Supporting Information

N-Methylene-C-Linked Nitropyrazoles and 1,2,4-triazolone-3-one: Thermally Stable Energetic Materials with Reduced Sensitivity

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1. Crystal stricture data

Table S1 Crystal data and structure refinement for compound 3.

Identification code	DK_KP_CDNPHY_0464_0m (1)
Empirical formula	$C_6H_7N_9O_5$
Formula weight	285.21
Temperature/K	108.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.2377(4)
b/Å	7.5343(4)
c/Å	38.309(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2089.0(2)
Z	4
ρ_{calc}g/cm^3	0.907
μ/mm^{-1}	0.079
F(000)	584.0
Crystal size/mm^3	0.16 × 0.104 × 0.047
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.252 to 54.22
Index ranges	$-9 \le h \le 9$, $-9 \le k \le 9$, $-49 \le l \le 49$
Reflections collected	29940
Independent reflections	2311 [R_{int} = 0.0671, R_{sigma} = 0.0297]
Data/restraints/parameters	2311/0/190
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0807
Final R indexes [all data]	R_1 = 0.0480, wR_2 = 0.0874
Largest diff. peak/hole / e Å^{-3}	0.28/-0.26
CCDC	2381173

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound 3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	8436.4(14)	6180.0(15)	4663.7(3)	21.5(3)

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 3. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	5746.5(15)	6999.9(15)	4860.5(3)	23.0(3)
O3	757.0(14)	3656.3(15)	4002.2(3)	20.3(3)
O4	2463.9(15)	2208.0(15)	3627.9(3)	21.2(3)
O5	4086.8(15)	2973.8(14)	2486.8(3)	19.9(3)
N1	5635.5(15)	3484.6(16)	3951.3(3)	12.1(3)
N2	6837.8(16)	4290.4(17)	4157.1(3)	13.1(3)
N3	6740.9(17)	6169.7(17)	4653.2(3)	16.0(3)
N4	2490.5(17)	5615.0(18)	4533.0(3)	18.2(3)
N5	2279.7(17)	3198.4(18)	3882.3(3)	15.7(3)
N6	6133.7(17)	4798.3(17)	3228.7(3)	15.9(3)
N7	5436.1(18)	4899.6(18)	2892.4(3)	16.9(3)
N8	5083.8(17)	2197.7(17)	3051.2(3)	14.8(3)
N9	4517.8(19)	419.9(18)	3077.3(4)	18.9(3)
C1	5825(2)	5160(2)	4392.5(4)	13.2(3)
C2	3897(2)	4941(2)	4348.1(4)	13.6(3)
C3	3850.0(19)	3845(2)	4054.8(4)	13.4(3)
C4	6347(2)	2383(2)	3665.3(3)	13.7(3)
C5	5869.0(19)	3156(2)	3317.9(4)	13.5(3)
C6	4804(2)	3328(2)	2774.3(4)	15.4(3)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	15.8(5)	27.7(7)	21.1(6)	-4.1(5)	-2.8(4)	-2.3(5)
O2	26.7(6)	24.0(7)	18.4(6)	-8.6(5)	2.2(5)	4.7(5)
O3	10.1(5)	25.7(7)	25.1(6)	2.6(5)	1.9(4)	2.2(5)
O4	18.1(5)	25.0(7)	20.6(6)	-6.9(5)	-0.9(5)	-2.2(5)
O5	27.8(6)	17.8(6)	14.2(5)	-1.1(5)	-7.4(4)	1.2(5)
N1	11.5(6)	14.0(6)	10.9(6)	0.0(5)	0.0(5)	-0.2(5)
N2	13.2(6)	14.7(7)	11.3(6)	0.4(5)	-0.7(5)	-1.1(5)
N3	19.1(6)	15.4(7)	13.4(6)	0.3(5)	0.5(5)	1.0(5)
N4	14.8(6)	21.8(7)	17.9(6)	-1.8(6)	3.2(5)	3.6(6)
N5	13.3(6)	16.8(7)	17.1(6)	3.8(6)	0.0(5)	-0.3(5)
N6	18.6(6)	17.5(7)	11.5(6)	-0.5(5)	-1.2(5)	-0.3(5)
N7	24.0(7)	13.1(7)	13.7(7)	0.4(6)	-2.4(5)	-1.0(6)
N8	18.7(6)	12.4(7)	13.2(6)	-0.7(5)	-1.5(5)	-1.3(5)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for compound 3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N9	23.7(7)	12.5(7)	20.5(7)	-0.8(6)	-2.5(6)	-3.9(6)
C1	14.2(7)	13.3(7)	12.1(7)	0.2(6)	-0.1(5)	1.0(6)
C2	14.4(7)	12.8(7)	13.6(7)	4.0(6)	1.6(6)	1.7(6)
C3	10.8(7)	14.5(8)	14.9(7)	3.4(6)	0.2(5)	-0.8(6)
C4	13.2(6)	14.6(8)	13.3(7)	-1.9(6)	1.1(5)	1.2(6)
C5	11.3(7)	15.8(8)	13.3(7)	-1.5(6)	1.0(5)	0.8(6)
C6	17.0(7)	15.3(8)	13.9(7)	-0.9(6)	0.0(6)	2.6(6)

Table S4 Bond Lengths for compound 3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N3	1.2278(16)	N5	C3	1.4022(19)
O2	N3	1.2409(16)	N6	N7	1.3857(17)
O3	N5	1.2428(16)	N6	C5	1.2982(19)
O4	N5	1.2346(16)	N7	C6	1.348(2)
O5	C6	1.2465(18)	N8	N9	1.4043(18)
N1	N2	1.3219(16)	N8	C5	1.3740(18)
N1	C3	1.3789(18)	N8	C6	1.3754(19)
N1	C4	1.4675(18)	C1	C2	1.415(2)
N2	C1	1.3340(18)	C2	C3	1.395(2)
N3	C1	1.4198(19)	C5	C4	1.4930(19)
N4	C2	1.3403(19)			

Table S5 Crystal data and structure refinement for compound 8.

Identification code	dk_kp_tzno_0666_0m
Empirical formula	$C_6H_6N_8O_6$
Formula weight	286.19
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.4322(6)
b/Å	6.1733(4)
c/Å	10.2585(7)
α/°	90
β/°	103.420(2)
γ/°	90
Volume/Å^3	519.42(6)
Z	2
ρ_{calc}g/cm^3	1.830
μ/mm^{-1}	0.163
F(000)	292.0
Crystal size/mm^3	0.58 × 0.33 × 0.144
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.082 to 53.63
Index ranges	$-10 \leq h \leq 10$, $-7 \leq k \leq 7$, $-12 \leq l \leq 12$
Reflections collected	13652
Independent reflections	2208 [R_{int} = 0.0397, R_{sigma} = 0.0214]
Data/restraints/parameters	2208/1/193
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0638
Final R indexes [all data]	R_1 = 0.0266, wR_2 = 0.0642
Largest diff. peak/hole / e Å^{-3}	0.24/-0.17
Flack parameter	0.3(4)
CCDC	2381172

Table S6 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound 8. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	1692.9(18)	-106(3)	4623.0(14)	23.0(3)

Table S6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 8. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2	365.3(19)	-502(3)	6189.0(15)	24.8(4)
O3	1108.1(19)	2483(3)	8468.7(15)	20.7(3)
O4	2928(2)	5917(3)	9879.8(15)	27.2(4)
O5	3779(2)	8294(3)	8628.9(17)	28.5(4)
O6	9932.7(17)	8834(2)	8902.2(13)	19.6(3)
N1	3535.3(19)	5178(3)	6629.2(15)	16.4(3)
N2	3075(2)	3544(3)	5790.9(16)	16.8(4)
N3	1343.5(19)	462(3)	5667.8(16)	16.6(4)
N4	3230(2)	6510(3)	8828.5(18)	20.4(4)
N5	6869(2)	4987(3)	7970.5(16)	17.2(3)
N6	8392(2)	5653(3)	8678.5(17)	17.5(4)
N7	7309(2)	8397(3)	7531.0(16)	14.8(3)
N8	6936(2)	10481(3)	7018.6(17)	17.9(4)
C1	2105(2)	2338(3)	6359(2)	15.7(4)
C2	1945(2)	3142(4)	7609(2)	16.5(4)
C3	2901(2)	4993(3)	7742.3(19)	17.2(4)
C4	4662(2)	6774(3)	6302(2)	17.4(4)
C5	6273(2)	6669(3)	7284.5(18)	15.2(4)
C6	8697(2)	7737(3)	8436.7(19)	16.0(4)

Table S7 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 8. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	27.2(8)	24.6(8)	18.6(7)	-5.6(7)	8.3(6)	-2.8(7)
O2	27.7(8)	25.1(8)	22.9(8)	-2.0(6)	8.6(6)	-10.7(7)
O3	26.7(8)	18.7(8)	19.4(7)	-2.1(6)	10.8(6)	-5.7(6)
O4	36.9(9)	27.5(8)	18.6(7)	-4.8(6)	9.2(6)	-4.8(7)
O5	33.9(9)	19.0(8)	35.9(9)	-8.1(7)	14.9(7)	-9.3(7)
O6	19.7(7)	22.8(8)	15.2(6)	-0.2(6)	1.8(5)	-6.2(6)
N1	16.2(7)	17.7(9)	14.3(7)	0.3(7)	1.7(6)	-1.7(7)
N2	14.3(7)	18.5(9)	16.5(8)	-1.3(7)	1.3(6)	-2.6(7)
N3	15.8(7)	17.4(9)	15.5(8)	-0.8(7)	1.7(6)	-1.6(7)
N4	20.3(8)	19.8(9)	21.2(8)	-3.4(7)	5.1(6)	-0.6(7)
N5	19.4(8)	16.1(8)	14.6(7)	-0.5(7)	0.6(6)	-1.5(7)
N6	18.6(8)	16.1(8)	15.4(8)	1.6(7)	-1.3(6)	1.2(7)
N7	17.1(8)	13.6(8)	13.2(7)	0.3(6)	2.5(6)	-0.6(6)

Table S7 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 8. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N8	23.6(9)	11.8(8)	18.0(8)	1.8(7)	4.1(7)	-0.5(7)
C1	13.7(9)	17.8(9)	14.6(9)	0.4(8)	1.5(7)	-0.5(7)
C2	16.2(8)	17.0(9)	15.6(9)	0.5(7)	2.1(7)	0.8(8)
C3	17.3(9)	18.1(10)	15.7(8)	-0.5(8)	3.1(7)	0.1(8)
C4	15.1(9)	18.1(10)	17.6(9)	4.0(8)	1.4(7)	-2.8(8)
C5	17.7(9)	14.9(9)	13.5(8)	-2.2(7)	5.2(7)	-1.5(7)
C6	18.6(9)	19.3(10)	10.2(8)	-0.9(7)	3.6(7)	-0.9(8)

Table S8 Bond Lengths for compound 8.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N3	1.227(2)	N4	C3	1.433(3)
O2	N3	1.235(2)	N5	N6	1.383(2)
O3	C2	1.316(3)	N5	C5	1.290(3)
O4	N4	1.220(3)	N6	C6	1.346(3)
O5	N4	1.230(3)	N7	N8	1.398(2)
O6	C6	1.242(3)	N7	C5	1.365(3)
N1	N2	1.324(2)	N7	C6	1.376(3)
N1	C3	1.373(2)	C1	C2	1.410(3)
N1	C4	1.461(3)	C2	C3	1.387(3)
N2	C1	1.335(3)	C4	C5	1.493(3)
N3	C1	1.430(3)			

2. Physical state of compounds 3-13:

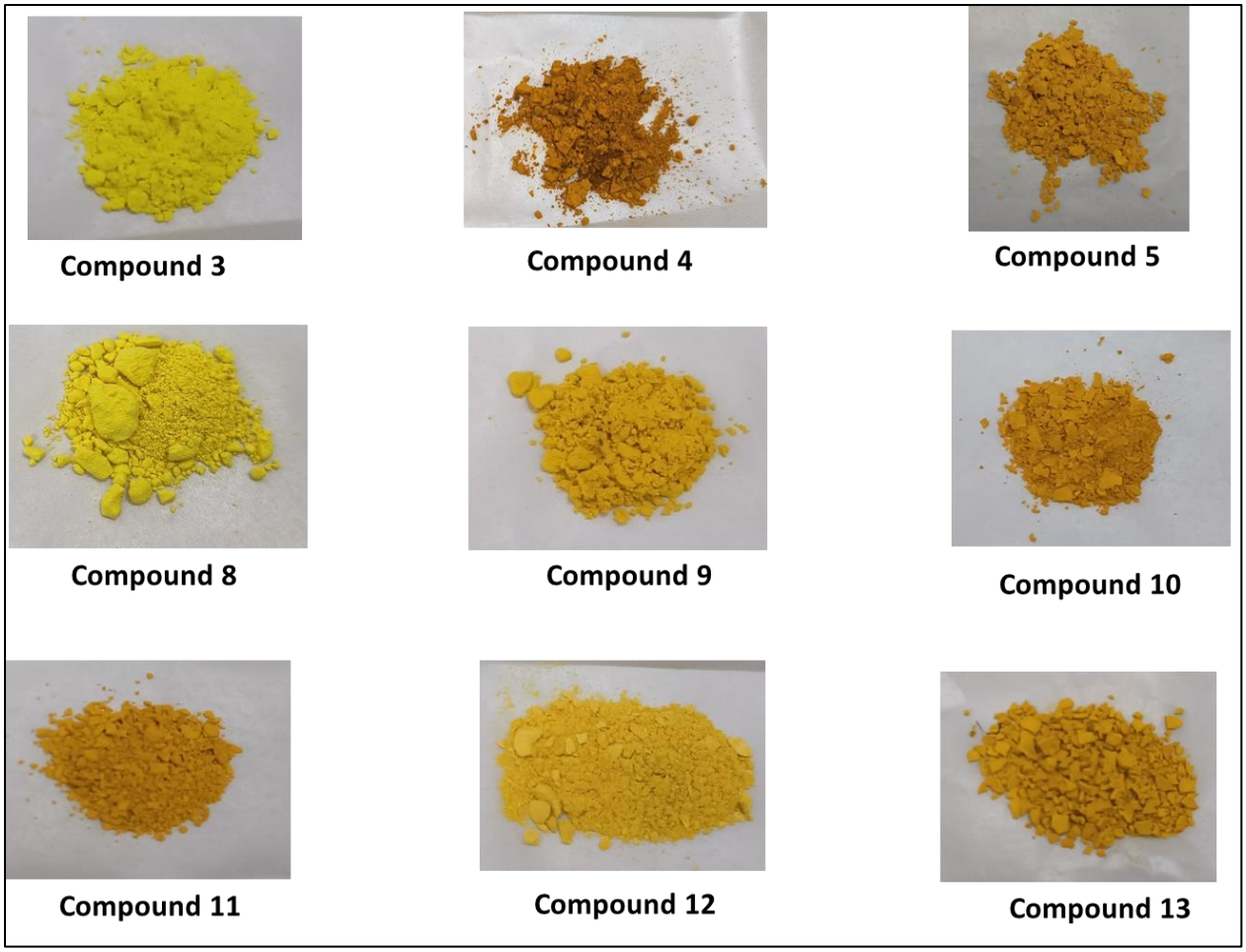
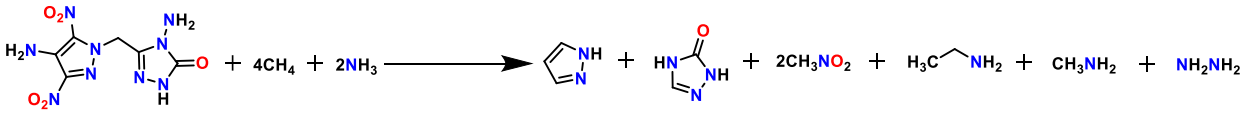


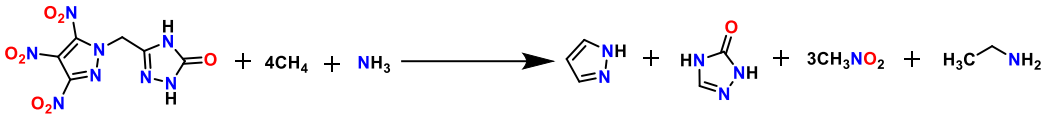
Figure S1. Physical state of compounds **3-13**.

4. Isodesmic reactions:

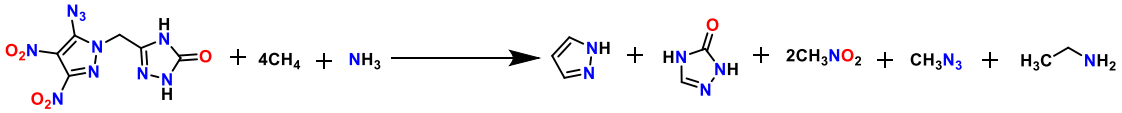
Compound 3:



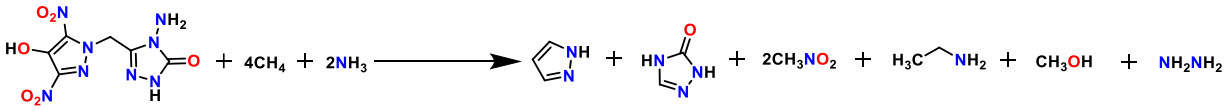
Compound 4:



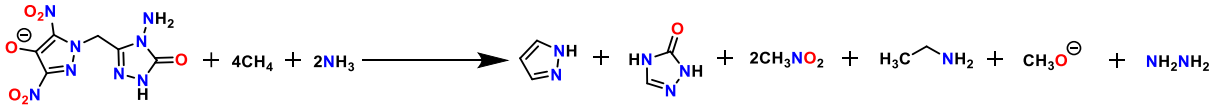
Compound 5:



Compound 8:



Anion for compounds 8-13:



5. NMR Result:

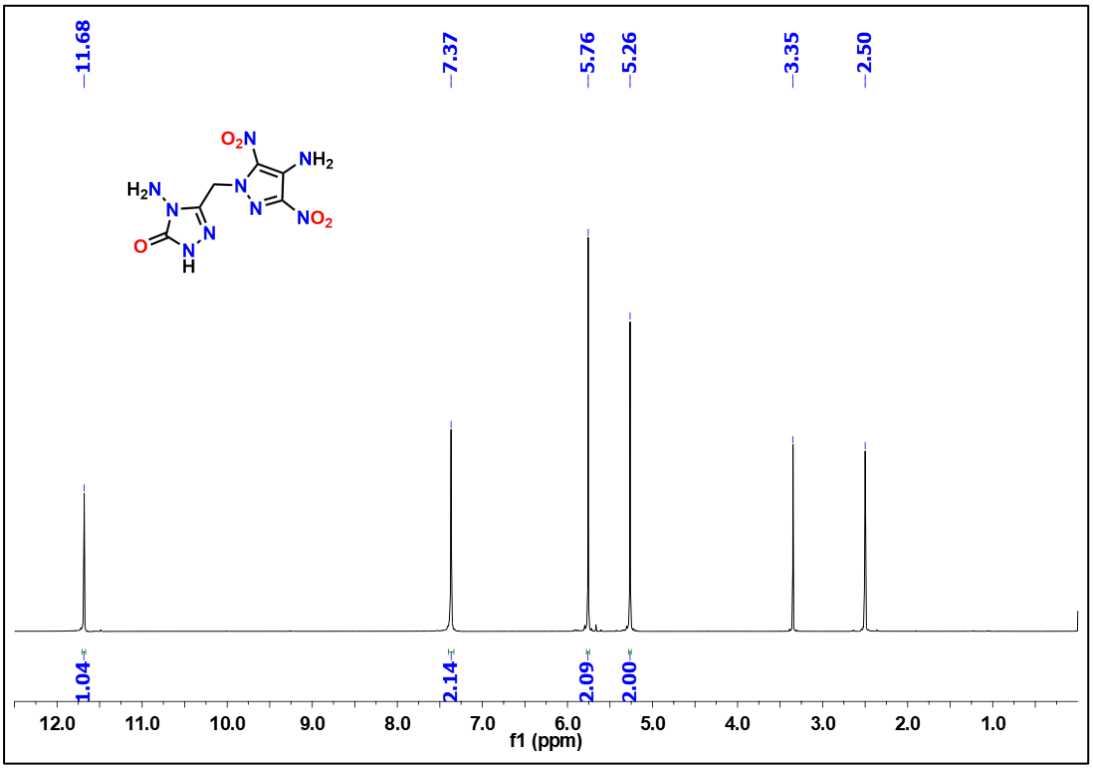


Figure S2. ^{1}H NMR Spectrum of compound **3** in DMSO-d_6 at 500 MHz.

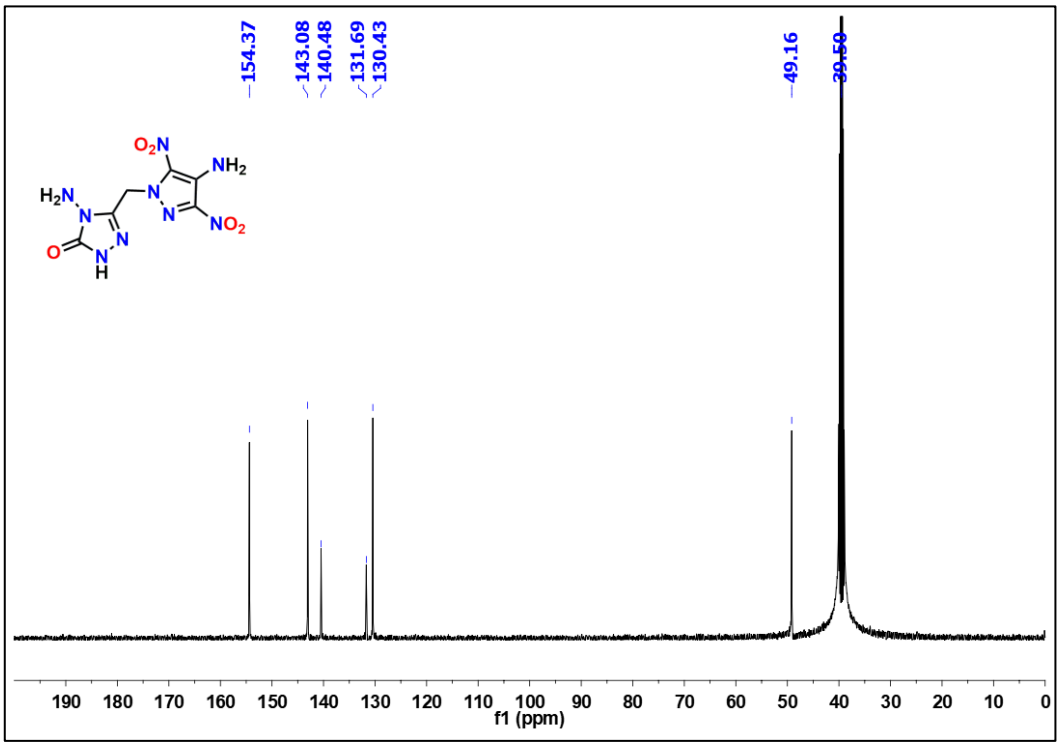


Figure S3. ^{13}C{^{1}H} NMR Spectrum of compound **3** in DMSO-d_6 at 125 MHz.

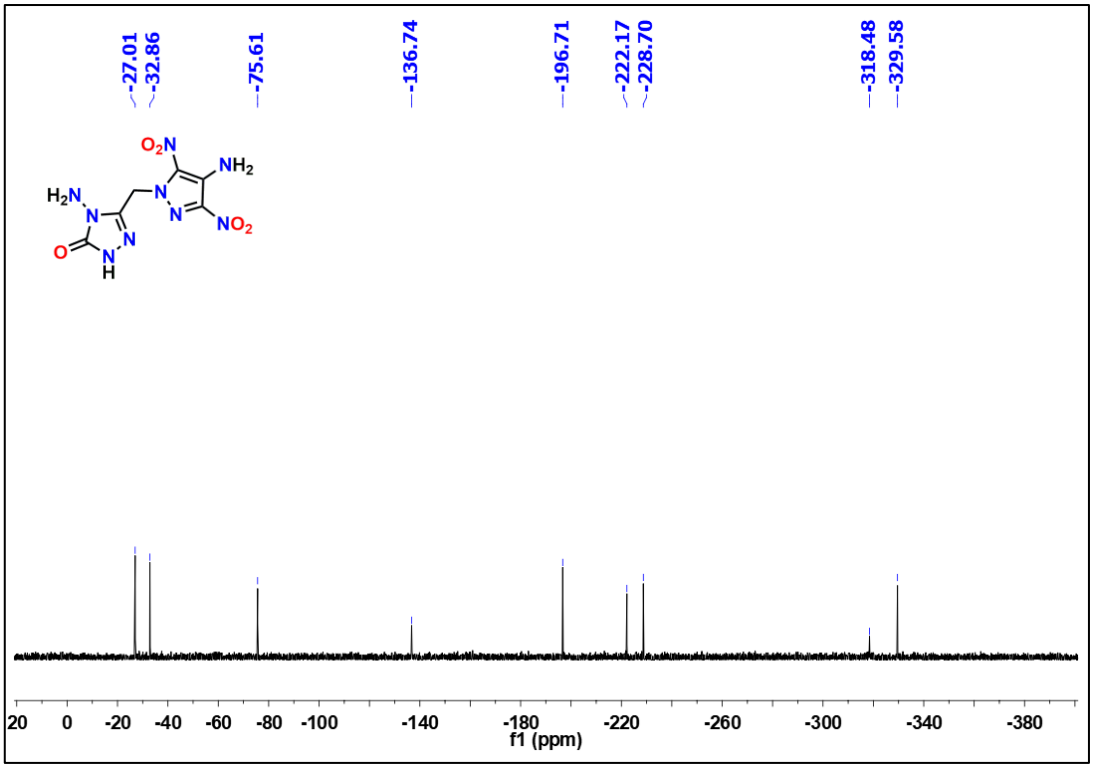


Figure S4. ^{15}N NMR Spectrum of compound **3** in DMSO-d_6 at 50.69 MHz.

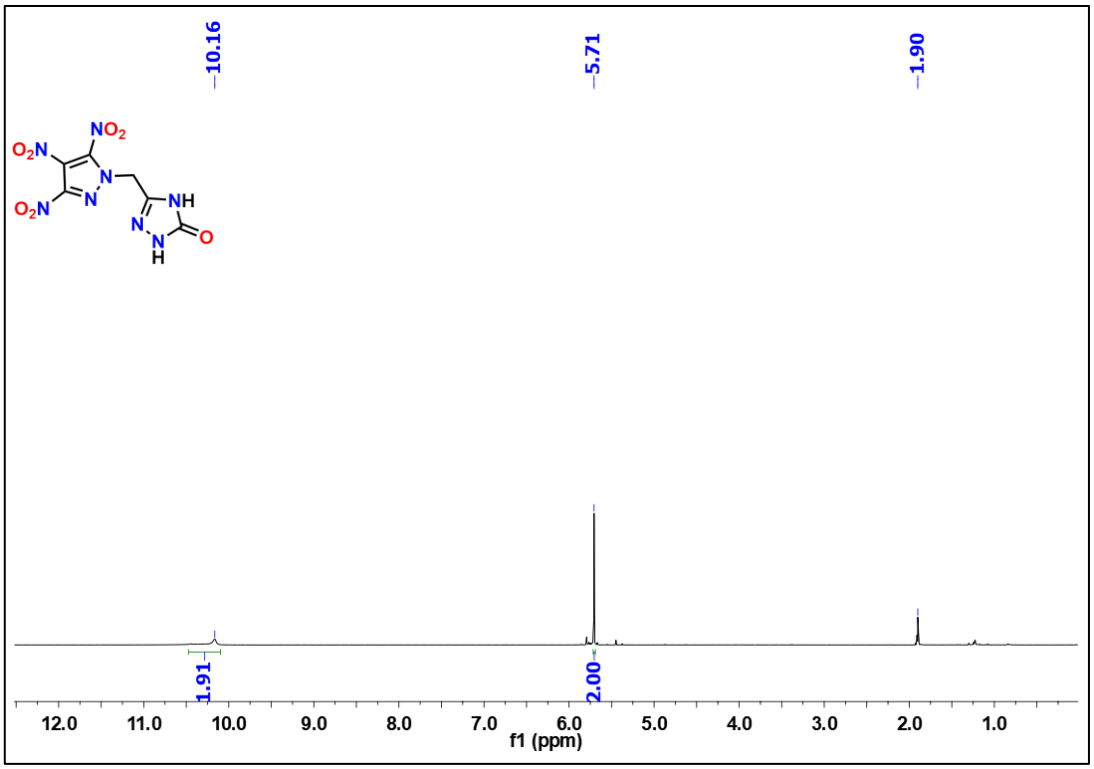


Figure S5. ^{1}H NMR Spectrum of compound **4** in CD_3CN-d_3 at 500 MHz.

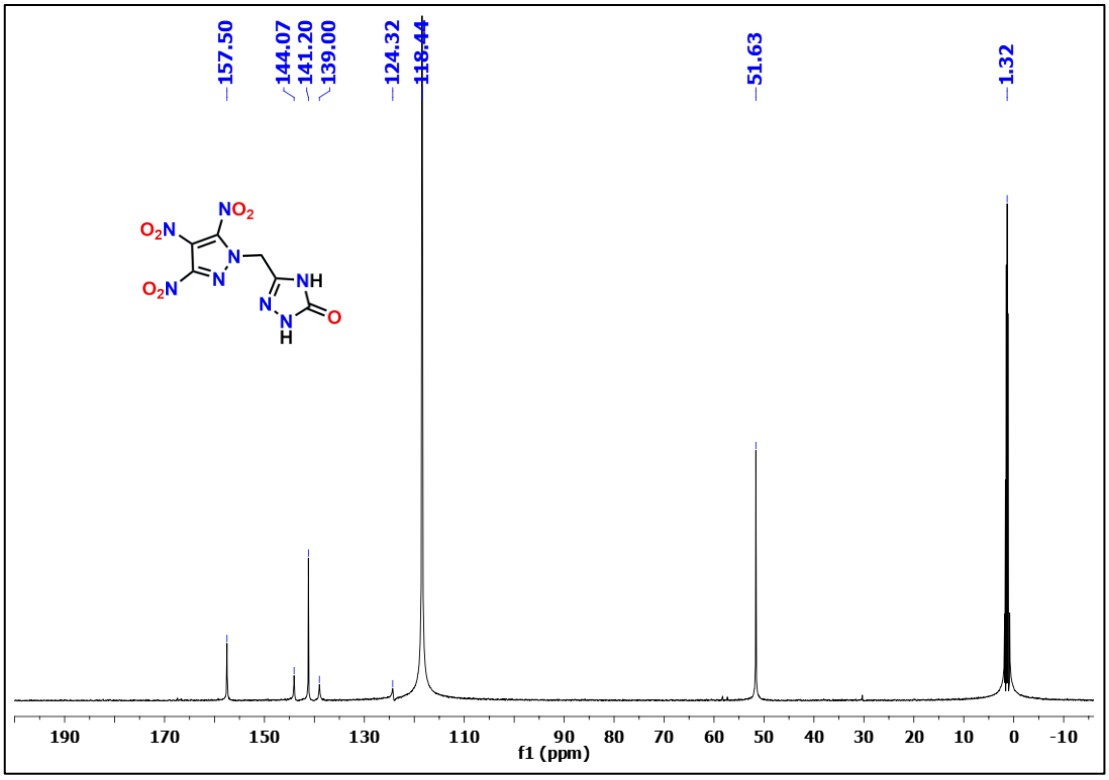


Figure S6. $^{13}C\{^{1}H\}$ NMR Spectrum of compound **4** in CD_3CN-d_3 at 125 MHz.

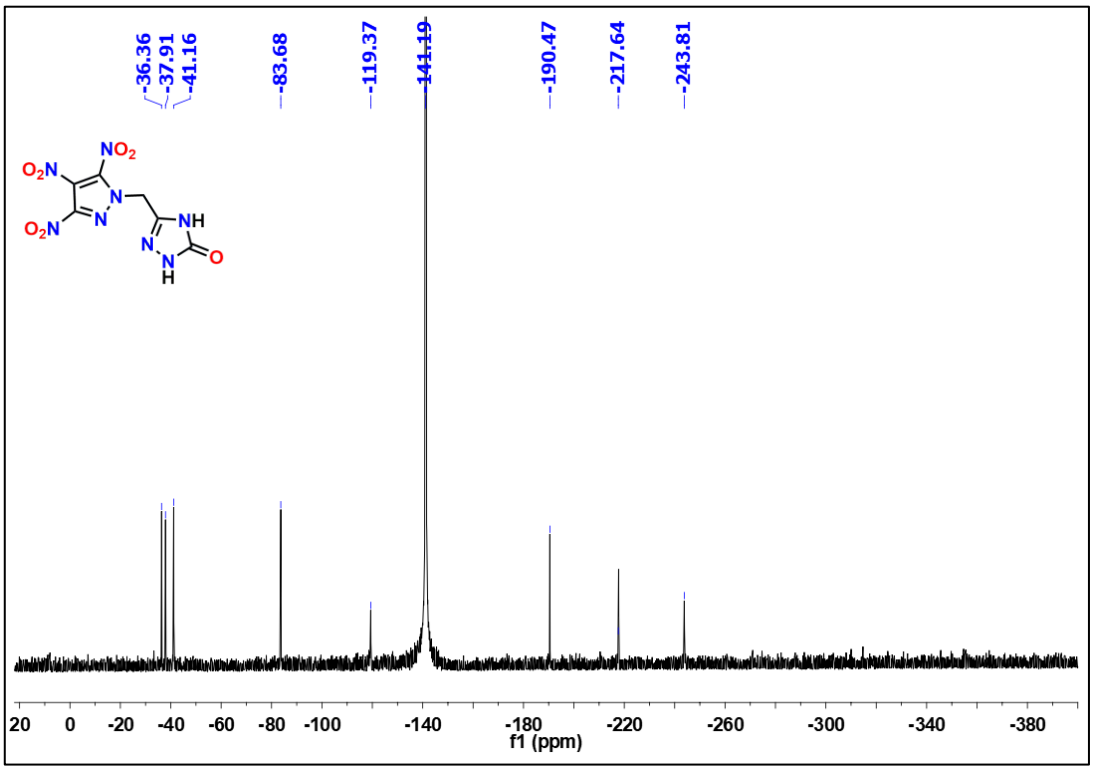


Figure S7. ^{15}N NMR Spectrum of compound **4** in CD_3CN-d_3 at 50.69 MHz.

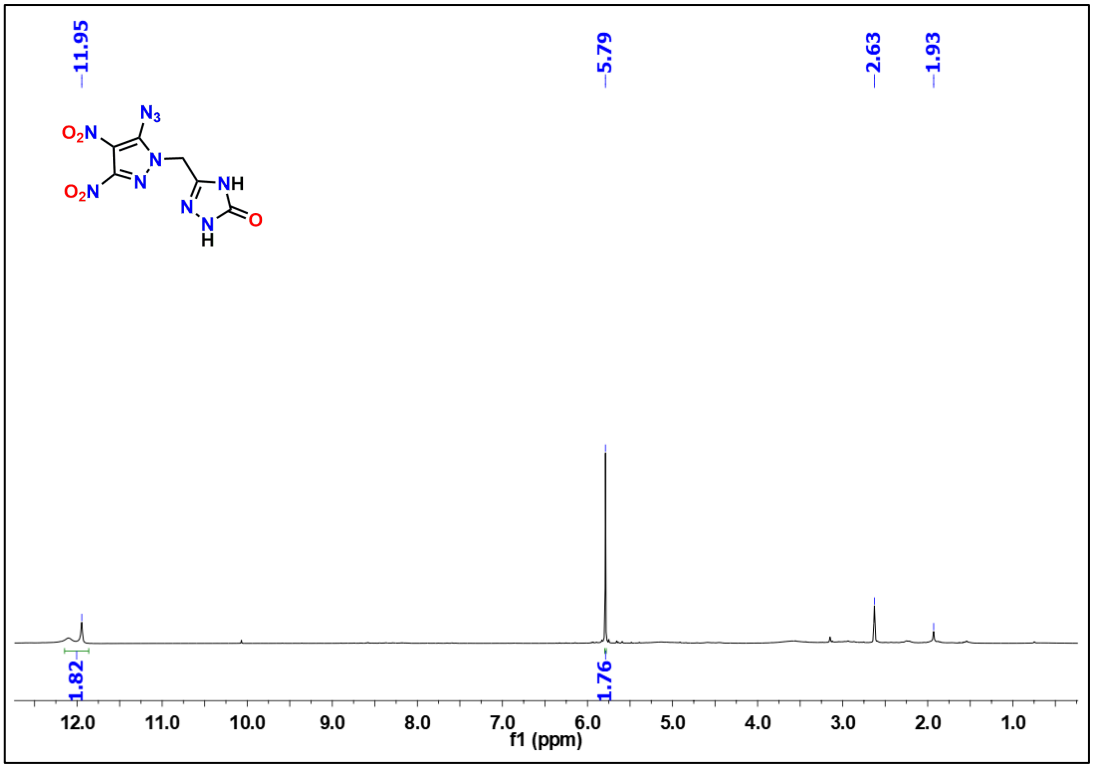


Figure S8 ^{1}H NMR Spectrum of compound **5** in CD_3CN-d_3 + DMSO-d_6 at 500 MHz.

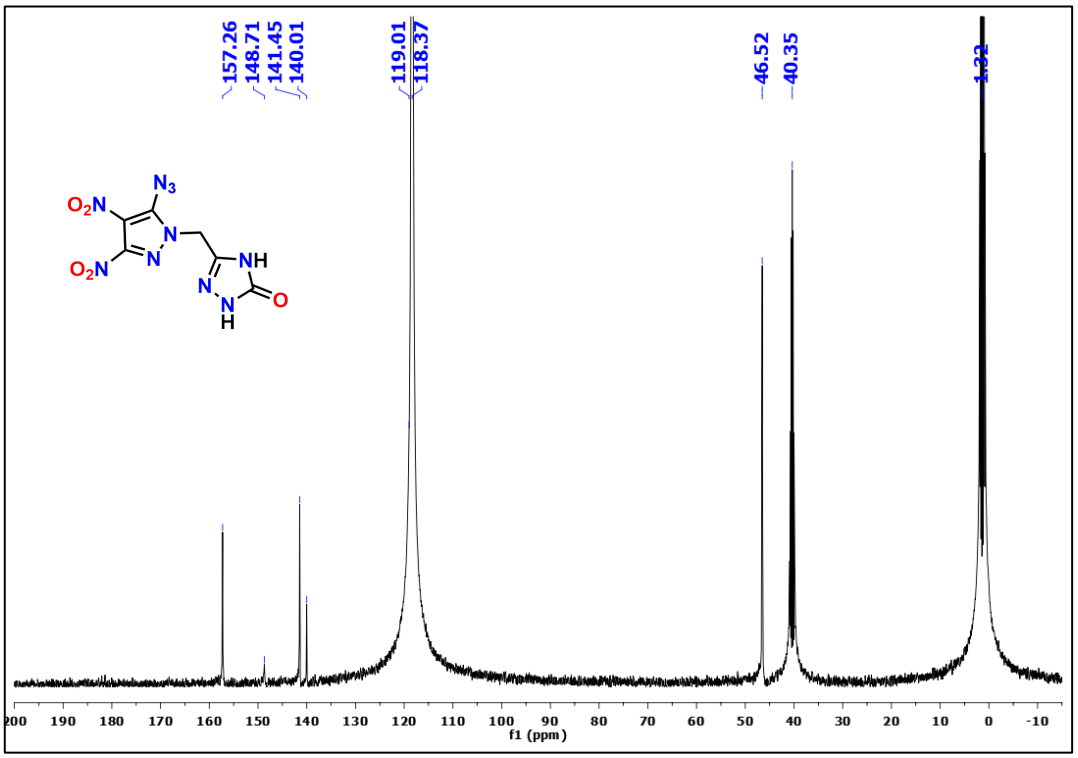


Figure S9. $^{13}C\{^{1}H\}$ NMR Spectrum of compound **5** in CD_3CN-d_3 + DMSO-d_6 at 125 MHz.

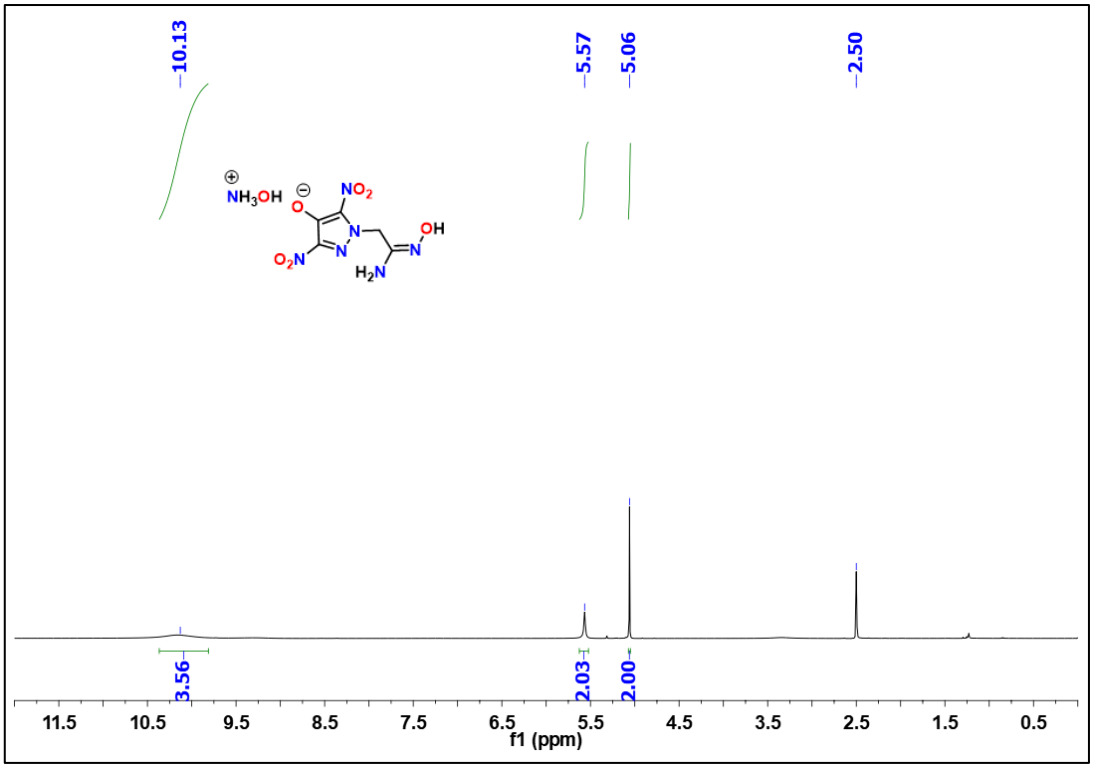


Figure S10. ^{1}H NMR Spectrum of compound **7** in DMSO-d_6 at 500 MHz.

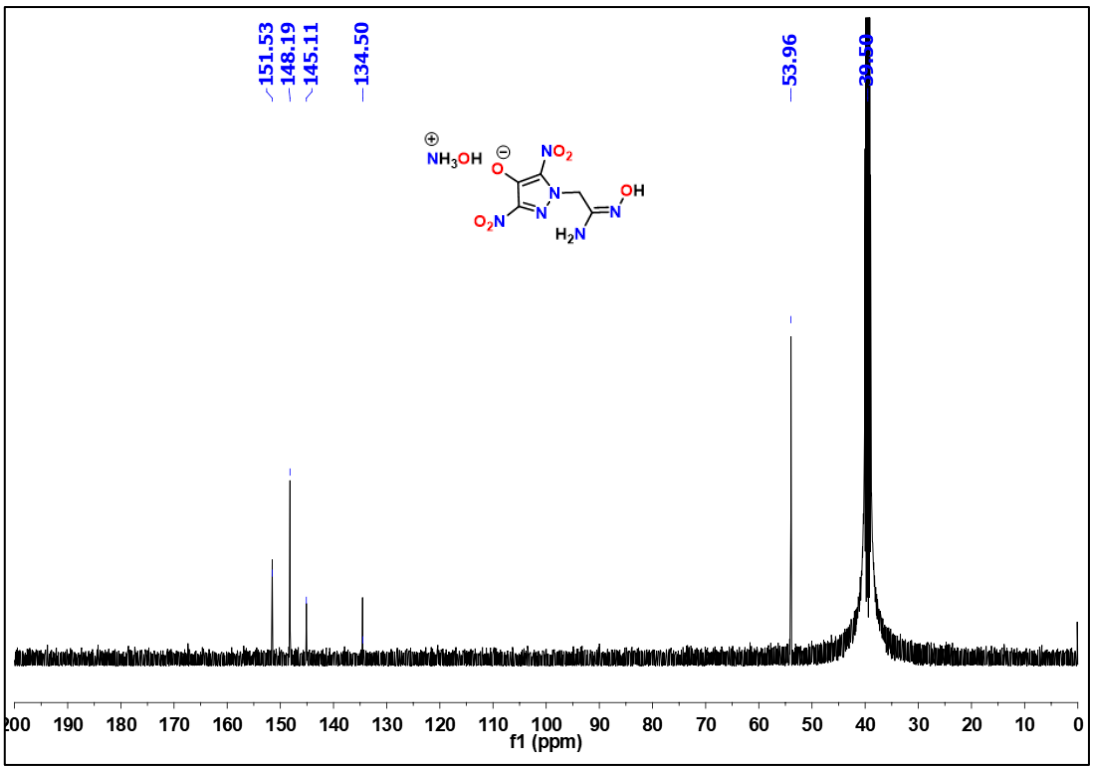


Figure S11. ^{13}C{^{1}H} NMR Spectrum of compound **7** in DMSO-d_6 at 125 MHz.

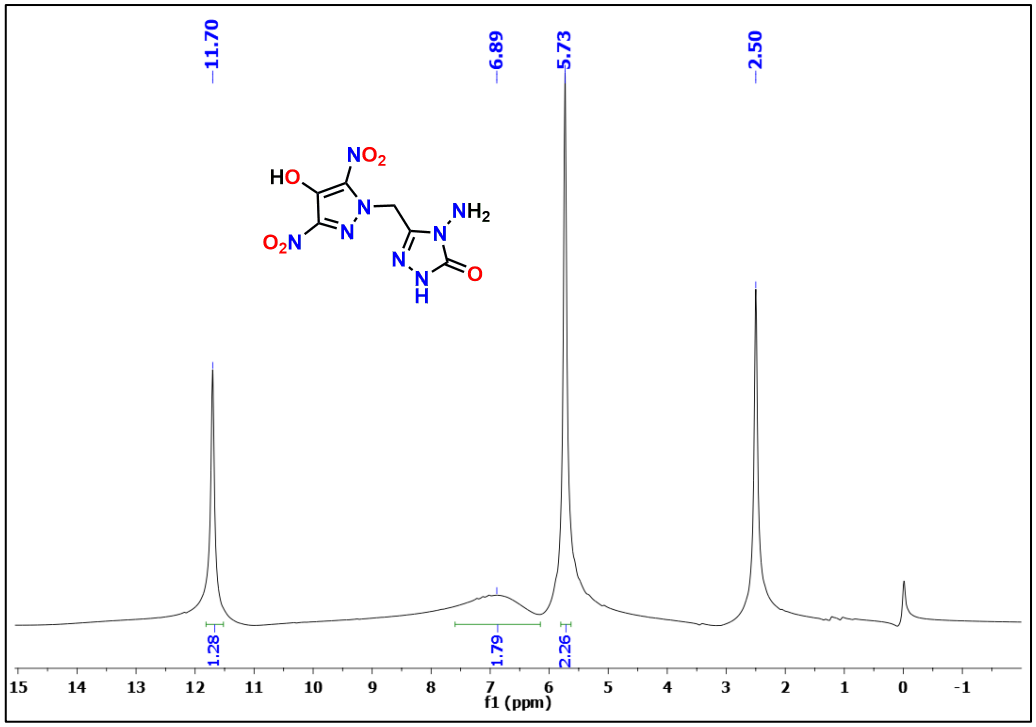


Figure S12. ^{1}H NMR Spectrum of compound **8** in DMSO-d_6 at 500 MHz.

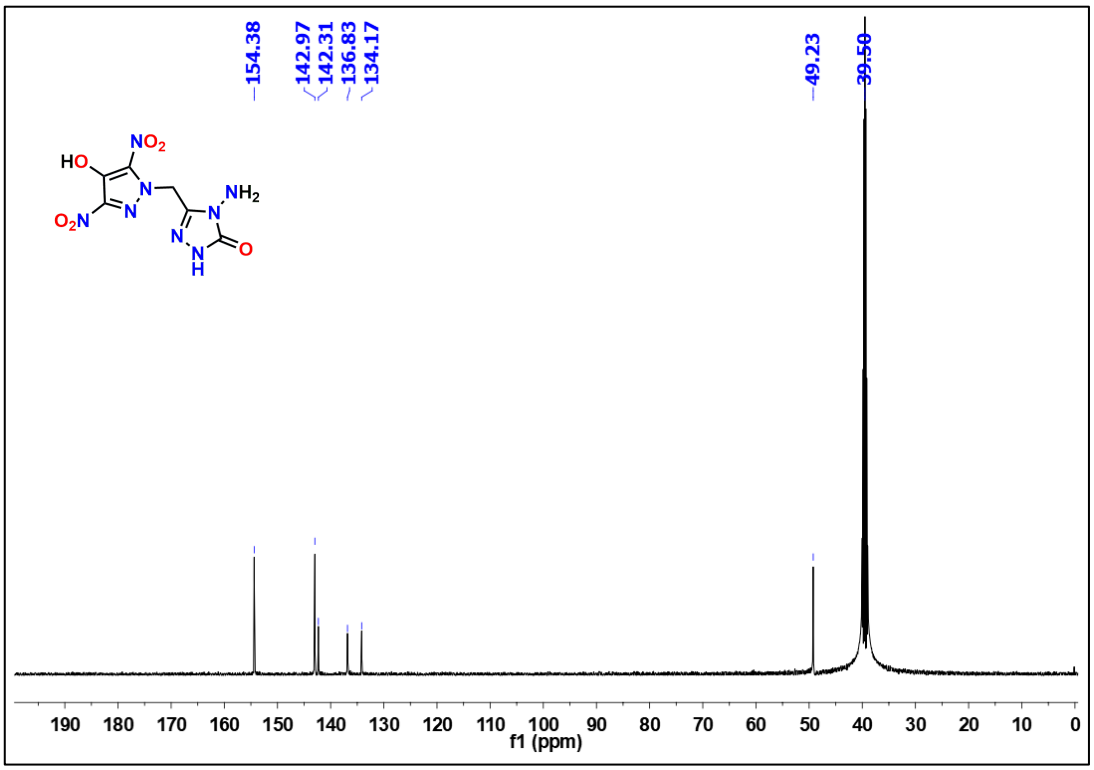


Figure S13. ^{13}C{^{1}H} NMR Spectrum of compound **8** in DMSO-d_6 at 125 MHz.

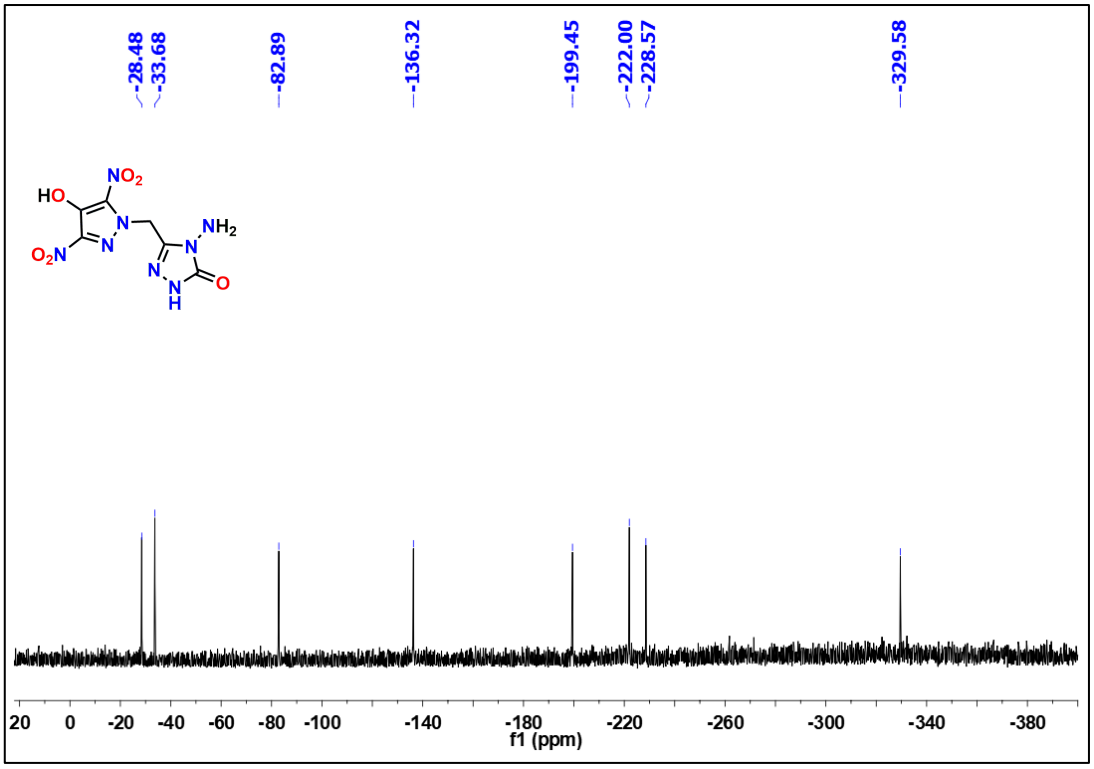


Figure S14. ^{15}N NMR Spectrum of compound **8** in DMSO-d_6 at 50.69 MHz.

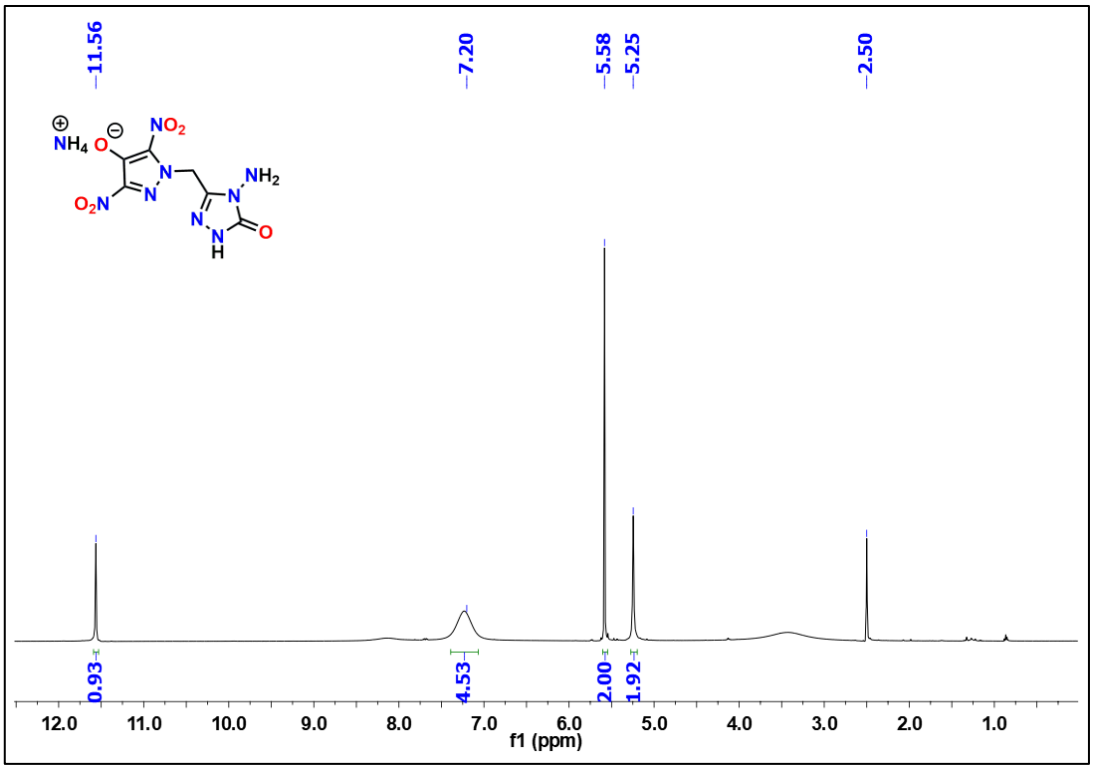


Figure S15. ^{1}H NMR Spectrum of compound **9** in DMSO-d_6 at 500 MHz.

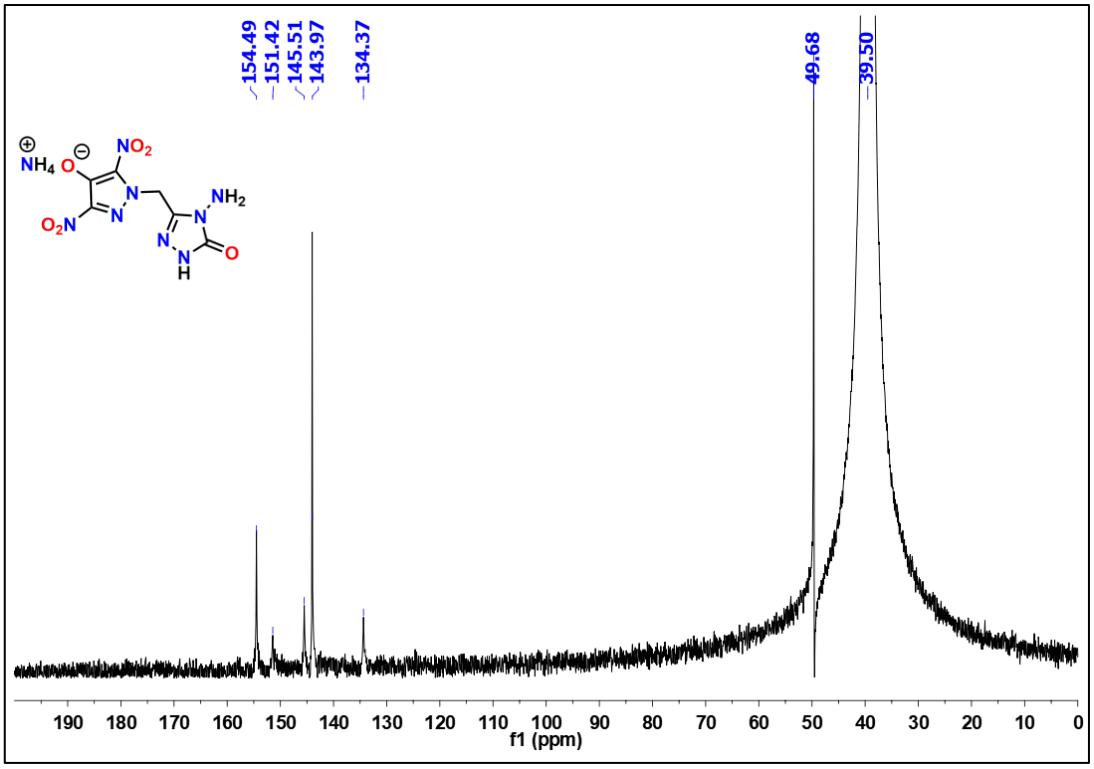


Figure S16. $^{13}C\{^{1}H\}$ NMR Spectrum of compound **9** in DMSO-d_6 at 125 MHz.

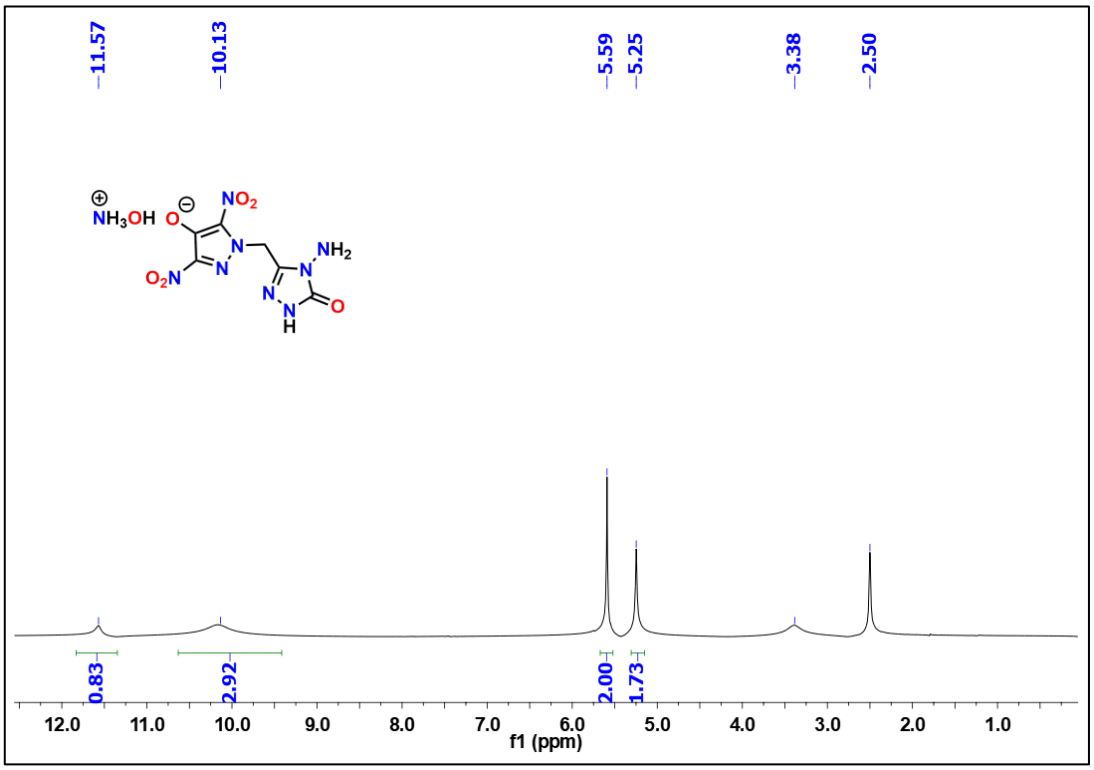


Figure S17. ^{1}H NMR Spectrum of compound **10** in DMSO-d_6 at 500 MHz.

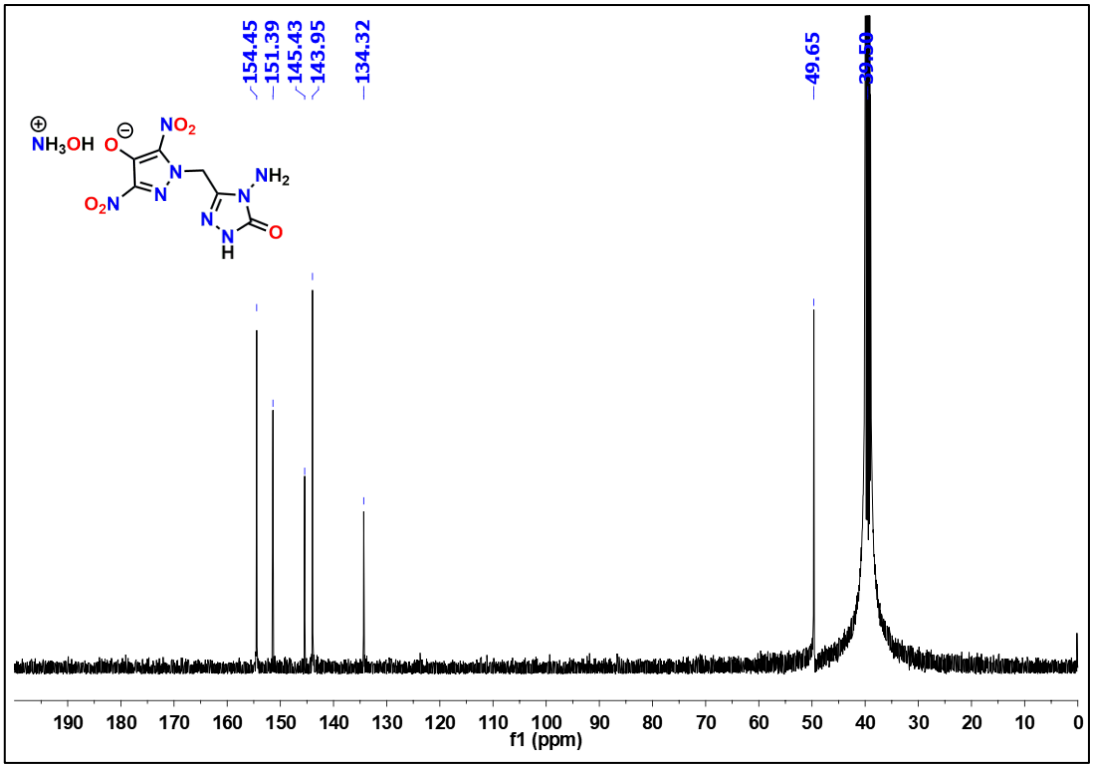


Figure S18. $^{13}C\{^{1}H\}$ NMR Spectrum of compound **10** in DMSO-d_6 at 125 MHz.

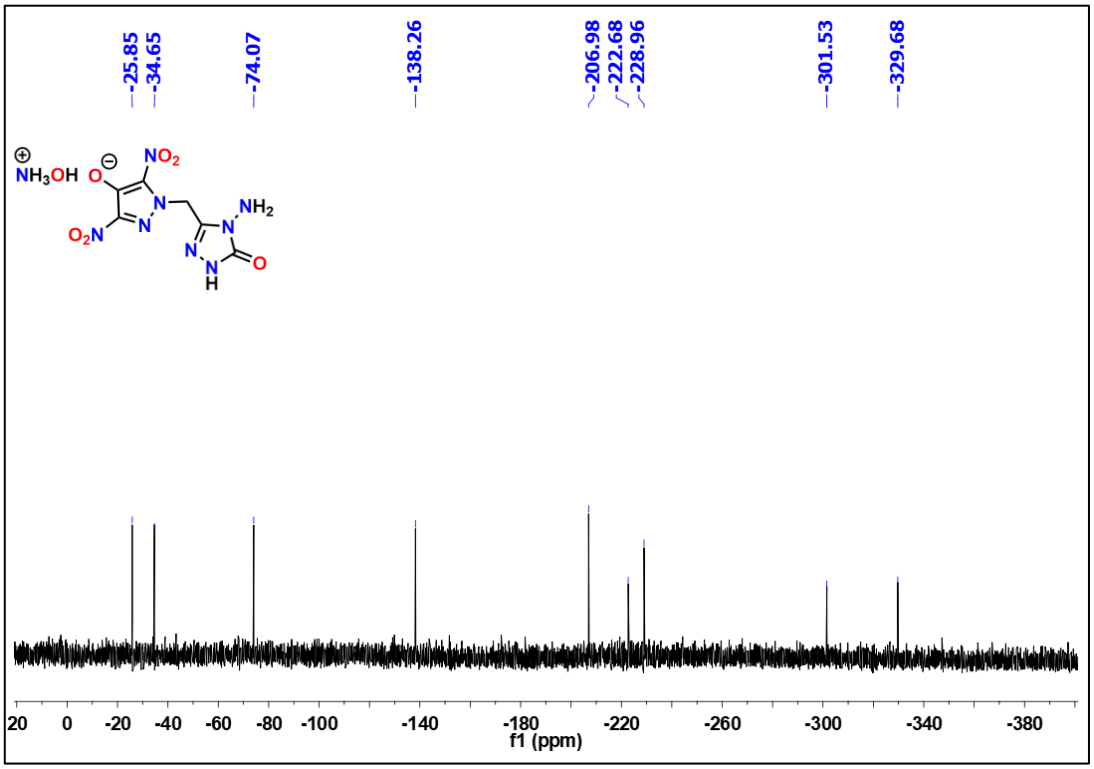


Figure S19. ^{15}N NMR Spectrum of compound **10** in DMSO-d_6 at 50.69 MHz.

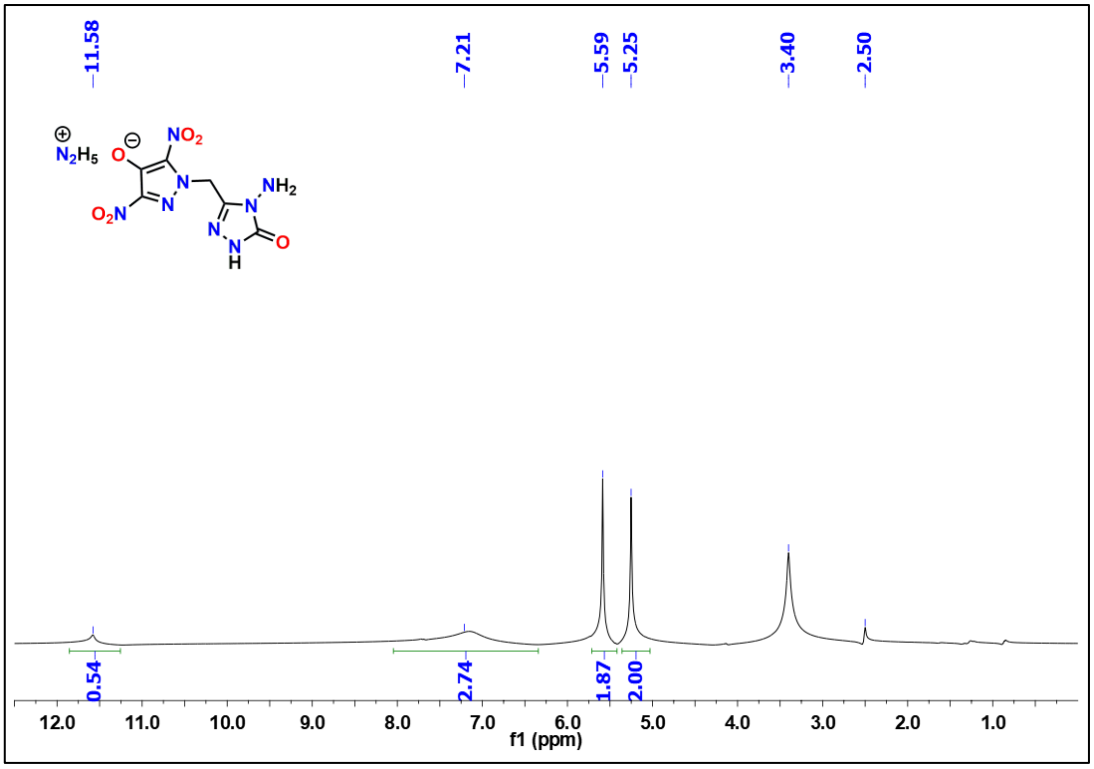


Figure S20. ^{1}H NMR Spectrum of compound **11** in DMSO-d_6 at 500 MHz.

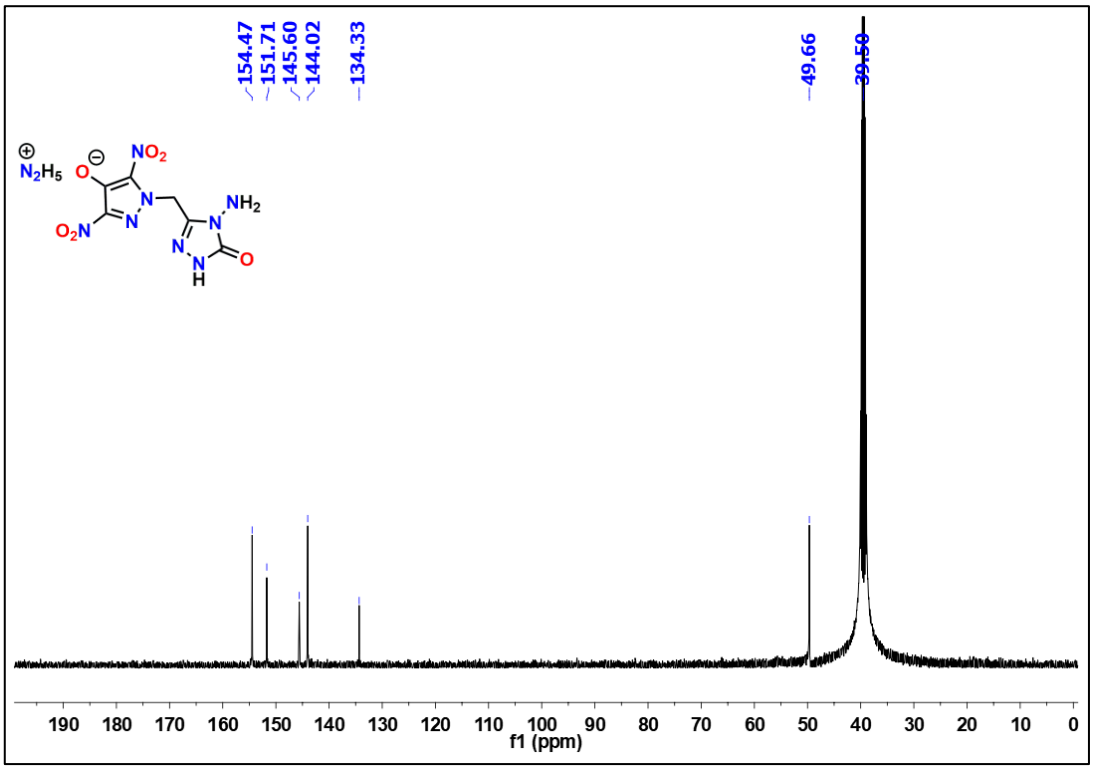


Figure S21. ^{13}C{^{1}H} NMR Spectrum of compound **11** in DMSO-d_6 at 125 MHz.

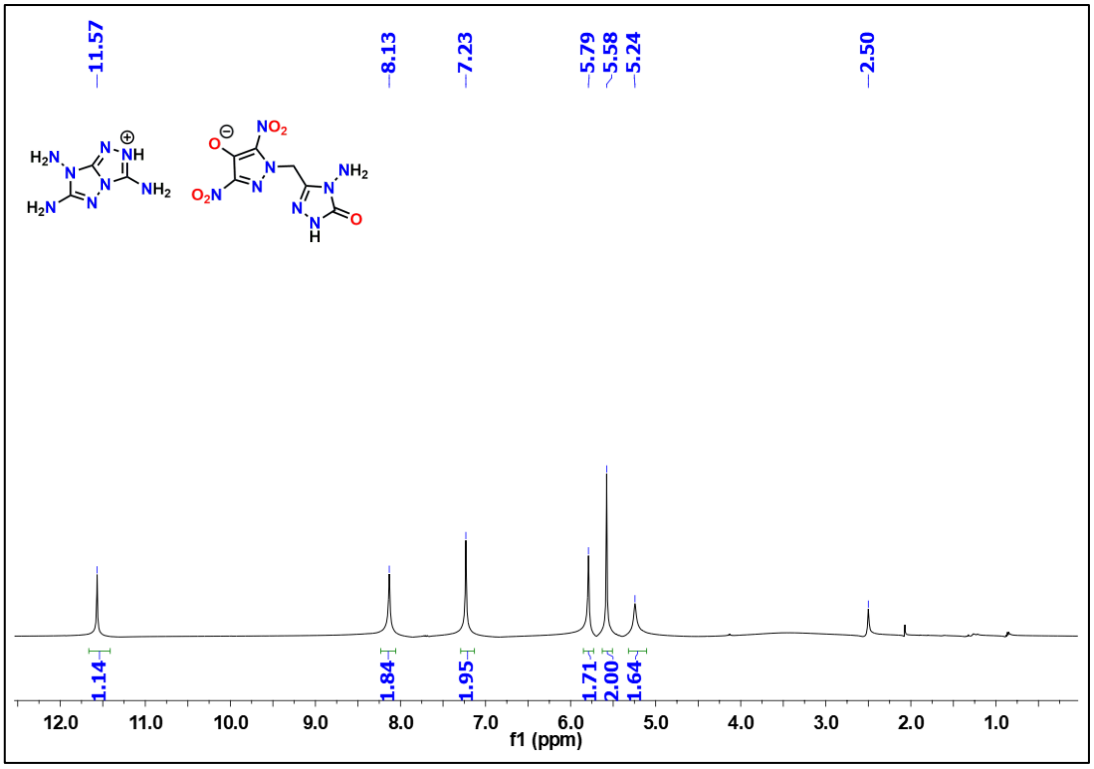


Figure S22. ^{1}H NMR Spectrum of compound **12** in DMSO-d_6 at 500 MHz.

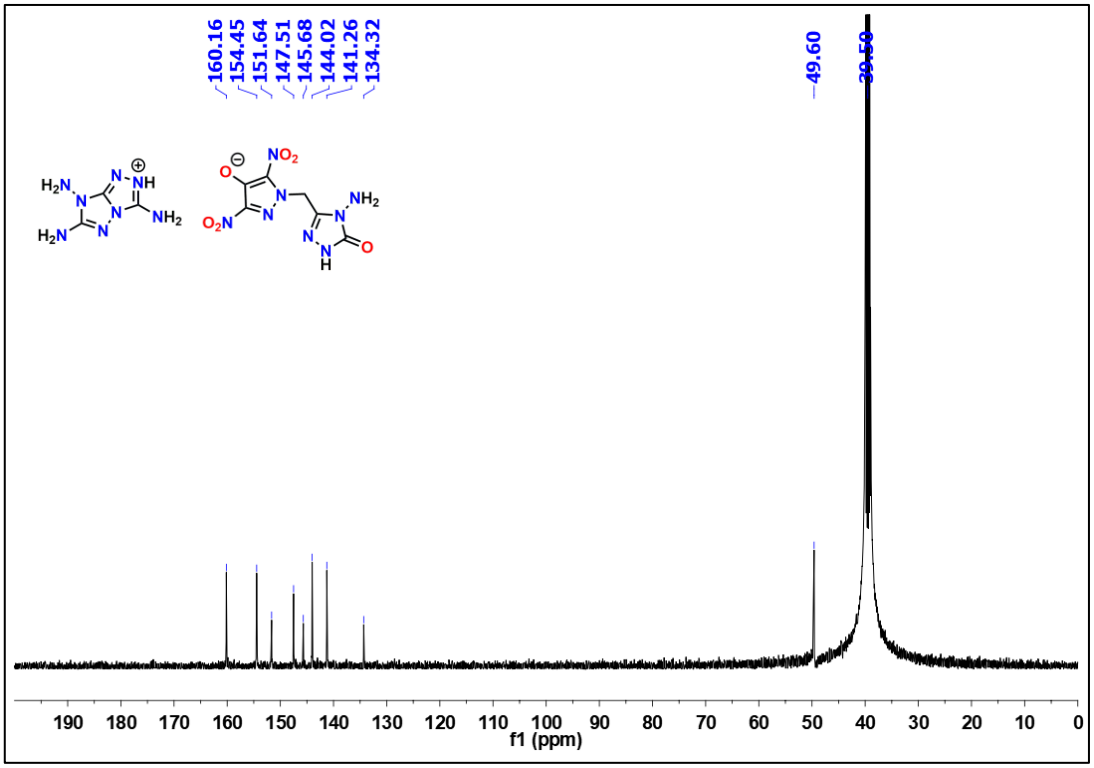


Figure S23. ^{13}C{^{1}H} NMR Spectrum of compound **12** in DMSO-d_6 at 125 MHz.

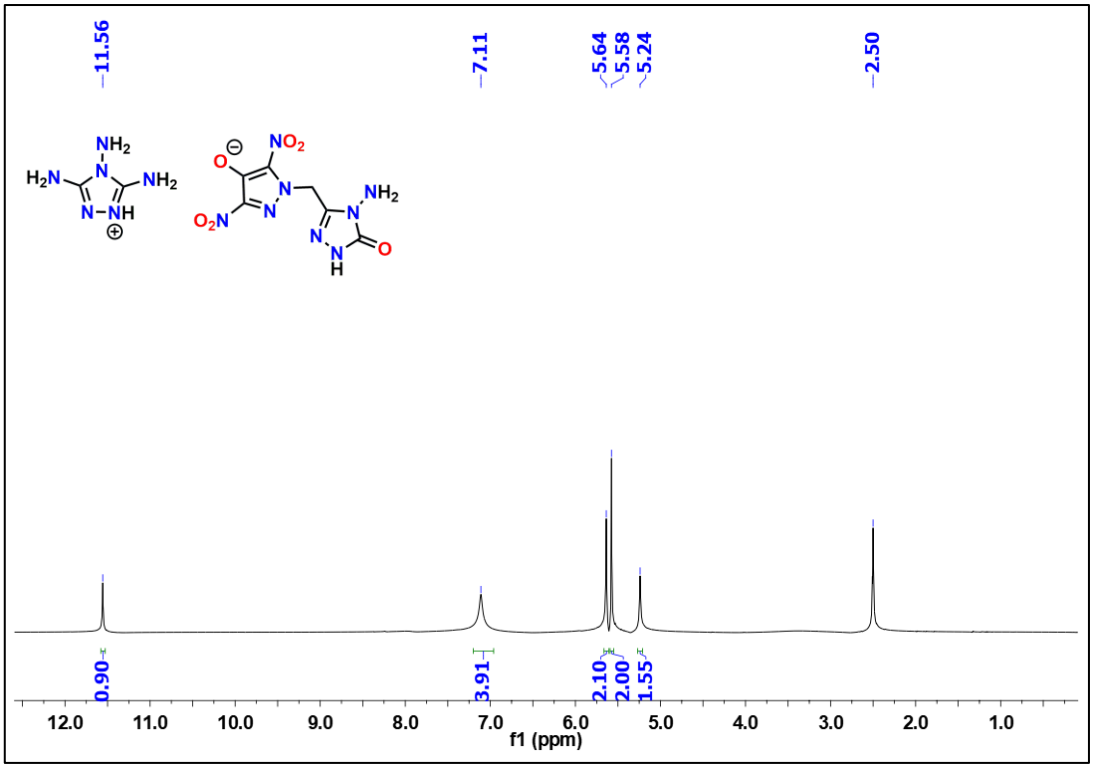


Figure S24. ^{1}H NMR Spectrum of compound **13** in DMSO-d_6 at 500 MHz.

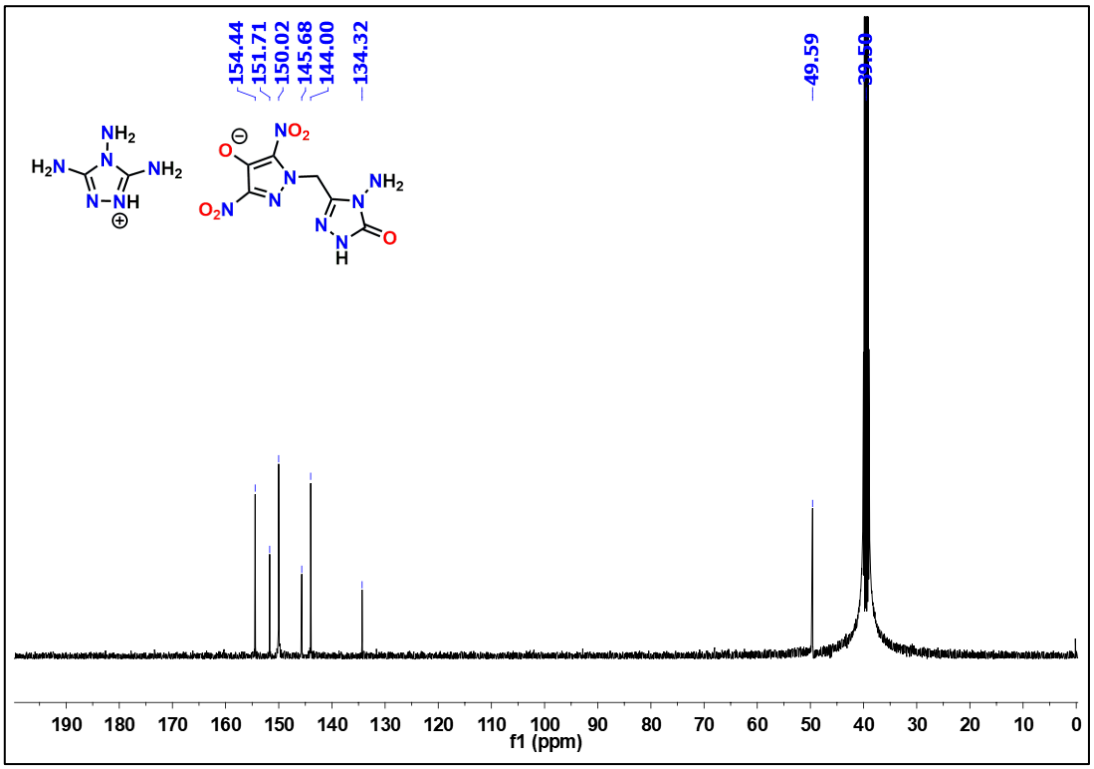


Figure S25. ^{13}C{^{1}H} NMR Spectrum of compound **14** in DMSO-d_6 at 125 MHz.

6. IR Results:

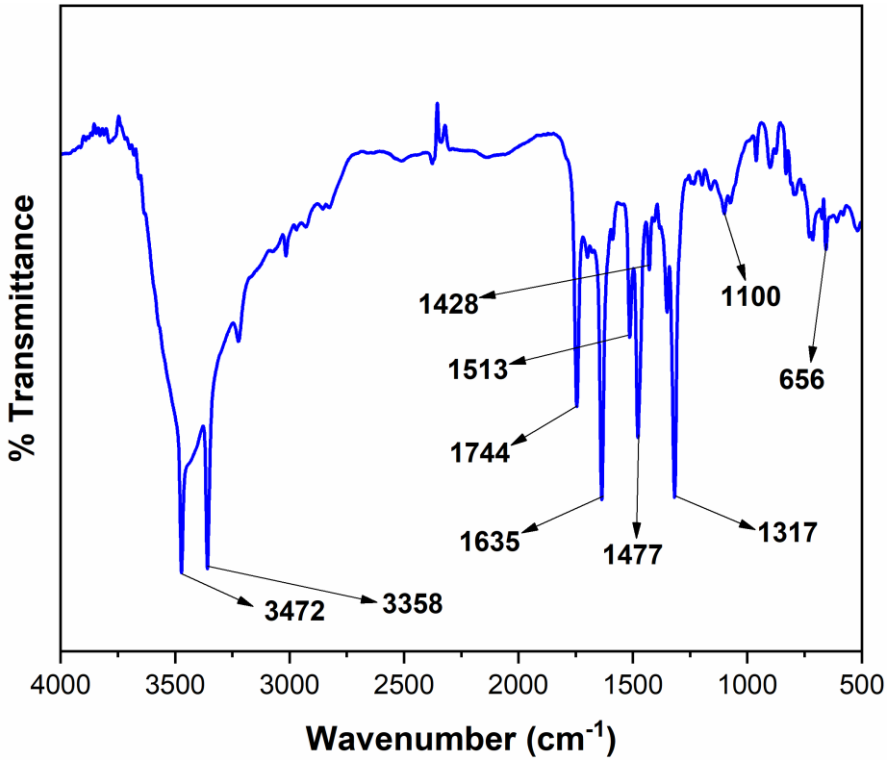


Figure S26. FTIR Spectra of compound **3.**

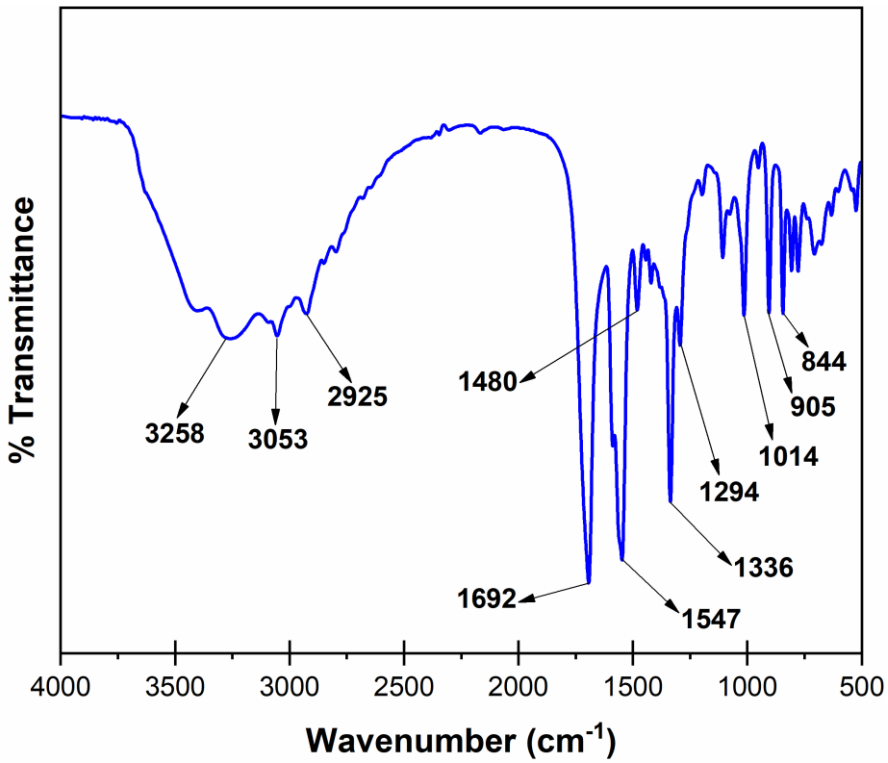


Figure S27. FTIR Spectra of compound **4.**

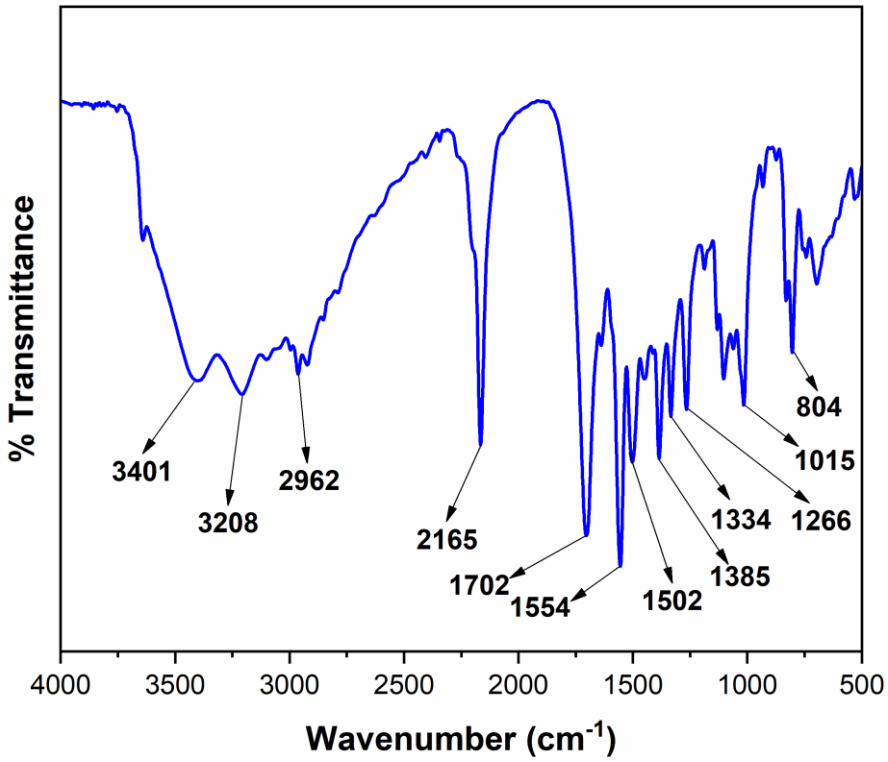


Figure S28. FTIR Spectra of compound **5.**

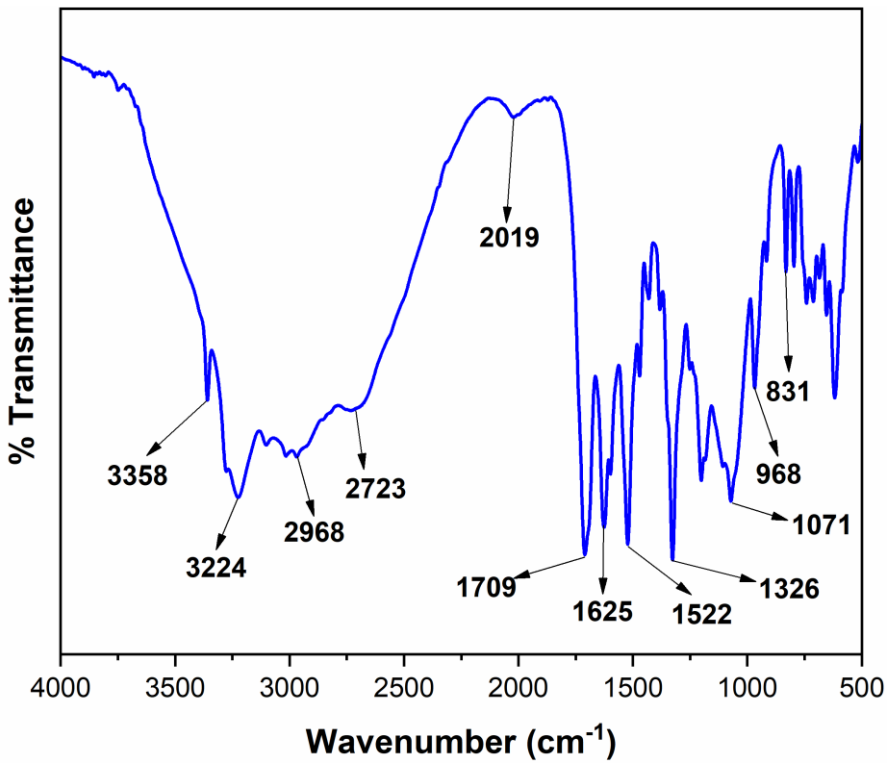


Figure S29. FTIR Spectra of compound **8.**

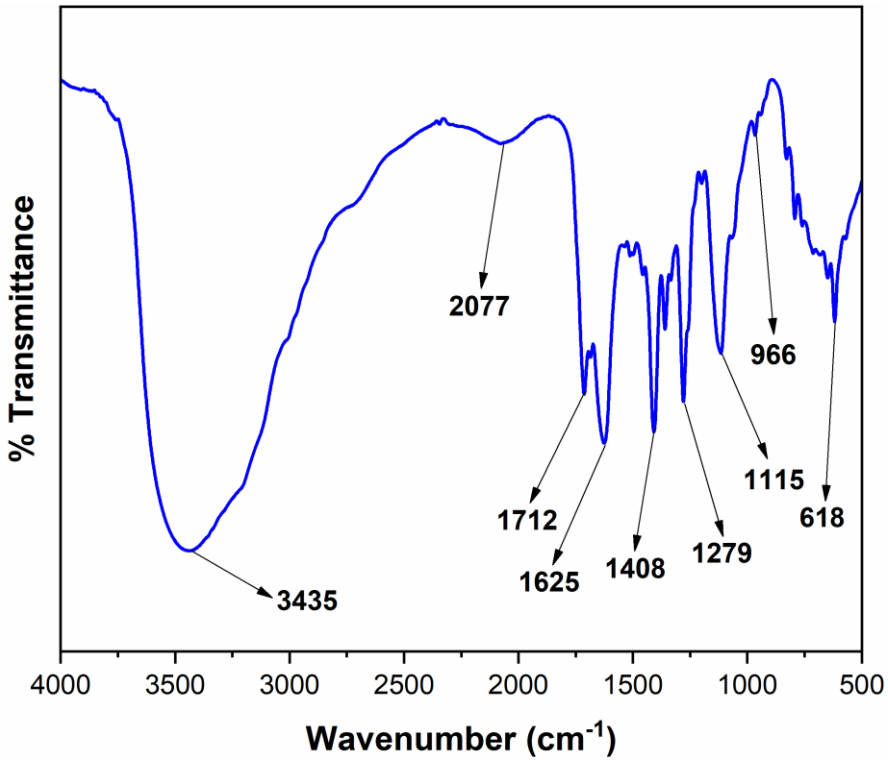


Figure S30. FTIR Spectra of compound **9.**

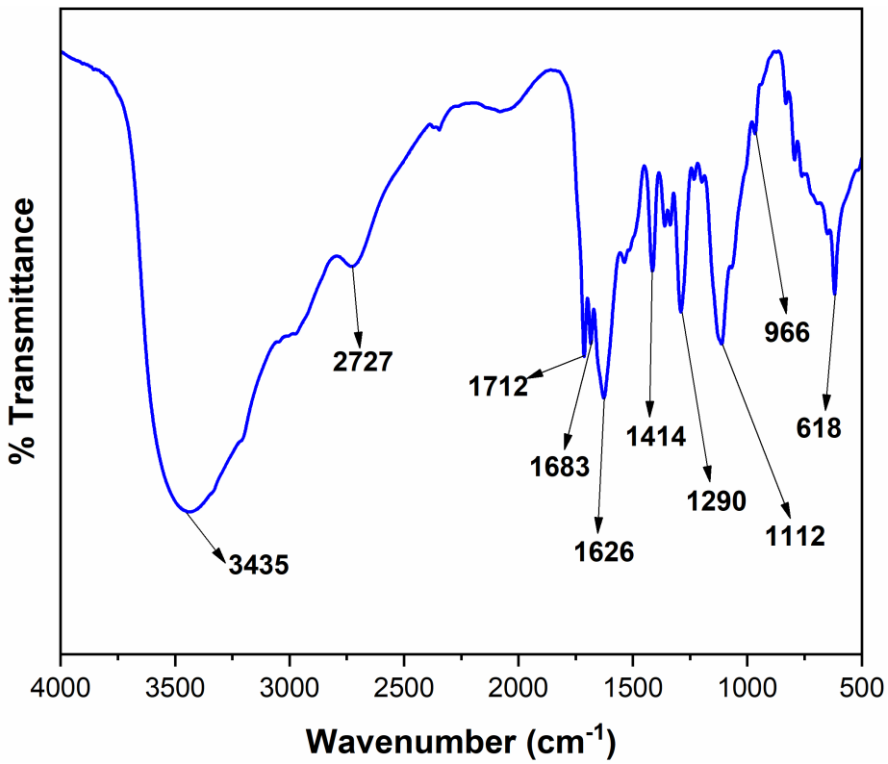


Figure S31. FTIR Spectra of compound **10.**

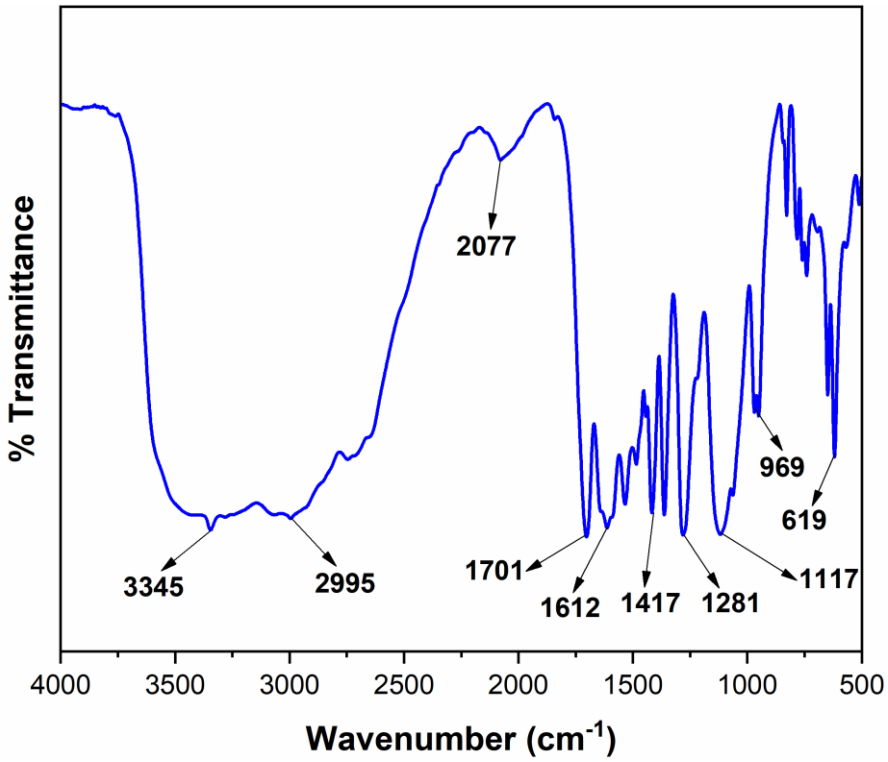


Figure S32. FTIR Spectra of compound **11.**

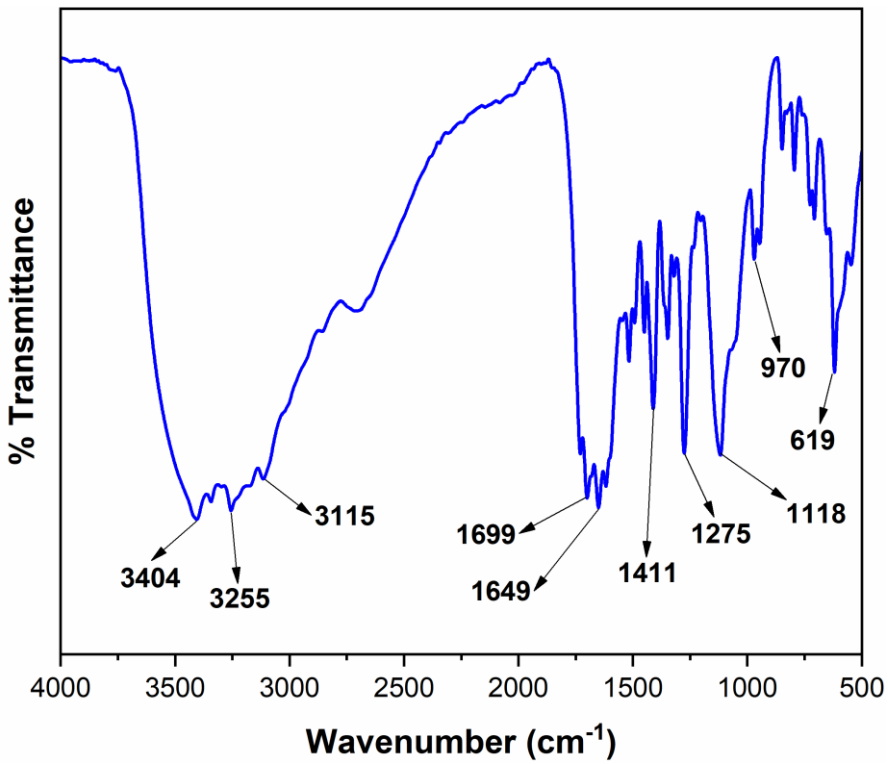


Figure S33. FTIR Spectra of compound **12.**

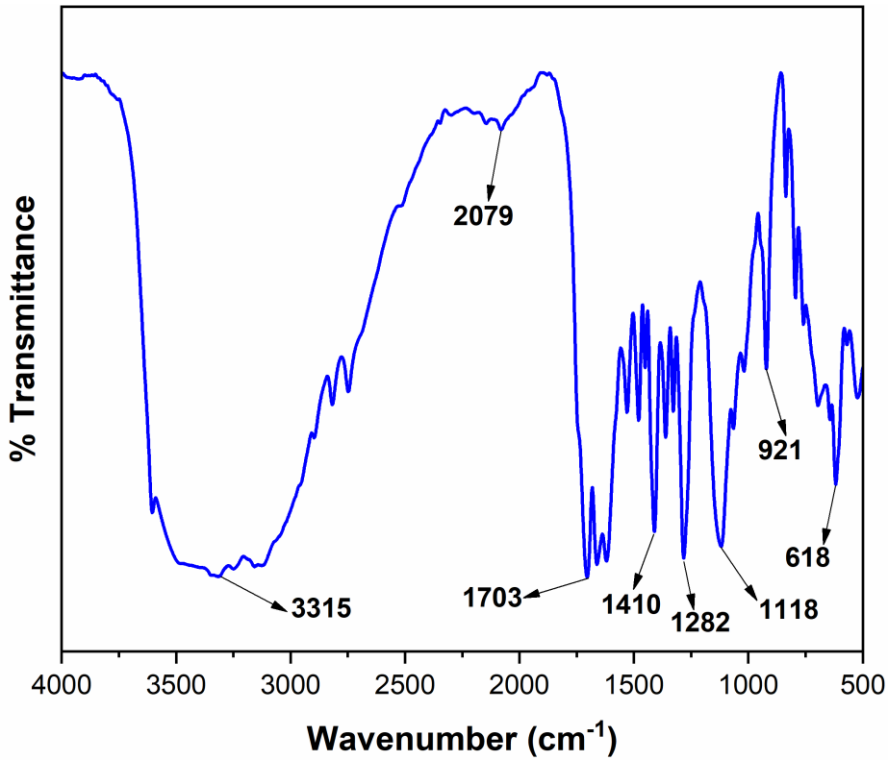


Figure S34. FTIR Spectra of compound **13.**

7. DSC Results:

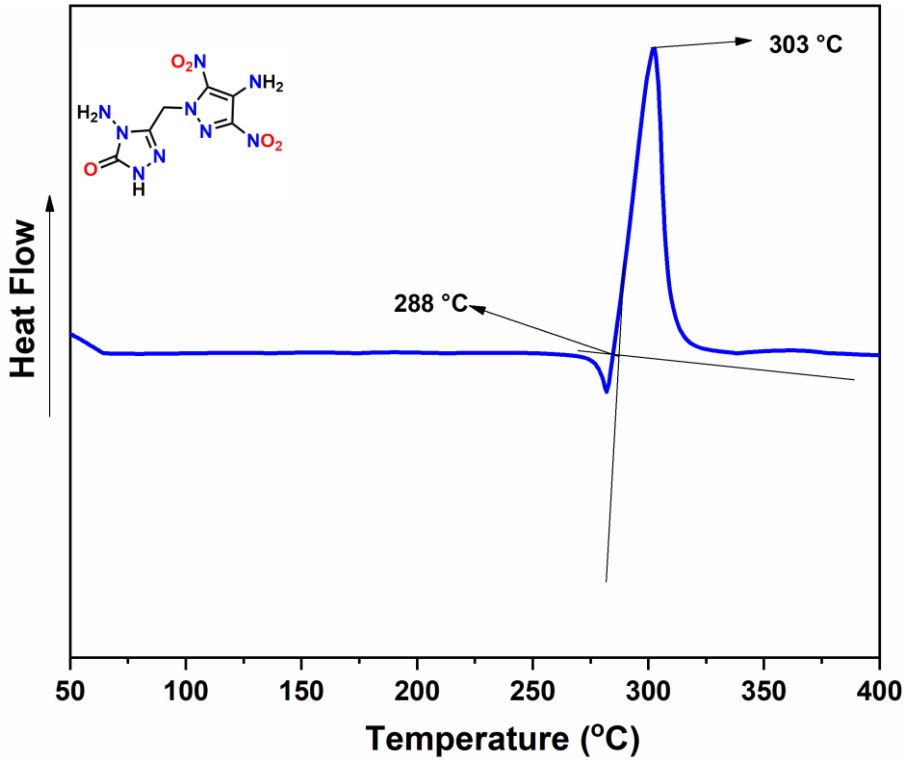


Figure S35. DSC curve of compound **3** at heating rate **5** °C/min.

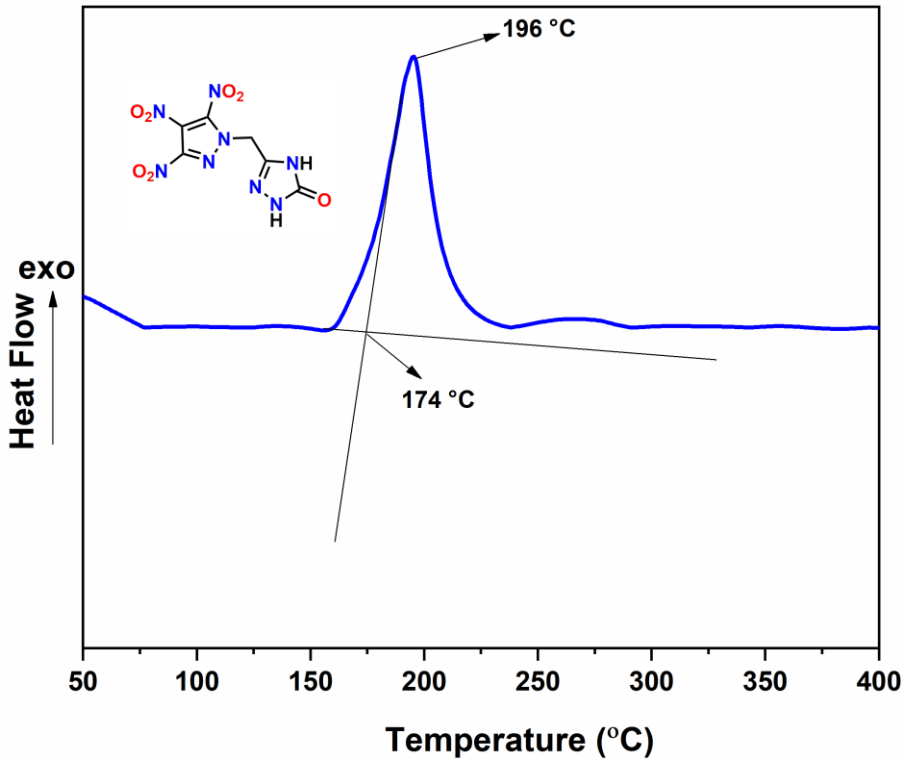


Figure S36. DSC curve of compound **4** at heating rate **5** °C/min.

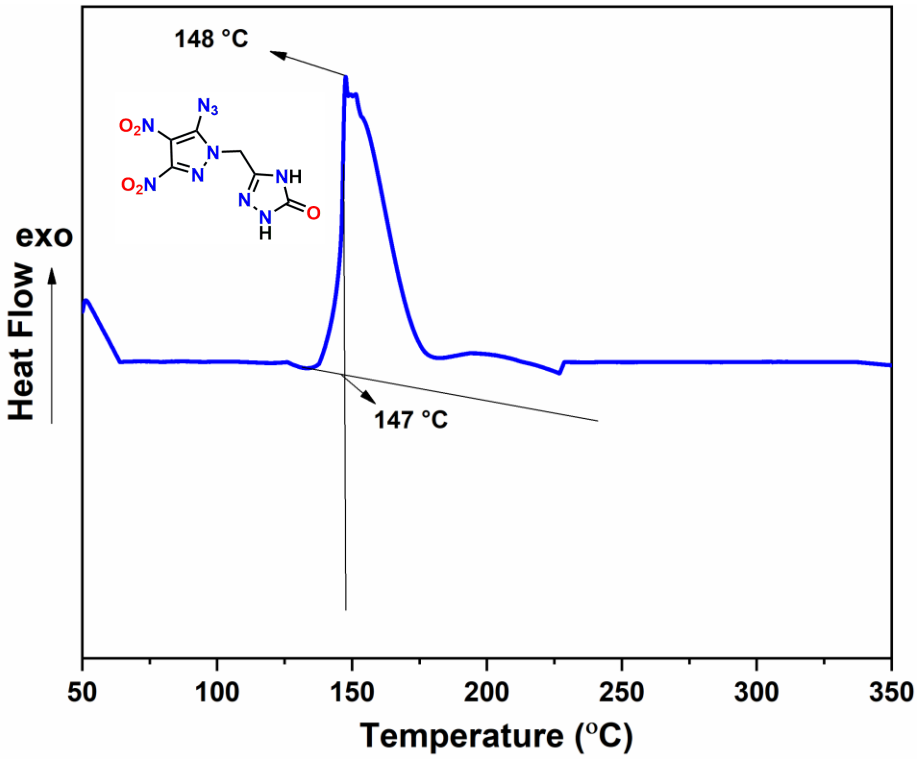


Figure S37. DSC curve of compound **5** at heating rate **5** °C/min.

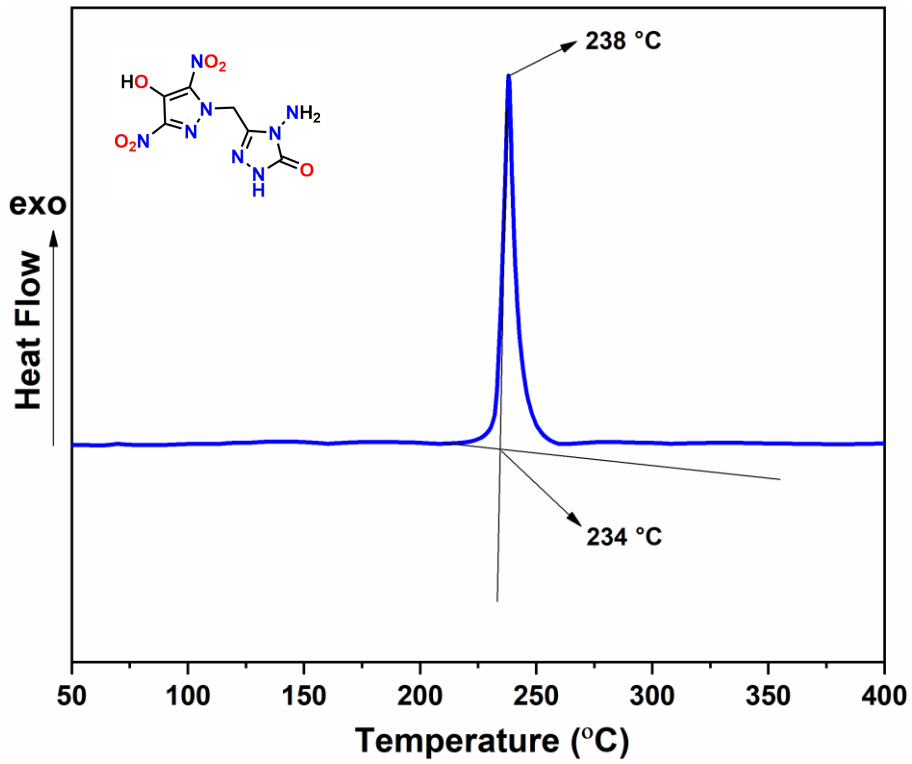


Figure S38. DSC curve of compound **8** at heating rate **5** °C/min.

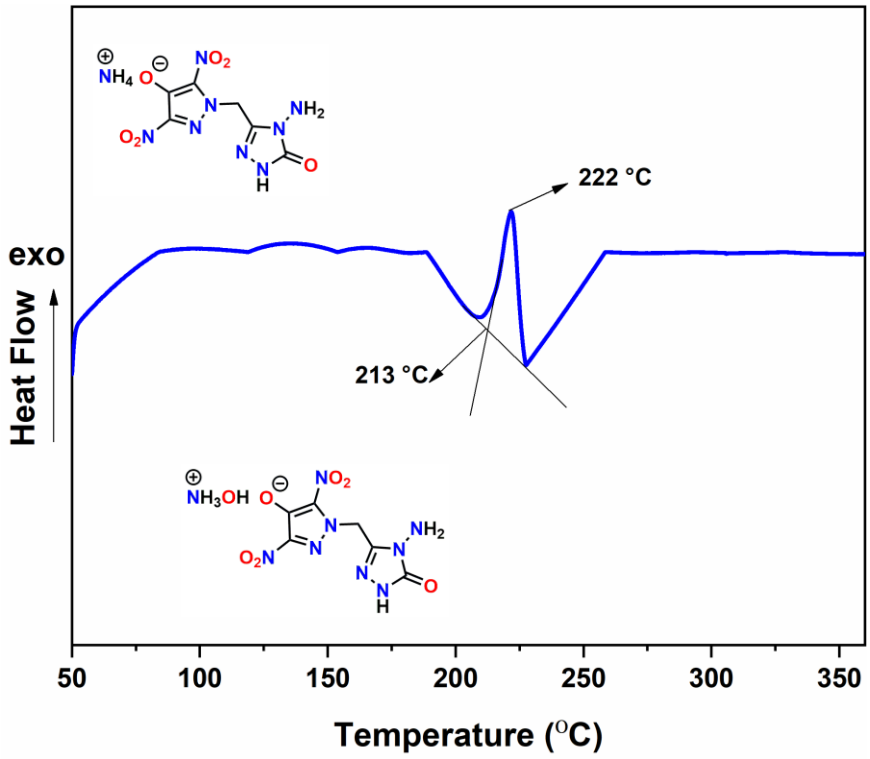


Figure S39. DSC curve of compound **9** at heating rate **5** °C/min.

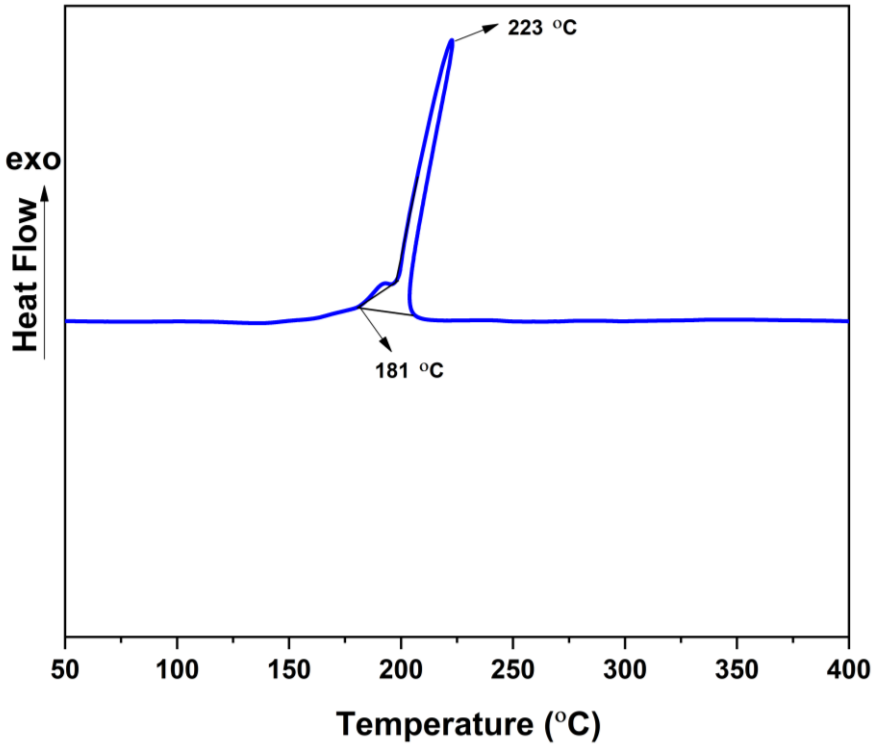


Figure S40. DSC curve of compound **10** at heating rate **5** °C/min.

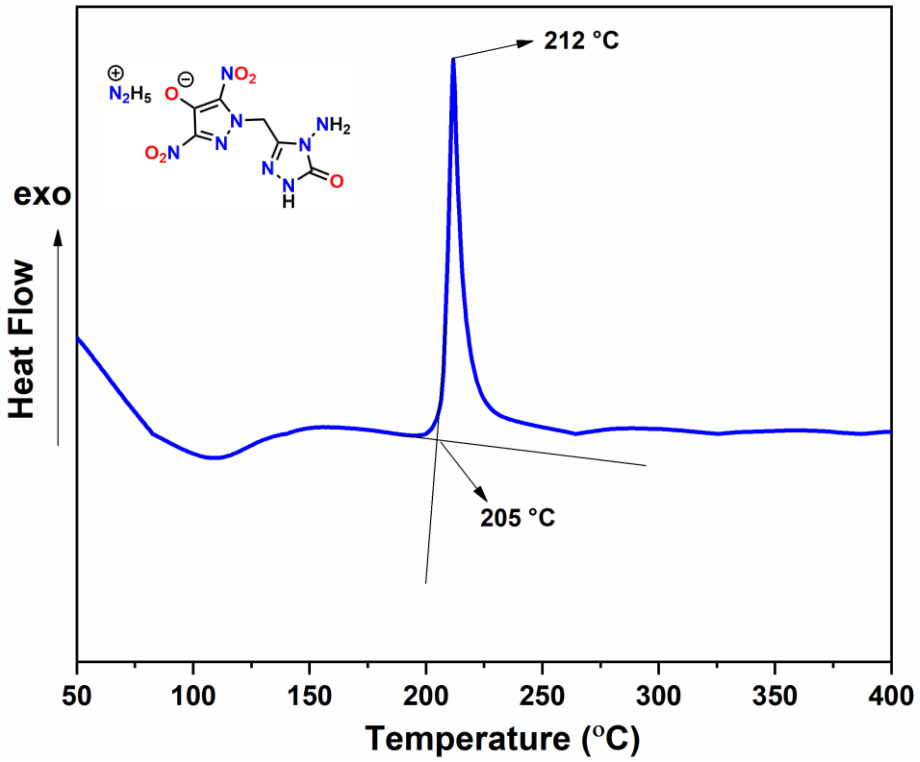


Figure S41. DSC curve of compound **11** at heating rate **5** °C/min.

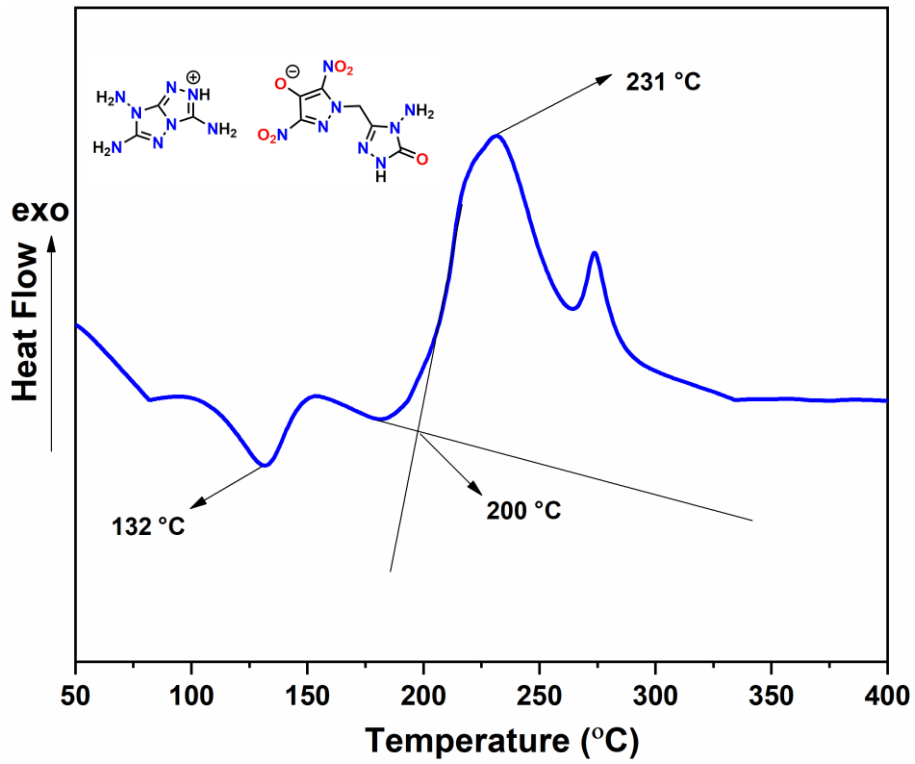


Figure S42. DSC curve of compound **12** at heating rate **5** °C/min.

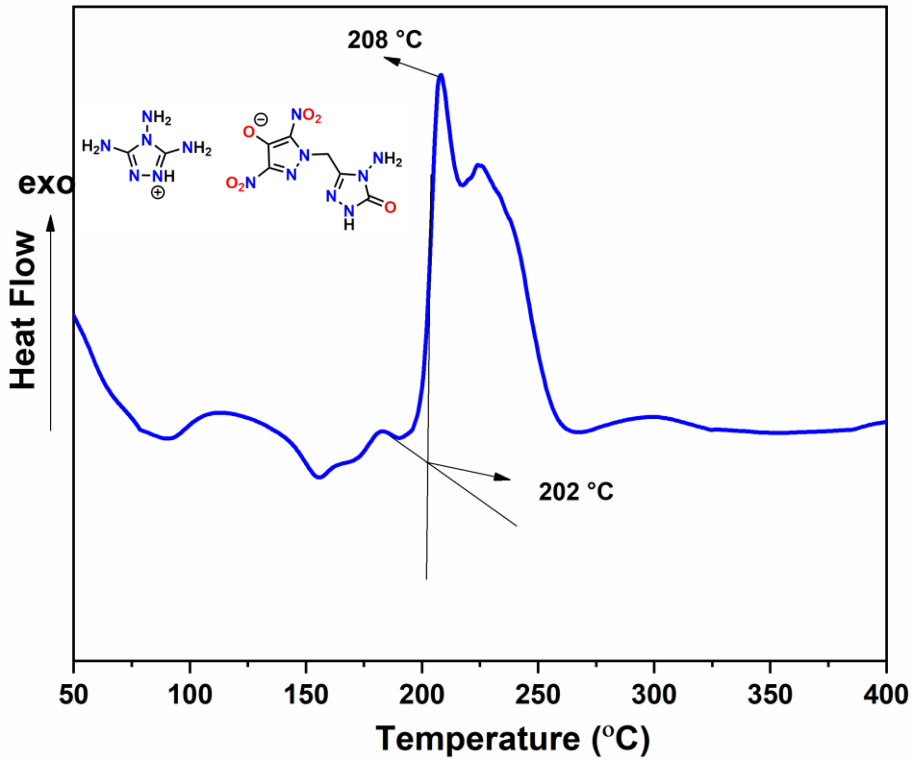


Figure S43. DSC curve of compound **13** at heating rate **5** °C/min.

8. Mass Results:

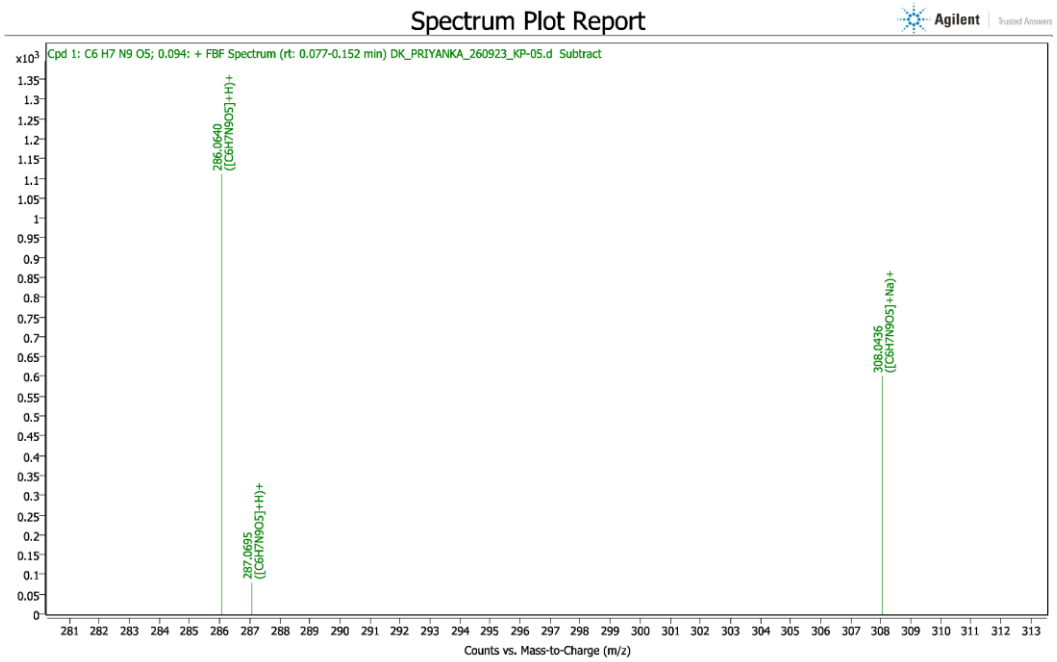


Figure S44. Mass Spectrum of Compound **3.**

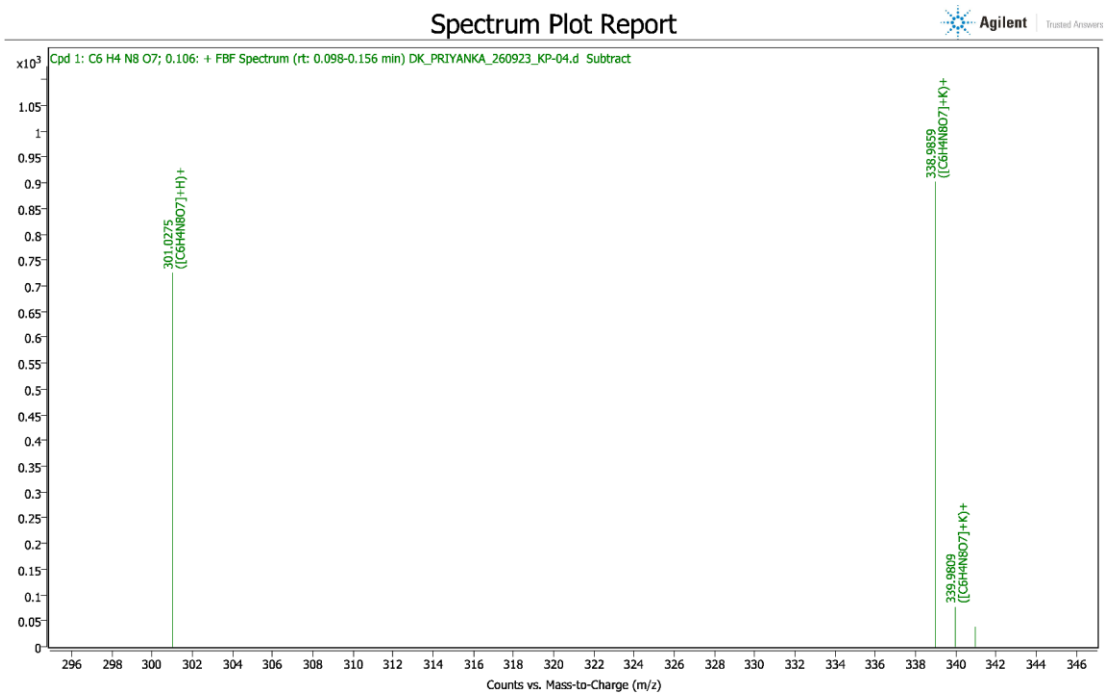


Figure S45. Mass Spectrum of Compound **4.**

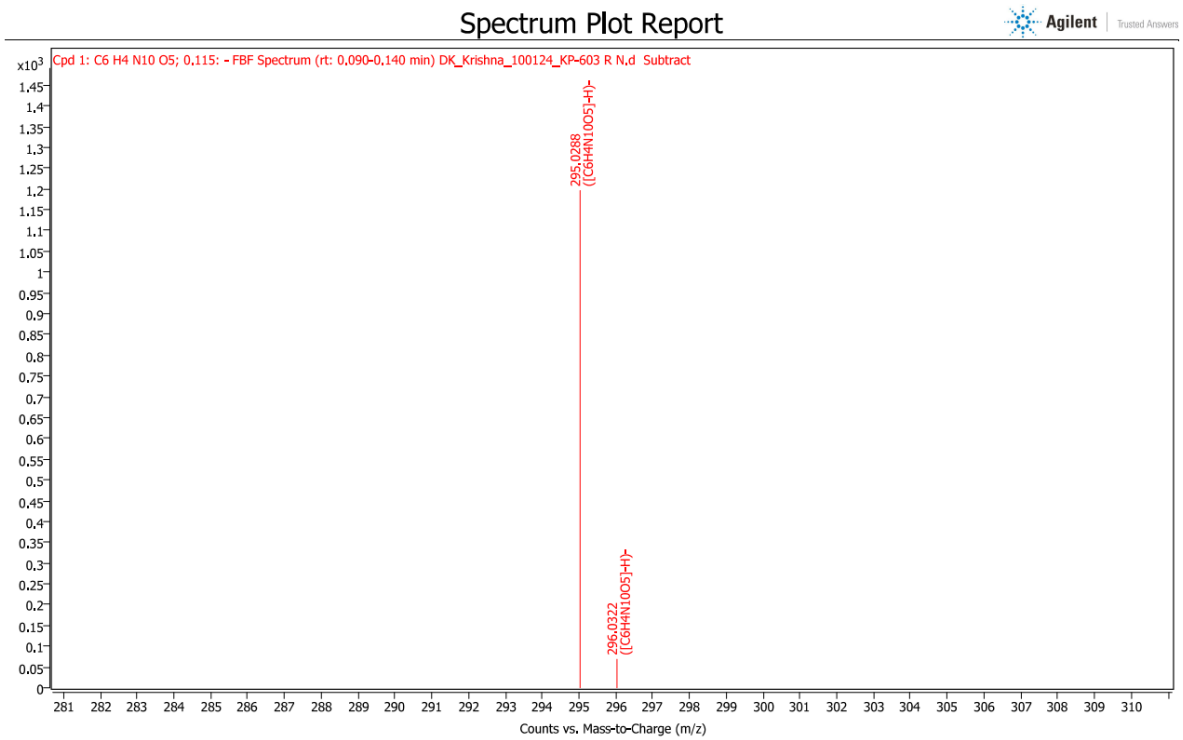


Figure S46. Mass Spectrum of Compound **5.**

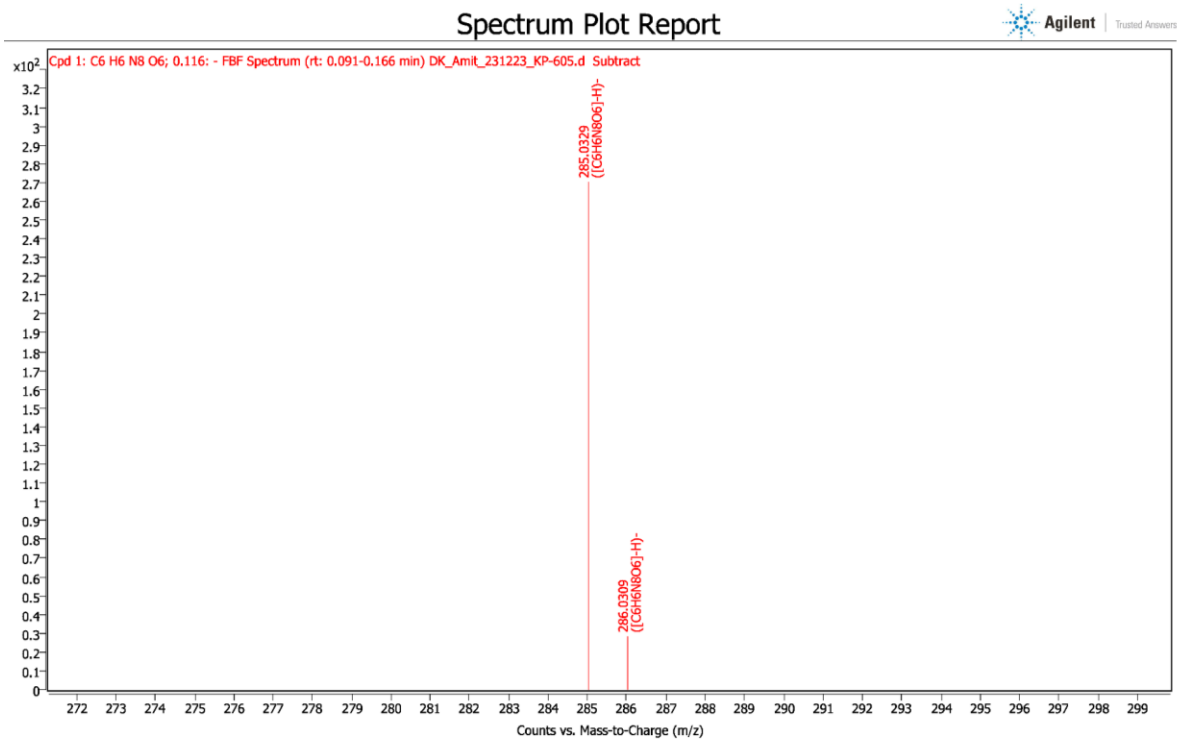


Figure S47. Mass Spectrum of Compound **8**.