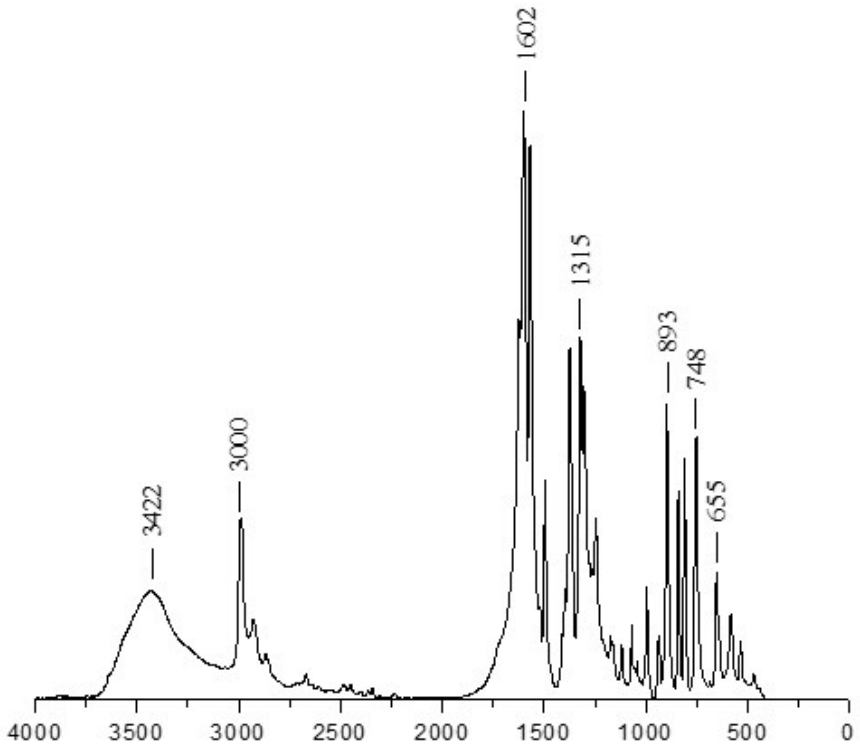
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

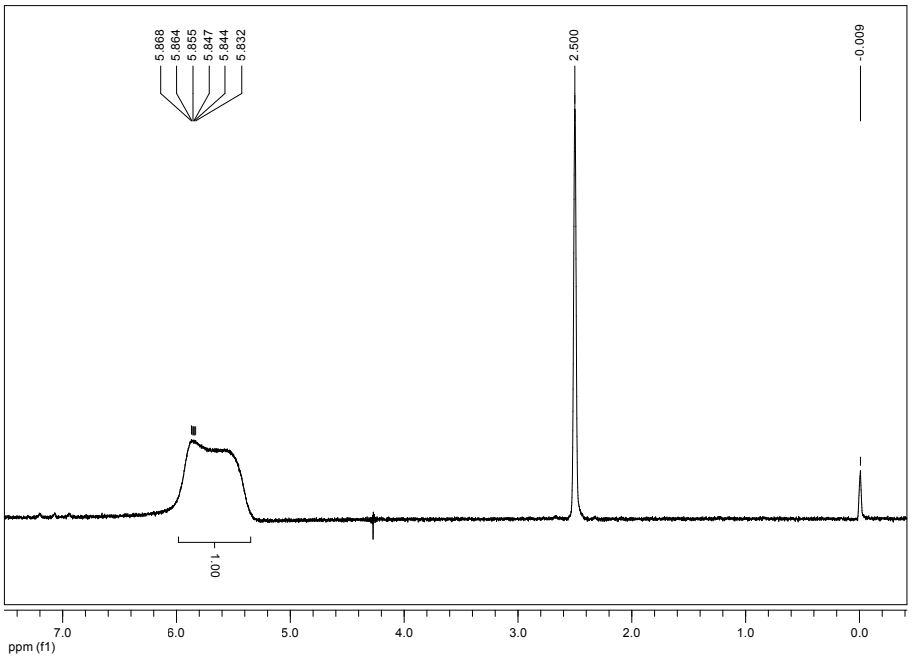
Design and Synthesis Energetic Materials towards High Density and Positive Oxygen Balance by N-dinitromethyl Functionalization of Nitroazoles

X. X. Zhao,[a] S. H. Li,[a] Y. Wang,[a] Y. C. Li,[a] F. Q. Zhao[b] and S. P. Pang*[a]

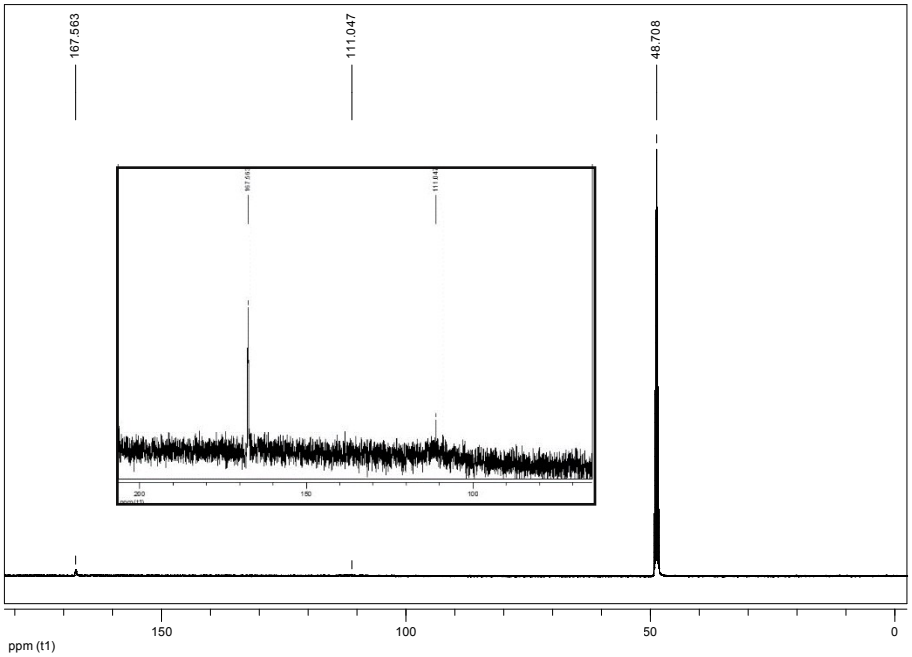
Content



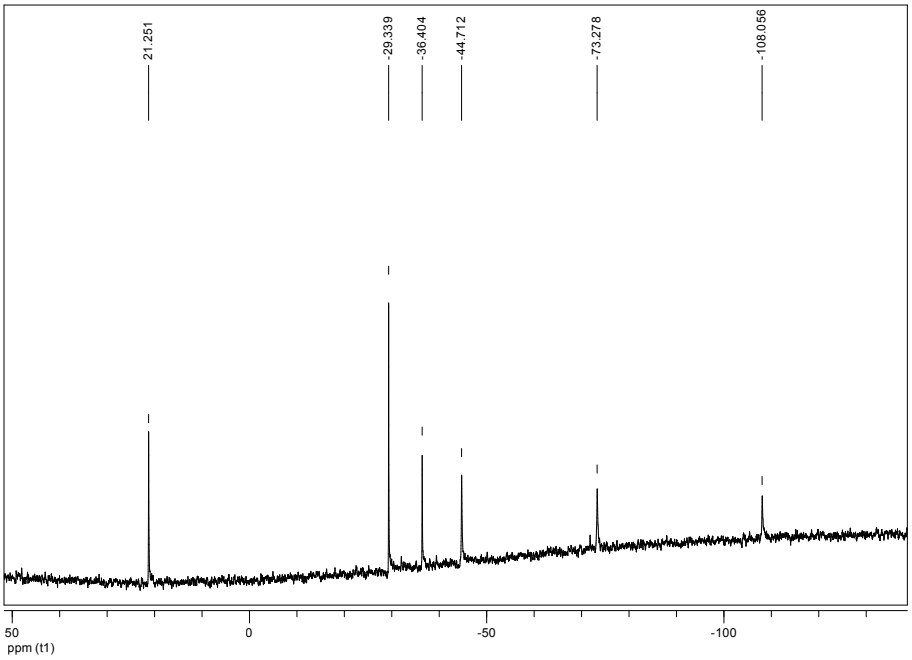
IR spectrum of **5**



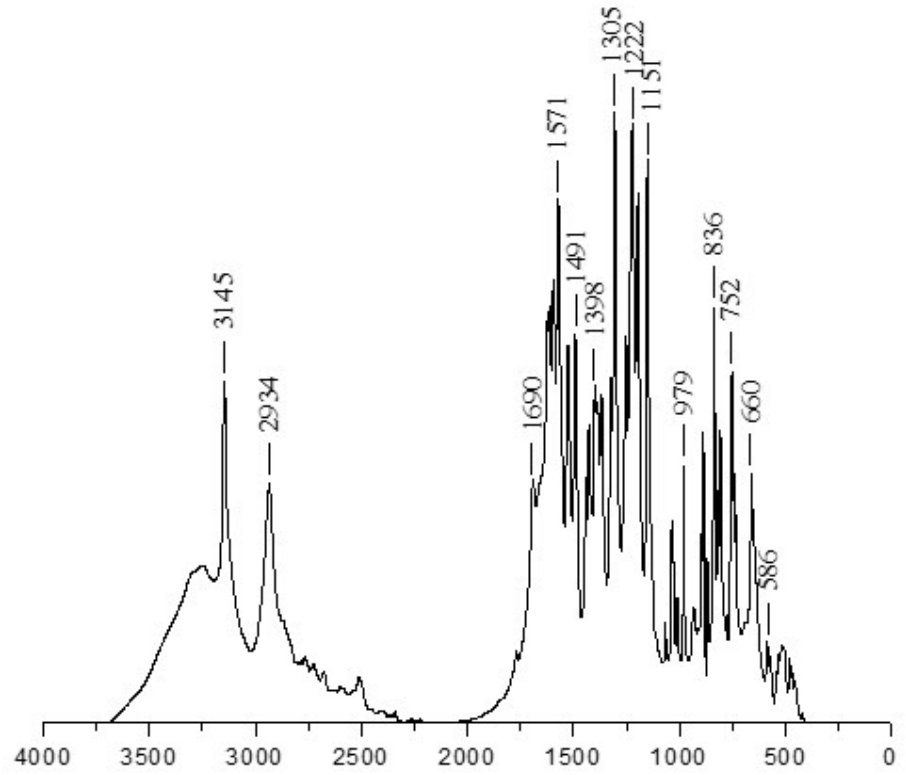
^{1}H NMR spectrum (400 MHz) of **5** in DMSO-d6 at 25 °C



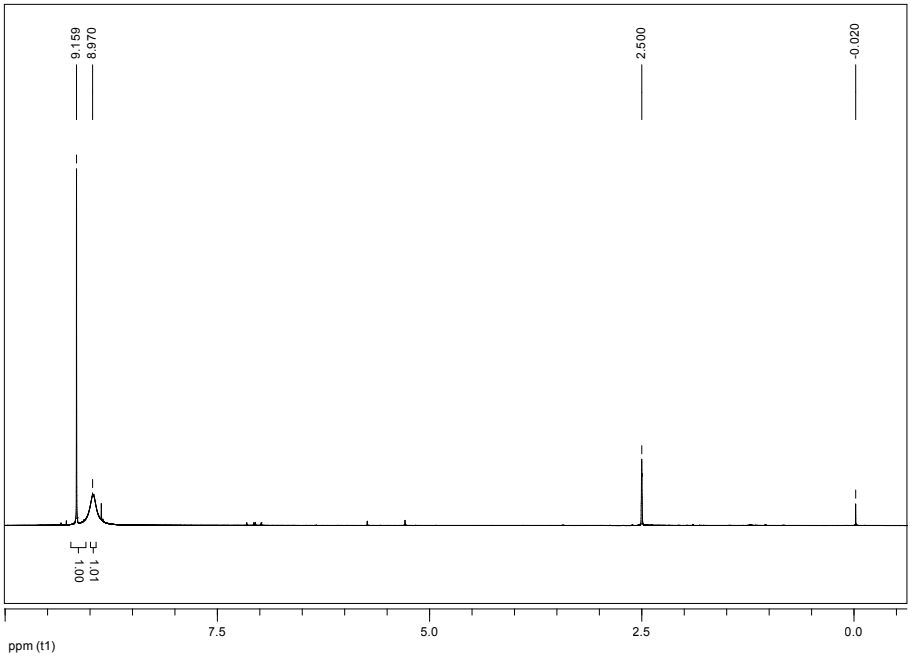
^{13}C NMR spectrum (400 MHz) of **5** in methnol-d4 at 25 °C



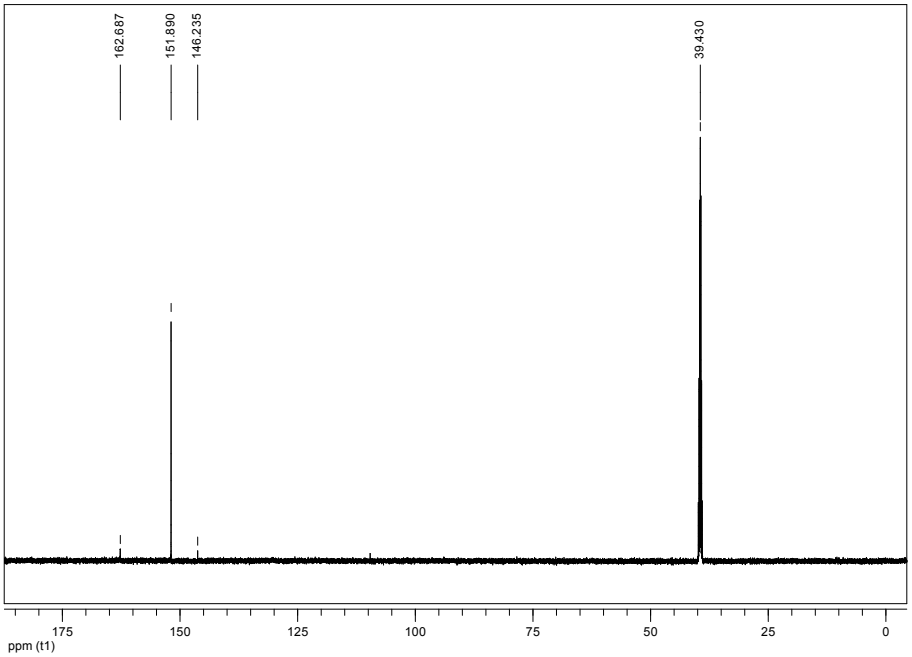
^{15}N NMR spectrum of **5** in methnol-d4 at 25 °C



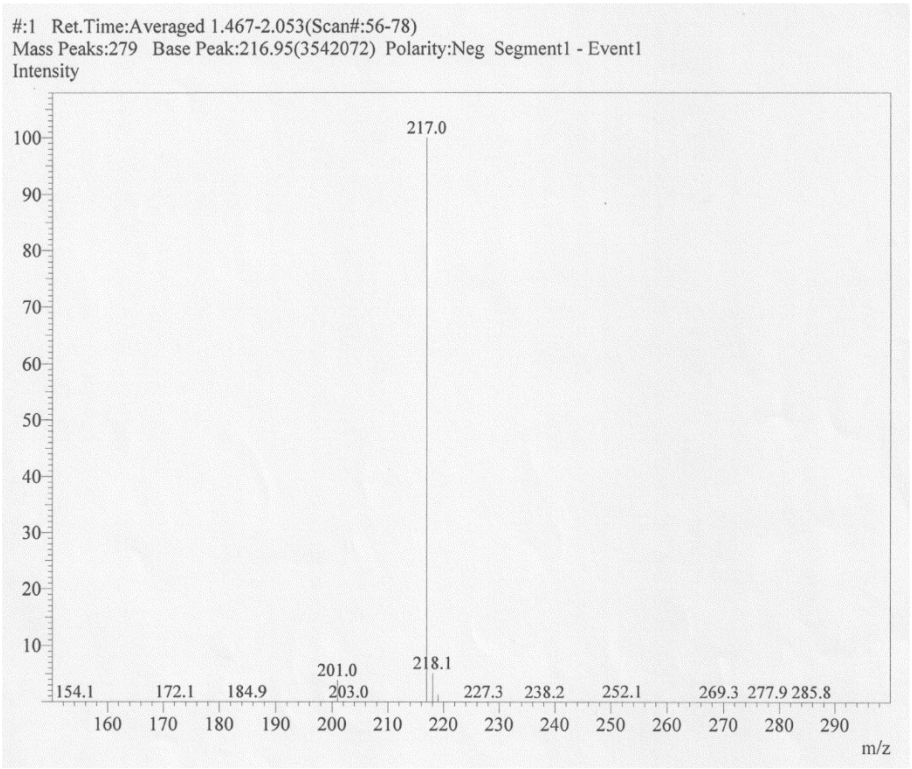
IR spectrum of **6**



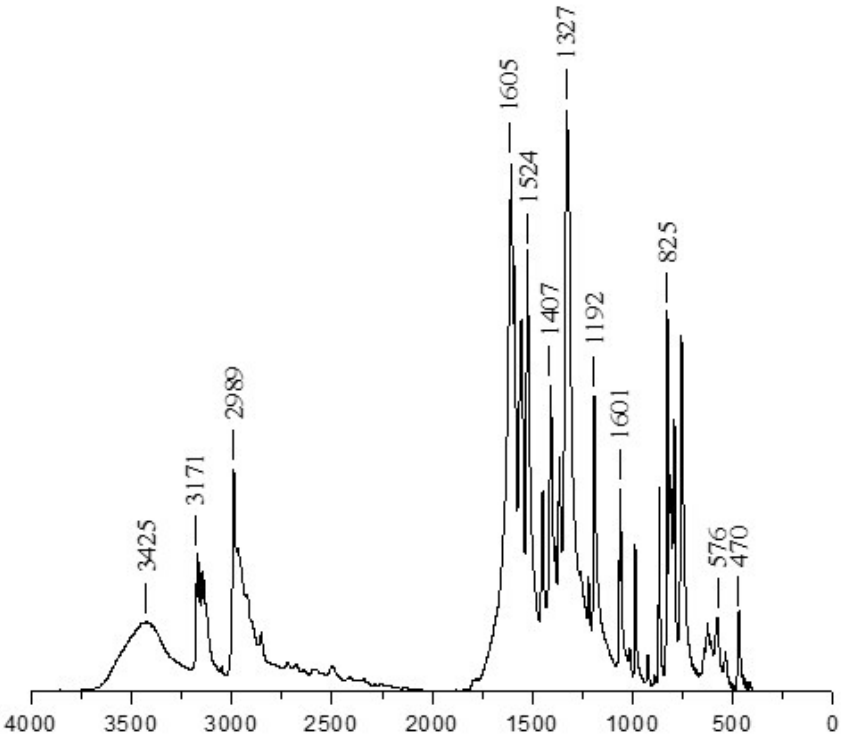
^{1}H NMR spectrum (400 MHz) of **6** in DMSO-d6 at 25 °C



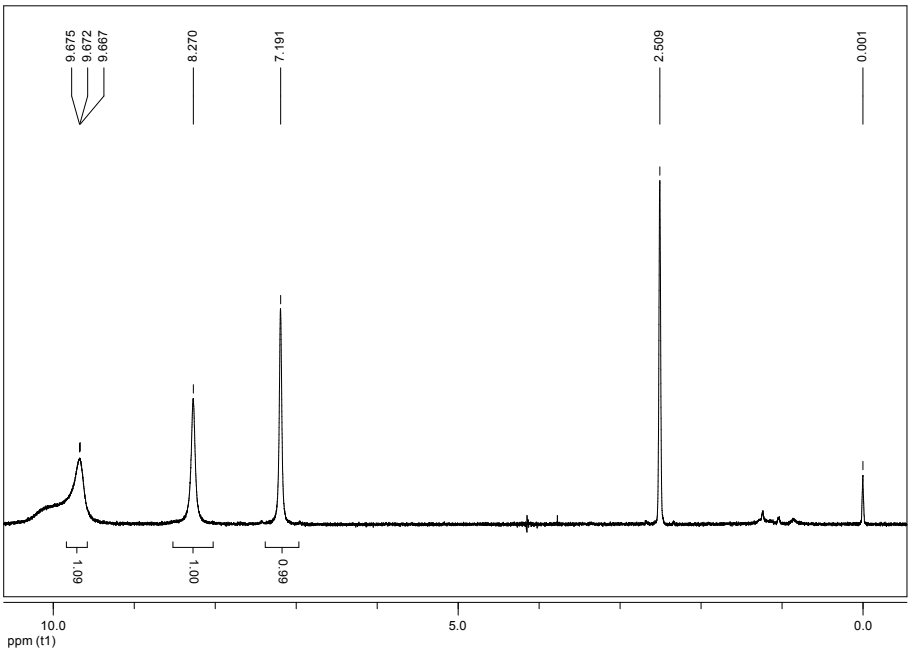
^{13}C NMR spectrum (400 MHz) of **6** in DMSO-d6 at 25 °C



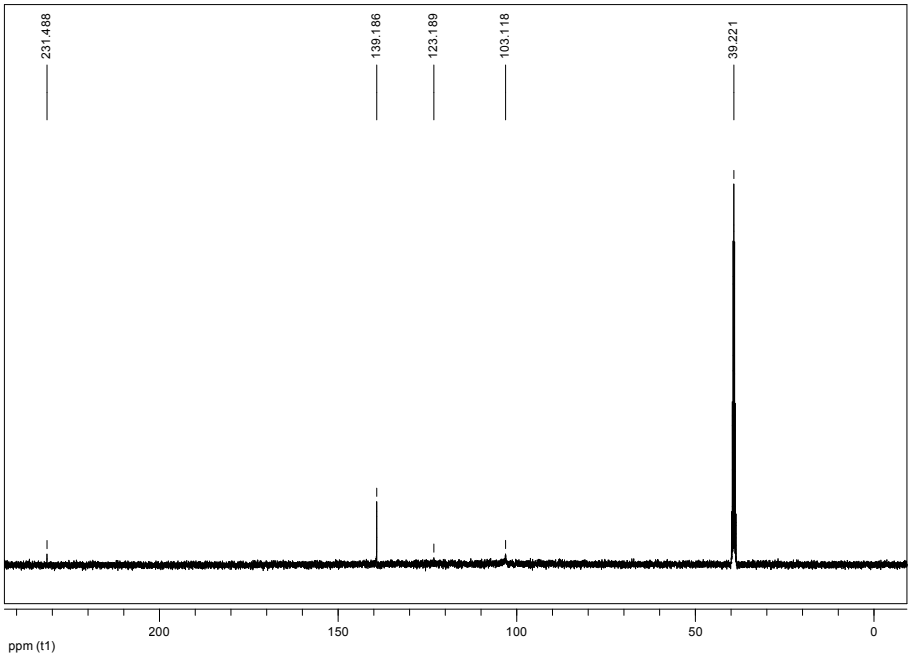
ESI spectrum of **6**



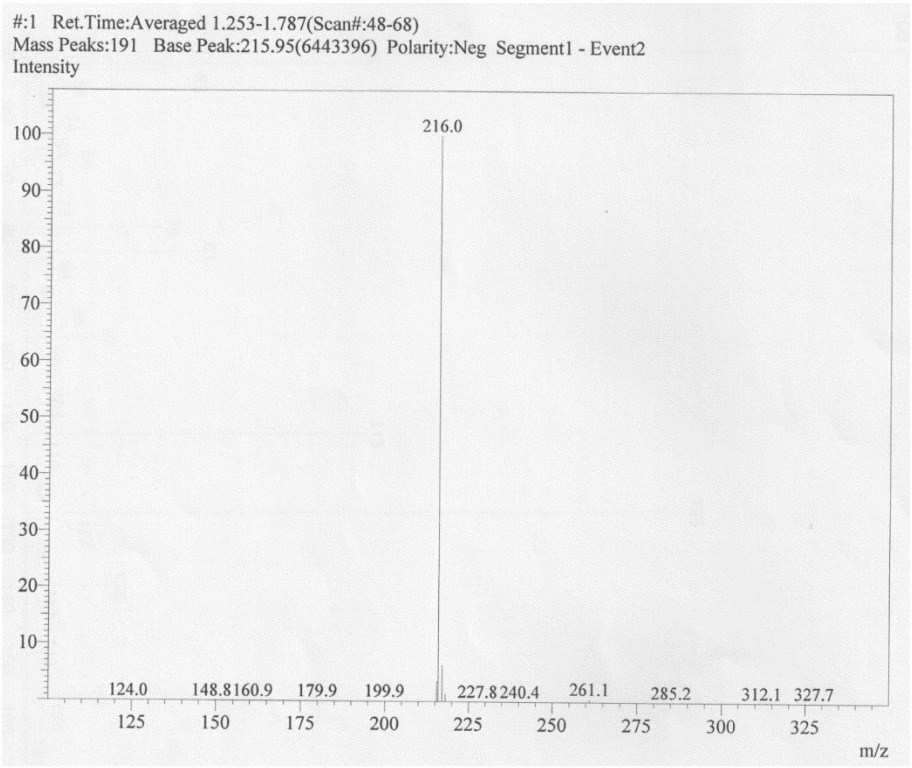
IR spectrum of **7**



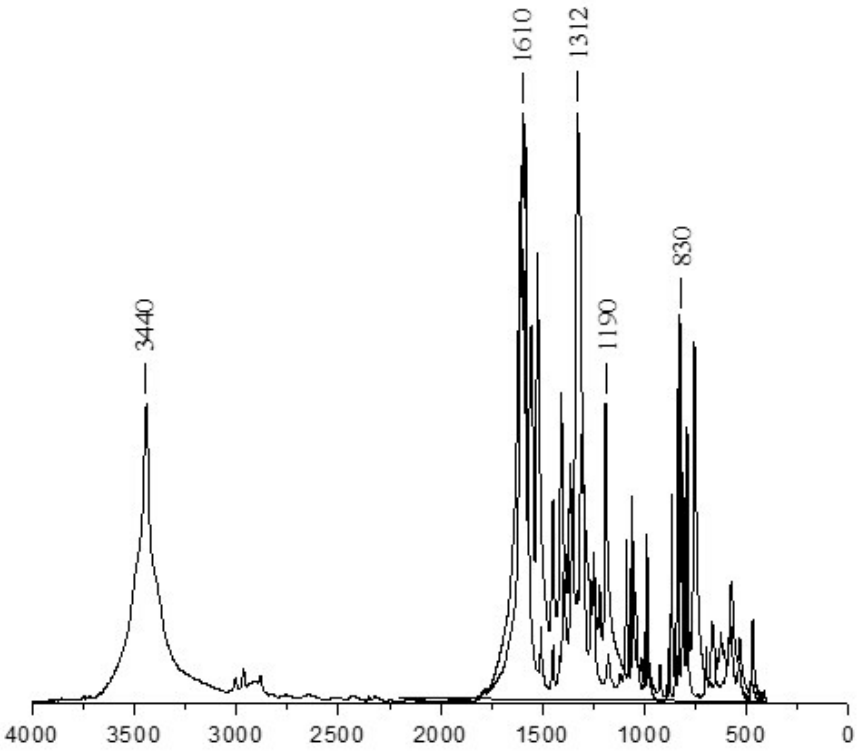
^{1}H NMR spectrum (400 MHz) of **7** in DMSO-d6 at 25 °C



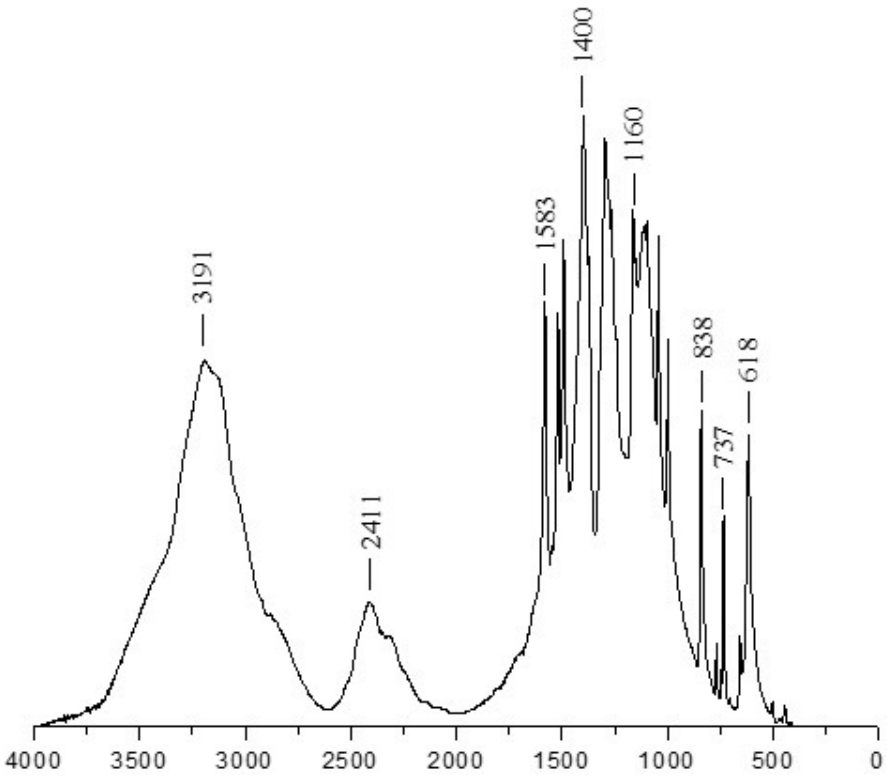
^{13}C NMR spectrum (400 MHz) of **7** in DMSO-d6 at 25 °C



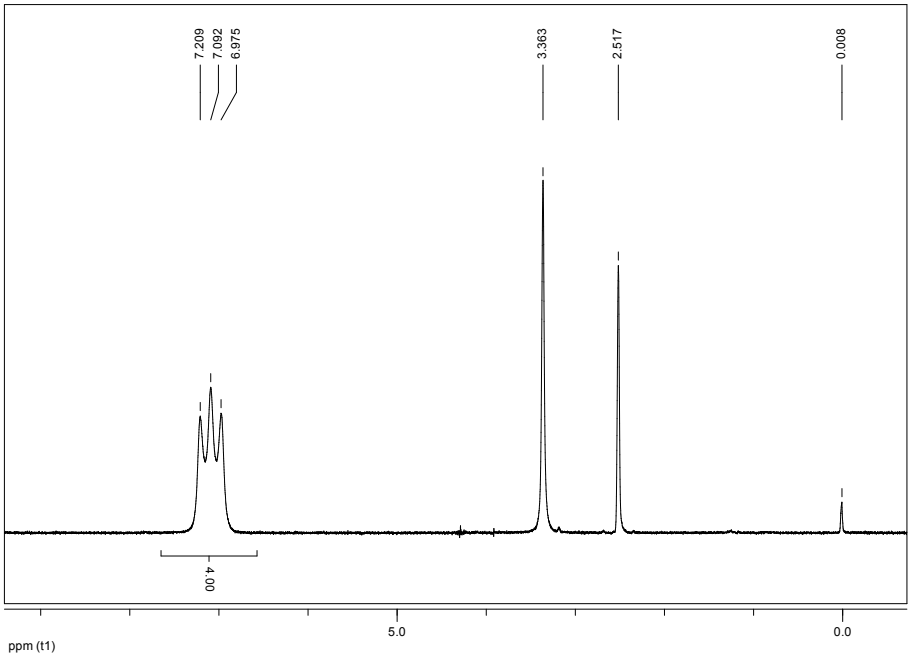
ESI spectrum of **7**



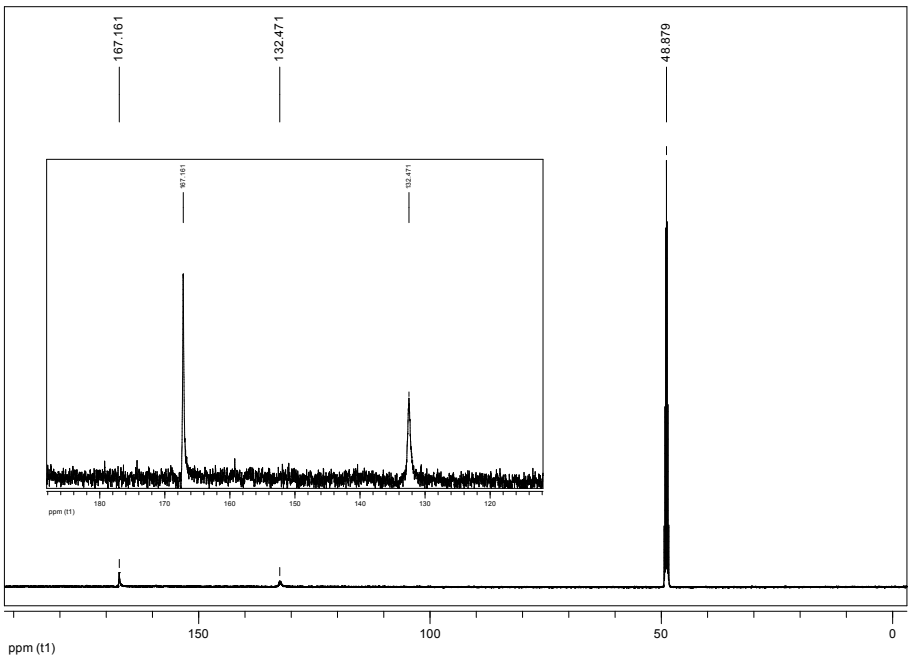
IR spectrum of **8**



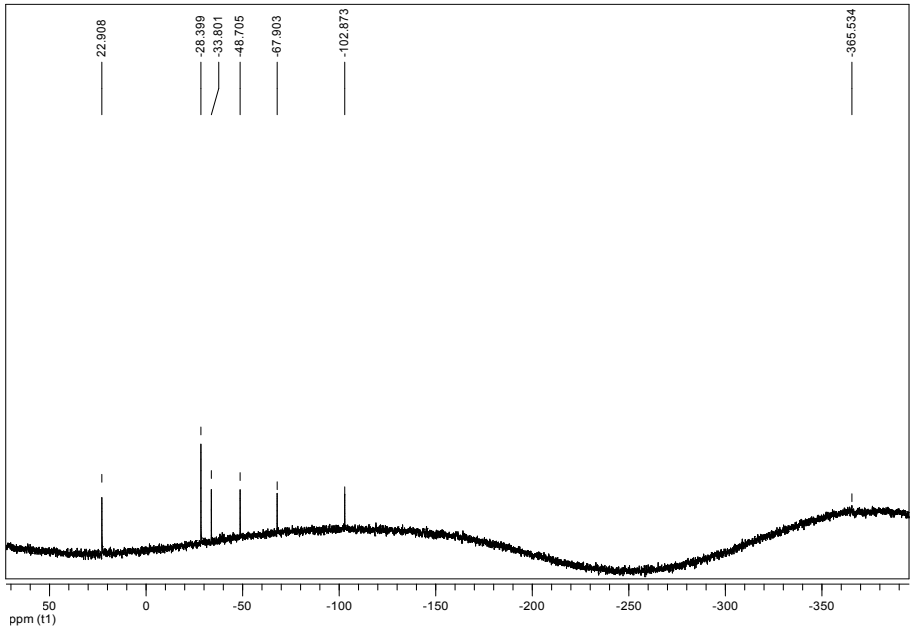
IR spectrum of **5a**



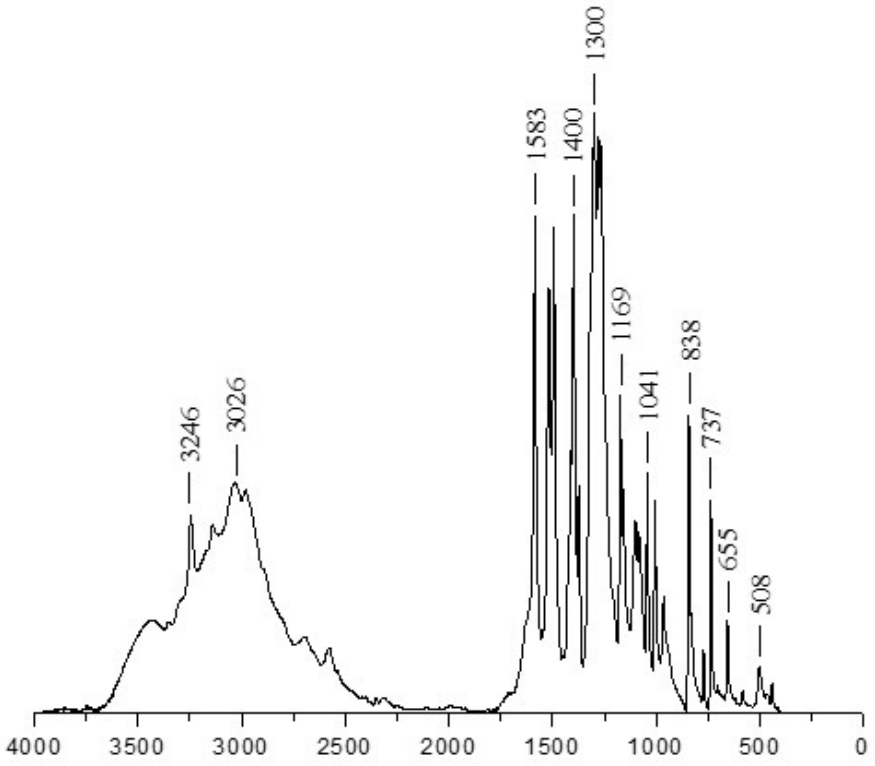
^{1}H NMR spectrum (400 MHz) of **5a** in DMSO-d6 at 25 °C



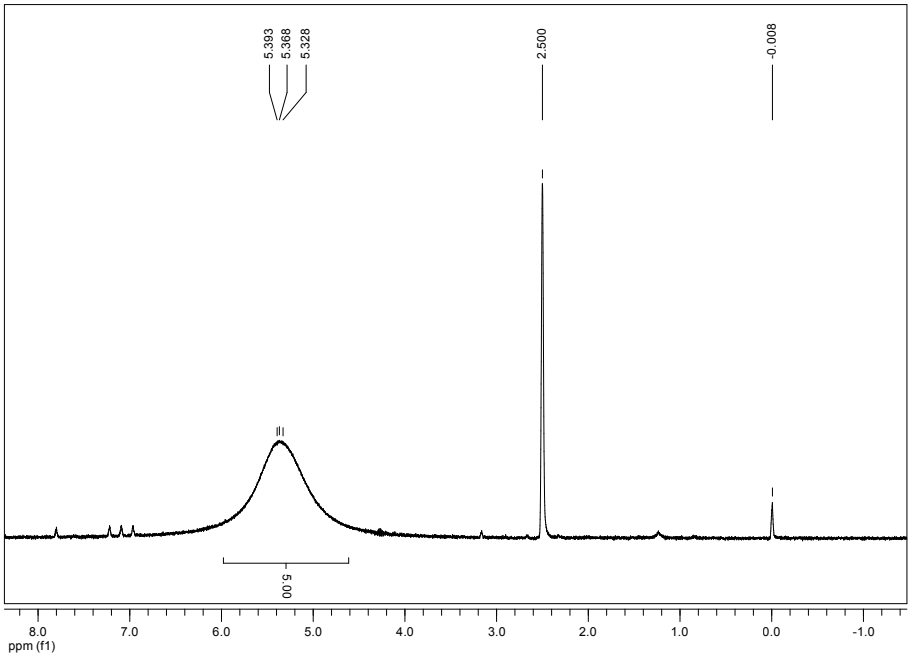
^{13}C NMR spectrum (400 MHz) of **5a** in methnol-d4 at 25 °C



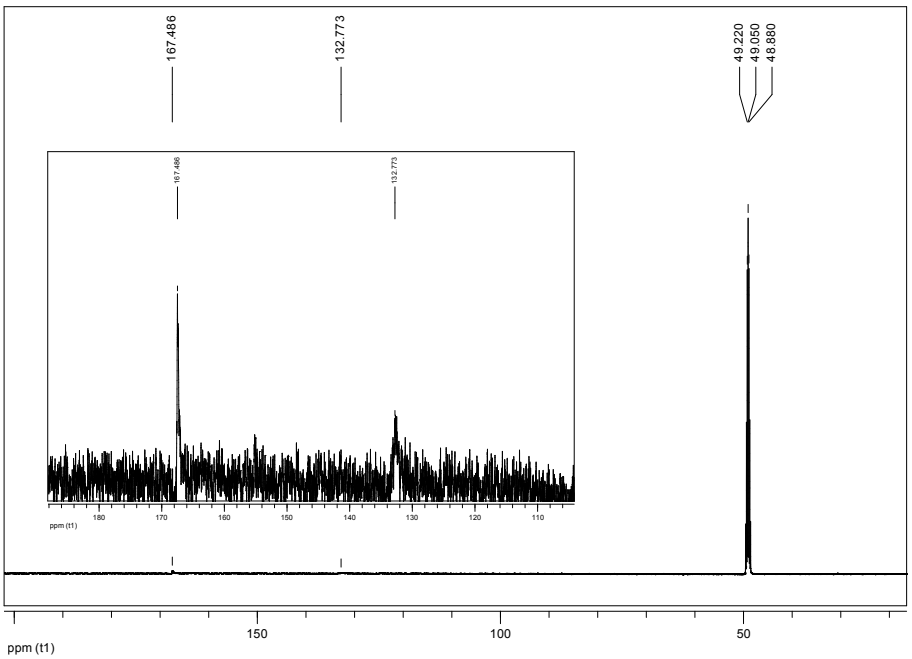
^{15}N NMR spectrum of **5a** in methnol-d4 at 25 °C



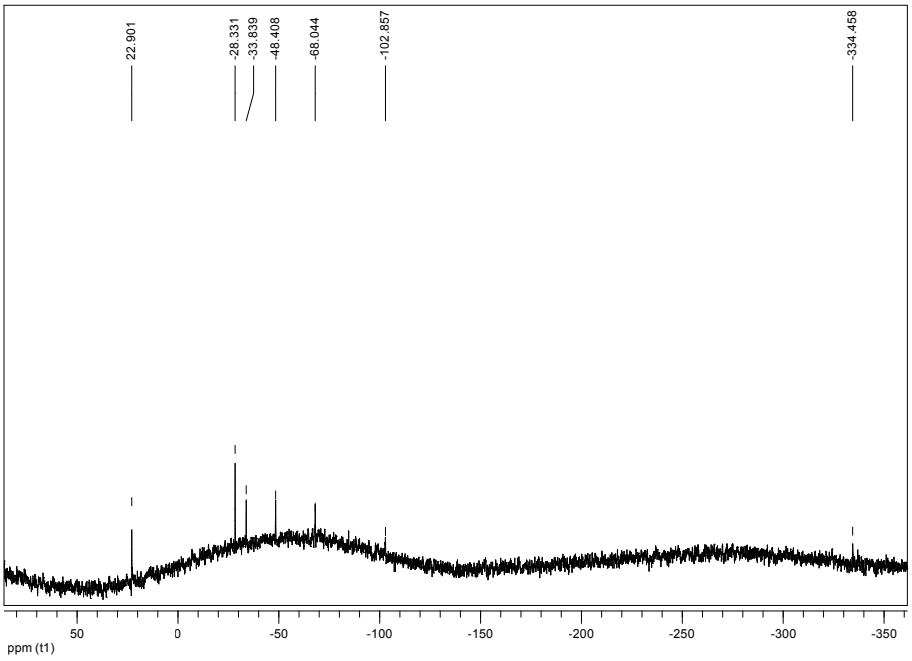
IR spectrum of **5b**



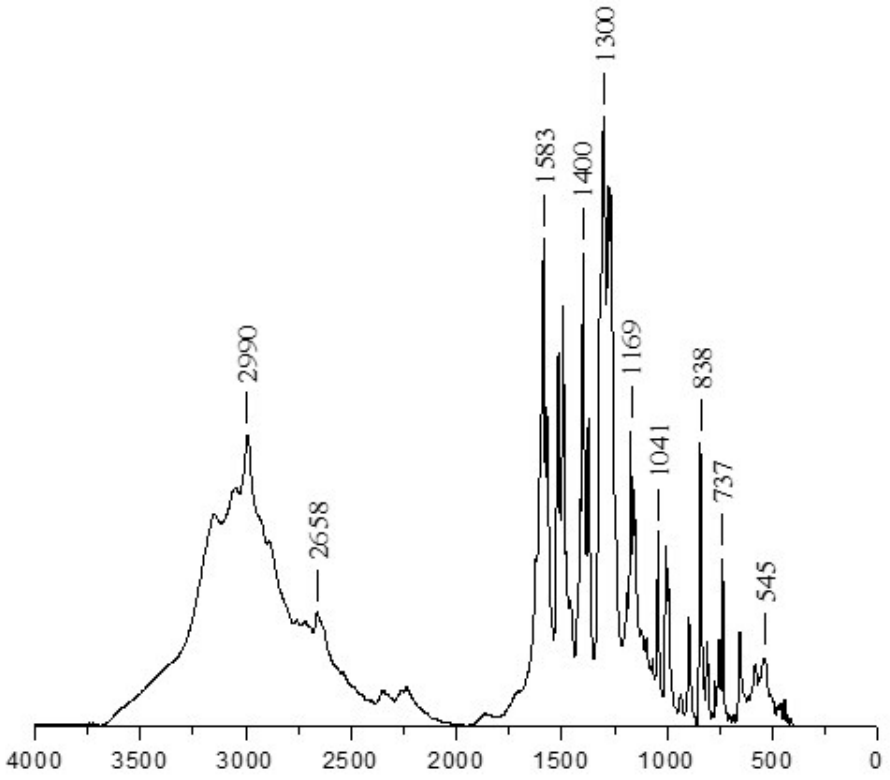
^{1}H NMR spectrum (400 MHz) of **5b** in DMSO-d6 at 25 °C



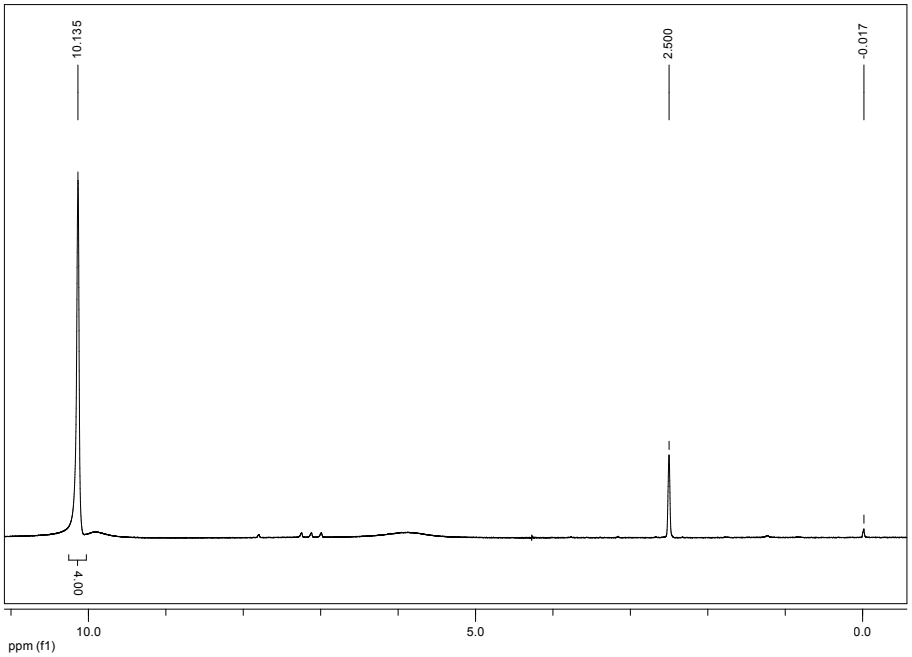
^{13}C NMR spectrum (400 MHz) of **5b** in methnol-d4 at 25 °C



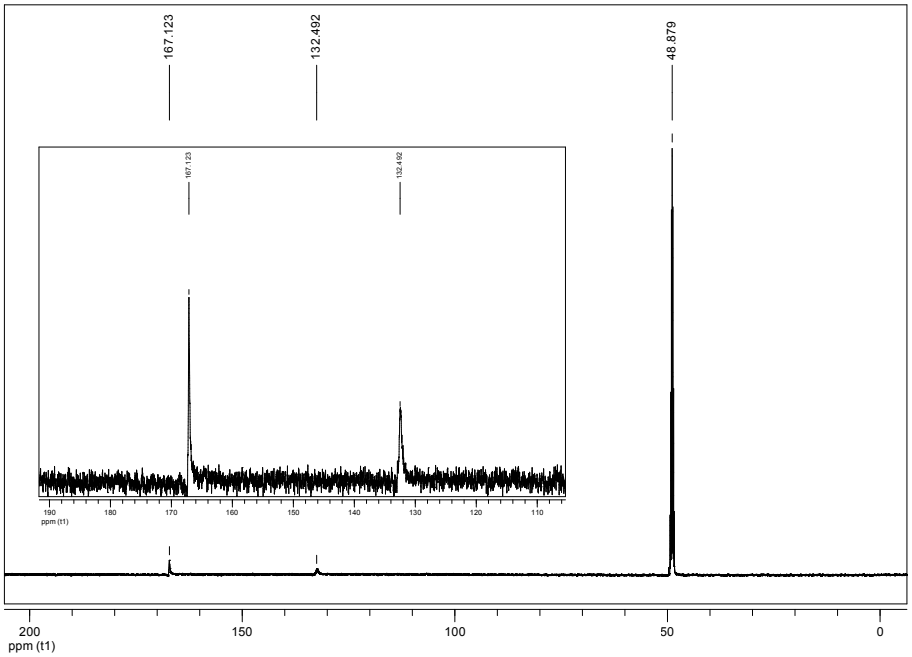
^{15}N NMR spectrum of **5b** in methnol-d4 at 25 °C



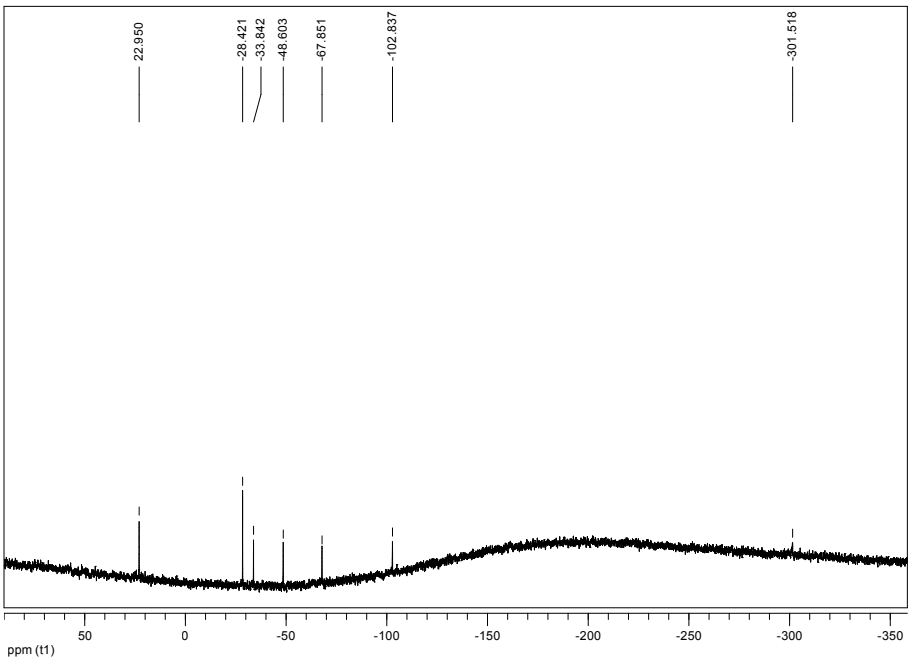
IR spectrum of **5c**



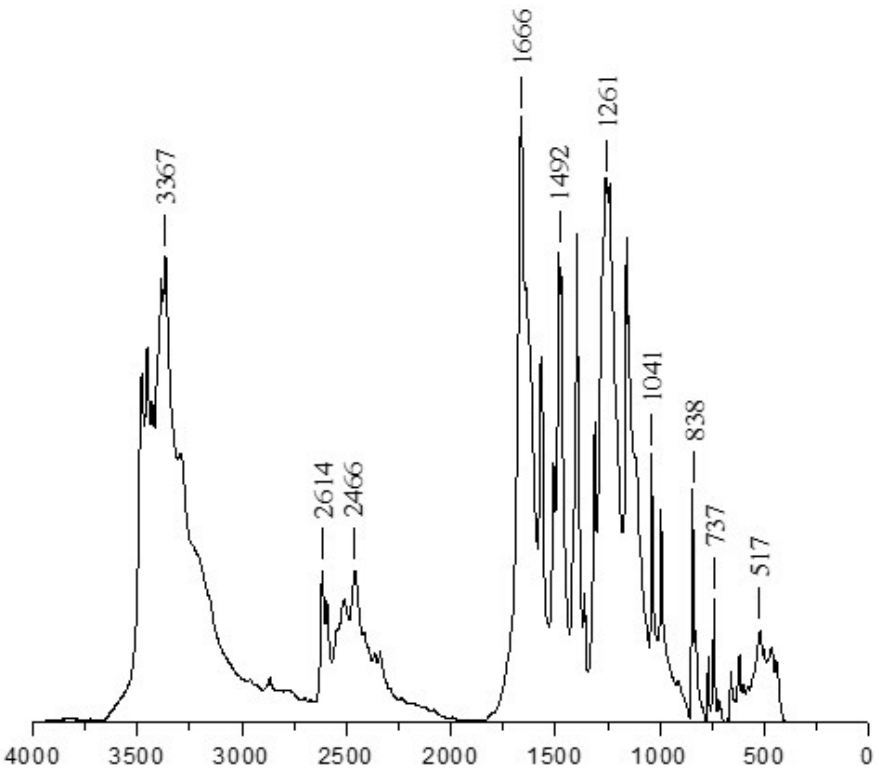
^{1}H NMR spectrum (400 MHz) of **5c** in DMSO-d6 at 25 °C



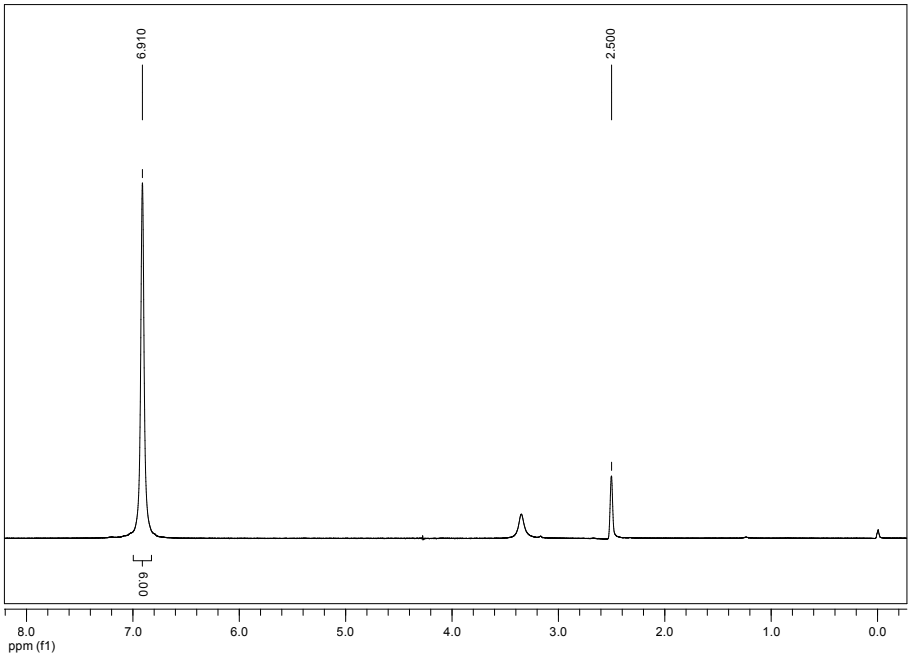
^{13}C NMR spectrum (400 MHz) of **5c** in methnol-d4 at 25 °C



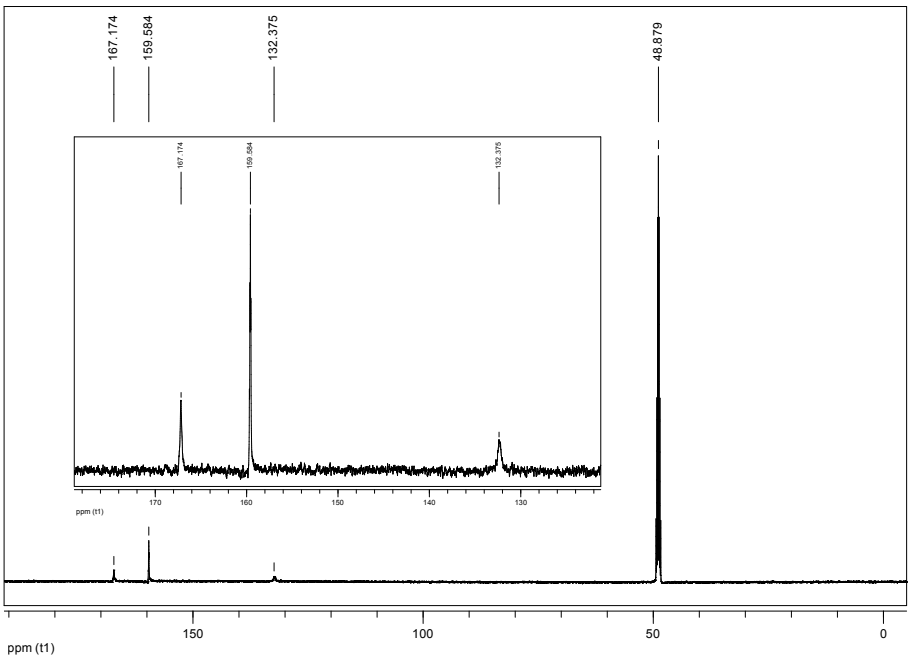
^{15}N NMR spectrum of **5c** in methnol-d4 at 25 °C



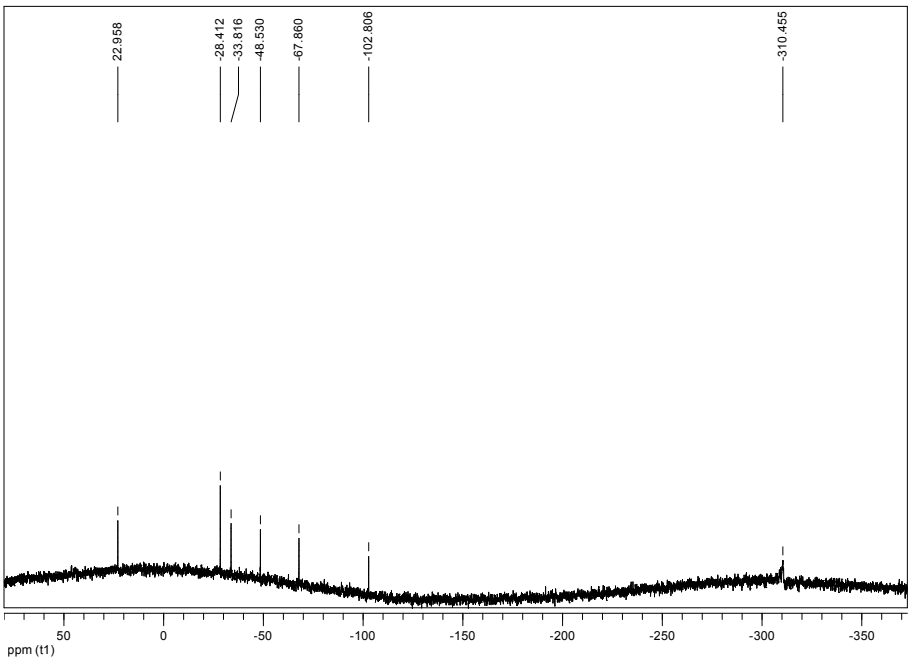
IR spectrum of **5d**



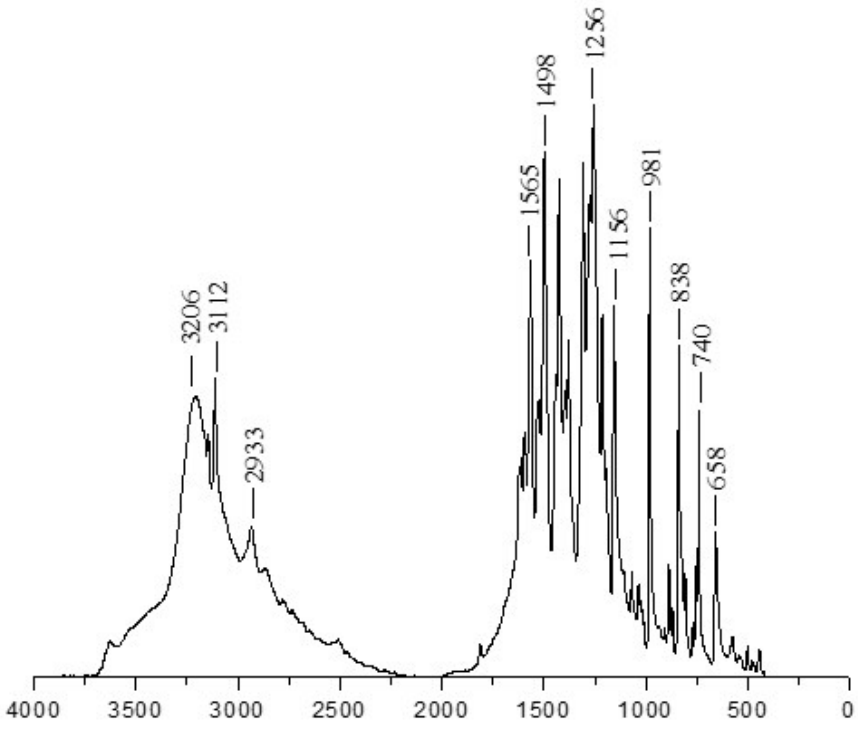
^{1}H NMR spectrum (400 MHz) of **5d** in DMSO-d6 at 25 °C



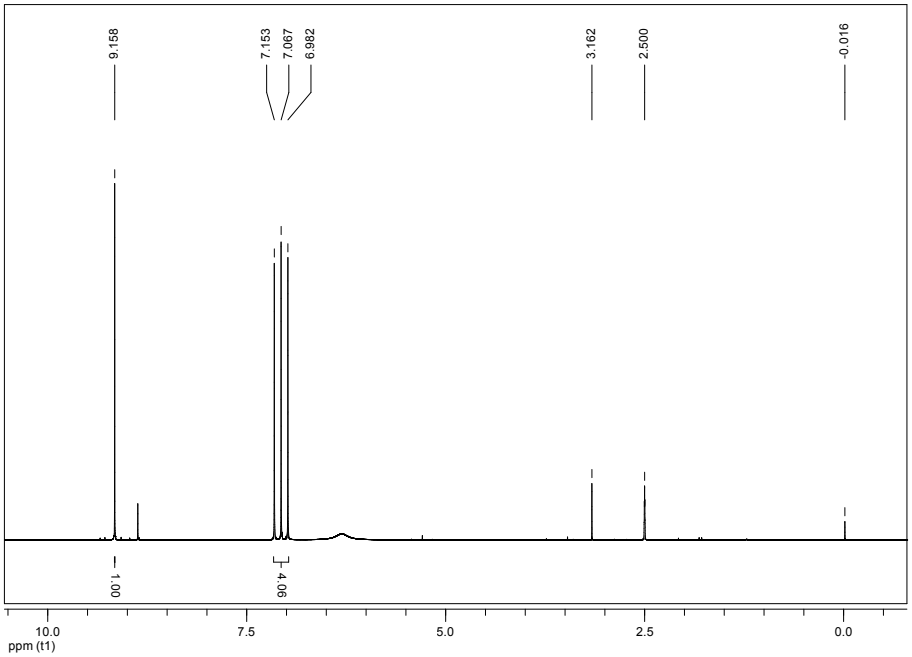
^{13}C NMR spectrum (400 MHz) of **5d** in methnol-d4 at 25 °C



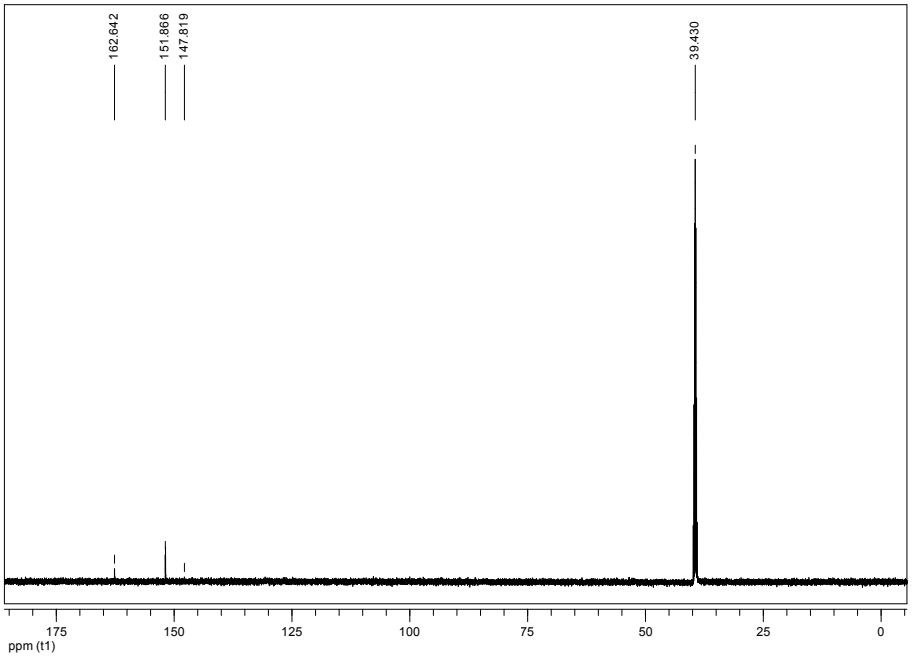
^{15}N NMR spectrum of **5d** in methnol-d4 at 25 °C



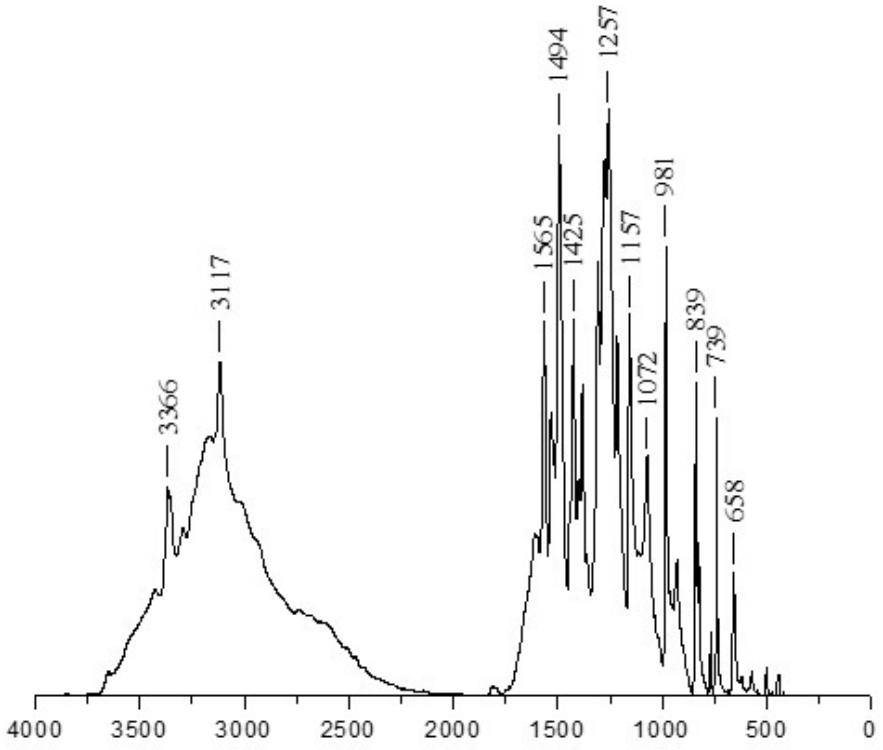
IR spectrum of **6a**



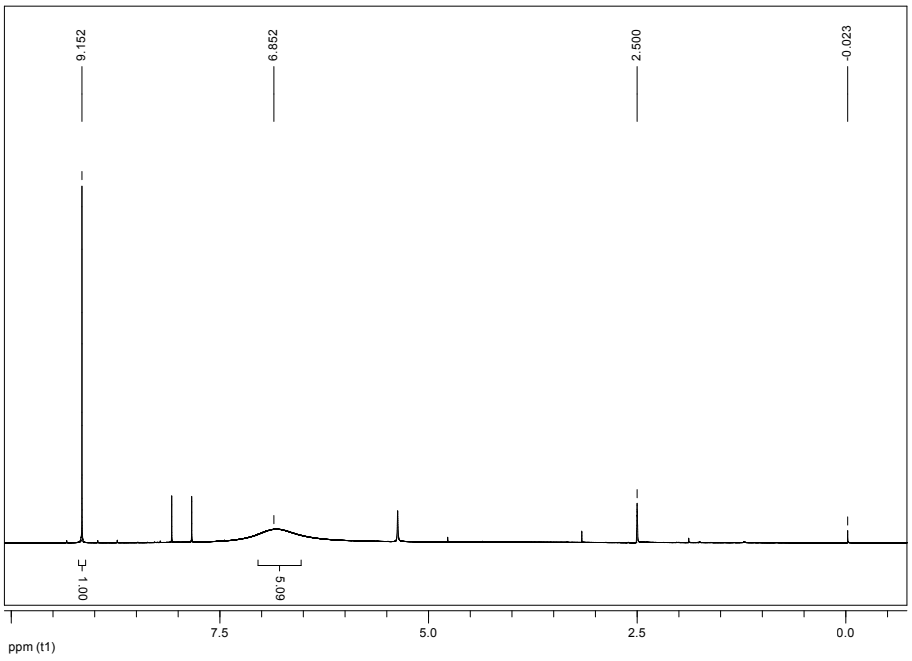
^{1}H NMR spectrum (400 MHz) of **6a** in DMSO-d6 at 25 °C



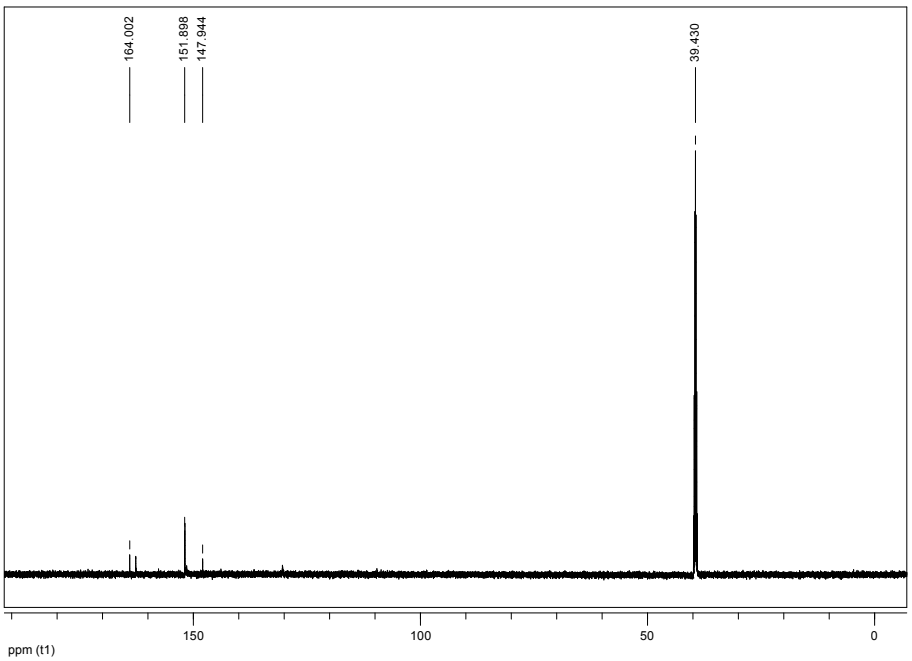
^{13}C NMR spectrum (400 MHz) of **6a** in DMSO-d6 at 25 °C



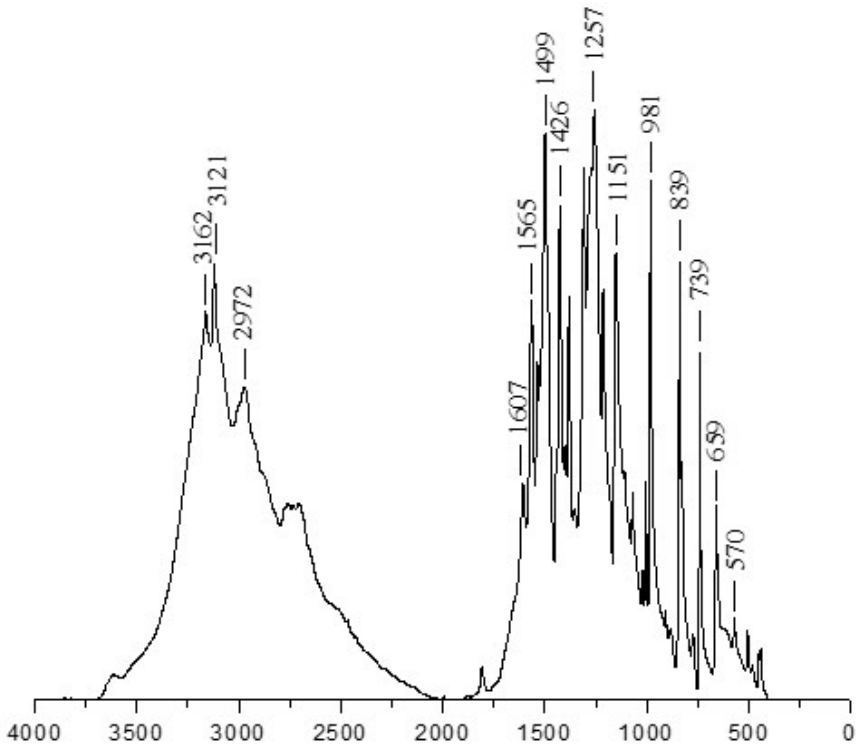
IR spectrum of **6b**



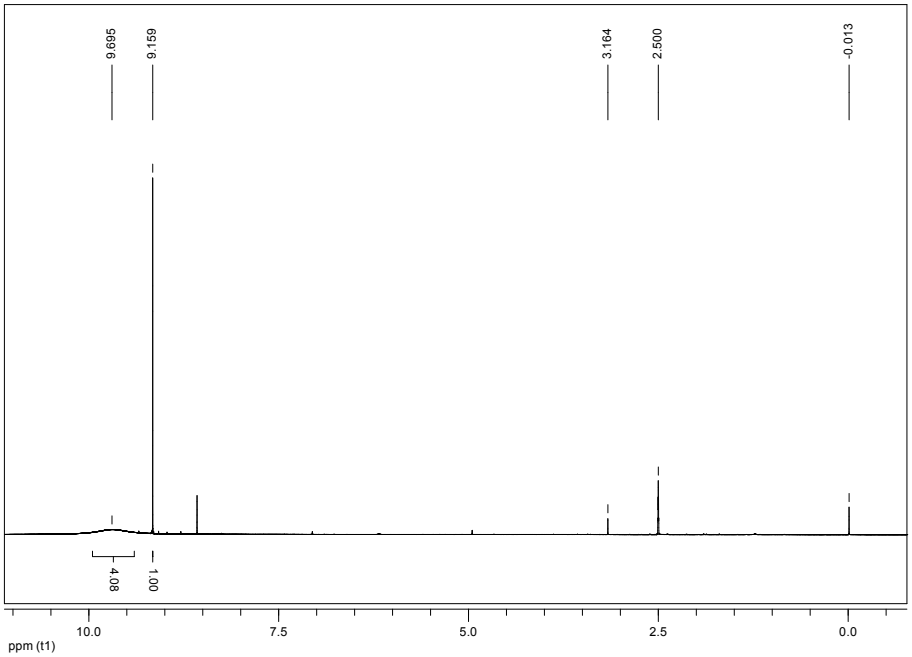
^{1}H NMR spectrum (400 MHz) of **6b** in DMSO-d6 at 25 °C



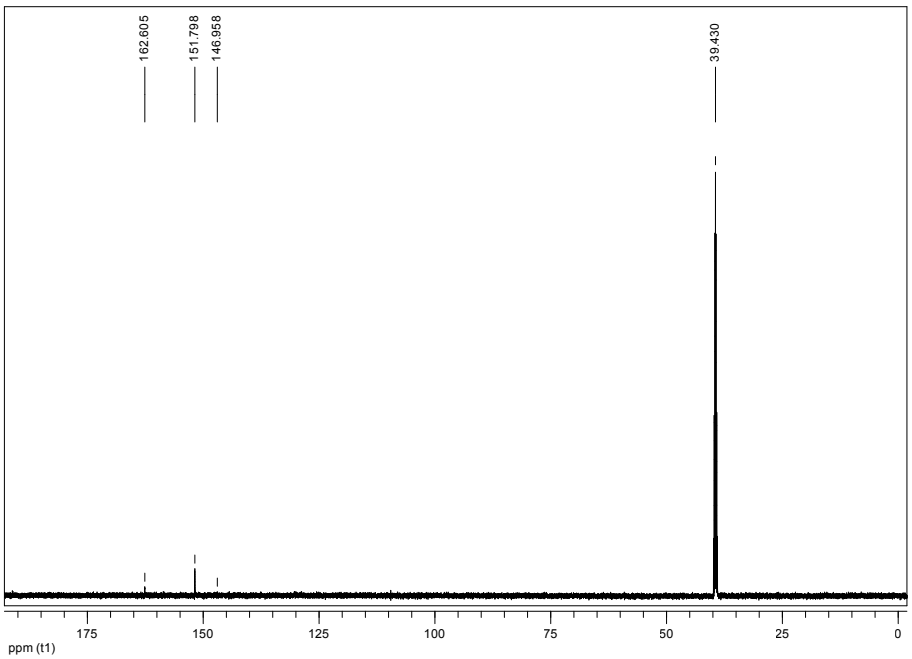
^{13}C NMR spectrum (400 MHz) of **6b** in DMSO-d6 at 25 °C



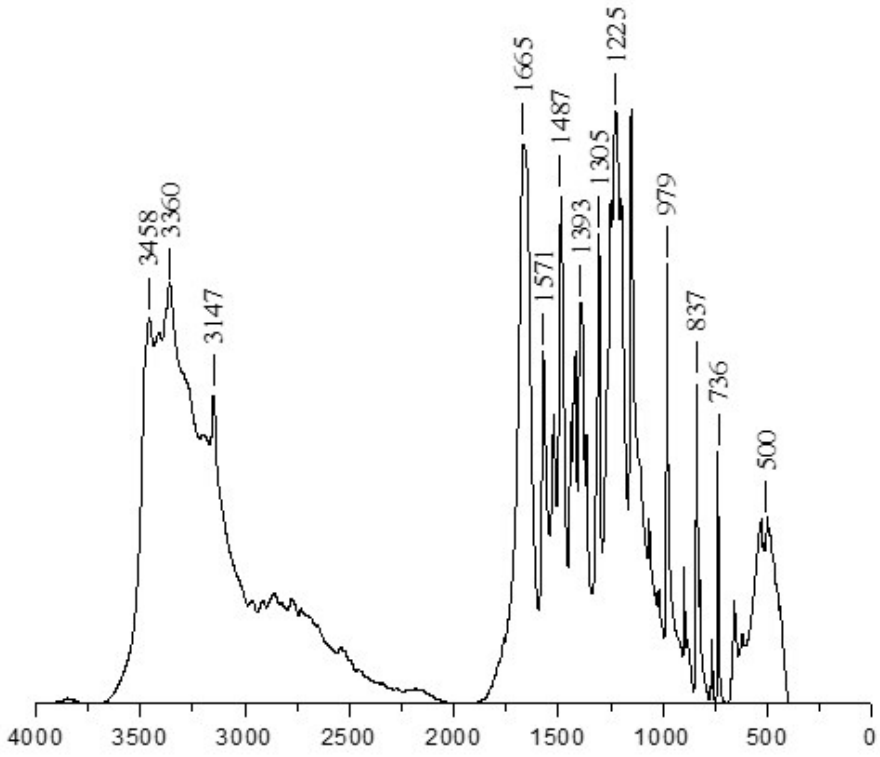
IR spectrum of **6c**



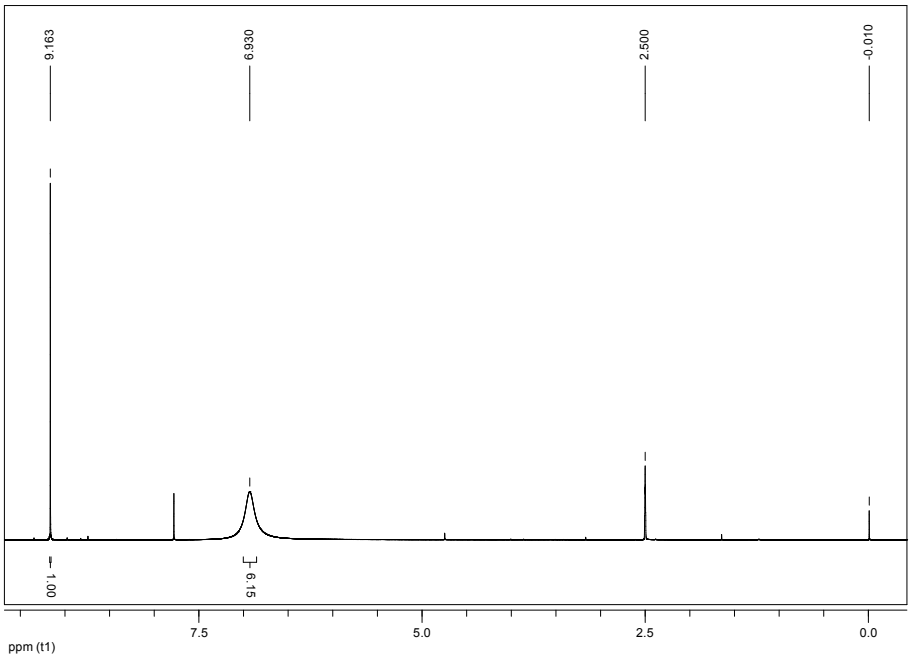
^{1}H NMR spectrum (400 MHz) of **6c** in DMSO-d6 at 25 °C



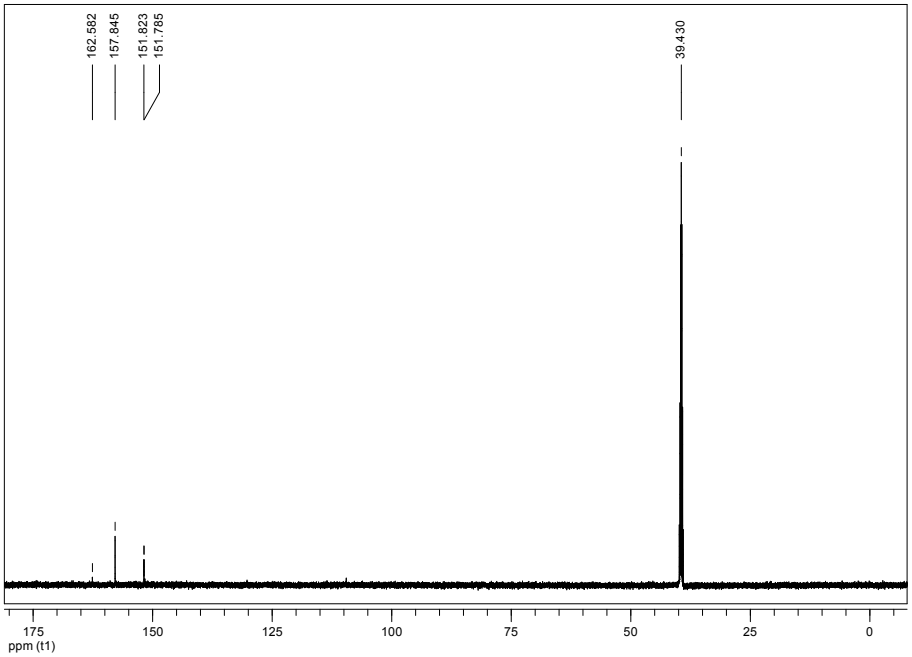
^{13}C NMR spectrum (400 MHz) of **6c** in DMSO-d6 at 25 °C



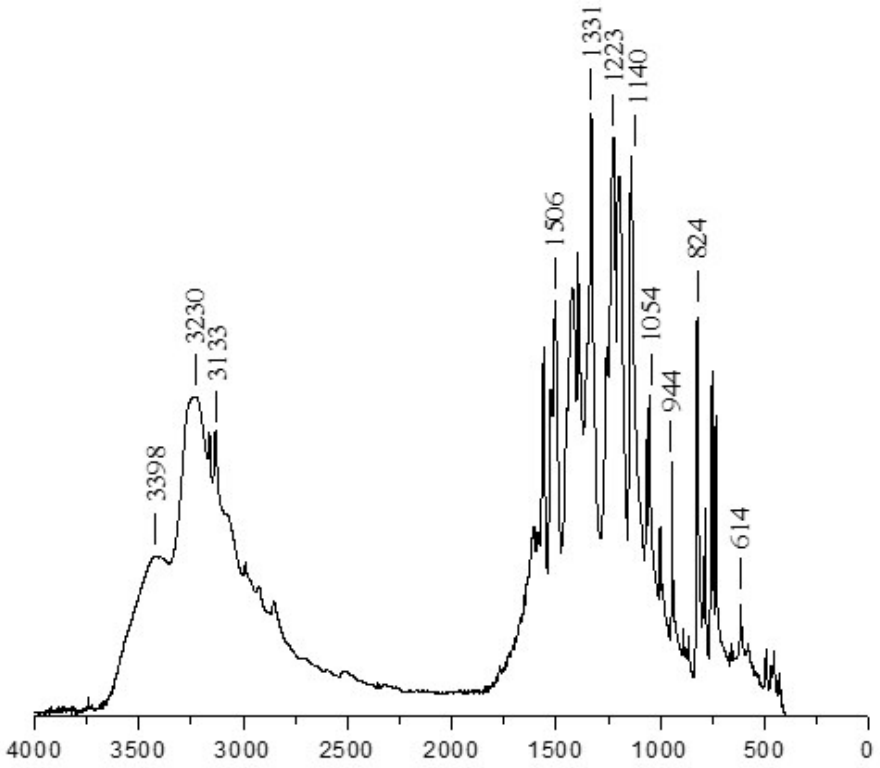
IR spectrum of **6d**



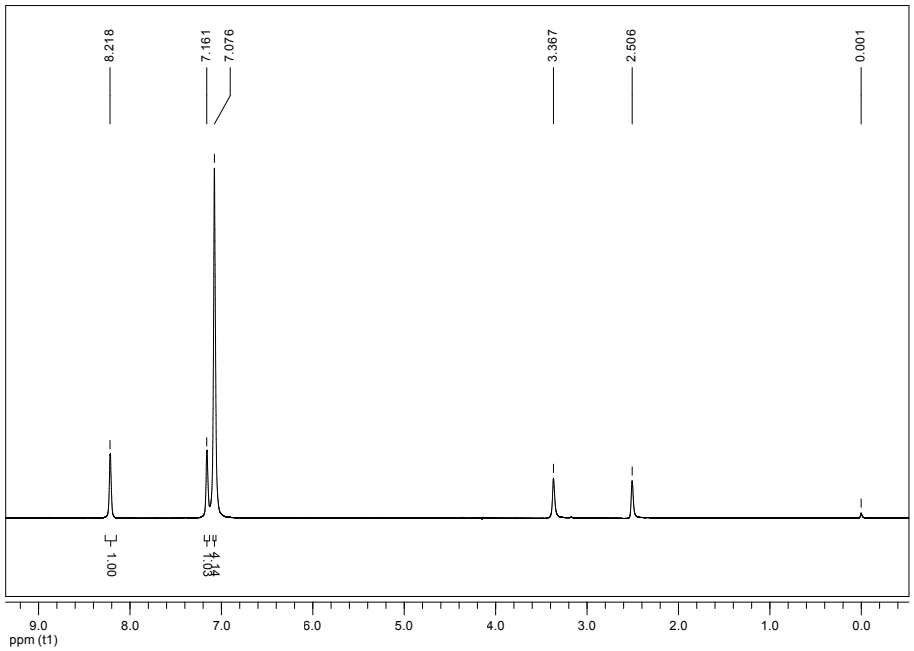
^{1}H NMR spectrum (400 MHz) of **6d** in DMSO-d6 at 25 °C



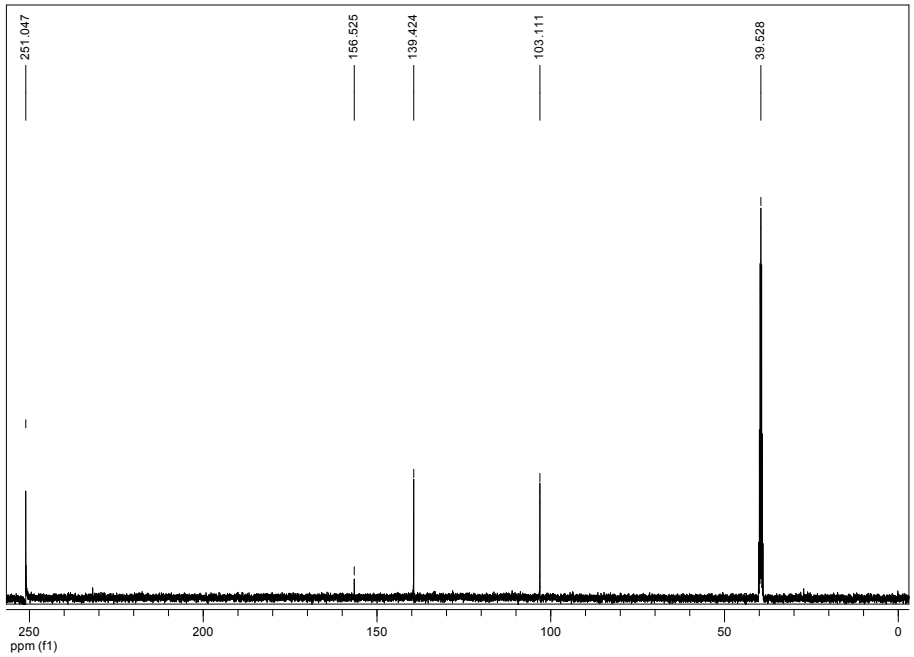
^{13}C NMR spectrum (400 MHz) of **6d** in DMSO-d6 at 25 °C



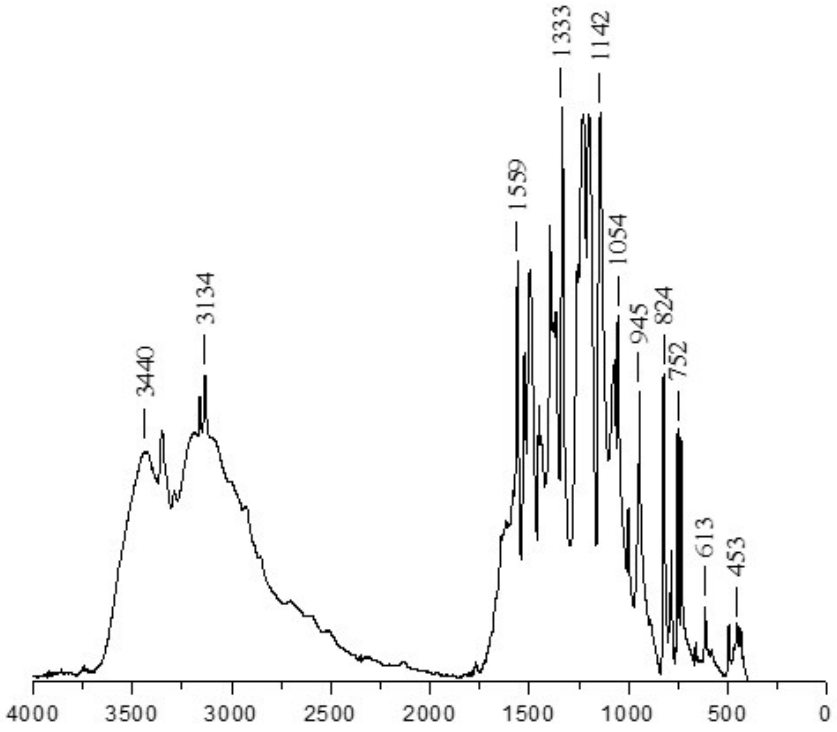
IR spectrum of **7a**



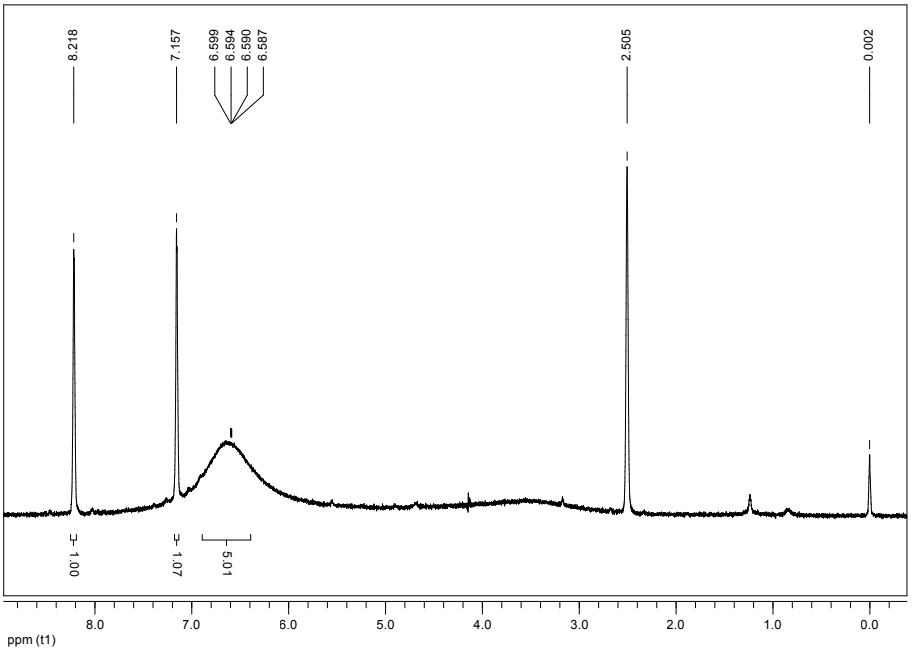
^{1}H NMR spectrum (400 MHz) of **7a** in DMSO-d6 at 25 °C



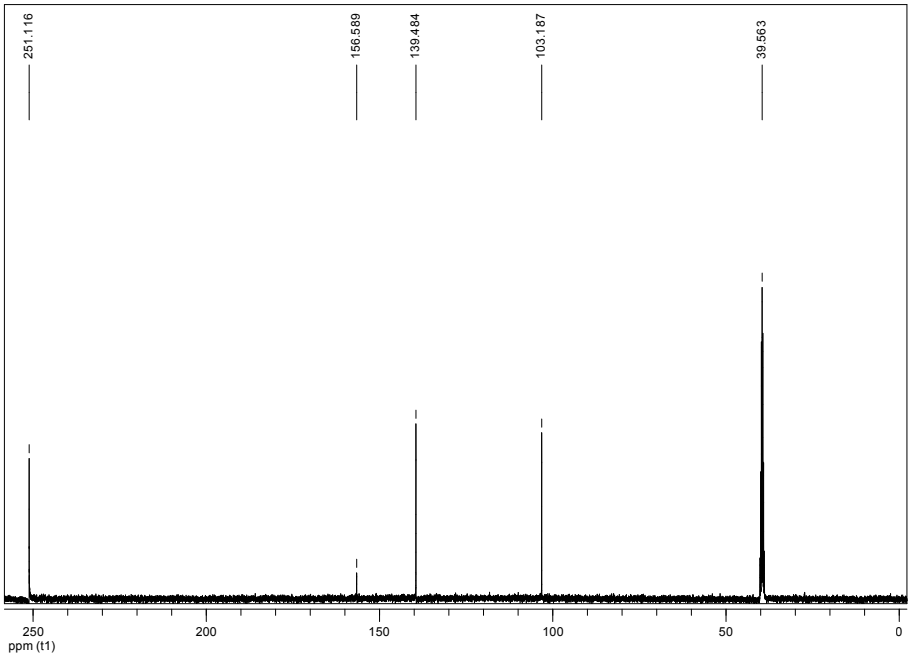
^{13}C NMR spectrum (400 MHz) of **7a** in DMSO-d6 at 25 °C



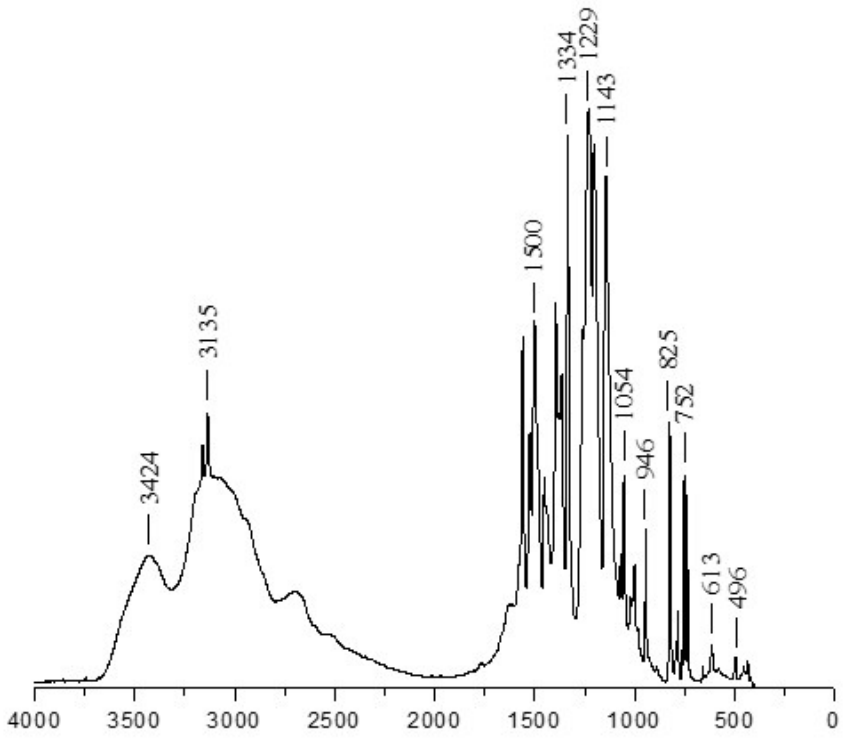
IR spectrum of **7b**



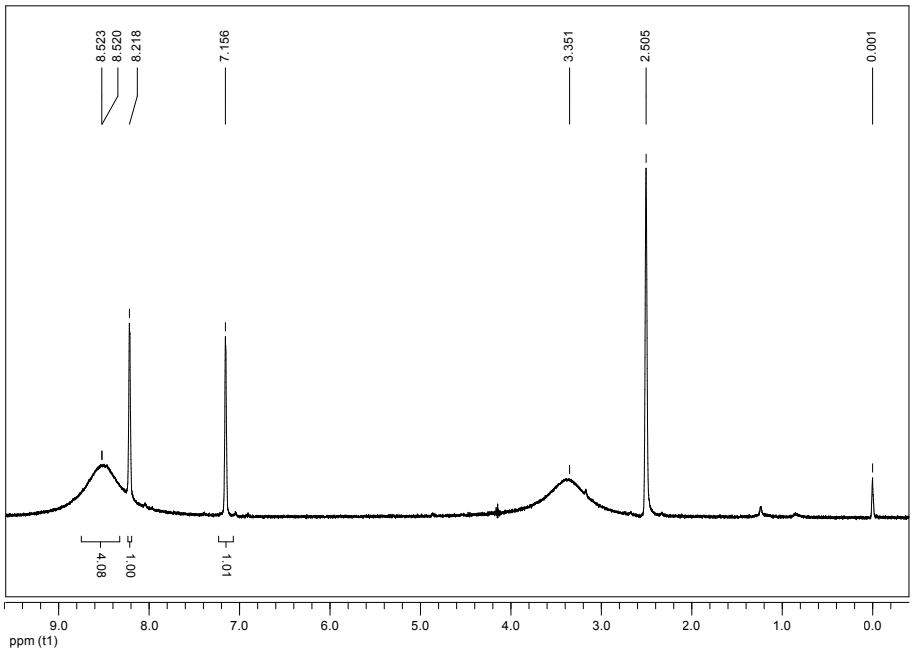
^{1}H NMR spectrum (400 MHz) of **7b** in DMSO-d6 at 25 °C



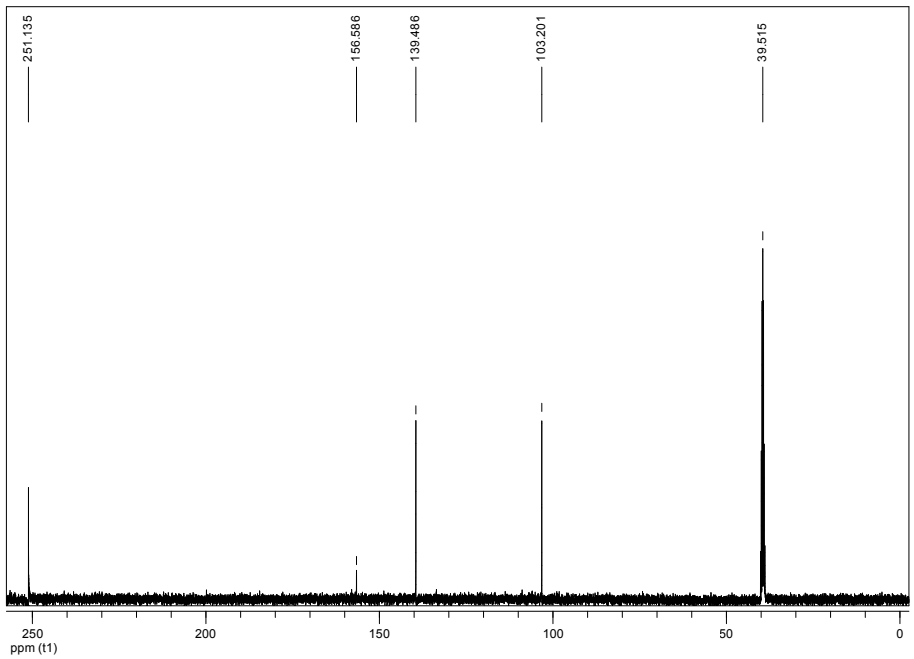
^{13}C NMR spectrum (400 MHz) of **7b** in DMSO-d6 at 25 °C



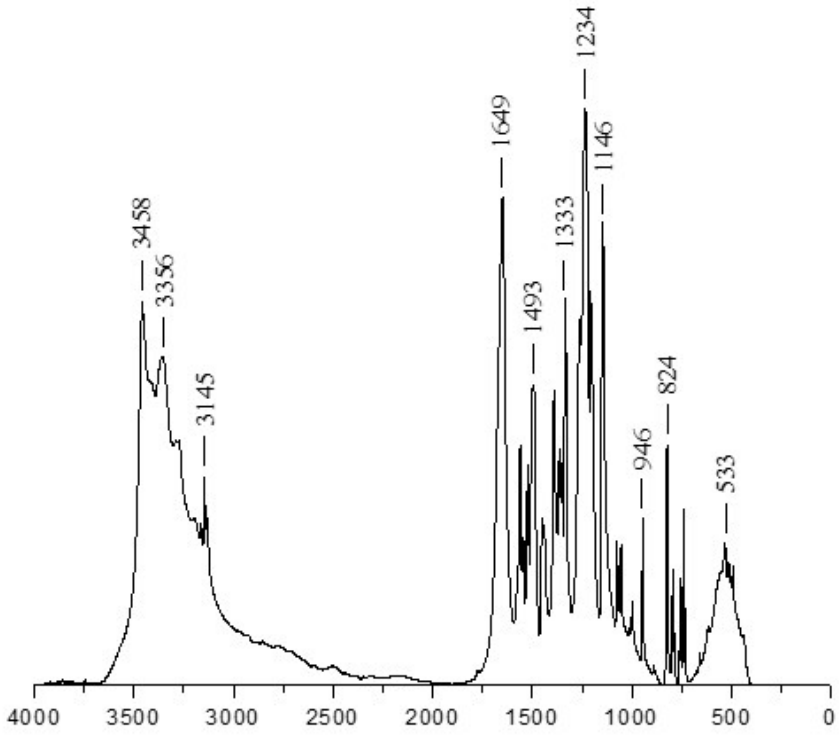
IR spectrum of **7c**



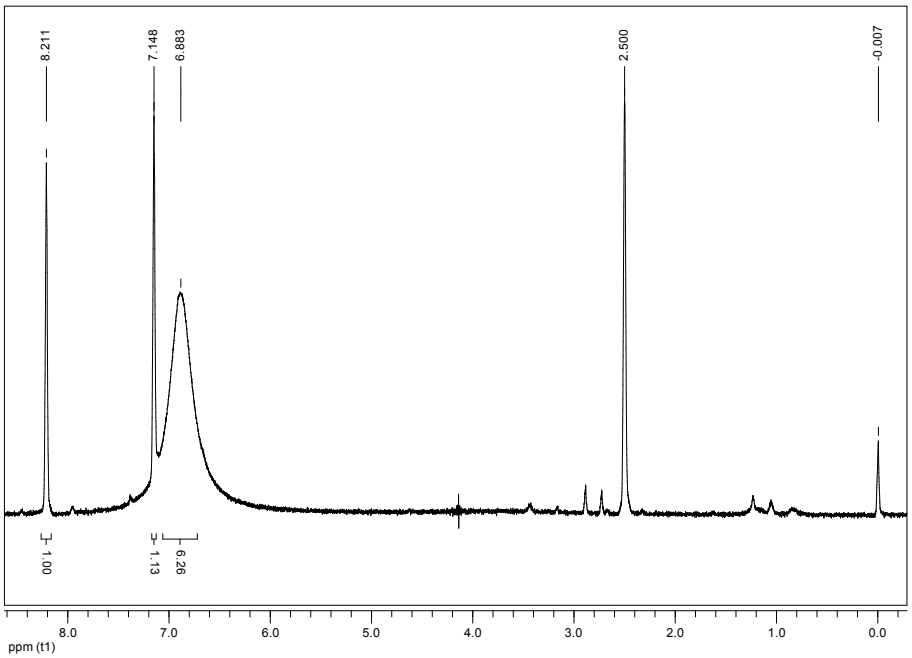
^{1}H NMR spectrum (400 MHz) of **7c** in DMSO-d6 at 25 °C



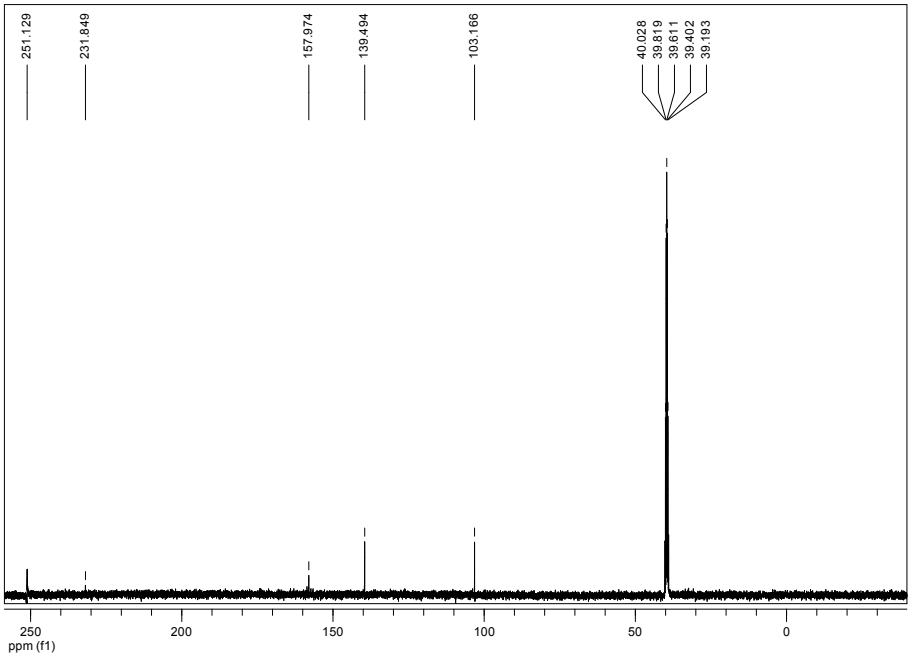
^{13}C NMR spectrum (400 MHz) of **7c** in DMSO-d6 at 25 °C



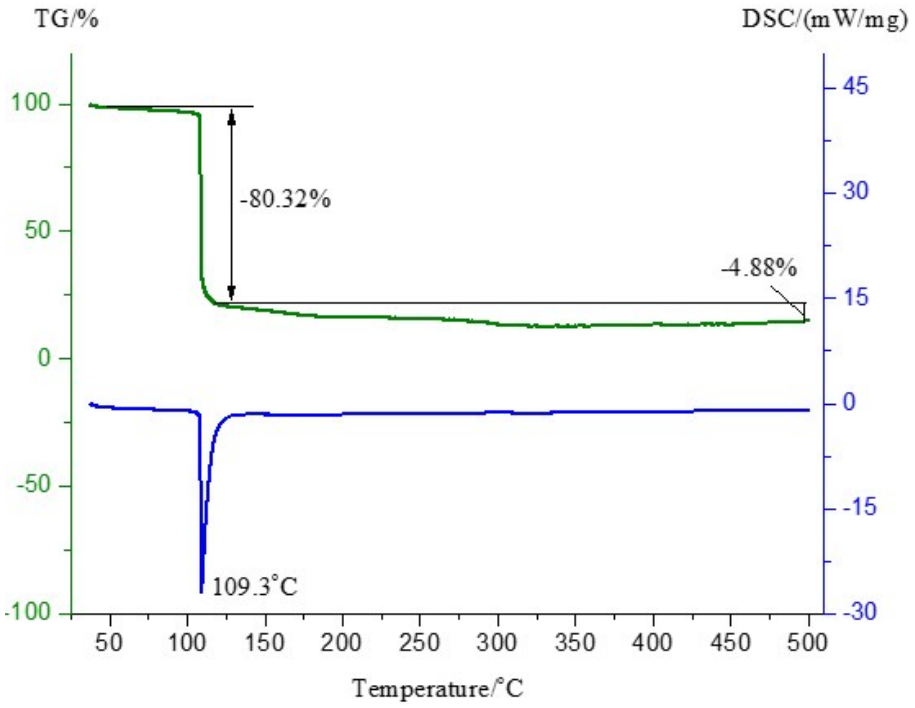
IR spectrum of **7d**



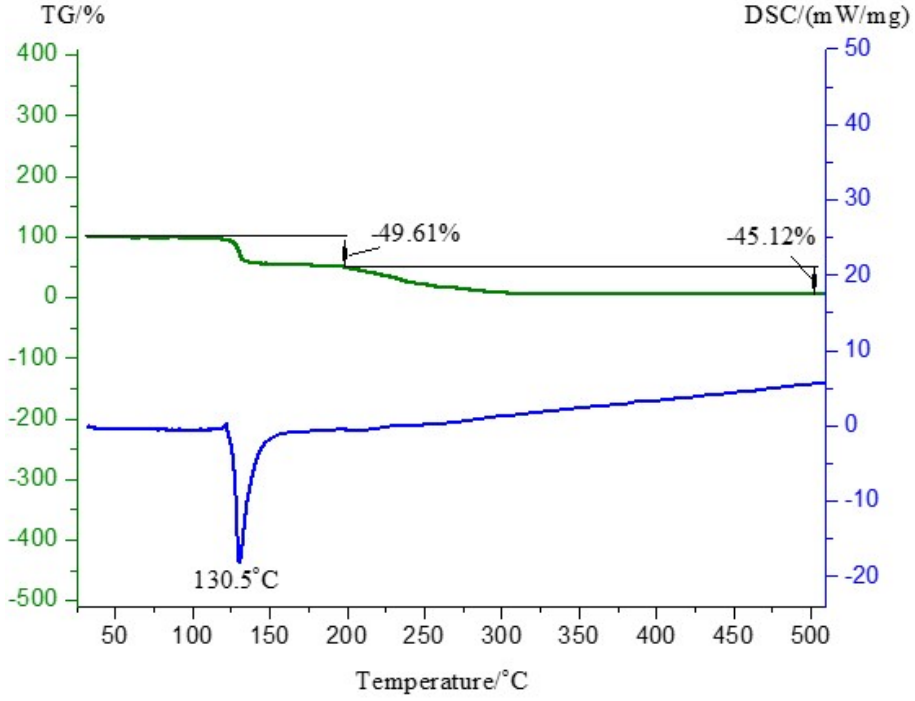
^{1}H NMR spectrum (400 MHz) of **7d** in DMSO-d6 at 25 °C



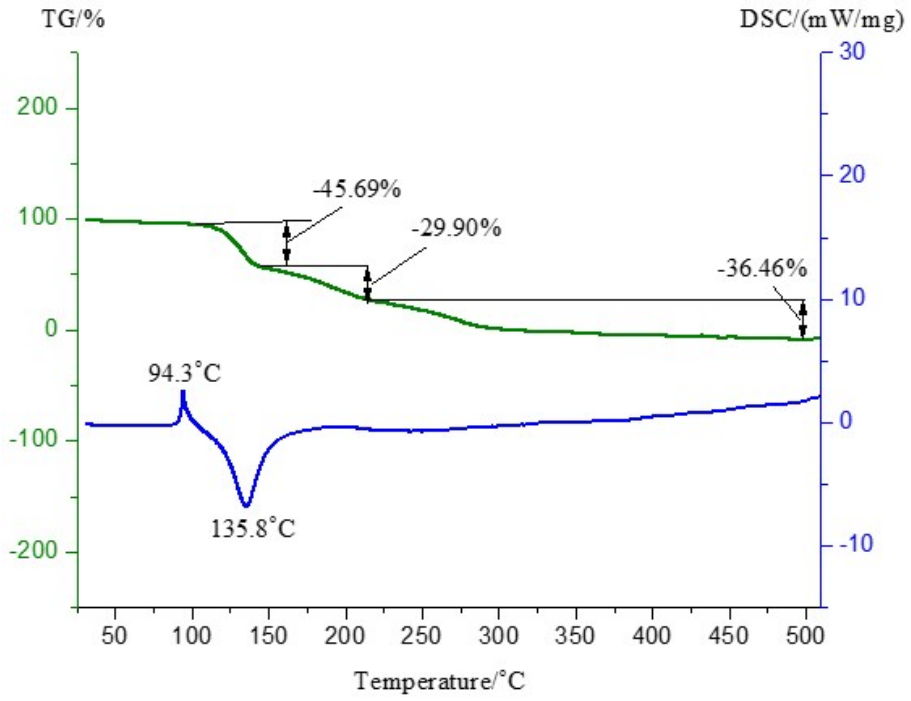
^{13}C NMR spectrum (400 MHz) of **7d** in DMSO-d6 at 25 °C



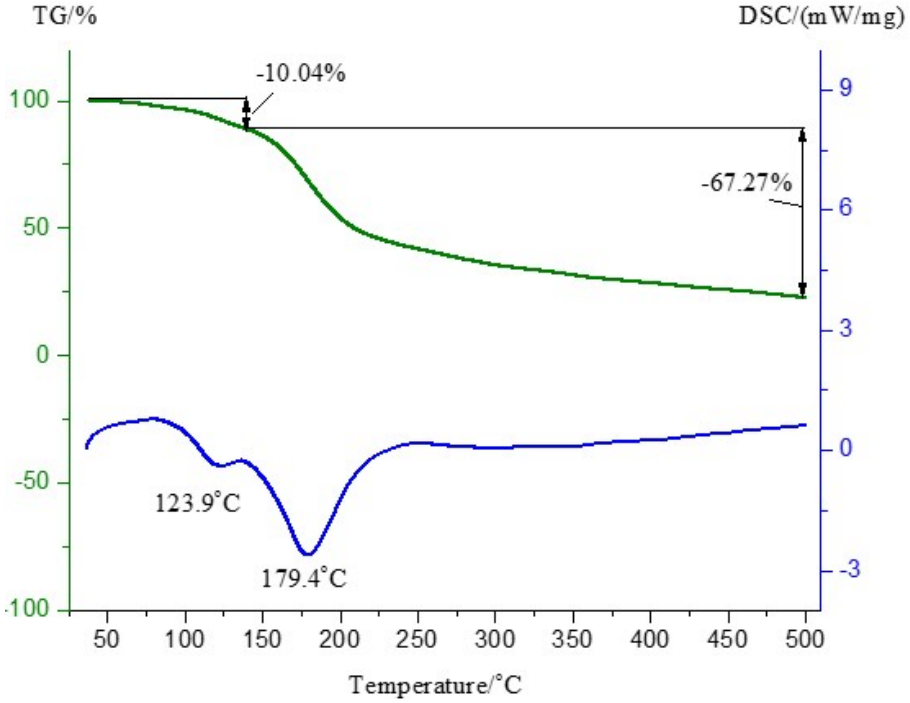
DSC spectrum of **5**



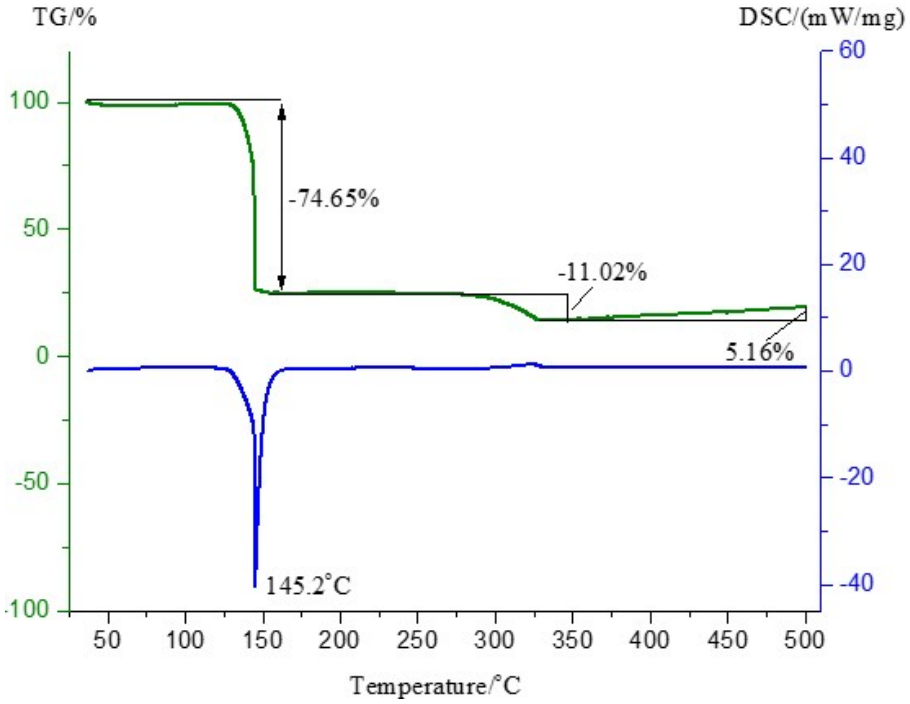
DSC spectrum of **6**



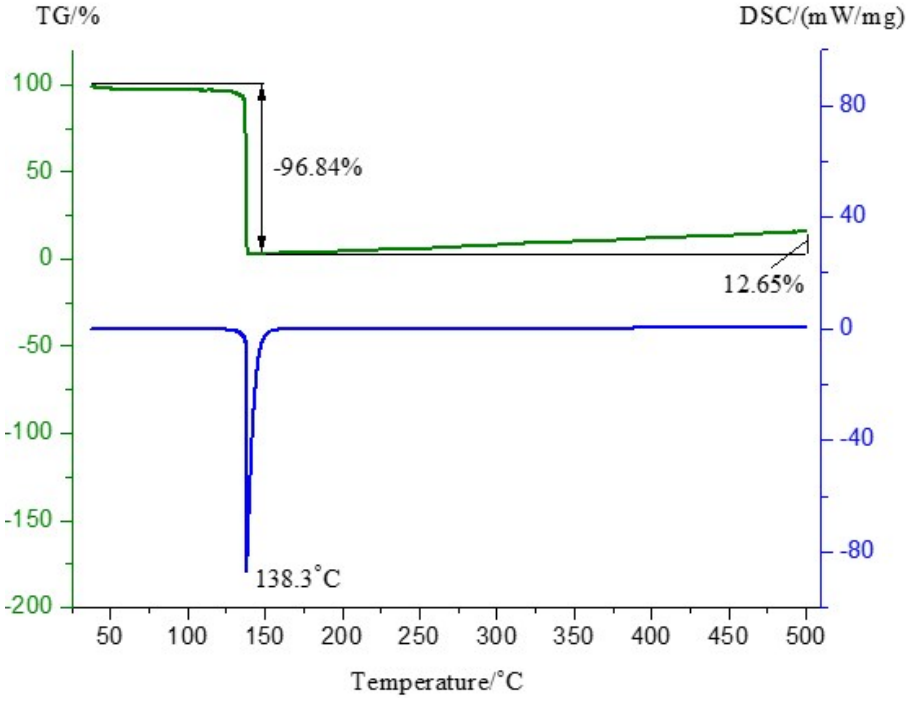
DSC spectrum of **7**



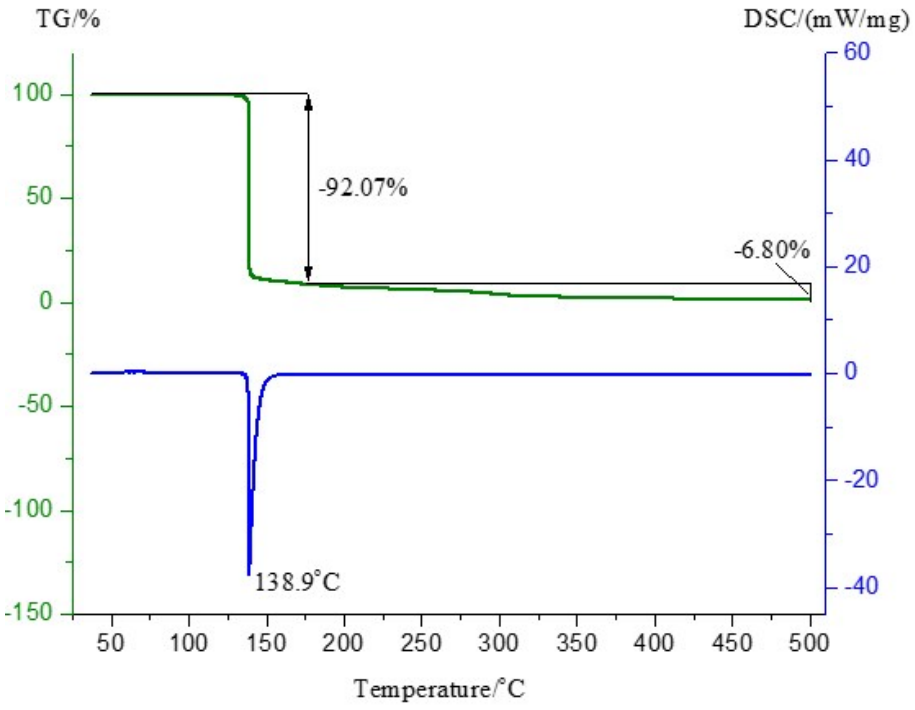
DSC spectrum of **8**



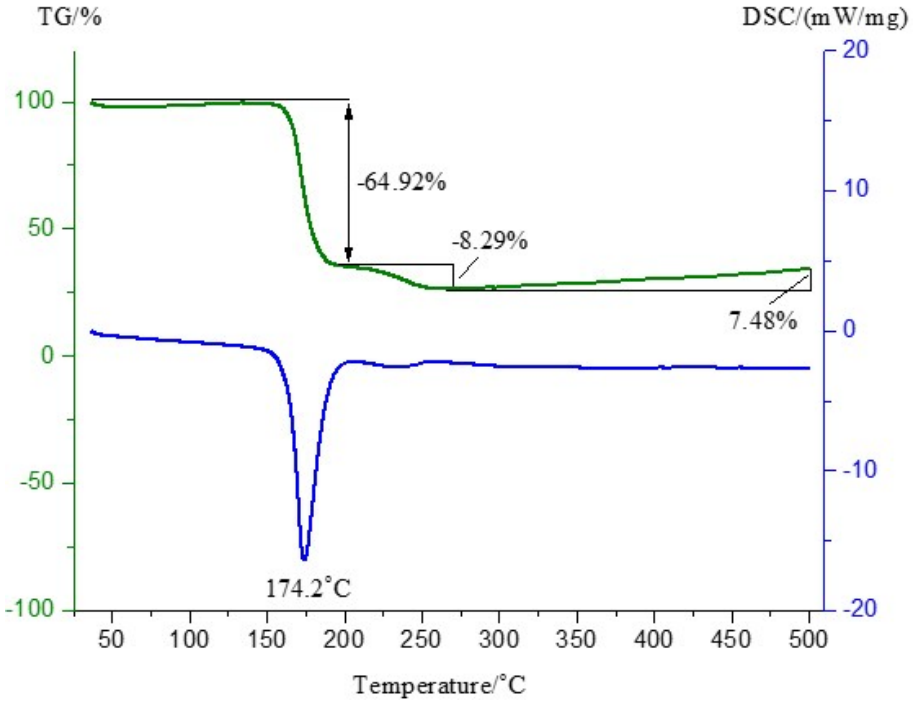
DSC spectrum of **5a**



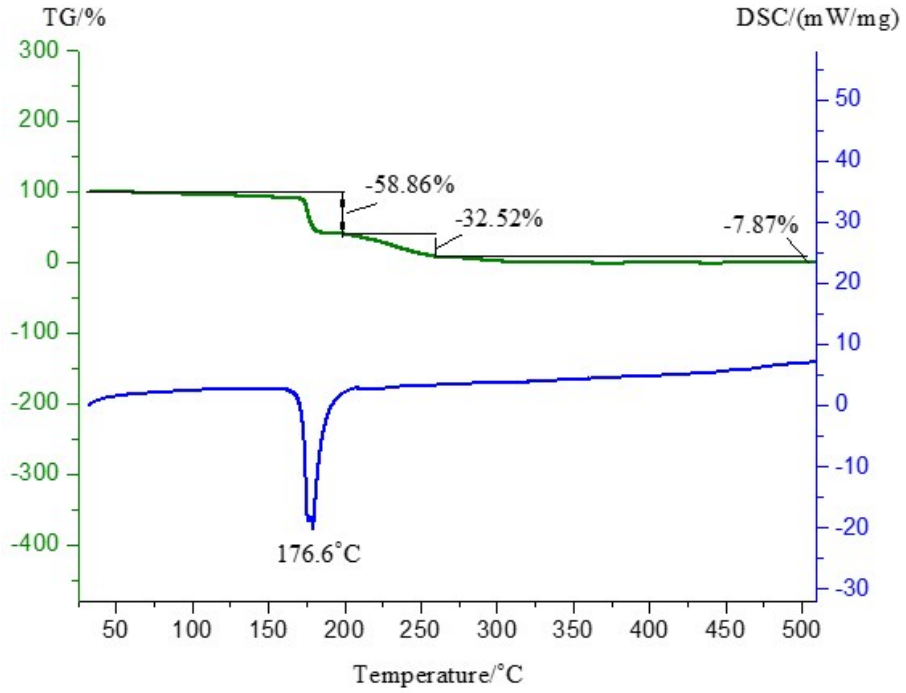
DSC spectrum of **5b**



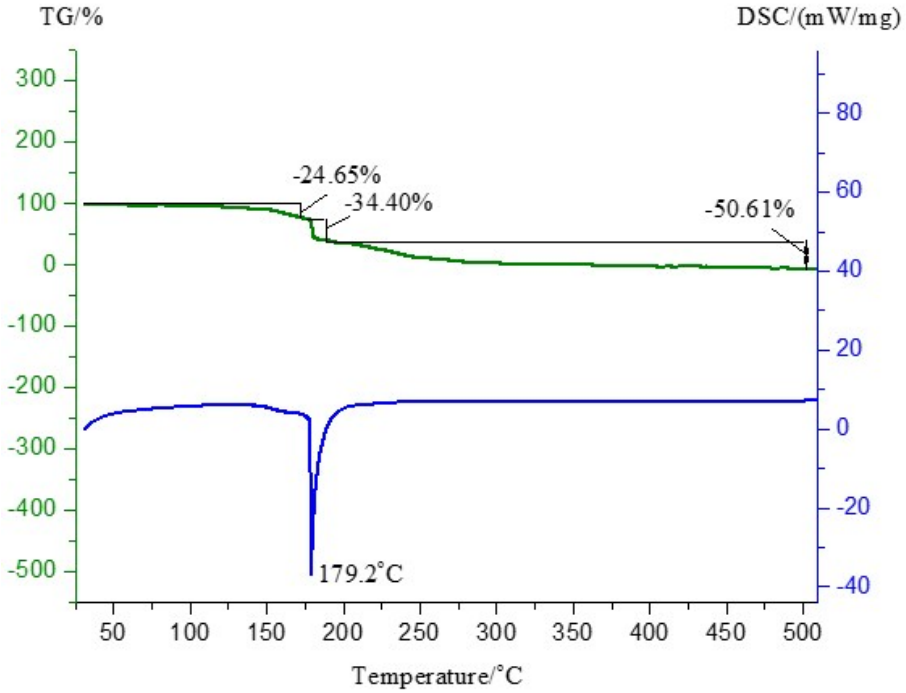
DSC spectrum of **5c**



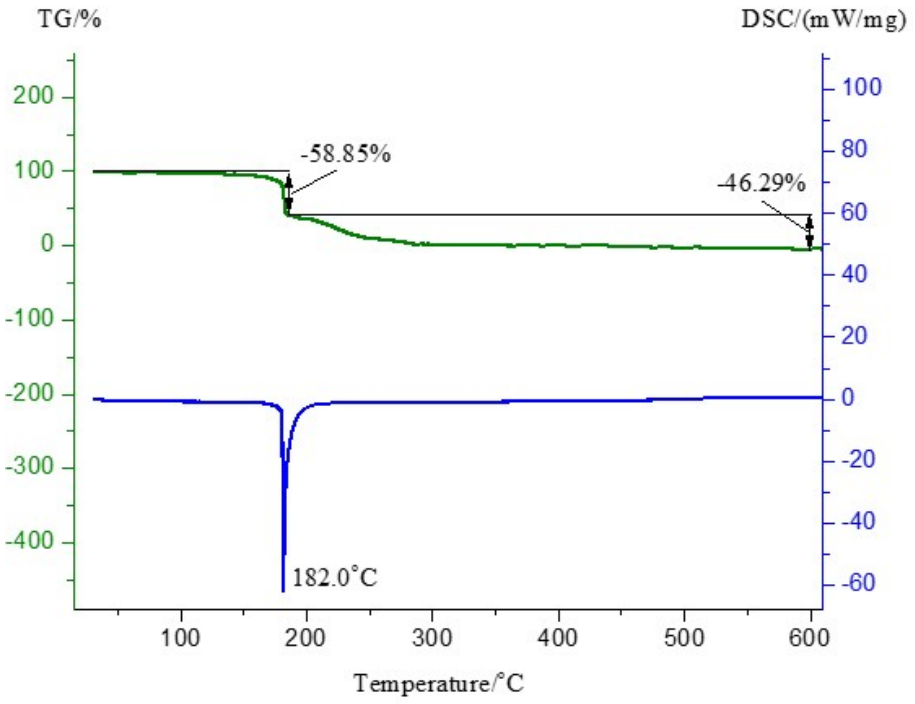
DSC spectrum of **5d**



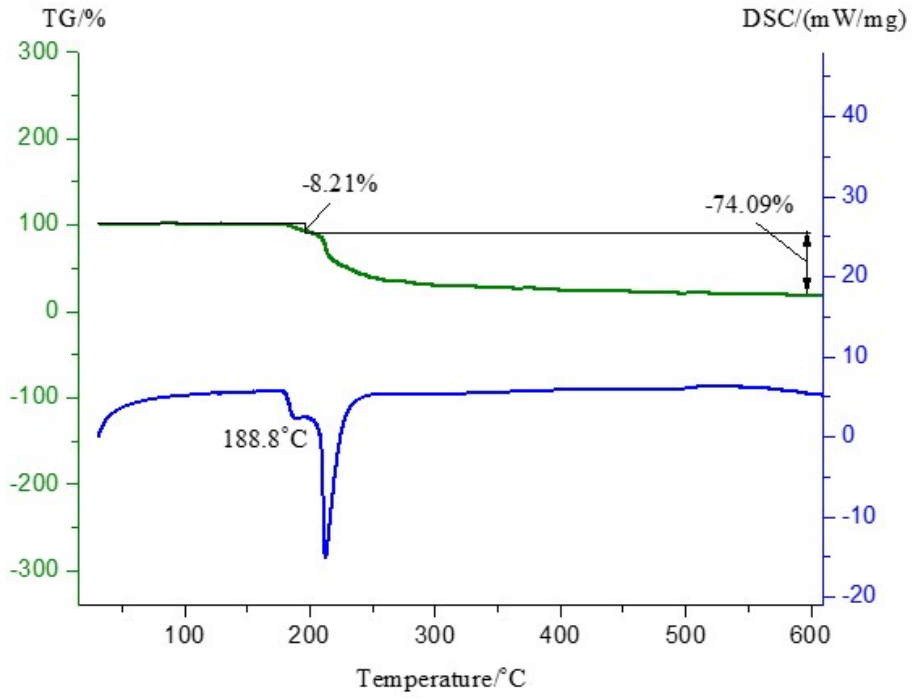
DSC spectrum of **6a**



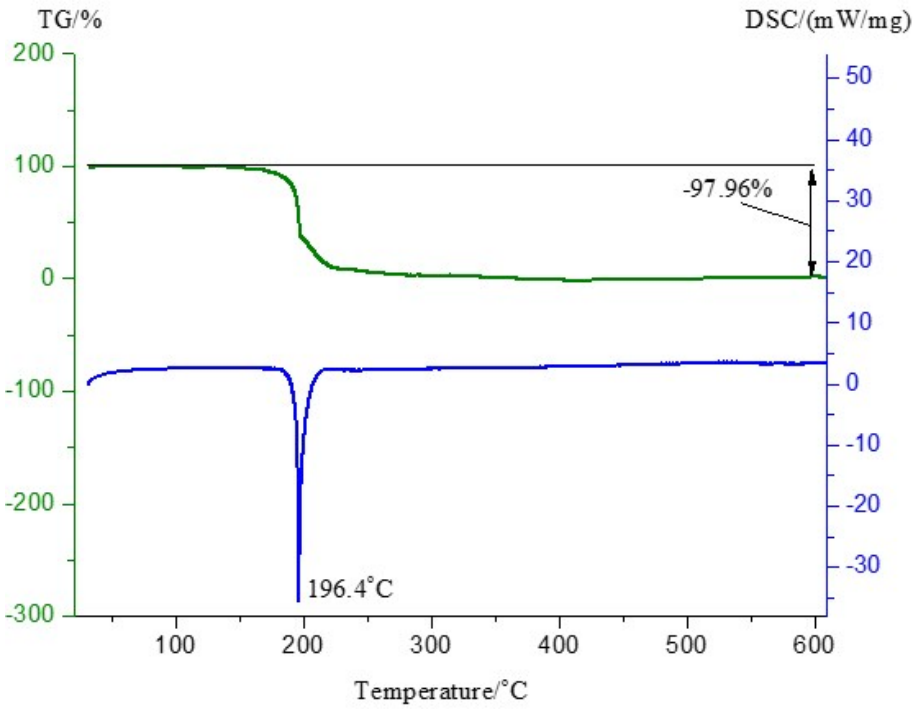
DSC spectrum of **6b**



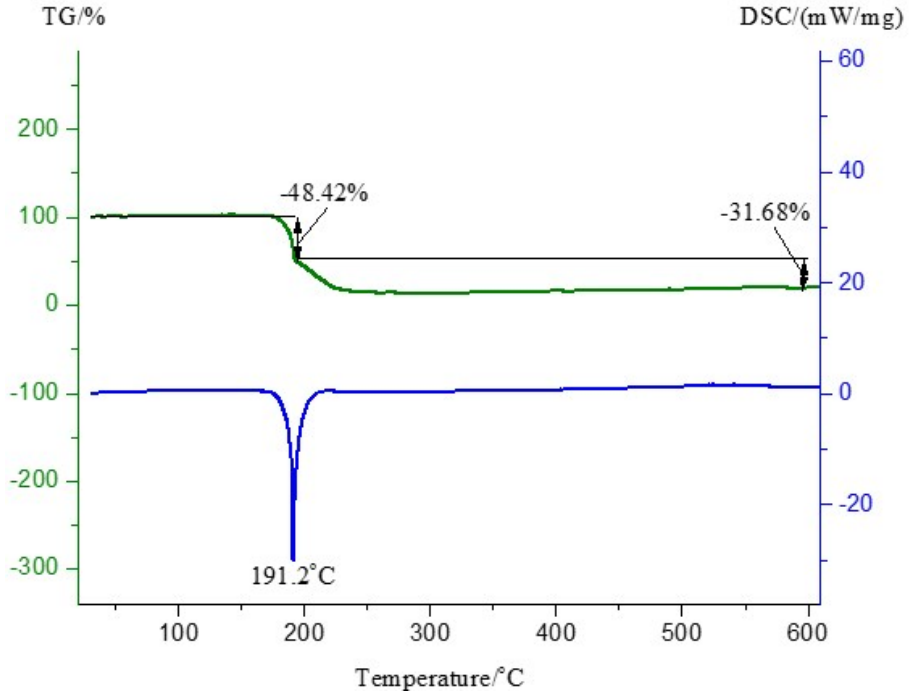
DSC spectrum of **6c**



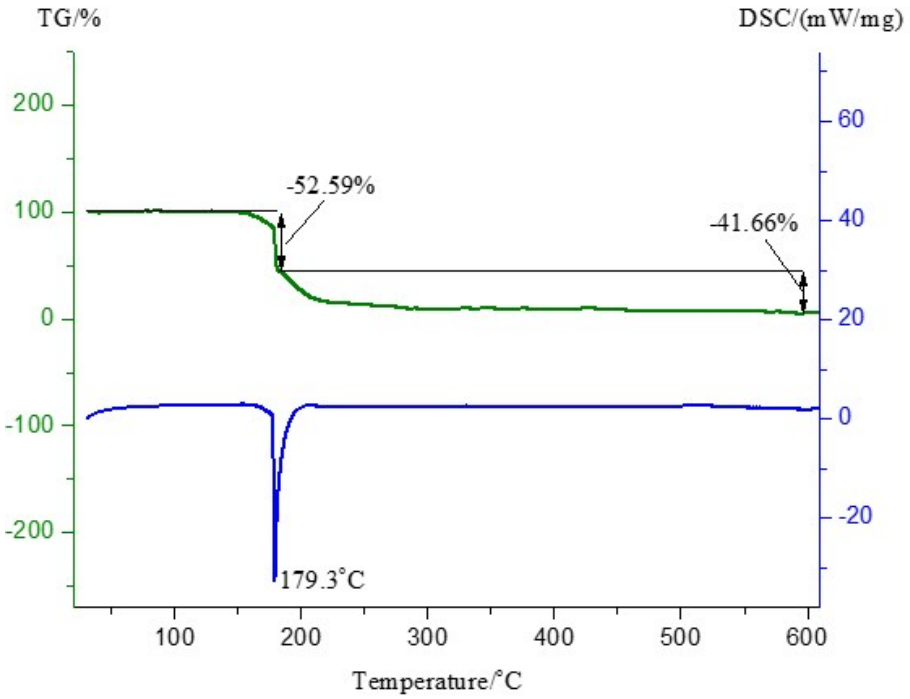
DSC spectrum of **6d**



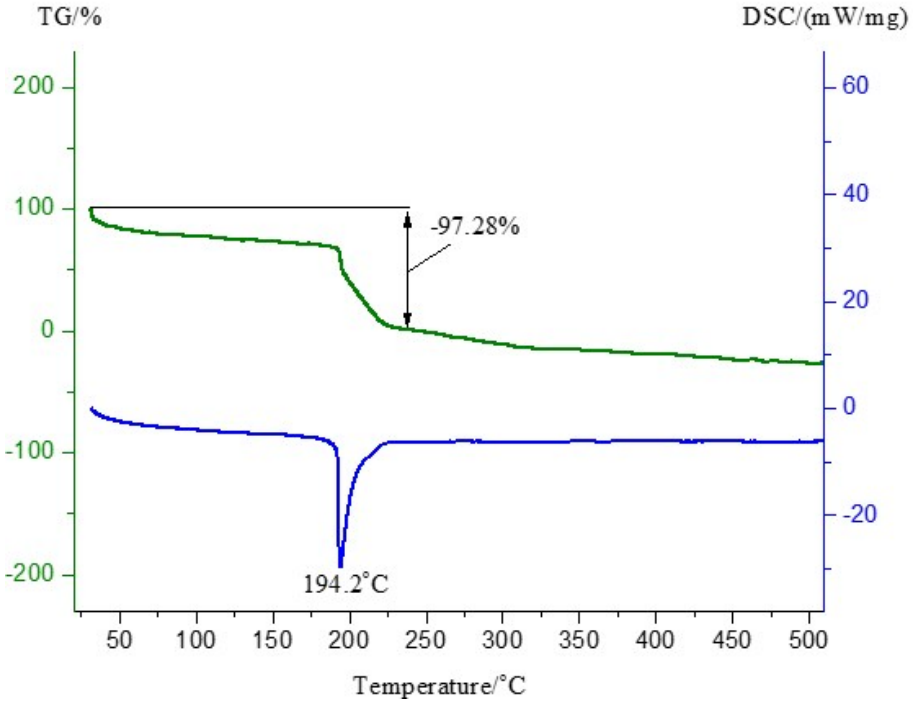
DSC spectrum of **7a**



DSC spectrum of **7b**



DSC spectrum of **7c**



DSC spectrum of **7d**

	5a	**5b**	**5d**
CCDC	1442351	1442350	1442346
Empirical formula	$C_2H_4N_8O_6$	$C_2H_5N_9O_6$	$C_3H_6N_{10}O_6$
Formula mass	236.13	251.15	278.18
Temperature (K)	98.7	99.4	98.7
Crystal system	Monoclinic	orthorhombic	Monoclinic
Space group	P_12_1/c_1	Pbca	P_12_1/c_1
a / Å, b / Å, c / Å	8.0847(3) 7.5557(3) 14.1232(6)	6.43139(19) 16.4647(4) 16.8638(5)	9.1227(5) 7.0640(4) 16.2597(11)
α / °, β / °, γ / °	90.00, 99.661(4), 90.00	90.00, 90.00, 90.00	90.00, 103.139(6), 90.00
Z	4	8	4
Volume (Å^3)	850.49(6)	1785.73(9)	1020.39(10)
ρ_{calc} (g·cm^{-3})	1.844	1.868	1.811
μ (mm^{-1})	0.177	0.178	0.168
F(000)	480	1024	568
Crystal size / mm^3	0.15 × 0.14 × 0.12	0.15 × 0.10 × 0.08	0.50 × 0.45 × 0.40
2θ range for data collection	5.86 to 52°	6.92 to 51.98°	6.06 to 52°
Index ranges	-9 ≤ h ≤ 9 -8 ≤ k ≤ 9 -16 ≤ l ≤ 17	-7 ≤ h ≤ 7 -12 ≤ k ≤ 20 -20 ≤ l ≤ 14	-11 ≤ h ≤ 11 -4 ≤ k ≤ 8 -19 ≤ l ≤ 20
Reflections collected	3503	4817	4294
Independent reflections	1669[R(int) = 0.0192 (inf-0.9Å)]	1743[R(int) =0.0244 (inf-0.9Å)]	1999[R(int) = 0.0235 (inf-0.9Å)]
Goodness-of-fit on F2	1.070	1.034	1.062
Final R indexes [I>2σ(I) i.e. Fo>4σ(Fo)]	R1 = 0.0319 wR2 = 0.0744	R_1 = 0.0333 wR_2 = 0.0772	R1 = 0.0368 wR2 = 0.0840
Final R indexes [all data]	R1 = 0.0393 wR2 = 0.0786	R1 = 0.0400 wR2 = 0.0808	R1 = 0.0448 wR2 = 0.0893

	6a	**6b**	**6c**
CCDC	1442343	1442345	1442398
Empirical formula	$C_3H_5N_7O_6 \cdot H_2O$	$C_3H_6N_8O_6$	$C_3H_5N_7O_7$
Formula mass	253.04	250.16	251.14
Temperature (K)	173	173	173
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å, b / Å, c / Å	6.3136(5) 15.3604(13) 9.3411(8)	6.4094(9) 16.106(2) 9.1462(11)	6.4054(9) 15.829(2) 8.9085(10)
α / °, β / °, γ / °	90.00, 98.223(2), 90.00	90.00, 100.123(4), 90.00	90.00, 99.085(4), 90.00
Z	4	4	4
Volume ($Å^3$)	896.58(13)	929.5(2)	891.9(2)
ρ_{calc} ($g \cdot cm^{-3}$)	1.759	1.788	1.870
μ (mm^{-1})	0.167	0.168	0.180
F(000)	458	512	512
Crystal size / mm^3	0.25 × 0.18 × 0.15	0.19 × 0.17 × 0.17	0.22 × 0.15 × 0.12
2θ range for data collection	6.90 to 50.50°	6.78 to 50.78°	6.44 to 50.06°
Index ranges	$-6 \le h \le 7$ $-18 \le k \le 18$ $-10 \le l \le 11$	$-7 \le h \le 4$ $-19 \le k \le 19$ $-11 \le l \le 9$	$-4 \le h \le 7$ $-19 \le k \le 17$ $-9 \le l \le 10$
Reflections collected	8925	5568	5074
Independent reflections	1589[R(int) = 0.0528 (inf-0.9Å)]	1676[R(int) = 0.0519 (inf-0.9Å)]	1601[R(int) = 0.0472 (inf-0.9Å)]
Goodness-of-fit on F2	1.020	1.027	1.030
Final R indexes [$I>2\sigma(I)$ i.e. $Fo>4\sigma(Fo)$]	R1 = 0.0424 wR2 = 0.0762	R1 = 0.0508 wR2 = 0.0931	R1 = 0.0458 wR2 = 0.0680
Final R indexes [all data]	R1 = 0.0763 wR2 = 0.0865	R1 = 0.1081 wR2 = 0.1107	R1 = 0.0941 wR2 = 0.0787

	7a	**7b**	**7c**
CCDC	1442352	1442349	1442347
Empirical formula	$C_4H_6N_6O_6$	$C_4H_7N_7O_6$	$C_4H_6N_6O_7$
Formula mass	234.15	249.17	250.03
Temperature (K)	101.7	101.7	101.7
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å, b / Å, c / Å	4.9037(3) 25.6452(14) 7.3737(4)	4.8027(2) 27.5834(14) 7.2531(4)	4.9109(4) 27.172(2) 6.9470(6)
α / °, β / °, γ / °	90.00, 106.189(6), 90.00	90.00, 104.940(6), 90.00	90.00, 106.073(8), 90.00
Z	4	4	4
Volume ($Å^3$)	890.53(9)	928.37(8)	890.77(13)
ρ_{calc} ($g \cdot cm^{-3}$)	1.746	1.783	1.806
μ (mm^{-1})	0.163	0.165	0.170
F(000)	480	512	495
Crystal size / mm^3	0.22 × 0.14 × 0.05	0.50 × 0.18 × 0.15	0.70 × 0.45 × 0.30
2θ range for data collection	5.96 to 51.98°	6 to 52°	6.28 to 52°
Index ranges	$-5 \le h \le 6$ $-22 \le k \le 31$ $-6 \le l \le 9$	$-5 \le h \le 5$ $-34 \le k \le 33$ $-8 \le l \le 8$	$-6 \le h \le 4$ $-33 \le k \le 31$ $-8 \le l \le 8$
Reflections collected	4027	5667	3676
Independent reflections	1732[R(int) =0.0335 (inf-0.9Å)]	1814[R(int) = 0.0199 (inf-0.9Å)]	1736[R(int) = 0.0284 (inf-0.9Å)]
Goodness-of-fit on F2	1.085	1.054	1.090
Final R indexes [I>2σ(I) i.e. Fo>4σ(Fo)]	R1 = 0.0397 wR2 = 0.0807	R1 = 0.0771 wR2 = 0.1669	R1 = 0.0436 wR2 = 0.0979
Final R indexes [all data]	R1 = 0.0542 wR2 = 0.0884	R1 = 0.0849 wR2 = 0.1726	R1 = 0.0542 wR2 = 0.1038

	6d	**7d**
CCDC	1442342	1442353
Empirical formula	$C_4H_7N_9O_6$	$C_5H_8N_8O_6$
Formula mass	227.19	276.19
Temperature (K)	173	101.8
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / Å, b / Å, c / Å	7.0482(7) 15.5415(18) 9.6301(9)	8.1268(5) 9.3064(4) 14.0786(9)
α / °, β / °, γ / °	90.00, 94.891(3), 90.00	90.00, 92.296(7), 90.00
Z	4	4
Volume ($Å^3$)	1051.04(19)	1063.92(10)
ρ_{calc} ($g \cdot cm^{-3}$)	1.752	1.724
μ (mm^{-1})	0.161	0.156
F(000)	568	568
Crystal size / mm^3	0.25 × 0.23 × 0.18	0.34 × 0.25 × 0.15
2θ range for data collection	6.36 to 46.56°	6.66 to 52°
Index ranges	$-6 \le h \le 8$ $-18 \le k \le 14$ $-11 \le l \le 9$	$-10 \le h \le 9$ $-11 \le k \le 11$ $-17 \le l \le 16$
Reflections collected	5981	4871
Independent reflections	1887[R(int) = 0.0375 (inf-0.9Å)]	2082[R(int) = 0.0344 (inf-0.9Å)]
Goodness-of-fit on F2	1.028	1.087
Final R indexes [I>2σ(I) i.e. Fo>4σ(Fo)]	R1 = 0.0392 wR2 = 0.0881	R1 = 0.0403 wR2 = 0.0943
Final R indexes [all data]	R1 = 0.0786 wR2 = 0.0881	R1 = 0.0512 wR2 = 0.1023

	7	**8**
CCDC	1442344	1442348
Empirical formula	$C_4H_3N_5O_6$	$C_3H_3N_7O_7$
Formula mass	217.11	249.01
Temperature (K)	101.7	153(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / Å, b / Å, c / Å	12.7070(8) 11.6741(8) 10.8273(8)	11.481(3) 6.6275(16) 12.722(3)
α / °, β / °, γ / °	90.00, 99.727(7), 90.00	90.00, 110.433(3), 90.00
Z	8	4
Volume ($Å^3$)	1583.06(19)	907.1(4)
ρ_{calc} ($g \cdot cm^{-3}$)	1.822	1.824
μ (mm^{-1})	0.172	0.177
F(000)	880	504
Crystal size / mm^3	0.50 × 0.45 × 0.45	0.42 × 0.38 × 0.28
2θ range for data collection	6.44 to 52°	6.56 to 61.02°
Index ranges	-15 ≤ h ≤ 15 -14 ≤ k ≤ 13 -13 ≤ l ≤ 13	-16 ≤ h ≤ 16 -8 ≤ 9 ≤ 31 -18 ≤ l ≤ 18
Reflections collected	7014	11121
Independent reflections	3111[R(int) = 0.0446 (inf-0.9Å)]	3017[R(int) = 0.0260 (inf-0.9Å)]
Goodness-of-fit on F2	1.054	0.999
Final R indexes [I>2σ(I) i.e. Fo>4σ(Fo)]	R1 = 0.0587 wR2 = 0.1484	R1 = 0.0402 wR2 = 0.0853
Final R indexes [all data]	R1 = 0.0748 wR2 = 0.1637	R1 = 0.0418 wR2 = 0.862

Heat of formation

Based on the Born-Haber energy cycle, heats of formation of ionic salts can be simplified by eqn. (1):

$\Delta H_f°$ (ionic salts, 298 K) = $\sum \Delta H_f°$ (cation, 298 K) + $\sum \Delta H_f°$(anion, 298 K) -ΔHL (1)

in which ΔHL is the lattice energy of the ionic salts, which could be predicted by using the formula suggested by Jenkins et al.[1]

$\Delta HL = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (2)

in which n_M and n_X depend on the nature of the ions M_{p+} and X_{q-}, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form [eqn. (3)]:

U_{POT} (kJ mol^{-1}) = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (3)

in which ρ_m is the density (g cm^{-3}) and Mm is the chemical formula mass of the ionic material (g mol^{-1}), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.

Table S1 Calculated total energy (E_0), zero-point energy (ZPE), thermal correction (HT), and heat of formation (HOF) of reference compounds.

Compd.	E_0/a.u.	ZPE (kJ/mol)	HT (kJ/mol)	HOF (kJ/mol)
5	-911.003790	215.27	35.12	301.3728
6	-895.005868	248.63	35.36	234.8022
7	-878.972332	280.05	35.56	175.75872
8	-1025.530974	301.75	41.02	98.22167
5 anion	-462.065951	83.93	20.31	8.7352
6 anion	-894.509467	215.23	34.60	-49.2789
7 anion	-878.459887	245.77	34.88	-67.0128
NH_4^+				645.8[2]
$N_2H_5^+$				774.1[2]
NH_4O^+				687.2[2]
G^+				571.9[2]

References

1. H. D. B. Jenkins, D. Tudeal and L. Glasser, L. *Inorg. Chem.*, 2002, **41**, 2364–2367.
2. D. Fischer, T. M. Klapçtke, M. Reymann and J. Stierstorfer, *Chem. Eur. J.*, 2014, **20**, 6401–6411.