Electronic Supplementary Information

Thermally Driven Tetrazine-to-Triazole Ring Contraction Mediated by Hydroxylammonium Cations

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. Wear personal protective equipment while handing hydrazine hydrate and use only 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. P1 was obtained following literature procedures.[1]

Synthesis of 1. To a stirred solution of **P1** (0.63 g, 4.0 mmol, 1.0 equiv.) in ethyl acetate (30 mL) at room temperature, a solution of NH_3 (2.0 equiv) in methanol (10 mL) was added. The resulting reaction mixture was stirred at room temperature for 1 hr. The red precipitate obtained was filtered and washed with methanol (2 x 2 mL). Isolated yield: (92%); $T_{dec\ onset.}$ = 161 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 7.37 (bs, 8H); ^{13}C NMR (125 MHz, d_6-DMSO): 165.7, 159.4; IR (cm^{-1}): 3160, 3024, 2846, 2363, 2325, 1626, 1524, 1426, 1325, 1298, 1058, 950, 809, 758; Calcd for $C_2H_8N_8O_3$: C, 12.50; H, 4.20; N, 58.32. Found: C, 12.66; H, 4.08; N, 58.57.

Synthesis of 2: To a stirred solution of **P1** (0.32 g, 2.0 mmol, 1.0 equiv.) in ethyl acetate (30 mL) at room temperature, a solution of $N_2H_4{\cdot}H_2O$ (2.0 equiv) in methanol (10 mL) was added. The resulting reaction mixture was stirred at room temperature for 1 hr. The red precipitate obtained was filtered and washed with methanol (2 x 2 mL). Isolated yield: (85%); $T_{dec\ onset.}$ = 117 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 7.18 (s, 10H); ^{13}C NMR (125 MHz, d_6-DMSO): 165.7, 159.3; IR (cm^{-1}): 3325, 3142, 1702, 1626, 1543, 1385, 1309, 1269, 1073, 975, 768; Calcd for $C_2H_{10}N_{10}O_3$: C, 10.81; H, 4.54; N, 63.05. Found: C, 10.87; H, 4.86; N, 61.06.

Synthesis of 3: To a stirred solution of **P1** (0.63 g, 4.0 mmol, 1.0 equiv.) in ethyl acetate (30 mL) at room temperature, a solution of $NH_2OH{\cdot}H_2O$ (2.0 equiv) in methanol (10 mL) was added. The resulting reaction mixture was stirred at room temperature for 1 hr. The red precipitate obtained was filtered and washed with methanol (2 x 2 mL). Isolated yield: (81%); $T_{dec\ onset.}$ = 119 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 9.14 (bs, 6H); ^{13}C NMR (125 MHz, D_2O): 164.7, 157.4; IR (cm^{-1}): 3445, 3135, 2709, 1634, 1579, 1521, 1384, 1356, 1297, 1190, 1064, 999; Calcd for $C_2H_8N_8O_5$: C, 10.72; H, 3.60; N, 49.99. Found: C, 11.03; H, 3.55; N, 50.75.

Synthesis of 4: To a stirred solution of **P1** (0.63 g, 4.0 mmol, 1.0 equiv.) in ethyl acetate (30 mL) at room temperature, a solution of $NH_2OH{\cdot}H_2O$ (2.0 equiv) in methanol (10 mL) was added. The

resulting reaction mixture was stirred at 50°C for 1 hr. The light brown precipitate obtained was filtered and washed with methanol (2 x 2 mL). Isolated yield: (88%); $T_{dec\ onset.}$ = 200 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 10.7 (bs, 2H), 7.28 (s, 4H); ^{13}C NMR (125 MHz, d_6-DMSO): 154.5, 148.6; IR (cm^{-1}): 3167, 3072, 2874, 2726, 1661, 1549, 1476, 1434, 1354, 1295, 1238, 1141, 1054, 1031, 994, 819, 767, 735; Calcd for $C_2H_6N_6O_3$: C, 14.82; H, 3.73; N, 51.84;. Found: C, 14.89; H, 3.75; N, 52.02.

Synthesis of 5: To a stirred solution of **1** (0.19 g, 1.0 mmol, 1.0 equiv.) in water (30 mL) at room temperature, a solution of TATOT.HCl (0.38 g, 2.0 mmol, 2.0 equiv.) in water (10 mL) was added. The resulting reaction mixture was stirred at room temperature for 1 hr. The red precipitate obtained was filtered and washed with methanol (2 x 2 mL). Isolated yield: (90%); $T_{dec\ onset.}$ = 184 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 6.89 (bs, 3H), 6.81 (s, 2H), 5.67 (s, 2H); ^{13}C NMR (125 MHz, d_6-DMSO): 159.4, 153.8, 152.3, 148.2, 142.2; IR (cm^{-1}): 3399, 3354, 3247, 3173, 3143, 2843, 2693, 1687, 1651, 1579, 1502, 1446, 1354, 1335, 1310, 1239, 1081, 1057, 976, 934, 898, 840, 744, 767, 745, 711, 676, 619; Calcd for $C_8H_{14}N_{22}O_3$: C, 20.60; H, 3.03; N, 66.08. Found: C, 20.75; H, 3.01; N, 65.87.

Synthesis of 6: To a stirred solution of **4** (0.16 g, 1.0 mmol, 1.0 equiv.) in water (30 mL) at room temperature, a solution of TATOT.HCl (0.19 g, 1.0 mmol, 1.0 equiv.) in water (10 mL) was added. The resulting reaction mixture was stirred at room temperature for 1 hr. The red precipitate obtained was filtered and washed with methanol (2 x 2 mL). Isolated yield: (87%); $T_{dec\ onset.}$ = 232 °C; ^{1}H NMR (500 MHz, d_6-DMSO): 10.5 (bs, 3H), 8.07 (s, 2H), 7.19 (s, 2H), 5.76 (s, 2H); ^{13}C NMR (125 MHz, d_6-DMSO): 160.0, 154.4, 148.4, 147.4, 141.2; IR (cm^{-1}): 3325, 3206, 3184, 3140, 3066, 2762, 2358, 1711, 1669, 1581, 1561, 1492, 1447, 1386, 1334, 1235, 1049, 1027, 1006,

976, 771, 722, 702, 623; Calcd for $C_5H_9N_{13}O_3$: C, 20.07; H, 3.03; N, 60.86. Found: C, 20.06; H, 3.19; N, 60.90.

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[2] solution program using dual methods and by using Olex2.[3] The model was refined with ShelXL[4] 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.

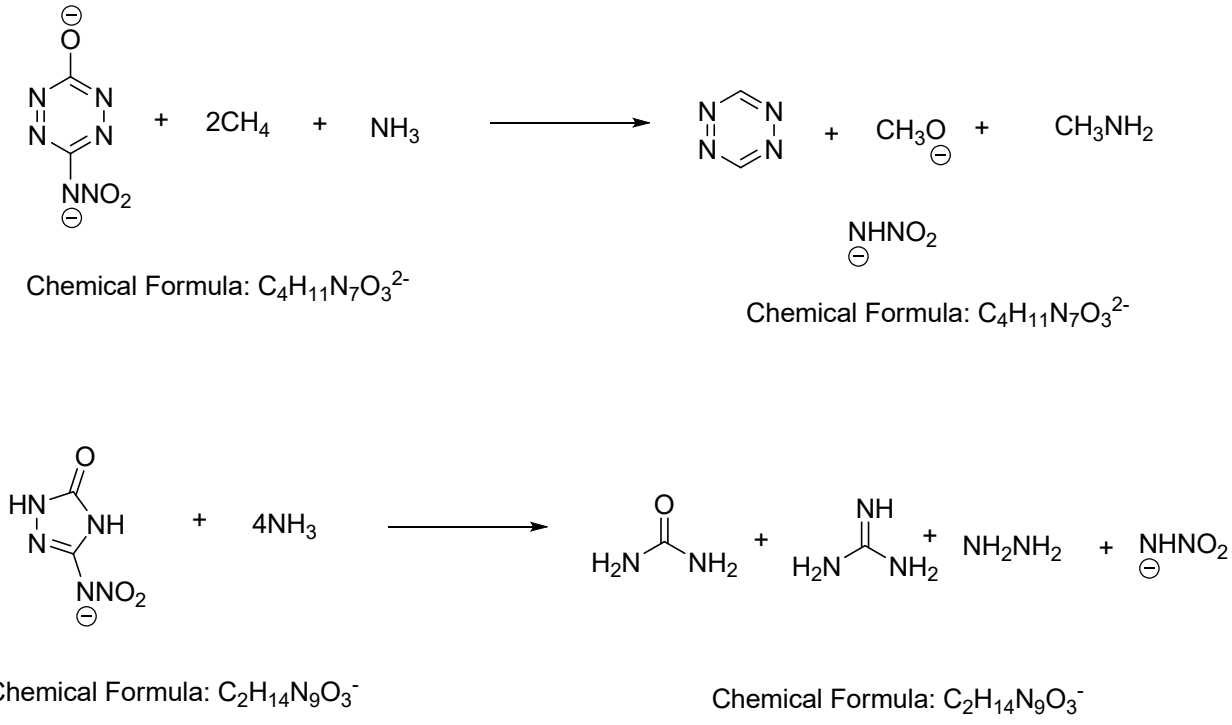
Table S1: Crystallographic data for compounds **1, 4** and **5**.

Compound	**1**	**4**	**5**
CCDC	2542795	2542796	2542797
Formula	$C_2H_8N_8O_3$	$C_8H_{24}N_{24}O_{12}$	$C_8H_{14}N_{22}O_3$
$D_{calc.}$/ g cm^{-3}	1.707	1.674	1.788
m/mm^{-1}	1.327	1.327	1.257
Formula Weight	192.16	648.51	466.41
Colour	red	yellow	red
Shape	needle-shaped	needle-shaped	irregular-shaped
Size/mm	0.11×0.04×0.02	0.11×0.05×0.02	0.21×0.12×0.03
T/K	100.00(10)	101(4)	100.00(10)
Crystal System	monoclinic	triclinic	triclinic
Space Group	$C2/c$	P-1	P-1
a/Å	13.1181(5)	7.2916(6)	9.0884(4)
b/Å	8.0305(2)	7.5502(8)	10.2064(5)
c/Å	15.6693(5)	13.1587(7)	10.7479(5)
a/°	90	94.215(7)	73.853(4)
b/°	115.049(4)	94.320(6)	66.266(5)
g/°	90	116.254(10)	75.743(4)
V/Å^3	1495.42(10)	643.21(11)	866.36(8)
Z	8	1	2
Z'	1	0.5	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K_a	Cu K_a	Cu K_a
Q_{min}/°	6.235	3.393	4.564
Q_{max}/°	79.950	80.495	80.200
Index range h	-16 ≥ h ≥ 16	-9 ≤ h ≤ 8	-
Index range k	-9 ≥ k ≥ 10	-8 ≤ k ≤ 9	-
Index range l	-9 ≥ l ≥ 19	-16 ≤ l ≤ 16	-
Measured Refl's.	5688	8577	10630
Indep't Refl's	1591	2712	3659
Refl's I≥2s(I)	1398	1338	3306
R_{int}	0.0241	0.0492	0.0296
Parameters	150	199	354
Restraints	0	0	0
Largest Peak/eÅ^3	0.180	0.614	0.267
Deepest Hole/eÅ^3	-0.223	-0.345	-0.266
GooF	1.063	1.103	1.019
R_1 (I≥2s(I) / all)	0.0297 / 0.0338	0.0737 / 0.1145	0.0378
wR_2 (I≥2s(I) / all)	0.0838 / 0.0864	0.2206 / 0.2496	0.0911

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.[5] The atomization energies for cations were calculated by using the G[2]*ab initio* method [6] 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.[7-8]

Section S4. References

1. J. Singh, R. J. Staples and J. M. Shreeve, *J. Mater. Chem. A*, 2025, **13**, 11475–11485.
2. G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* 2008, 64, 112–122.
3. G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* 2015, **71**, 3–8.
4. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339–341.
5. R. G. Parr, Y. Weitao, *Density-Functional Theory of Atoms and Molecules* (Oxford University Prss, 1995).
6. Suleimenov and T.-K. Ha, *Chem. Phys. Lett.* 1998, **290**, 451–457.
7. H. D. B. Jenkins, D. Tudela and L. Glasser, *Inorg. Chem.* 2002, **41**, 2364–2367.
8. 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

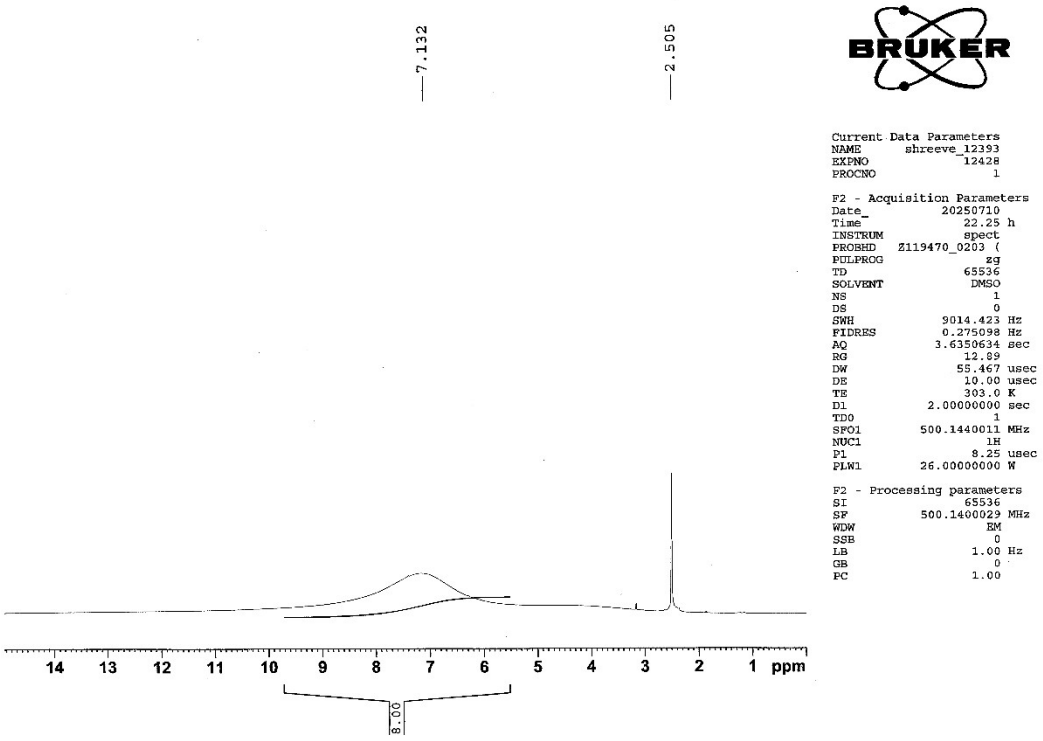


Fig. S1. [1]H NMR spectrum for compound **1**.

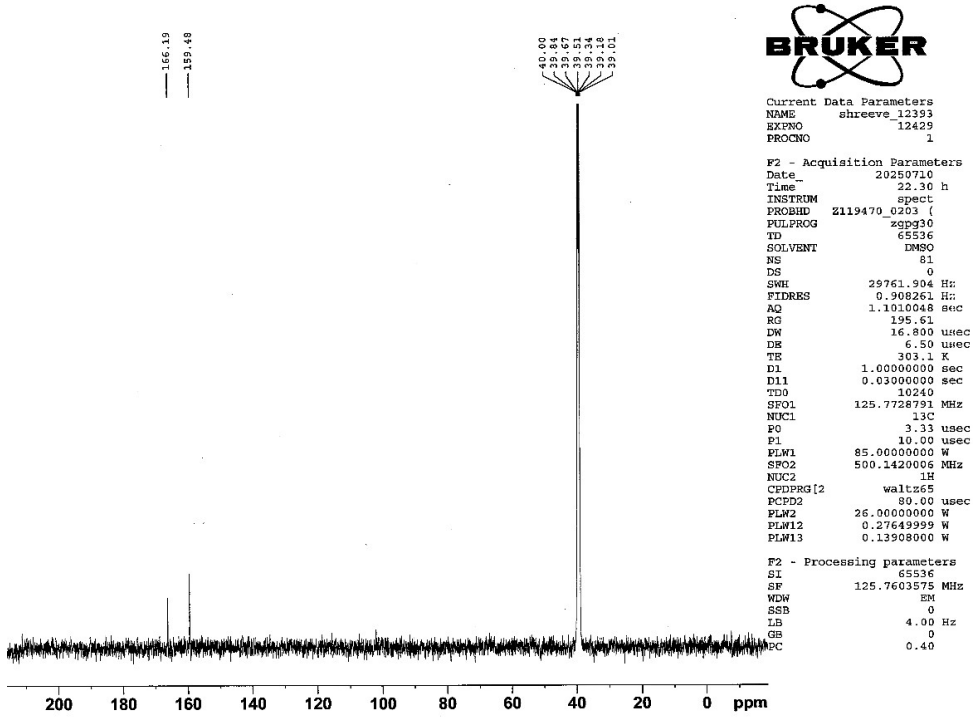


Fig. S2. [13]C NMR spectrum for compound **1**

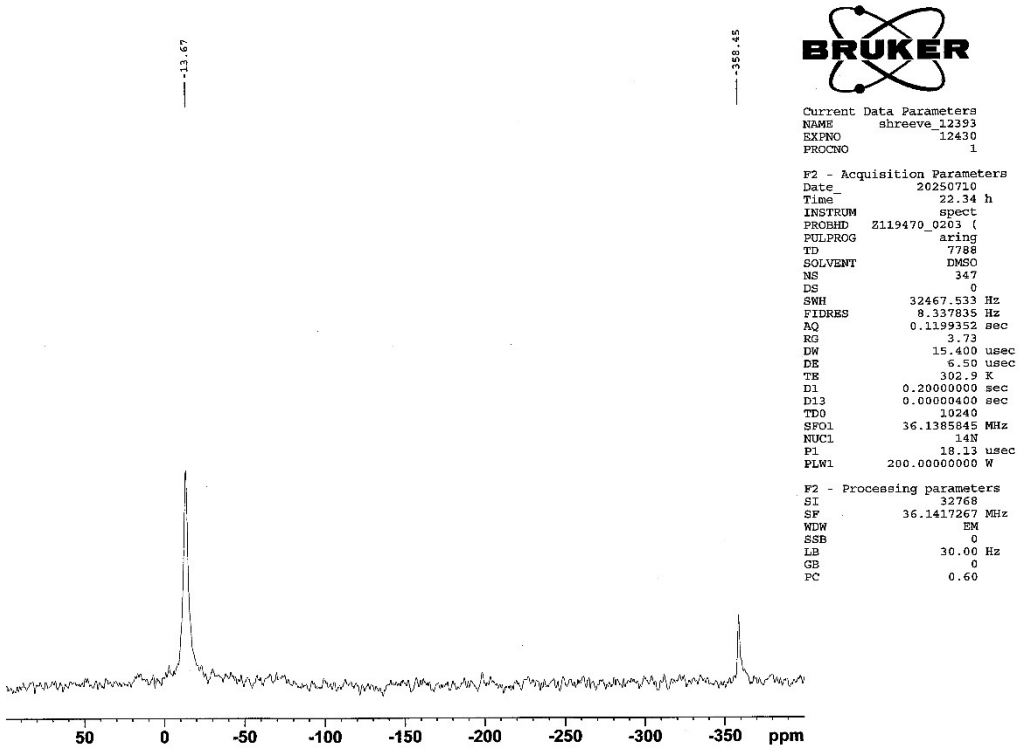


Fig. S3: ^{14}N NMR spectrum for compound **1**.

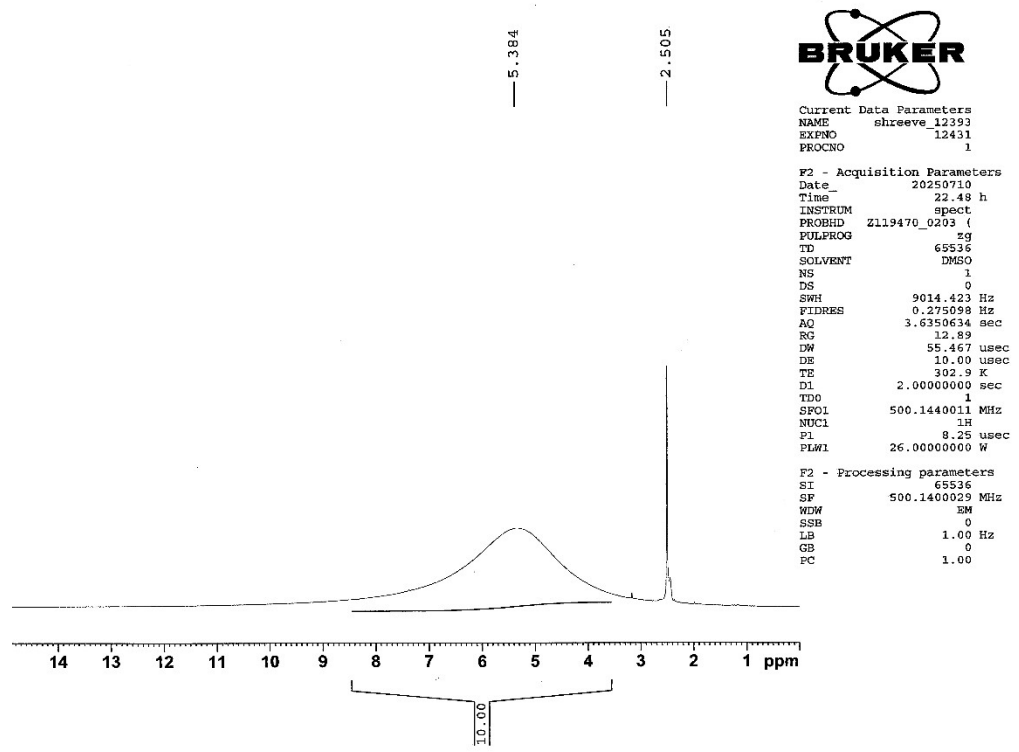


Fig. S4. ^{1}H NMR spectrum for compound **2**.

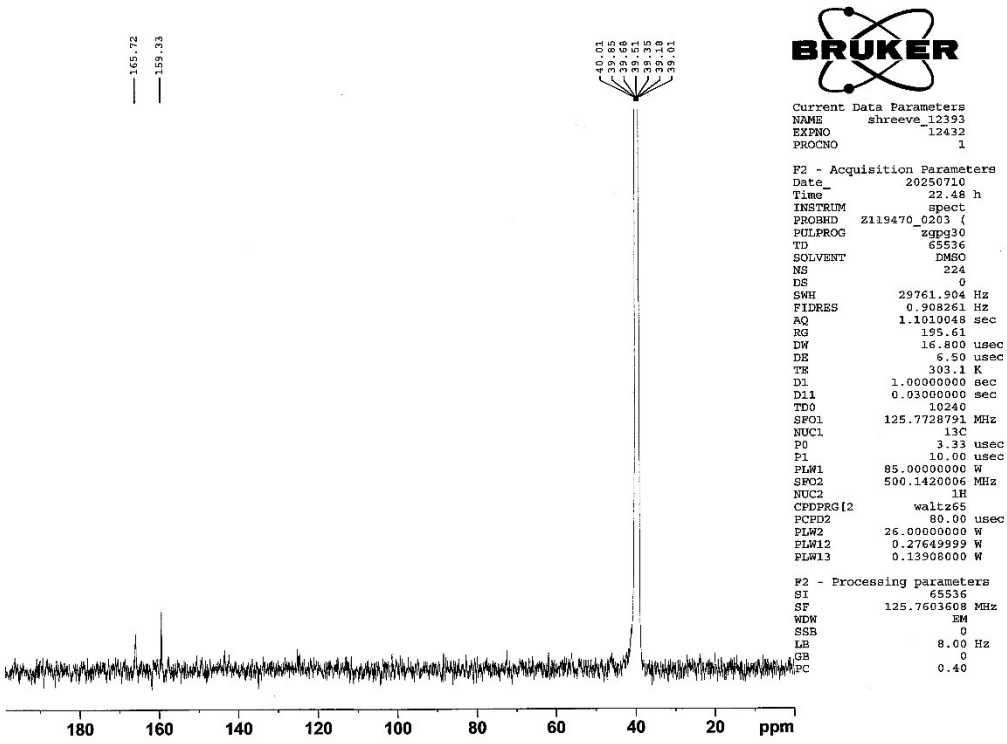


Fig. S5. ^{13}C NMR spectrum for compound **1**

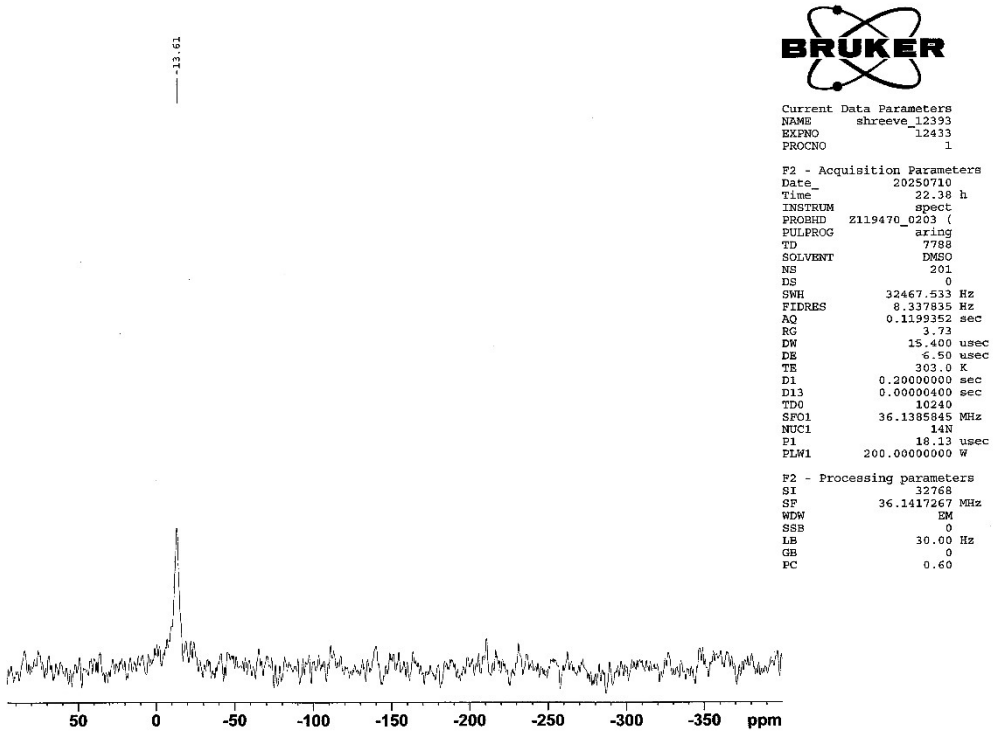


Fig. S6: ^{14}N NMR spectrum for compound **2**.

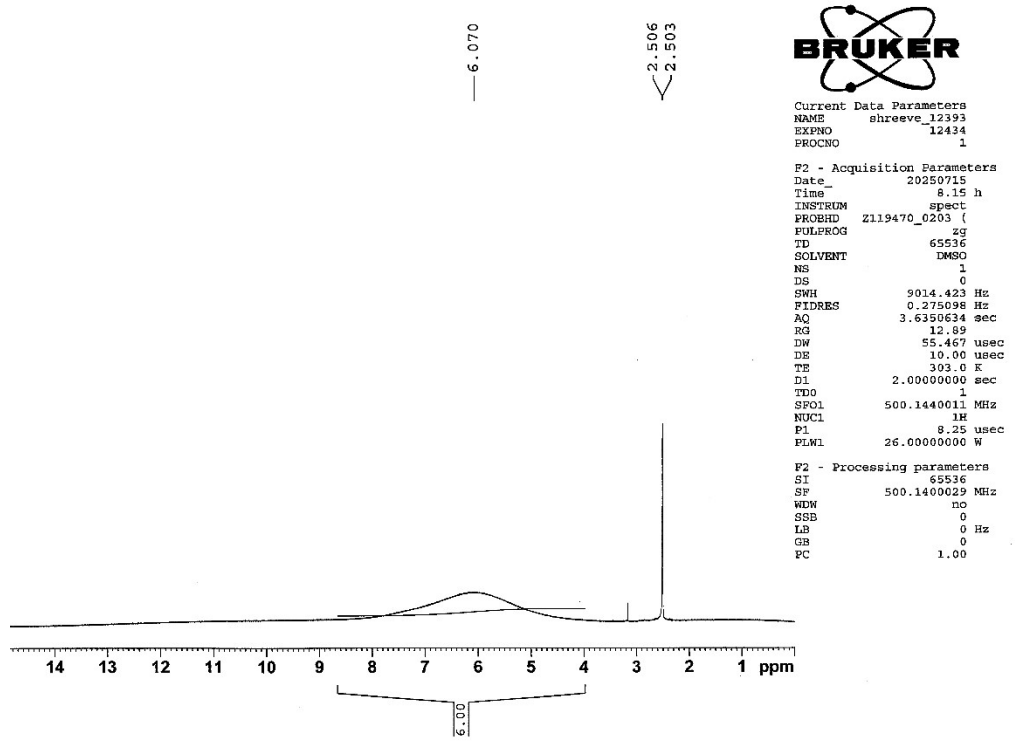


Fig. S7. [1]H NMR spectrum for compound **3**.

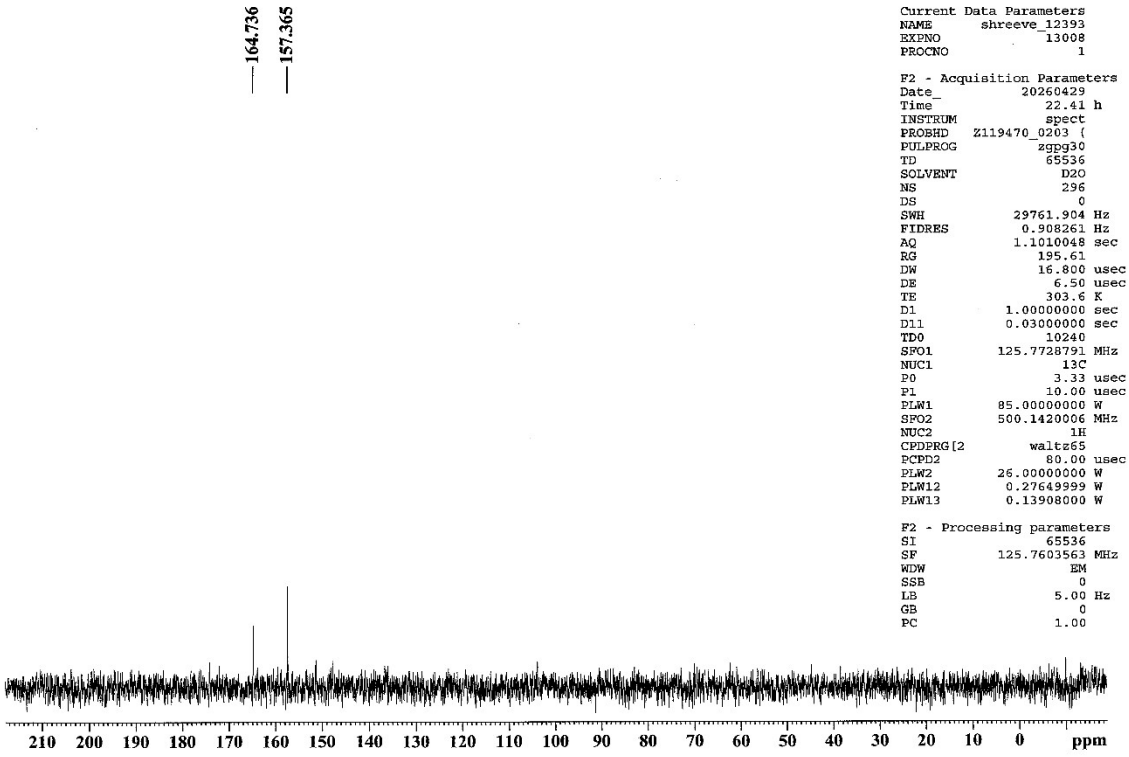


Fig. S8. [13]C NMR spectrum for compound **3**.

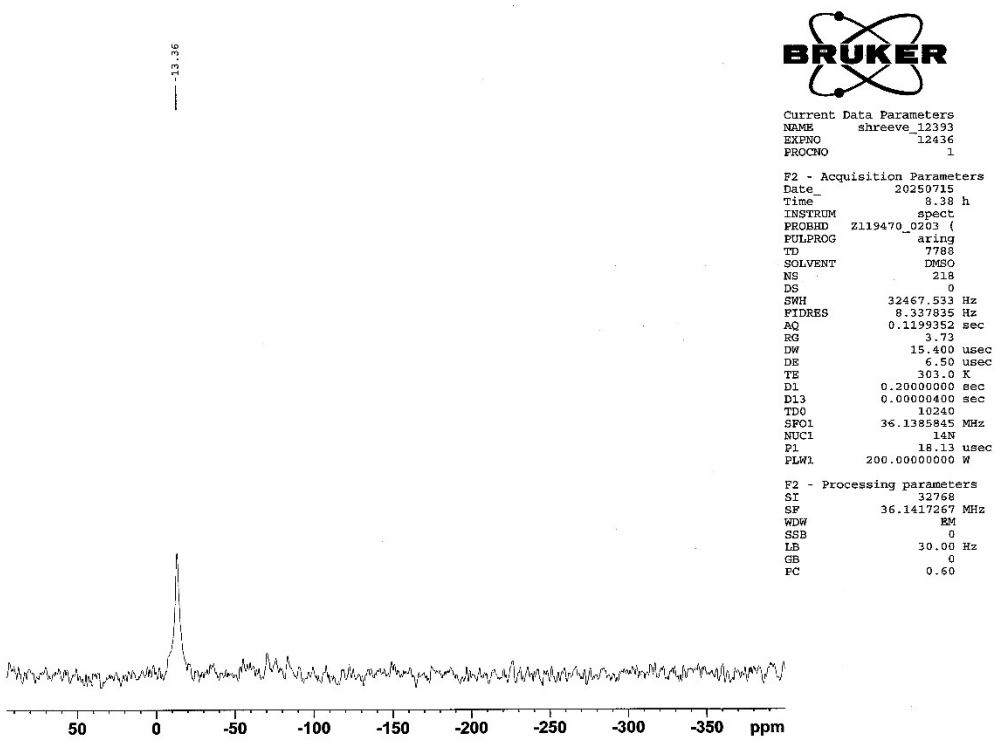


Fig. S9: ^{14}N NMR spectrum for compound **3**.

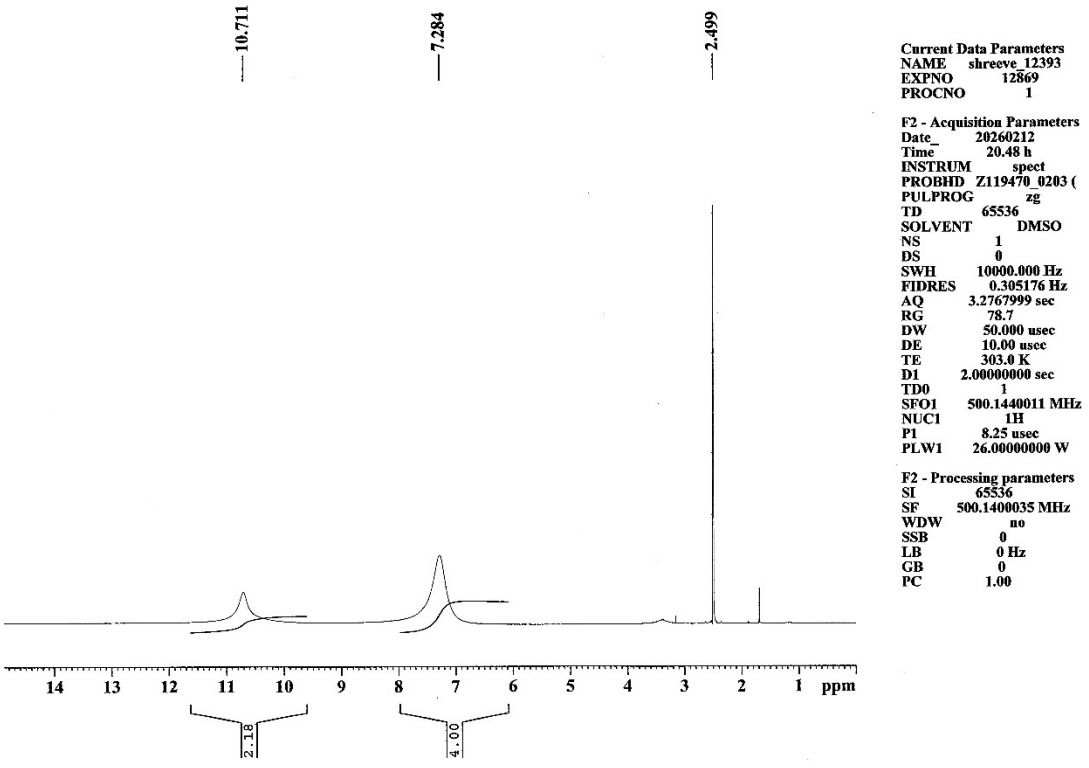


Fig. S10. ^{1}H NMR spectrum for compound **4**.

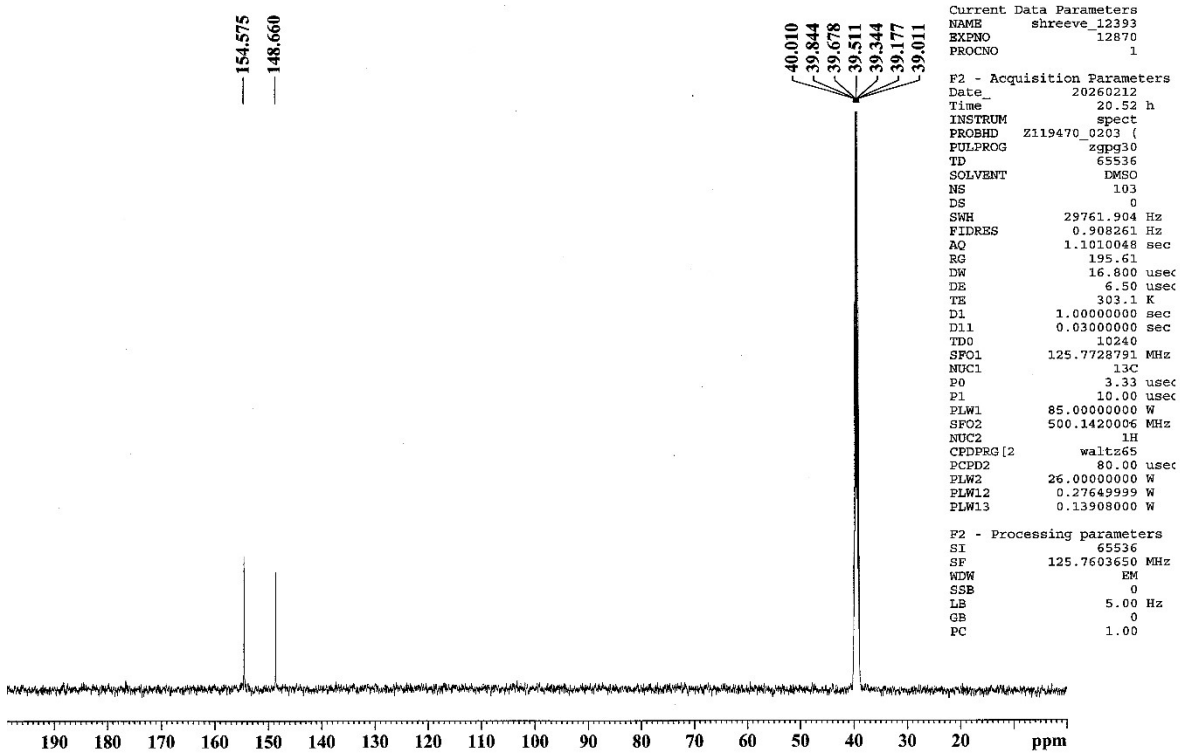


Fig. S11. ^{13}C NMR spectrum for compound **4**

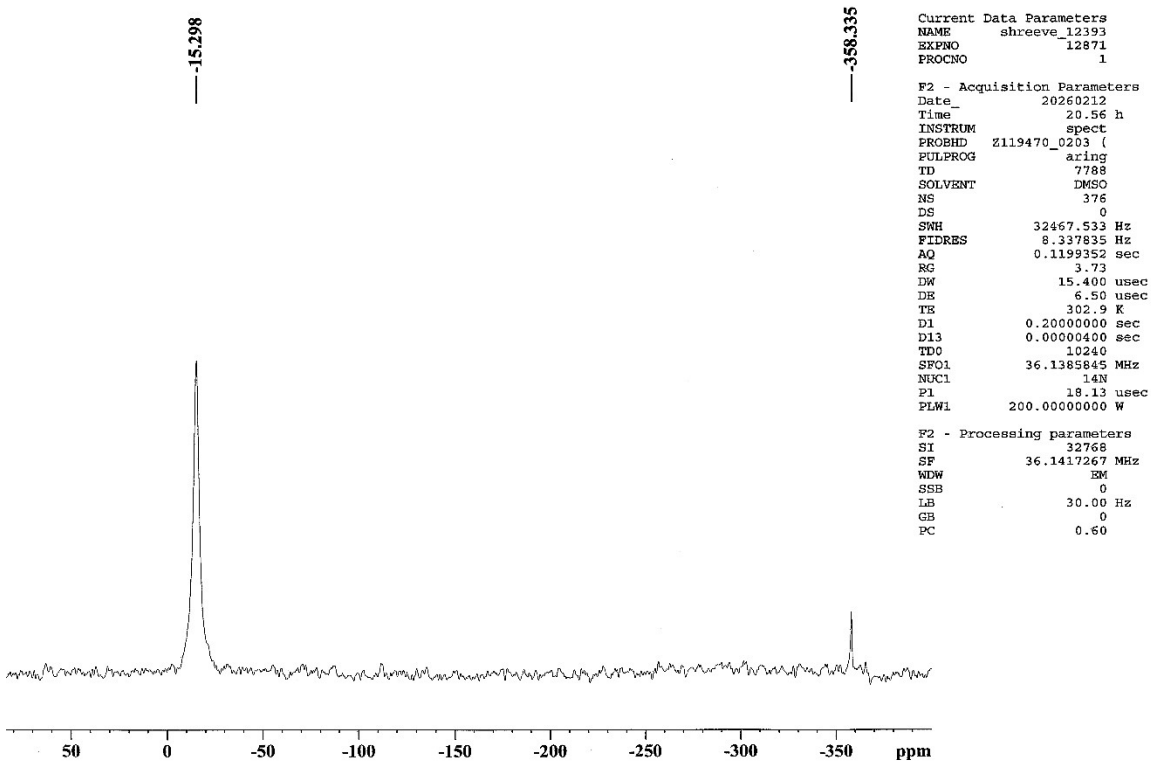


Fig. S12: ^{14}N NMR spectrum for compound **4**.

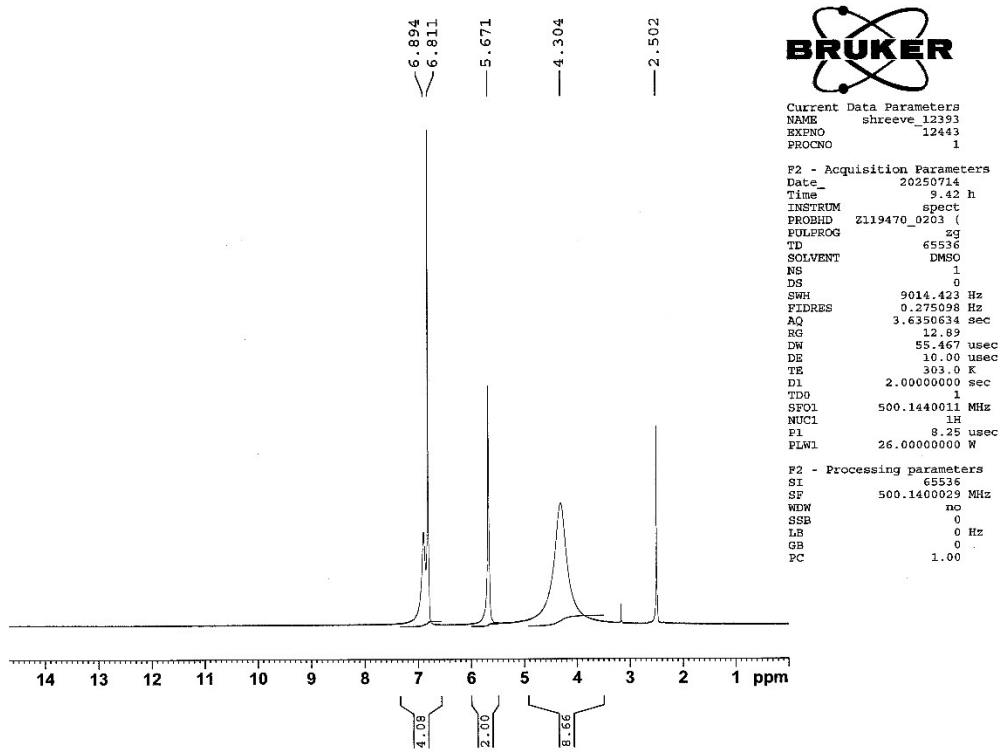


Fig. S13. [1]H NMR spectrum for compound **5**.

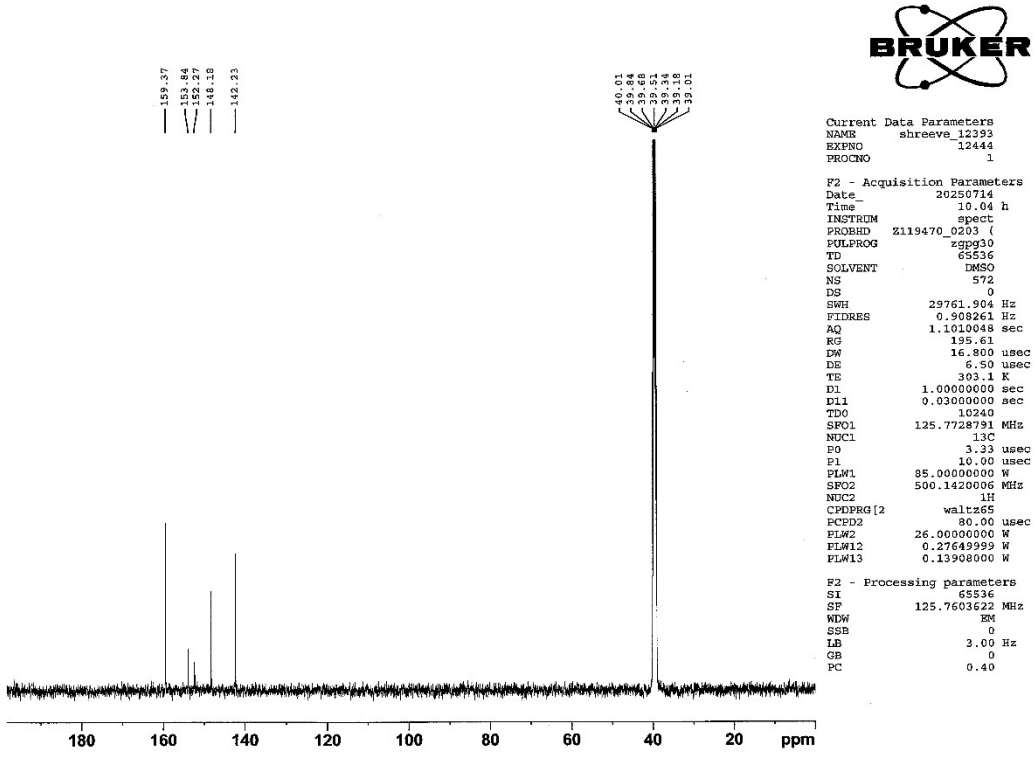


Fig. S14. [13]C NMR spectrum for compound **5**

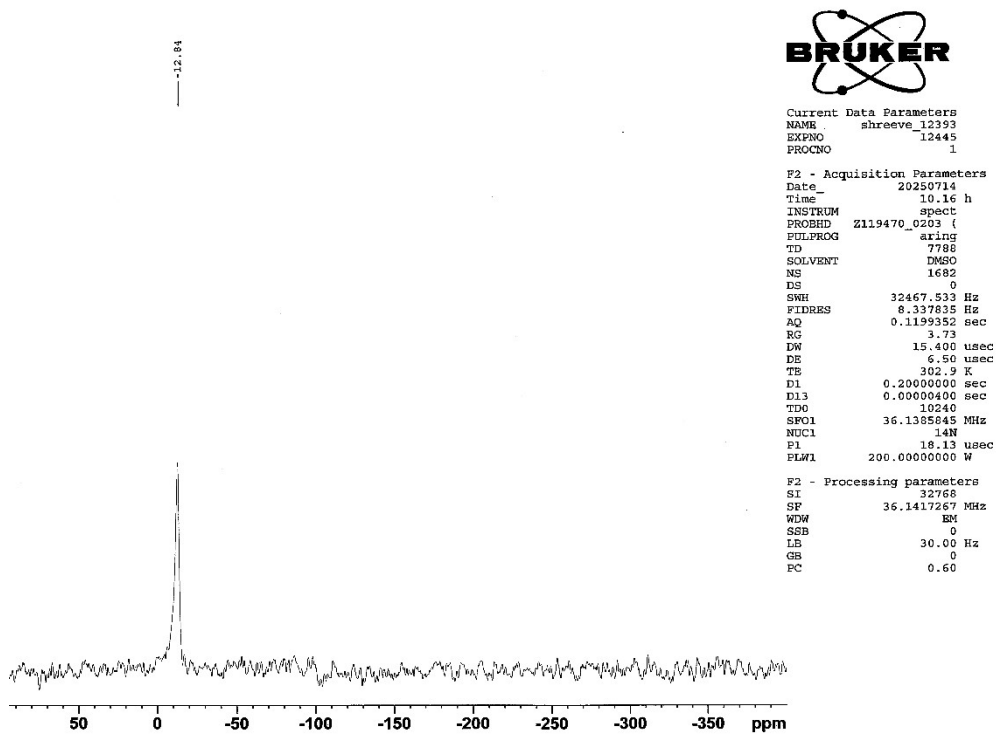


Fig. S15: ^{14}N NMR spectrum for compound **5**.

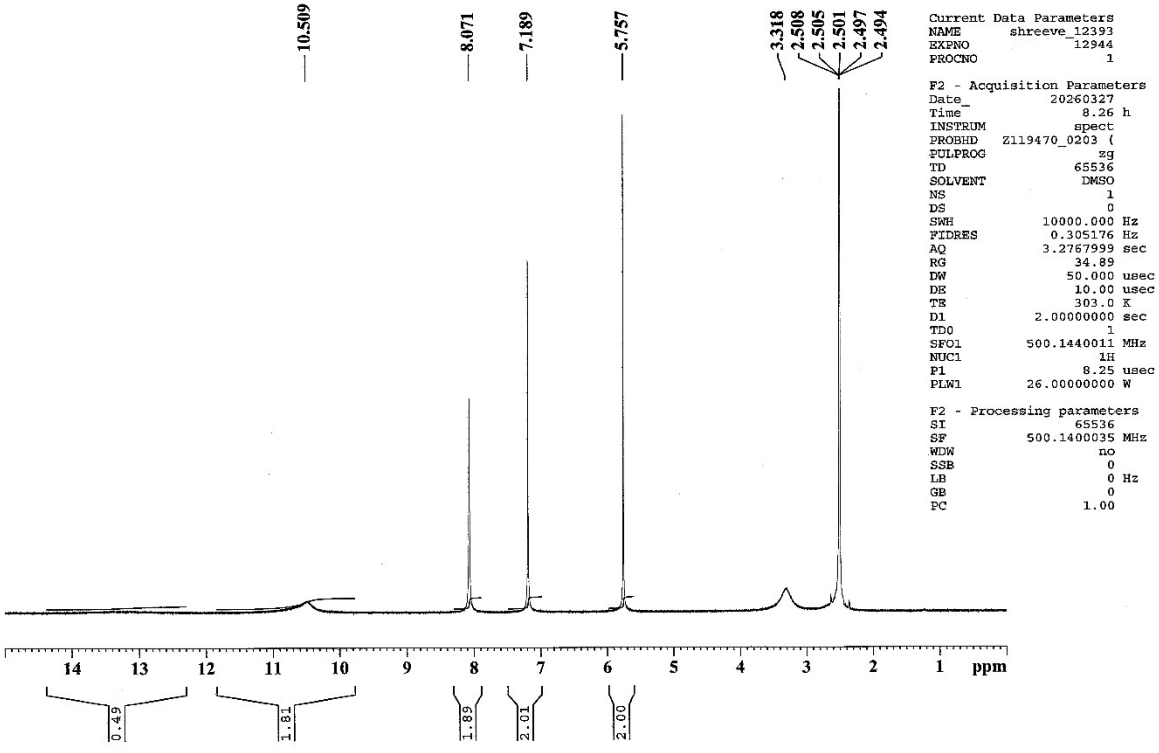


Fig. S16. ^{1}H NMR spectrum for compound **6**.

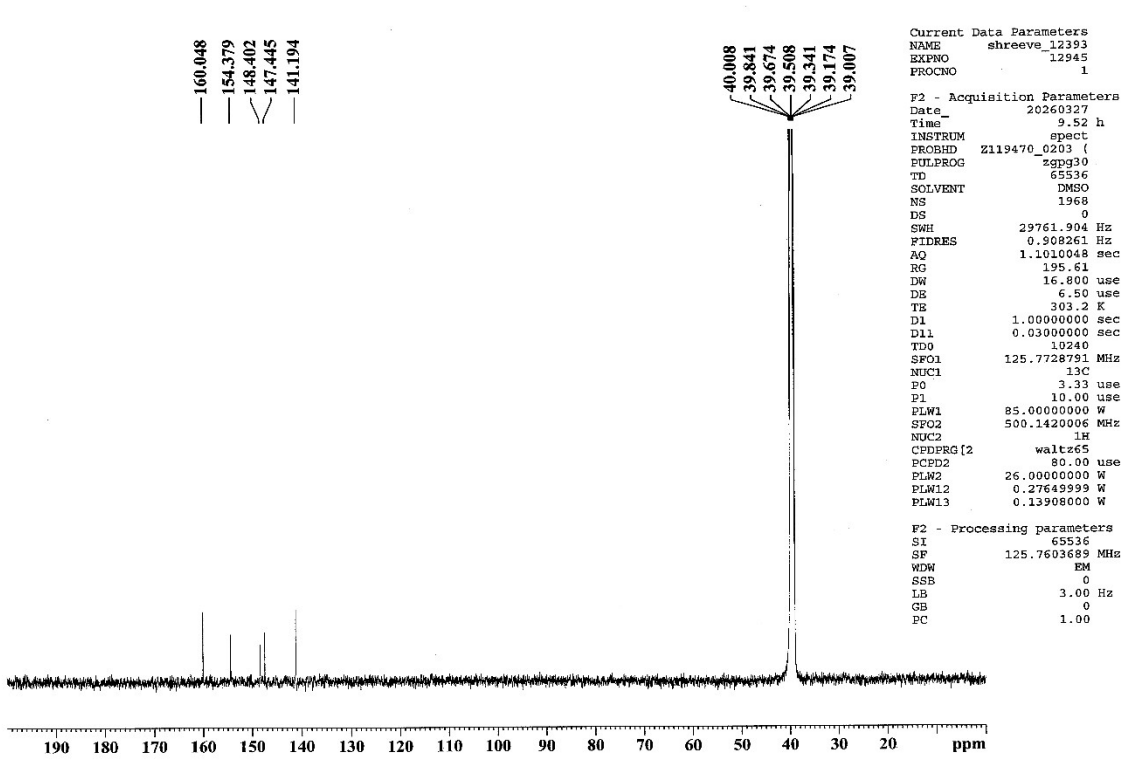


Fig. S17. ^{13}C NMR spectrum for compound **6**

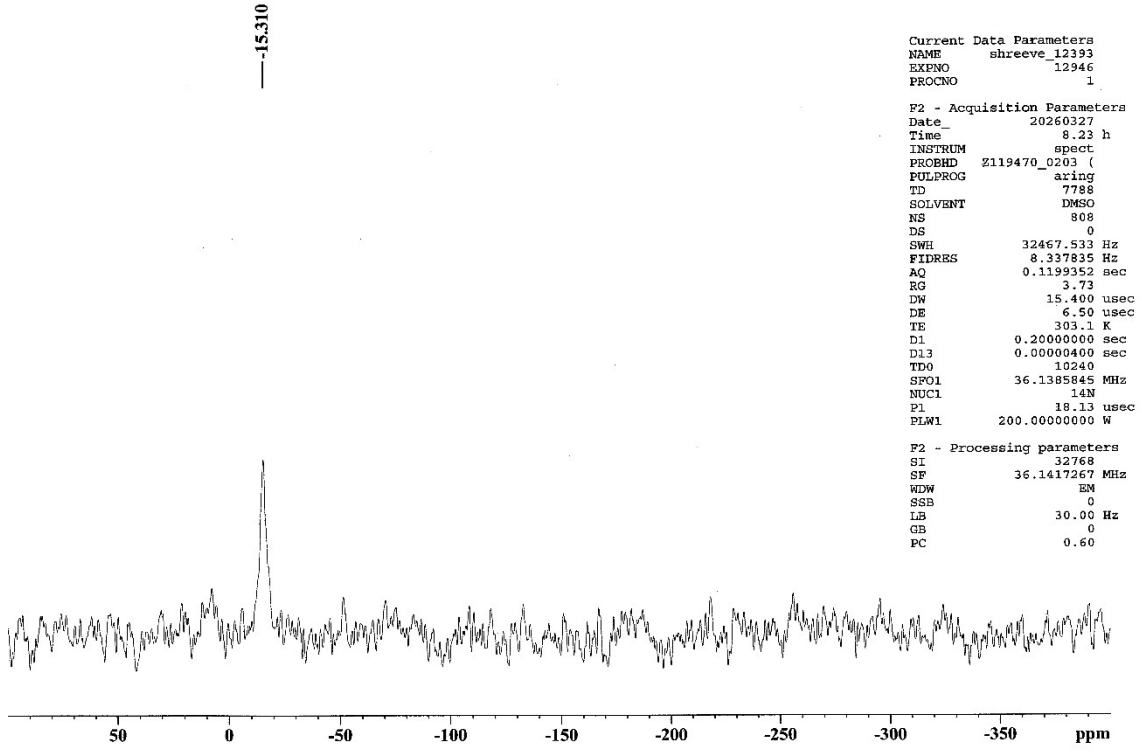


Fig. S18: ^{14}N NMR spectrum for compound **6**.

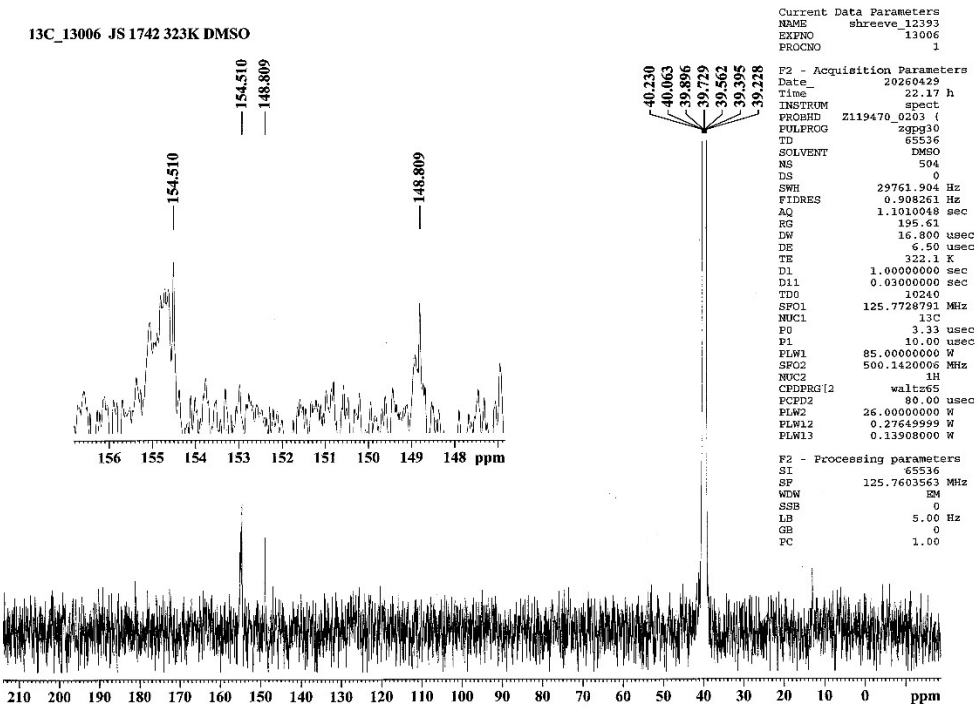


Fig S19. ^{13}C NMR spectra of compound **3** in DMSO-d_6 at 50°C.

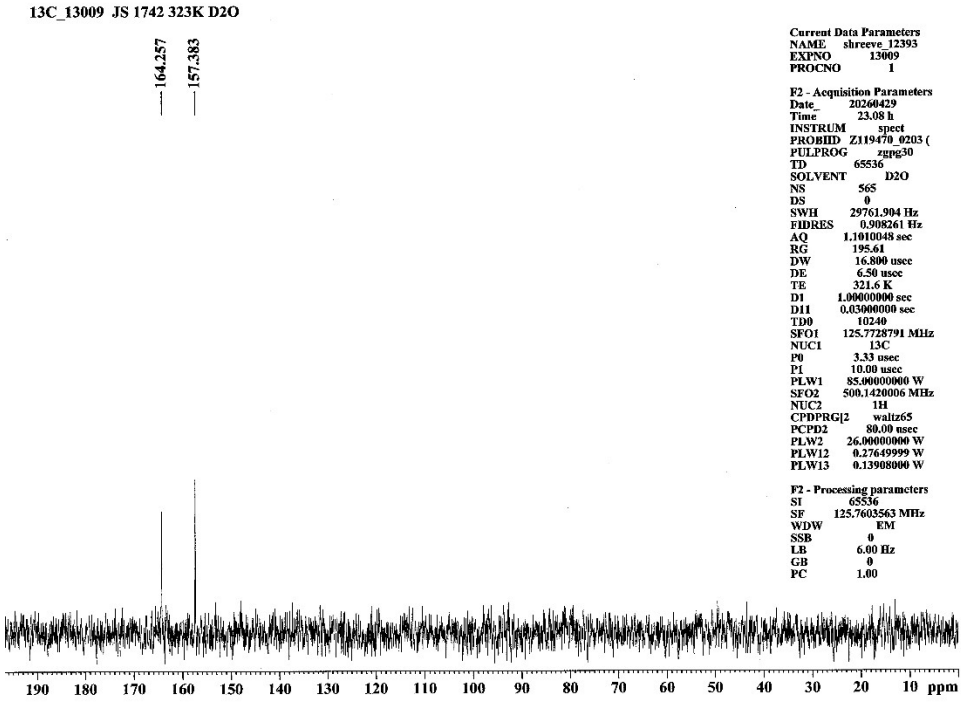


Fig S20. ^{13}C NMR spectra of compound **3** in D_2O at 50°C (0 min).

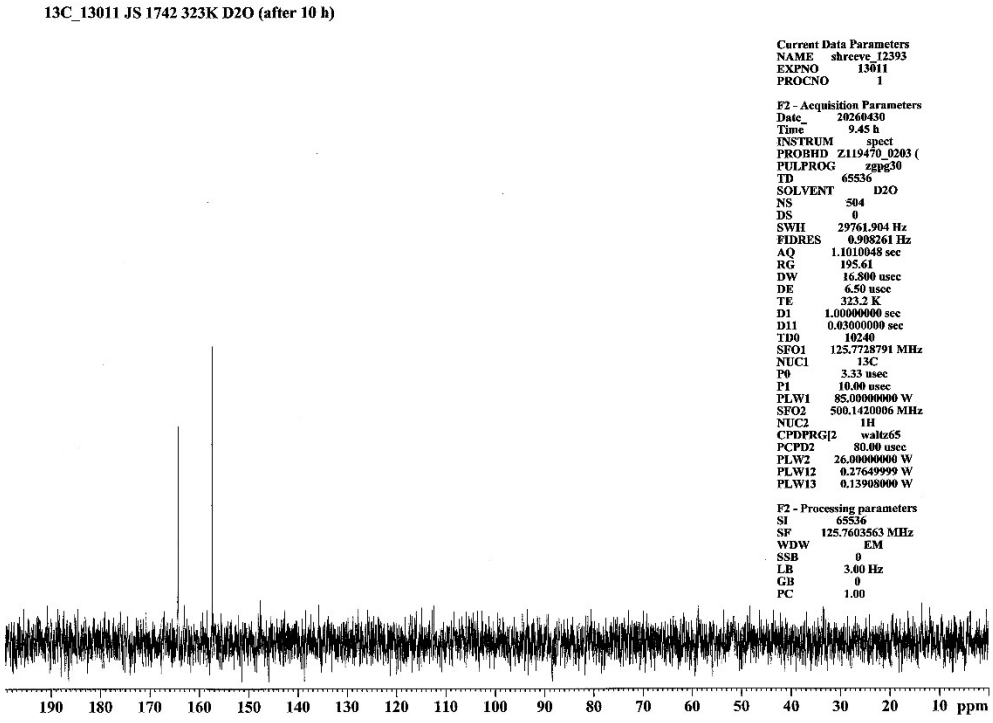


Fig S21. ^{13}C NMR spectra of compound **3** in D_2O at 50°C (10 hr).

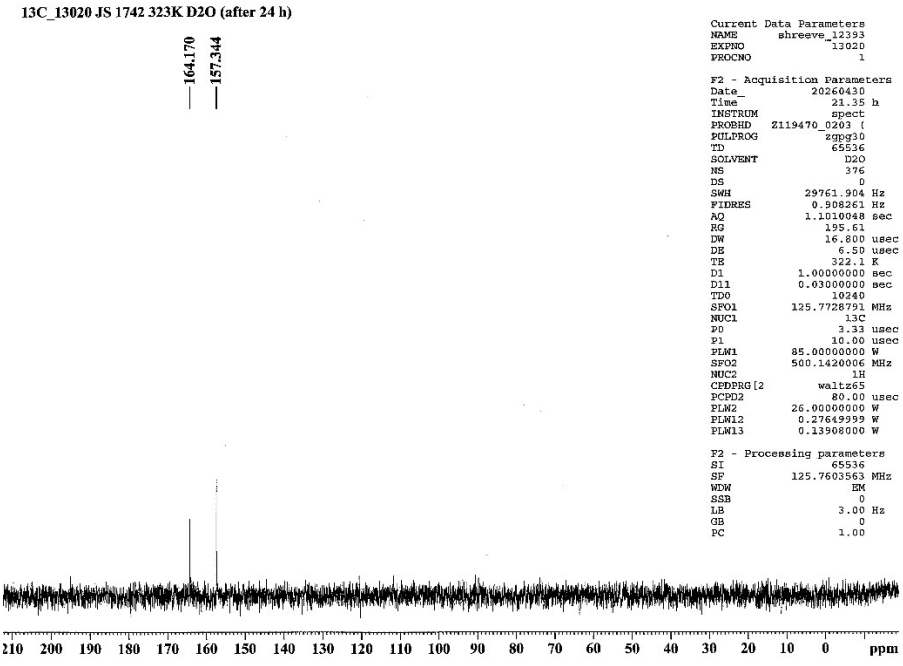


Fig S22. ^{13}C NMR spectra of compound **3** in D_2O at 50°C (24 hr).