Electronic Supplementary Information

Design and Synthesis of Thermally Robust Pyrazine–Tetrazole Hybrids as High-Nitrogen Energetic Materials

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Section S1. Experimental section

Section S1.1. *Caution*!

The new compounds are energetic materials which show increased sensitivity toward various stimuli (e.g., higher temperatures, impact, and friction). Proper safety precautions such as leather gloves, face shield, and eye protection must be taken at all times while synthesizing and handling these materials. All materials should be synthesized in milligram amounts. Wear personal protective equipment while handing hydrazine hydrate and use only in fume hood.

Section S1.2. General methods

All reagents (analytical grade) were purchased from AK Scientific, VWR or Oakwood Chemicals and were used as supplied. ^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded using a 500 MHz (Bruker AVANCE 500) NMR spectrometer operating at 500.19, 125.78, 36.14, and 50.69 MHz, respectively. Chemical shifts in ^{1}H and ^{13}C NMR spectra are reported relative to Me_4Si; ^{14}N and ^{15}N NMR spectra to $MeNO_2$ as an external standard. Abbreviations for multiplicities and descriptors are: s = singlet, br = broad, m = multiplet (denotes complex pattern), and q = quartet. The decomposition points (onset temperature) were obtained on a differential scanning calorimeter (TA Instruments Company, Model: Q2000). Infrared spectra were recorded on a FT-IR spectrometer (Thermo Nicolet 6700) equipped with an ATR assembly. The densities were measured at ambient temperatures by employing a gas pycnometer (Micromeritics AccuPyc II 1340). The impact and friction sensitivities were determined by using a standard BAM drop hammer and BAM friction tester. Elemental analyses were carried out on a Vario Micro cube Elementar Analyser.

Section S1.3. Synthesis and characterization data

Synthesis of P2, 1 and 3. **P2**, **1** and **3** were obtained following literature procedures.[1-2]

Synthesis of 2. To a 100 mL round-bottomed flask was added **1** (2.00 g, 12.5 mmol, 1.0 equiv.), sodium azide (2.03 g, 31.2 mmol, 2.5 equiv.), and DMSO (10 mL). The reaction mixture was

stirred at reflux for 24 h. After cooling, HCl (1M, 50 mL) was added to the reaction mixture with vigorous stirring. The reaction mixture was heated at 50 °C, cooled and the resulting precipitate was filtered and washed with distilled water (3 x 30 mL) to obtain **2** as a brown solid. (**2**): Physical description: Amorphous brown solid. Isolated yield: (2.50 g, 81%); $T_{dec.}$ = 305 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 11.3 (bs, 2H), 7.59 (bs, 4H); ^{13}C NMR (125 MHz, d_6-DMSO): 155.2, 151.3, 130.2; IR ($\tilde{\nu}$, cm^{-1}): 3493, 3452, 3382, 3334, 1686, 1659, 1615, 1594, 1513, 1396, 1336, 1300, 1209, 1087, 1010, 848, 803; Calcd for C_6H_6N12: C, 29.27; H, 2.46; N, 68.27. Found: C, 29.17; H, 2.70; N, 65.78.

Synthesis of 5. To a 100 mL round-bottomed flask was added **1** (2.00 g, 12.5 mmol, 1.0 equiv.), sodium azide (2.03 g, 31.2 mmol, 2.5 equiv.), zinc bromide (1.40 g, 6.3 mmol, 0.5 equiv.), and DMSO (10 mL). The reaction mixture was stirred at reflux for 24 h. After cooling, HCl (1M, 50 mL) was added to the reaction mixture with vigorous stirring. The reaction mixture was heated at 50 °C, cooled and the resulting precipitate was filtered and washed with distilled water (3 x 30 mL) to obtain **5** as a brown solid. (**5**): Physical description: Amorphous brown solid. Isolated yield: (2.60 g, 85%); $T_{dec.}$ = 320 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 16.5 (bs, 2H), 6.88 (bs, 4H); ^{13}C NMR (125 MHz, d_6-DMSO): 153.1, 144.2, 124.5; IR ($\tilde{\nu}$, cm^{-1}): 3461, 3426, 3325, 3229, 3175, 1639, 1580, 1514, 1412, 1309, 1236, 1080, 1010, 875; Calcd for $C_6H_6N_{12}$: C, 29.27; H, 2.46; N, 68.27. Found: C, 29.31; H, 2.45; N, 66.08.

Synthesis of 6. To red fuming acid (5 mL), stirred at 0 °C, was added compound **5** (1.00 g, 4.1 mmol, 1.0 equiv.) in small portions. Stirring continued at the same temperature for 1 h and the mixture was poured into ice (20 g). The resulting brown precipitate was filtered and washed with water (3 × 20 mL). (**6**): Physical description: Amorphous brown solid. Isolated yield: (1.00 g, 74%); $T_{dec.}$ = 212 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 11.3 (bs, 4H); ^{13}C NMR (125 MHz, d_6-

DMSO): 154.0, 148.8, 131.7; IR ($\tilde{\nu}$, cm^{-1}): 3415, 3250, 3126, 3011, 2942, 2852, 1749, 1649, 1491, 1384, 1309, 1257, 1192, 1167, 1113, 1049, 963, 896, 722; Calcd for $C_6H_4N_{14}O_4$: C, 21.44; H, 1.20; N, 58.33; Found: C, 21.40; H, 1.59.; N, 57.08.

Section S2. X-ray crystallographic details and crystallographic data

Data collection

Crystals with suitable dimensions were mounted on a nylon loop with Paratone oil. Data were collected using a XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 99.9(4) K. The structures were solved with the ShelXT[4] solution program using dual methods and by using Olex2.[5] The model was refined with ShelXL[6] using full matrix least squares minimization on F^2 (Table S1). The thermal ellipsoids and packing diagrams of X-ray structures in the main article and supplementary material are plotted using Diamond 3.2 software.

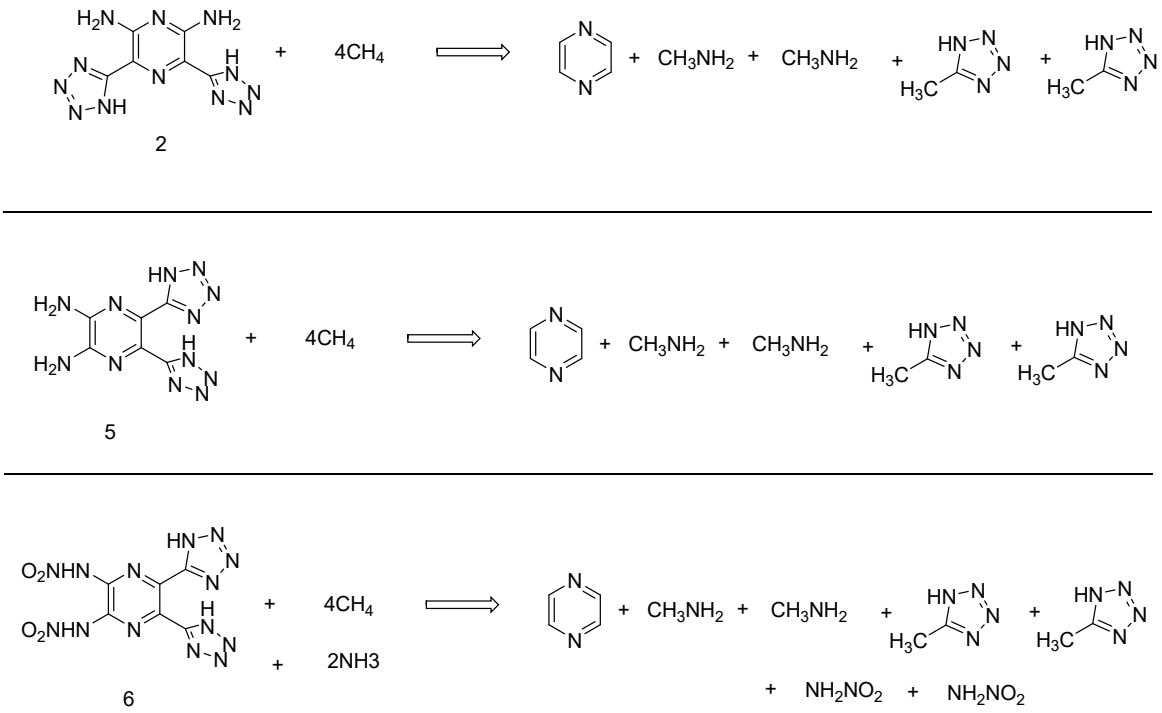
Table S1: Crystallographic data for **2.DMSO**.

Compound	**2•2DMSO**
CCDC #	2492520
Formula	$C_{10}H_{18}N_{12}O_2S_2$
$D_{calc.}$/ g cm^{-3}	1.509
m/mm^{-1}	3.056
FW	402.48
Color	yellow
Shape	needle-shaped
Size/mm^3	0.26×0.08×0.03
T/K	100.00(10)
Crystal System	triclinic
Space Group	P-1
a/Å	7.70178(17)
b/Å	10.3479(3)
c/Å	11.8168(3)
α/°	72.911(2)
β/°	89.9231(19)
γ/°	80.201(2)
V/Å^3	885.87(4)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_a
Q_{min}/°	3.919
Q_{max}/°	80.012
Measured Refl's.	14079
Indep't Refl's	3815
Refl's I≥2 s(I)	3553
R_{int}	0.0406
Parameters	292
Restraints	0
Largest Peak	0.398
Deepest Hole	-0.406
GooF	1.062
wR_2 (all data)	0.1043
wR_2	0.1026
R_1 (all data)	0.0392
R_1	0.0374

Section S3. Enthalpy of formation

Section S3.1. Isodesmic reactions

The $\Delta\mathbf{H_f}$ (enthalpy of formation) for new compounds was calculated by using isodesmic reactions (Scheme S1).



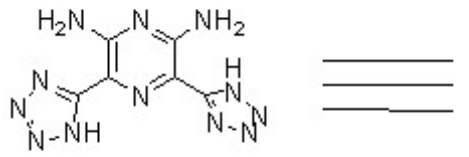
Scheme S1: Isodesmic reactions.

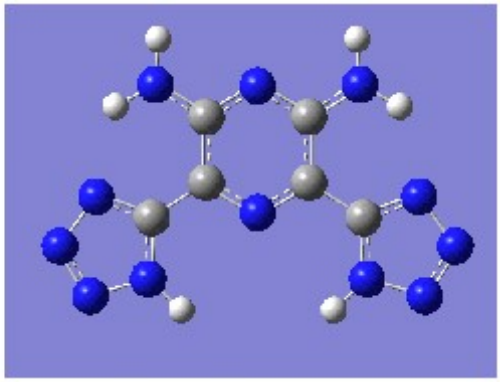
The single crystal structure was used for the geometric optimization and frequency analyses using the B3LYP functional with the 6-31+G** basis set. The single-point energies were obtained at the MP2/6-311++G** level.[7] The atomization energies for cations were calculated by using the G[2]*ab initio* method [8] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. In case of the energetic salts, the solid-phase heats of formation were obtained based on a Born–Haber energy cycle.[9]

Section S3.2. Gas phase heats of formation

Table S2: Gas phase heats of formation

Compd	ZPE	Hcorr	scaled ZPE	ΔHT	Mp-6-311++g**	Corrected	ΔHr	ΔHr (kJ/mol)	ΔHf (kJ/mol)
2	0.165819	0.180557	0.15919	0.014738	-887.1156709	-886.94175	0.10205656	267.9494726	731.9598152
5	0.165589	0.180246	0.15897	0.014657	-887.1047897	-886.93117	0.09147716	240.1732605	759.7360273
6	0.168932	0.188725	0.16217	0.019793	-1295.230674	-1295.04871	0.06461784	169.6541226	909.8351652





MP2=-887.1156709

Number of imaginary frequencies (NImag) = 0

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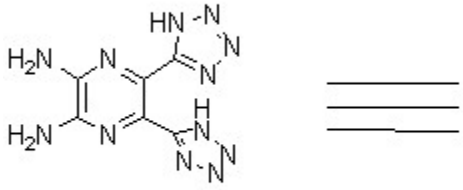
Zero-point correction=                           0.165819 (Hartree/Particle)
Thermal correction to Energy=                    0.179612
Thermal correction to Enthalpy=                  0.180557
Thermal correction to Gibbs Free Energy=         0.124318
Sum of electronic and zero-point Energies=           -889.097852
Sum of electronic and thermal Energies=              -889.084059
Sum of electronic and thermal Enthalpies=            -889.083114
Sum of electronic and thermal Free Energies=         -889.139353
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.000025	2.407878	-0.000130
2	7	0	-0.000007	-0.379495	-0.000153
3	7	0	2.299091	2.436764	0.000107
4	1	0	2.237216	3.443631	0.000044
5	1	0	3.195834	1.959331	0.000146
6	7	0	-2.299097	2.436785	0.000027
7	1	0	-2.237195	3.443654	0.000291
8	1	0	-3.195861	1.959374	0.000253
9	7	0	2.458480	-1.834155	-0.000247
10	1	0	1.716114	-2.517907	-0.000562
11	7	0	3.760505	-2.205179	-0.000121
12	7	0	4.446315	-1.112521	0.000247
13	7	0	3.630236	-0.024839	0.000257
14	7	0	-2.458420	-1.834194	0.000142
15	1	0	-1.716056	-2.517951	0.000092
16	7	0	-3.760463	-2.205173	0.000081
17	7	0	-4.446317	-1.112546	0.000135
18	7	0	-3.630252	-0.024873	-0.000028
19	6	0	1.153493	1.728608	-0.000032
20	6	0	1.153463	0.289467	-0.000022
21	6	0	-1.153489	0.289446	-0.000156
22	6	0	-1.153530	1.728594	-0.000191
23	6	0	2.381084	-0.485478	-0.000006
24	6	0	-2.381085	-0.485517	-0.000005



MP2=-887.1047897

Number of imaginary frequencies (NImag) = 0

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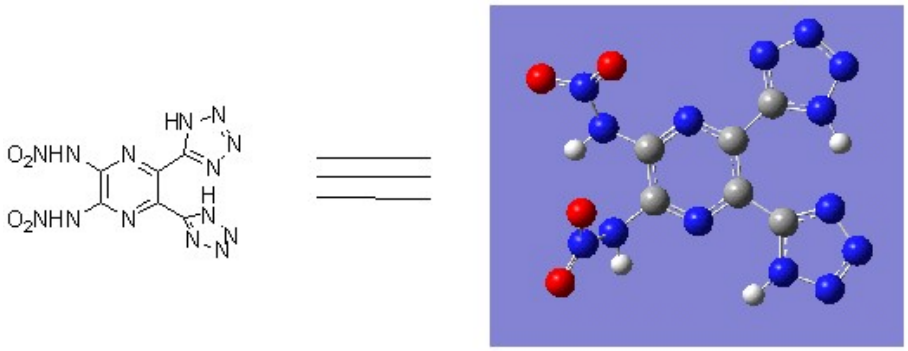
Thermal correction to Energy=	0.179302
Thermal correction to Enthalpy=	0.180246
Thermal correction to Gibbs Free Energy=	0.123944
Sum of electronic and zero-point Energies=	-889.074843
Sum of electronic and thermal Energies=	-889.061131
Sum of electronic and thermal Enthalpies=	-889.060187
Sum of electronic and thermal Free Energies=	-889.116489

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	1.389270	-1.464425	0.061946
2	7	0	1.481135	1.286676	-0.054889
3	7	0	3.708922	-1.573690	0.099646
4	1	0	3.559236	-2.562023	0.267374
5	1	0	4.482224	-1.178259	0.619984
6	7	0	-0.632439	2.928917	-0.000703
7	1	0	0.248938	3.422903	-0.029140
8	7	0	-1.818607	3.565365	0.027237
9	7	0	-2.722600	2.643750	0.058802
10	7	0	-2.149354	1.412479	0.052501
11	6	0	2.543895	-0.838419	0.059330
12	6	0	2.597790	0.592873	-0.052087
13	6	0	0.281895	0.641583	-0.005655
14	6	0	0.230466	-0.766702	0.011192
15	6	0	-0.833575	1.592626	0.013627
16	7	0	3.817709	1.240318	-0.089995
17	1	0	3.757748	2.232346	-0.283552
18	1	0	4.552719	0.772935	-0.607195
19	7	0	-0.909261	-2.966995	-0.066413
20	7	0	-2.188357	-3.390524	-0.076747
21	7	0	-3.016839	-2.386167	-0.032121
22	7	0	-2.262314	-1.279105	0.008221
23	1	0	-2.648875	-0.324191	0.040999
24	6	0	-0.959277	-1.635275	-0.013217



MP2=-1295.2306737

Number of imaginary frequencies (NImag) = 0

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Thermal correction to Energy=                    0.187781
Thermal correction to Enthalpy=                  0.188725
Thermal correction to Gibbs Free Energy=         0.117265
Sum of electronic and zero-point Energies=          -1298.001845
Sum of electronic and thermal Energies=             -1297.982996
Sum of electronic and thermal Enthalpies=           -1297.982052
Sum of electronic and thermal Free Energies=        -1298.053512
```

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.856204	0.697448	-0.166196
2	6	0	0.996357	-0.720467	-0.196843
3	7	0	-0.094356	-1.495016	-0.366992
4	6	0	-1.282170	-0.943541	-0.493363
5	6	0	-1.420821	0.468200	-0.480095
6	7	0	-0.361658	1.238757	-0.330249
7	7	0	-2.664169	1.039787	-0.721215
8	1	0	-3.427523	0.445269	-1.022019
9	7	0	-2.395463	-1.797639	-0.723894
10	1	0	-2.177603	-2.673583	-1.192965
11	7	0	-3.183158	2.147673	0.005045
12	8	0	-2.445601	2.733865	0.767373
13	8	0	-4.357926	2.380358	-0.252334
14	7	0	-3.215846	-2.106529	0.407869
15	8	0	-3.259132	-1.269366	1.295550
16	8	0	-3.829348	-3.157739	0.329271
17	7	0	1.693405	3.020453	-0.021196
18	7	0	2.891882	3.604581	0.137087
19	7	0	3.840227	2.711644	0.243899
20	7	0	3.485126	-1.160509	0.101938
21	7	0	4.219757	-2.298911	0.180942
22	7	0	3.457545	-3.336617	0.077582
23	7	0	2.203792	-2.873529	-0.071883
24	1	0	1.412683	-3.496156	-0.168227
25	7	0	3.246048	1.519320	0.152810
26	1	0	3.754480	0.623780	0.195015
27	6	0	1.916643	1.705342	-0.012165
28	6	0	2.219137	-1.522069	-0.056821

Section S3.3. Solid state enthalpy of formation

The gas state $\Delta\mathbf{H_f}$ of compound **2** is 731.6 kJ mol^{-1}.

The gas state $\Delta\mathbf{H_f}$ of compound **5** is 759.7 kJ mol^{-1}.

The gas state $\Delta\mathbf{H_f}$ of compound **6** is 909.8 kJ mol^{-1}.

The calculated gas-phase enthalpy for compounds **2, 5** and **6** is converted to solid phase values by subtracting the empirical heat of sublimation obtained based on Trouton's rule.[10]

Compound 2: ΔH_{sub} (kJ mol^{-1}) = 0.188·(273+305) = 108.7 kJ mol^{-1}

Compound 5: ΔH_{sub} (kJ mol^{-1}) = 0.188·(273+320) = 111.5 kJ mol^{-1}

Compound 6; ΔH_{sub} (kJ mol^{-1}) = 0.188·(273+212) = 91.2 kJ mol^{-1}

Table S3: Solid state $\Delta\mathbf{H_f}$ for compounds using Trouton's rule.

Compound	ΔH_f (g) kJ mol^{-1}	ΔH_{sub} kJ mol^{-1}	ΔH_f(s) kJ mol^{-1}
2	731.6	108.7	622.9
5	759.7	111.5	648.2
6	909.8	91.2	818.6

Section S4. References

[1] T. G. Witkowski, E. Sebastiao, B. Gabidullin, A. Hu, F. Zhang and M. Murugesu, *ACS Appl. Energy Mater.*, 2018, **1**, 589–593.

[2] Y. Wang, J. Liu, J. He, X. Ren, L. Hu and S. Pang, *Chem. Commun.*, 2025, **61**, 13433–13436.

[3] D. E. Chavez and M. A. Hiskey, *J. Heterocycl. Chem.*, 1998, **35**, 1329–1332.

[4] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* 2008, 64, 112–122.

[5] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* 2015, **71**, 3–8.

[6] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339–341.

[7] R. G. Parr, Y. Weitao, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, 1995).

[8] O. Suleimenov and T.-K. Ha, *Chem. Phys. Lett.* 1998, **290**, 451–457.

[9] H. D. B. Jenkins, D. Tudela and L. Glasser, *Inorg. Chem.* 2002, **41**, 2364–2367.

[10] M. S. Westwell, M. S. Searle, D. J. Wales, D. H. Williams, *J. Am. Chem. Soc.* 1995, **117**, 5013–5015.

Section S5. Spectrum Analysis

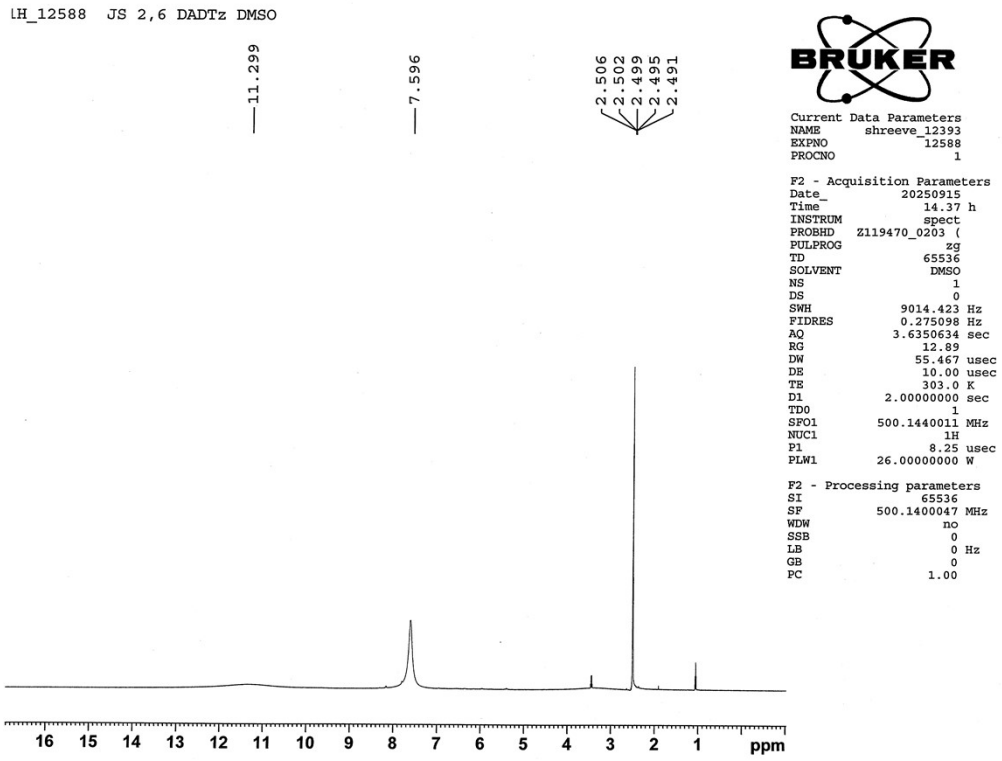

Figure S1: ^{1}H NMR spectrum for compound **2**.

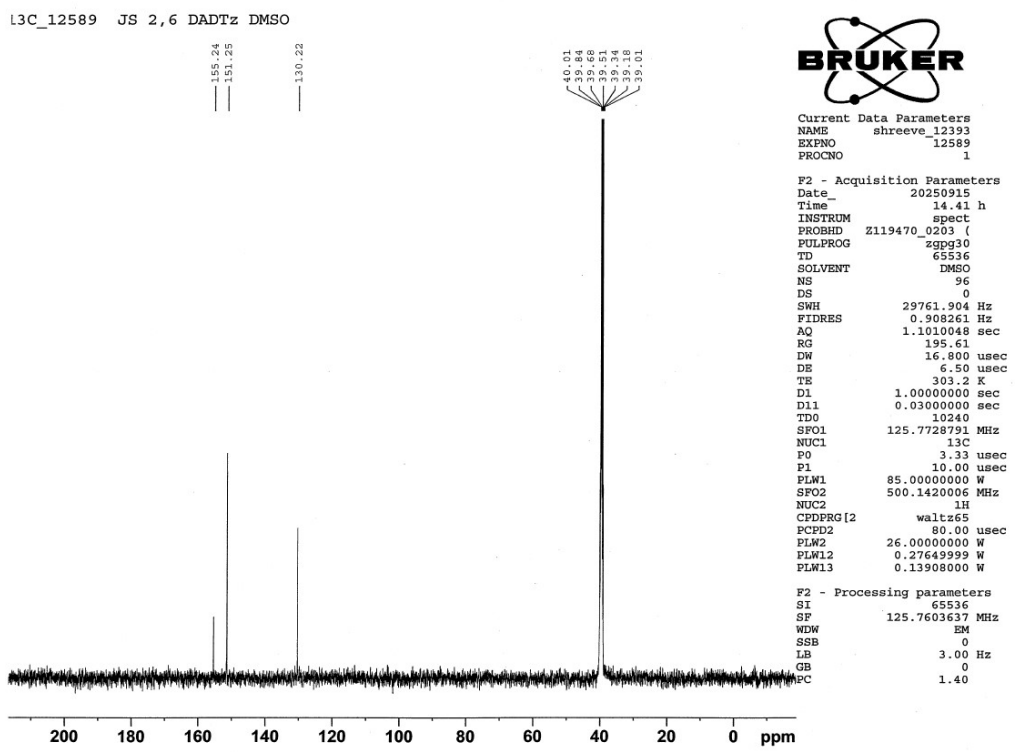

Figure S2: ^{13}C NMR spectrum for compound **2**.

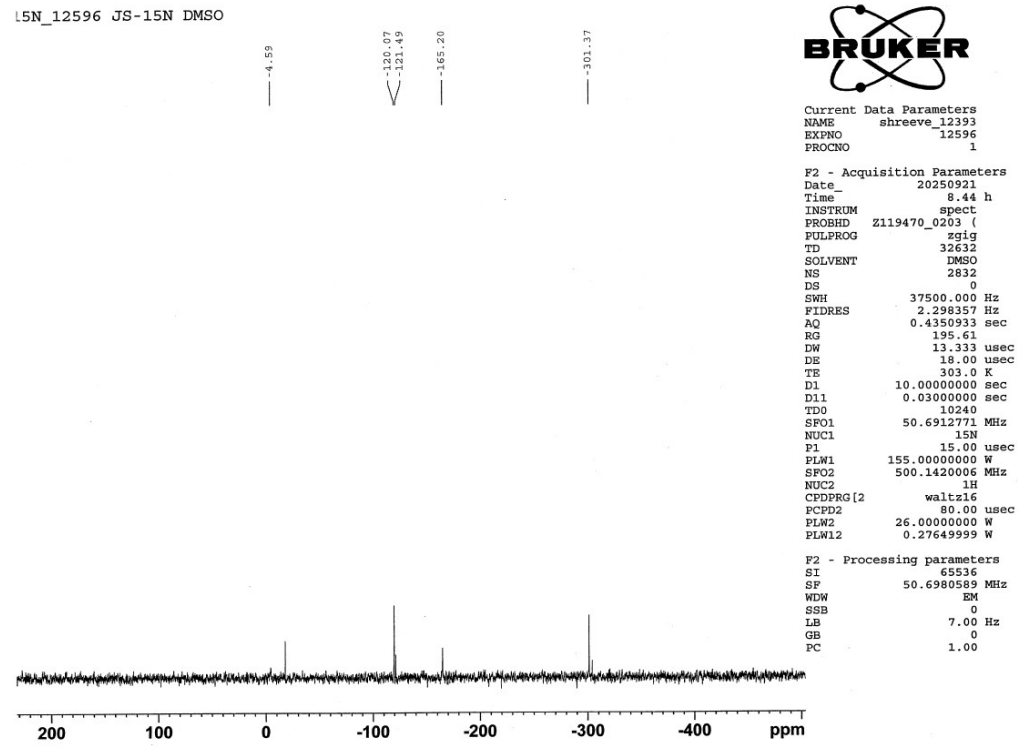

Figure S3: ^{15}N NMR spectrum for compound **2**.

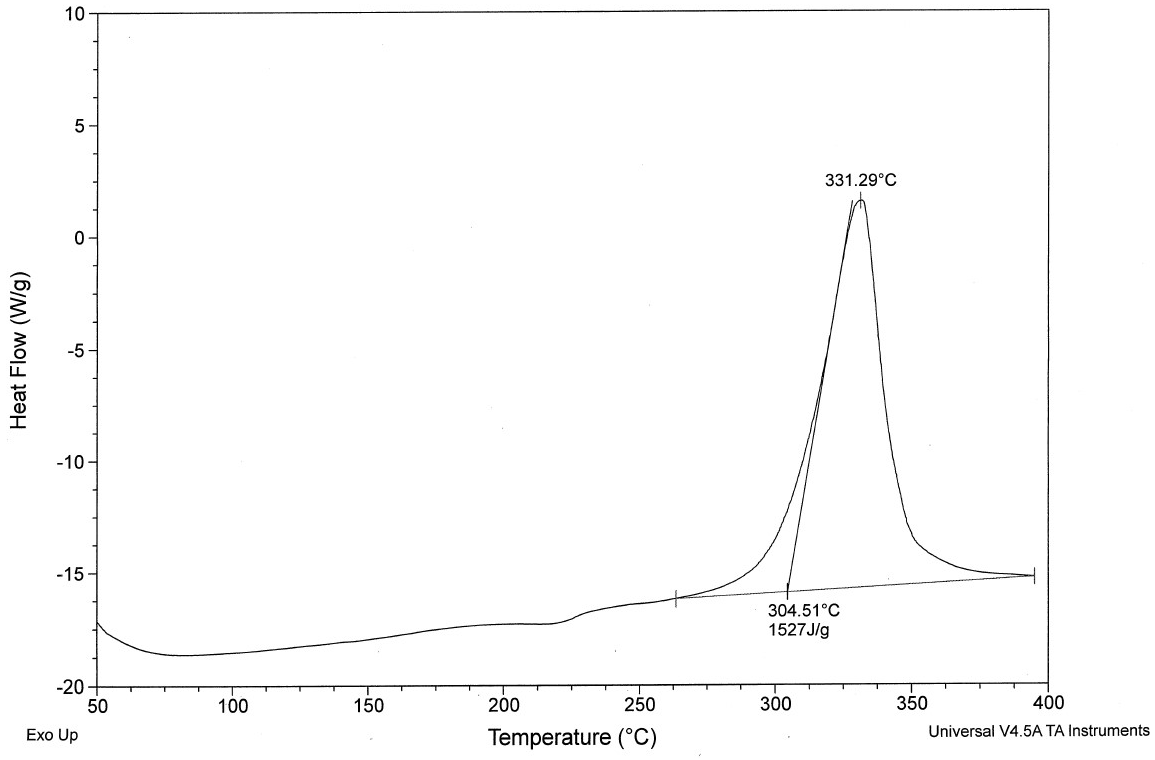

Figure S4: DSC plot for compound **2.**

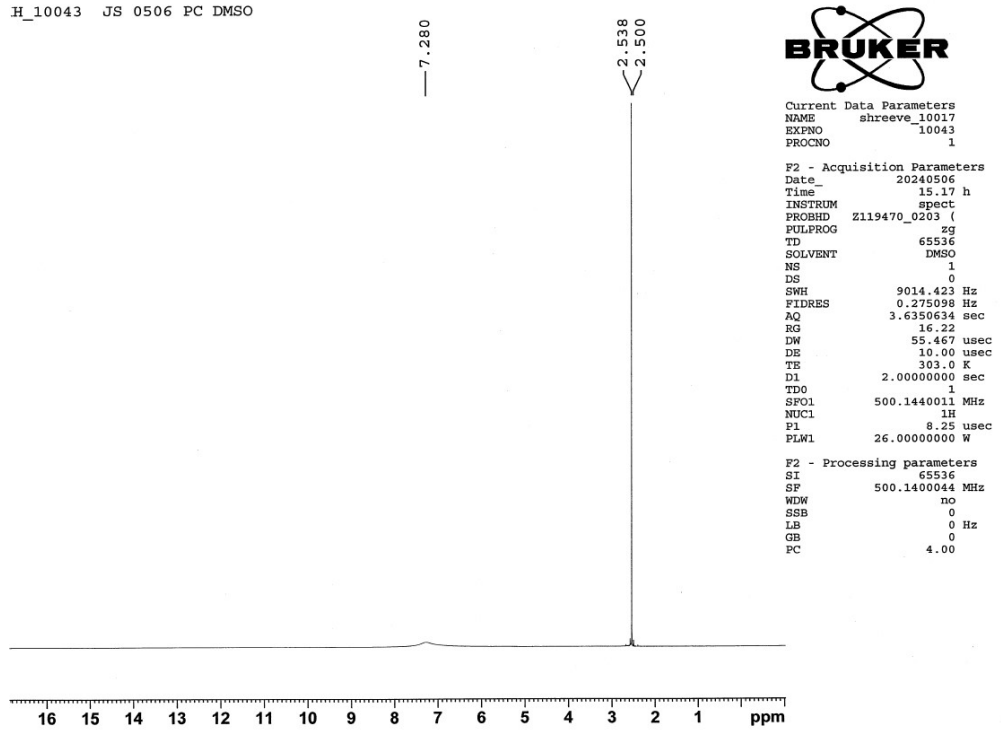

Figure S5: ^{1}H NMR spectrum for compound **4**.

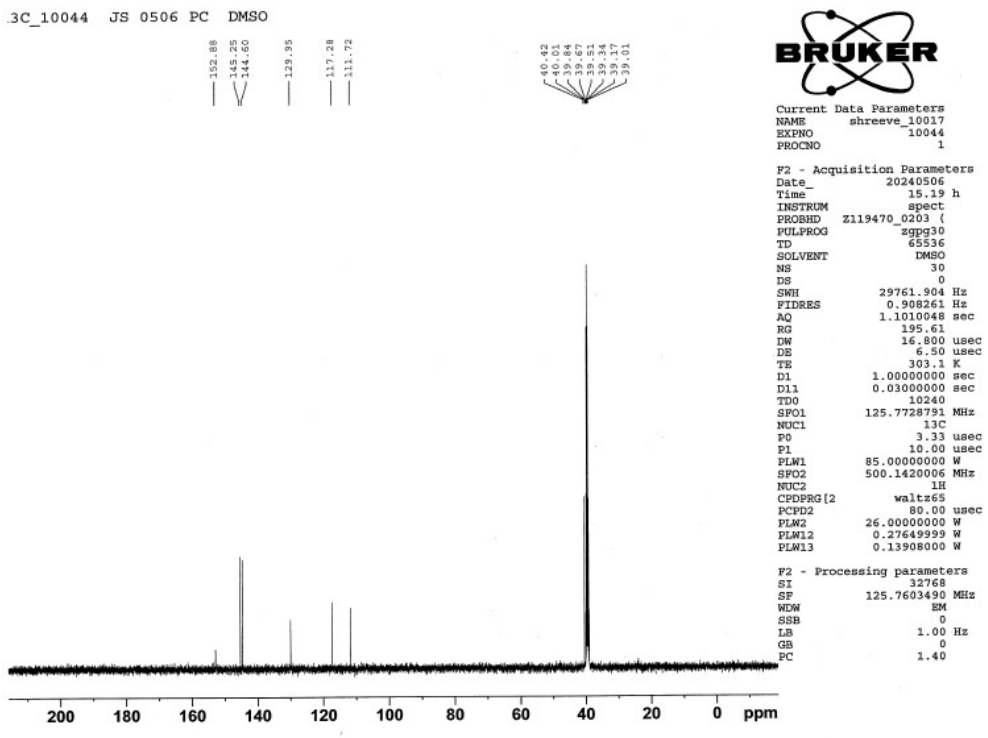

Figure S6: ^{13}C NMR spectrum for compound **4**.

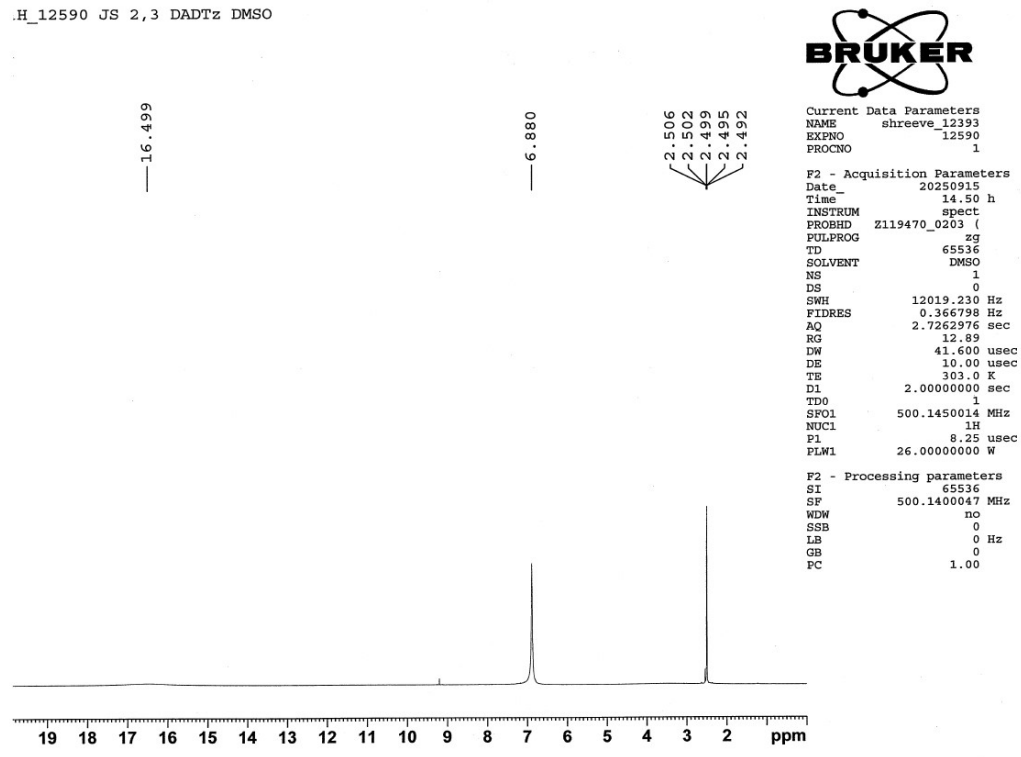

Figure S7: ^{1}H NMR spectrum for compound **5**.

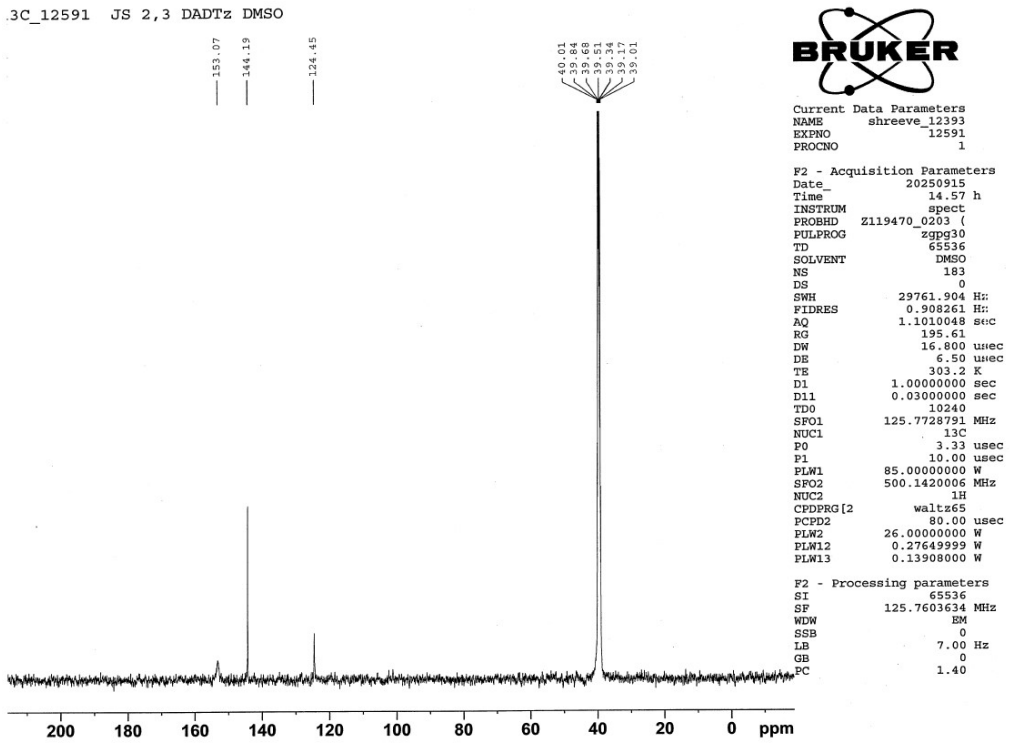

Figure S8: ^{13}C NMR spectrum for compound **5**.

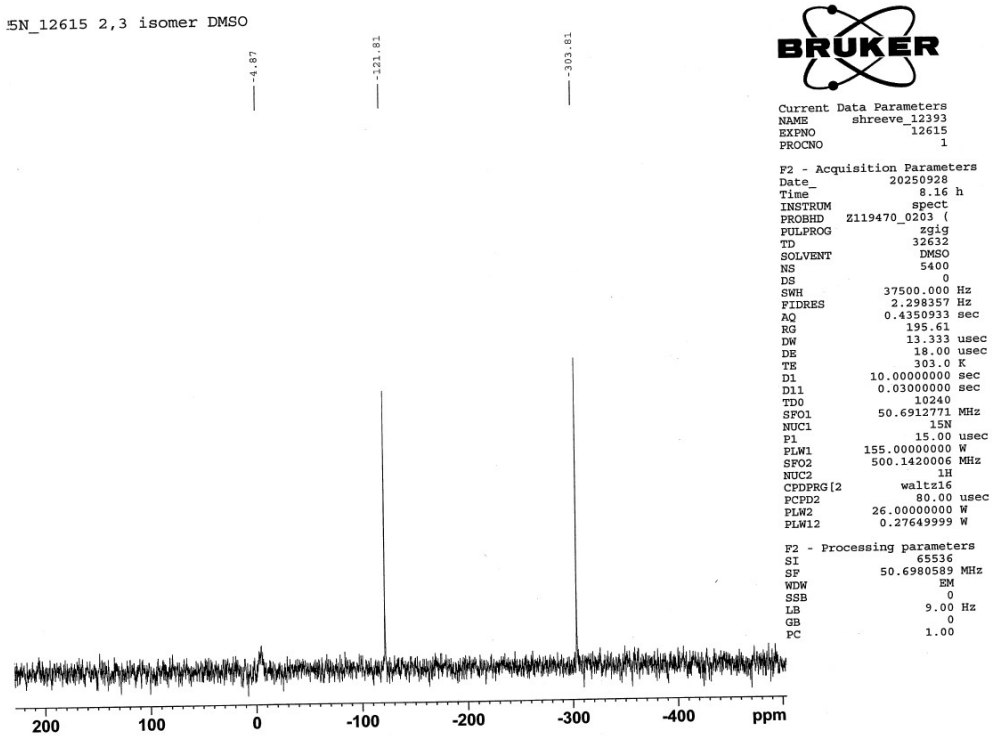

Figure S9: ^{15}N NMR spectrum for compound **5**.

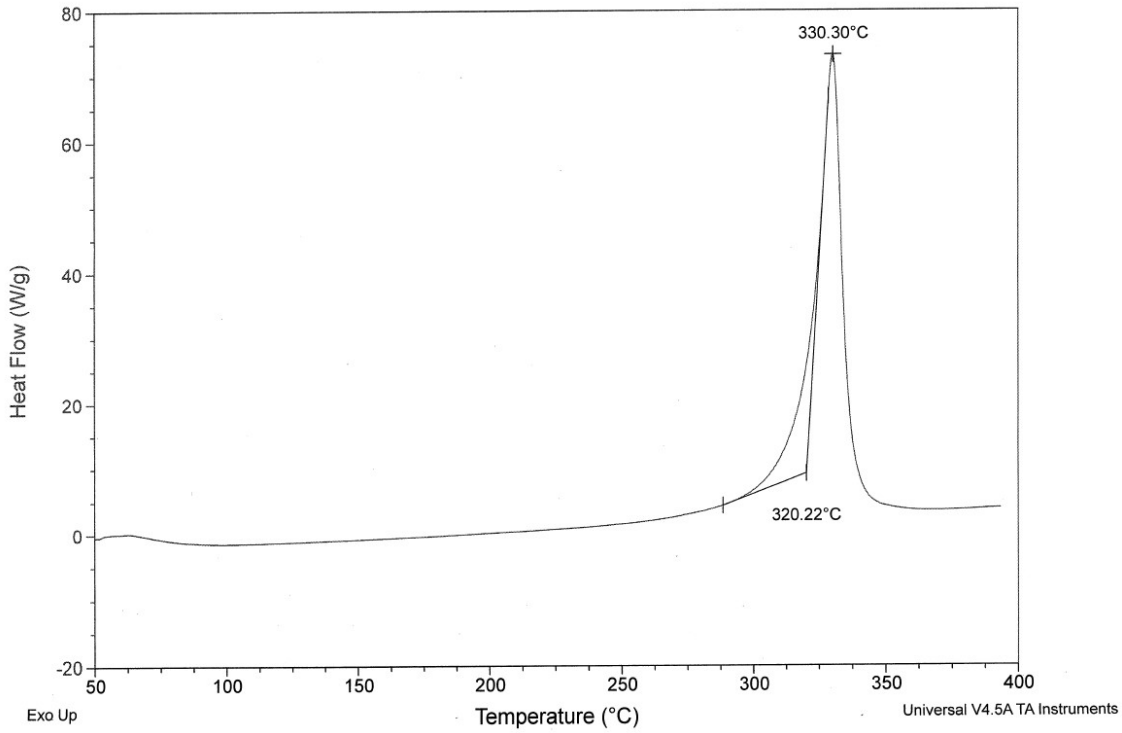

Figure S10: DSC plot for compound **5.**

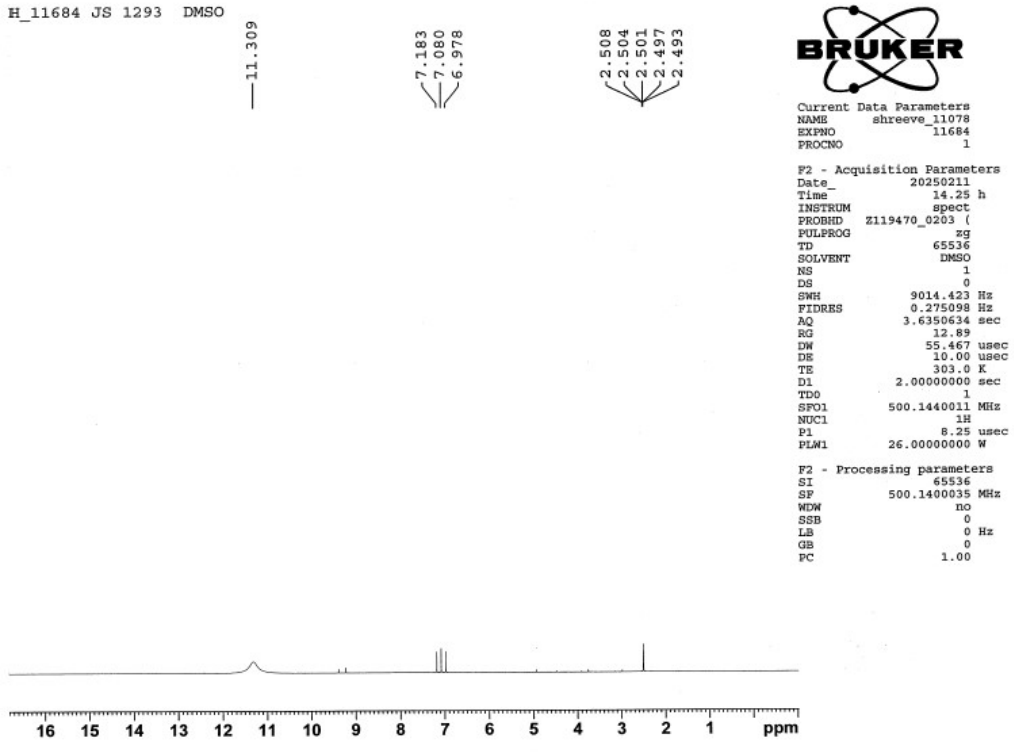

Figure S11: ^{1}H NMR spectrum for compound **6**.

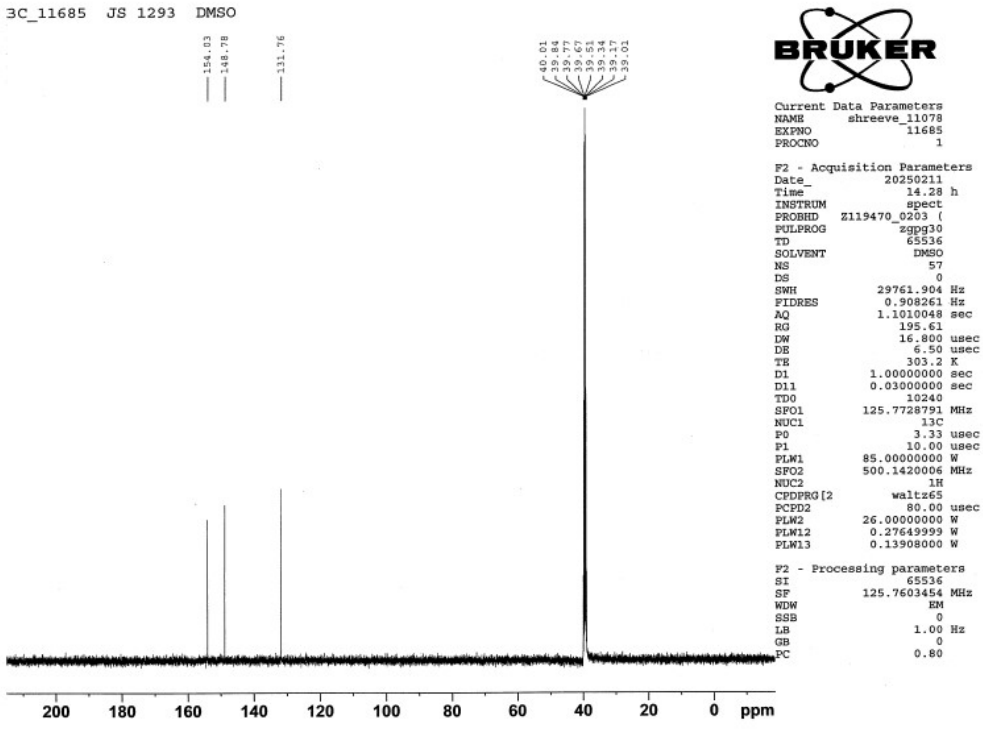

Figure S12: ^{13}C NMR spectrum for compound **6**.

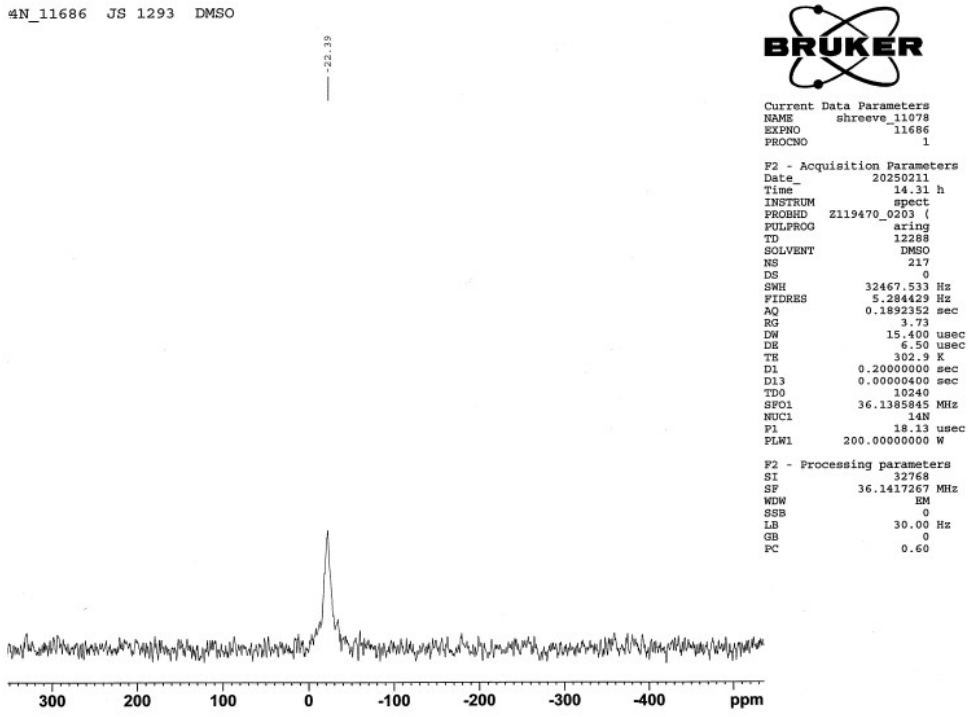

Figure S13: ^{14}N NMR spectrum for compound **6**.

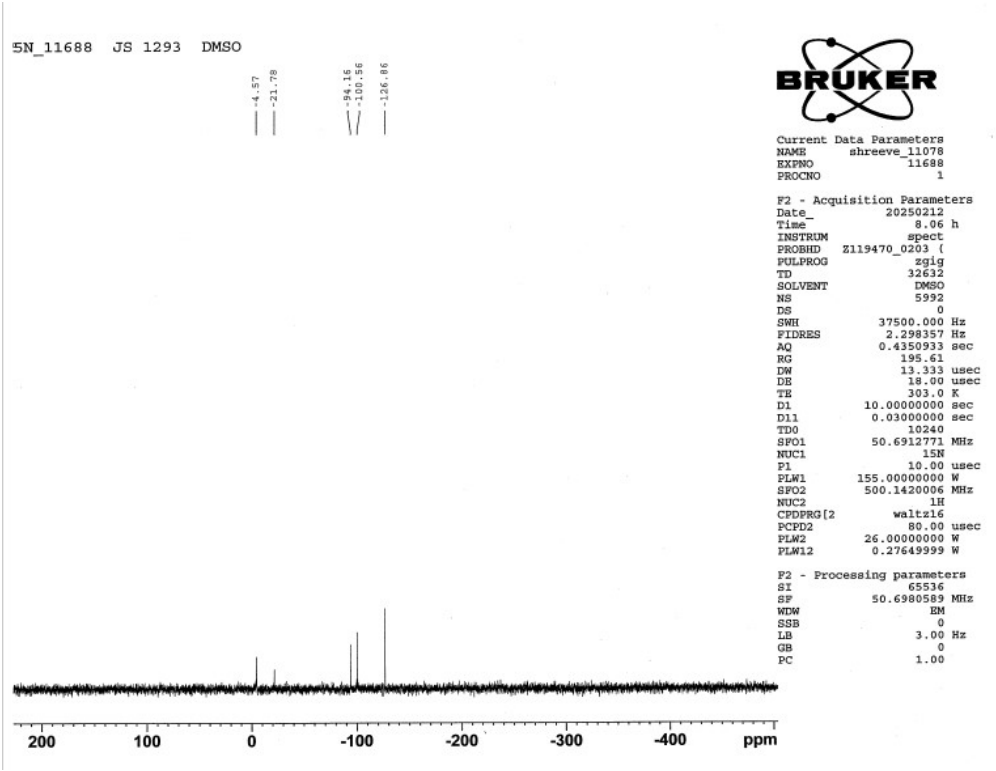

Figure S14: ^{15}N NMR spectrum for compound **6**.

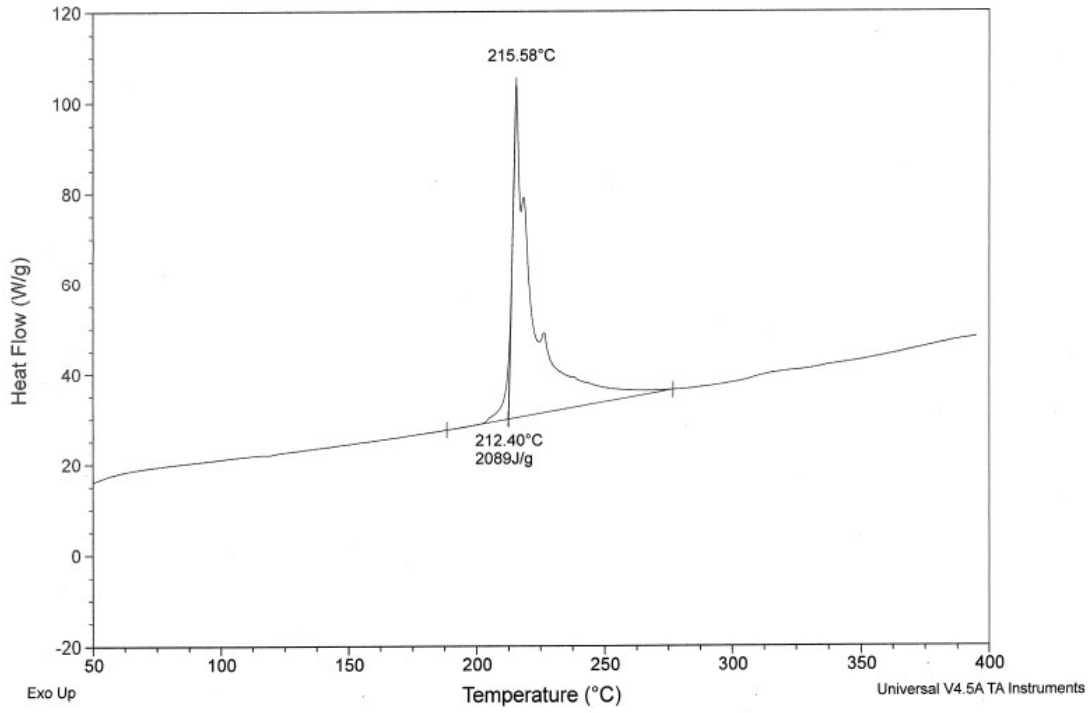

Figure S15: DSC plot for compound **6.**