

Electronic Supplementary Information

Polynitro Functionalized 4-Phenyl-1H-pyrazoles as Heat-Resistant Explosives

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1. Crystal structure data:

Table 1: Crystal data and structure refinement for compound 6.

Identification code	compd 6
Empirical formula	C ₁₀ H ₅ N ₇ O ₁₀
Formula weight	383.21
Temperature/K	299(2)
Crystal system	Monoclinic
Space group	P2 ₁ /n
a/Å	6.911(2)
b/Å	20.066(7)
c/Å	11.124(4)
α/°	90
β/°	106.903(15)
γ/°	90
Volume/Å ³	1476.0(9)
Z	4
ρ _{calc} /cm ³	1.724
μ/mm ⁻¹	0.157
F(000)	776
Crystal size/mm ³	0.23 × 0.20 × 0.18
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.06 to 56.622
Index ranges	-9 ≤ h ≤ 9, -26 ≤ k ≤ 26, -14 ≤ l ≤ 14
Reflections collected	47494
Independent reflections	3669 [R _{int} = 0.0551, R _{sigma} = 0.0207]
Data/restraints/parameters	3669/0/245
Goodness-of-fit on F ²	0.923
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0478, wR ₂ = 0.1454
Final R indexes [all data]	R ₁ = 0.0647, wR ₂ = 0.1557
Largest diff. peak/hole / e Å ⁻³	0.42/-0.34
CCDC number	2178043

Table 2: Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å²×103) for compound 6. U_{eq} is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
N1	3339(2)	5432.4(7)	2435.2(13)	36.5(3)
N2	5124(2)	5359.2(7)	3292.6(14)	38.4(3)

O2	8192(2)	5405.1(8)	5371.6(17)	62.3(4)
O1	6709(2)	6155.4(10)	6169.4(16)	65.6(5)
O10	460(3)	8357.9(8)	4127.0(17)	70.0(5)
N3	6758(2)	5771.1(8)	5338.2(16)	41.6(4)
N7	412(3)	8168.6(8)	5161.3(17)	46.3(4)
O5	1689(3)	5592.4(9)	8085.1(16)	71.5(5)
O9	-140(3)	8508.8(8)	5898.1(18)	69.5(5)
N5	1146(3)	6165.3(9)	7948.1(15)	47.5(4)
O6	380(3)	6456.5(10)	8645.3(17)	77.5(6)
N6	-50(3)	7562.4(9)	7460.2(17)	52.7(4)
O7	1111(3)	7817.4(10)	8376.5(16)	74.0(5)
O8	-1885(3)	7585.9(10)	7165.9(19)	76.4(6)
N4	128(3)	6020.2(10)	2127.8(17)	54.7(5)
C4	5004(2)	5732.7(8)	4253.4(16)	33.2(3)
C5	2401(2)	6462.5(8)	4951.8(15)	32.2(3)
C3	3146(2)	6055.5(8)	4065.3(15)	33.0(3)
C6	2196(3)	6163.9(8)	6034.6(15)	34.3(3)
C10	1833(3)	7121.3(9)	4696.8(16)	35.7(4)
O3	-515(3)	5823.8(13)	1076.9(18)	91.7(7)
C8	830(3)	7189.0(9)	6603.1(16)	36.9(4)
C2	2138(3)	5846.2(9)	2869.2(16)	36.8(4)
C9	1052(3)	7476.3(8)	5516.2(16)	35.9(4)
C7	1412(3)	6524.8(9)	6846.5(15)	35.9(4)
C1	2955(4)	5052.4(10)	1256.5(19)	52.6(5)
O4	-840(4)	6359.6(19)	2624(3)	160.3(17)

Table 3: Table containing bond lengths for selected bonds

Atom	Atom	Length/Å
N1	N2	1.330(2)
N1	C1	1.473(2)
N3	C4	1.443(2)
N7	C9	1.476(2)

N5	C7	1.479(2)
N6	C8	1.476(2)
N4	C2	1.437(2)
C5	C3	1.483(2)

Table 4: Table containing selected bond angles

Atom	Atom	Atom	Angle/°
N2	N1	C1	118.08(15)
C2	N1	C1	131.49(17)
N2	C4	C3	114.24(15)
N2	C4	N3	118.01(15)
C3	C4	N3	127.74(15)
C9	C8	N6	121.50(17)
C7	C8	N6	120.60(16)
N1	C2	N4	122.22(16)
C3	C2	N4	127.88(16)
C10	C9	N7	116.87(16)
C8	C9	N7	121.59(15)
C6	C7	N5	116.86(16)
C8	C7	N5	121.89(15)

Table 5: Crystal data and structure refinement for compound 14.

Identification code	dk_kp_hncptot_0016_0ma_a
Empirical formula	C ₁₃ H ₁₅ N ₁₅ O ₁₃
Formula weight	589.36
Temperature/K	150.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	13.2502(4)
b/Å	22.4477(7)
c/Å	7.5544(2)
α/°	90
β/°	96.143(1)
γ/°	90
Volume/Å ³	2234.05(11)
Z	4
ρ _{calc} /g/cm ³	1.7521
μ/mm ⁻¹	0.155
F(000)	1208.8
Crystal size/mm ³	0.08 × 0.03 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.58 to 41.54

Index ranges	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -7 ≤ l ≤ 7
Reflections collected	126143
Independent reflections	2321 [R _{int} = 0.0732, R _{sigma} = 0.0167]
Data/restraints/parameters	2321/3/382
Goodness-of-fit on F ²	1.106
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0361, wR ₂ = 0.0892
Final R indexes [all data]	R ₁ = 0.0382, wR ₂ = 0.0913
Largest diff. peak/hole / e Å ⁻³	0.38/-0.25
CCDC Number	2270163

Table 6: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for Compound 14. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O7	1717.7(13)	4697.6(8)	6150(2)	23.5(5)
O3	5629.7(15)	4683.9(9)	6225(3)	32.1(5)
O8	1664.8(16)	5625.1(9)	8407(3)	40.1(6)
O9	2453.5(15)	5511.1(9)	11013(3)	35.7(5)
O10	5185.5(15)	4204.4(9)	12114(3)	37.5(6)
O11	5843.2(15)	3747.8(10)	10006(3)	39.5(6)
O4	6887.5(15)	4277(1)	5037(3)	39.6(6)
O1	3515.0(16)	2786.5(9)	8477(3)	38.6(6)
C5	4119.7(19)	3979.3(11)	7612(3)	20.2(7)
C4	4795(2)	2933.4(12)	6770(3)	24.3(7)
C2	5642(2)	3680.6(12)	5954(3)	23.2(7)
C12	-131.2(19)	6304.0(12)	3228(4)	20.9(7)
C9	3681.7(19)	4664.9(11)	9903(4)	21.3(7)
C1	6909(2)	3045.8(15)	4410(5)	44.9(9)
O13	836.7(16)	7173.8(9)	7591(3)	37.7(6)
O12	1591.0(18)	6804.8(9)	11010(3)	44.8(6)
O6	2935.7(17)	4164.4(9)	3553(3)	41.1(6)
N10	-45.0(16)	5816.3(9)	2205(3)	20.5(6)
N8	824.1(16)	5709(1)	4695(3)	24.9(6)
O2	4149.6(17)	2009(1)	7305(3)	46.6(6)
N12	-819.6(16)	6658.9(10)	2257(3)	24.3(6)
N6	2282.1(17)	5359.3(10)	9441(3)	25.6(6)
N11	-692.8(16)	5825.3(10)	609(3)	23.6(6)
N5	2916.2(16)	3877.1(11)	4905(3)	23.2(6)
O5	2582.0(17)	3370.6(10)	4919(3)	44.7(6)
N7	5169.0(17)	4047.6(10)	10556(3)	25.9(6)
N9	388.6(17)	6276.9(10)	4789(3)	25.4(6)
N14	766.6(17)	4871.1(10)	2761(3)	27.7(6)
N3	4101.1(19)	2546.7(11)	7557(3)	29.9(6)

N4	6085.3(18)	4252.7(11)	5707(3)	27.8(6)
N1	6052.5(17)	3158.7(11)	5441(3)	29.7(6)
N15	-1828.7(17)	6589.3(10)	-487(3)	30.3(6)
N13	-1162(2)	7229.3(11)	2608(3)	32.6(7)
N2	5520.2(18)	2692.9(10)	5931(3)	32.0(6)
C11	541.2(19)	5419.3(12)	3179(4)	21.2(7)
C6	3239.5(19)	4159.7(11)	6628(3)	19.5(7)
C13	-1138(2)	6349.1(12)	717(4)	22.3(7)
C8	2849.0(19)	4864.1(11)	8808(3)	20.5(7)
C10	4307.0(19)	4232.5(11)	9327(3)	19.9(7)
C7	2528(2)	4597.9(11)	7120(3)	18.9(7)
C3	4814.8(19)	3555.6(12)	6836(3)	20.9(7)

Table 7: Table containing bond lengths for selected bonds

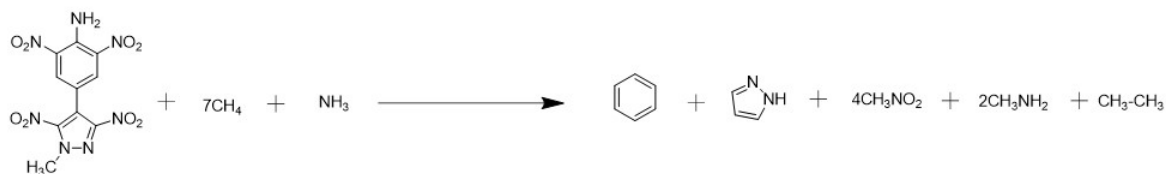
Atom	Atom	Length/Å	Atom	Atom	Length/Å
O7	C7	1.254(3)	C9	C10	1.377(4)
O3	N4	1.227(3)	C1	N1	1.465(4)
O8	N6	1.224(3)	O6	N5	1.210(3)
O9	N6	1.233(3)	N10	N11	1.403(3)
O10	N7	1.227(3)	N10	C11	1.348(3)
O11	N7	1.226(3)	N8	N9	1.404(3)
O4	N4	1.226(3)	N8	C11	1.335(3)
O1	N3	1.221(3)	O2	N3	1.225(3)
C5	C6	1.375(4)	N12	N13	1.393(3)
C5	C10	1.412(4)	N12	C13	1.382(3)
C5	C3	1.488(4)	N6	C8	1.451(3)
C4	N3	1.438(4)	N11	C13	1.322(3)
C4	N2	1.322(4)	N5	O5	1.221(3)
C4	C3	1.398(4)	N5	C6	1.470(3)
C2	N4	1.433(4)	N7	C10	1.453(3)
C2	N1	1.365(3)	N14	C11	1.313(3)
C2	C3	1.372(4)	N1	N2	1.335(3)
C12	N10	1.351(3)	N15	C13	1.333(3)
C12	N12	1.364(3)	C6	C7	1.439(4)
C12	N9	1.302(3)	C8	C7	1.431(4)
C9	C8	1.380(4)			

Table 8: Table containing selected bond angles

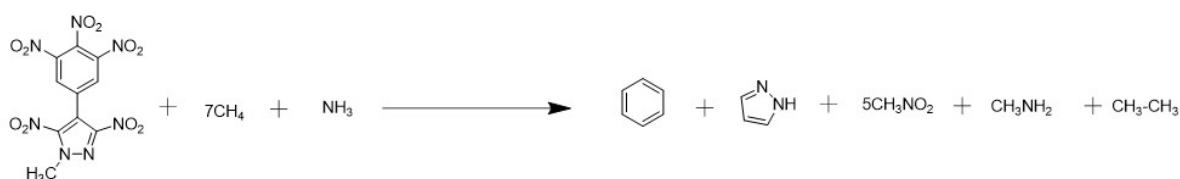
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	C5	C6	115.7(2)	C4	N3	O1	116.3(2)
C3	C5	C6	120.0(2)	O2	N3	O1	124.7(2)
C3	C5	C10	124.3(2)	O2	N3	C4	119.0(2)
N2	C4	N3	118.8(3)	O4	N4	O3	125.1(2)
C3	C4	N3	126.8(3)	C2	N4	O3	116.3(2)
C3	C4	N2	114.4(2)	C2	N4	O4	118.6(2)
N1	C2	N4	123.4(2)	C1	N1	C2	130.8(3)
C3	C2	N4	127.4(2)	N2	N1	C2	110.8(2)
C3	C2	N1	109.0(2)	N2	N1	C1	118.3(2)
N12	C12	N10	105.0(2)	N1	N2	C4	104.2(2)
N9	C12	N10	114.3(2)	N8	C11	N10	103.8(2)
N9	C12	N12	140.6(3)	N14	C11	N10	128.4(2)
C10	C9	C8	120.6(2)	N14	C11	N8	127.8(2)
N11	N10	C12	113.4(2)	N5	C6	C5	120.1(2)
C11	N10	C12	107.6(2)	C7	C6	C5	127.1(2)
C11	N10	N11	137.9(2)	C7	C6	N5	112.8(2)
C11	N8	N9	114.0(2)	N11	C13	N12	113.7(2)
N13	N12	C12	130.3(2)	N15	C13	N12	119.7(2)
C13	N12	C12	106.5(2)	N15	C13	N11	126.6(2)
C13	N12	N13	123.1(2)	N6	C8	C9	117.4(2)
O9	N6	O8	121.4(2)	C7	C8	C9	122.7(2)
C8	N6	O8	119.8(2)	C7	C8	N6	119.9(2)
C8	N6	O9	118.7(2)	C9	C10	C5	121.4(2)
C13	N11	N10	101.3(2)	N7	C10	C5	121.3(2)
O5	N5	O6	123.0(2)	N7	C10	C9	117.3(2)
C6	N5	O6	119.1(2)	C6	C7	O7	121.0(2)
C6	N5	O5	117.8(2)	C8	C7	O7	126.9(2)
O11	N7	O10	123.0(2)	C8	C7	C6	112.1(2)
C10	N7	O10	117.6(2)	C4	C3	C5	130.0(2)
C10	N7	O11	119.4(2)	C2	C3	C5	128.4(2)
N8	N9	C12	100.2(2)	C2	C3	C4	101.6(2)

2. Isodesmic Reactions:

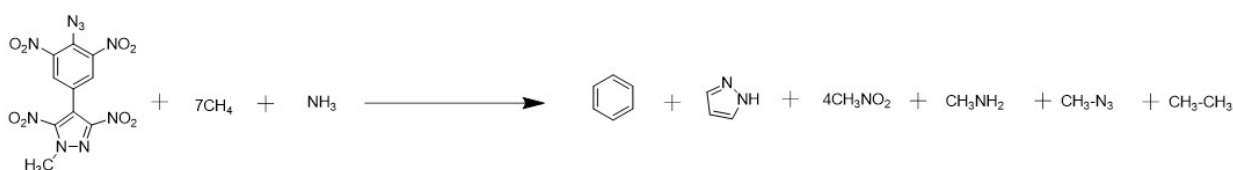
Compound 5:



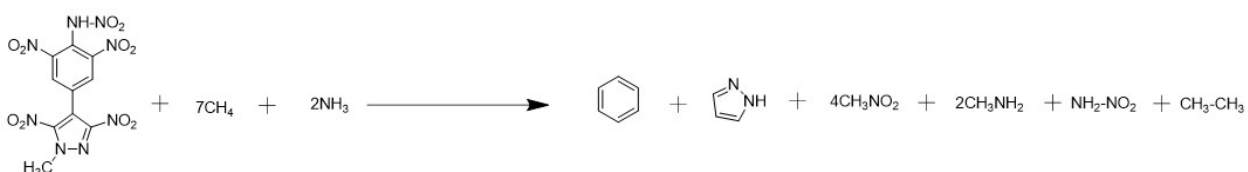
Compound 6:



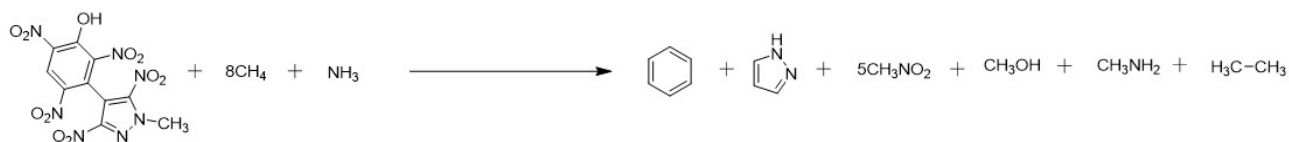
Compound 7:



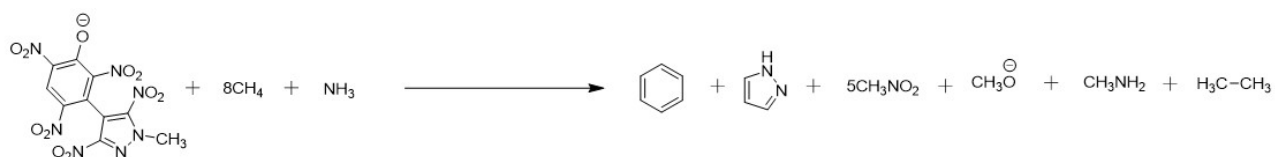
Compound 8:



Compound 10:



Energetic Anion for salts 11-14:



3. NMR Spectra:

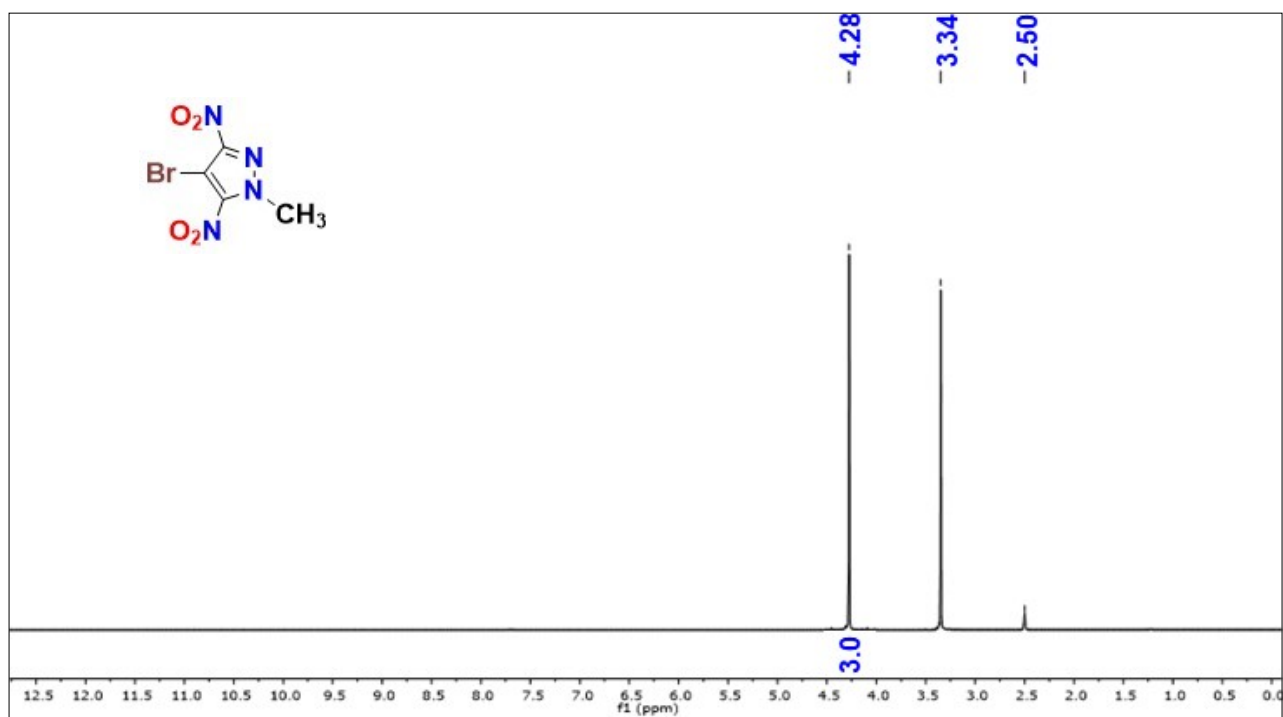


Fig.1: ^1H NMR Spectra of compound 2

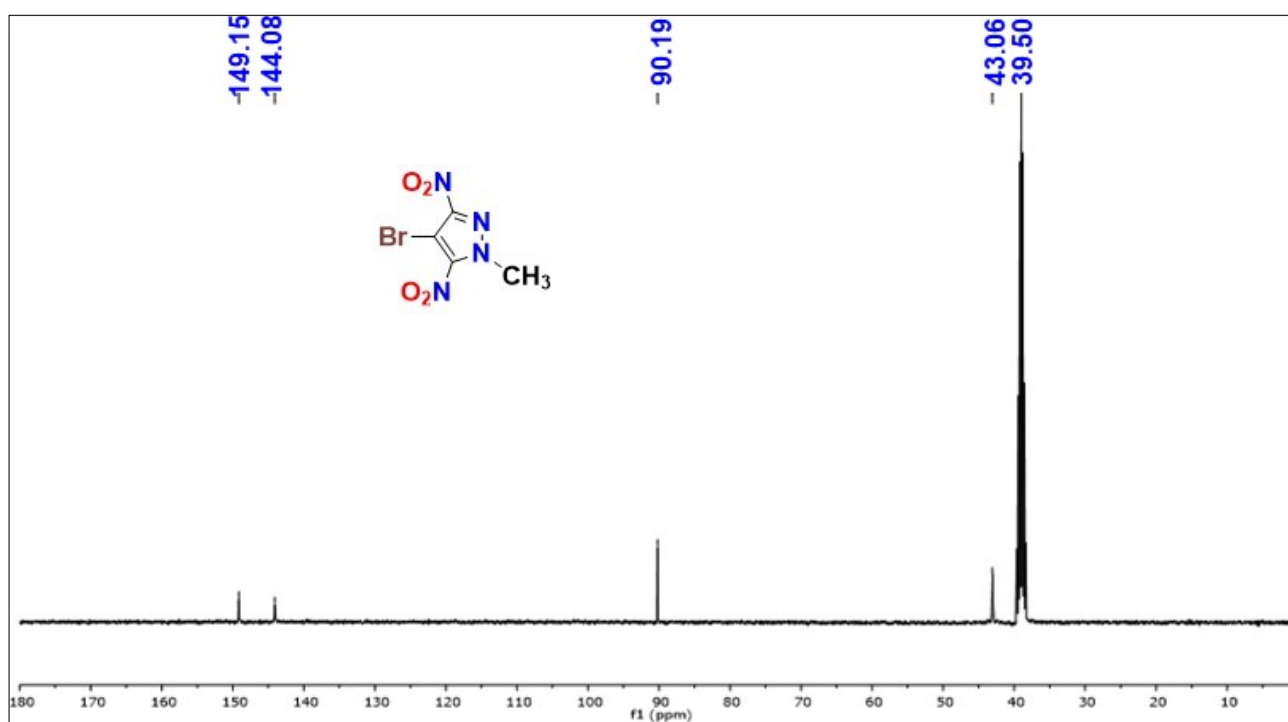


Fig.2: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound 2

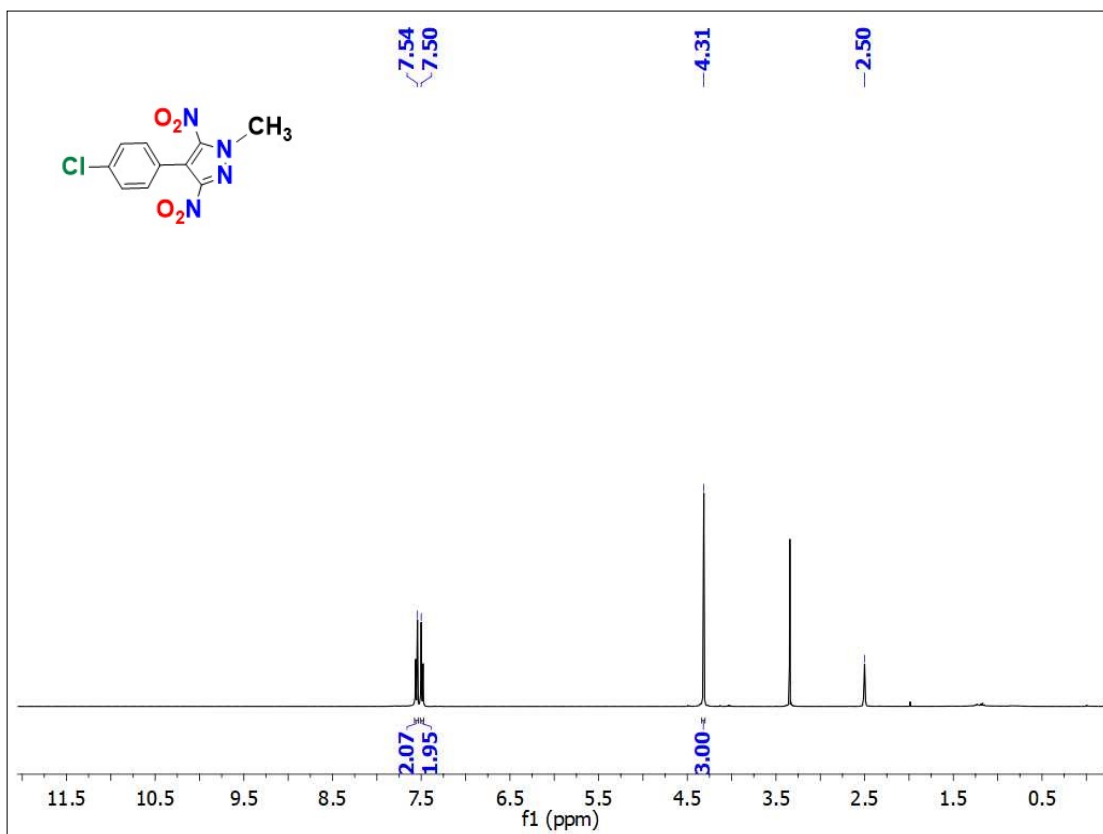


Fig.3: ^1H NMR Spectra of compound **3**

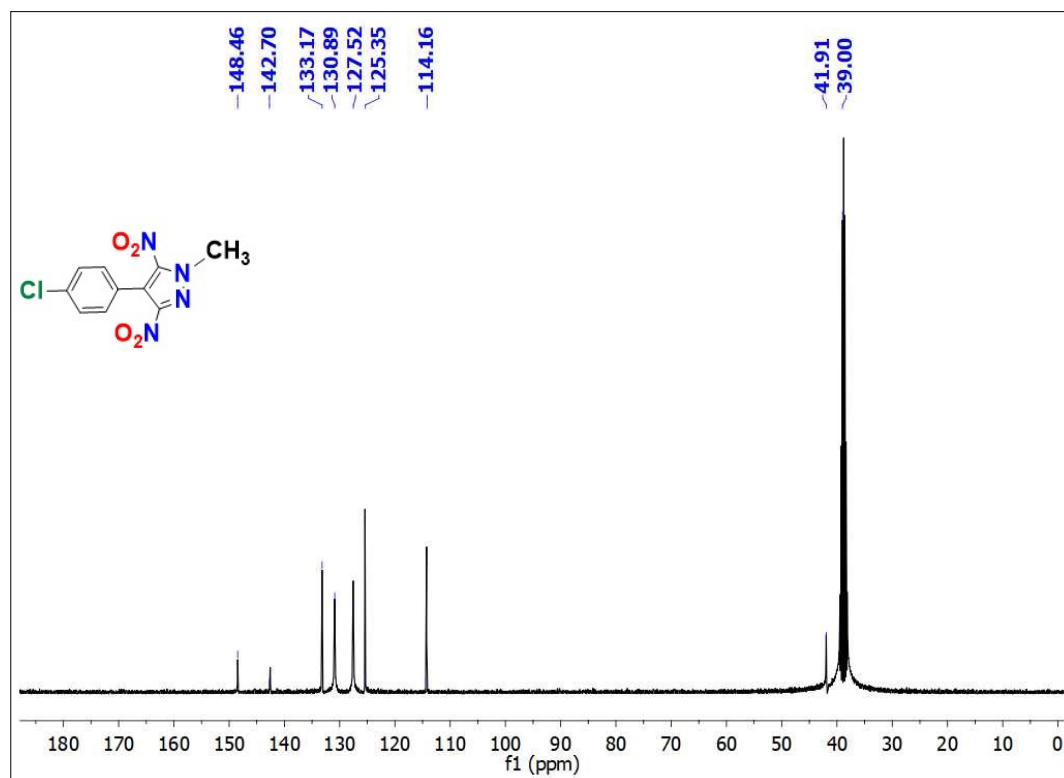


Fig.4: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound **3**

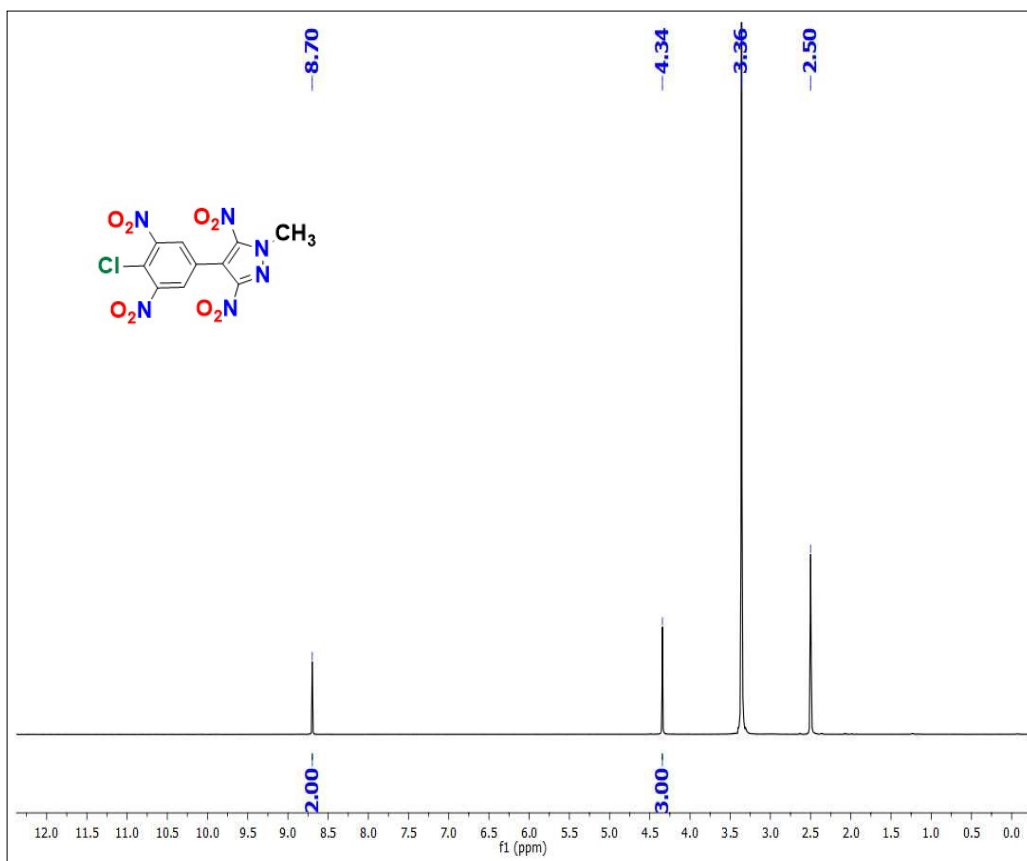


Fig.5: ^1H NMR Spectra of compound 4

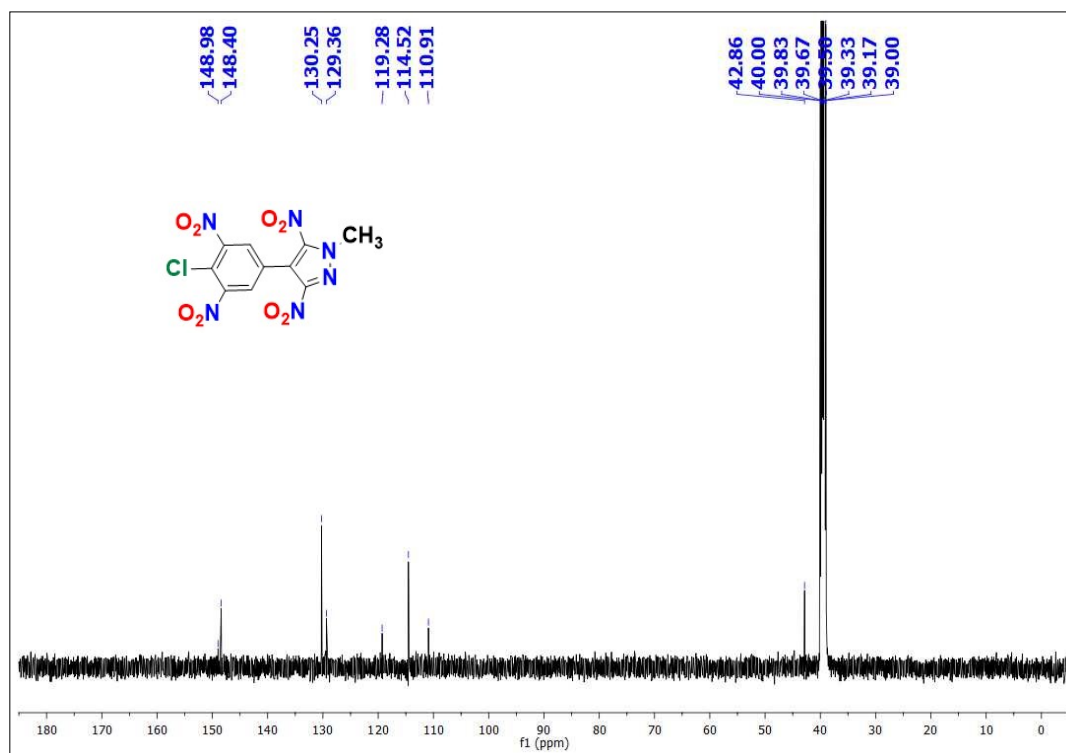


Fig.6: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound 4

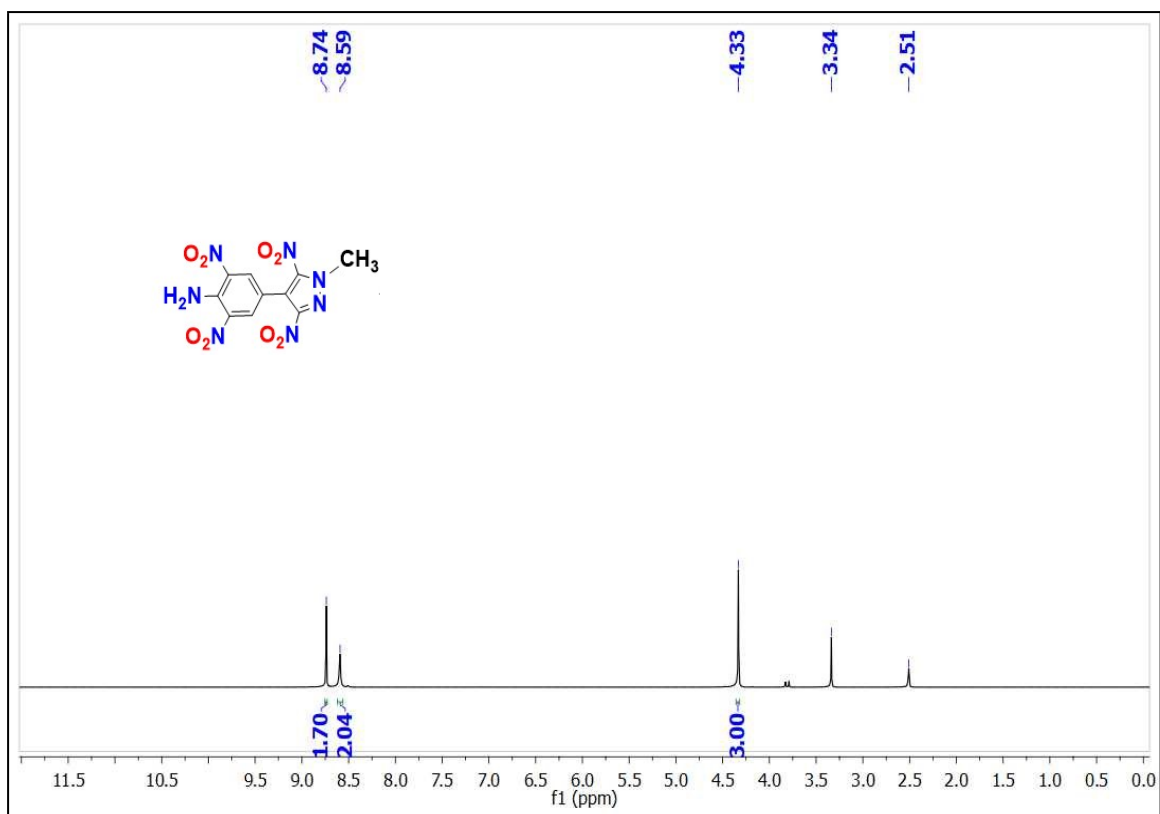


Fig.7: ^1H NMR Spectra of compound 5

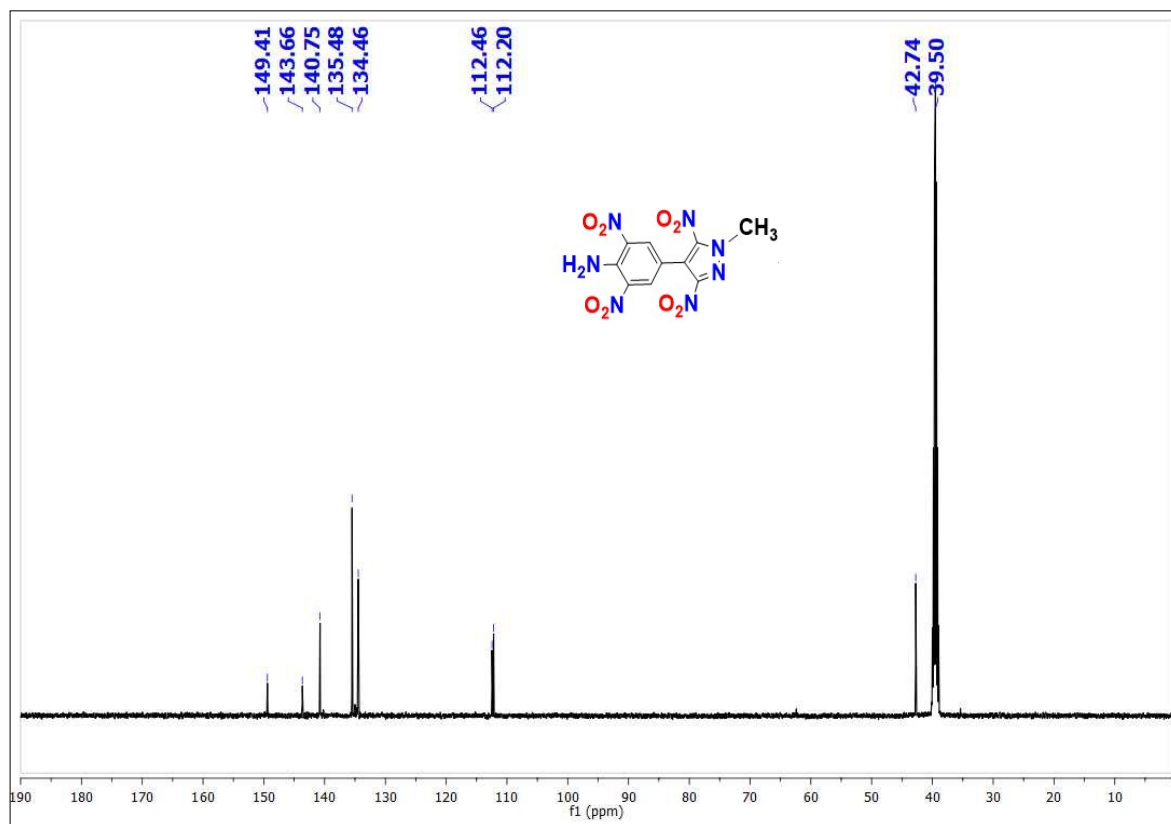


Fig.8: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound 5

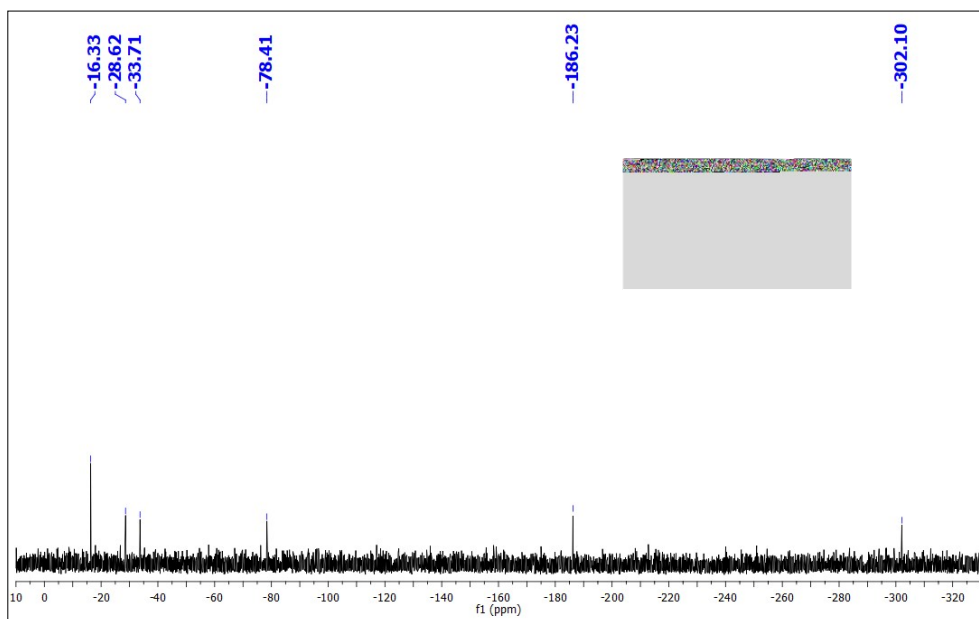


Fig.9: ^{15}N NMR Spectra of compound **5**

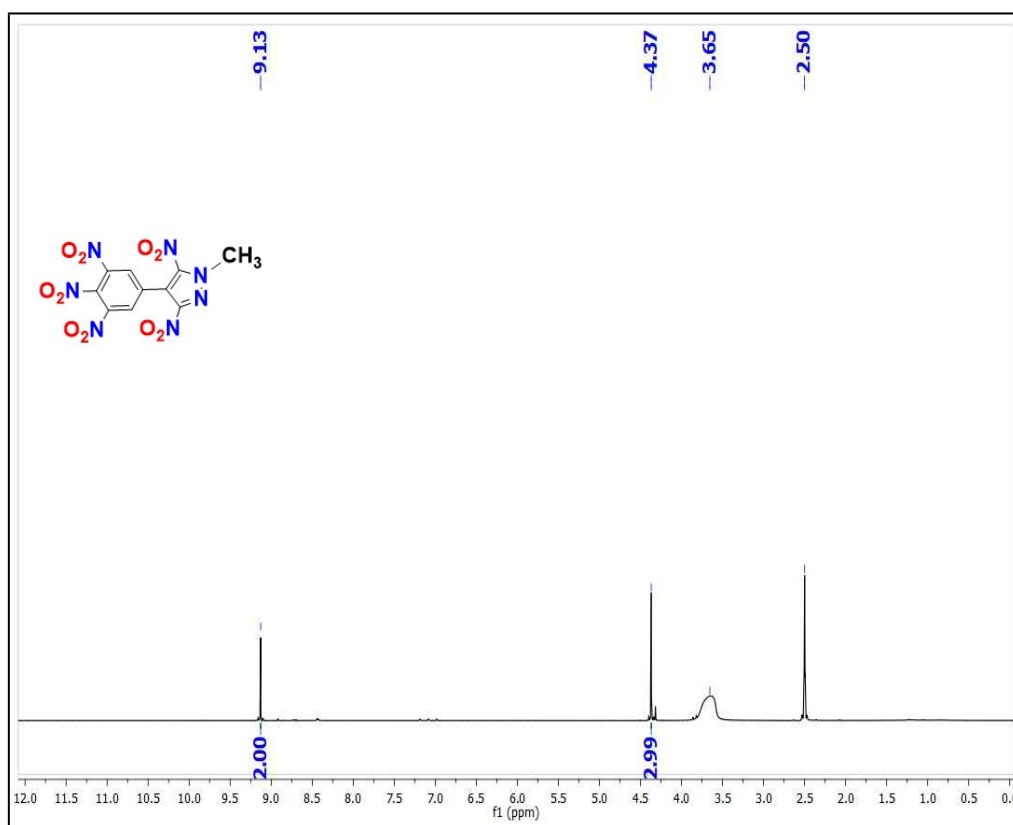


Fig.10: ^1H NMR Spectra of compound **6**

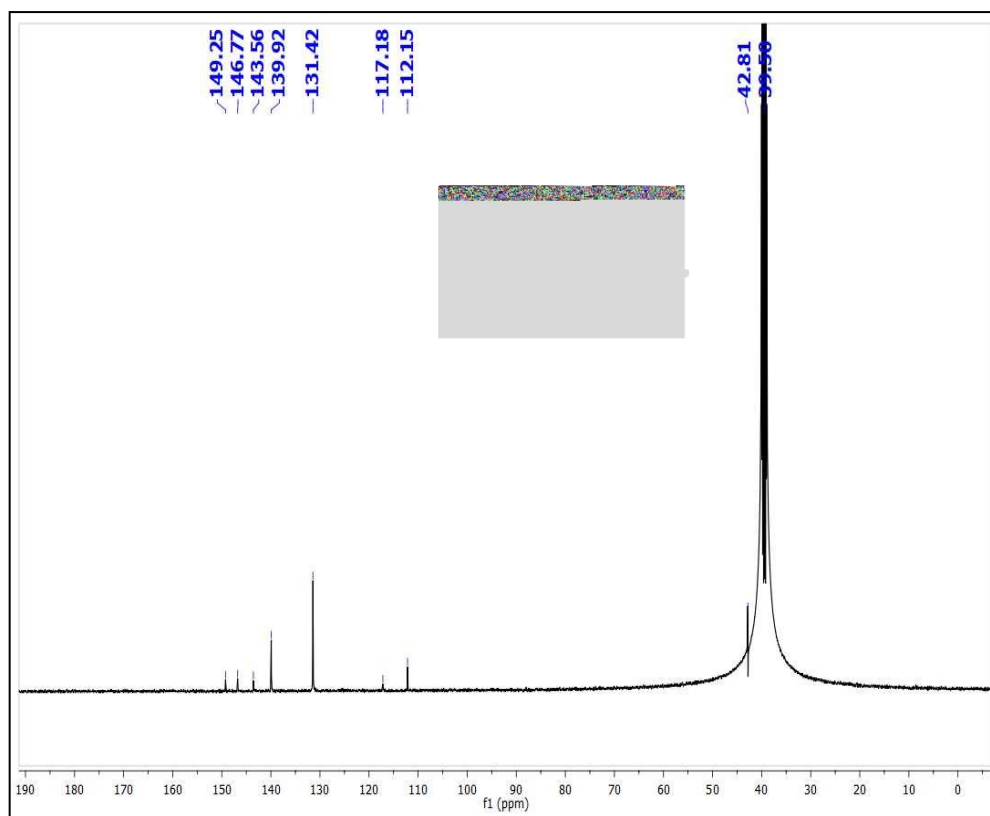


Fig.11: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound **6**

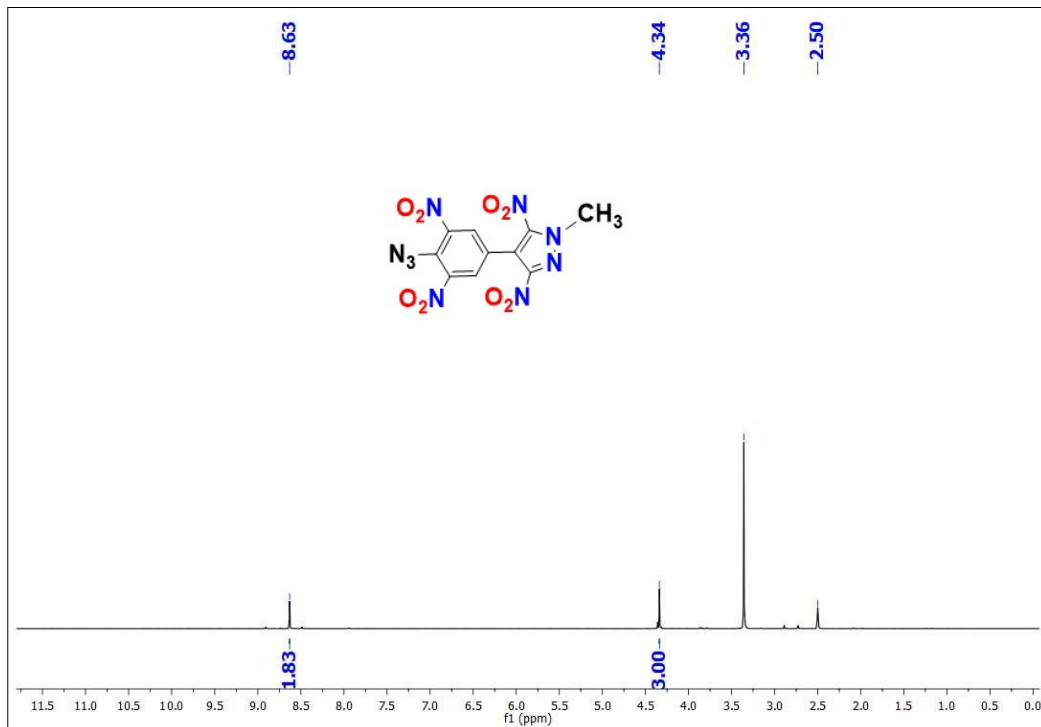


Fig.12: ^1H NMR Spectra of compound **7**

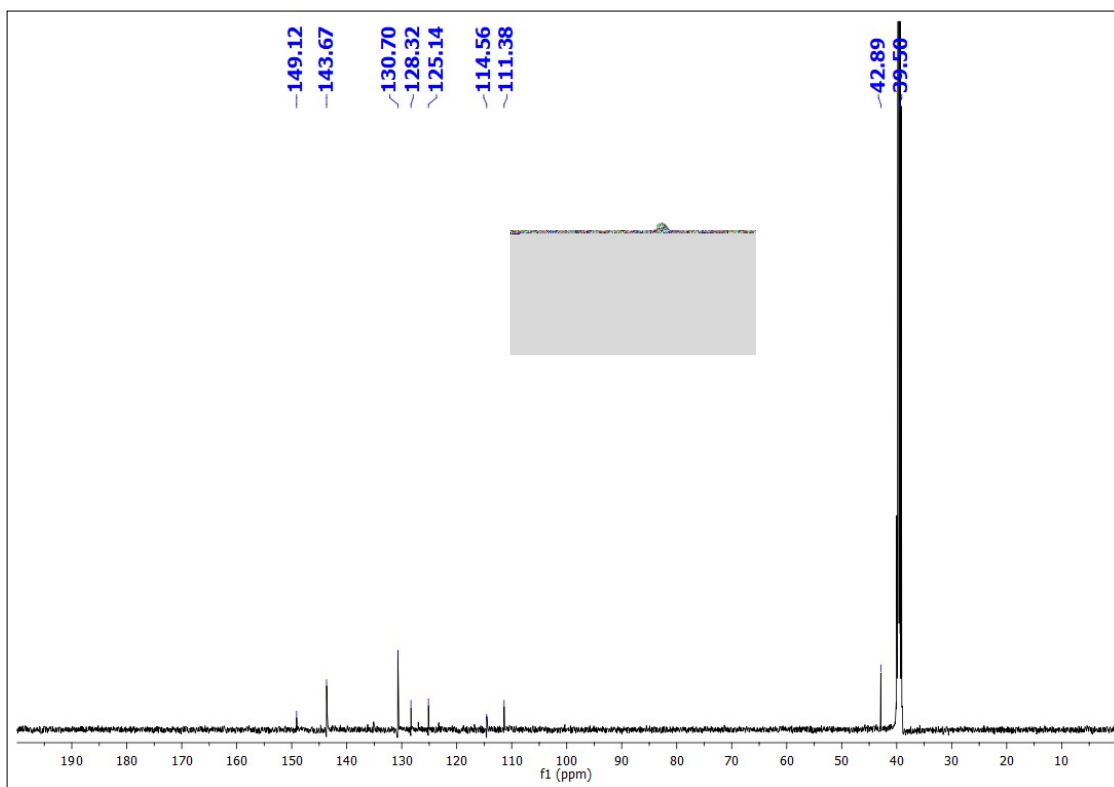


Fig.13: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound 7

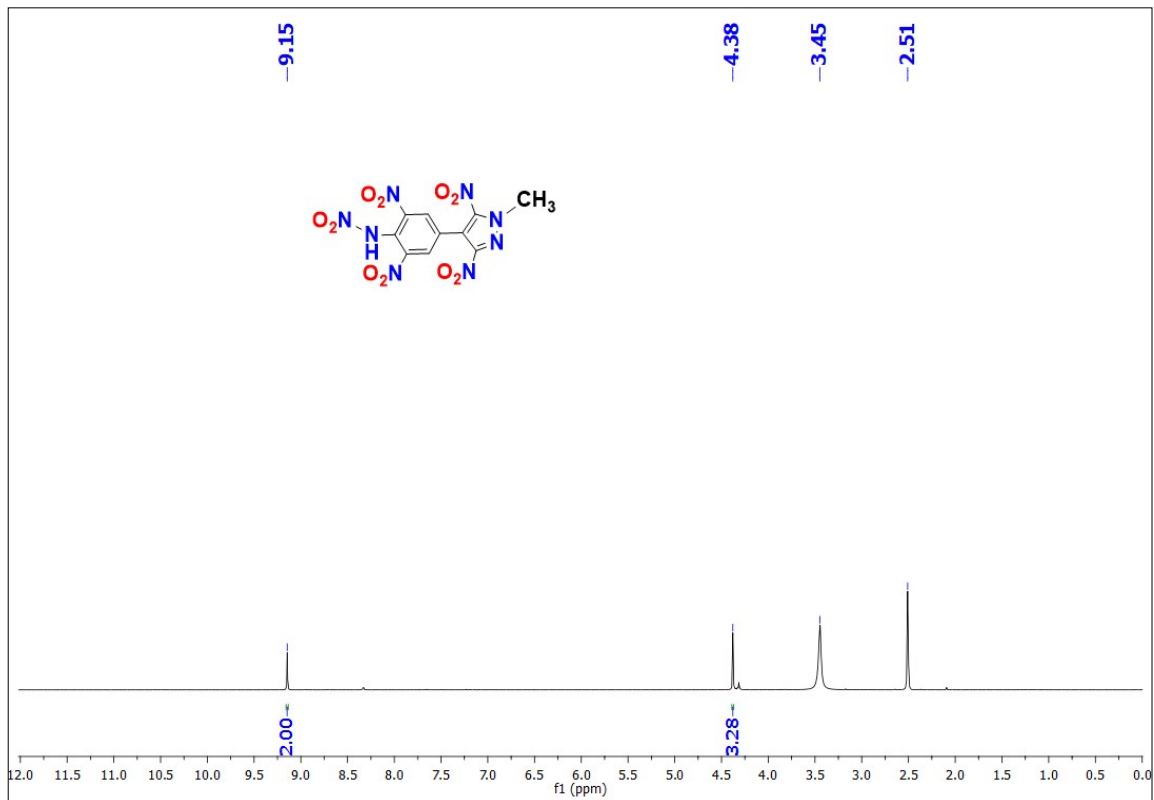


Fig.14: ^1H NMR Spectra of compound 8

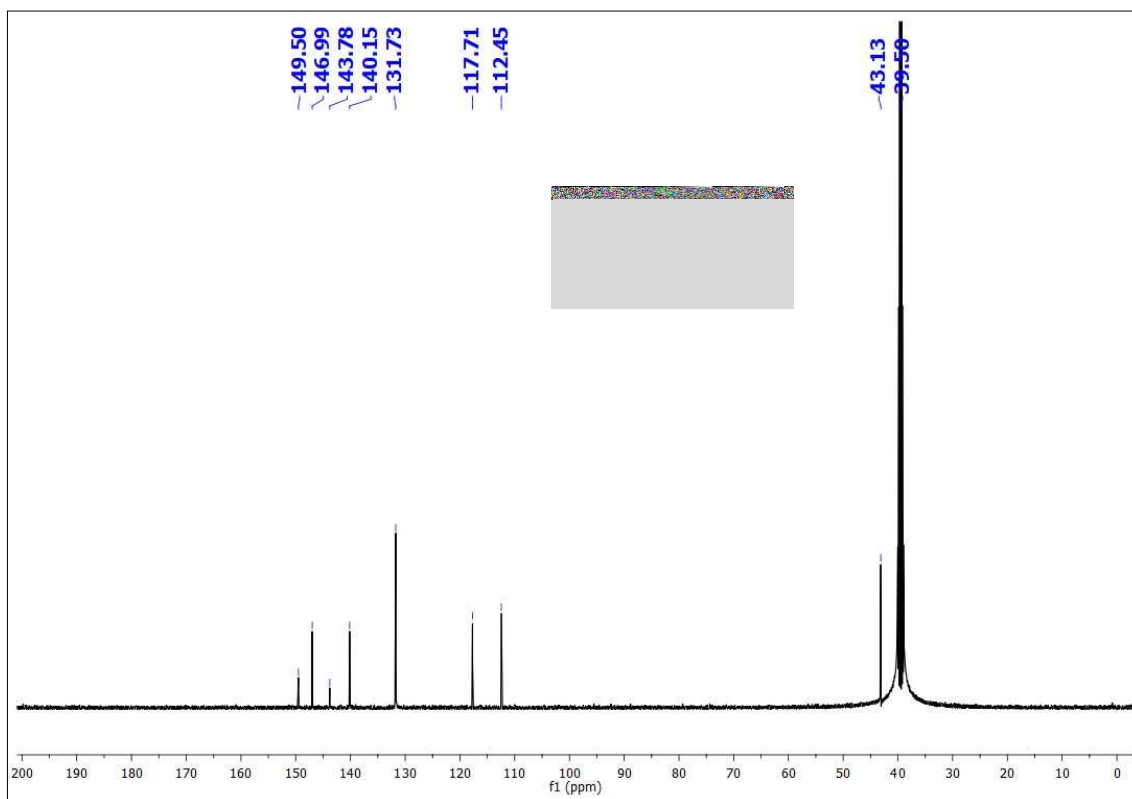


Fig.15: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound **8**

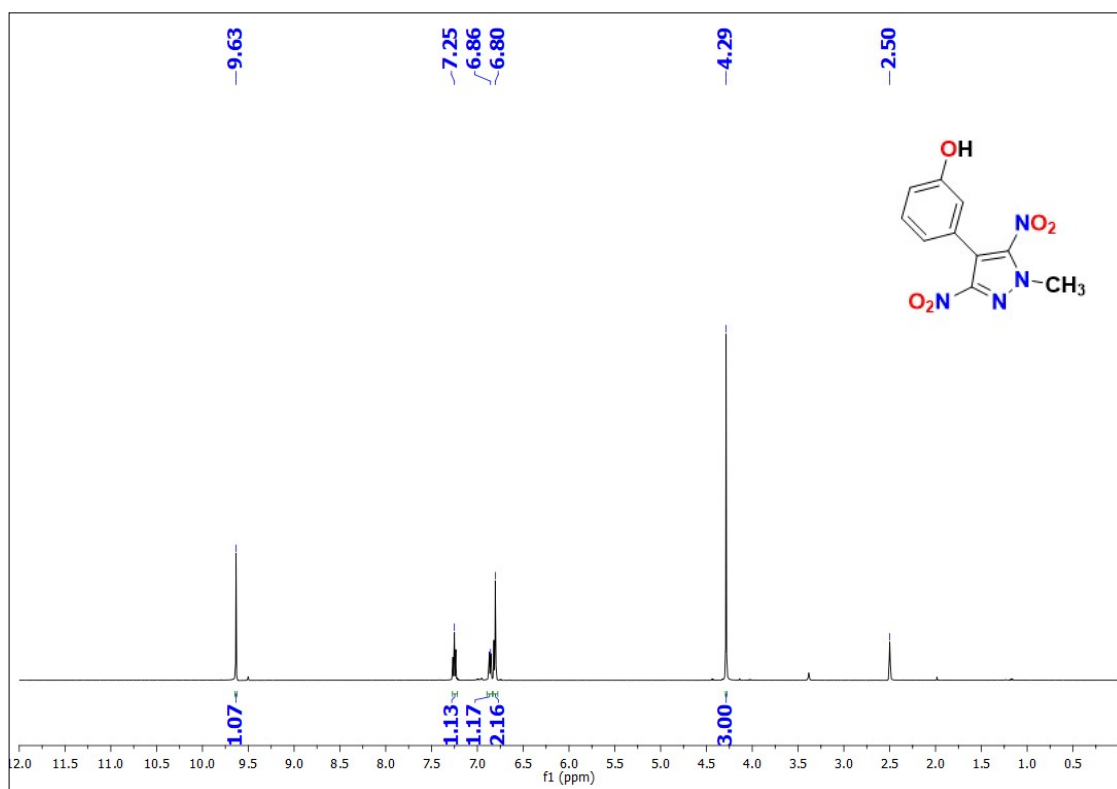


Fig.16: ^1H NMR Spectra of compound **9**

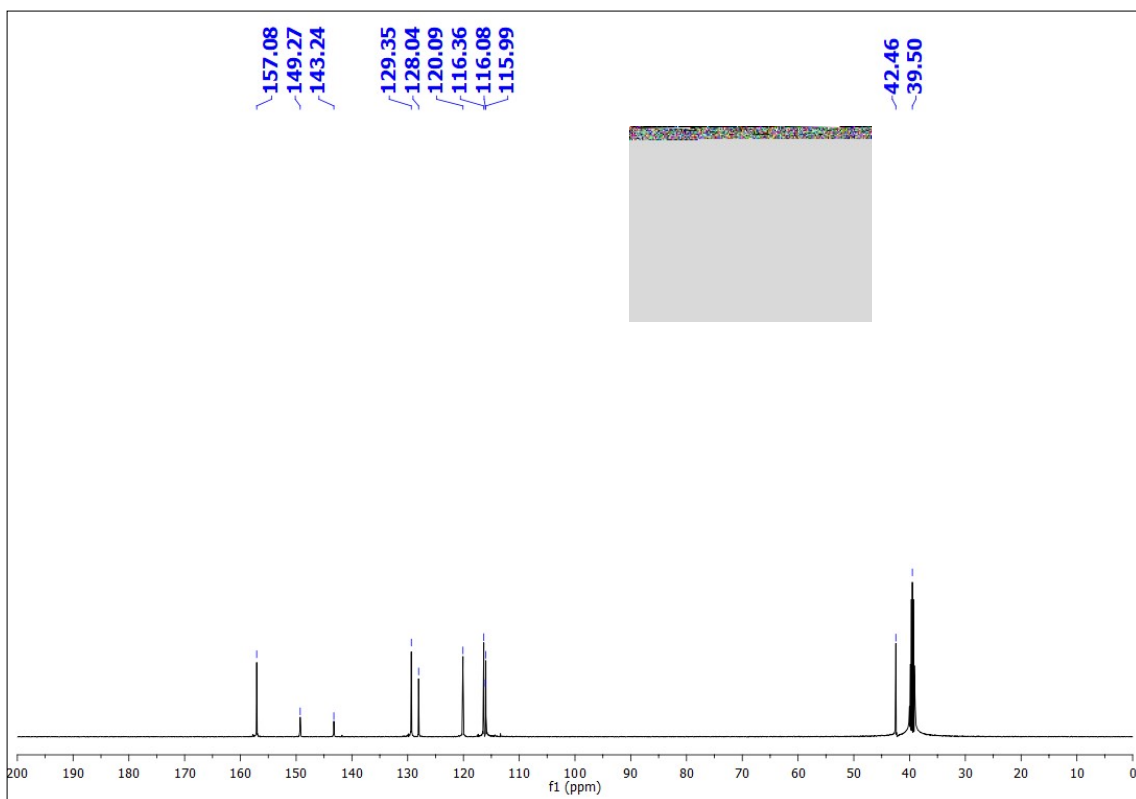


Fig.17: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound **9**

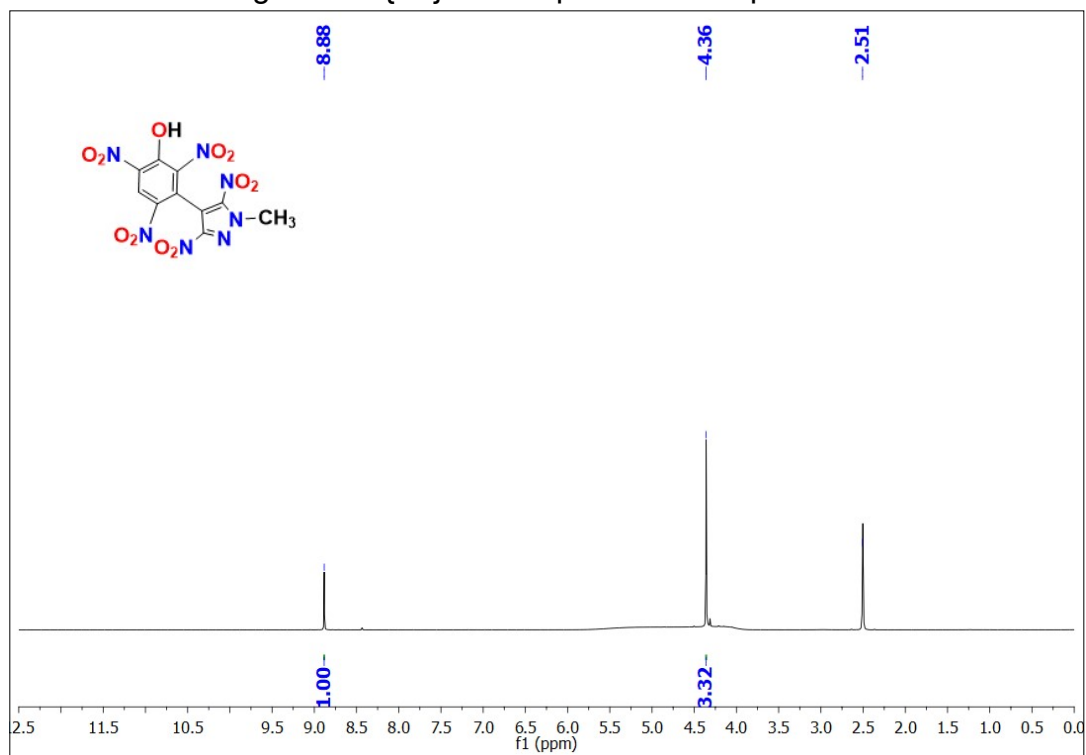


Fig.18: ^1H NMR Spectra of compound **10**

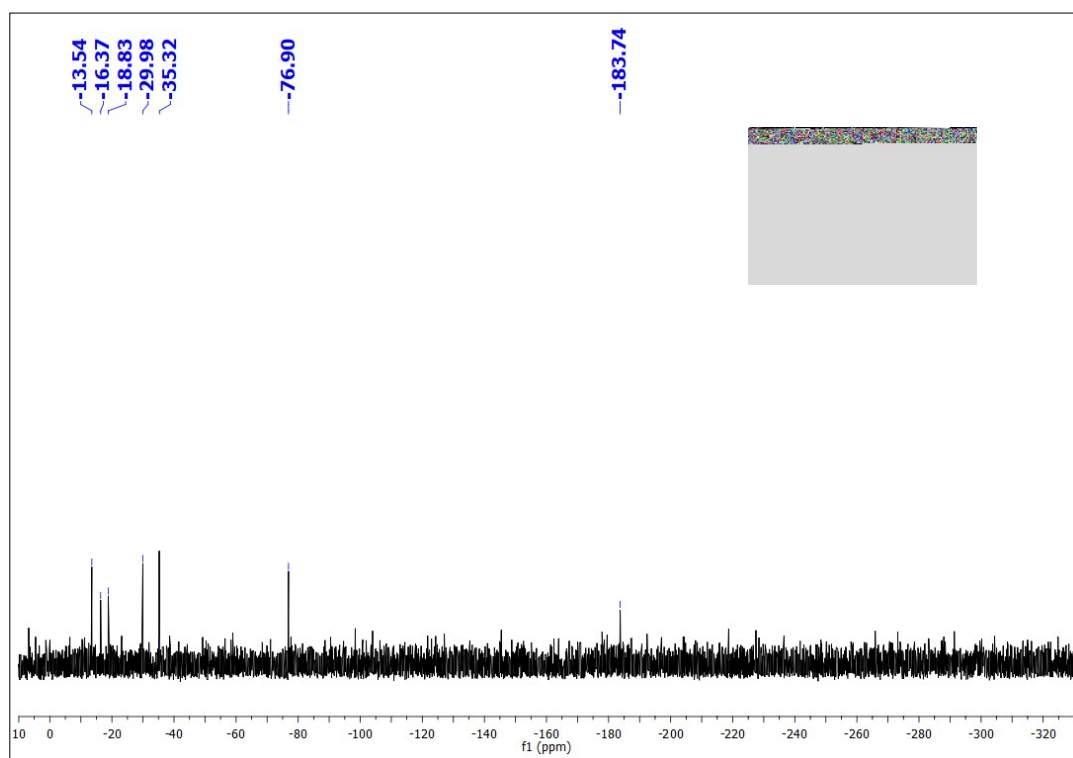


Fig.21: ^{15}N NMR Spectra of compound **10**

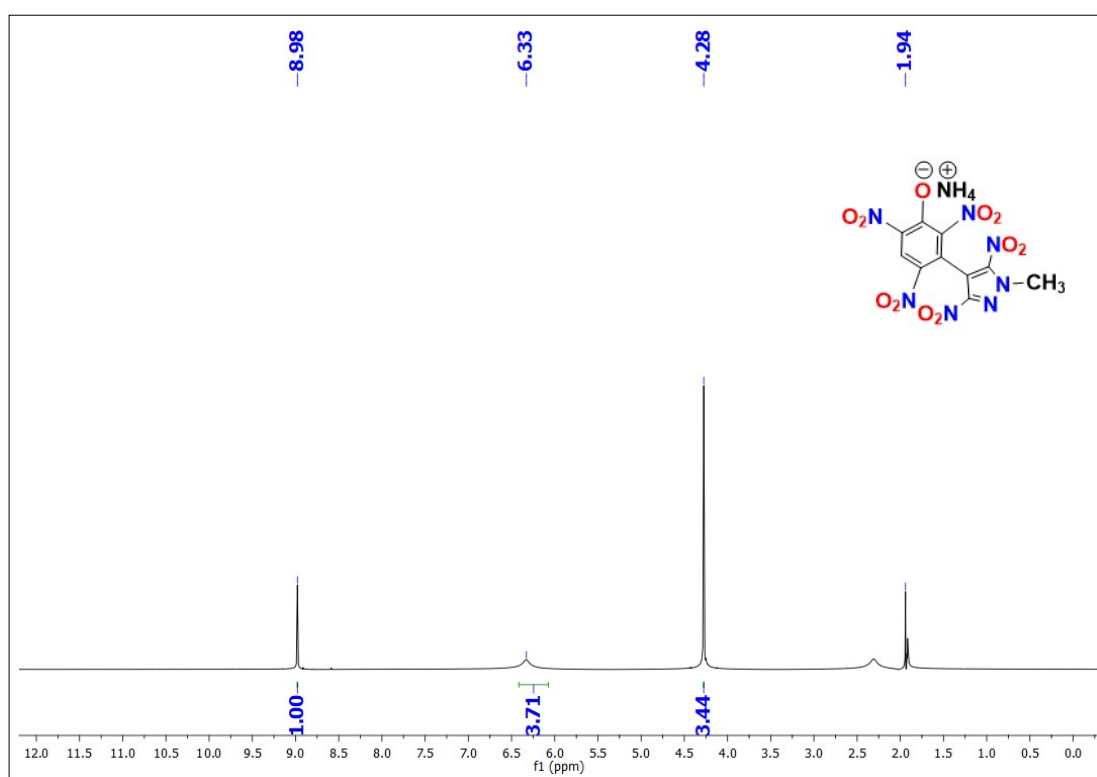


Fig.22: ^1H NMR Spectra of compound **11**

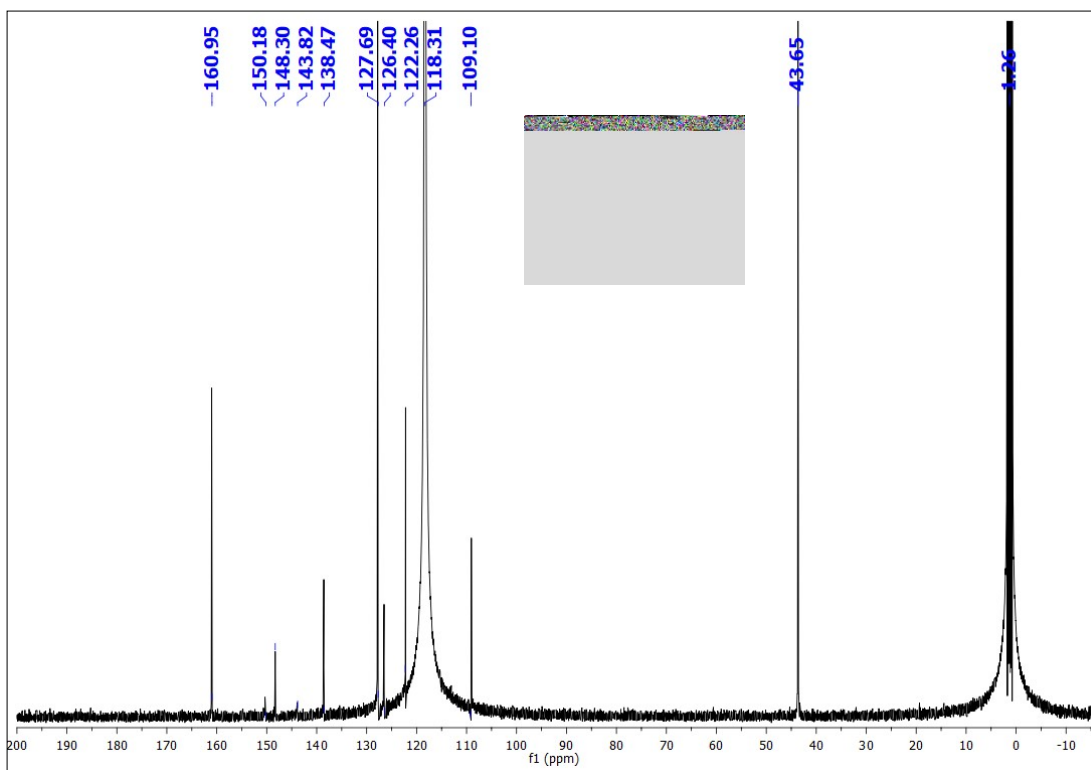


Fig.23: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound **11**

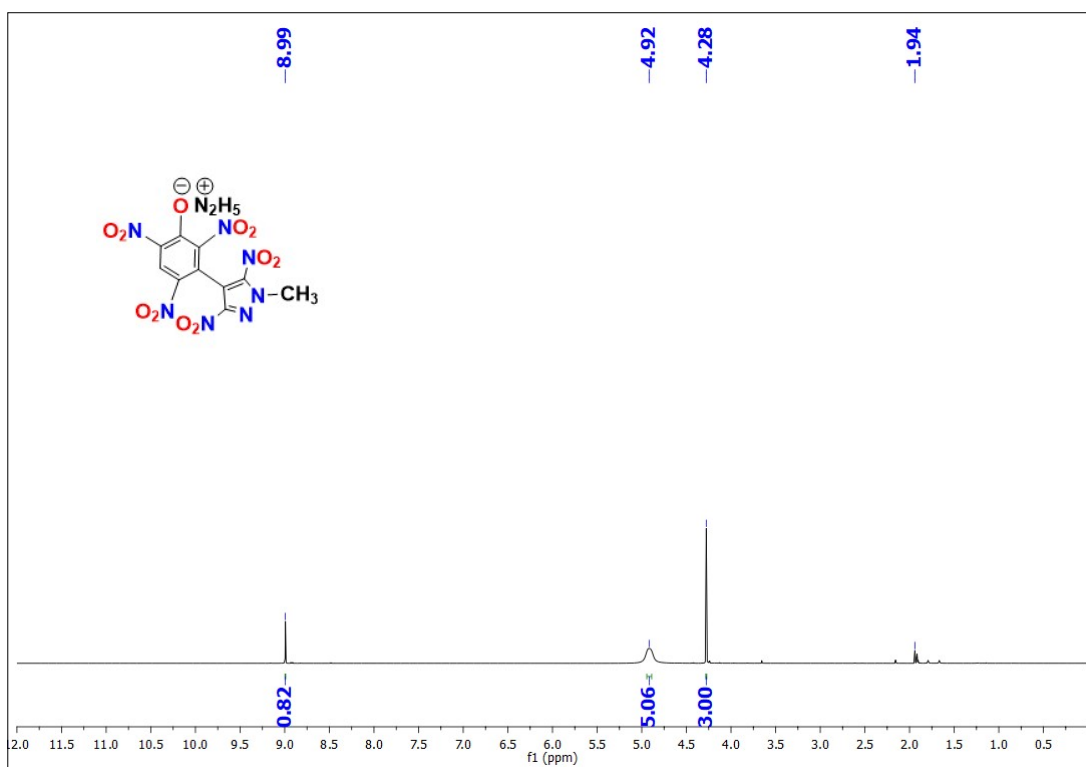


Fig.24: ^1H NMR Spectra of compound **12**

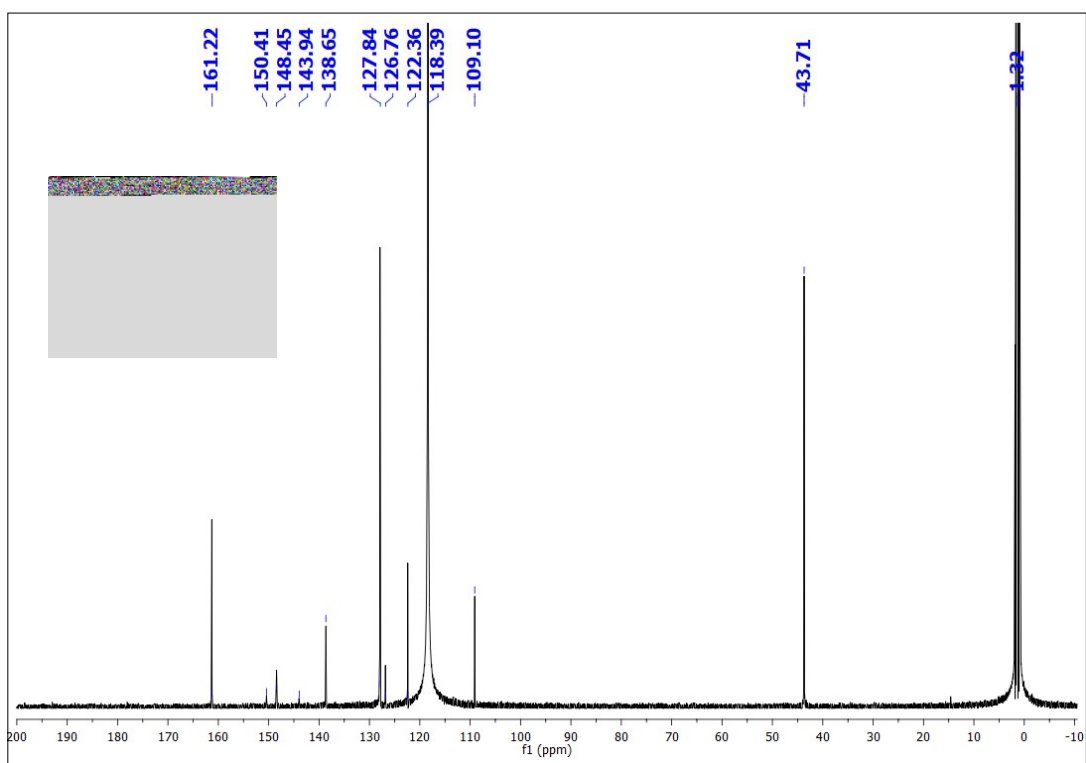


Fig.25: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound **12**

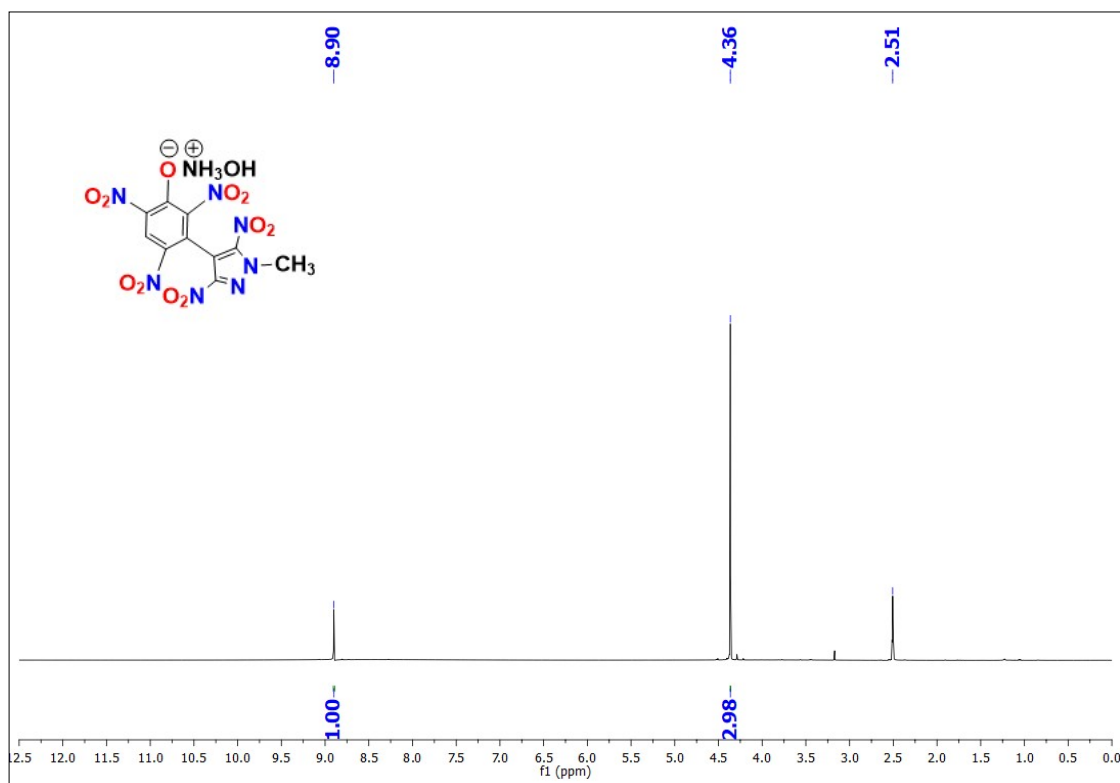


Fig.26: ^1H NMR Spectra of compound **13**

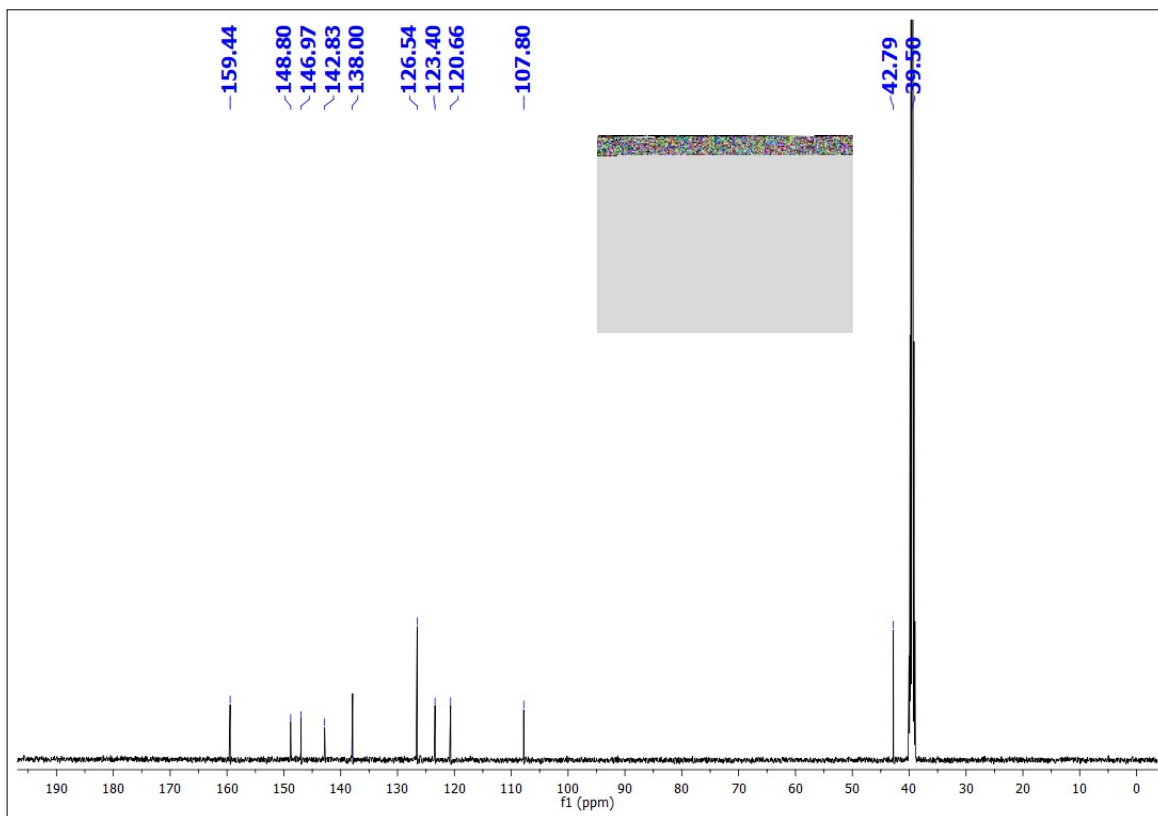


Fig.27: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound **13**

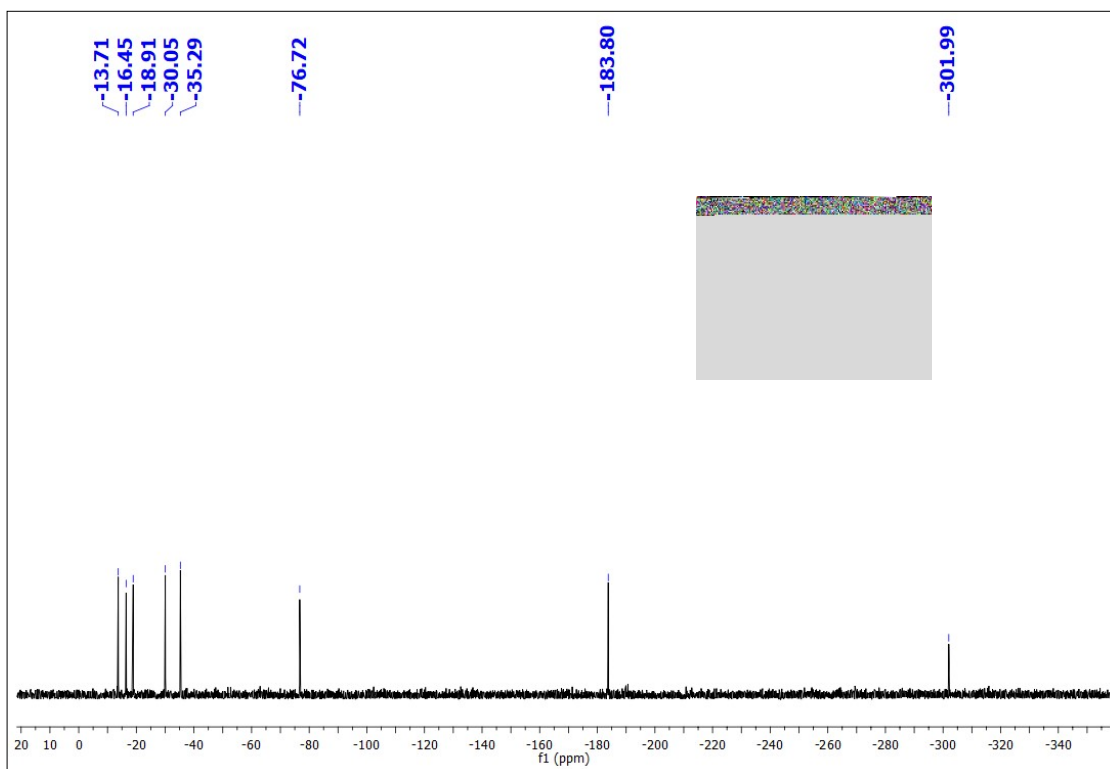


Fig.28: ^{15}N NMR Spectra of compound **13**

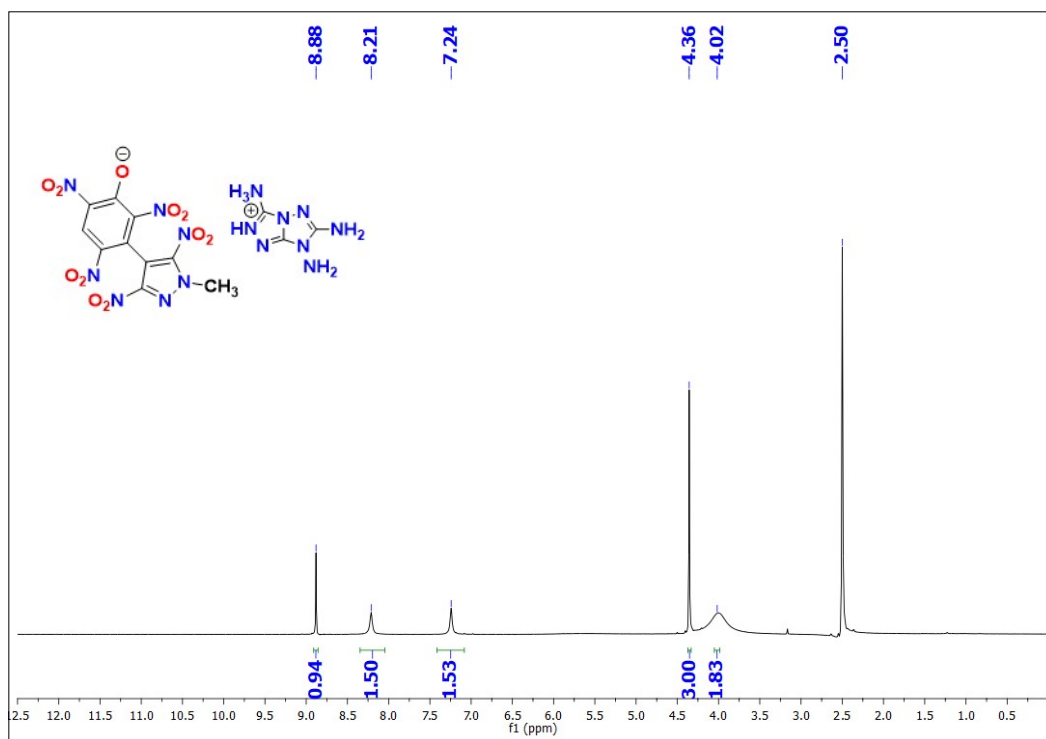


Fig.29: ^1H NMR Spectra of compound 14

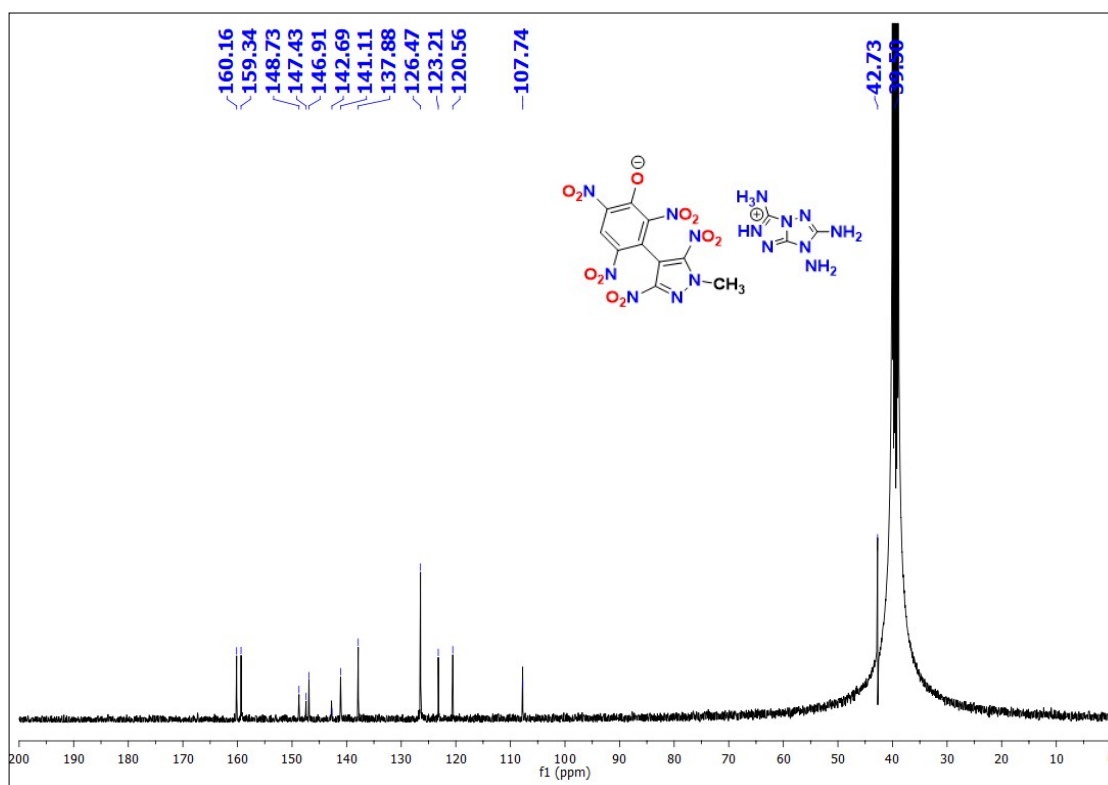


Fig.30: $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of compound 14

4. Mass Spectra

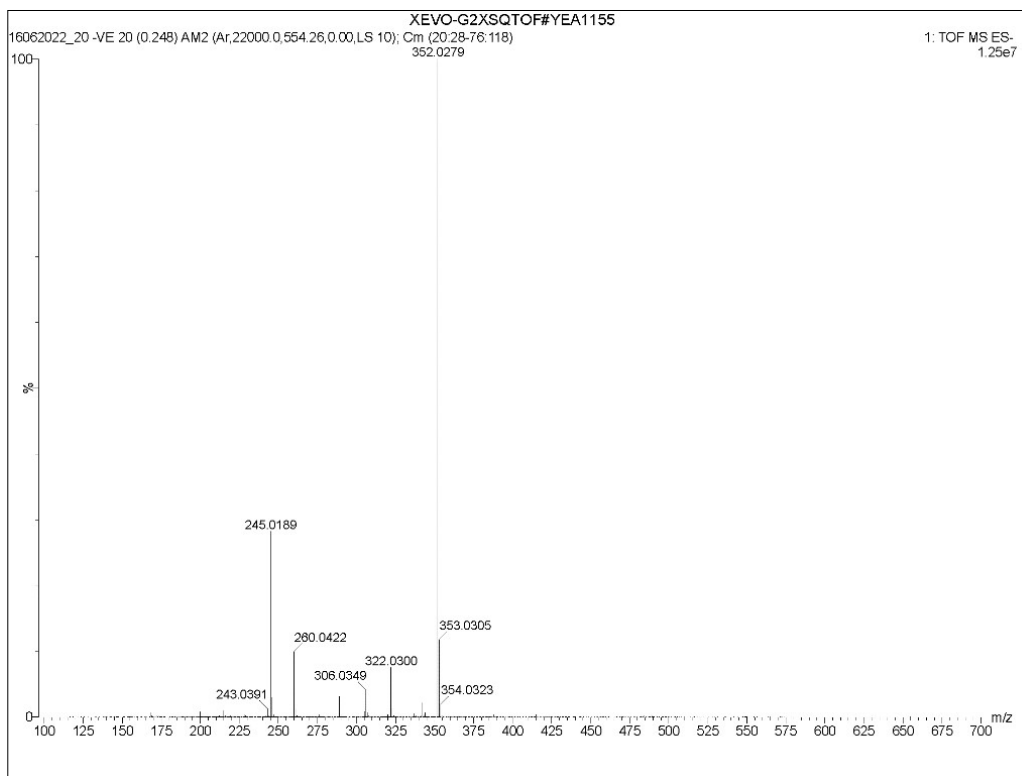


Fig.31: Mass Spectrum of Compound 5

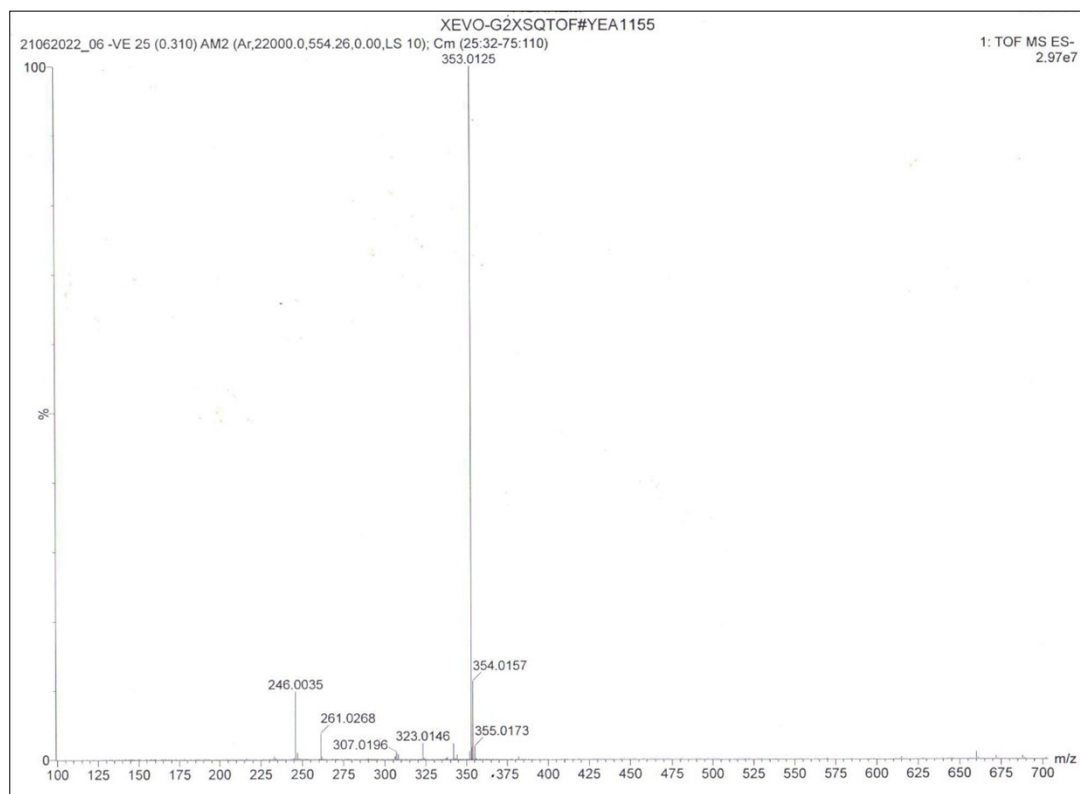


Fig.32: Mass Spectrum of Compound 6

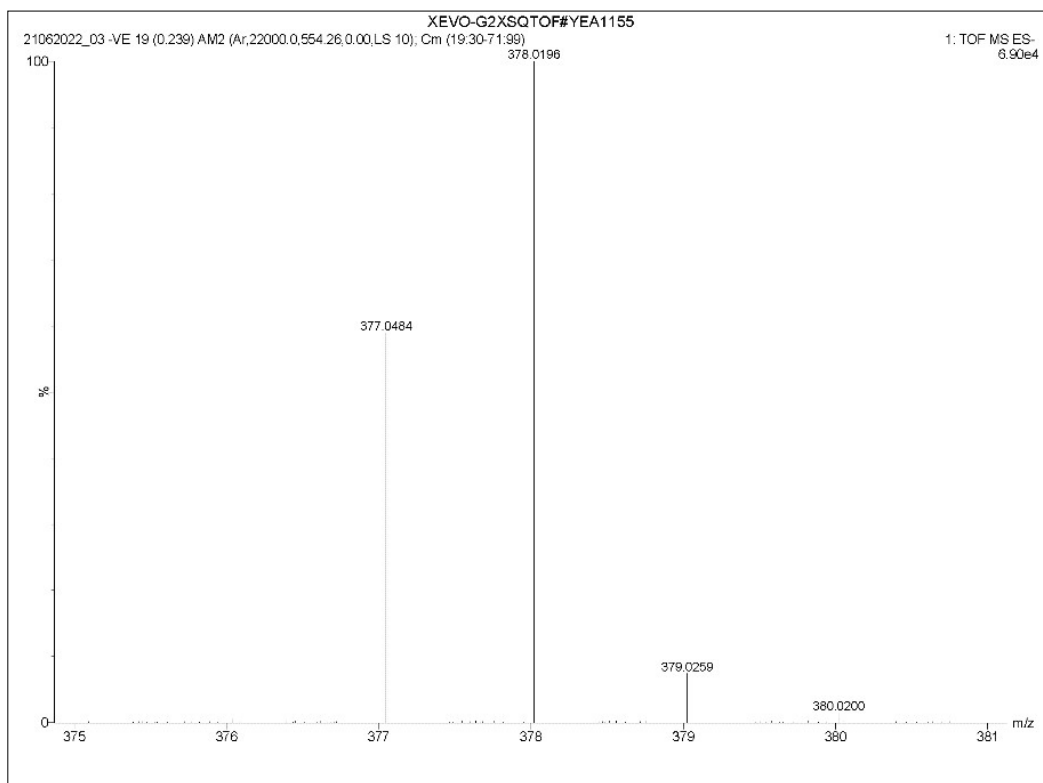


Fig.33: Mass Spectrum of Compound 7

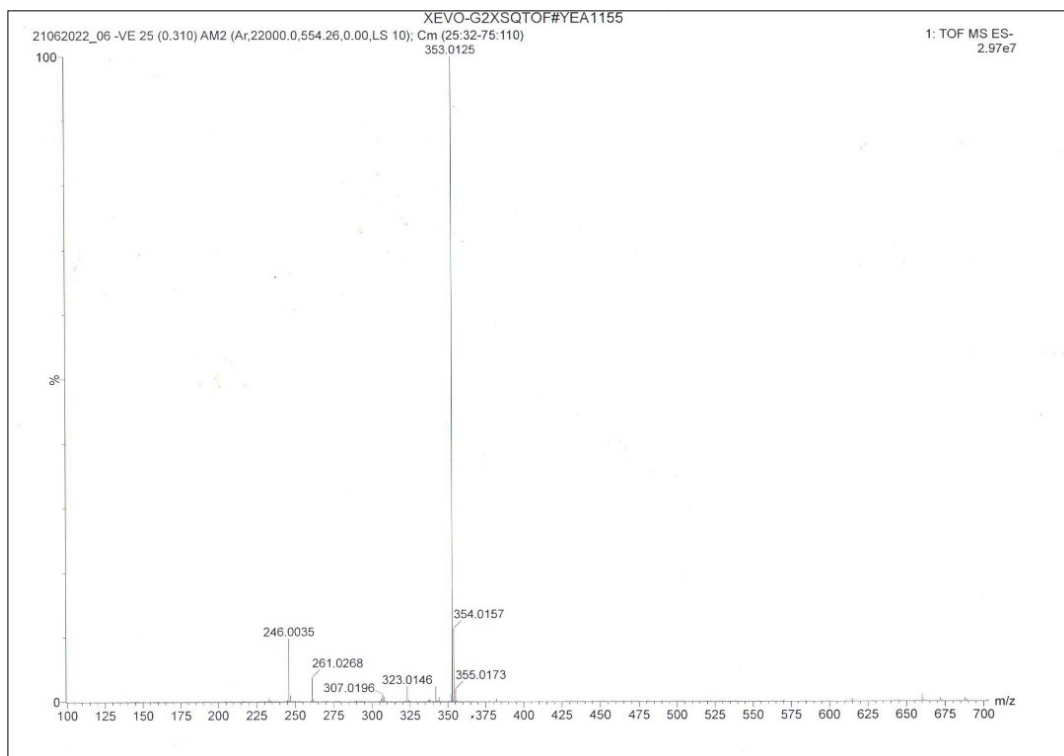


Fig.34: Mass Spectrum of Compound 8

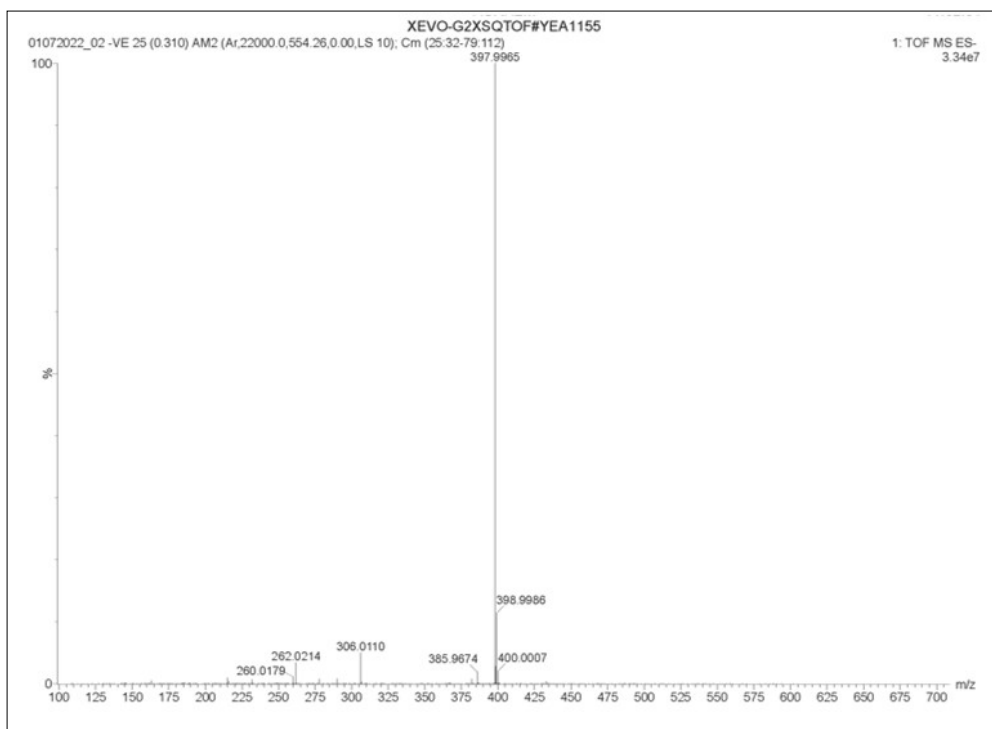


Fig.35: Mass Spectrum of Compound **10**

5. IR Data

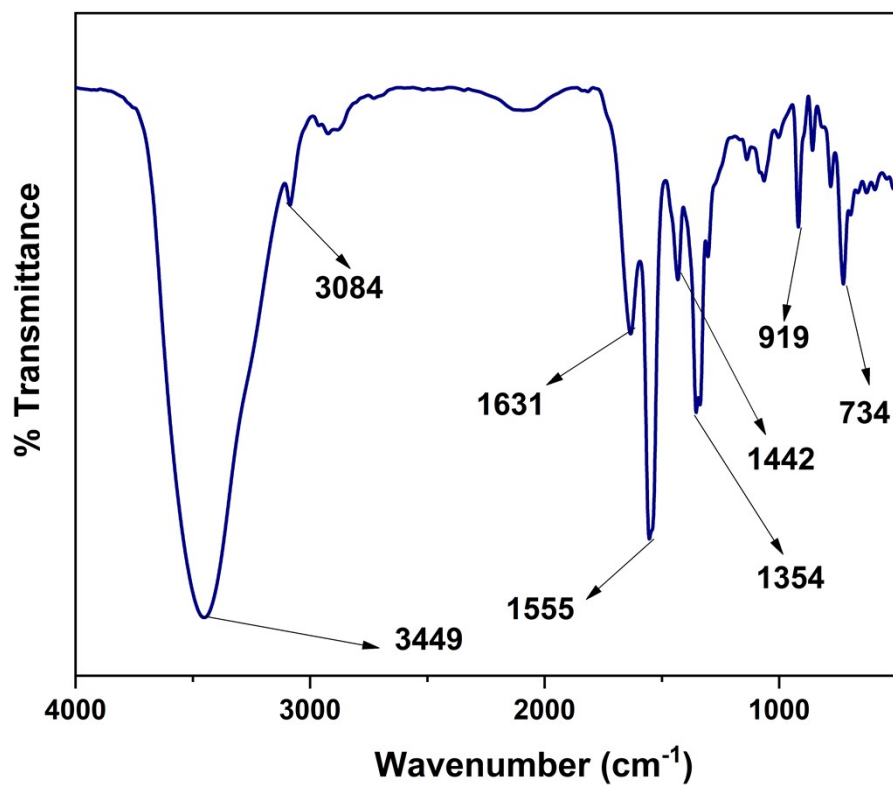


Fig.36: FTIR Spectra of compound 3

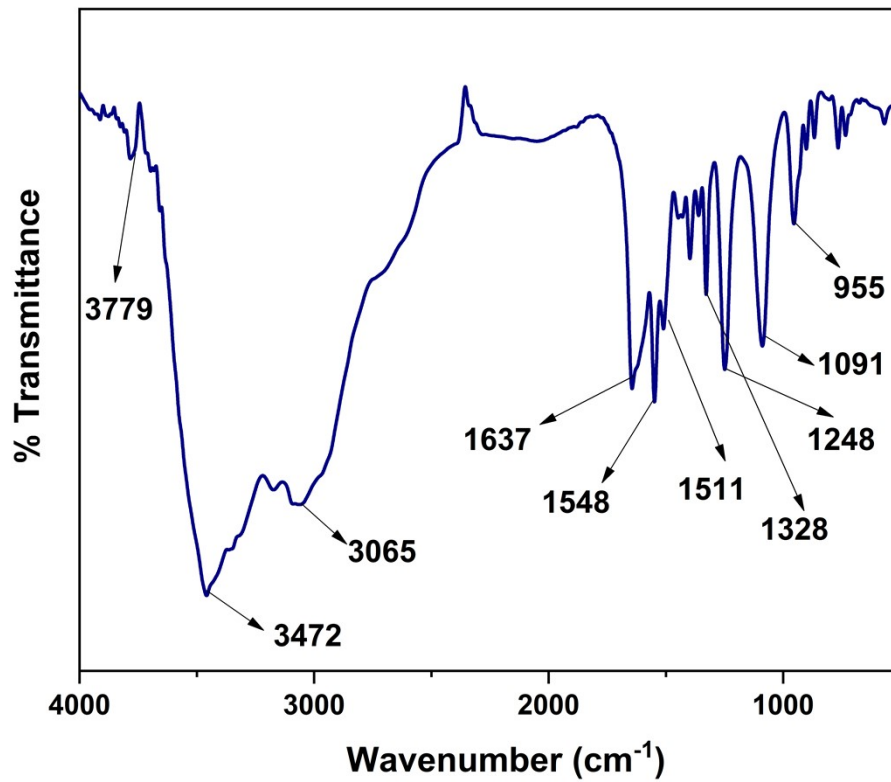


Fig.37: FTIR Spectra of compound 4

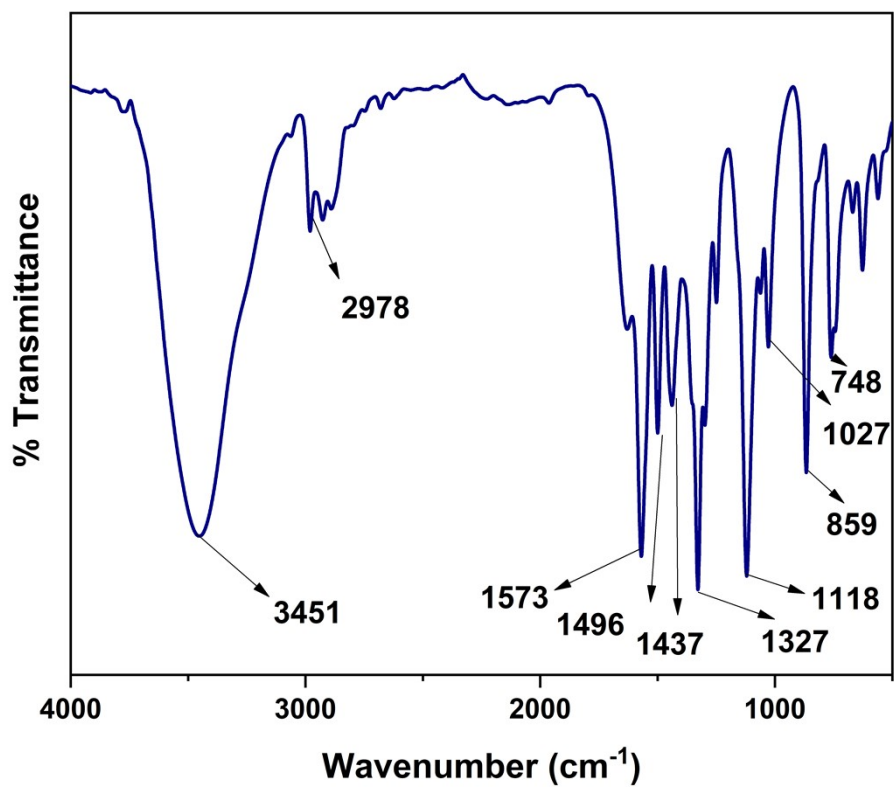


Fig.38: FTIR Spectra of compound 5

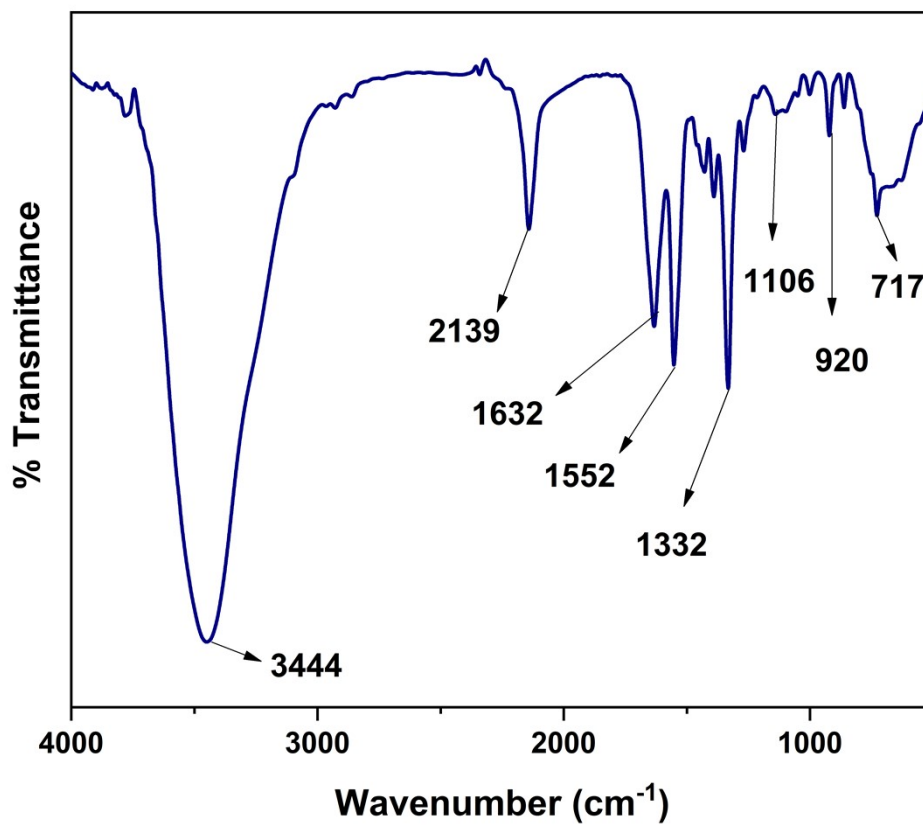


Fig.39: FTIR Spectra of compound 6

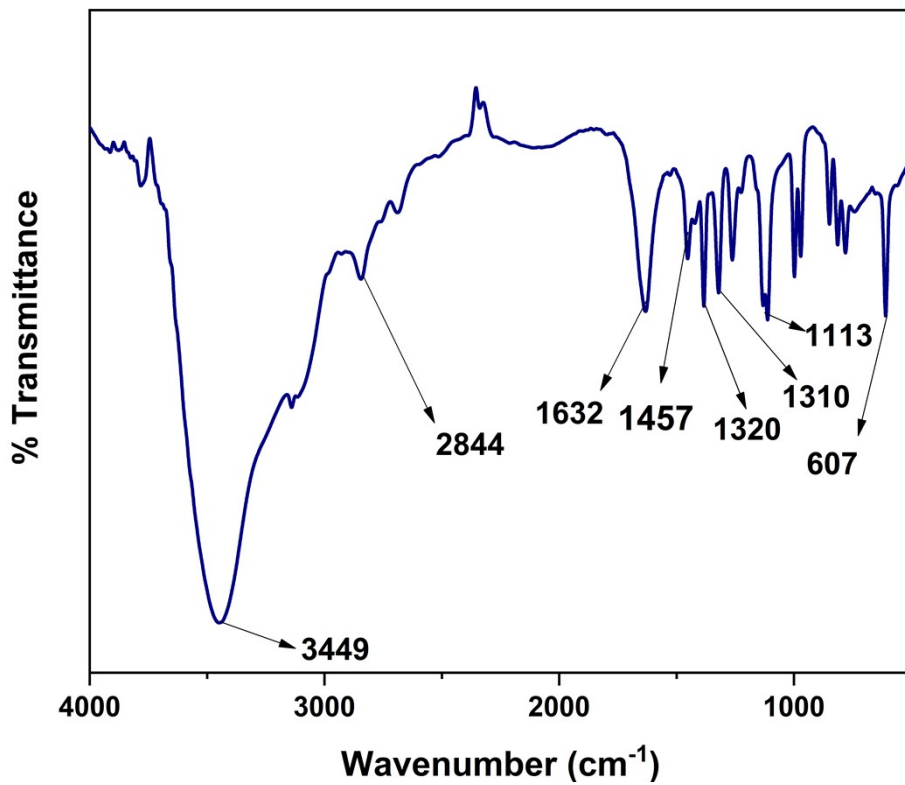


Fig.40: FTIR Spectra of compound 7

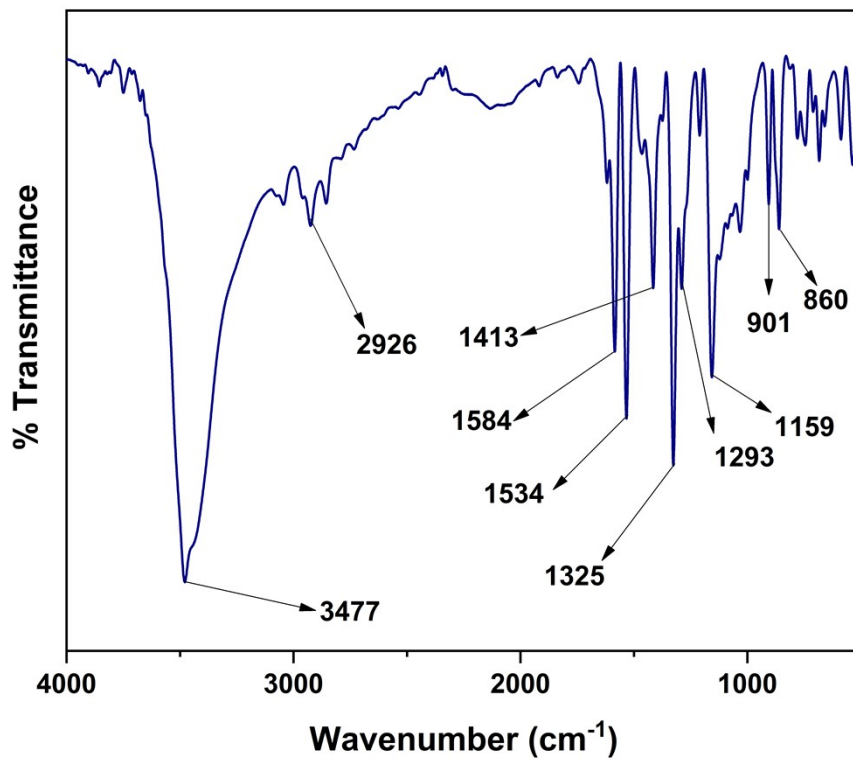


Fig.41: FTIR Spectra of compound 8

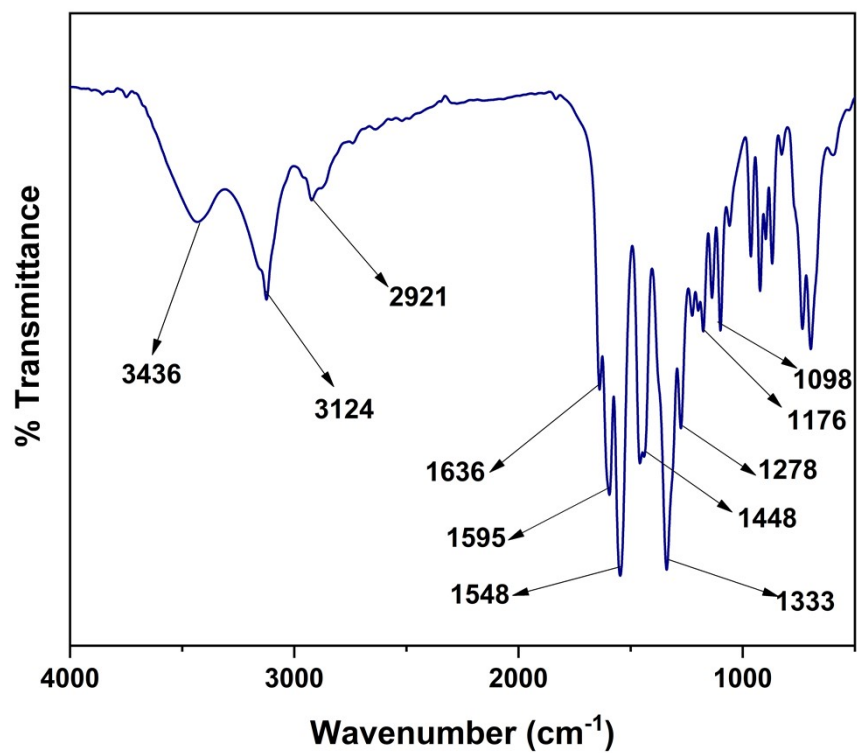


Fig.42: FTIR Spectra of compound 10

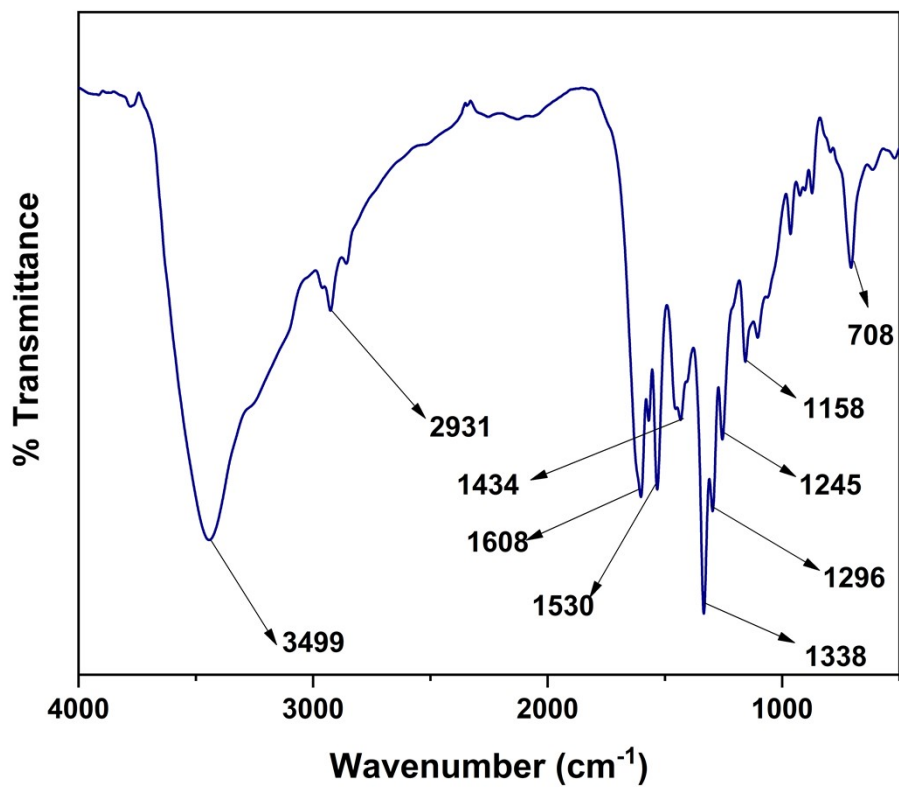


Fig.43: FTIR Spectra of compound 11

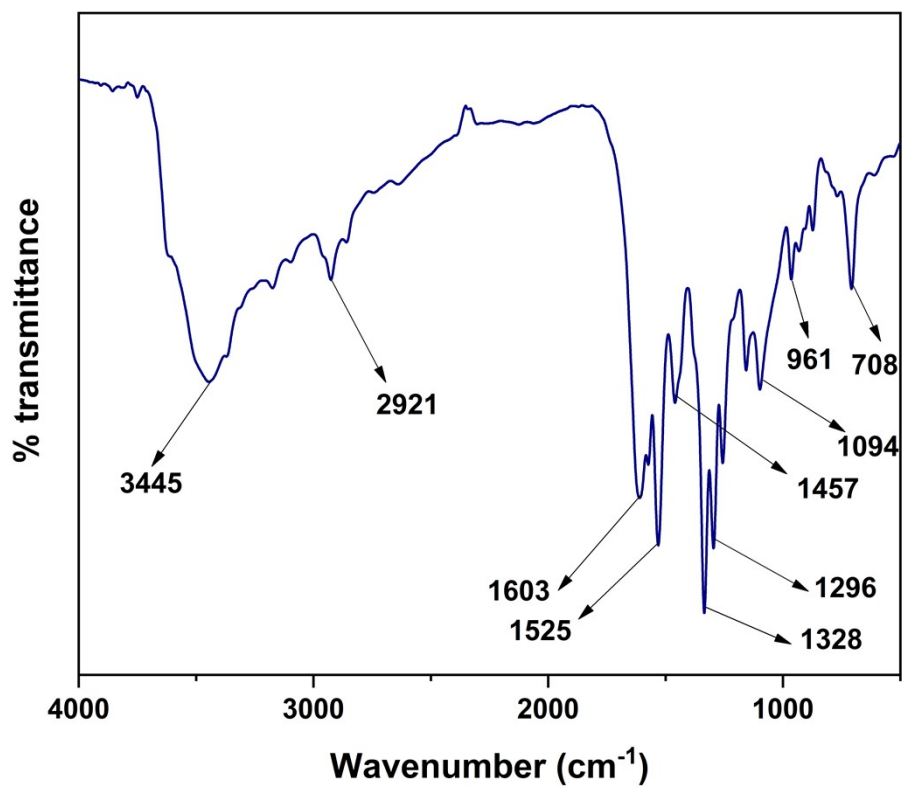


Fig.44: FTIR Spectra of compound 12

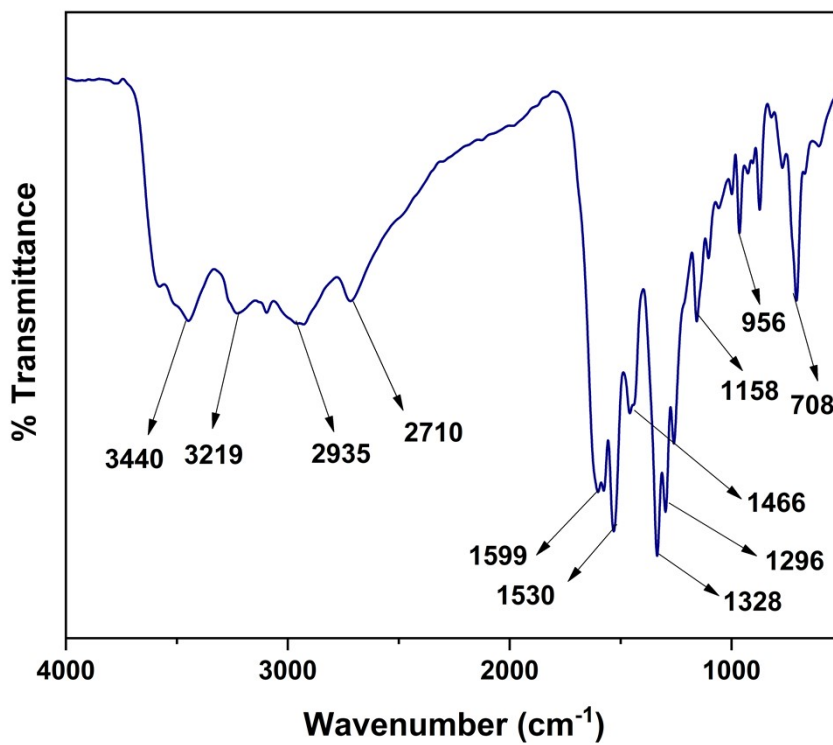


Fig.45: FTIR Spectra of compound 13

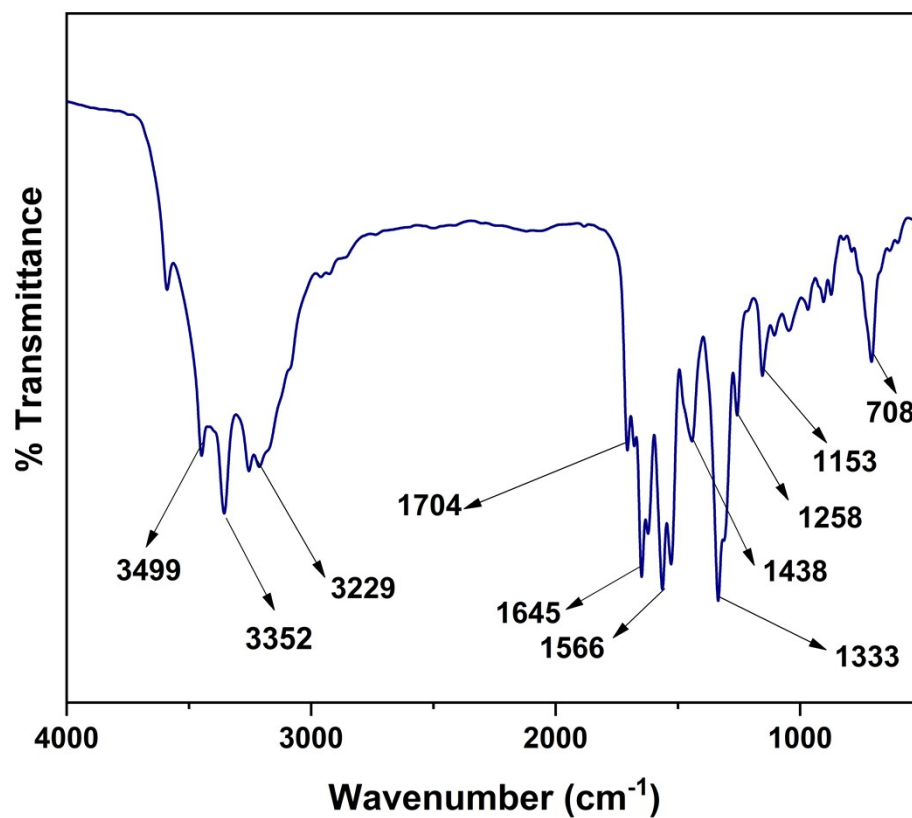


Fig.46: FTIR Spectra of compound **14**

6. DSC Analysis

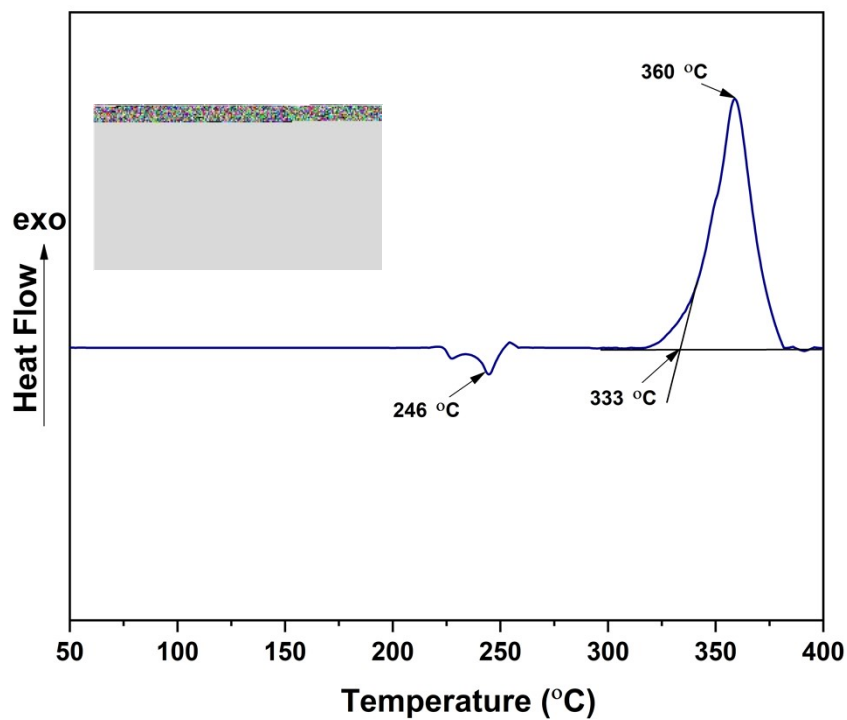


Fig.47: DSC curve of compound 5 at heating rate 5 °C/min.

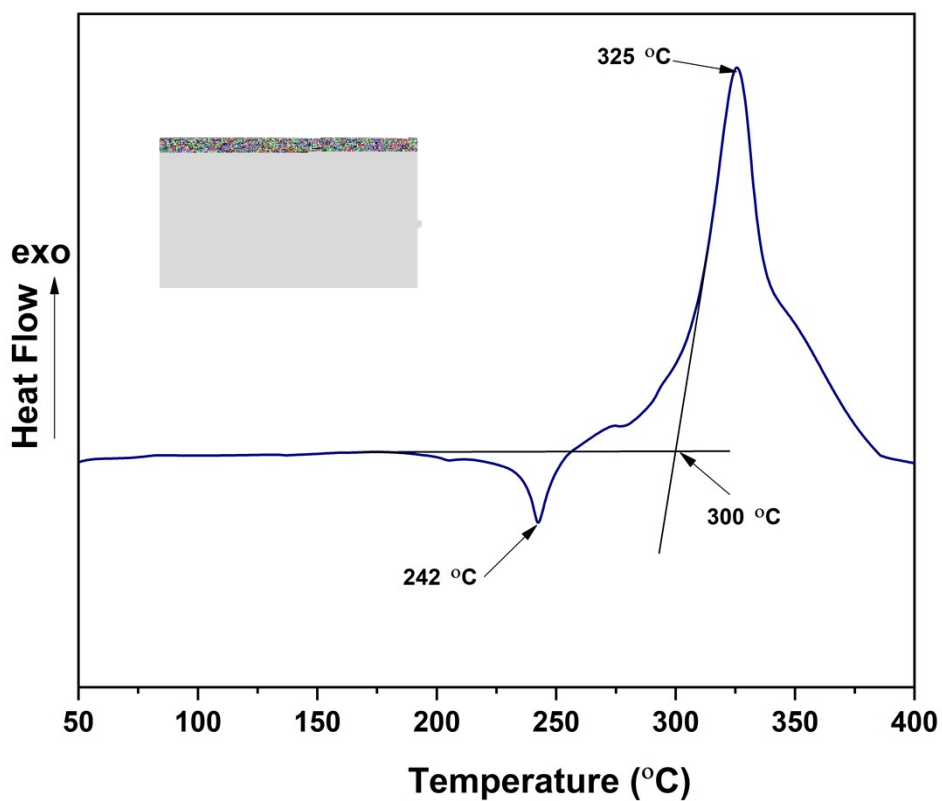


Fig.48: DSC curve of compound 6 at heating rate 5 °C/min.

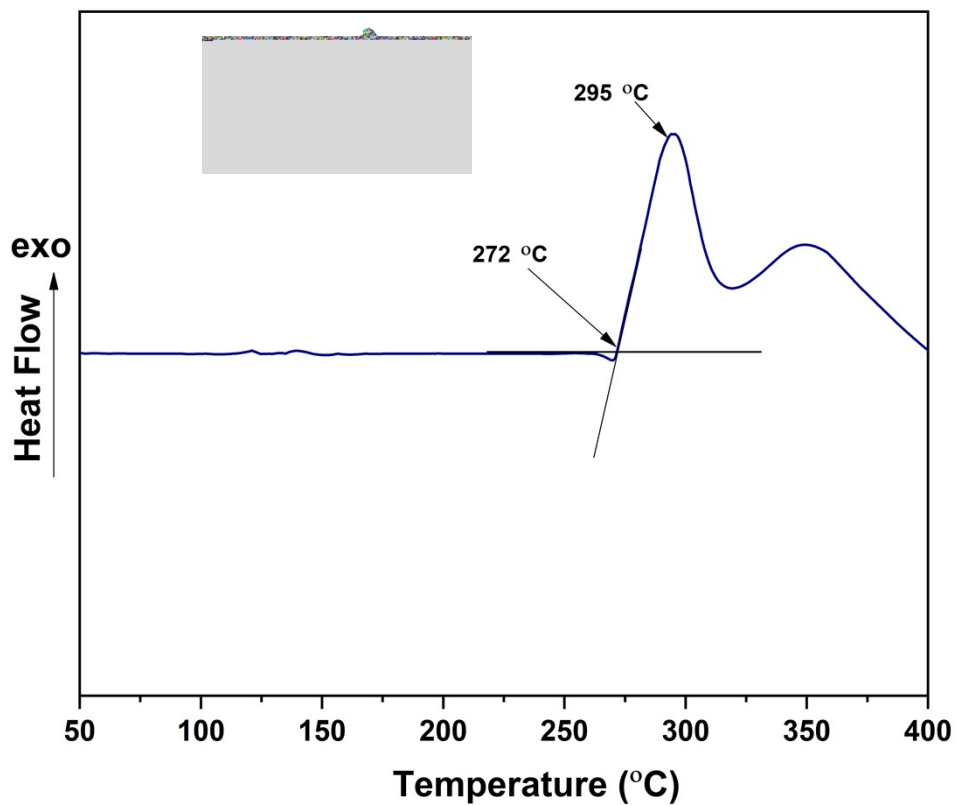


Fig.49: DSC curve of compound **7** at heating rate 5 °C/min.

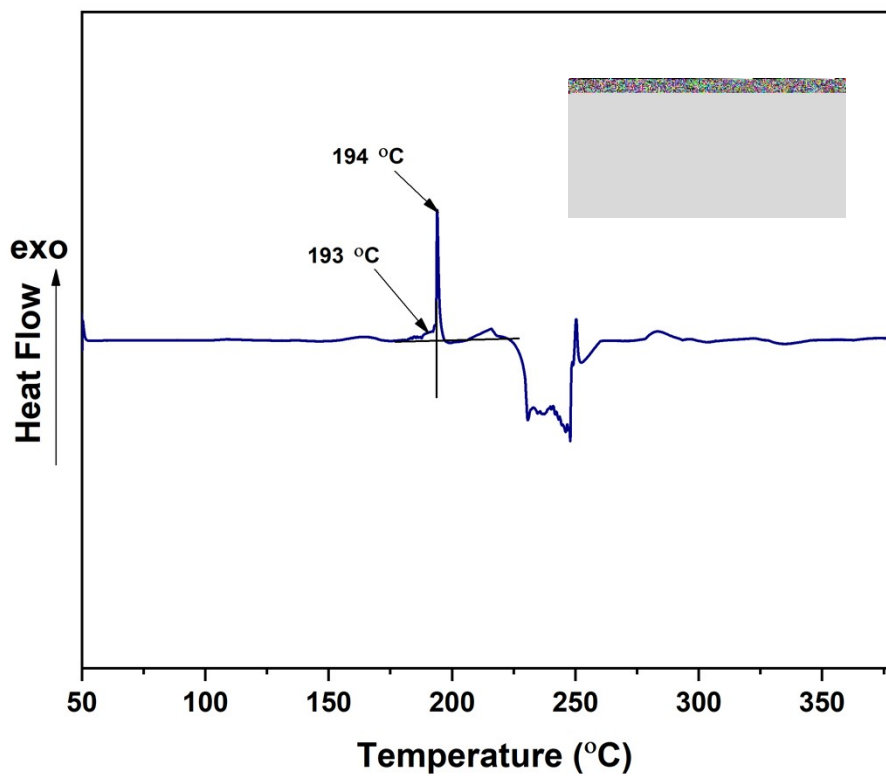


Fig.50: DSC curve of compound **8** at heating rate 5 °C/min.

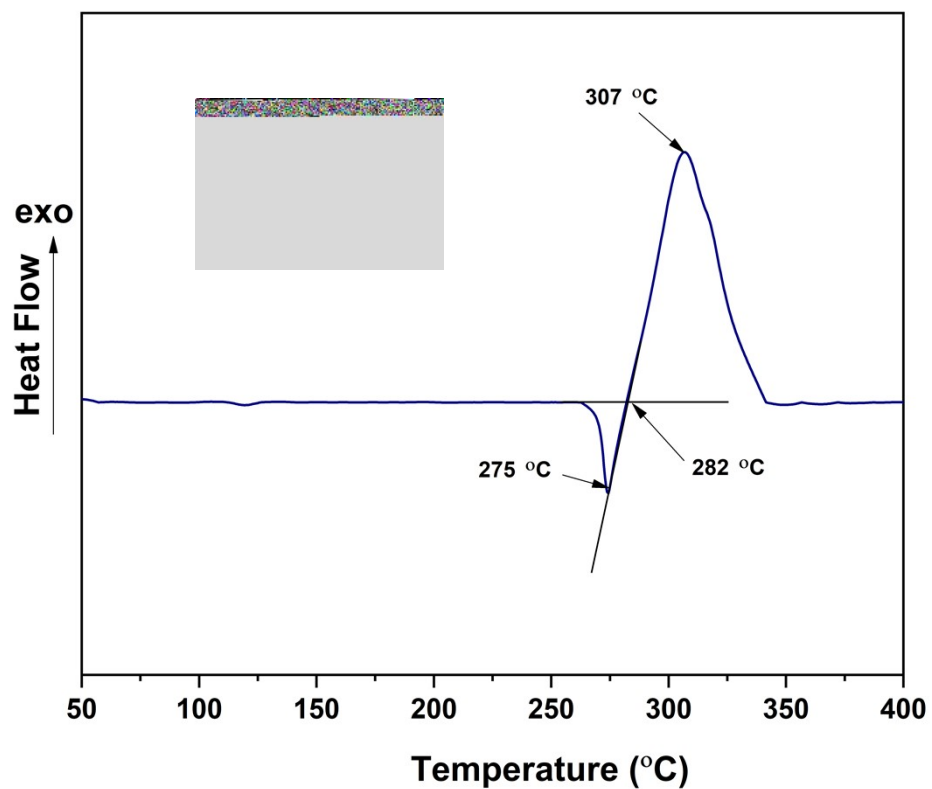


Fig.51: DSC curve of compound **10** at heating rate 5 °C/min.

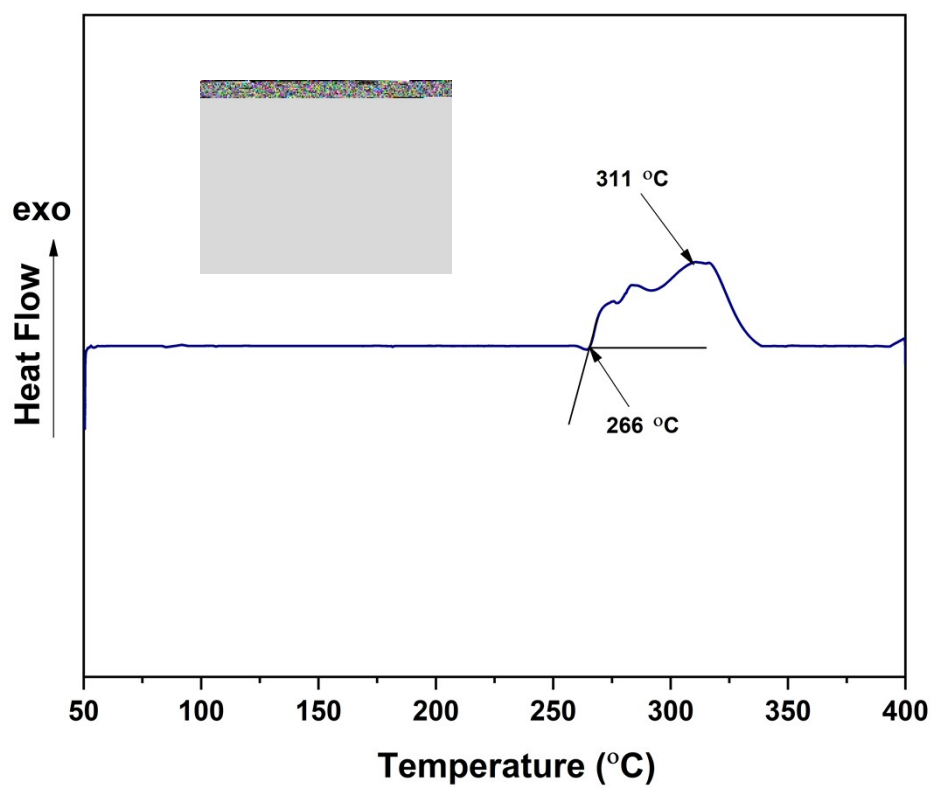


Fig.52: DSC curve of compound **11** at heating rate 5 °C/min.

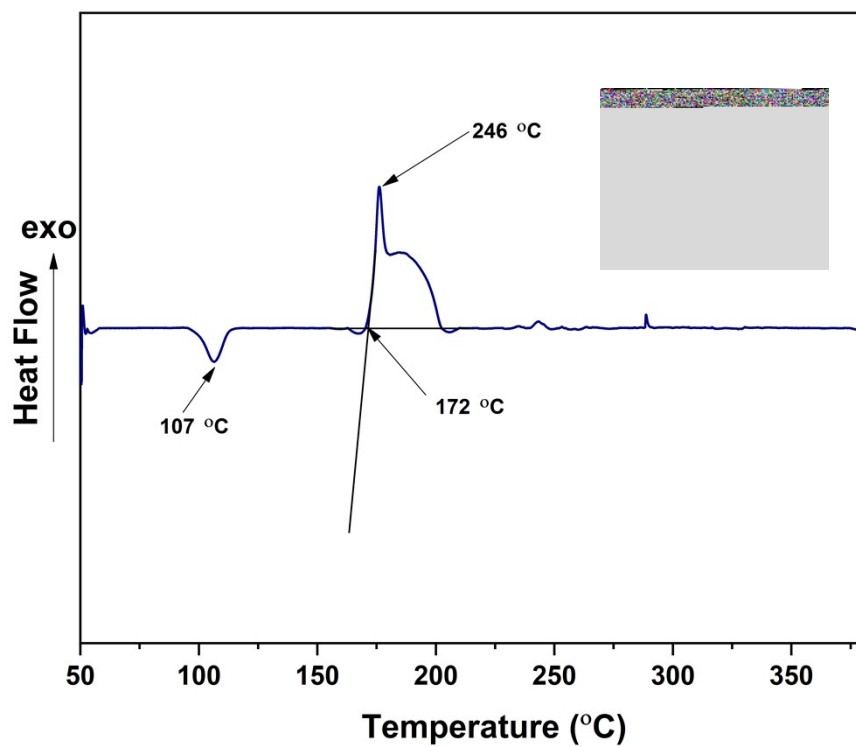


Fig.53: DSC curve of compound **12** at heating rate 5 °C/min.

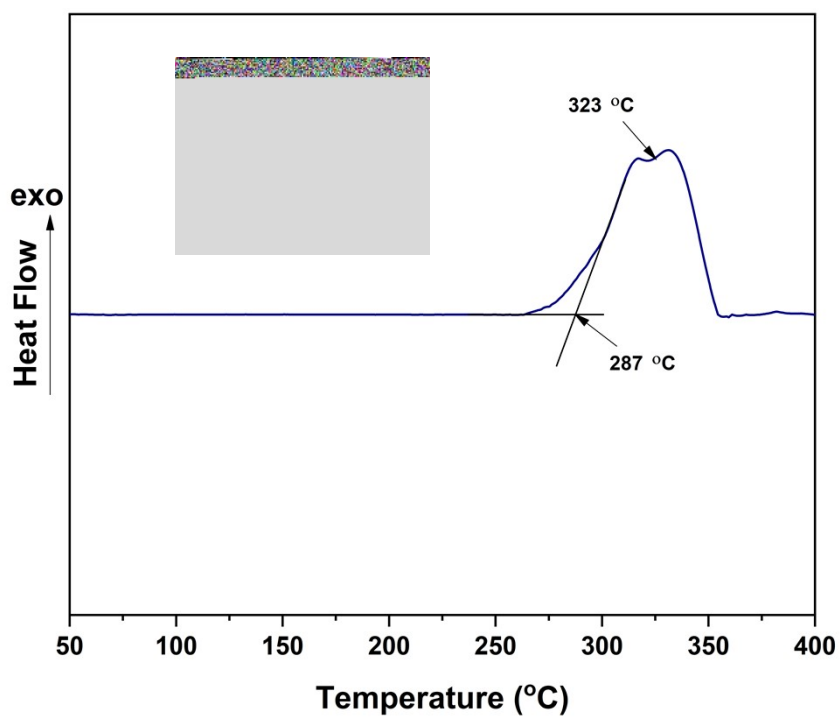


Fig.54: DSC curve of compound **13** at heating rate 5 °C/min.

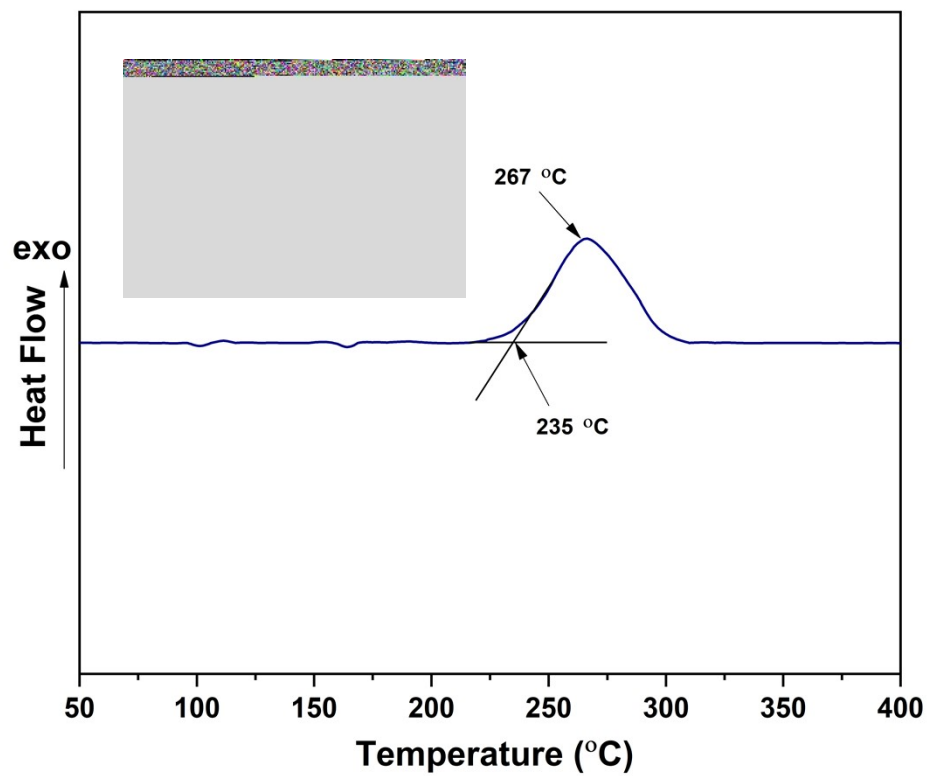


Fig.55: DSC curve of compound 14 at heating rate 5 °C/min.