Electronic Supplementary Information

From Anion-Centric to Cation-Enabled Energetics: Planar Tetrazine Frameworks with Enhanced Stability

Jatinder Singh,[a] Richard J. Staples,[b] Jean'ne M. Shreeve*[a]

[a] Department of Chemistry, University of Idaho, Moscow, Idaho, 83844-2343, United States.

[b] Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States.

Corresponding Author

Jean'ne M. Shreeve − Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, United States.

Email: jshreeve@uidaho.edu; Fax: (+1) 208-885-5173.

Table of contents

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 only. Personal protective equipment must be worn while handling hydrazine hydrate and it should be only used in a fume hood.

Section S1.2. General methods

All reagents (analytical grade) were purchased from AK Scientific or 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 in infrared spectra 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 P1-P3 . P1-P3 were obtained following literature procedures.[1-2]

Synthesis of L1. To a stirred solution of guanidine·HCl (3.53 g, 4.9 mmol, 2.0 equiv.) in methanol (30 mL) at room temperature, a solution of sodium methoxide (1.00 g, 4.9 mmol, 2.0 equiv) in methanol (10 mL) was added. After stirring for 15 min, **P1** (5.00 g, 18.5 mmol, 1.0 equiv.) was added in portions. The resulting reaction mixture was stirred at room temperature for 3 hr. The red precipitate was filtered and washed with hot water (3 x 20 mL). Isolated yield: (2.80 g, 77%); $T_{dec\ onset.}$ = 274 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 6.74 (s, 8H); ^{13}C NMR (125 MHz, d_6-DMSO): 162.6, 158.0; IR ($\tilde{\nu}$, cm^{-1}): 3441, 3370, 3170, 3098, 1666, 1617, 1546, 1434, 1151, 1047, 938, 832, 742; Calcd for $C_4H_8N_{10}$: C, 24.49; H, 4.11; N, 71.40. Found: C, 25.10; H, 4.40; N, 69.40.

Synthesis of L1-2Cl. To a stirred solution of L1 (2.00 g, 10.2 mmol, 1.0 equiv.) in water (30 mL) at room temperature, aq HCl (2mL of 2M solution) was added. The resulting reaction mixture was stirred at room temperature for 3 hr. The orange precipitate obtained was filtered and washed with water (2 x 10 mL). Isolated yield: (2.00 g, 73%); $T_{dec\ onset.}$ = 358 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 8.28 (s, 10H); ^{13}C NMR (125 MHz, d_6-DMSO): 158.5, 154.4; IR ($\tilde{\nu}$, cm^{-1}): 3390, 3264, 3034, 2936, 2844, 2790, 2351, 1700, 1601, 1417, 1306, 1186, 1063, 951, 762; Calcd for $C_4H_{10}C_{l2}N_{10}$: C, 17.85; H, 3.75; N, 52.05. Found: C, 17.93; H, 3.91; N, 51.23.

Synthesis of L2. To a stirred solution of guanidine·HCl (1.00 g, 10.5 mmol, 1.0 equiv.) in methanol (30 mL) at room temperature, a solution of sodium methoxide (0.56 g, 10.5 mmol, 1.0 equiv) in methanol (10 mL) was added. After stirring for 15 min, **P2** (2.00 g, 10.5 mmol, 1.0 equiv.) was added in portions The resulting reaction mixture was stirred at room temperature for 3 hr. A red precipitate was filtered and washed with hot water (3 x 20 mL). Isolated yield: (1.21 g, 75%); $T_{dec.\ onset.}$ = 265 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 6.90 (s, 2H), 6.70 (s, 4H); ^{13}C NMR (125 MHz, d_6-DMSO): 164.4, 160.1, 157.7; IR ($\tilde{\nu}$, cm^{-1}): 3377, 3334, 3179, 1617, 1548, 1435,

1132, 1061, 936, 603; Calcd for $C_3H_6N_8$: C, 23.38; H, 3.92; N, 72.70. Found: C, 23.64; H, 3.98; N, 70.42.

Synthesis of L2-Cl. To a stirred solution of **L2** (1.00 g, 1.0 equiv.) in water (30 mL) at room temperature, aq HCl (2ml of 2M solution) was added. The resulting reaction mixture was stirred at room temperature for 3 hr. The orange precipitate was filtered and washed with water (2 x 10 mL). Isolated yield: (1.10 g, 92%); $T_{dec.\ onset}$ = 327 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 8.17 (s, 5H), 7.94 (s, 2H); ^{13}C NMR (125 MHz, d_6-DMSO): 162.9, 156.1, 154.9; IR ($\tilde{\nu}$, cm^{-1}): 3340, 3293, 3185, 2987, 2897, 1676, 1631, 1522, 1469, 1421, 1353, 1318, 1147, 1064, 1028, 964, 865, 739, 623; Calcd for $C_3H_7ClN_8$: C, 18.91; H, 3.70; N, 58.79. Found: C, 18.81; H, 3.77; N, 58.02.

Synthesis of compounds A1-L1, A1-2L2, A2-L1, A2-2L2, A3-L1, A3-2L2, A4-L1, A4-2L2, 2A5-L1, A5-L1: The sodium or potassium or ammonium salts of compounds A1–A6 were reacted with the hydrochlorides (L1·2Cl and L2·Cl) in aqueous solution to give the assembled products. The resulting mixture was stirred at room temperature, and the precipitate was filtered, washed with water (2 × 10 mL), and dried to yield the desired energetic salts in quantitative yields.

A1-L1. $T_{dec\ onset.}$ = 163°C; ^{1}H NMR (500 MHz, d_6-DMSO): 7.66 (s, 10H); ^{13}C NMR (125 MHz, d_6-DMSO): 169.6, 159.5, 156.4; IR ($\tilde{\nu}$, cm^{-1}): 3382, 2366, 1689, 1626, 1478, 1390, 1351, 1075, 1033, 739; Calcd for $C_6H_{10}N_{20}\cdot H_2O$: C, 18.95; H, 3.18; N, 73.66. Found: C, 18.79; H, 3.38; N, 71.35.

A1-2L2. $T_{dec.\ onset}$ = 195 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 7.97 (s, 4H), 7.90 (s, 2H); ^{13}C NMR (125 MHz, d_6-DMSO): 172.7, 162.8, 156.6, 154.8; IR ($\tilde{\nu}$, cm^{-1}): 3375, 3314, 3197, 3122, 1695, 1624, 1476, 1425, 1385, 1352, 1319, 1189, 1070, 1026, 974, 857, 733; Calcd for $C_8H_{14}N_{26}\cdot H_2O$: C, 19.51; H, 3.28; N, 73.96. Found: C, 19.59; H, 3.67; N, 73.36.

A2-L1. $T_{dec.\ onset}$ = 317 °C; IR ($\tilde{\nu}$, cm^{-1}): ^{1}H NMR (500 MHz, d_6-DMSO): 7.93 (bs, 8H), 8.19 (s, 2H); 3394, 3318, 3256, 3097, 3007, 1701, 1658, 1613, 1543, 1477, 1418, 1386, 1303, 1262, 1231, 1110, 1078, 1037, 947, 854, 811, 754, 623; Calcd for $C_{10}H_{10}N_{18}O_8.H_2O$: C, 22.73; H, 2.29; N, 47.72. Found: C, 22.38; H, 2.53; N, 49.93.

A2-2L2. $T_{dec.onset}$ = 320 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 8.19 (s, 4H), 7.93 (s, 2H); ^{13}C NMR (125 MHz, d_6-DMSO): 162.9, 156.3, 154.6, 143.9, 140.4; IR ($\tilde{\nu}$, cm^{-1}): 3571, 3387, 3183, 3111, 1686, 1615, 1477, 1377, 1300, 1209, 1114, 1044, 963, 805, 644; Calcd for $C_{12}H_{14}N_{24}O_8$: C, 23.16; H, 2.27; N, 54.01; Found: C, 23.24; H, 2.90; N, 53.50.

A3-L1. $T_{dec\cdot onset.}$ = 216 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 12.31 (bs, 2H), 7.64 (s, 8H); ^{13}C NMR (125 MHz, d_6-DMSO): 159.4, 156.5, 153.3; IR ($\tilde{\nu}$, cm^{-1}): 3396, 3273, 3142, 2792, 1701, 1601, 1541, 1479, 1421, 1382, 1283, 1057, 1039, 948, 844, 758, 679; Calcd for $C_6H_{10}N_{18}O_4$: C, 18.09; H, 2.53; N, 63.31; Found: C, 18.67; H, 2.89; N, 62.76.

A3-2L2. $T_{dec.\ onset}$ = 256 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 7.99 (bs, 4H), 7.93 (s, 2H); ^{13}C NMR (125 MHz, d_6-DMSO): 163.9, 162.9, 156.2, 154.7; IR ($\tilde{\nu}$, cm^{-1}): 3446, 3389, 3293, 3113, 2889, 1698, 1616, 1478, 1403, 1379, 1271, 1069, 1026, 970, 850, 770; Calcd for $C_8H_{14}N2_4O_4$: C, 18.83; H, 2.76; N, 65.87; Found: C, 18.61; H, 2.87; N, 65.47.

A4-L1. $T_{dec.onset}$ = 186 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 8.13 (bs, 10H); ^{13}C NMR (125 MHz, d_6-DMSO): 159.4, 158.5, 154.3, 121.7; IR ($\tilde{\nu}$, cm^{-1}): 3636, 3402, 3213, 2893, 1687, 1615, 1562, 1487, 1431, 1372, 1236, 1132, 1076, 1050, 973, 945, 856, 823, 782, 748, 634 ; Calcd for $C_8H_{10}N_{16}O_9$: C, 20.26; H, 2.13; N, 47.25; Found: C, 19.89; H, 2.49; N, 46.53.

A4-2L2. $T_{dec\cdot\ onset.}$ = 222 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 11.26 (bs, 2H), 7.95 (s, 4H), 7.84 (s, 4H); ^{13}C NMR (125 MHz, d_6-DMSO): 162.8, 159.4, 156.1, 154.4, 121.6; IR ($\tilde{\nu}$, cm^{-1}): 3319,

3199, 2897, 3795, 1689, 1604, 1552, 1468, 1405, 1376, 1233, 1141, 1069, 970, 854, 826, 778, 746, 619; Calcd for $C_{10}H_{14}N_{22}O_9$: C, 20.48; H, 2.41; N, 52.55; Found: C, 20.58; H, 2.52; N, 52.64.

2A5-L1. $T_{dec.\cdot onset}$ = 200 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 8.72 (bs, 10H), 6.77 (bs, 6H), 7.84 (s, 4H); ^{13}C NMR (125 MHz, d_6-DMSO): 162.5, 158.0, 157.9, 128.1; IR ($\tilde{\nu}$, cm^{-1}): 3404, 3331, 3298, 3085, 1667, 1626, 1535, 1441, 1394, 1351, 1221, 1167, 1136, 1056, 1025, 936, 858, 837, 791, 752, 604; Calcd for $C_8H_{16}N_{18}O_8$: C, 19.52; H, 3.28; N, 51.21; Found: C, 19.60; H, 3.37; N, 51.29.

A5-L2. $T_{dec.\cdot onset}$ = 243 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 8.73 (bs, 4H), 6.89 (bs, 2H), 6.66 (s, 4H); ^{13}C NMR (125 MHz, d_6-DMSO): 164.3, 160.0, 157.9, 157.5, 128.1; IR ($\tilde{\nu}$, cm^{-1}): 3399, 3331, 3293, 3183, 1613, 1537, 1429, 1352, 1220, 1166, 1066, 1024, 933, 860, 841, 791, 752, 620; Calcd for $C_5H_{10}N_{12}O_4$: C, 19.87; H, 3.34; N, 55.62; Found: C, 19.73; H, 3.38; N, 54.63.

Synthesis of compound 1.

To a stirred solution of guanidine·HCl (1.21 g, 12.7 mmol, 2.0 equiv.) in methanol (30 mL) at room temperature, a solution of sodium methoxide (0.68 g, 12.7 mmol, 2.0 equiv) in methanol (10 mL) was added. After stirring for 15 min, precursor **P3** (1.50, 6.4 mmol, 1.0 equiv.) in methanol (10 mL) at room temperature, was added. The resulting reaction mixture was stirred for 1 hr. The red precipitate was filtered and washed with hot water (3 x 20 mL). Isolated yield: (1.50 g, 91%); $T_{dec\ \cdot onset.}$ = 263 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 1.07 (bs, 11H), ^{13}C NMR (125 MHz, d_6-DMSO): 164.3, 161.7, 159.1, 158.1; IR ($\tilde{\nu}$, cm^{-1}): 3339, 3179, 2807, 1638, 1544, 1452, 1357, 1304, 1146, 1056, 954, 803, 767, 748, 723, 610; Elemental analysis: Calcd for $C_4H_{10}N_{12}O_2$: C, 18.61; H, 3.90; N, 65.10. Found: C, 18.83; H, 3.95; N, 64.76.

Synthesis of compound 2.

To a stirred solution of **1** (1.00 g, 3.9 mmol, 1.0 equiv.) in water (30 mL) at room temperature, aq HCl (2ml of 2M solution) was added. The resulting reaction mixture was stirred at room temperature for 3 hr. The red precipitate was filtered and washed with hot water (2 x 10 mL). Isolated yield: (0.65 g, 84%); $T_{dec\cdot onset}$ = 247 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 11.64 (bs, 1H), 7.99 (bs, 4H); ^{13}C NMR (125 MHz, d_6-DMSO): 165.9, 155.9, 154.3; IR ($\tilde{\nu}$, cm^{-1}): 3384, 3302, 3105, 1695, 1602, 1470, 1391, 1302, 1248, 1072, 1021, 935, 770, 722, 625; Elemental analysis: Calcd for $C_3H_5N_9O_2$: C, 18.09; H, 2.53; N, 63.31;. Found: C, 18.18; H, 2.80; N, 62.57.

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. The thermal ellipsoids and packing diagrams of X-ray structures in the main article and supplementary material are plotted using Diamond 3.2 software.

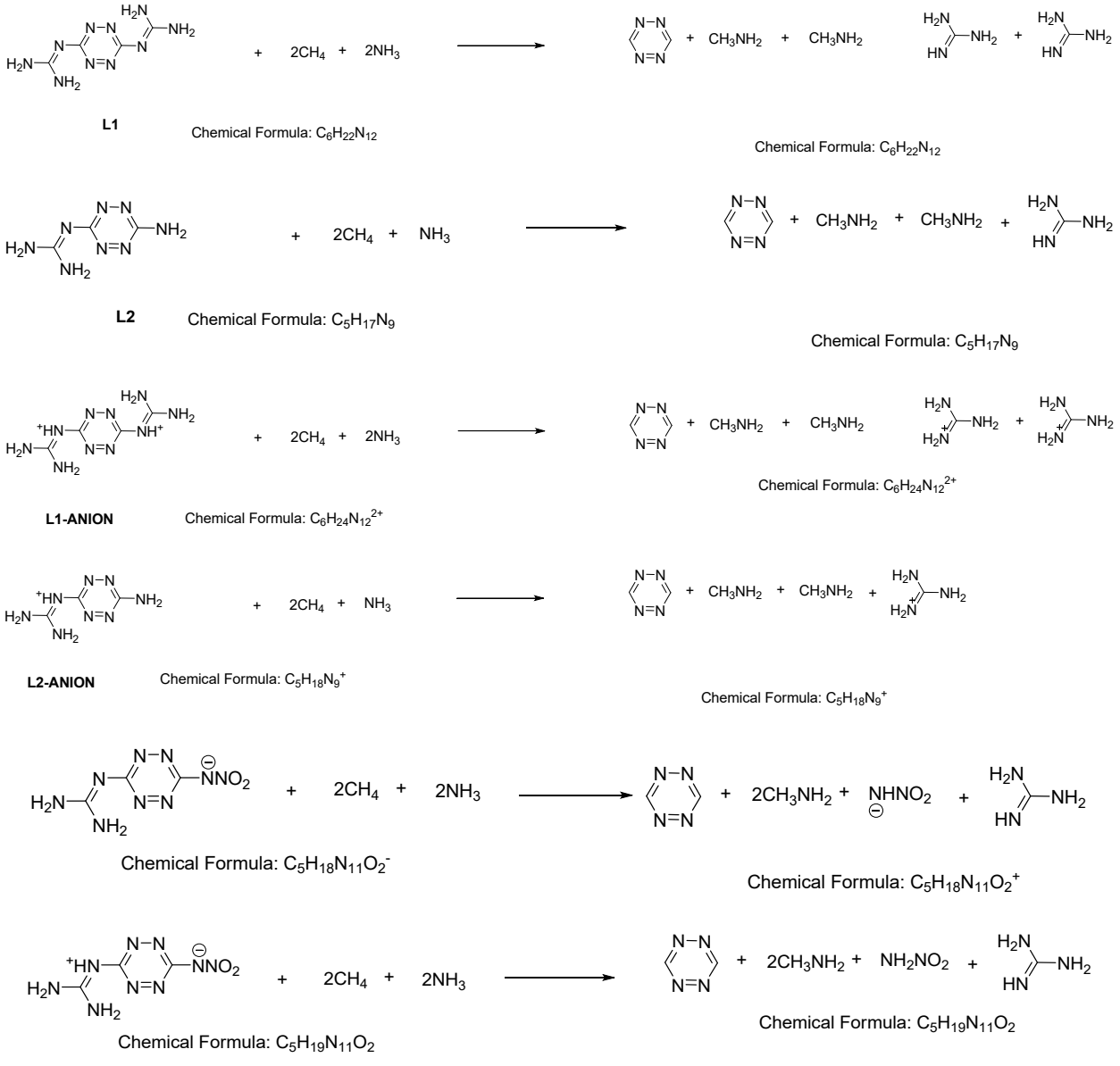
Table S1: Crystallographic data for **L2, A1-L1,** and **A3-2L2**.

Compound	**L2**	**A1-L1**	**A3-2L2**
CCDC #	2491019	2491020	2491021
Formula	$C_3H_6N_8$	$C_6H_{10}N_{20}$	$C_8H_{14}N_{24}O_4$
$D_{calc.}$/ g cm^{-3}	1.677	1.715	1.811
m/mm^{-1}	1.086	1.142	1.303
FW	308.32	362.34	510.43
Color	dark red	red	red
Shape	block-shaped	needle-shaped	needle-shaped
Size/mm^3	0.17×0.12×0.03	0.39×0.07×0.05	0.22×0.03×0.02
T/K	100	100	100
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/n$	$I2/a$
a/Å	7.2311(2)	7.4904(2)	21.5286(11)
b/Å	13.5439(3)	7.3959(2)	6.4729(5)
c/Å	6.9938(2)	12.6706(4)	13.4466(6)
α/°	90	90	90
β/°	116.974(4)	91.508(3)	92.573(5)
γ/°	90	90	90
V/Å^3	610.44(3)	701.69(3)	1871.92(19)
Z	2	2	4
Z'	0.5	0.5	0.5
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K_a	Cu K_a	Cu K_a
Q_{min}/°	6.537	6.789	6.591
Q_{max}/°	79.875	80.202	79.943
Measured Refl's.	4048	4933	6517
Indep't Refl's	1286	1428	1939
Refl's I≥2 s(I)	1145	1319	1638
R_{int}	0.0278	0.0361	0.0642
Parameters	124	138	191
Restraints	0	0	0
Largest Peak	0.258	0.467	0.290
Deepest Hole	-0.257	-0.299	-0.405
GooF	1.083	1.090	1.051
wR_2 (all data)	0.0989	0.1068	0.1513
wR_2	0.0965	0.1046	0.1424
R_1 (all data)	0.0386	0.0406	0.0620
R_1	0.0351	0.0382	0.0536

Section S3. Enthalpy of formation

Section S3.1. Isodesmic reactions

The ΔH_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 S4. References

[1] M. D. Coburn, G. A. Buntain, B. W. Harris, M. A. Hiskey, K. -Y Lee and D. G. Ott, *J. Heterocycl. Chem.*, 1991, **28**, 2049–2050.

[2] G. F. Rudakov, T. V. Ustinova, I. B. Kozlov and V. F. Zhilin, *Chem. Heterocycl. Compd.*, 2014, **50**, 53–64.

[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 and D. H. Williams, *J. Am. Chem. Soc.* 1995, **117**, 5013–5015.

Section S5. Spectral Analysis

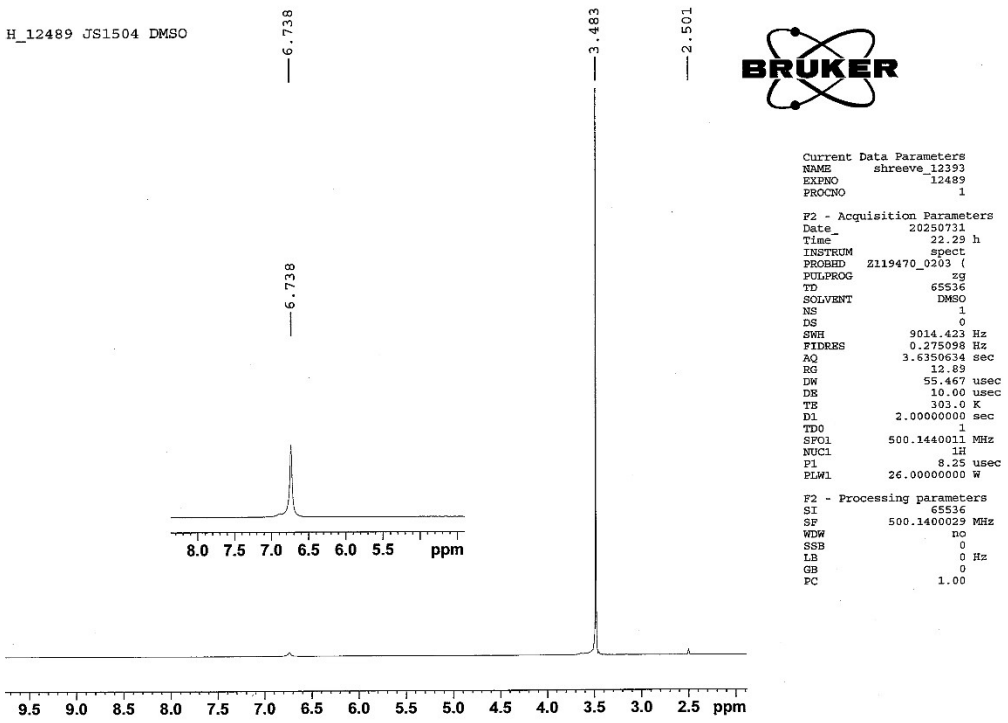


Figure S1: ^{1}H NMR spectrum for compound **L1**.

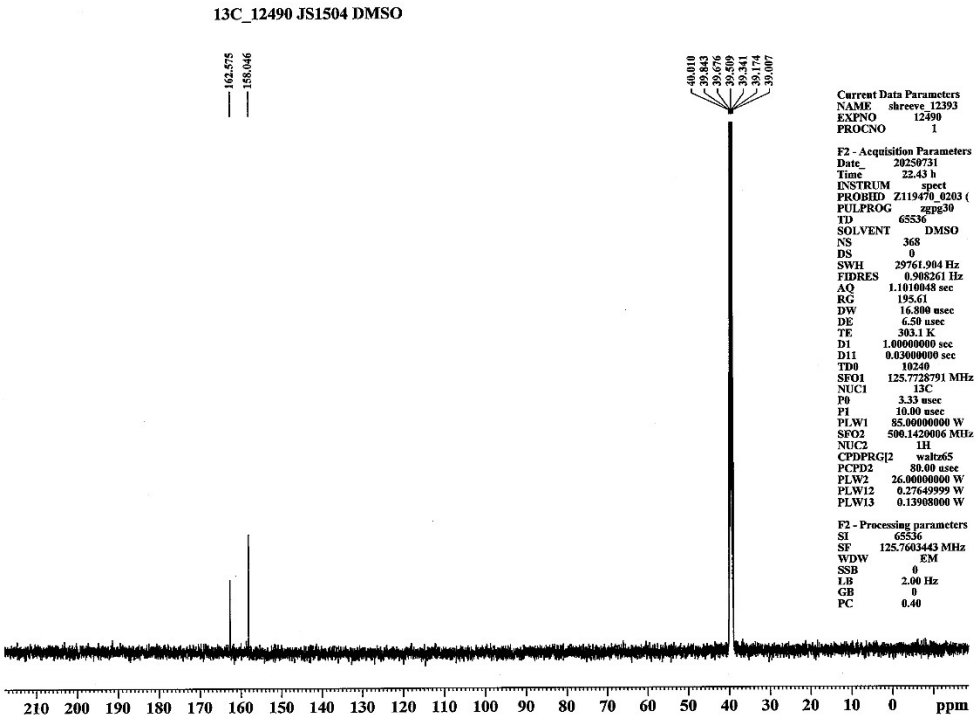


Figure S2: ^{13}C NMR spectrum for compound **L1**.

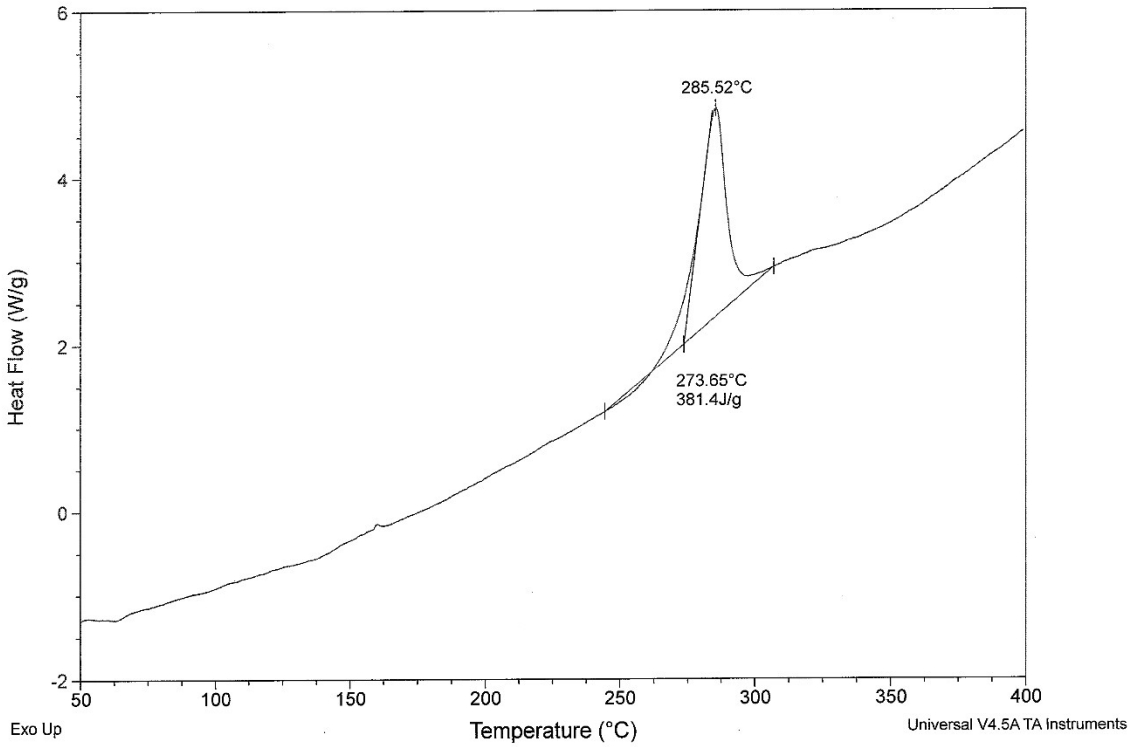


Figure S3: DSC plot for compound **L1.**

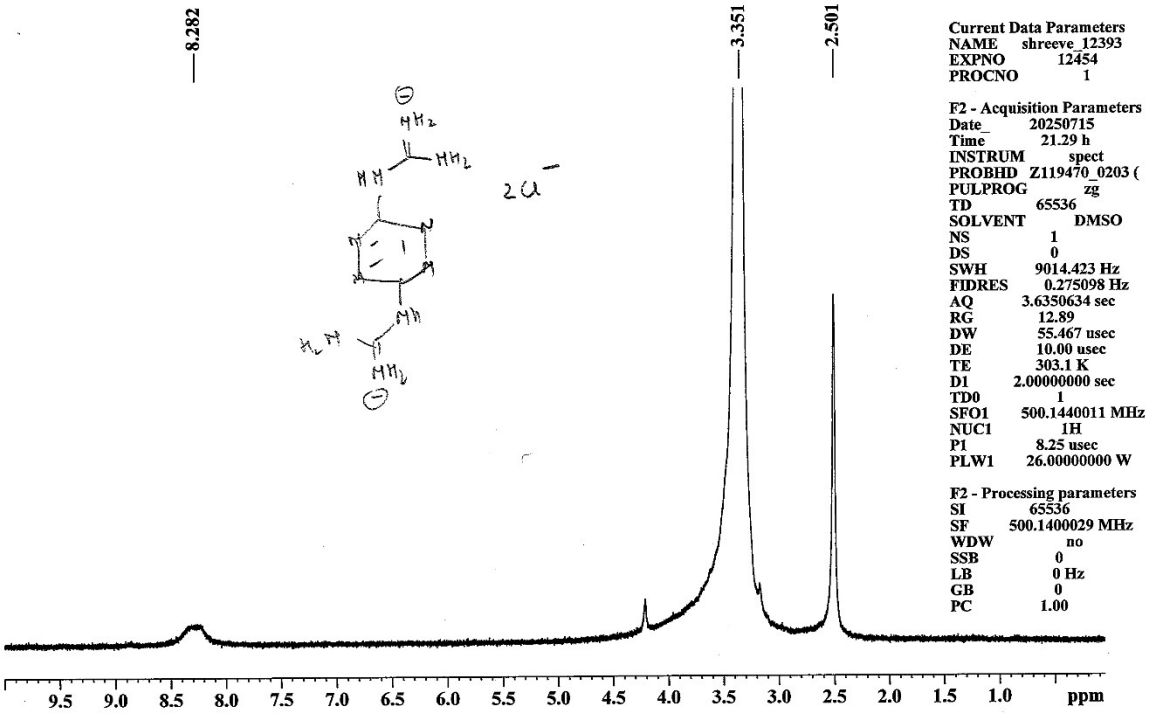


Figure S4: ^{1}H NMR spectrum for compound **L1-2Cl**.

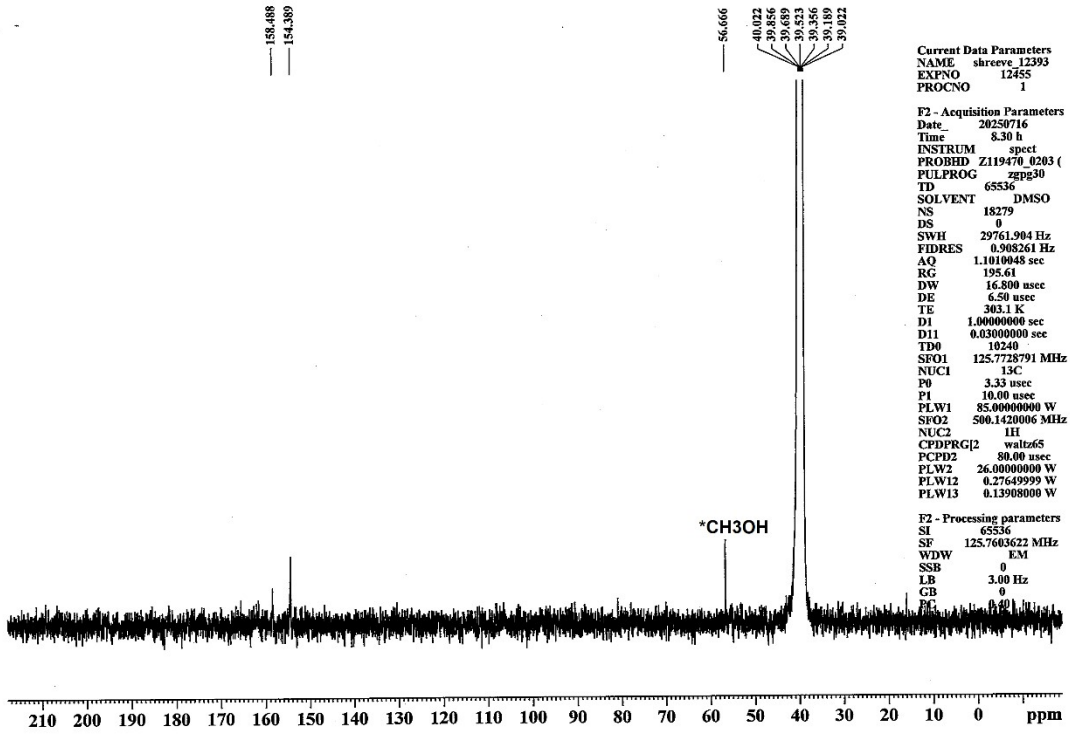


Figure S5: ^{13}C NMR spectrum for compound **L1-2Cl**.

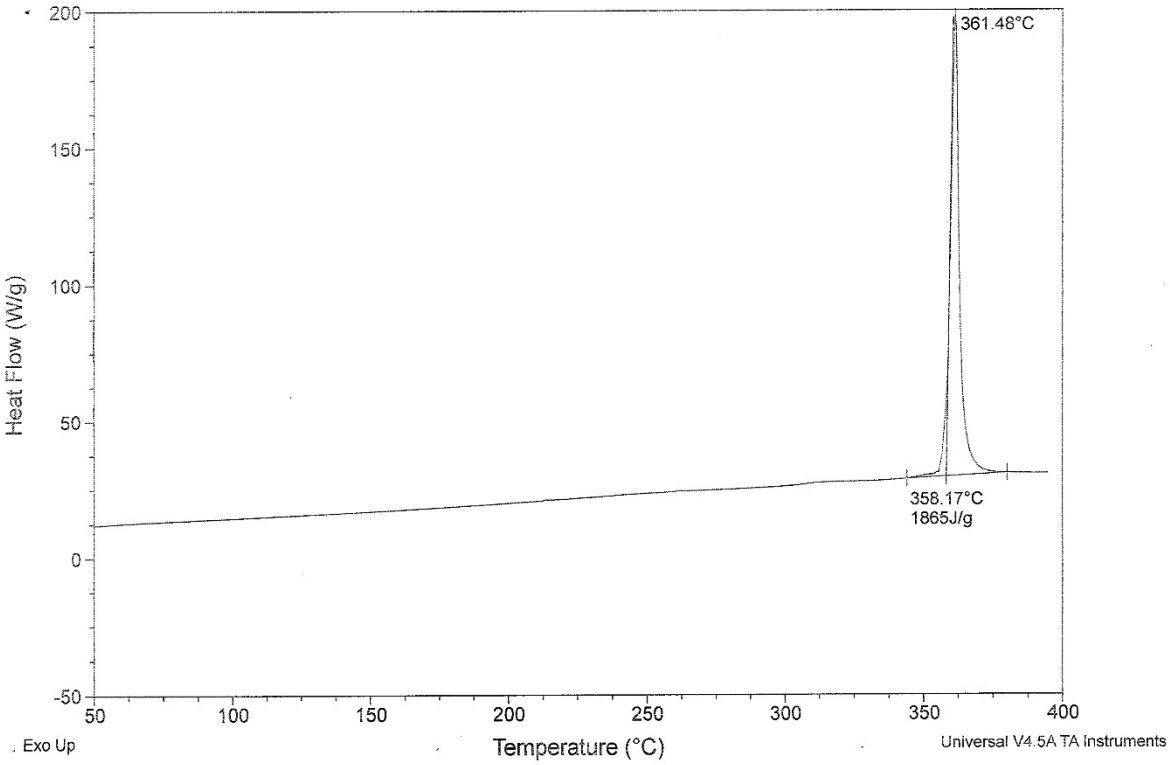


Figure S6: DSC plot for compound **L1-2Cl.**

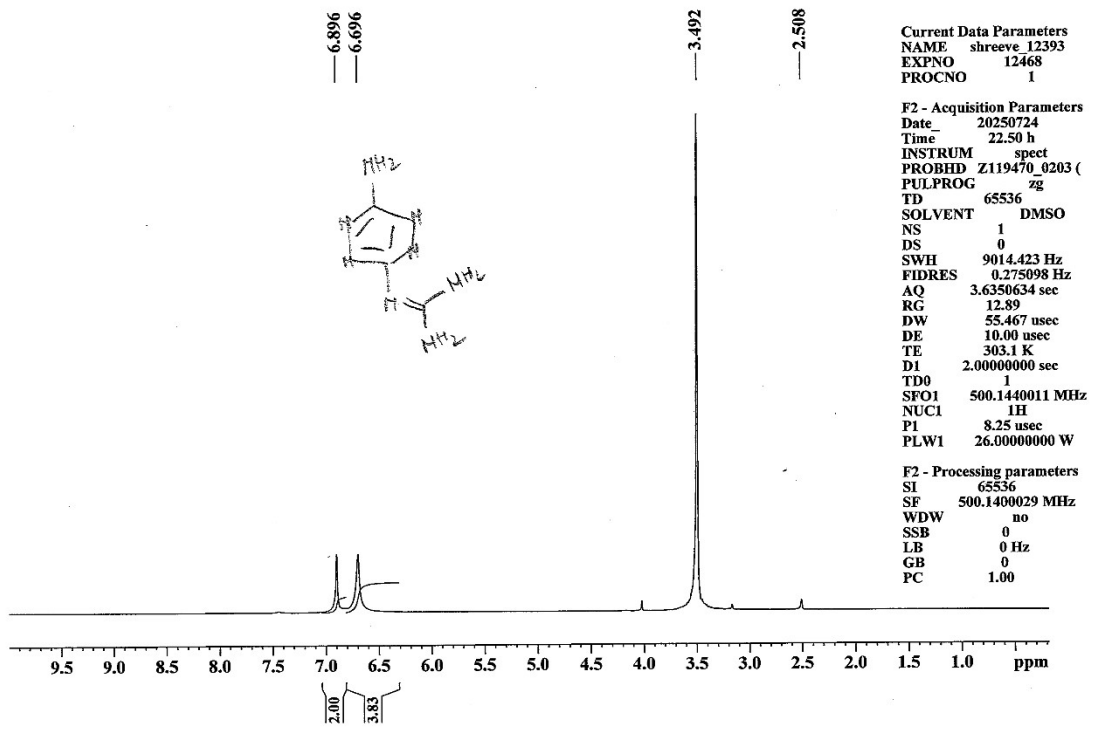


Figure S7: ^{1}H NMR spectrum for compound **L2**.

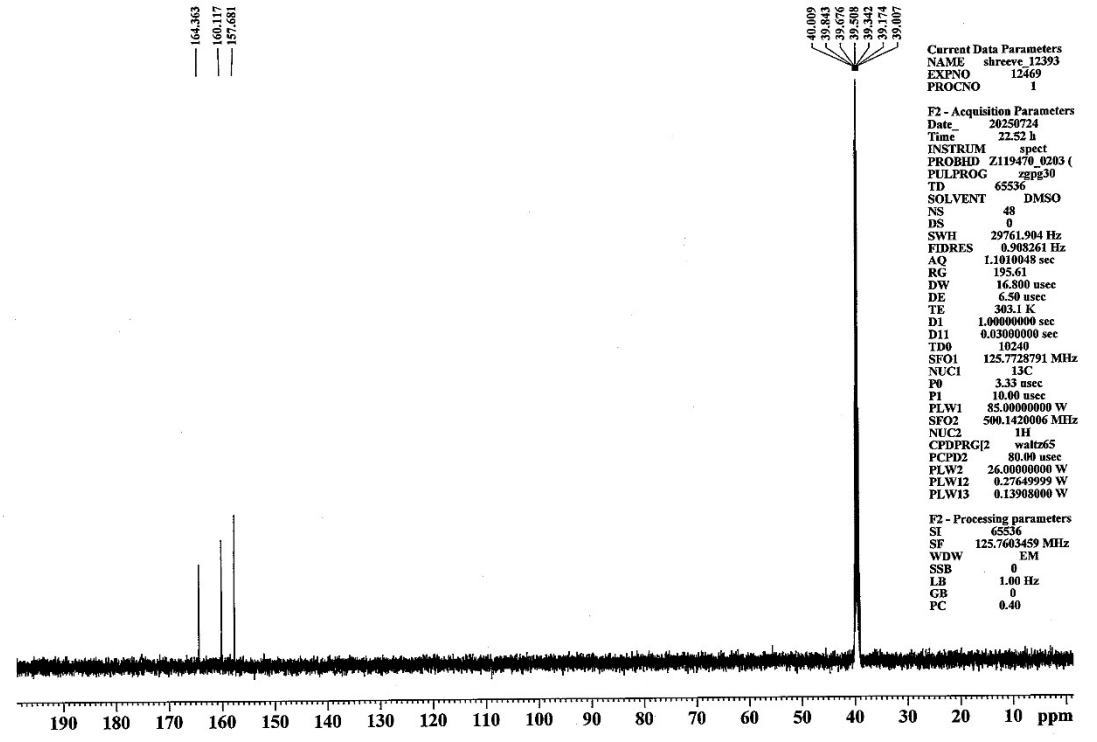


Figure S8: ^{13}C NMR spectrum for compound **L2**.

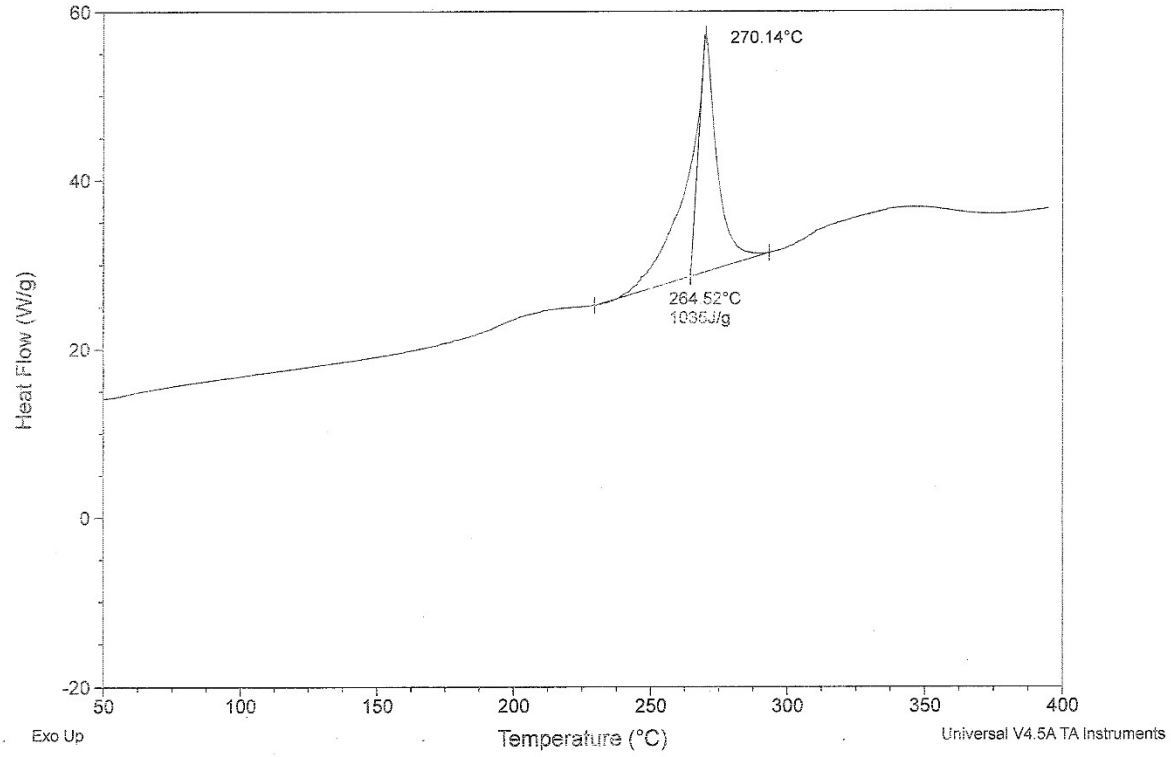


Figure S9: DSC plot for compound **L2.**

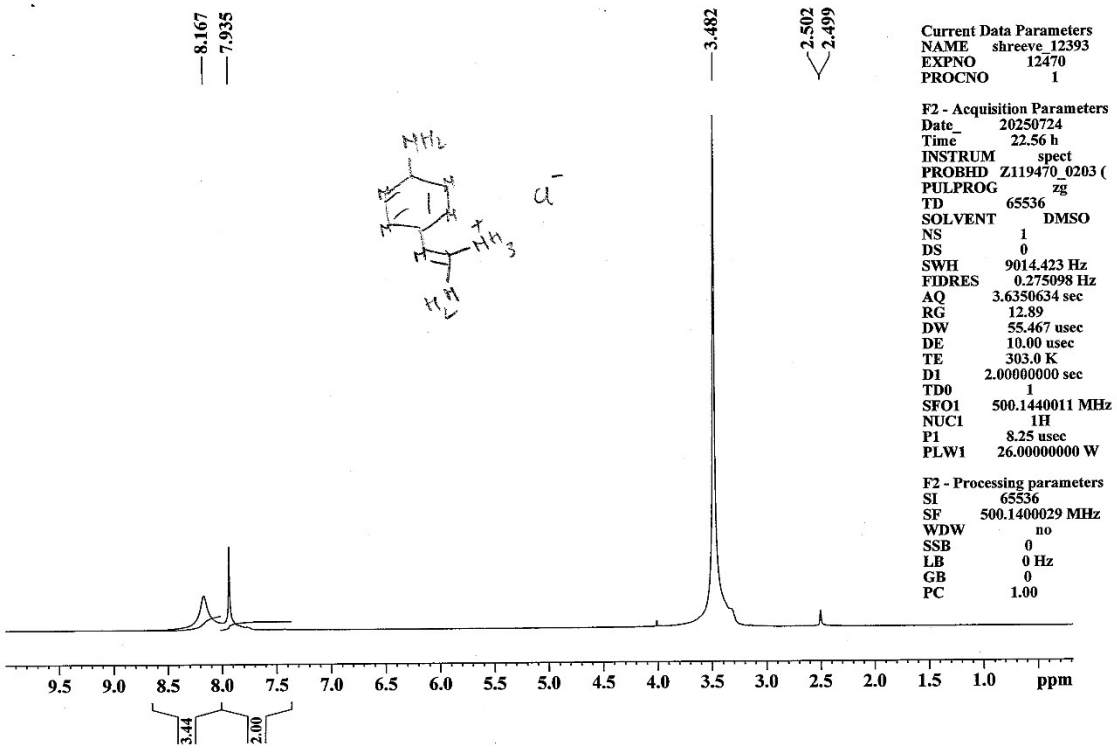


Figure S10: ^{1}H NMR spectrum for compound **L2-Cl**.

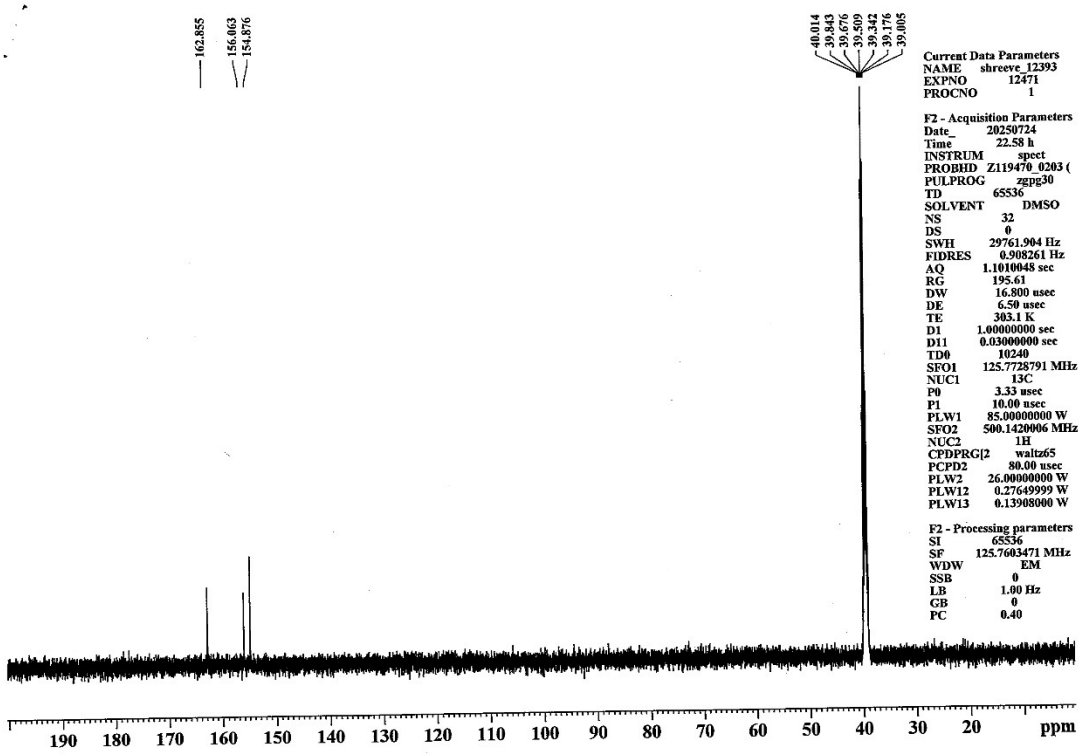


Figure S11: ^{13}C NMR spectrum for compound **L2-Cl**.

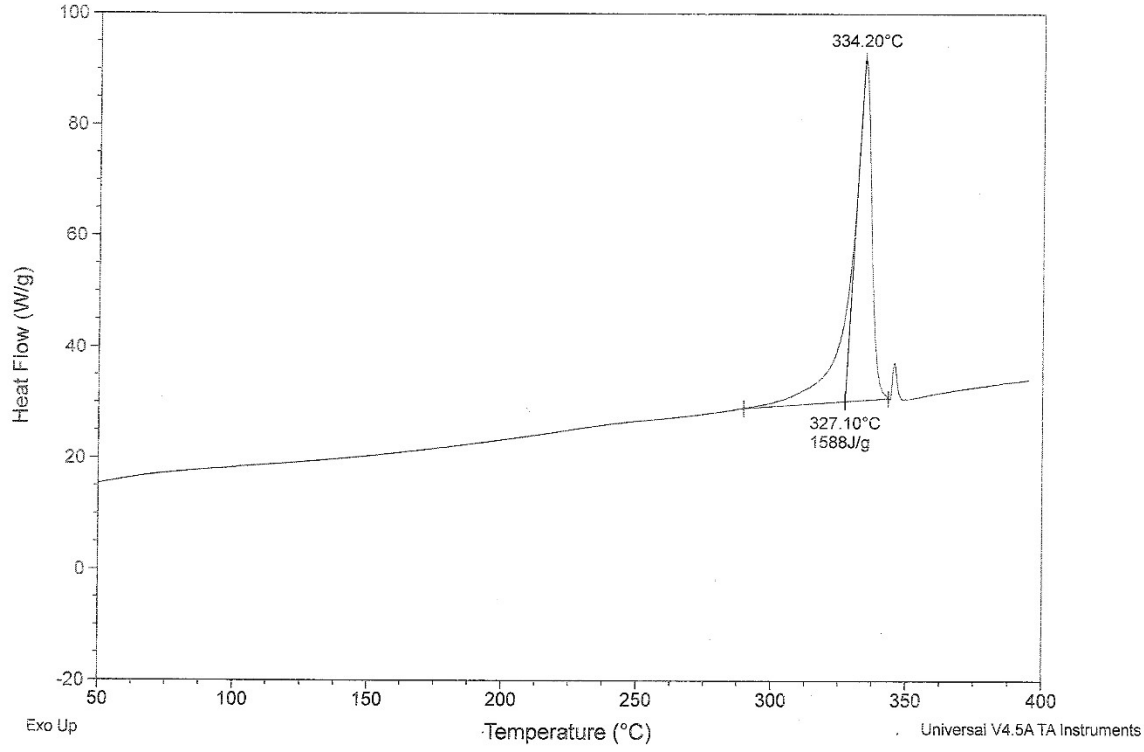


Figure S12: DSC plot for compound **L2-Cl.**

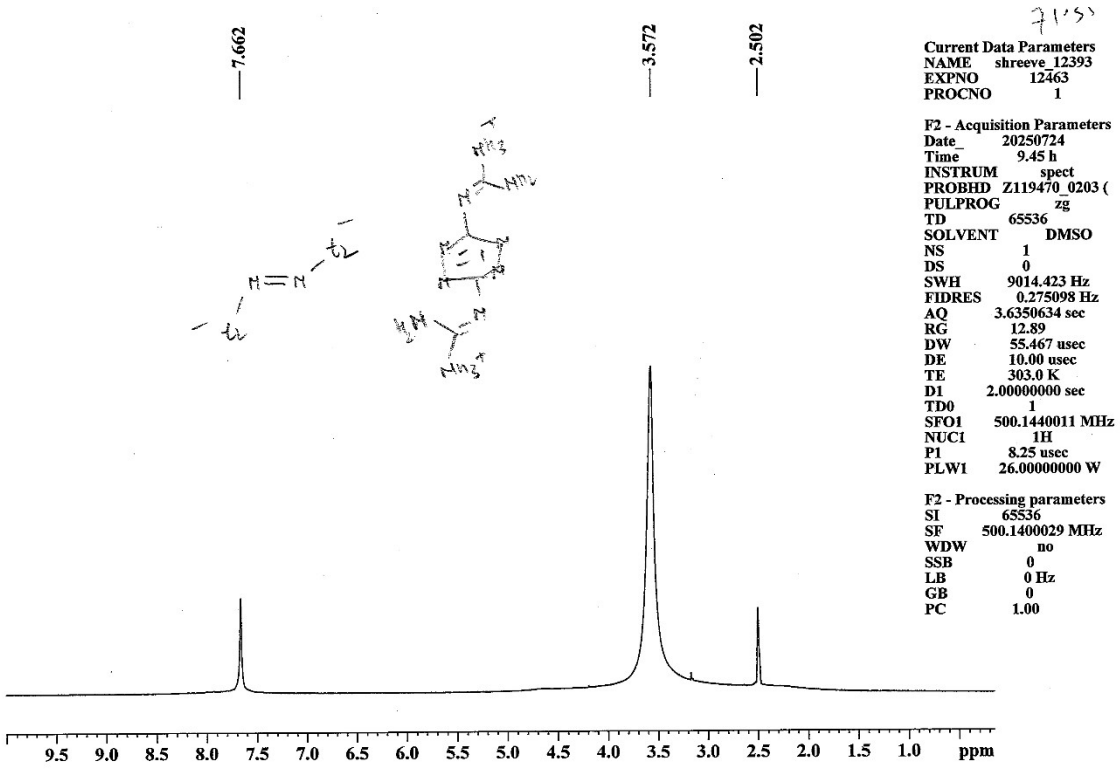


Figure S13: ^{1}H NMR spectrum for compound **A1-L1**.

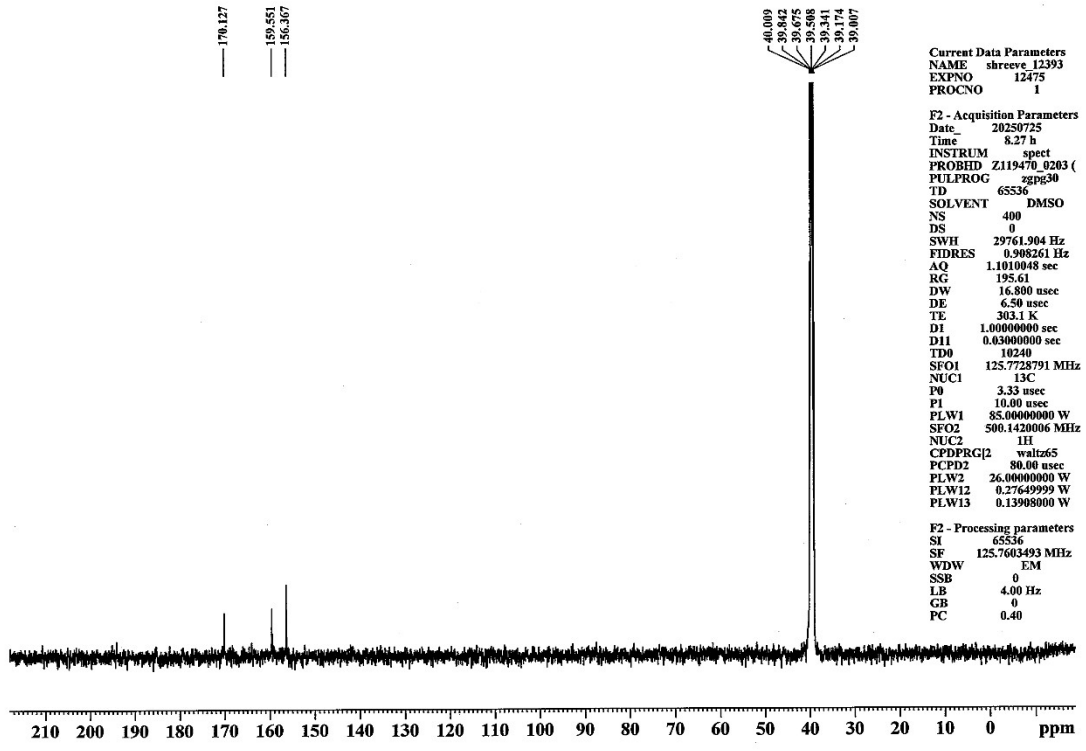


Figure S14: ^{13}C NMR spectrum for compound **A1-L1**.

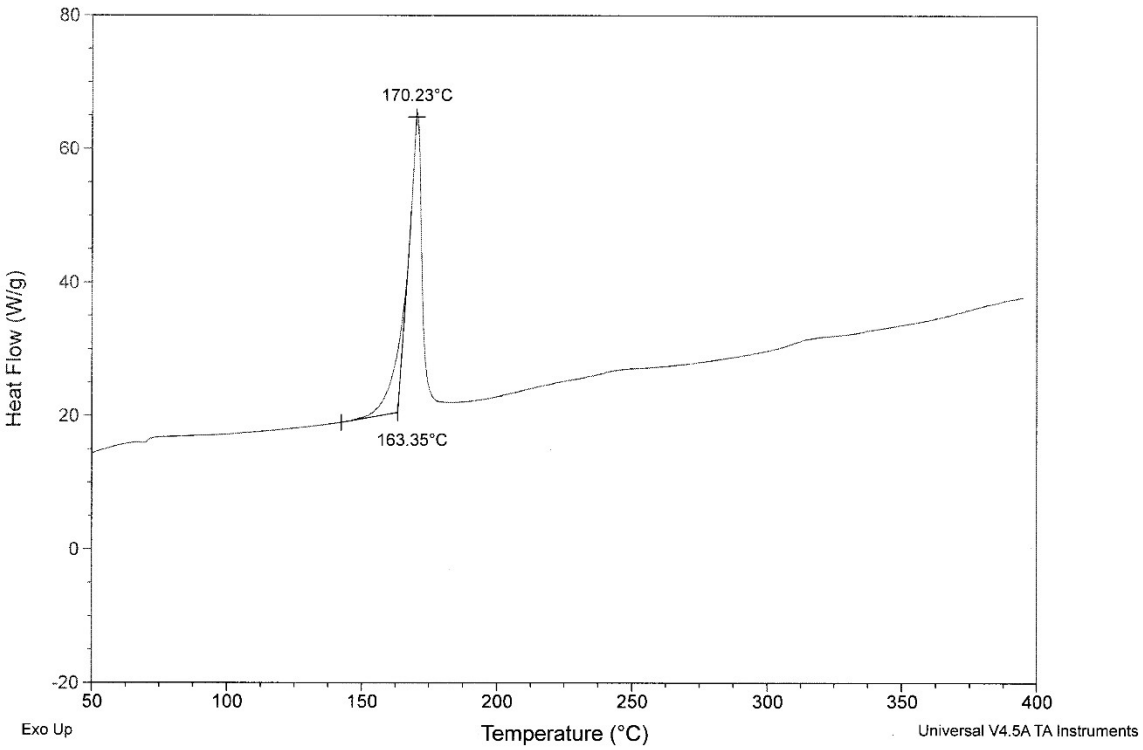


Figure S15: DSC plot for compound **A1-L1.**

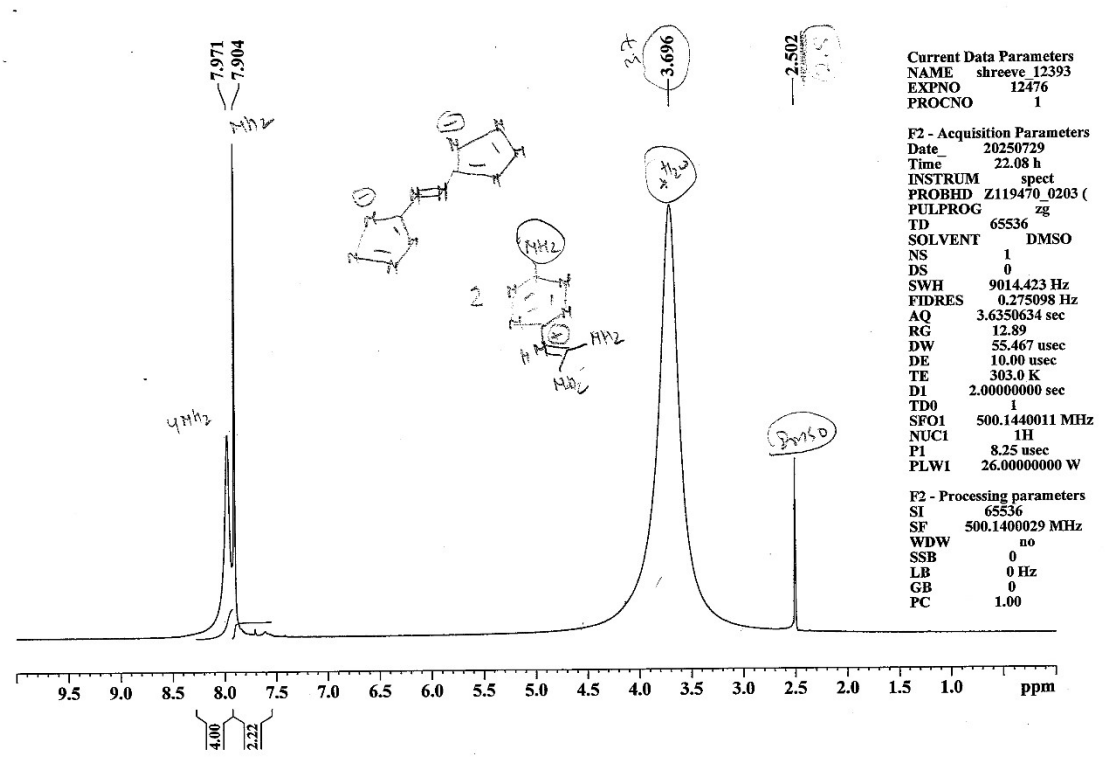


Figure S16: ^{1}H NMR spectrum for compound **A1-2L2**.

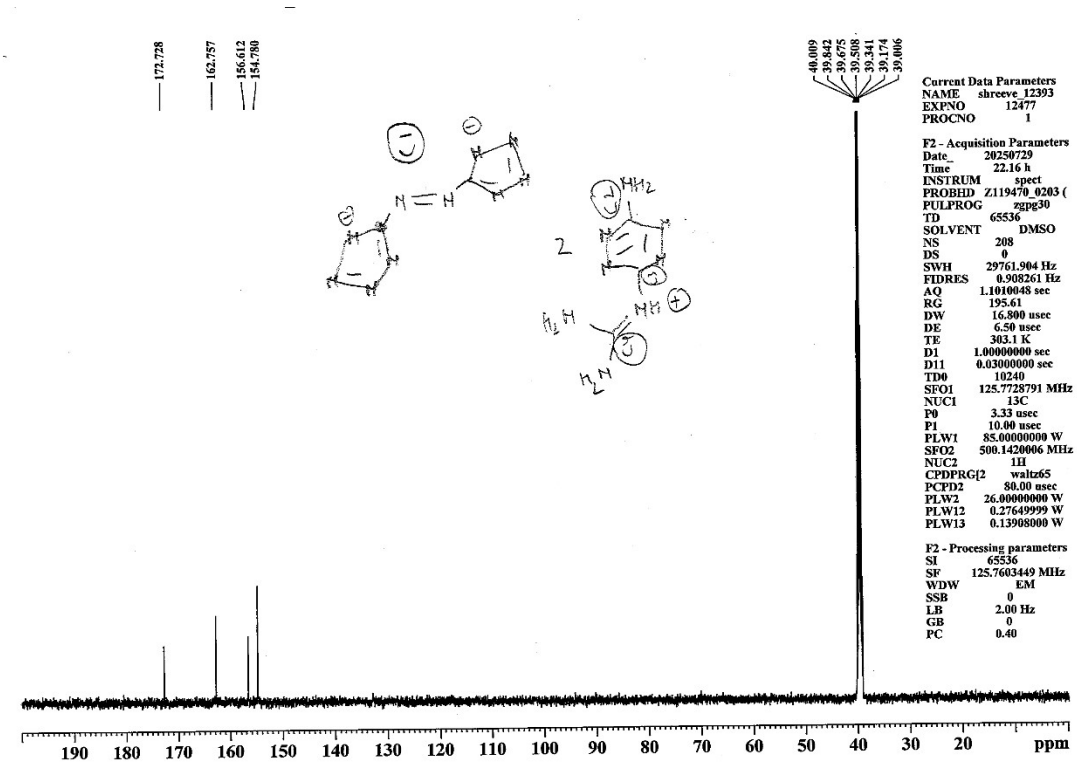


Figure S17: ^{13}C NMR spectrum for compound **A1-2L2**.

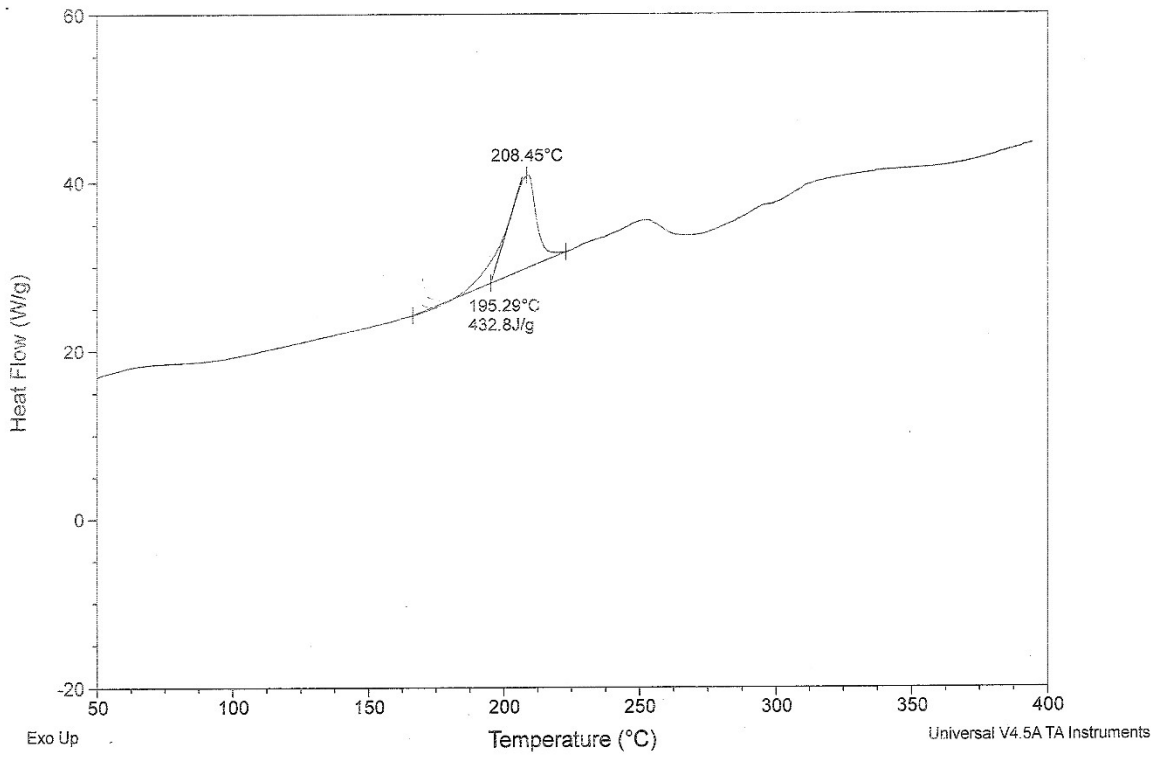


Figure S18: DSC plot for compound **A1-2L2.**

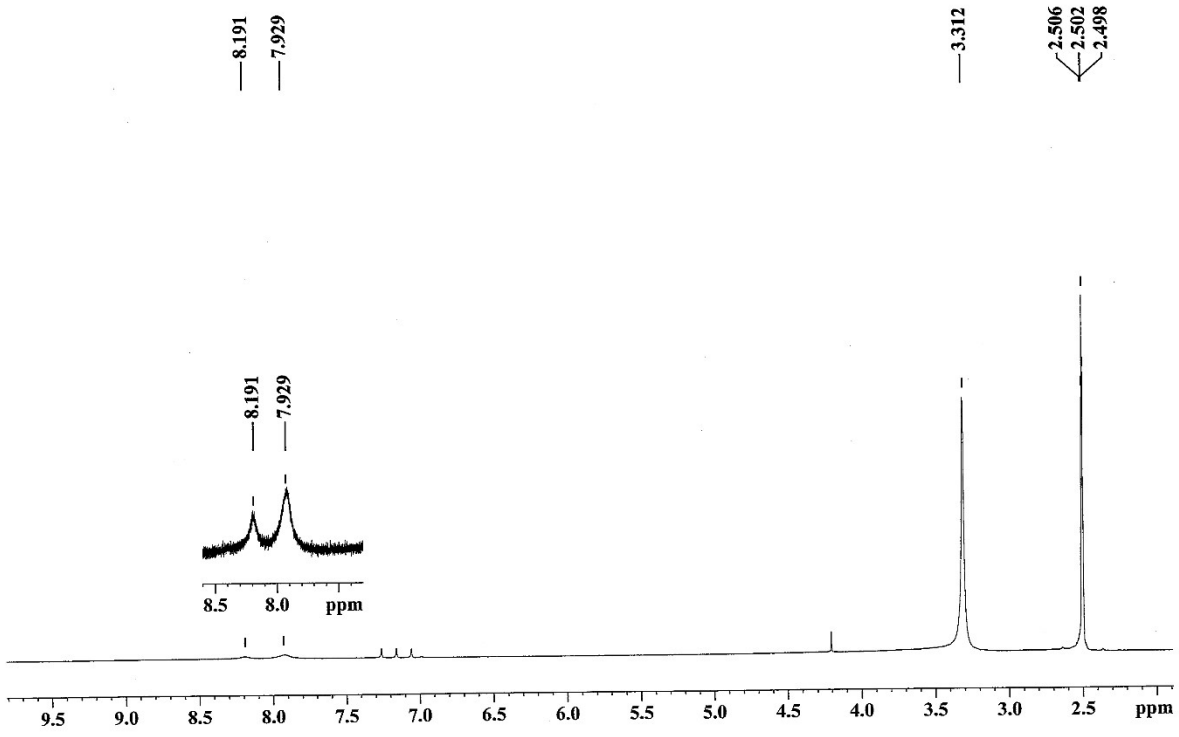


Figure S19: ^{1}H NMR spectrum for compound **A2-L1**.

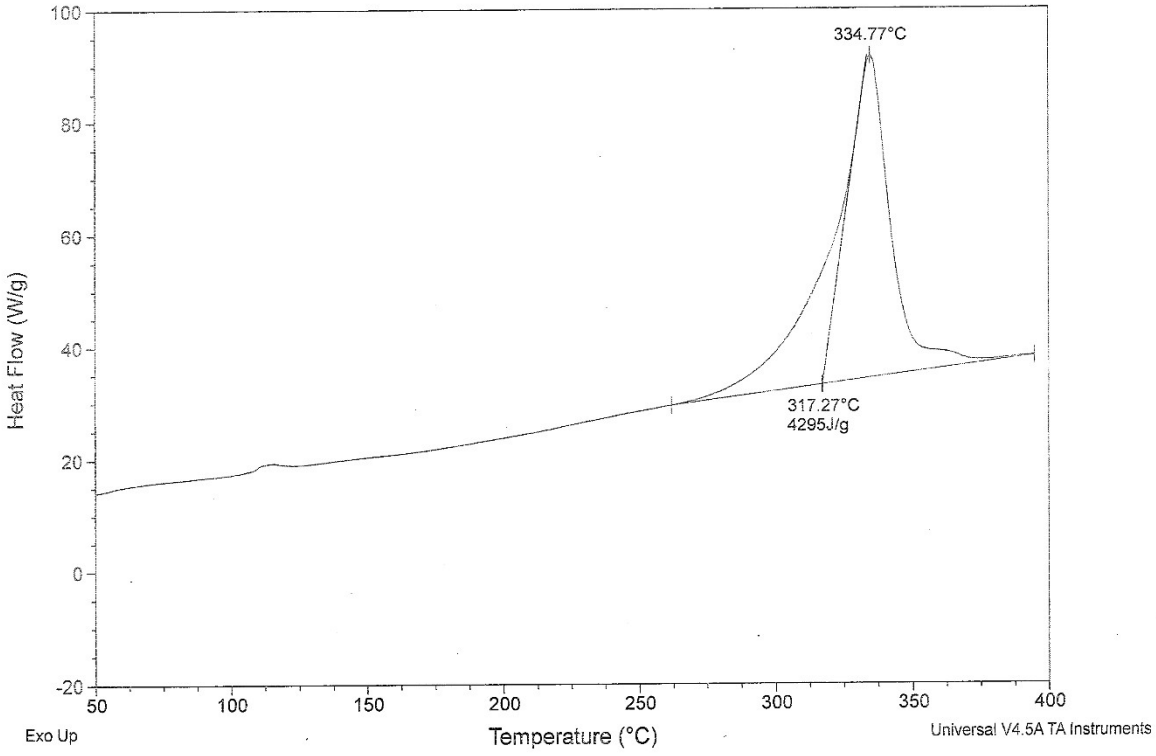


Figure S20: DSC plot for compound **A2-L1.**

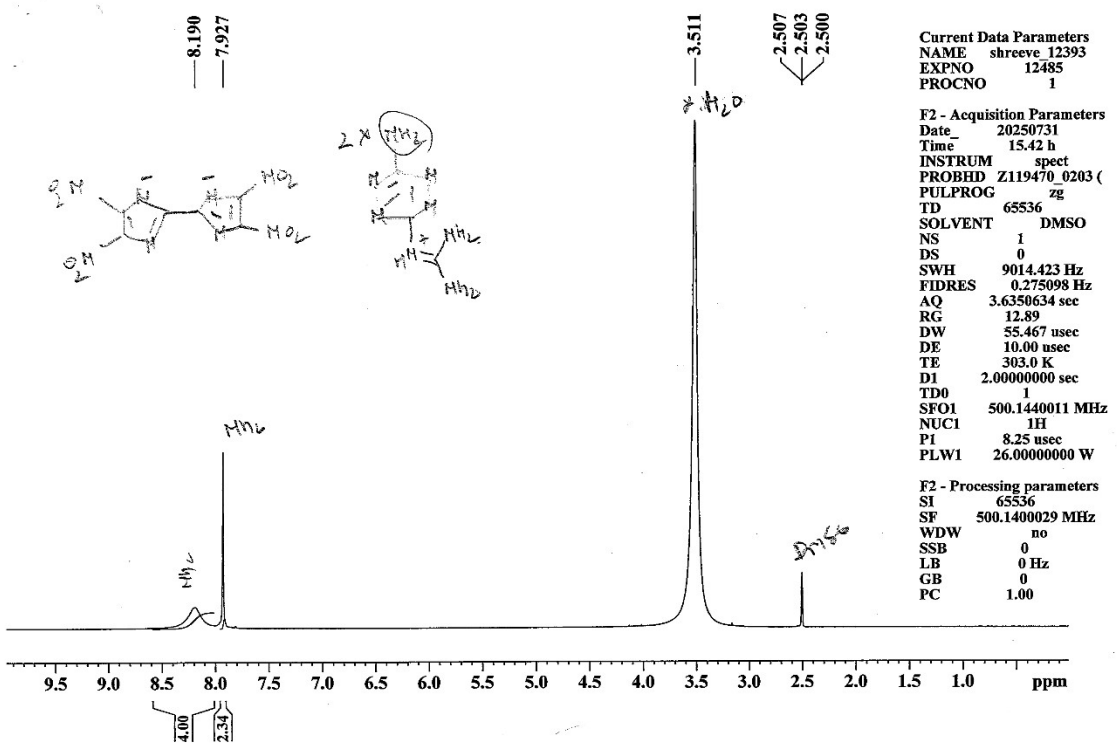


Figure S21: ^{1}H NMR spectrum for compound **A2-2L2**.

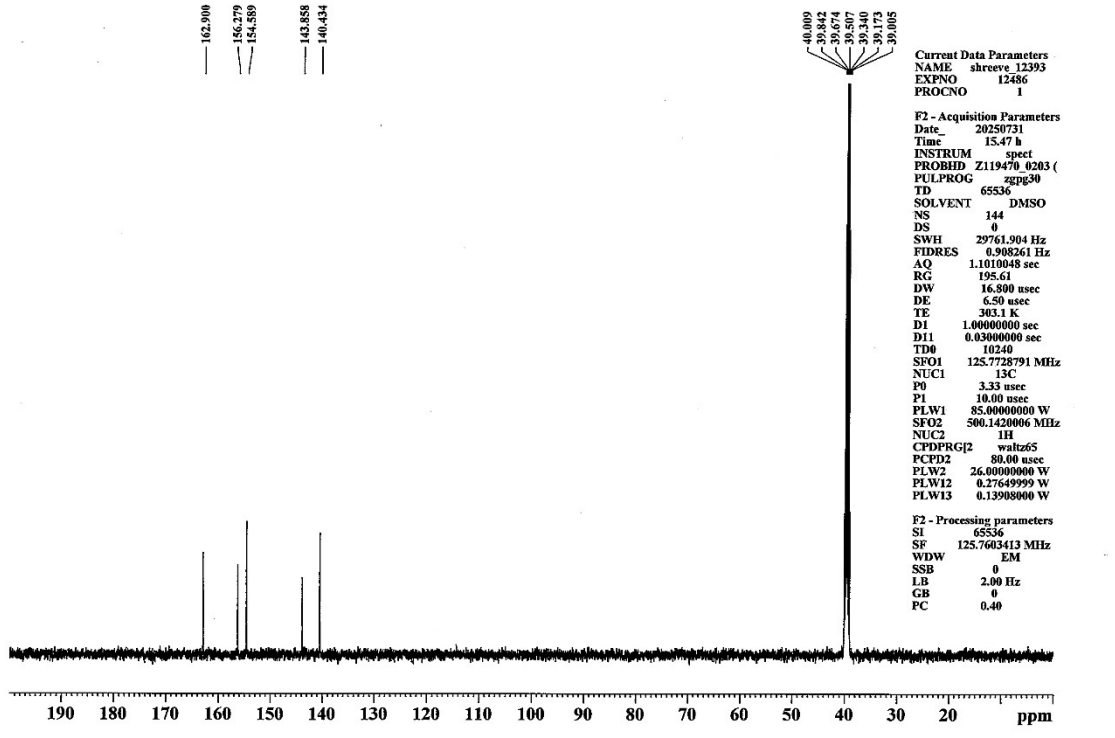


Figure S22: ^{13}C NMR spectrum for compound **A2-2L2**.

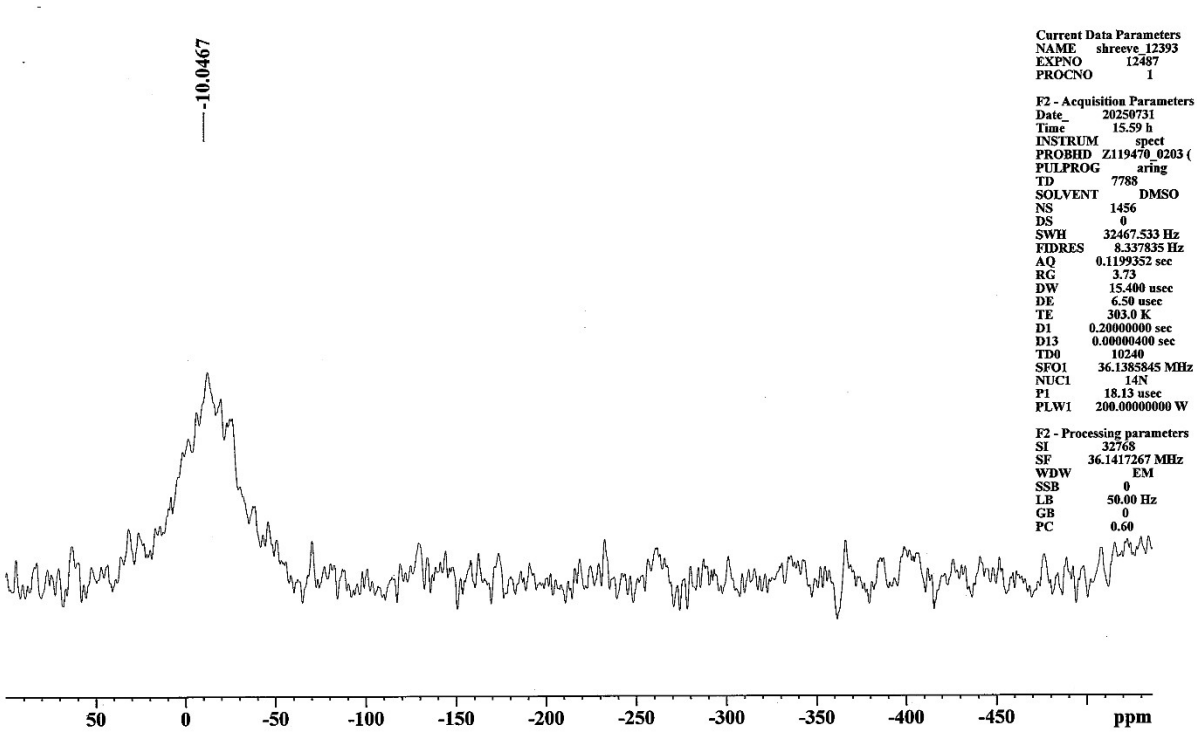


Figure S23: ^{14}N NMR spectrum for compound **A2-2L2**.

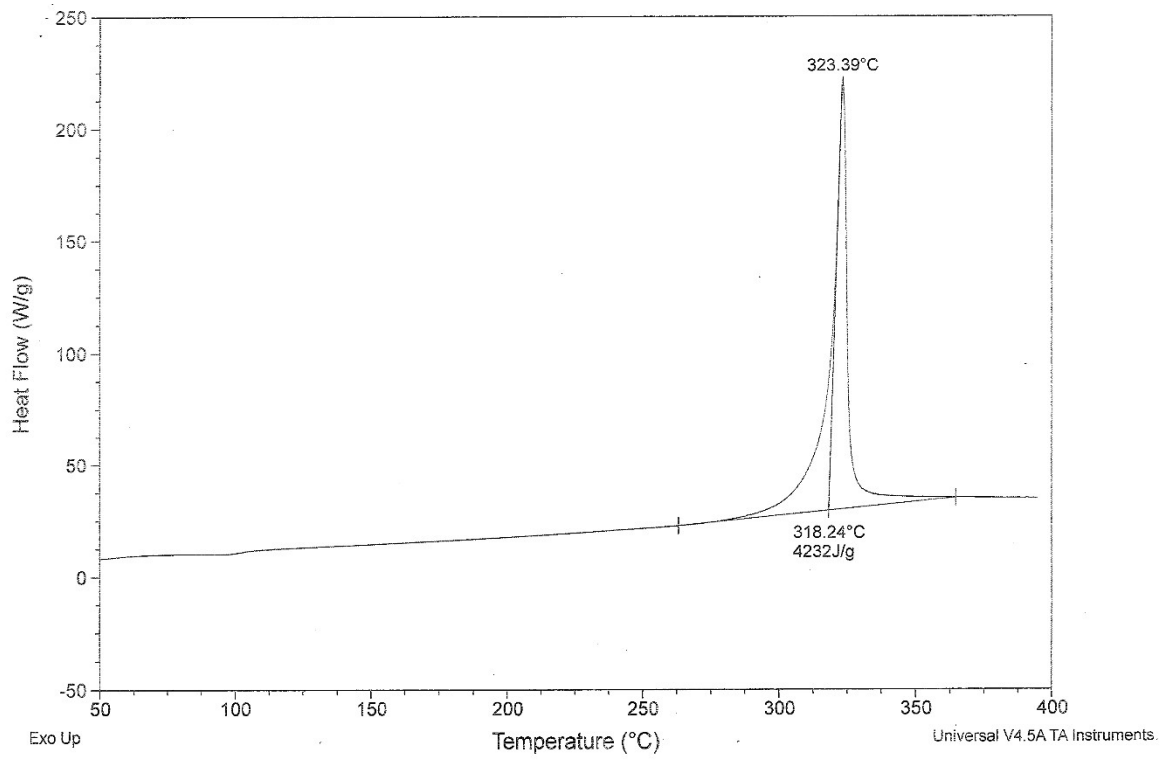


Figure S24: DSC plot for compound **A2-2L2.**

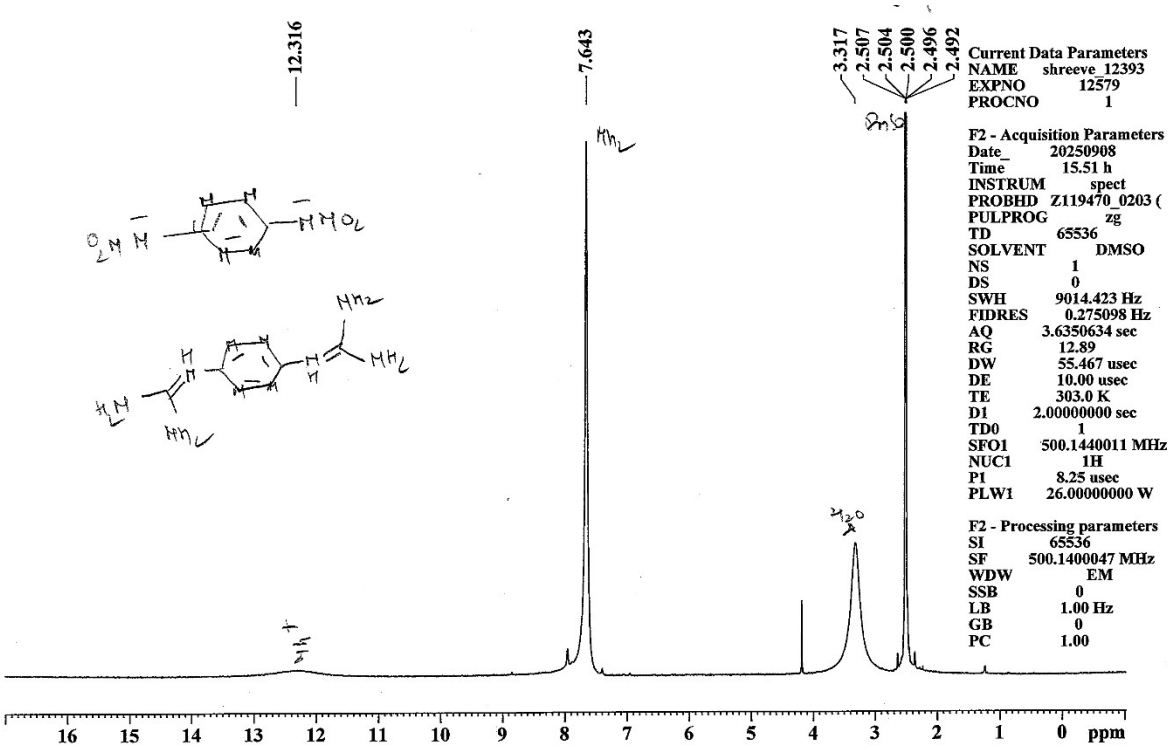


Figure S25: [1]H NMR spectrum for compound **A3-L1**.

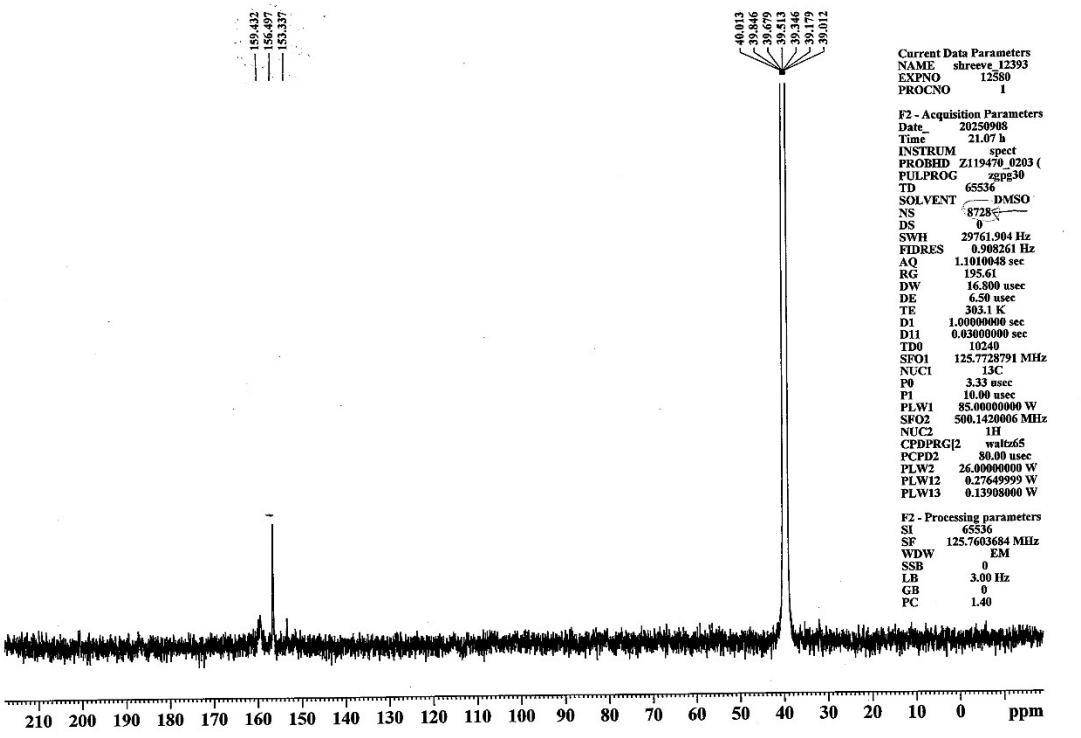


Figure S26: [13]C NMR spectrum for compound **A3-L1**.

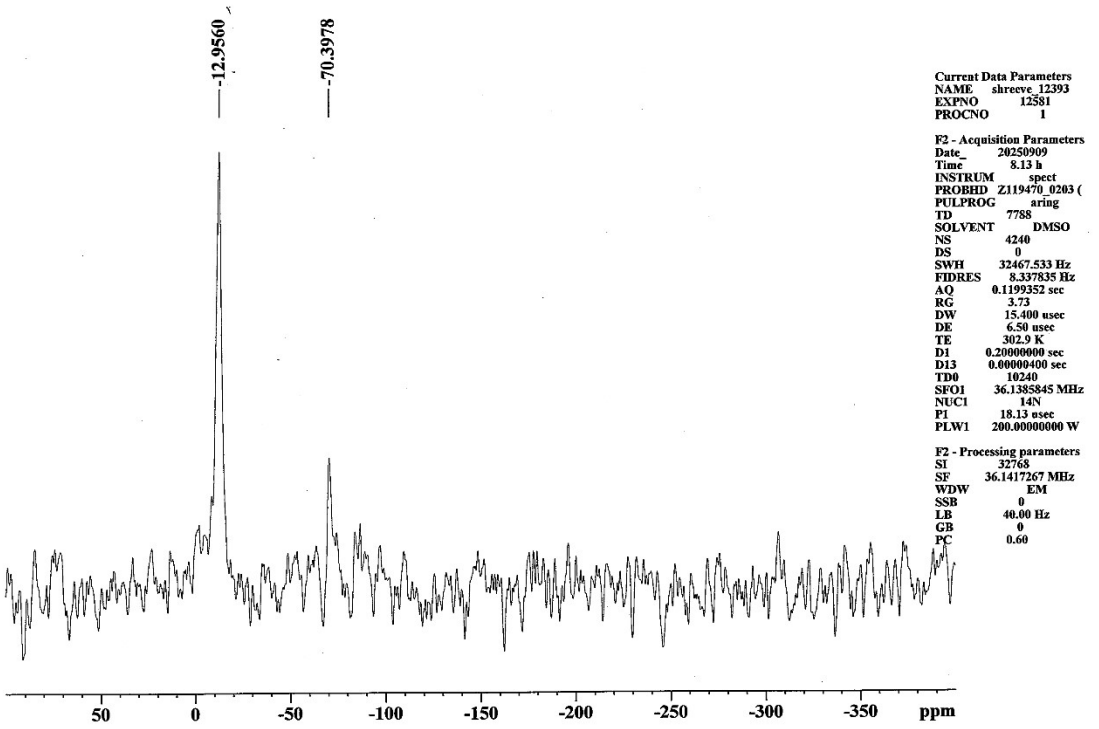


Figure S27: ^{14}N NMR spectrum for compound **A3-L1**.

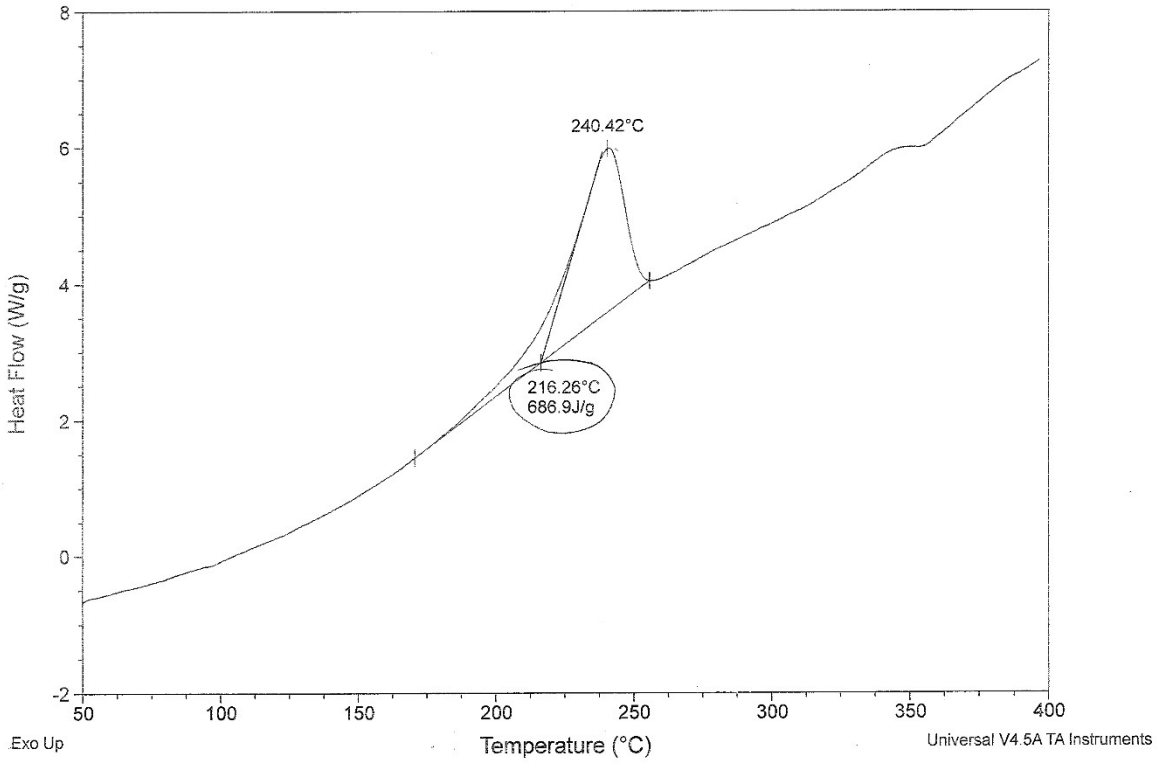


Figure S28: DSC plot for compound **A3-L1**.

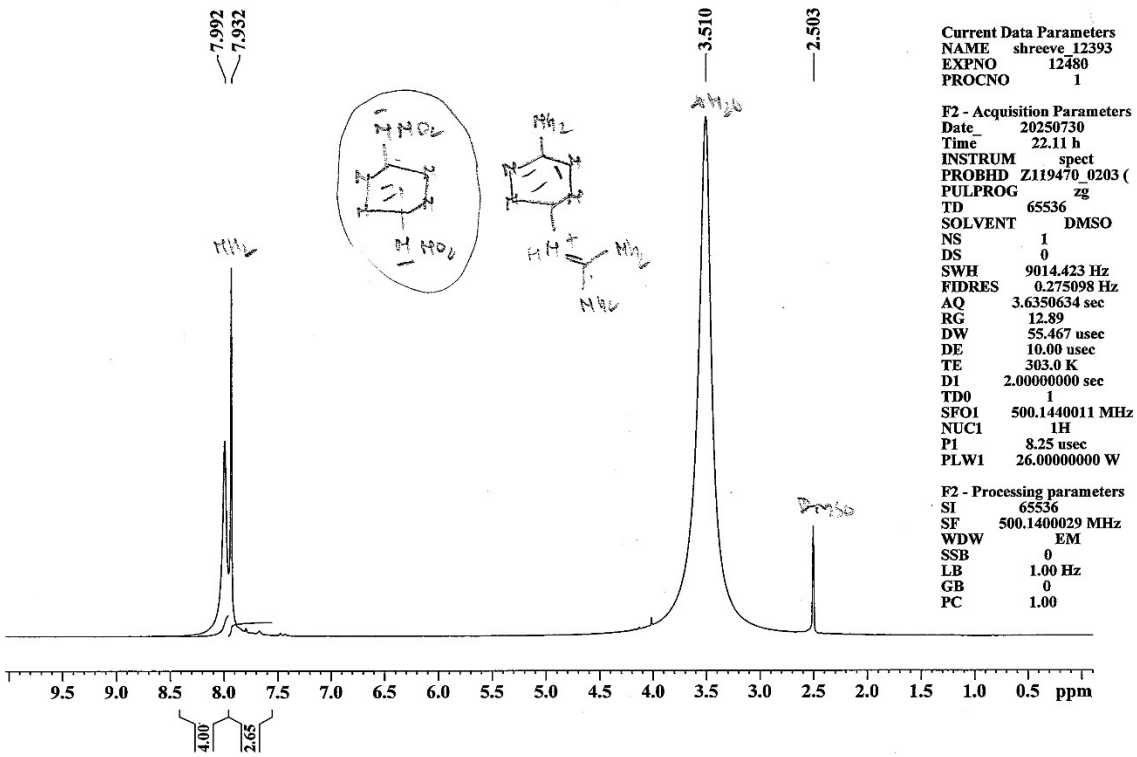


Figure S29: [1]H NMR spectrum for compound **A3-2L2**.

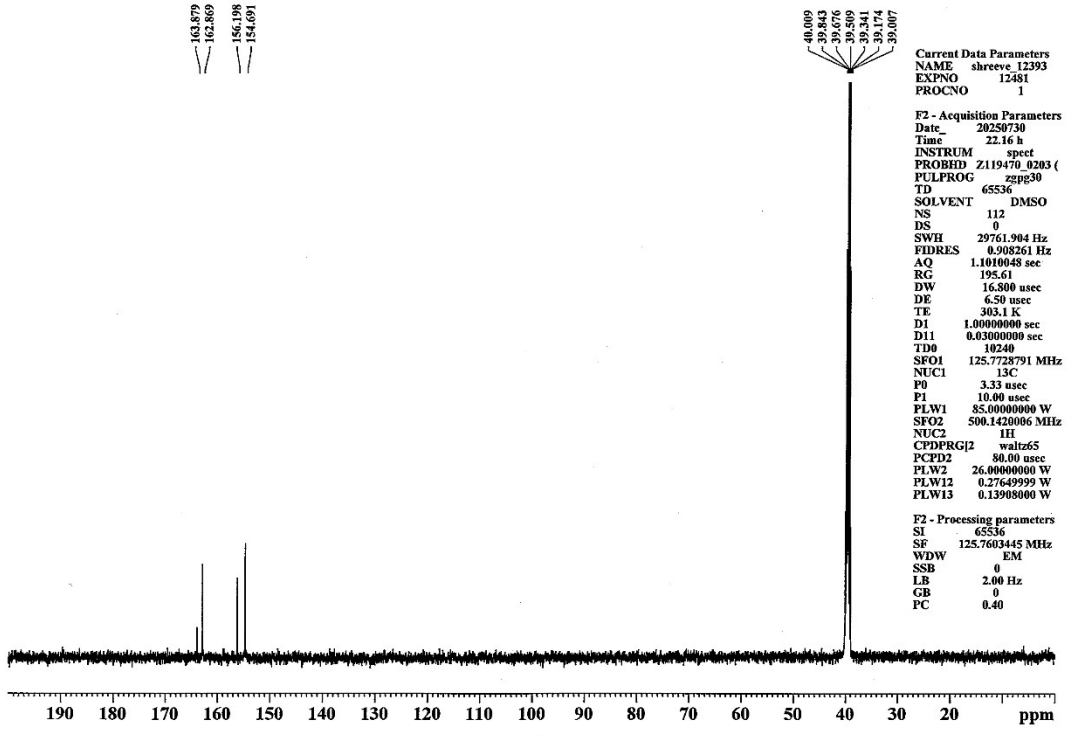


Figure S30: [13]C NMR spectrum for compound **A3-2L2**.

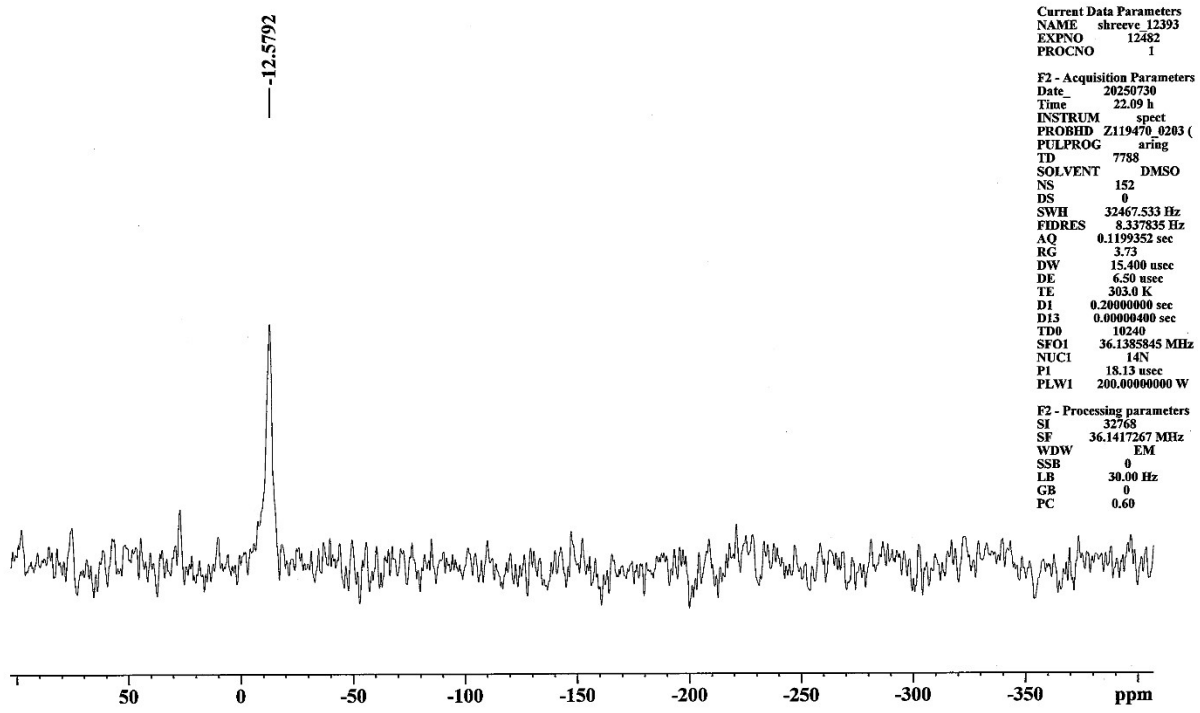


Figure S31: ^{14}N NMR spectrum for compound **A3-2L2**.

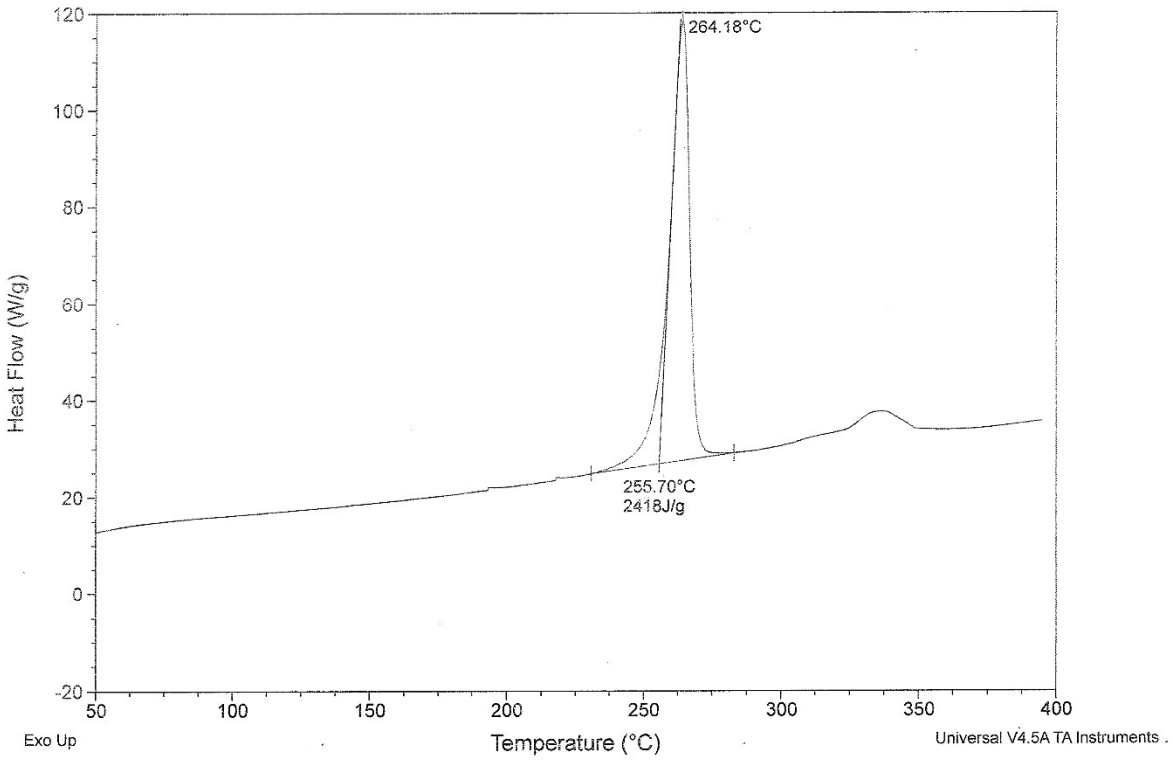


Figure S32: DSC plot for compound **A3-2L2**.

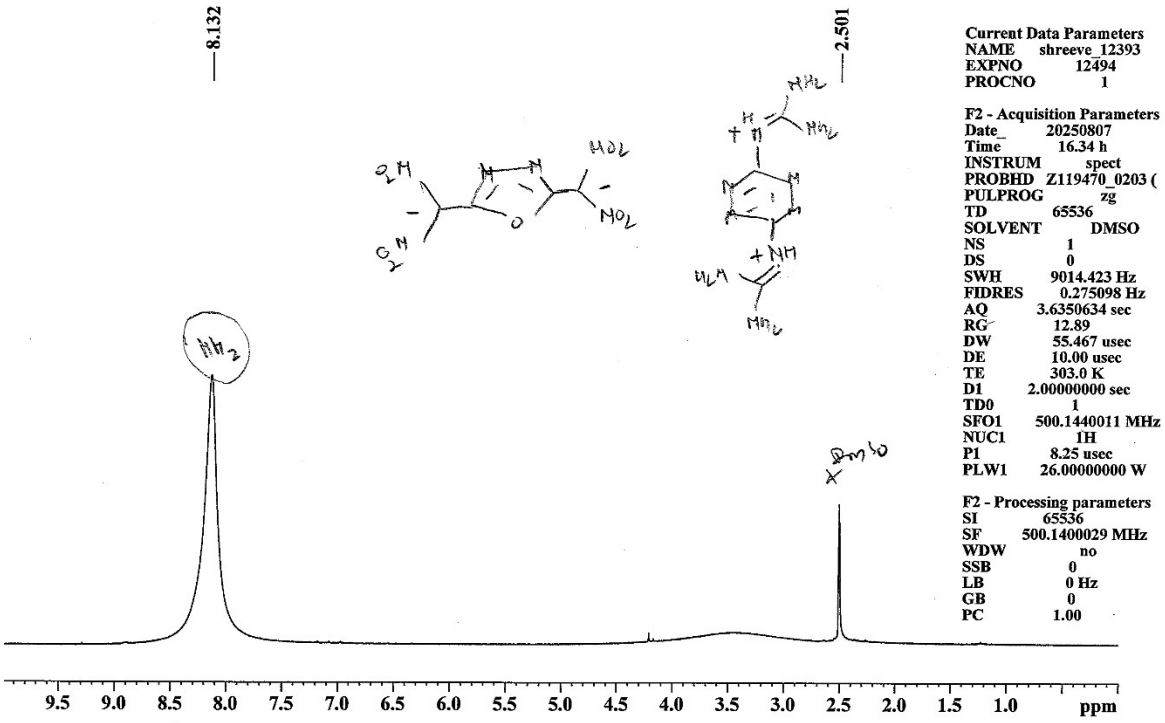


Figure S33: ^{1}H NMR spectrum for compound **A4-L1**.

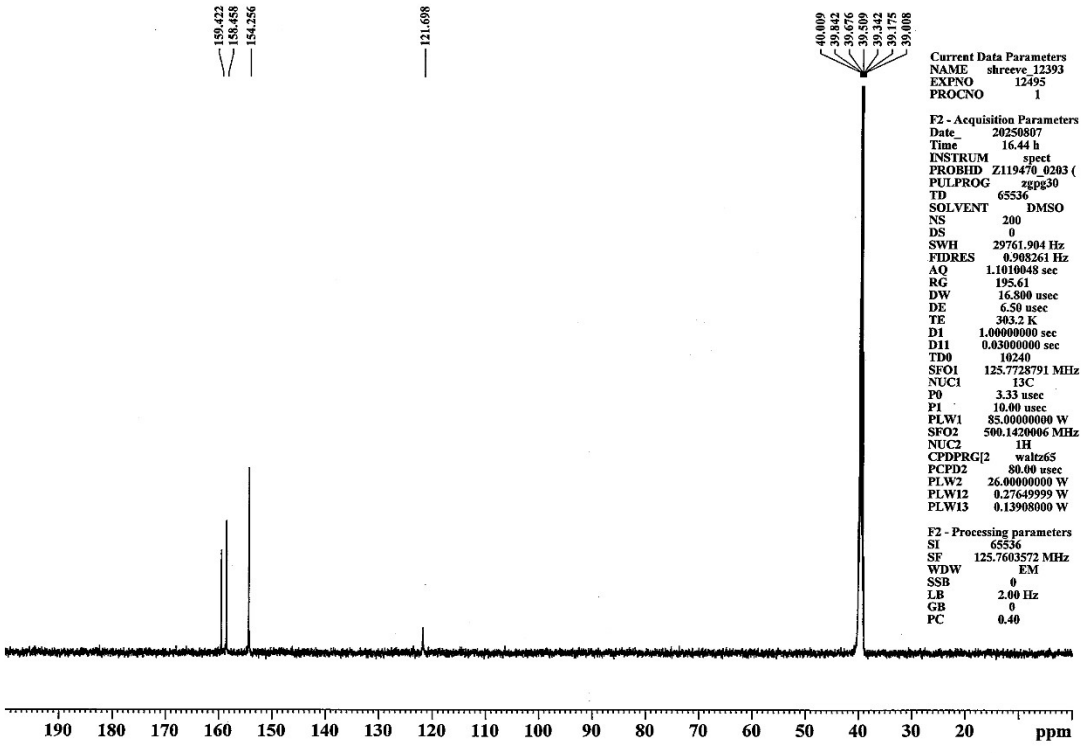


Figure S34: ^{13}C NMR spectrum for compound **A4-L1**.

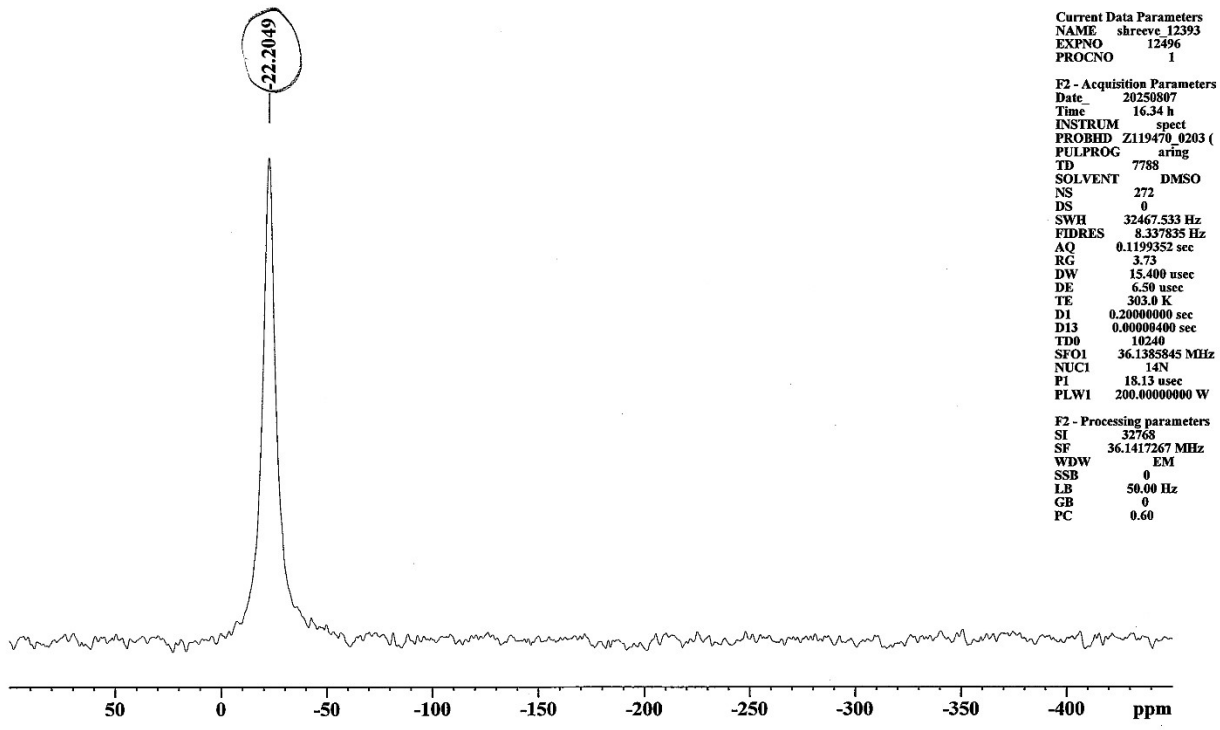


Figure S35: ^{14}N NMR spectrum for compound **A4-L1**.

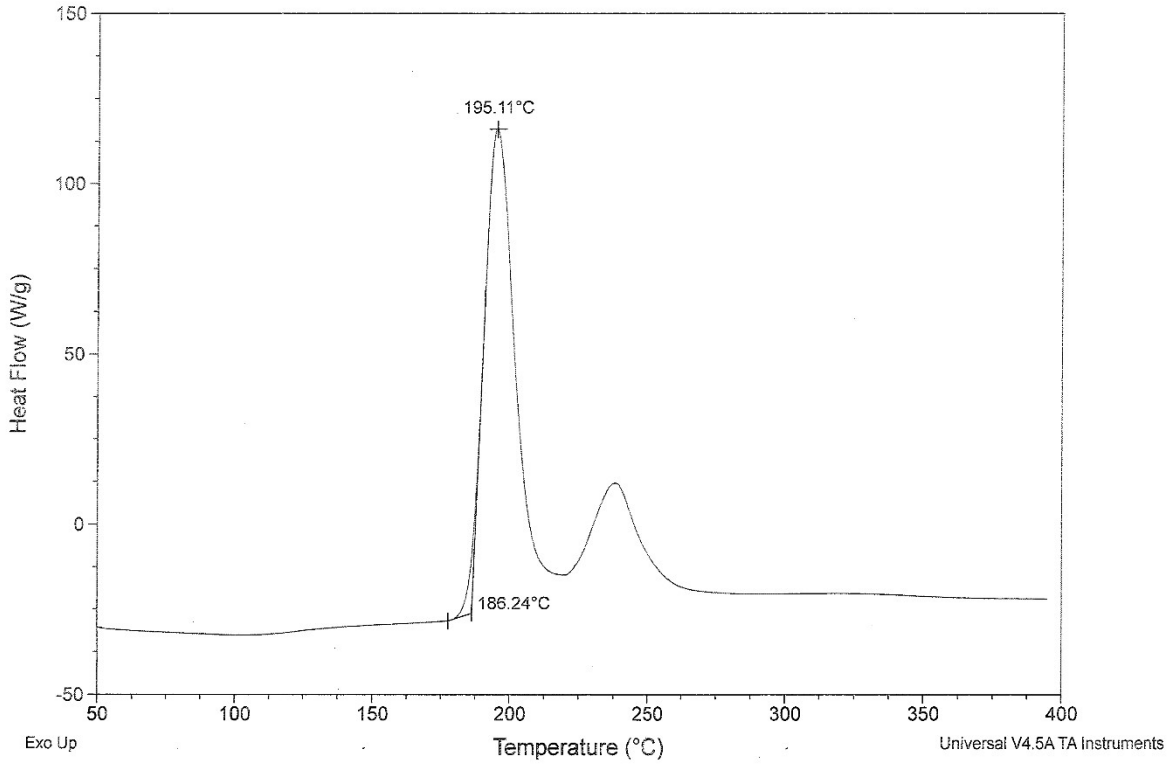


Figure S36: DSC plot for compound **A4-L1**.

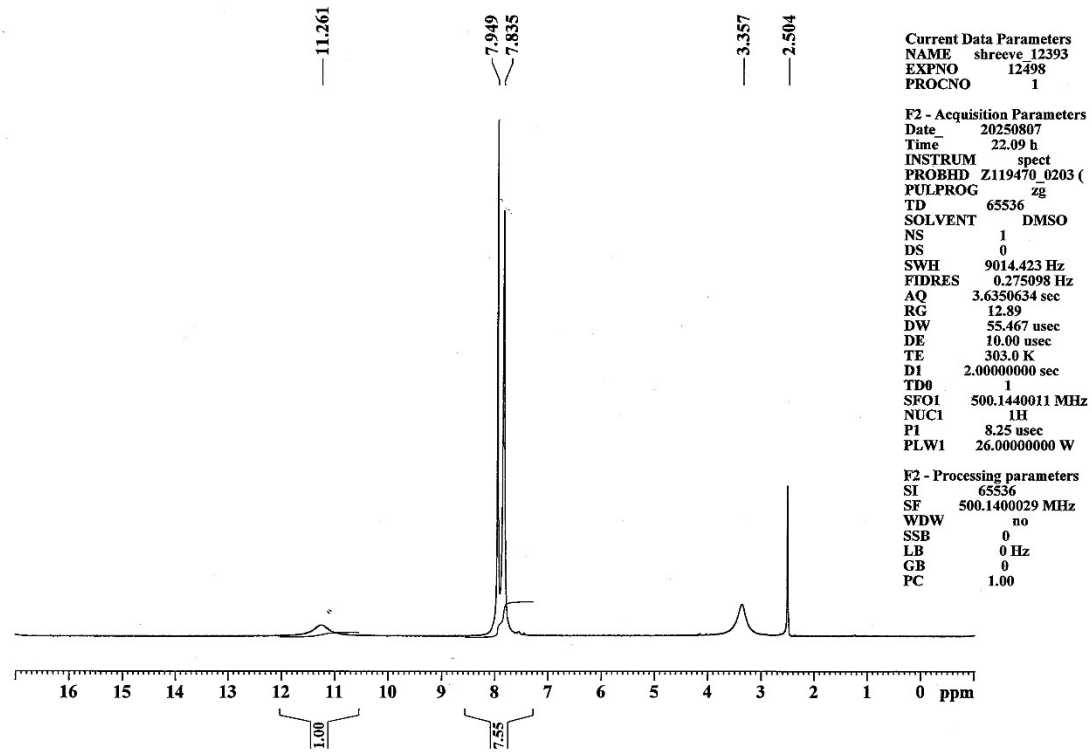


Figure S37: ^{1}H NMR spectrum for compound **A4-2L2**.

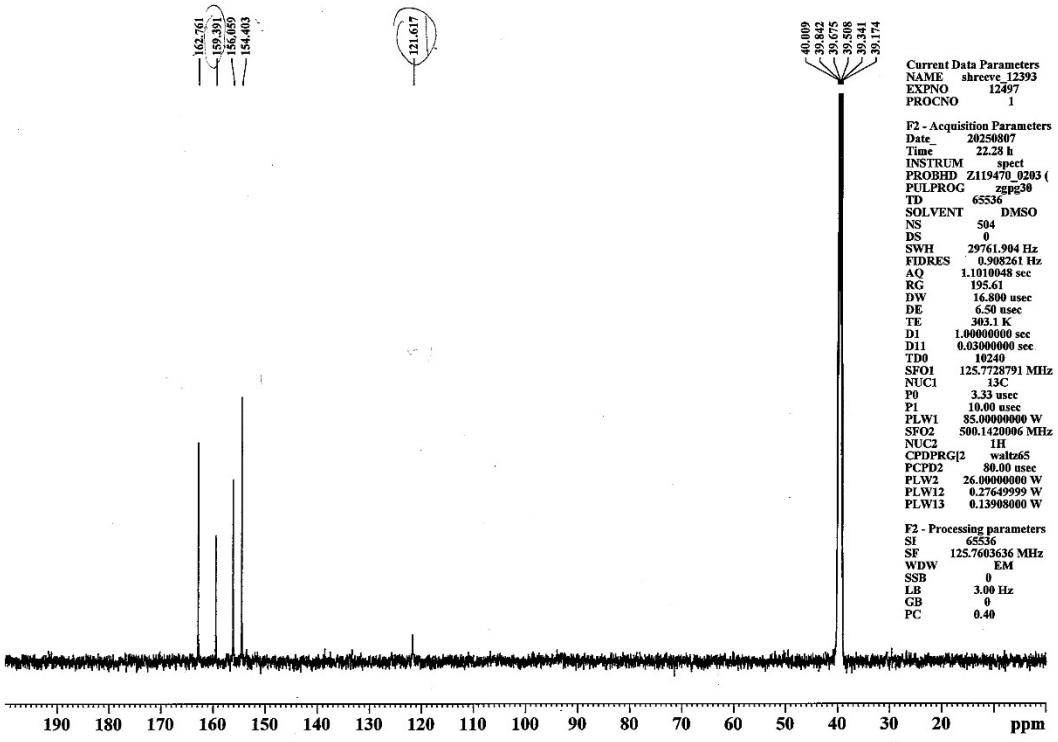


Figure S38: ^{13}C NMR spectrum for compound **A4-2L2**.

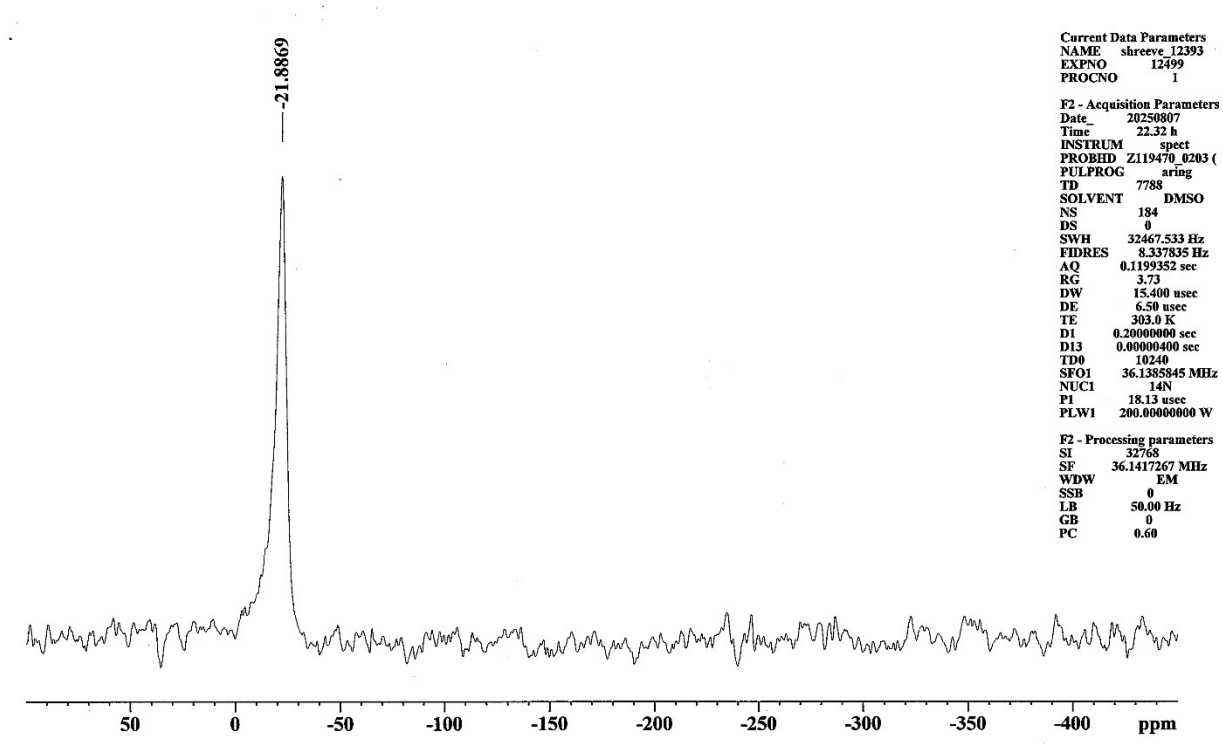


Figure S39: ^{14}N NMR spectrum for compound **A4-2L2**.

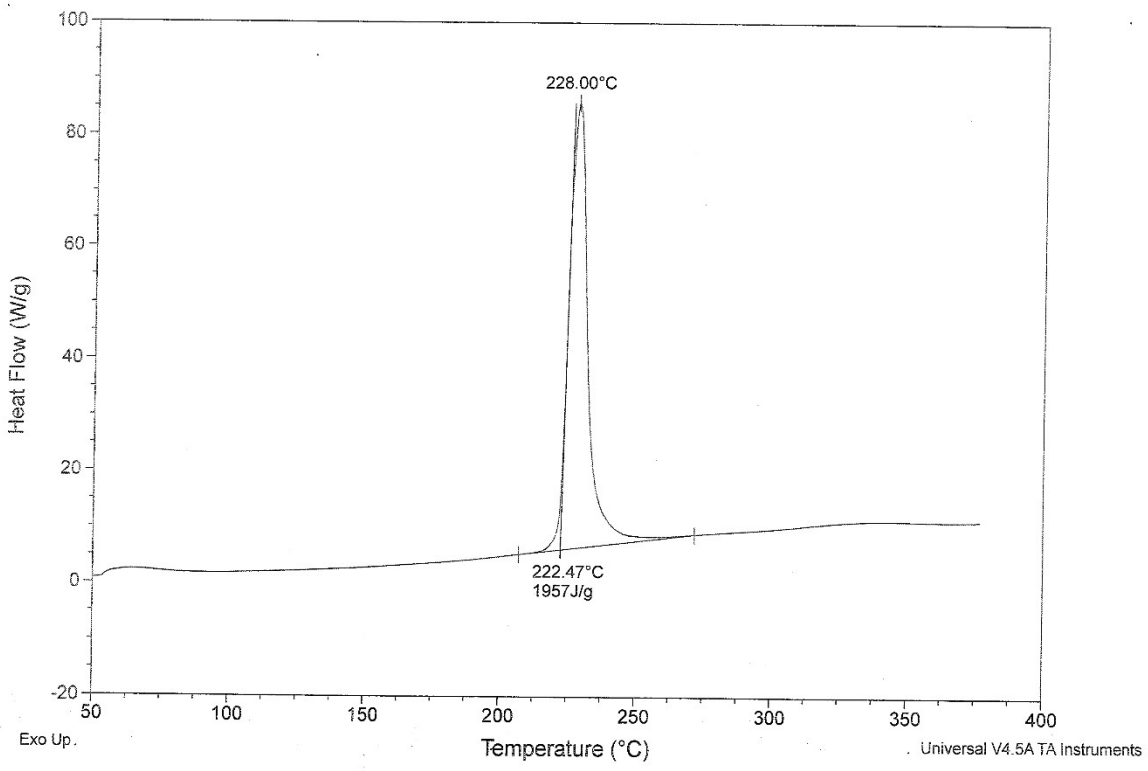


Figure S40: DSC plot for compound **A4-2L2**.

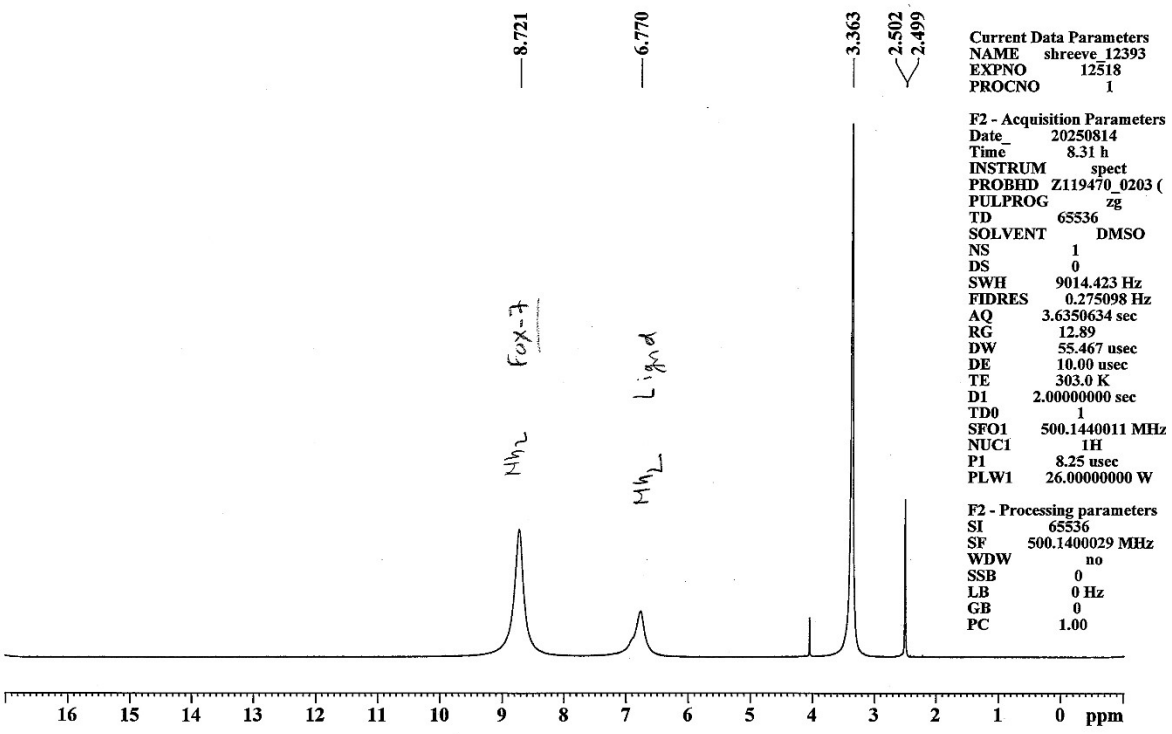


Figure S41: ^{1}H NMR spectrum for compound **2A5-L1**.

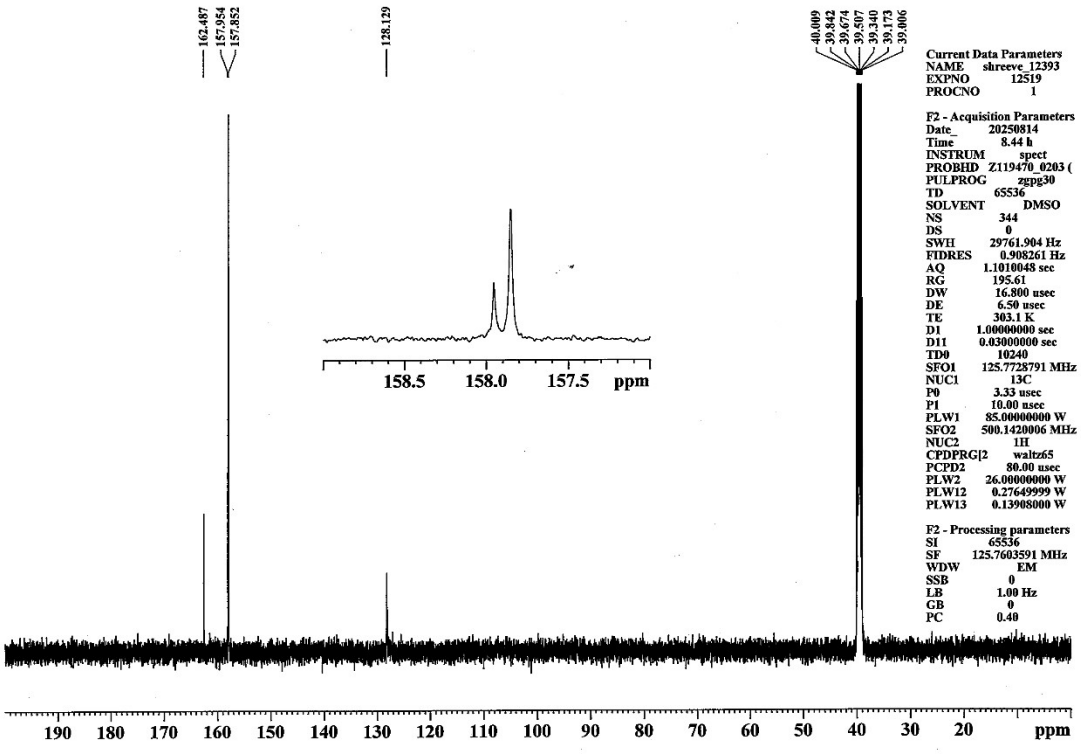


Figure S42: ^{13}C NMR spectrum for compound **2A5-L1**.

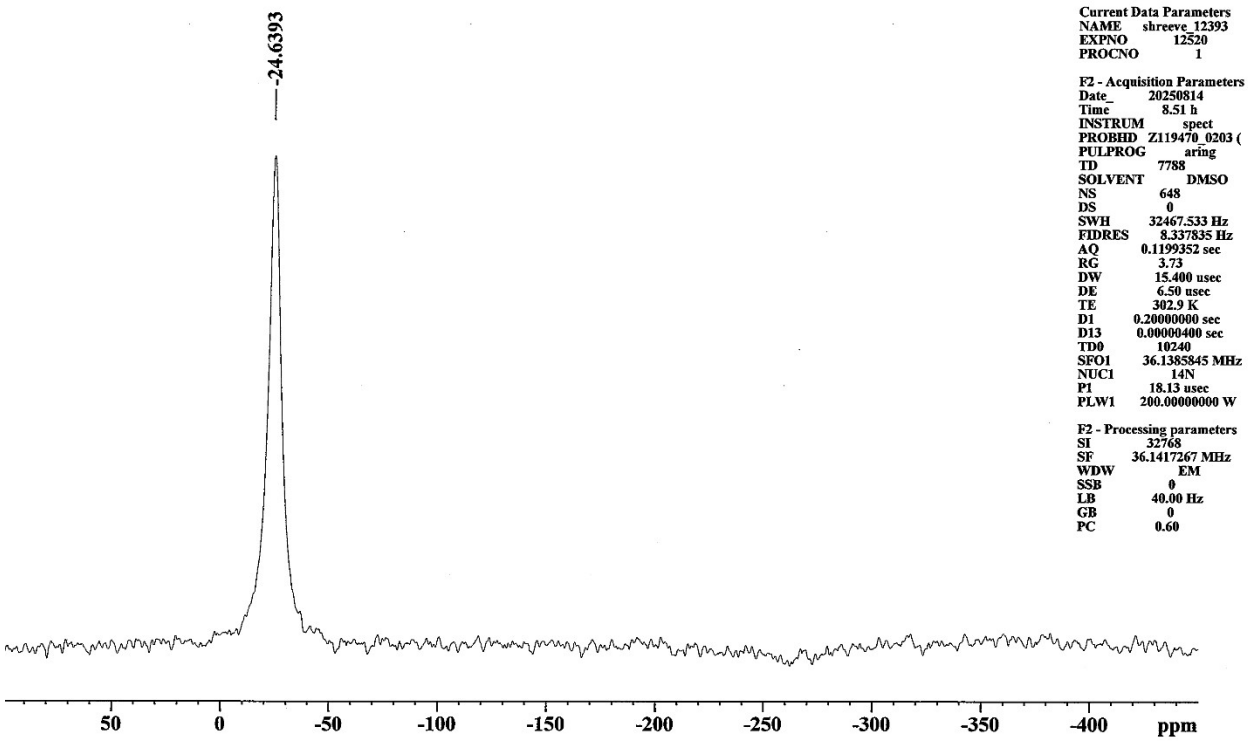


Figure S43: ^{14}N NMR spectrum for compound **2A5-L1**.

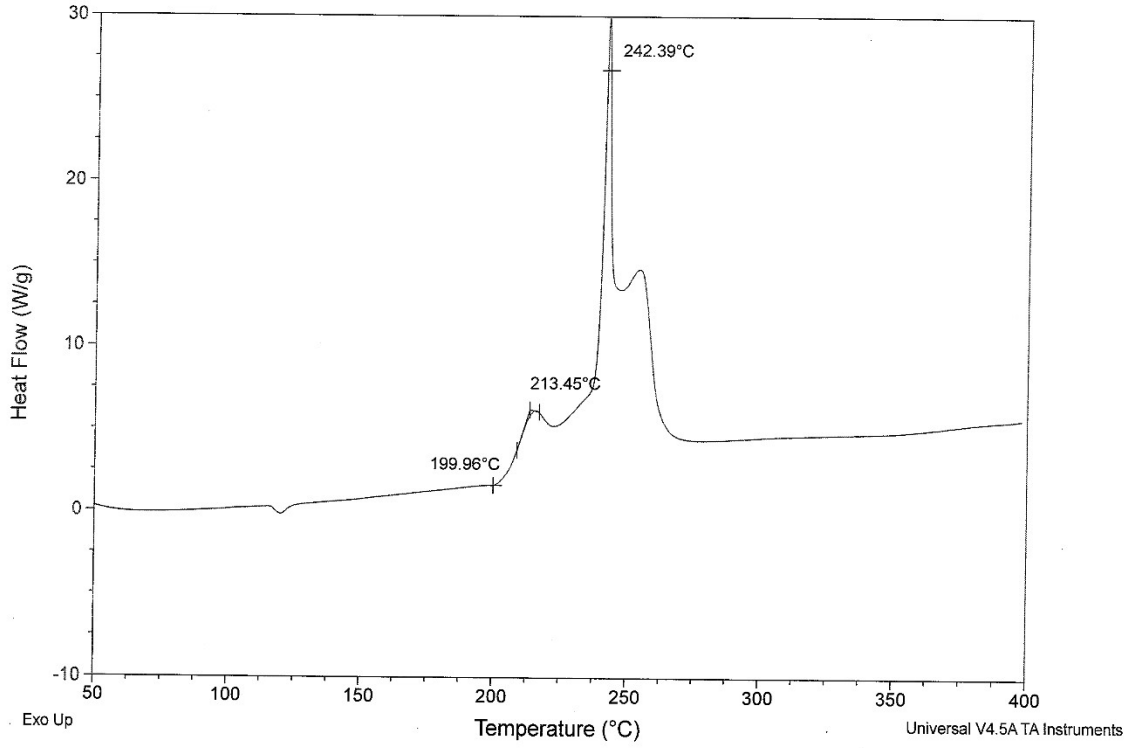


Figure S44: DSC plot for compound **2A5-L1**.

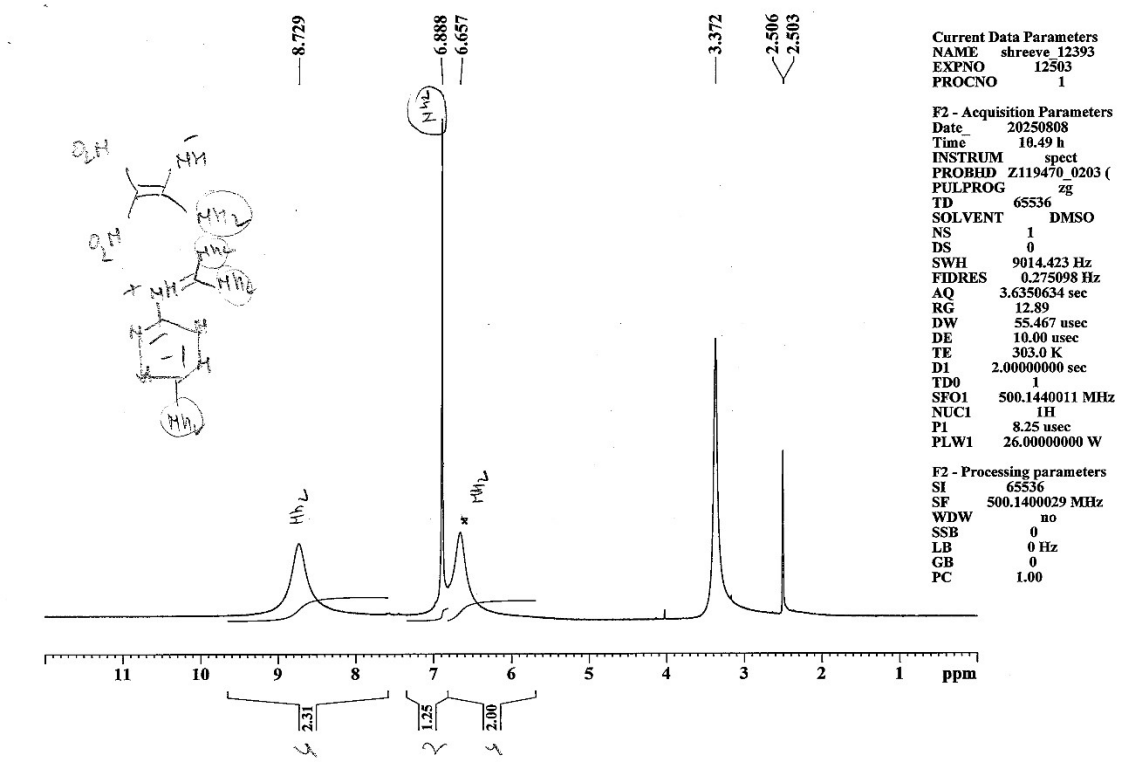


Figure S45: ^{1}H NMR spectrum for compound **A5-L2**.

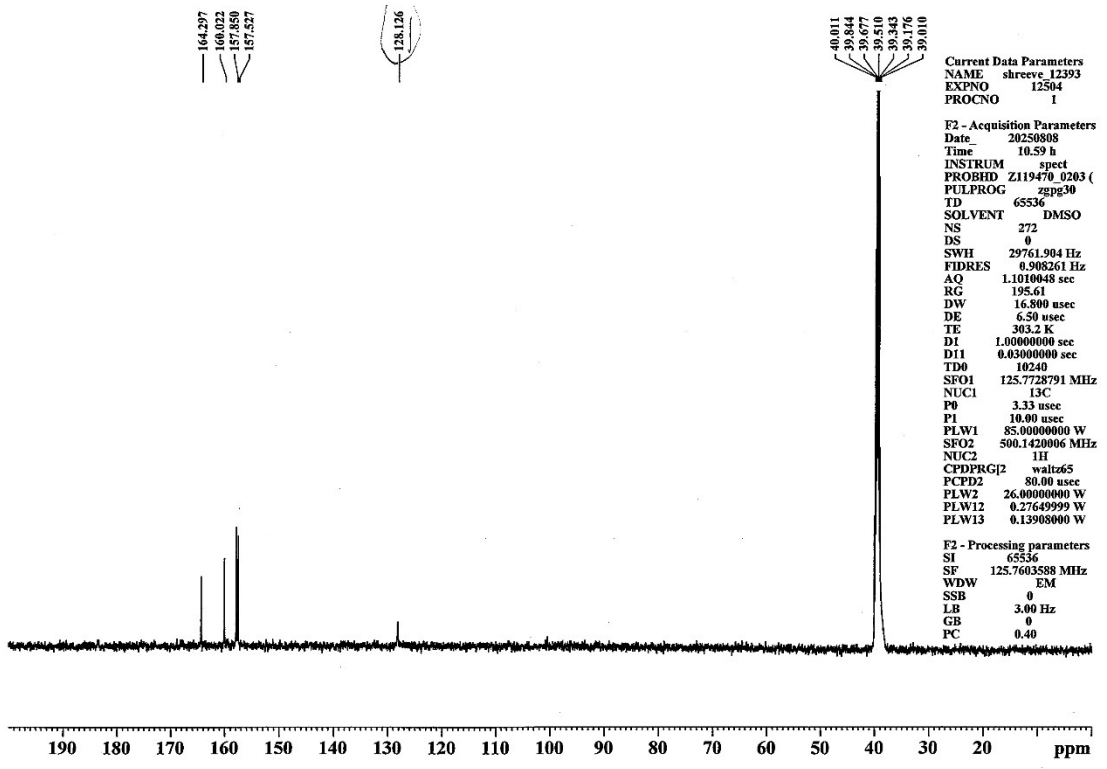


Figure S46: ^{13}C NMR spectrum for compound **A5-L2**.

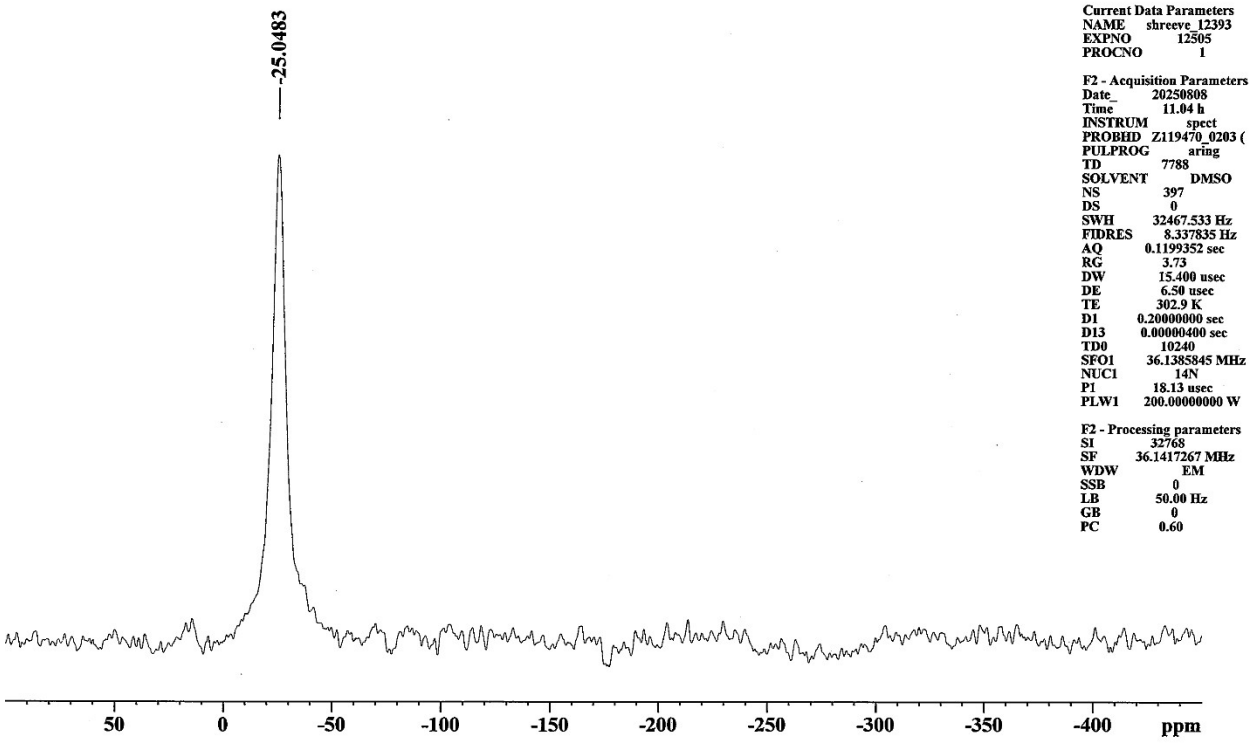


Figure S47: ^{14}N NMR spectrum for compound **A5-L2**.

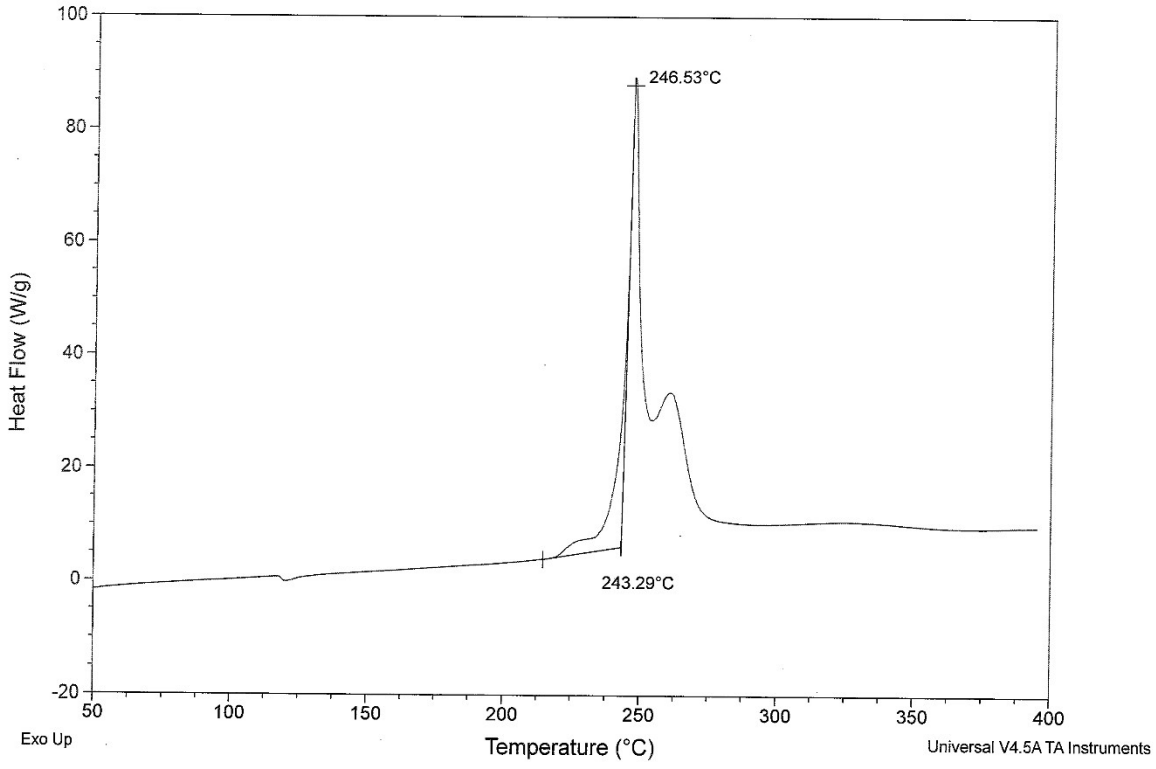


Figure S48: DSC plot for compound **A5-L2**.

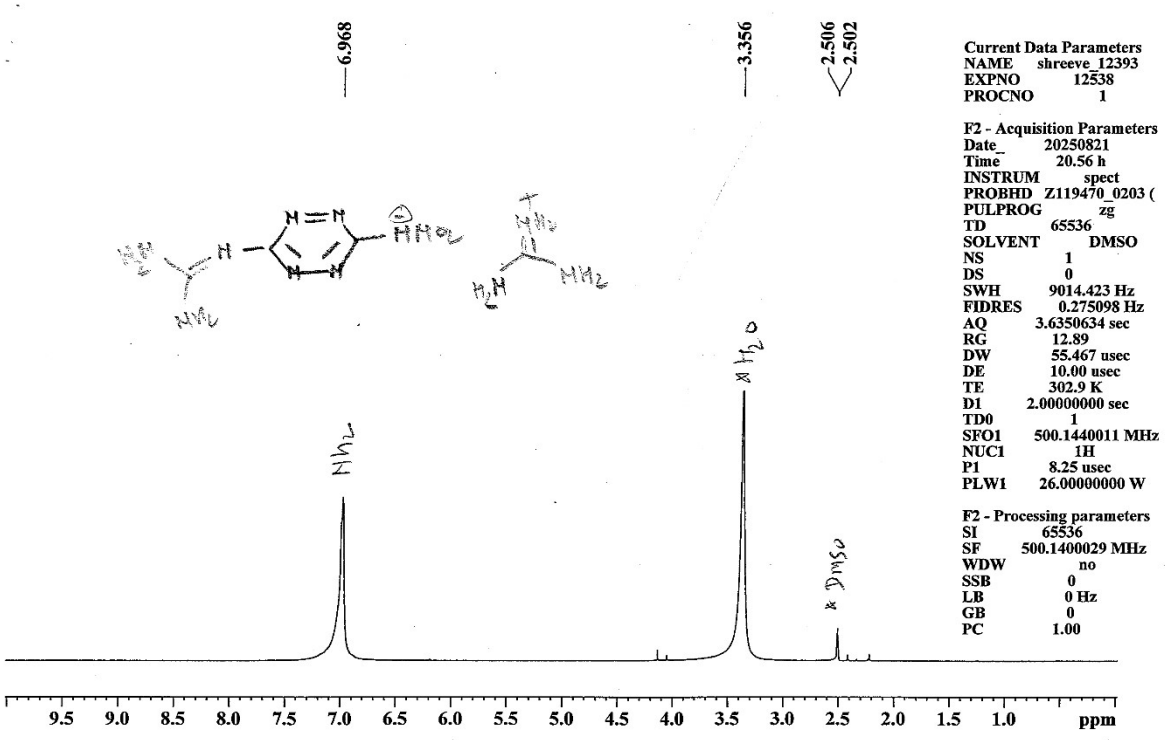


Figure S49: ^{1}H NMR spectrum for compound **1**.

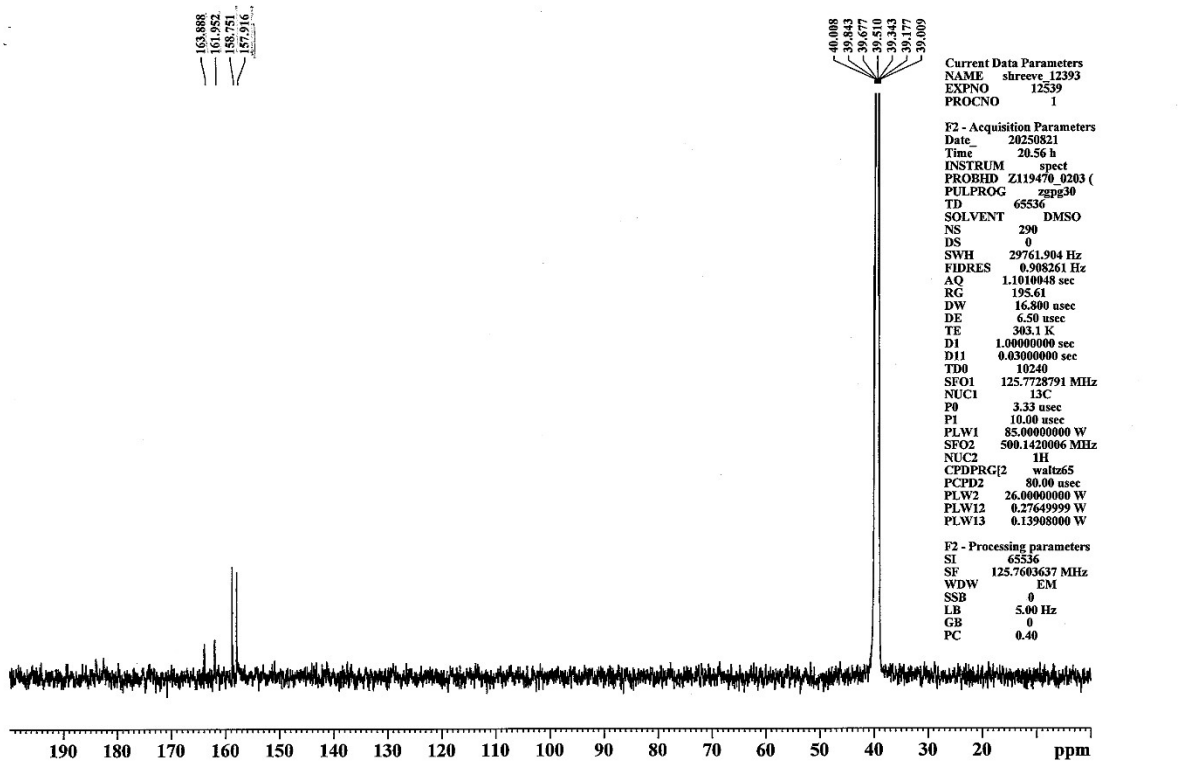


Figure S50: ^{13}C NMR spectrum for compound **1**.

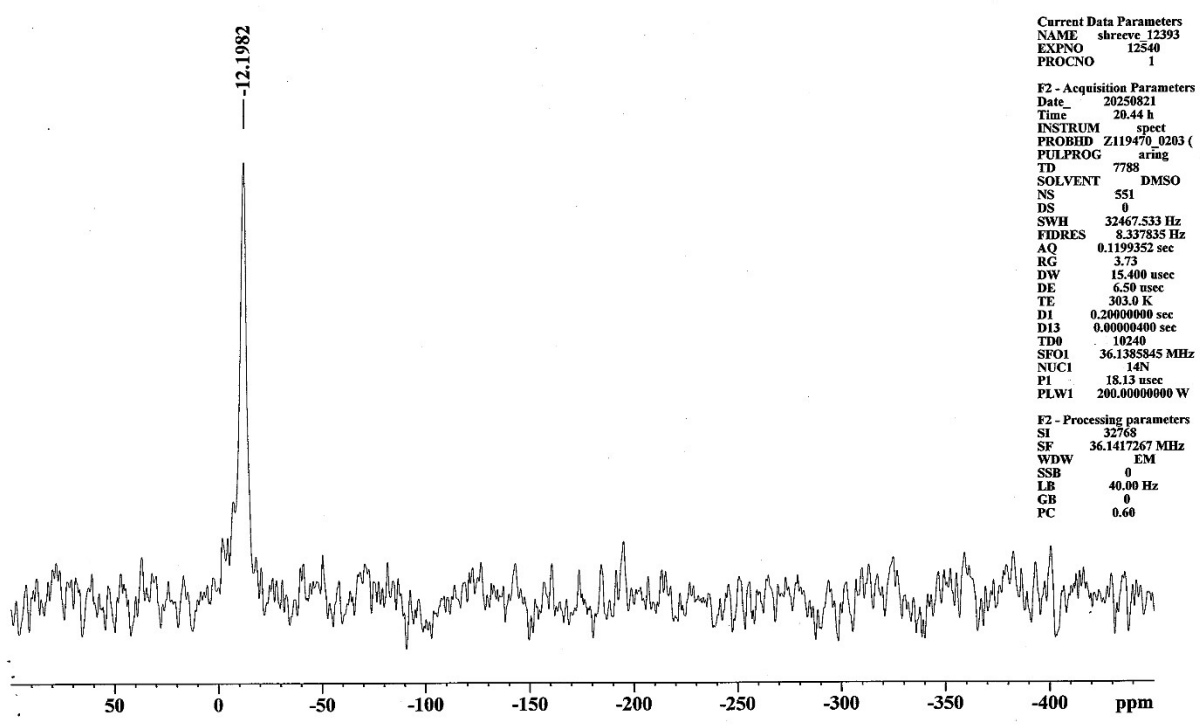


Figure S51: ^{14}N NMR spectrum for compound **1**.

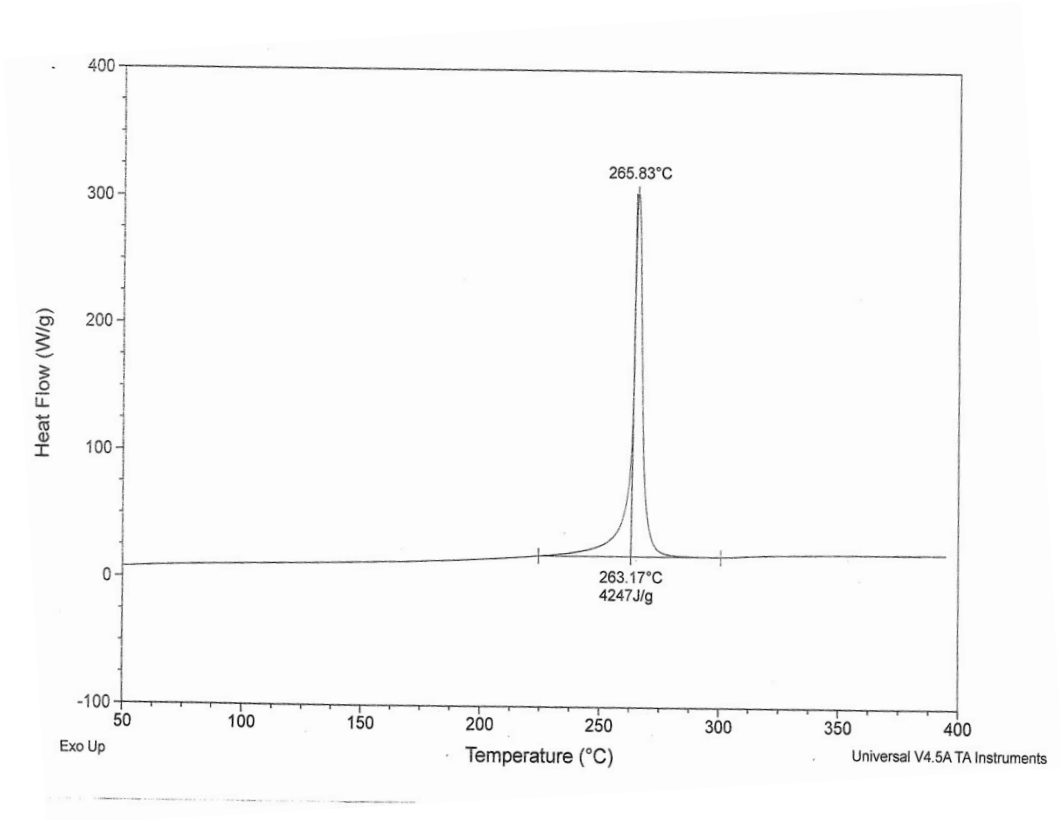


Figure S52: DSC plot for compound **1**.

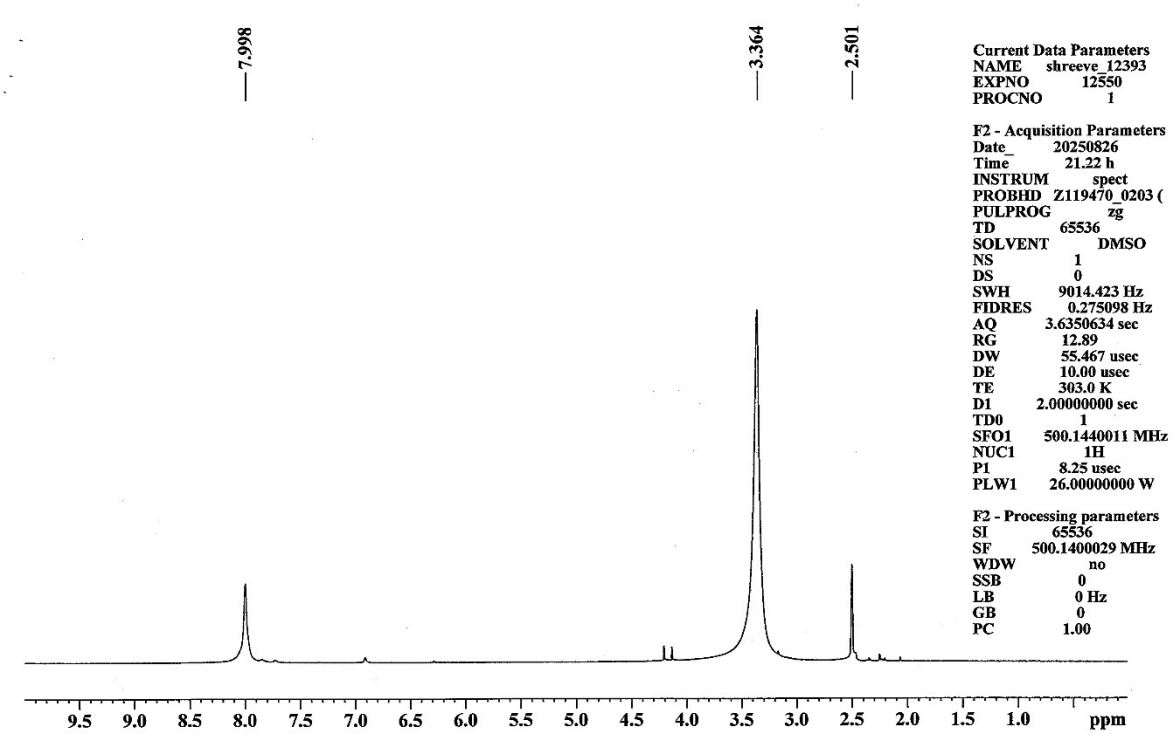


Figure S53: ^{1}H NMR spectrum for compound **2**.

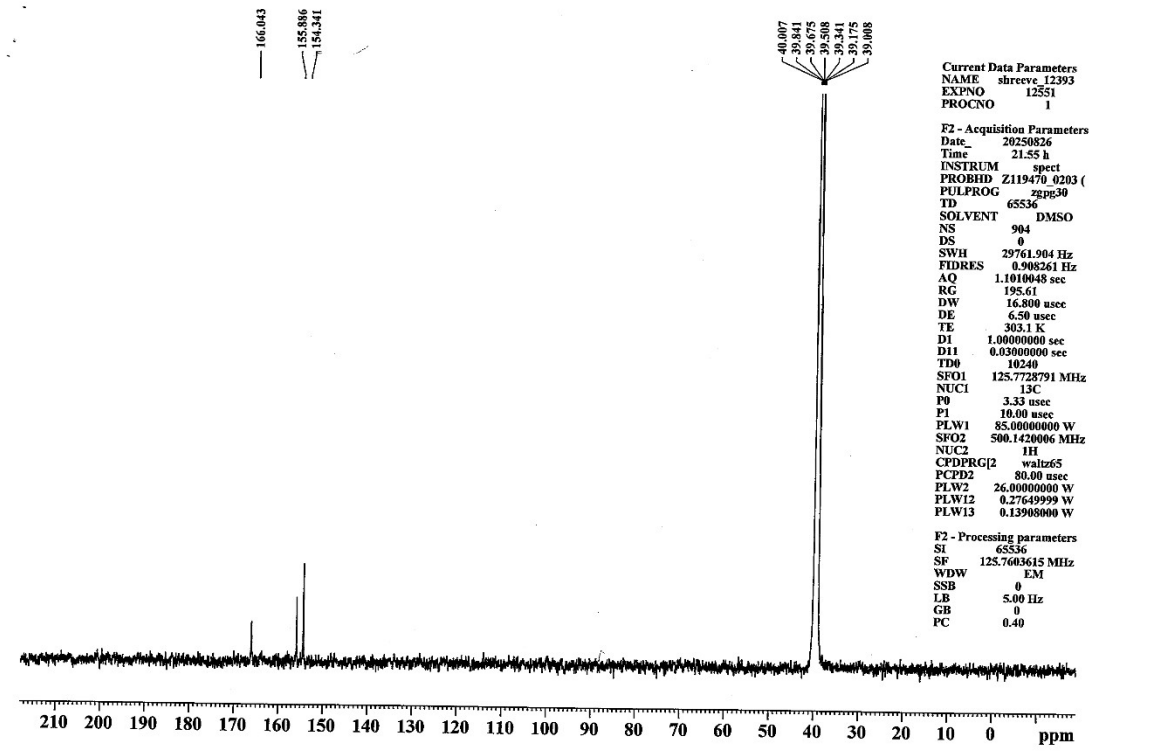


Figure S54: ^{13}C NMR spectrum for compound **2**.

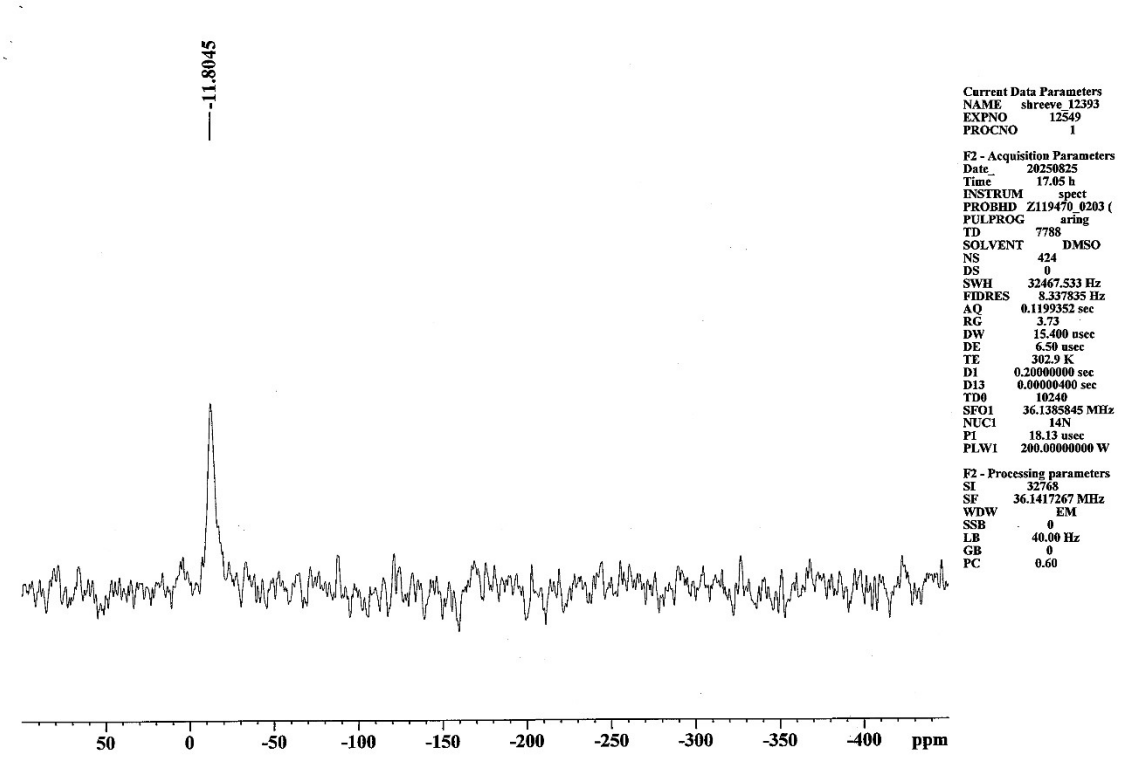


Figure S55: ^{14}N NMR spectrum for compound **2**.

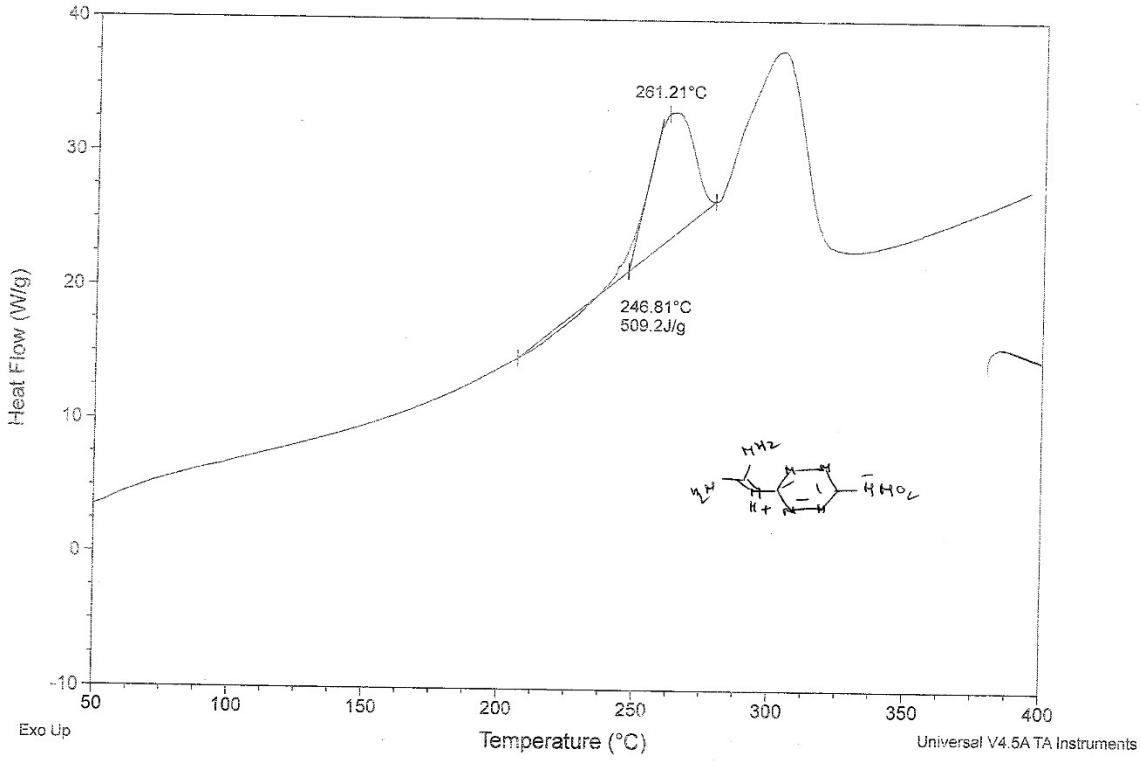


Figure S56: DSC plot for compound **2**.