Up
Universal V4.5A TA I
DSC
O_2N
NO_2
I
N
N
80.67°C
368.90°C

Experimental Details

X-ray crystallography

An irregular yellow crystal of dimensions 0.17 x 0.10 x 0.07 mm^3 was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK$_\alpha$ radiation (λ= 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) °K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX2* [v2010.3-0].[2] The crystal was a non-merohedral twin. The data was refined and solved using the major component. Data reduction was performed using *SAINT* [v7.68A][3] and *XPREP* [v2008/2].[4] Corrections were applied for Lorentz, polarization, and absorption effects using TWINABS v2008/2.[5] The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* [v2008/4] system of programs.[6] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

Table 3: Crystallographic data for compound 5

Compound	5
Formula	$C_4H_3IN_4O_4$
CCDC number	1031880
M_w	298.00
Crystal size [mm^3]	0.17 x 0.10 x 0.07
Crystal system	Monoclinic
Space group	$P2_1$
a [Å]	6.082(9)
b [Å]	8.835(14)
c [Å]	8.067(13)
α[°]	90
β [°]	107.606(19)
γ [°]	90
V [Å^3]	413.2(11)

Z	2
T [K]	150(2)
ρ_{calcd} [Mg m^{-3}]	2.395
μ [mm^{-1}]	3.866
F(000)	280
ϑ[°]	2.65 to 28.21
Index ranges	-8<=h<=7 0<=k<=11 0<=l<=10
Reflections collected	1073
Independent reflections (R_{int})	1073 [R_{int} = 0.0000]
Data/restraints/parameters	1073 / 1 / 119
GOF on F^2	0.970
R_1 ($I > 2\delta(I)$)^a	0.0229
wR_2 ($I > 2\delta(I)$)^b	0.0394
R_1 (all data)	0.0252
wR_2 (all data)	0.0398
Largest diff. peak and hole [e. Å-3]	1.030 and -0.782
$_a\, R_1 = \sum\lvert\lvert F_0\rvert - \lvert F_c\rvert\rvert / \sum\lvert F_0\rvert$ $_b R_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$	

1-Methyl-3, 4, 5-triodopyrazole (2)

A procedure similar to that for **1** was followed. 1-Methylpyrazole (3 g, 36.5 mmol), iodine (15.24 g, 60.0 mmol), potassium persulfate (16.2 g, 60.0 mmol), trifluoroacetic acid (48 mL), sulfuric acid (2.16 mL), and DCE (50 mL) were reacted in 500 mL round-bottomed flask to obtain a white solid (yield, 13.8 g, 82.7 %).

T_{melt} = 153.9 °C; T_{dec} (onset) = 400°C; IR (KBr) ν 2929, 1645, 1359, 1325, 1258, 1161, 1076, 972, 947, 829, 714, 637, 447 cm^{-1} ; ^{1}H NMR δ 3.95 (CH_3) ; ^{13}C NMR δ 107.1, 98.6; elemental analysis: (%) calculated for $C_4H\,I_3\,N_2$ (459.79): C, 10.45; H, 0.66; N, 6.09; found C, 10.61; H, 0.65; N, 5.84.

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