

Electronic Supplementary Information

Advancing Energy Safety via Stepwise Nucleophilic Substitution on Tetrazine

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

Experimental section	Section S1
X-ray crystallography details and crystallographic data	Section S2
Enthalpy of formation	Section S3
References	Section S4
Spectral Analysis	Section S5

Section S1. Experimental section

Section S1.1. Caution!

The new compounds are energetic materials which show increased sensitivities 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 handling hydrazine hydrate and use only in 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. ^1H , ^{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 ^1H 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 of compounds 2-6

Compounds **1**, **2** and **3** were obtained following the literature procedures.¹⁻²

Synthesis of compound 4. To a stirred solution of compound **3** (1.50 g, 6.4 mmol, 1.0 equiv.) in ethanol (30 mL) at 0°C, a solution of 85% hydrazine hydrate (0.64 g, 12.7 mmol, 2.0 equiv.) in ethanol (10 mL) was added. The resulting reaction mixture was stirred for 1 hr. The red precipitate obtained was filtered and washed with CH₃CN (2 x 10 mL). The compound (**4**) was further purified by recrystallization with methanol. Isolated yield: (0.80 g, 63%); T_{dec} = 114 °C; ¹H NMR (500 MHz, d₆-DMSO): 8.88 (bs, 1H), 6.91 (bs, 5H), 4.44 (bs, 2H); ¹³C NMR (125 MHz, d₆-DMSO): 163.8, 162.3; IR (ν̄, cm⁻¹): 3448, 3299, 3183, 2926, 2639, 1626, 1553, 1403, 1336, 1290, 1174, 1134, 1060, 955, 762, 682, 531; Calcd for C₂H₈N₁₀O₂: C, 11.77; H, 3.95; N, 68.61. Found: C, 12.77; H, 3.62; N, 68.55.

The synthesis of compound **4** was also carried out, increasing the scale by threefold. To a stirred solution of compound **3** (4.54 g, 19 mmol, 1.0 equiv.) in ethanol (100 mL) at 0°C, a solution of 85% hydrazine hydrate (1.92 g, 38 mmol, 2.0 equiv.) in ethanol (30 mL) was added. The resulting reaction mixture was stirred for 1 hr. The red precipitate obtained was filtered and washed with CH₃CN (2 x 30 mL). Isolated yield: (2.5 g, 64%); Calcd for C₂H₈N₁₀O₂·(0.2CH₃CN): C, 13.57; H, 4.08; N, 67.28. Found: C, 13.32; H, 3.93; N, 66.79.

Synthesis of compound 5. Compound **4** (0.50 g, 2.4 mmol) was dissolved in water and TATOT·HCl (0.47 g, 2.4 mmol) was added in portions. The resulting reaction mixture was stirred at room temperature for 3 h. The orange solid (**5**) was filtered off, washed with water and dried. Isolated yield: (0.60 g, 77%); T_{dec.} = 159 °C; ¹H NMR (500 MHz, d₆-DMSO): 9.07 (bs, 1H), 7.94 (s, 2H), 7.15 (s, 2H), 5.76 (s, 2H), 4.18 (s, 2H); ¹³C NMR (125 MHz, d₆-DMSO): 163.6, 162.1, 160.0, 147.6, 141.4; IR (ν̄, cm⁻¹): 3310, 2995, 2717, 1680, 1638, 1546, 1465, 1352, 1311, 1160, 1060, 980, 937, 835, 773, 720, 603, 540; Elemental analysis: Calcd for C₅H₁₀N₁₆O₂: C, 18.41; H, 3.09; N, 68.69. Found: C, 18.50; H, 3.18; N, 68.33.

Synthesis of compound 6. Compound **4** (0.50 g, 2.4 mmol) was dissolved in water and MA·HCl (0.39 g, 2.4 mmol) was added in portions. The resulting reaction mixture was stirred at room temperature for 3 h. The orange solid (**6**) was filtered off, washed with water and dried. Isolated yield: (0.50 g, 76%); $T_{\text{dec.}} = 162\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (500 MHz, d_6 -DMSO): 9.02 (s, 1H), 7.40 (s, 6H), 3.45 (bs, 3H); $^{13}\text{C NMR}$ (125 MHz, d_6 -DMSO): 163.3, 162.1, 160.8; IR ($\tilde{\nu}$, cm^{-1}): 3395, 3293, 3121, 1679, 1638, 1522, 1462, 1379, 1294, 1177, 1147, 1031, 886, 778, 653, 571; Elemental analysis: Calcd for $\text{C}_5\text{H}_{10}\text{N}_{14}\text{O}_2$: C, 20.14; H, 3.38; N, 65.75. Found: C, 20.40; H, 3.41; N, 64.10.

Synthesis of compound 7. Compound **4** (0.5 g, 2.4 mmol) was dissolved in water and sulfuric acid (10% in water) was added dropwise. The resulting reaction mixture was stirred at room temperature for 1 h. The red solid (**7**) was filtered off, washed with water and dried. Isolated yield: (0.30 g, 73%); $T_{\text{dec.}} = 139\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (500 MHz, d_6 -DMSO): 4.09 (s, 3H); $^{13}\text{C NMR}$ (125 MHz, d_6 -DMSO): 161.1, 160.1; IR ($\tilde{\nu}$, cm^{-1}): 3481, 3399, 3150, 2929, 2708, 1608, 1546, 1503, 1465, 1359, 1287, 1206, 1113, 1047, 966, 896, 837, 771, 571; Elemental analysis: Calcd for $\text{C}_2\text{H}_4\text{N}_8\text{O}_2$: C, 13.96; H, 2.34; N, 65.11. Found: C, 13.95; H, 2.54; N, 64.44.

The synthesis of compound **7** was also carried out, increasing the scale by threefold. Compound **4** (1.5 g, 7.3 mmol) was dissolved in 20 ml water and sulfuric acid (10% in water) was added dropwise. The resulting reaction mixture was stirred at room temperature for 1 h. The red solid (**7**) was filtered off, washed with water and dried. Isolated yield: (0.9 g, 75%).

Synthesis of compound 8. To the stirred solution of compound **3** (1.50 g, 6.4 mmol, 1.0 equiv.) in ethanol (30 mL), a solution of 28% aqueous ammonia (2 mL) in ethanol (10 mL) was added. The resulting reaction mixture was stirred for 6 hr. The red precipitate obtained was filtered and washed with CH_3CN (2 x 10mL). The compound (**8**) was further purified by recrystallization with methanol. Isolated yield: (0.80 g, 73%); $T_{\text{dec.}} = 174\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (500 MHz, d_6 -DMSO): 7.43 (s,

2H), 7.27 (s, 4H); ^{13}C NMR (125 MHz, $\text{d}_6\text{-DMSO}$): 163.4, 161.9; IR ($\tilde{\nu}$, cm^{-1}): 3481, 3328, 3175, 1646, 1524, 1454, 1358, 1299, 1062, 1025, 972, 884, 850, 772, 641, 570; Calcd for $\text{C}_2\text{H}_6\text{N}_8\text{O}_2$: C, 13.80; H, 3.47; N, 64.35. Found: C, 13.83; H, 3.28; N, 64.04.

Synthesis of compound 9. Compound **8** (0.5 g, 2.9 mmol) was dissolved in water (20 mL) and TATOT·HCl (0.55 g, 2.9 mmol) was added in portions. The resulting reaction mixture was stirred at room temperature for 3 h. The orange solid (**9**) was filtered off, washed with water (2 x 10 mL) and dried. Isolated yield: (0.60 g, 67%); $T_{\text{dec.}} = 241\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, $\text{d}_6\text{-DMSO}$): 8.00 (s, 2H), 7.44 (s, 2H), 7.17 (s, 2H), 5.77 (s, 2H); ^{13}C NMR (125 MHz, $\text{d}_6\text{-DMSO}$): 163.1, 161.7, 160.1, 147.6, 141.3; IR ($\tilde{\nu}$, cm^{-1}): 3360, 3244, 3187, 3146, 1664, 1590, 1509, 1418, 1373, 1357, 1290, 1057, 950, 838, 600; Elemental analysis: Calcd for $\text{C}_5\text{H}_9\text{N}_{15}\text{O}_2$: C, 19.30; H, 2.91; N, 67.51. Found: C, 19.26; H, 2.96; N, 66.85.

Synthesis of compound 10. Compound **8** (0.5 g, 2.9 mmol) was dissolved in water (20 mL) and MA·HCl (0.47 g, 2.9 mmol) (MA = melamine) was added in portions. The resulting reaction mixture was stirred at room temperature for 3 h. The orange solid (**10**) was filtered off, washed with water (2 x 10 mL) and dried. Isolated yield: (0.65 g, 79%); $T_{\text{dec.}} = 252\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, $\text{d}_6\text{-DMSO}$): 7.54 (s, 9H); ^{13}C NMR (125 MHz, $\text{d}_6\text{-DMSO}$): 162.6, 161.7, 160.3; IR ($\tilde{\nu}$, cm^{-1}): 3421, 3363, 31261673, 1622, 1557, 1513, 1409, 1344, 1300, 1126, 1067, 859, 774; Elemental analysis: Calcd for $\text{C}_5\text{H}_9\text{N}_{13}\text{O}_2$: C, 21.20; H, 3.20; N, 64.29. Found: C, 21.41; H, 3.29; N, 63.93.

Synthesis of compound 11. Compound **8** (0.5 g, 2.9 mmol) was dissolved in water and sulfuric acid (10% in water) was added dropwise. The resulting reaction mixture was stirred at room temperature for 1 h. The yellow solid (**11**) was filtered off, washed with water and dried. Isolated yield: (0.39 g, 86%); $T_{\text{dec.}} = 152\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, $\text{d}_6\text{-DMSO}$): 12.9 (s, 1H), 8.41 (s, 2H);

^{13}C NMR (125 MHz, d_6 -DMSO): 162.7, 154.8; IR ($\tilde{\nu}$, cm^{-1}): 3324, 3199, 1643, 1612, 1521, 1467, 1431, 1323, 1268, 1072, 1010, 980, 868, 816, 750, 705; Elemental analysis: Calcd for $\text{C}_2\text{H}_3\text{N}_7\text{O}_2$: C, 15.29; H, 1.92; N, 62.41. Found: C, 15.28; H, 2.13; N, 63.00.

Synthesis of compound 12. Compound **8** (0.5 g, 2.9 mmol) was dissolved in water and AgNO_3 (0.49 g, 2.9 mmol) was added in portions. The resulting reaction mixture was stirred at room temperature for 3 h. The red solid was filtered off, washed with water and dried. The dried Ag^+ salt was taken in water (50 mL) and the solution of $\text{N}_2\text{H}_4\cdot\text{HCl}$ (0.2 g, 2.9 mmol) in water was added. The resulting reaction mixture was stirred at room temperature for 3 h. The insoluble AgCl was filtered off and the remaining solution was evaporated to give an orange-red powder (**12**). Isolated yield: (0.35 g, 64%); $T_{\text{dec.}} = 135\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, d_6 -DMSO): 7.39 (s, 2H), 7.09 (s, 5H); ^{13}C NMR (125 MHz, d_6 -DMSO): 163.6, 161.7; IR ($\tilde{\nu}$, cm^{-1}): 3319, 3195, 1651, 1527, 1361, 1108, 1071, 964, 940, 891, 769, 573; Elemental analysis: Calcd for $\text{C}_2\text{H}_7\text{N}_9\text{O}_2$: C, 12.70; H, 3.73; N, 66.65. Found: C, 12.67; H, 3.42; N, 66.64.

Synthesis of compound 13. Compound **7** (0.3 g, 1.7 mmol) was dissolved in ethanol (10 mL) and gaseous ammonia until a red precipitate appeared. The red precipitate (**13**) was removed by filtration, washed with ethanol (2 x 10 mL) and dried. Isolated yield: (0.20 g, 63%); $T_{\text{dec.}} = 123\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, d_6 -DMSO): 8.96 (bs, 1H), 7.26 (bs, 4H), 3.56 (bs, 2H); ^{13}C NMR (125 MHz, d_6 -DMSO): 163.7, 162.3; IR ($\tilde{\nu}$, cm^{-1}): 3321, 3179, 1645, 1526, 1463, 1422, 1354, 1295, 1061, 1026, 977, 883, 848, 772; Elemental analysis: Calcd for $\text{C}_2\text{H}_7\text{N}_9\text{O}_2$: C, 12.70; H, 3.73; N, 66.65. Found: C, 12.75; H, 3.49; N, 66.78.

Section S2. X-ray crystallographic details and crystallographic data

Section S2.1. Sample preparation

The single crystals of compounds **5**, **9**·H₂O and **11** suitable for single-crystal X-ray analysis were obtained from CH₃OH:H₂O mixtures.

Section S2.2. 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 ShelXT³ solution program using dual methods and by using Olex2.⁴ The model was refined with ShelXL⁵ 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.

Section S2.3. Crystal structures and crystallographic data.

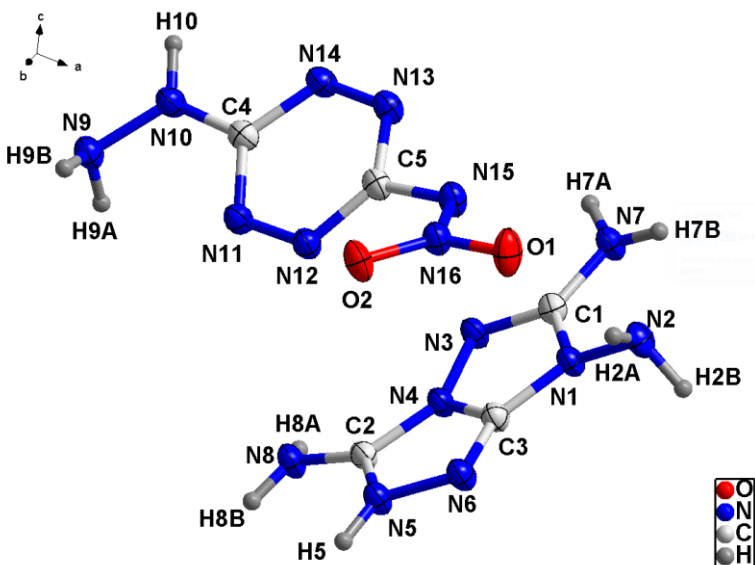


Figure S1: Thermal ellipsoid plot for compound **5**. Thermal ellipsoids are drawn at 50% probability level. Data collected at 100 K. CCDC # 2378050.

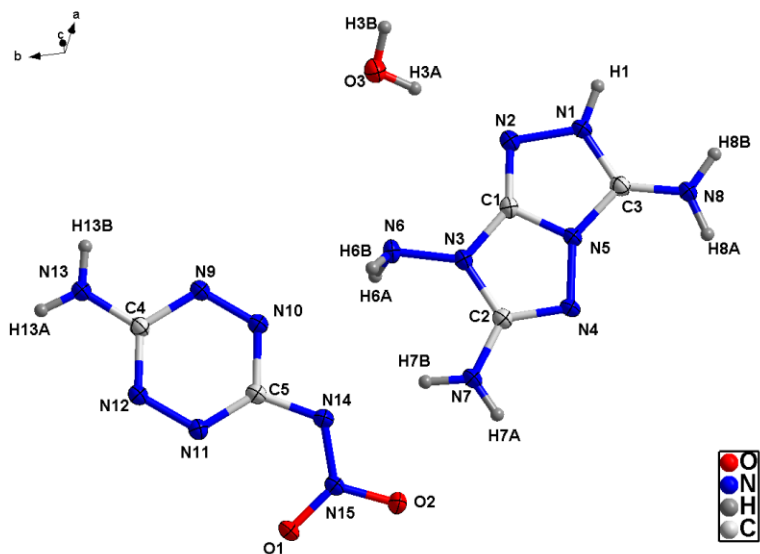


Figure S2: Thermal ellipsoid plot for compound **9**·H₂O. Thermal ellipsoids are drawn at 50% probability level. Data collected at 100 K. CCDC # 2378051.

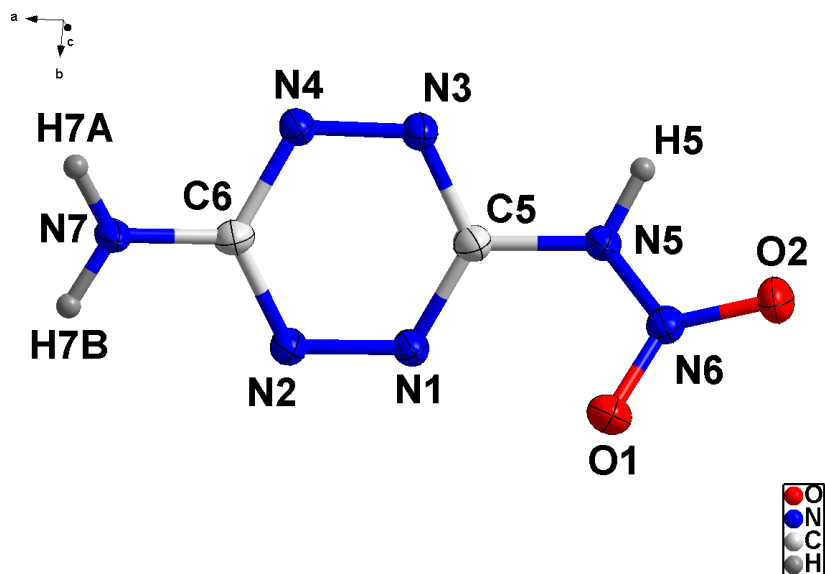


Figure S3: Thermal ellipsoid plot for compound **11**. Thermal ellipsoids are drawn at 50% probability level. Data collected at 100 K. CCDC # 2378052.

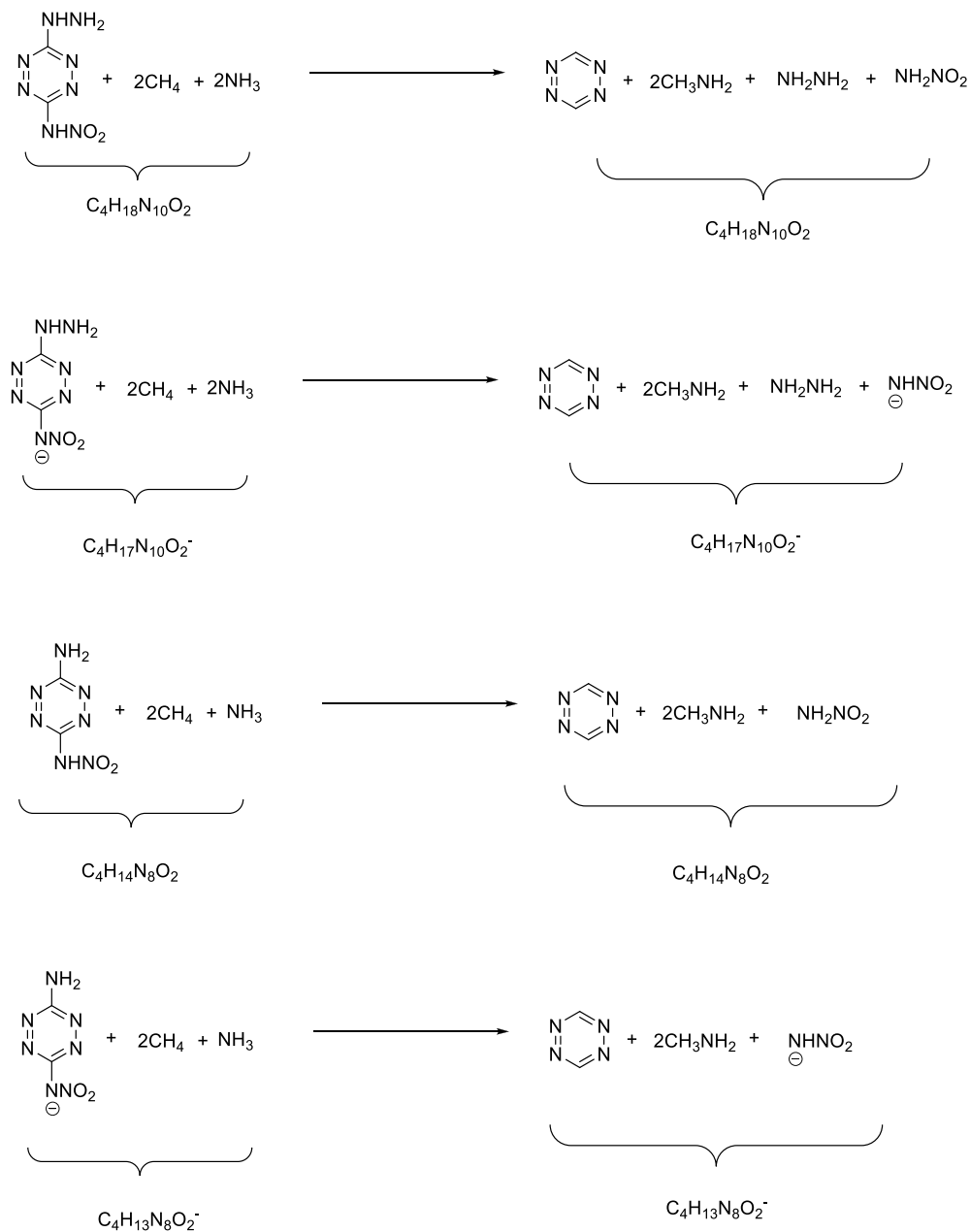
Table S1: Crystallographic data for **5**, **9·H₂O** and **11**.

Compound	5	9·H₂O	11
CCDC #	2378050	2378051	2378052
Formula	C ₅ H ₁₀ N ₁₆ O ₂	C ₅ H ₁₁ N ₁₅ O ₃	C ₂ H ₃ N ₇ O ₂
<i>D</i> _{calc.} / g cm ⁻³	1.798	1.805	1.868
<i>m</i> /mm ⁻¹	1.272	1.309	1.433
Formula Weight	326.29	329.29	157.11
Color	reddish yellow	red	yellow
Shape	needle-shaped	prism-shaped	plate-shaped
Size/mm ³	0.35×0.06×0.01	0.18×0.14×0.07	0.14×0.11×0.02
<i>T</i> /K	100.00(10)	99.99(10)	100.00(10)
Crystal System	triclinic	triclinic	orthorhombic
Flack Parameter	-	-	-
Hooft Parameter	-	-	-
Space Group	<i>P</i> -1	<i>P</i> -1	<i>Pbca</i>
<i>a</i> /Å	7.5670(4)	7.8417(3)	9.3390(3)
<i>b</i> /Å	8.0991(5)	8.7831(3)	7.8421(3)
<i>c</i> /Å	10.3845(5)	9.5513(4)	15.2539(6)
<i>α</i> [°]	75.305(5)	102.593(3)	90
<i>β</i> [°]	87.190(4)	102.923(3)	90
<i>γ</i> [°]	78.201(5)	100.960(3)	90
<i>V</i> /Å ³	602.60(6)	605.70(4)	1117.15(7)
<i>Z</i>	2	2	8
<i>Z</i> '	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K _α	Cu K _α	Cu K _α
<i>Q</i> _{min} [°]	4.402	4.937	5.801
<i>Q</i> _{max} [°]	79.562	77.706	78.965
Measured Refl's.	8176	7580	6601
Indep't Refl's	2563	2488	1187
Refl's I≥2 <i>s</i> (I)	2227	2215	1013
<i>R</i> _{int}	0.0403	0.0321	0.0399
Parameters	248	252	112
Restraints	0	0	0
Largest Peak	0.314	0.243	0.396
Deepest Hole	-0.346	-0.274	-0.269
GooF	1.052	1.045	1.041
<i>wR</i> ₂ (all data)	0.1326	0.1060	0.1494
<i>wR</i> ₂	0.1273	0.1027	0.1393
<i>R</i> ₁ (all data)	0.0497	0.0410	0.0588
<i>R</i> ₁	0.0443	0.0371	0.0518

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.⁶ The atomization energies for cations were calculated by using the *G²ab initio* method.⁷ 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.⁸

Section S3.2. Gas-phase enthalpy of formation to solid state enthalpy of formation

The gas state ΔH_f of compounds **7** and **11** are 575.1 and 479.3 kJ mol⁻¹, respectively.

All calculated gas-phase enthalpies for covalent materials are converted to solid phase values by subtracting the empirical heat of sublimation obtained based on Trouton's rule.⁹

$$\text{For } \mathbf{7}: \Delta H_{\text{sub}} (\text{kJ mol}^{-1}) = 0.188 \cdot (273+139) = 77.5 \text{ kJ mol}^{-1}$$

$$\text{For } \mathbf{11}: \Delta H_{\text{sub}} (\text{kJ mol}^{-1}) = 0.188 \cdot (273+175) = 84.2 \text{ kJ mol}^{-1}$$

Table S2: Solid state ΔH_f for compounds **7** and **11** using Trouton's rule.

	ΔH_f (g) kJ mol ⁻¹	ΔH_{sub} kJ mol ⁻¹	ΔH_f (s) kJ mol ⁻¹
7	575.1	77.5	497.6
11	479.3	84.2	395.1

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. G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* 2008, **64**, 112–122.
4. G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* 2015, **71**, 3–8.
5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339–341.
6. R. G. Parr, Y. Weitao, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, 1995).
7. O. Suleimenov, T.-K. Ha, *Chem. Phys. Lett.* 1998, **290**, 451–457.
8. H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* 2002, **41**, 2364–2367.
9. M. S. Westwell, M. S. Searle, D. J. Wales, D. H. Williams, *J. Am. Chem. Soc.* 1995, **117**, 5013–5015.

Section S5. Spectral Analysis

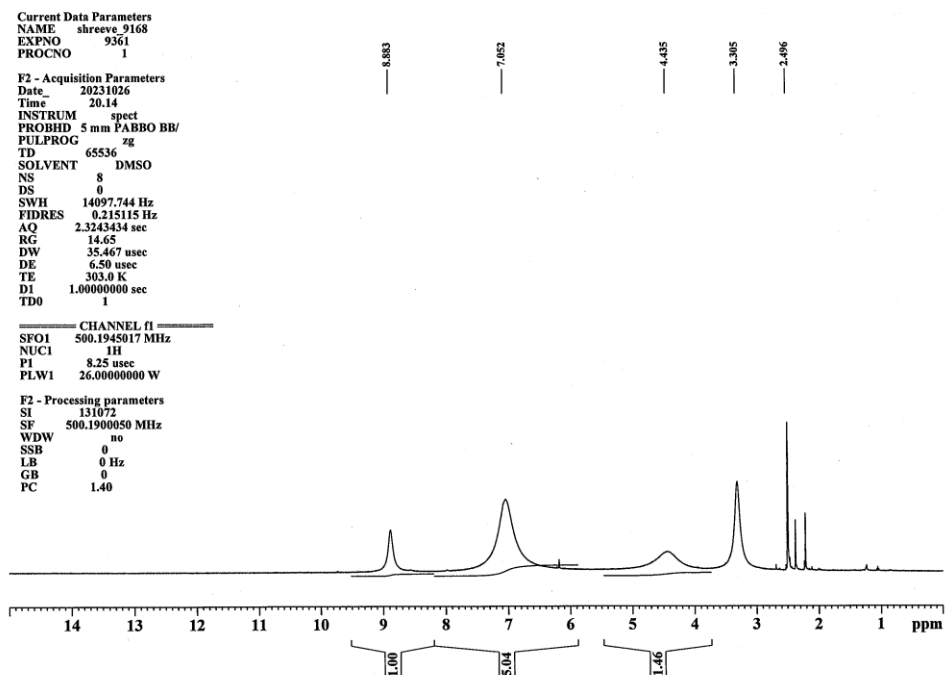


Figure S4: ^1H NMR spectrum of 4.

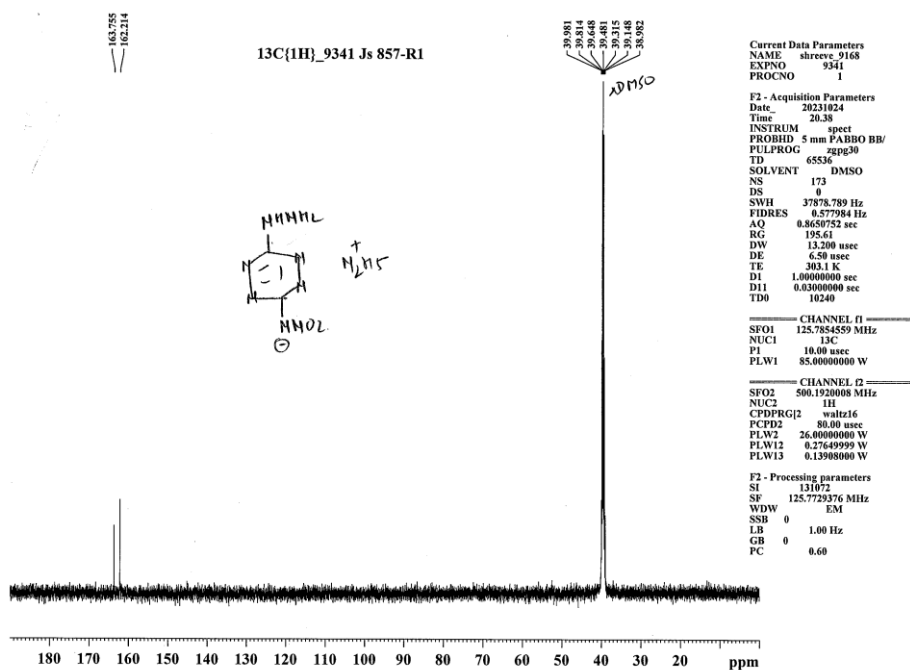


Figure S5: ^{13}C NMR spectrum of 4.

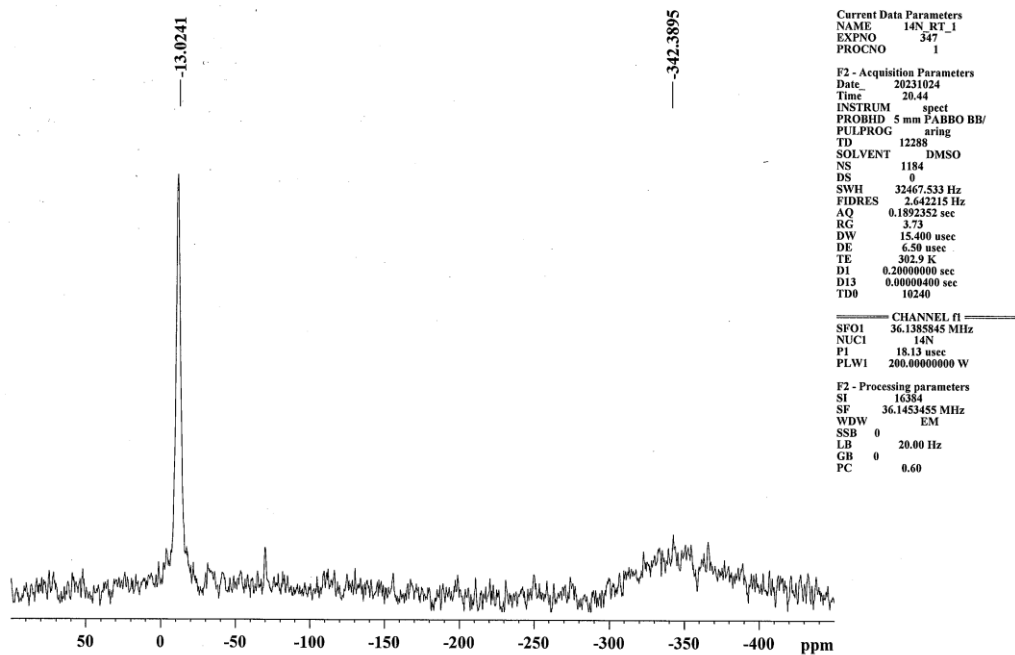


Figure S6: ^{14}N NMR spectrum of compound 4.

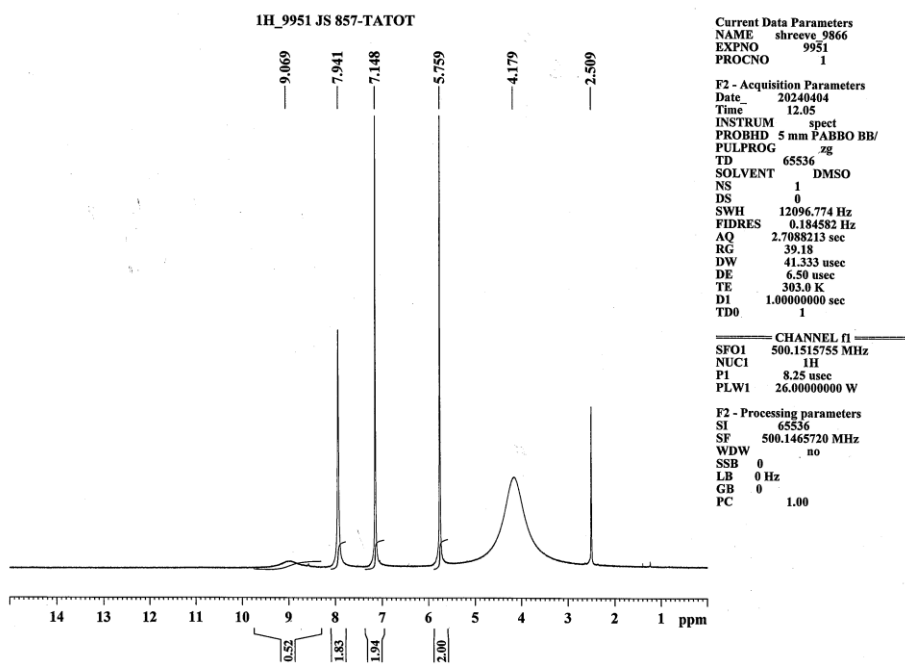


Figure S7: ^1H NMR spectrum of 5.

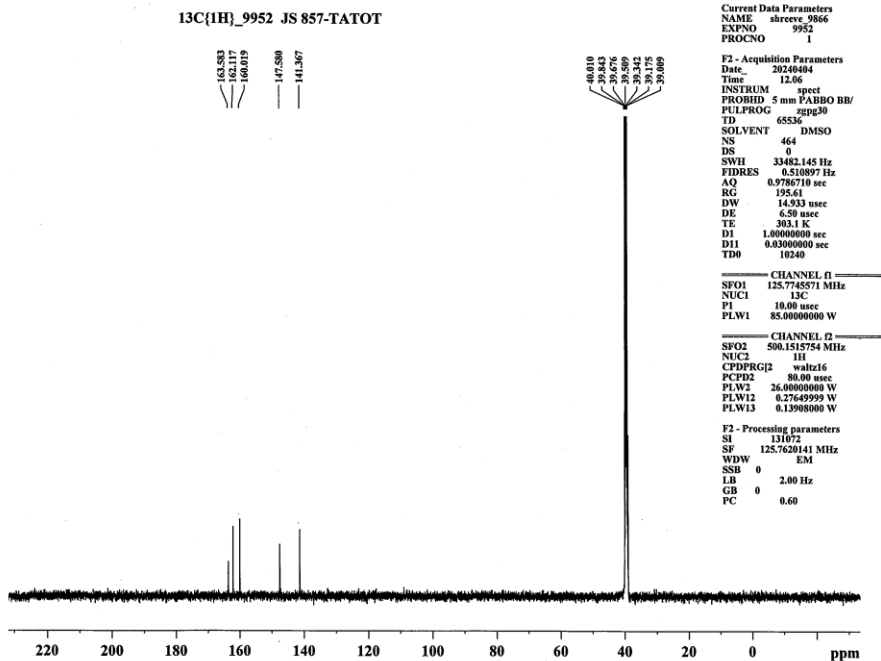


Figure S8: ^{13}C NMR spectrum of 5.

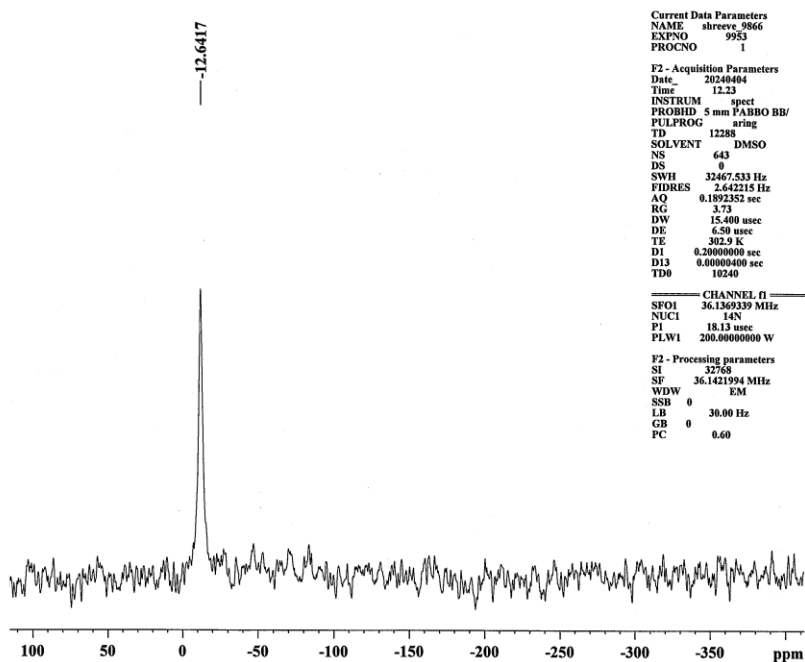


Figure S9: ^{14}N NMR spectrum of compound 5.

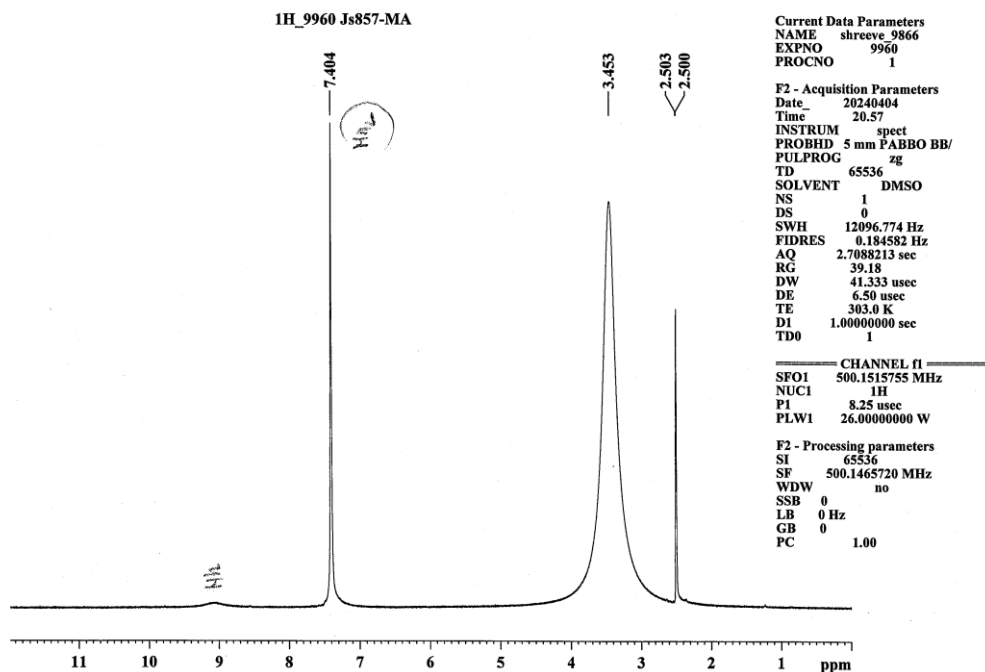


Figure S10: ¹H NMR spectrum of 6.

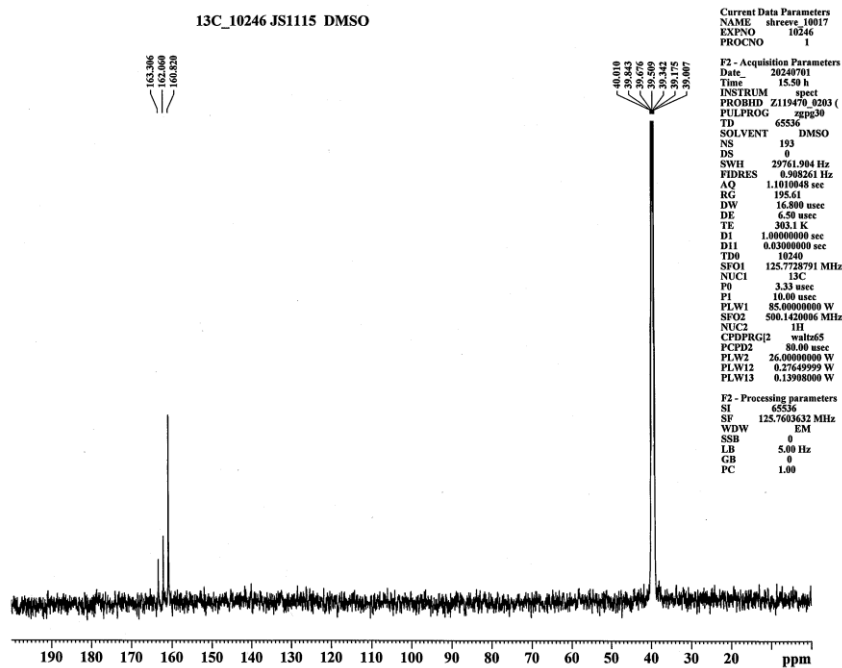


Figure S11: ¹³C NMR spectrum of 6.

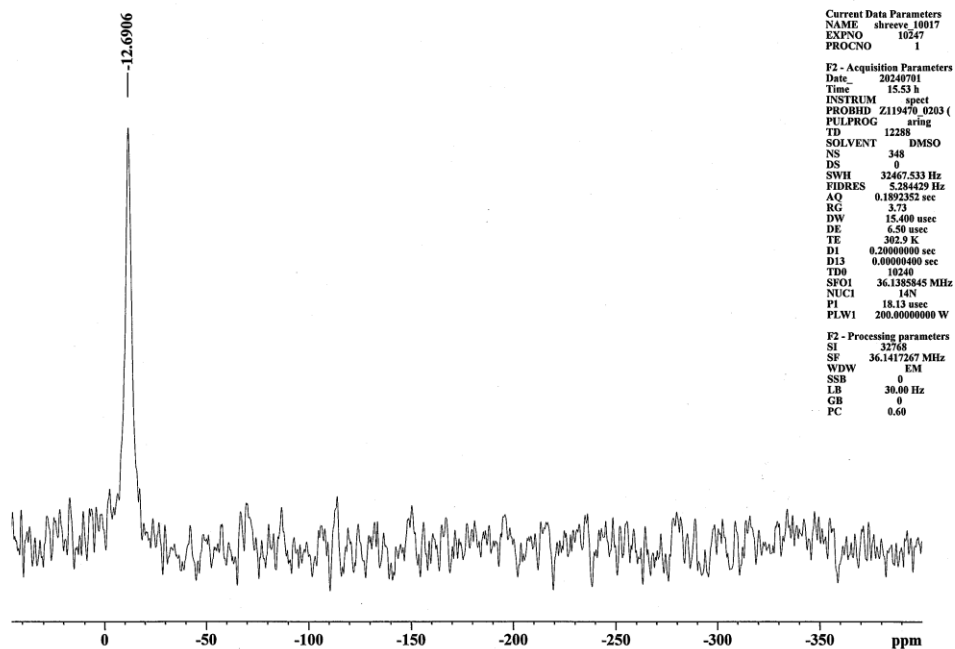


Figure S12: ^{14}N NMR spectrum of compound 6.

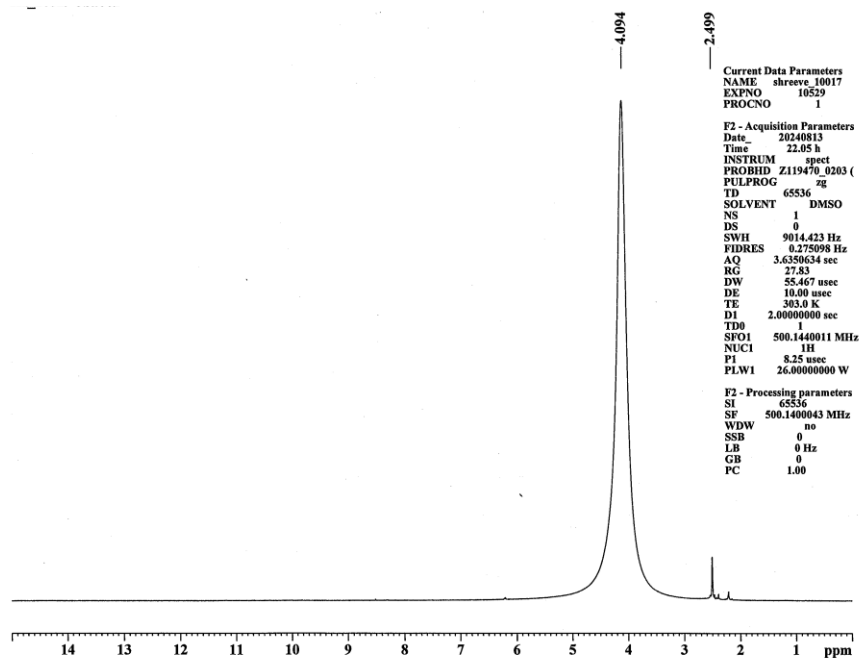


Figure S13: ^1H NMR spectrum of 7.

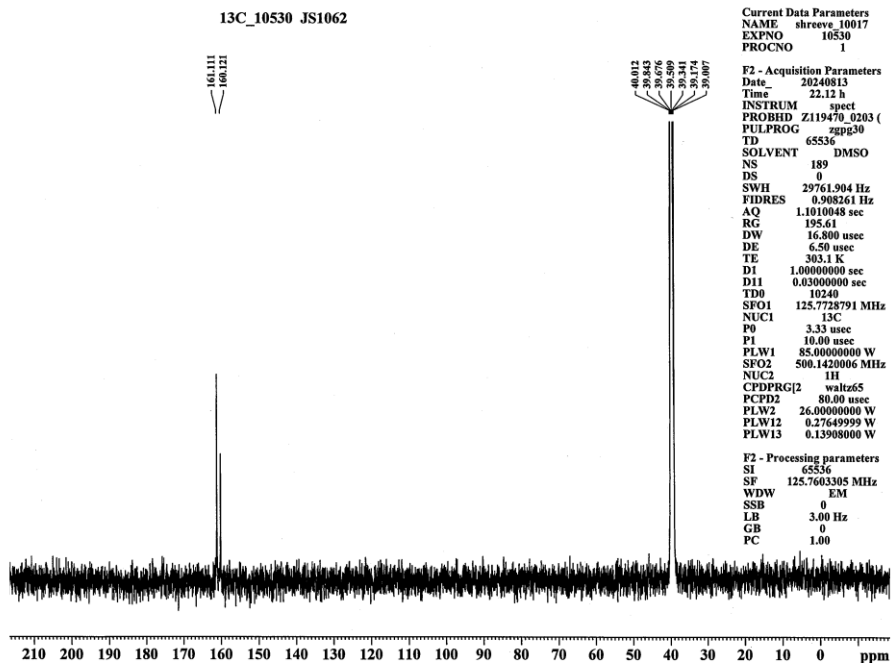


Figure S14: ^{13}C NMR spectrum of 7.

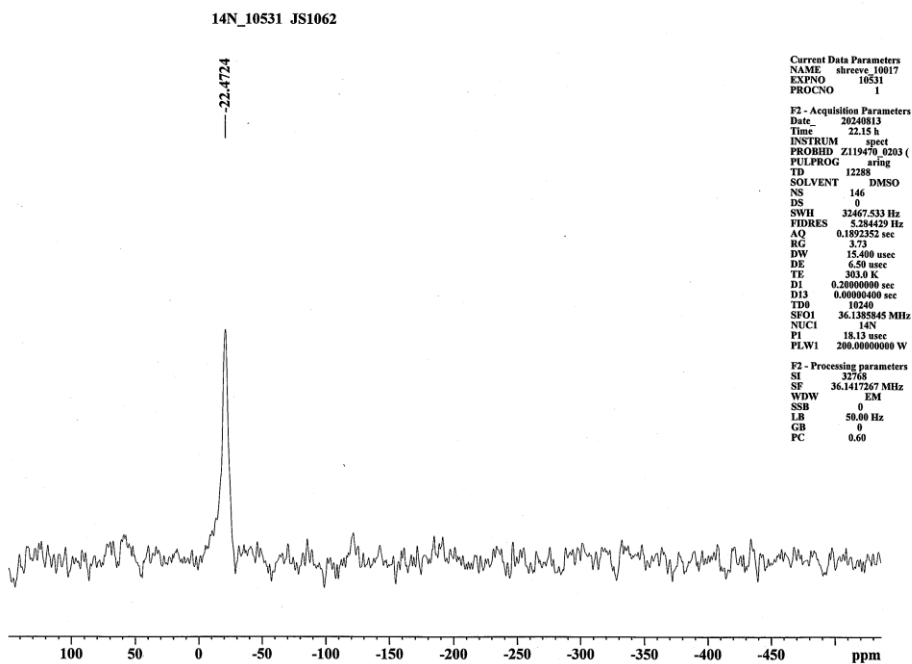


Figure S15: ^{14}N NMR spectrum of compound 7.

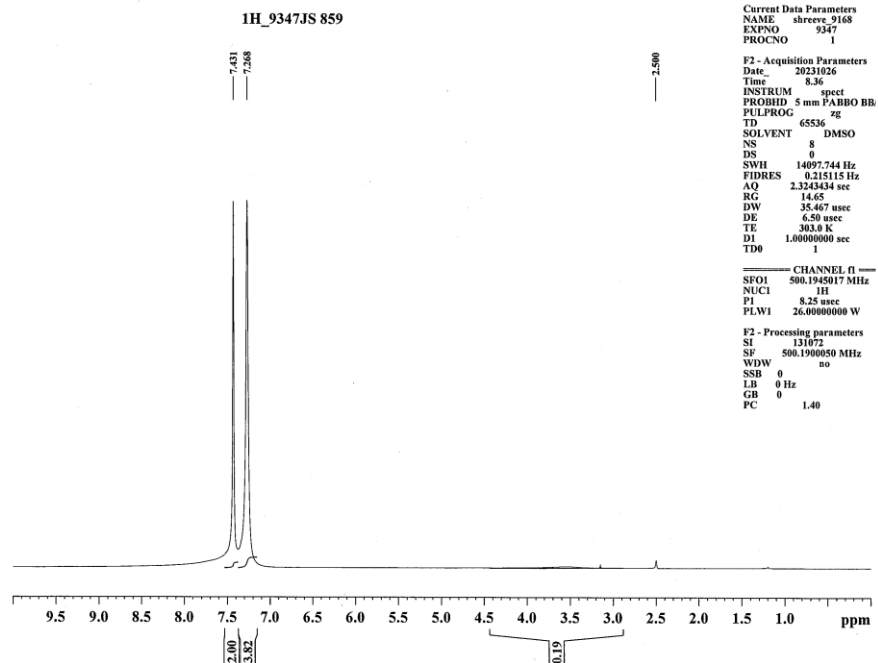


Figure S16: ¹H NMR spectrum of **8**.

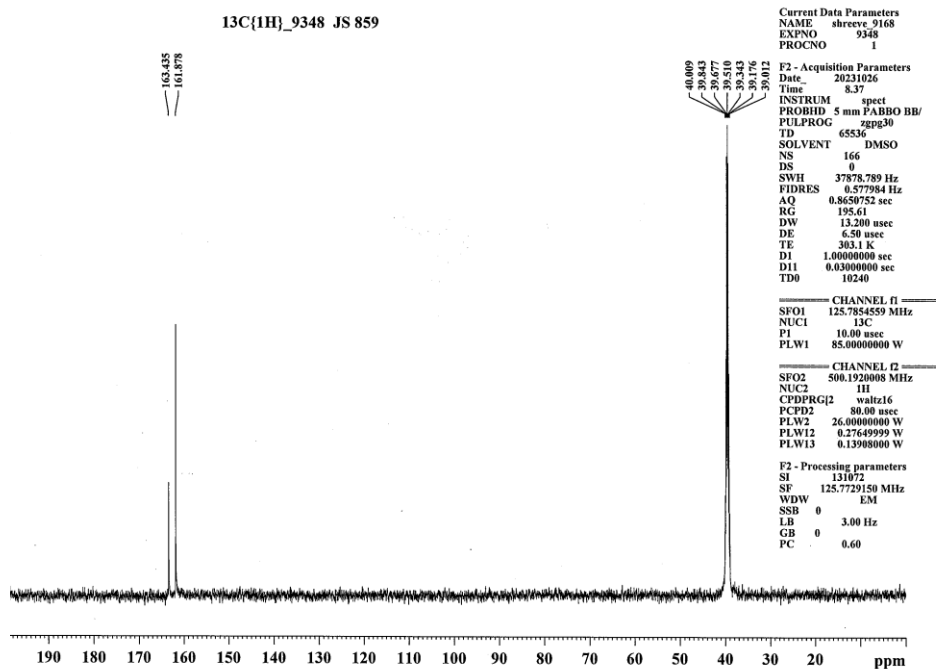


Figure S17: ¹³C NMR spectrum of **8**.

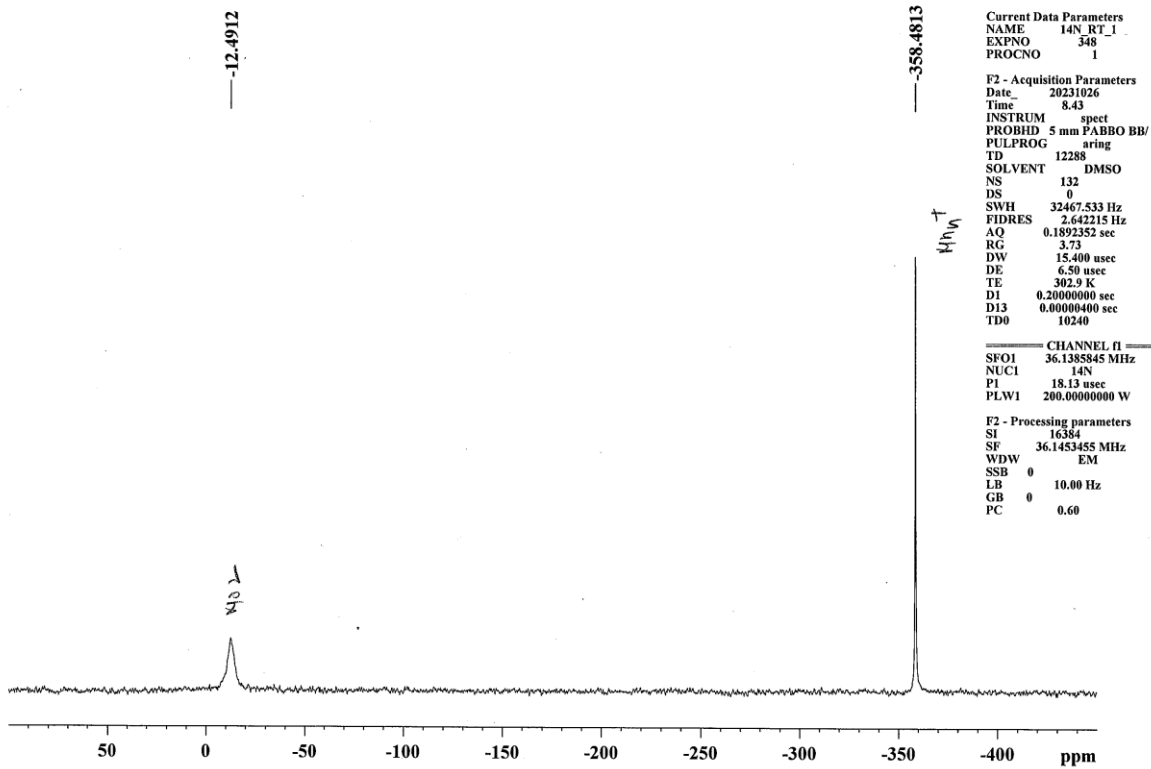


Figure S18: ^{14}N NMR spectrum of compound 8.

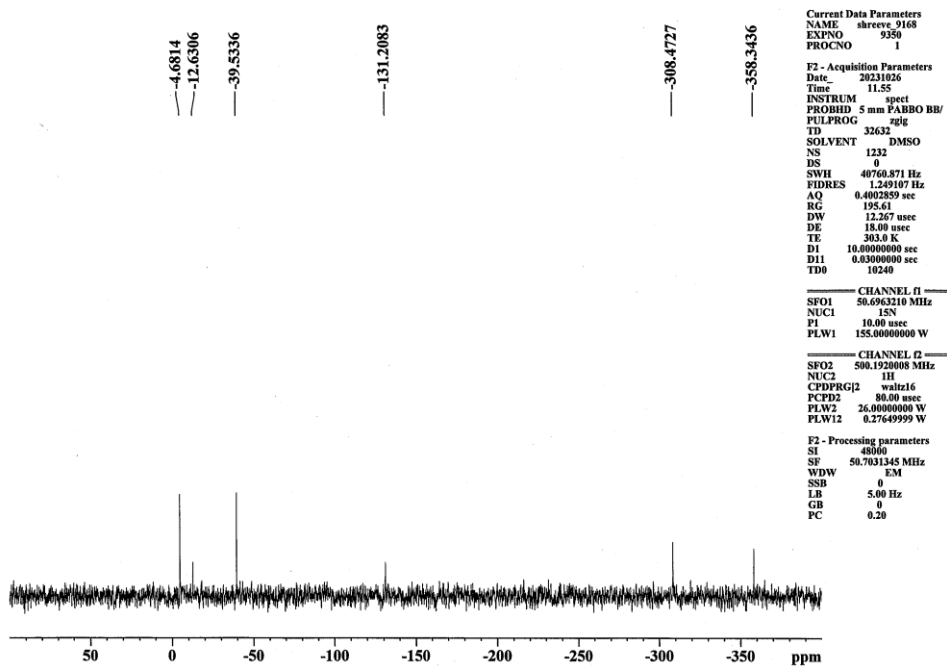


Figure S19: ^{15}N NMR spectrum of compound 8.

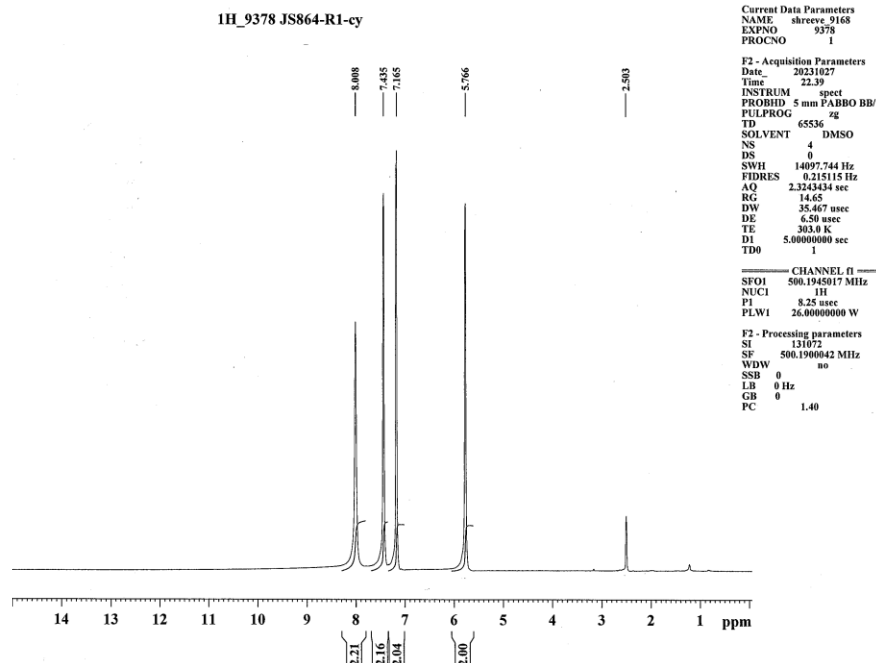


Figure S20: ¹H NMR spectrum of 9.

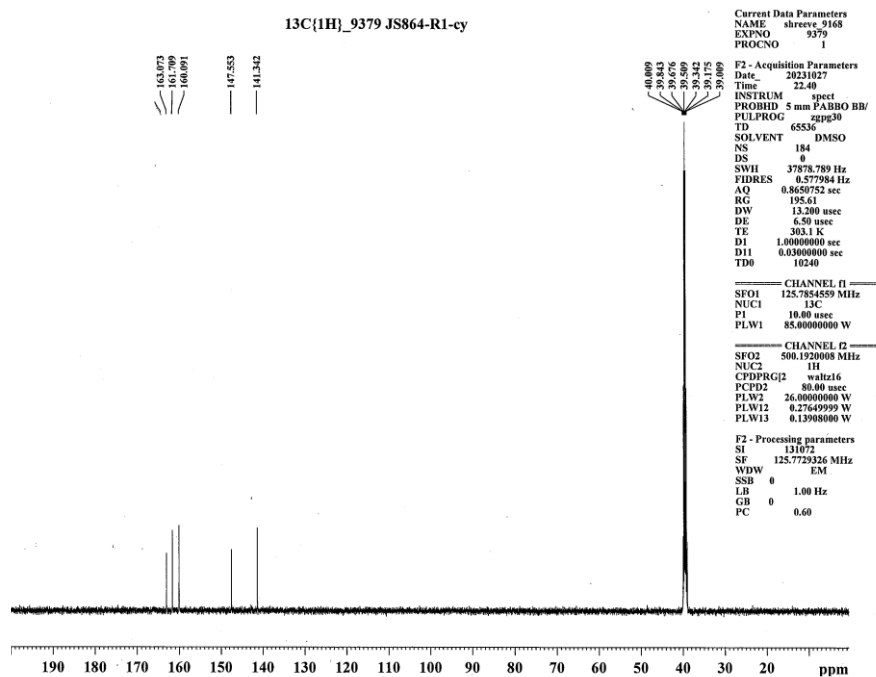


Figure S21: ¹³C NMR spectrum of 9.

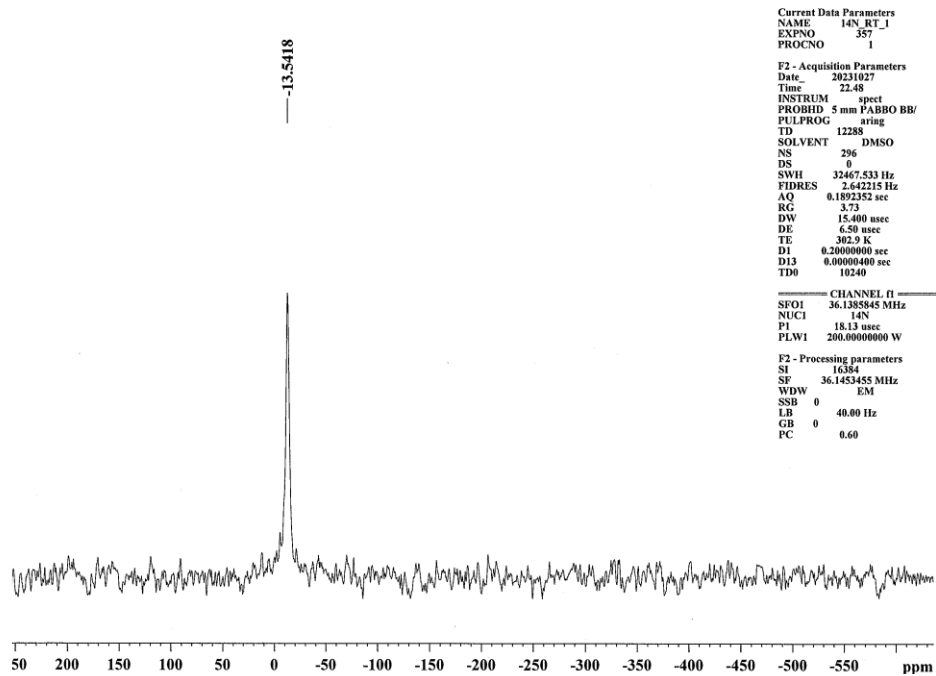


Figure S22: ^{14}N NMR spectrum of compound 9.

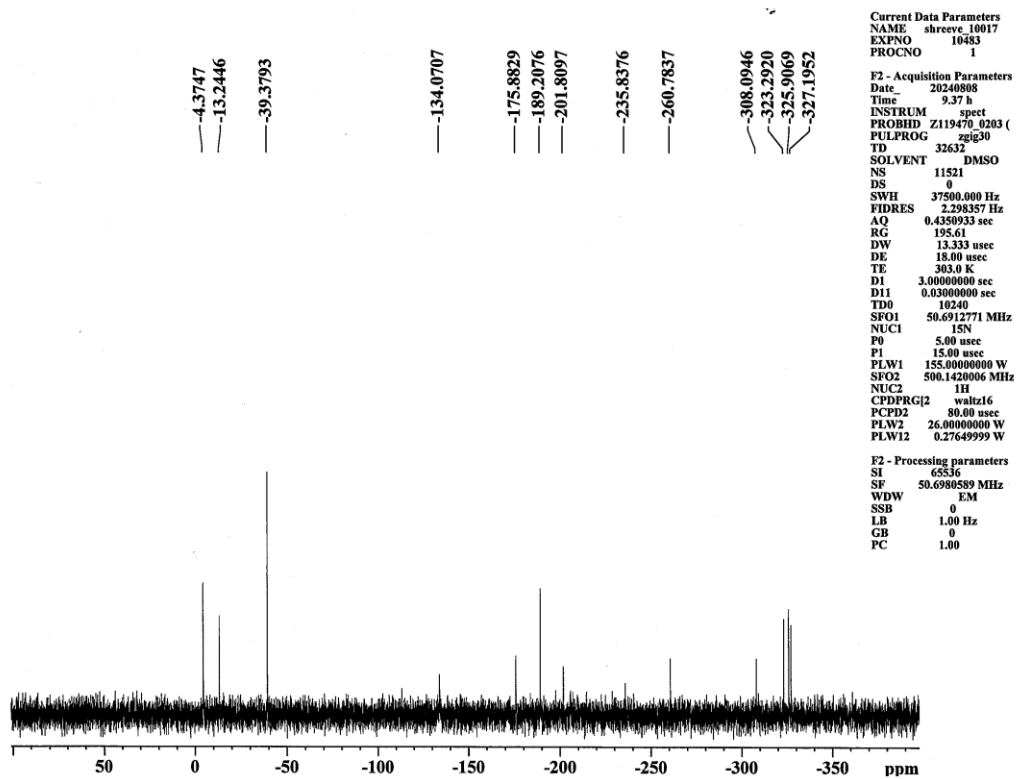


Figure S23: ^{15}N NMR spectrum of compound 9.

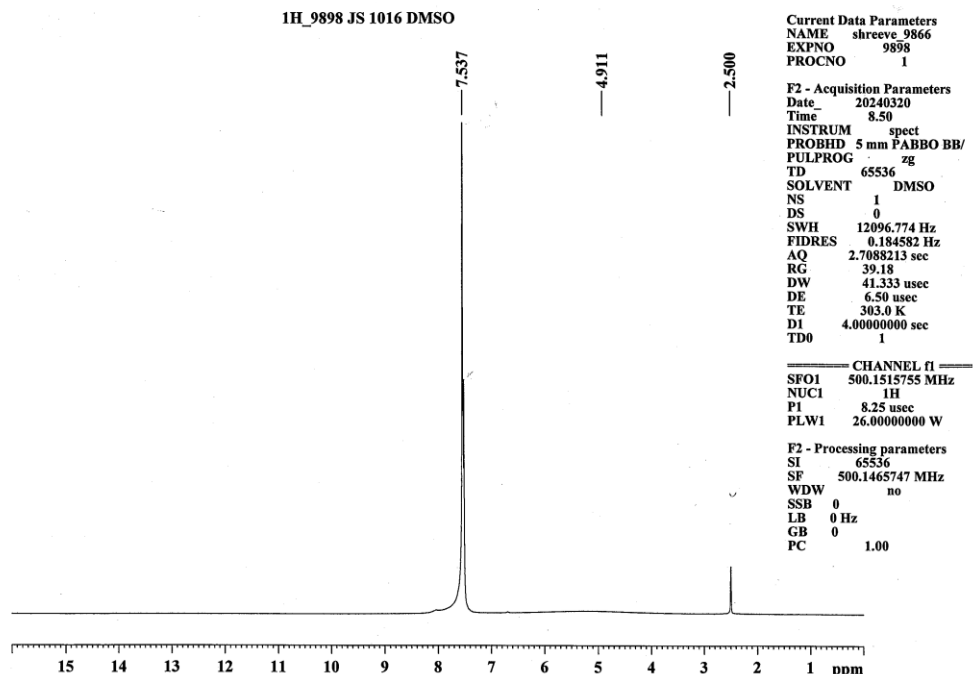


Figure S24: ¹H NMR spectrum of 10.

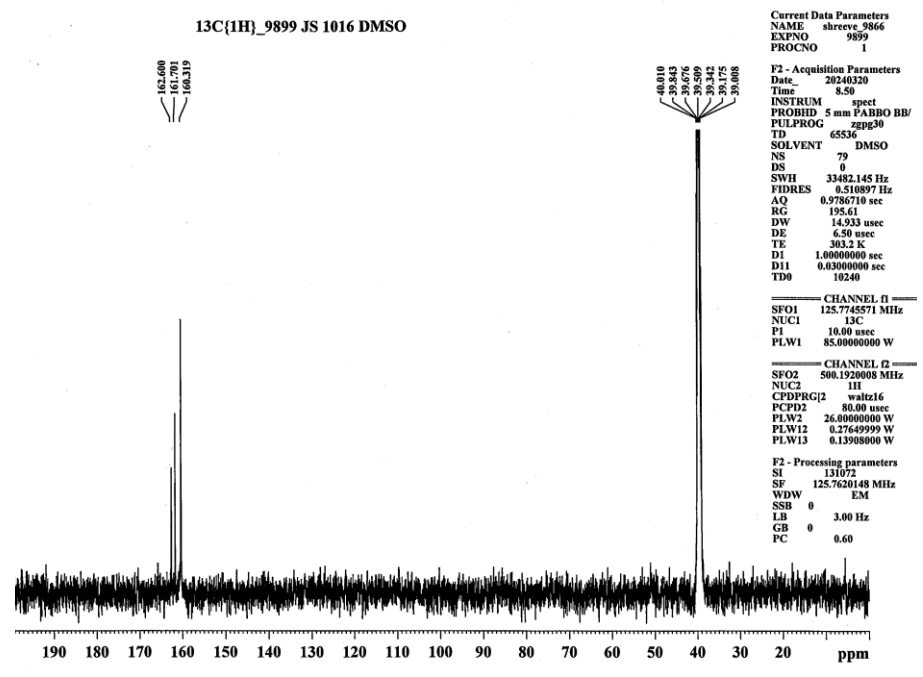


Figure S25: ¹³C NMR spectrum of 10.

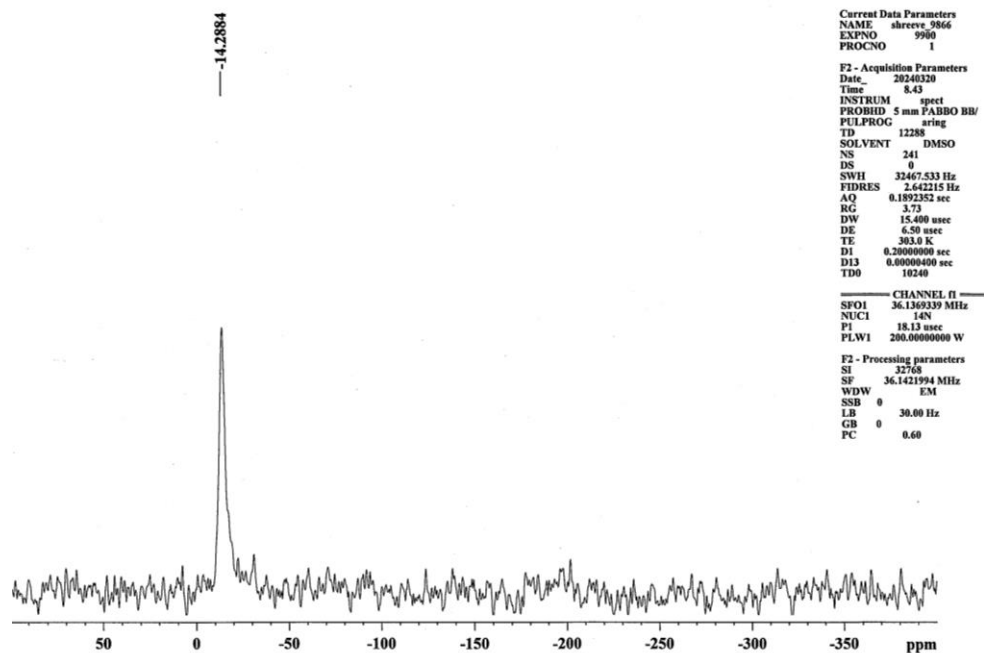


Figure S26: ^{14}N NMR spectrum of compound 10.

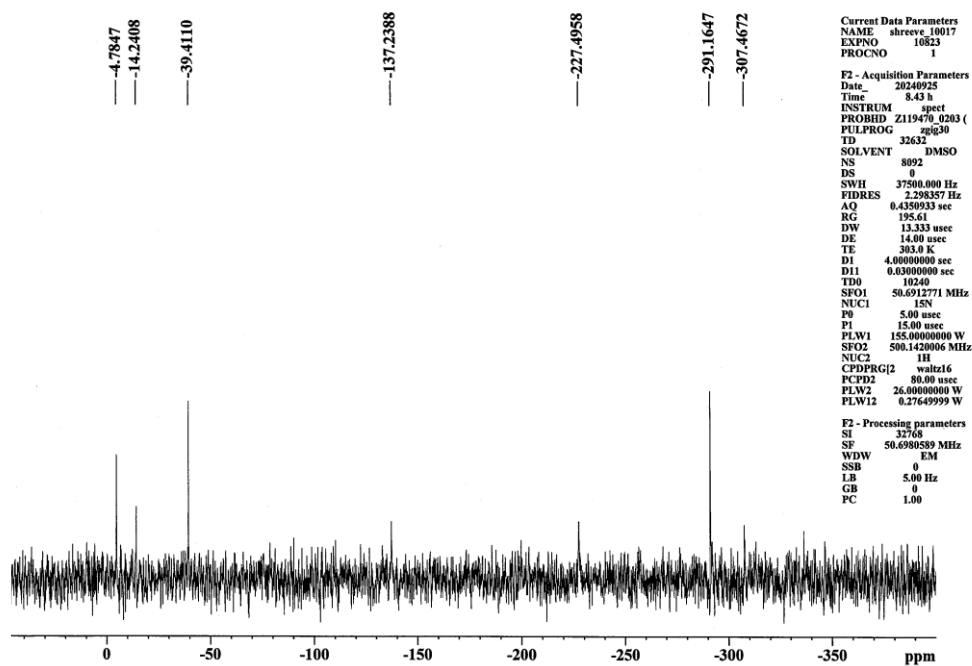


Figure S27: ^{15}N NMR spectrum of compound 10.

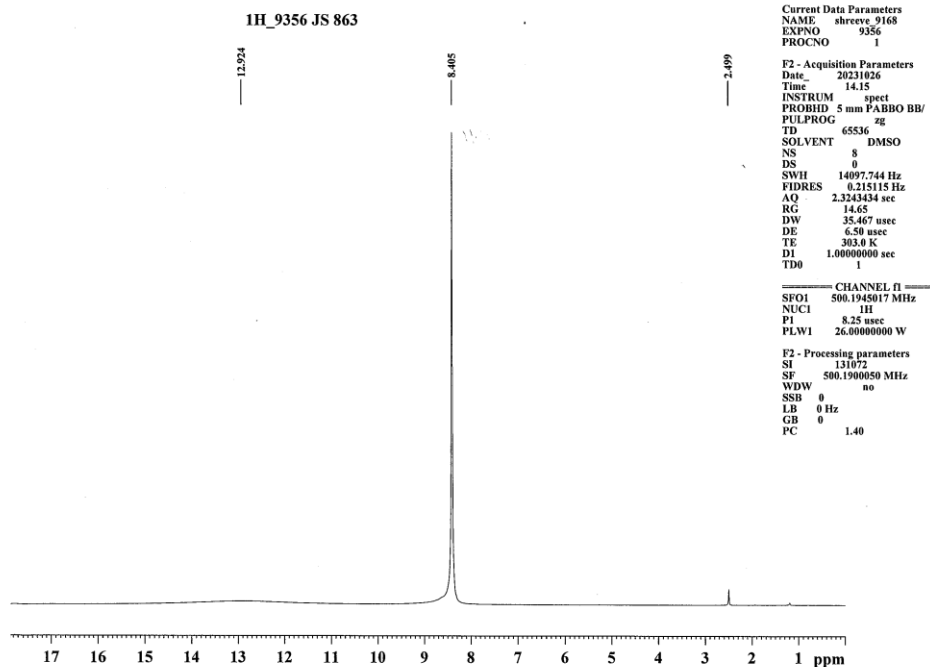


Figure S28: ^1H NMR spectrum of 11.

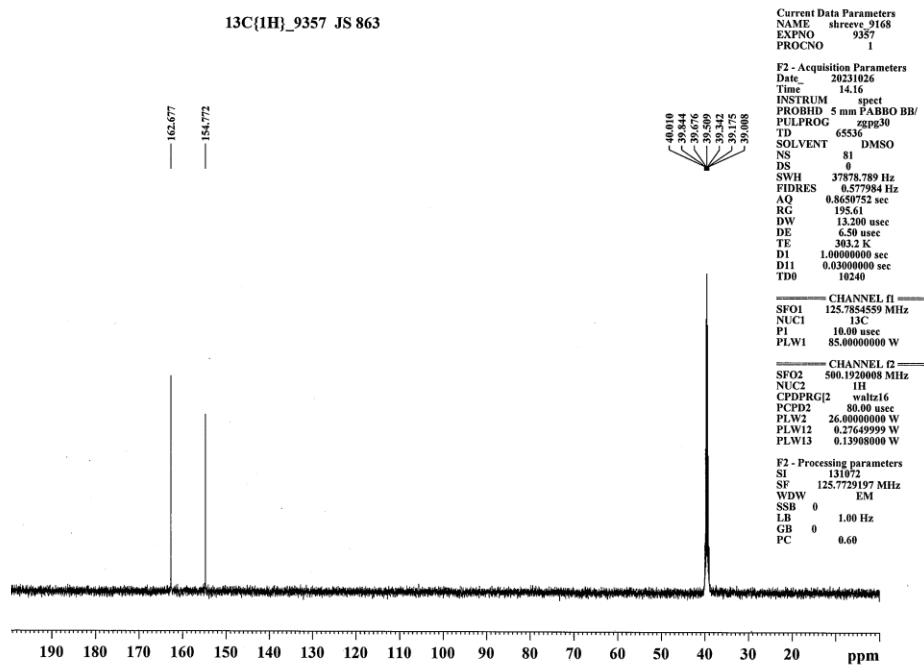


Figure S29: ^{13}C NMR spectrum of 11.

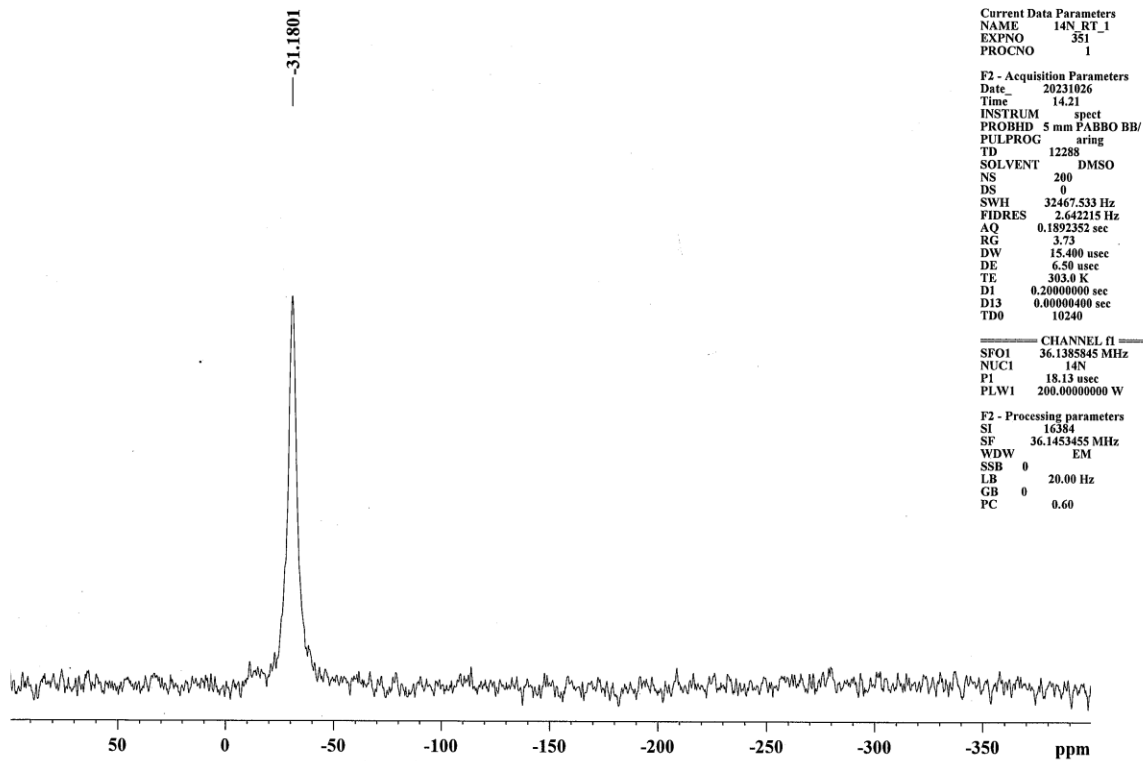


Figure S30: ^{14}N NMR spectrum of compound 11.

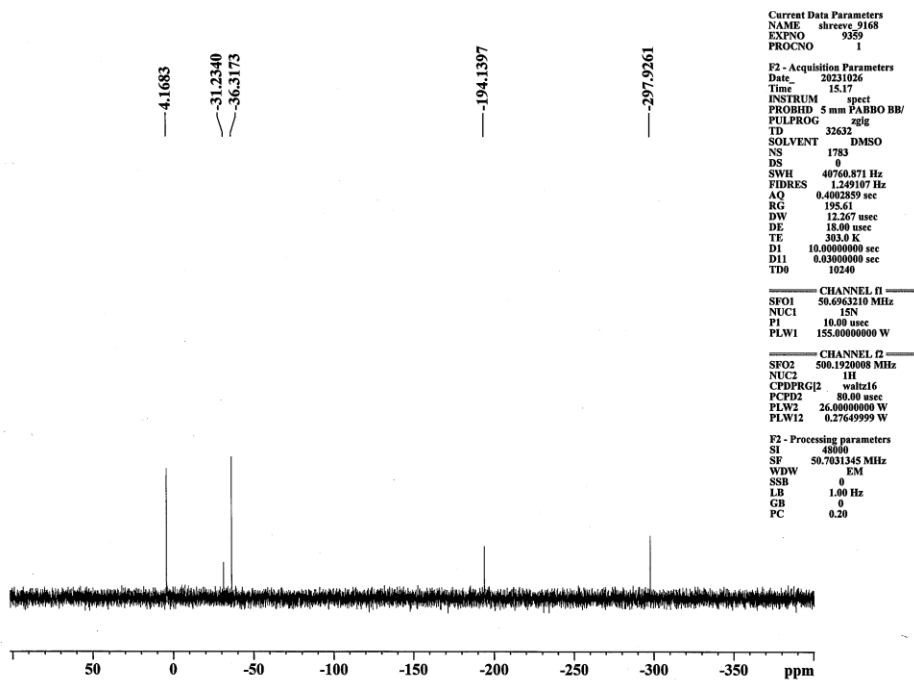


Figure S31: ^{15}N NMR spectrum of compound 11.

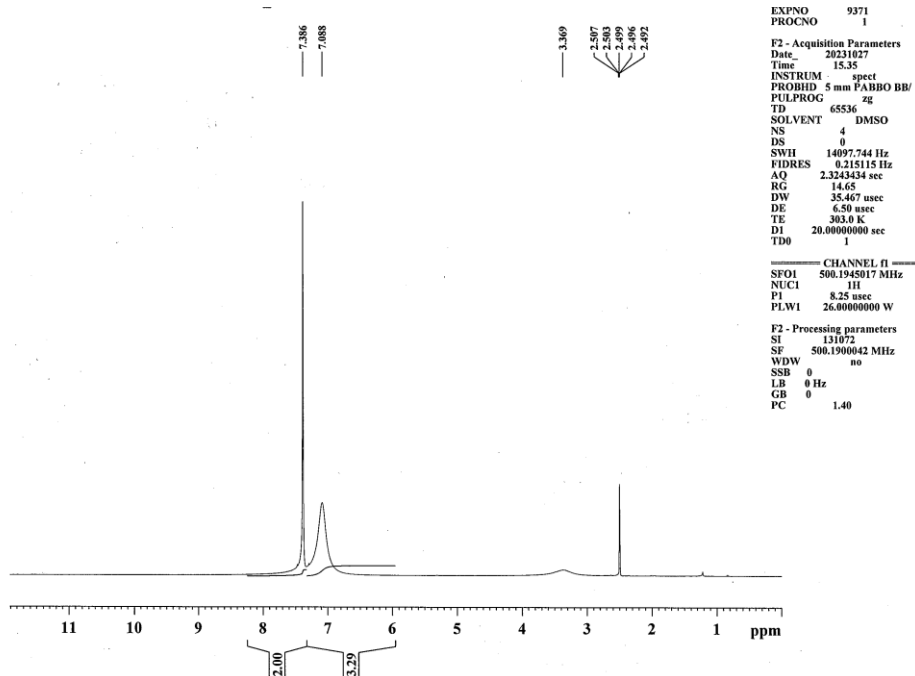


Figure S32: ¹H NMR spectrum of 12.

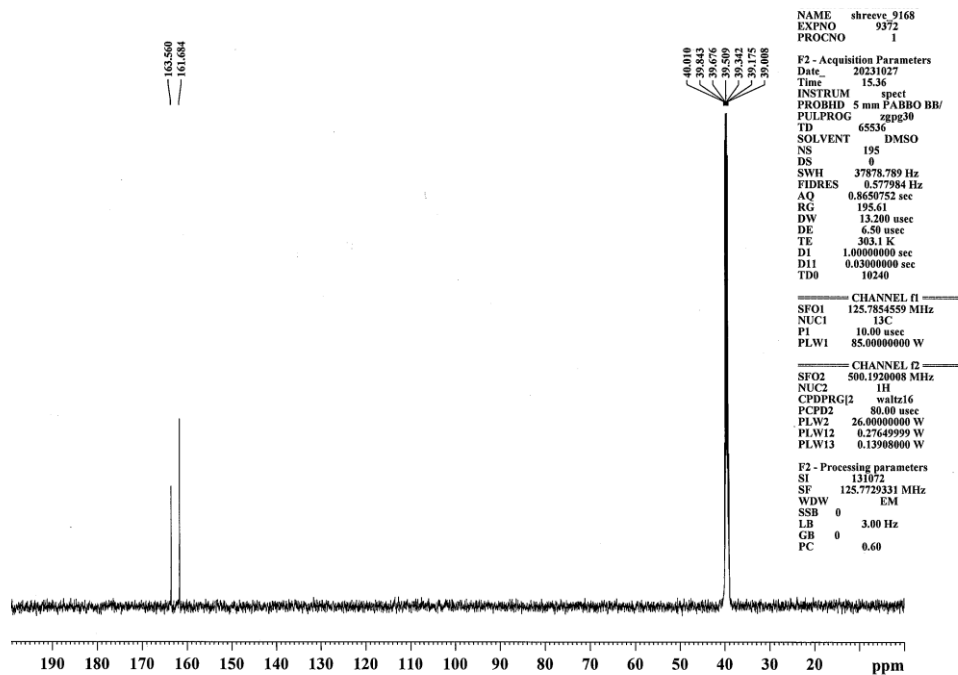


Figure S33: ¹³C NMR spectrum of 12.

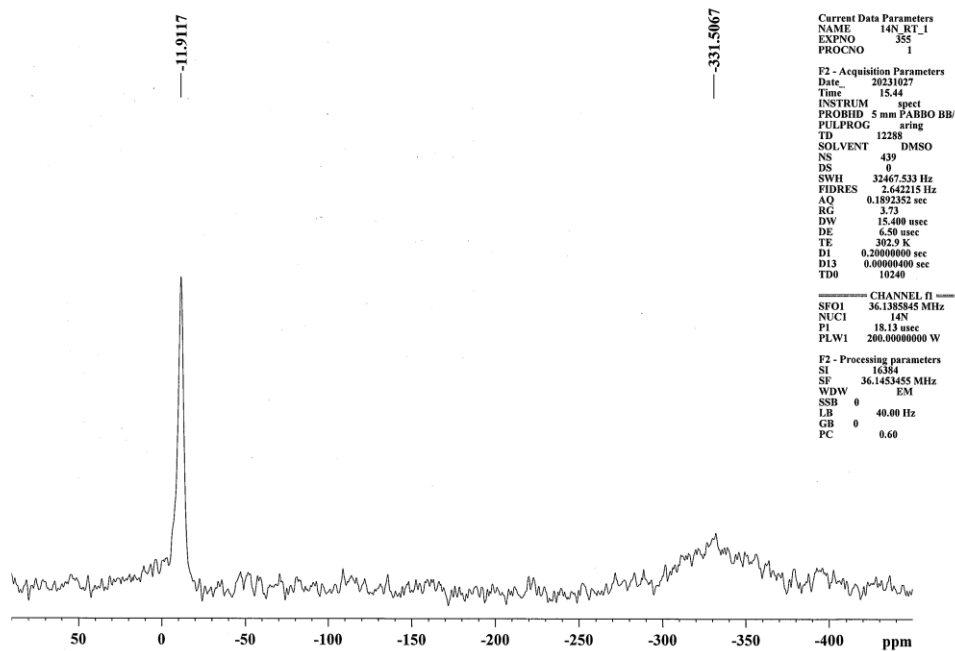


Figure S34: ^{14}N NMR spectrum of compound 12.

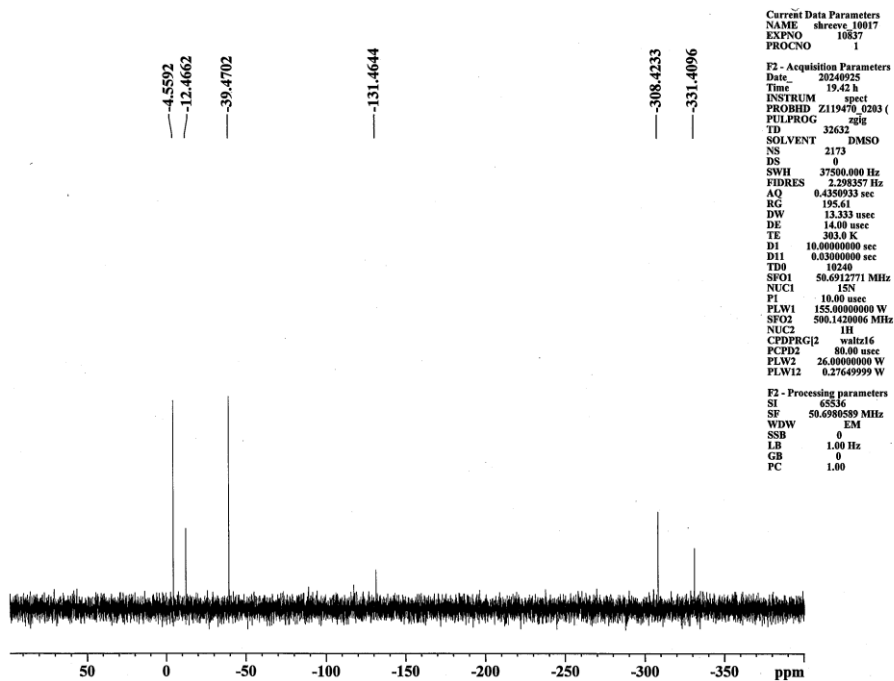


Figure S35: ^{15}N NMR spectrum of compound 12.

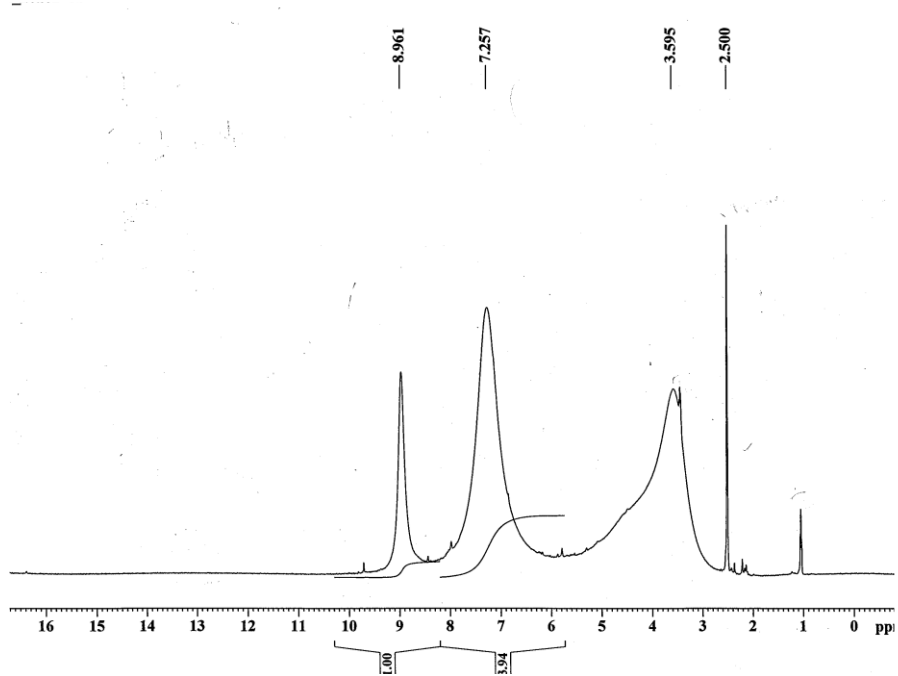


Figure S36: ^1H NMR spectrum of 13.

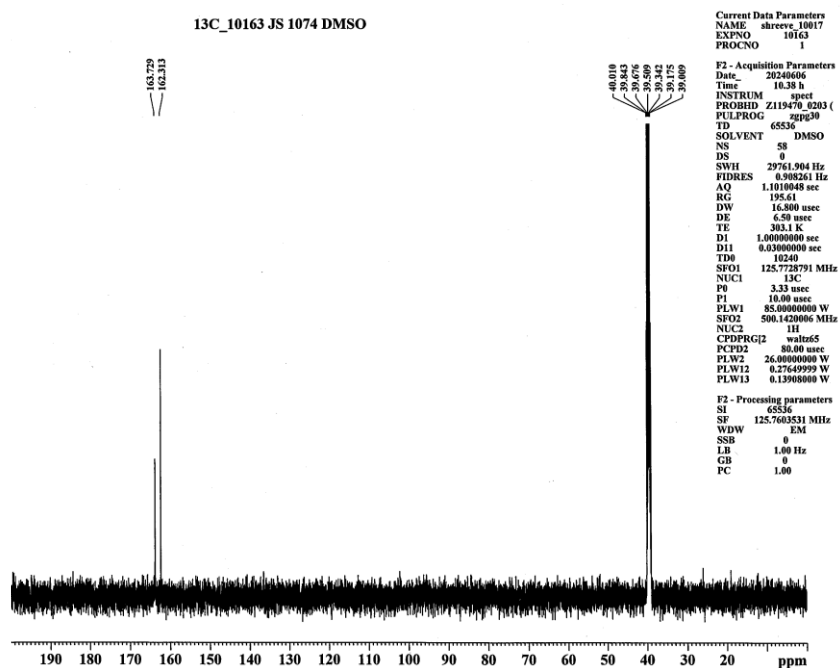


Figure S37: ^{13}C NMR spectrum of 13.

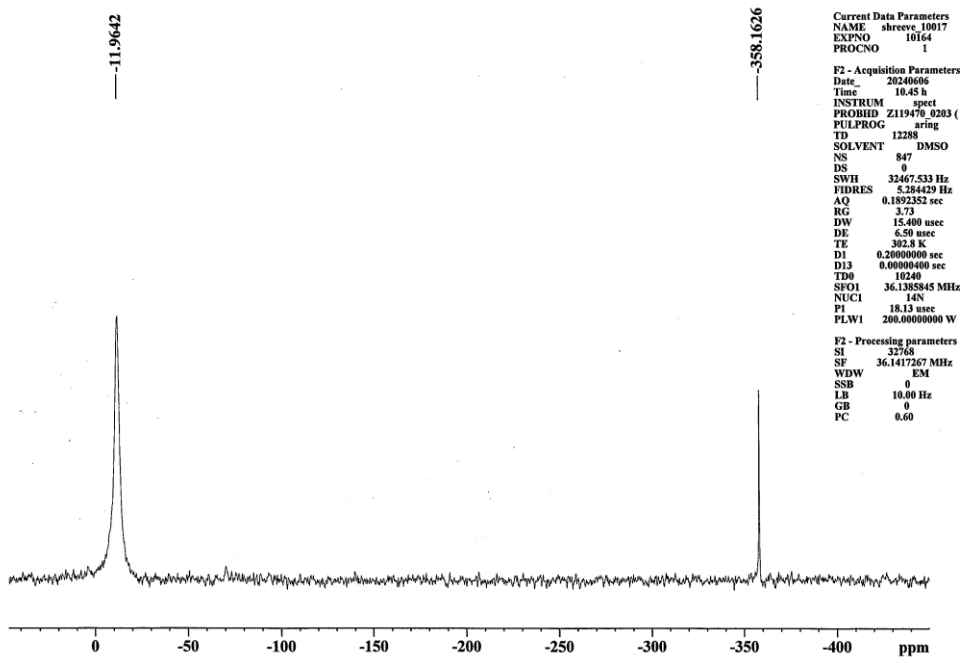


Figure S38: ^{14}N NMR spectrum of compound 13.

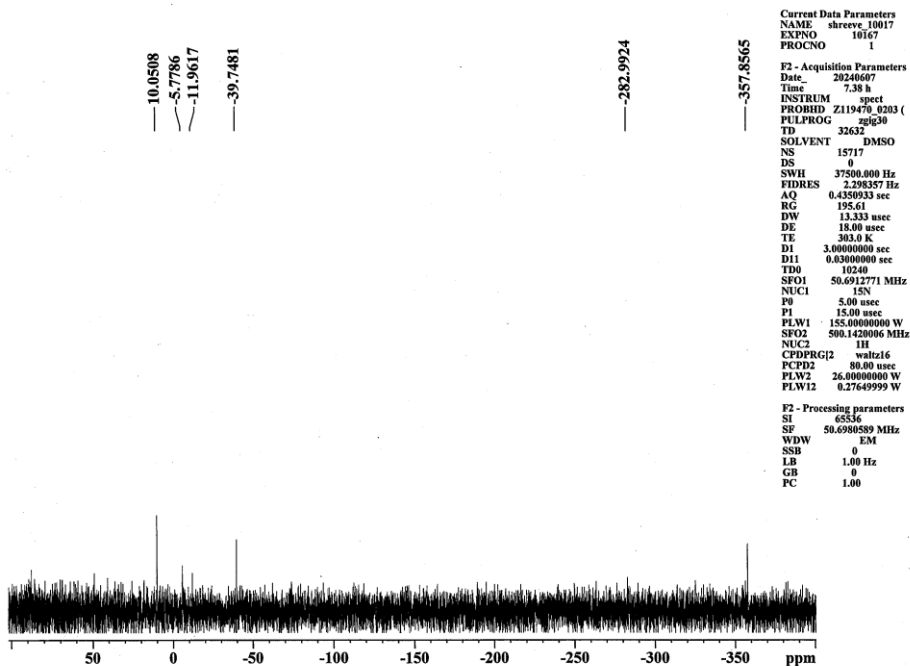


Figure S39: ^{15}N NMR spectrum of compound 13.