Serendipitous formation of 2*H*-pyrazolo[3,4-*d*]pyridazin-7(6*H*)-ones from 3-arylsydnones

Mahadev N. Kumbar‡, Saba Kauser J. Shaikh‡, Ravindra R. Kamble*,‡, Praveen K. Bayannavar‡, Atulkumar A. Kamble‡ and Raveendra K. Hunnur†

‡Department of Chemistry, Karnatak University, Dharwad-580003, Karnataka, India

† APL Research Centre, A Division of Aurobindo Pharma Ltd. 313, Batchupally, Hyderabad 500 072, India

Supporting Information

Table of Contents

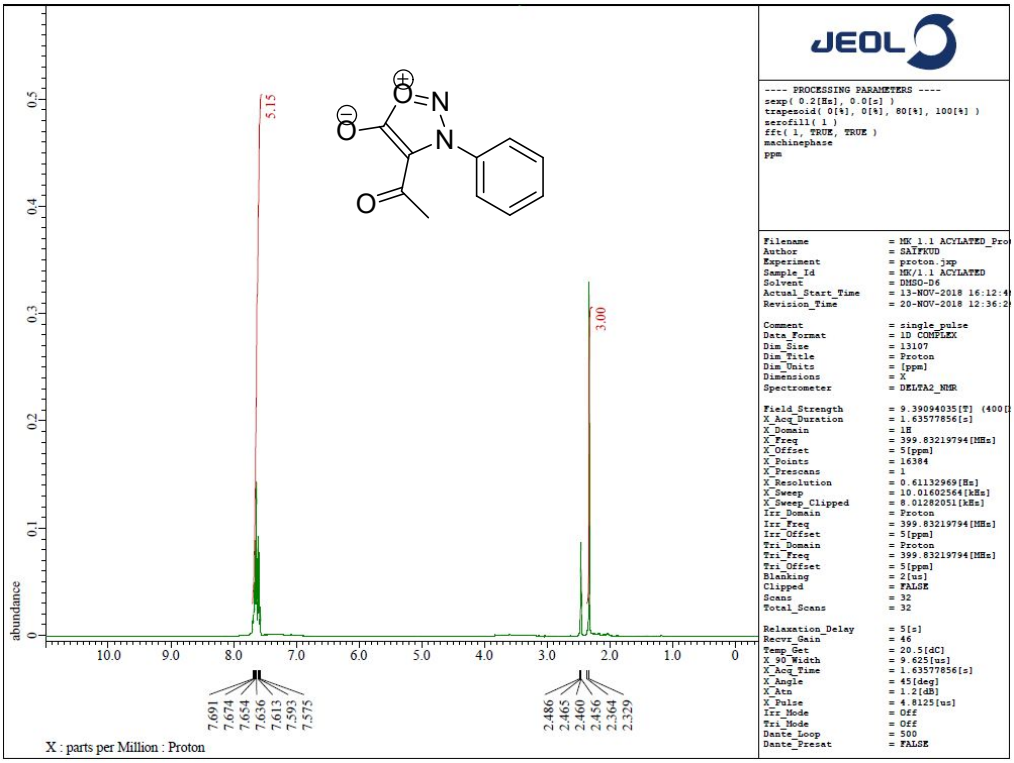


Figure S1: ^{1}H NMR Spectrum (DMSO-d$_6$) of Compound 2a

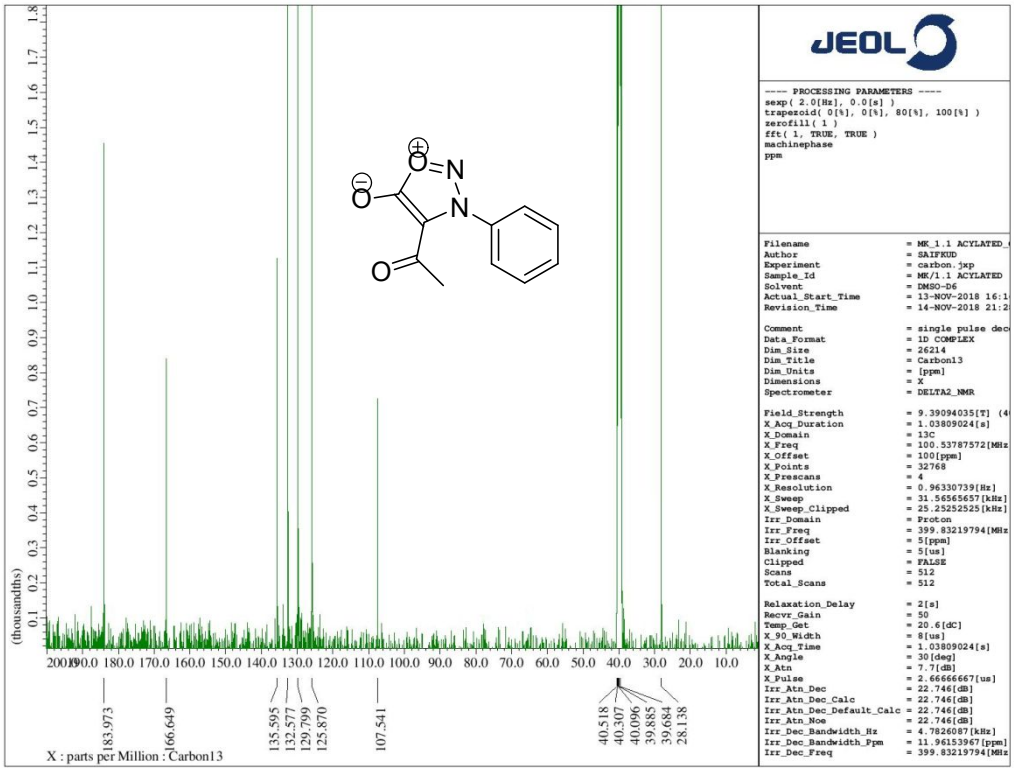


Figure S2: ^{13}C NMR Spectrum (DMSO-d$_6$) of Compound 2a

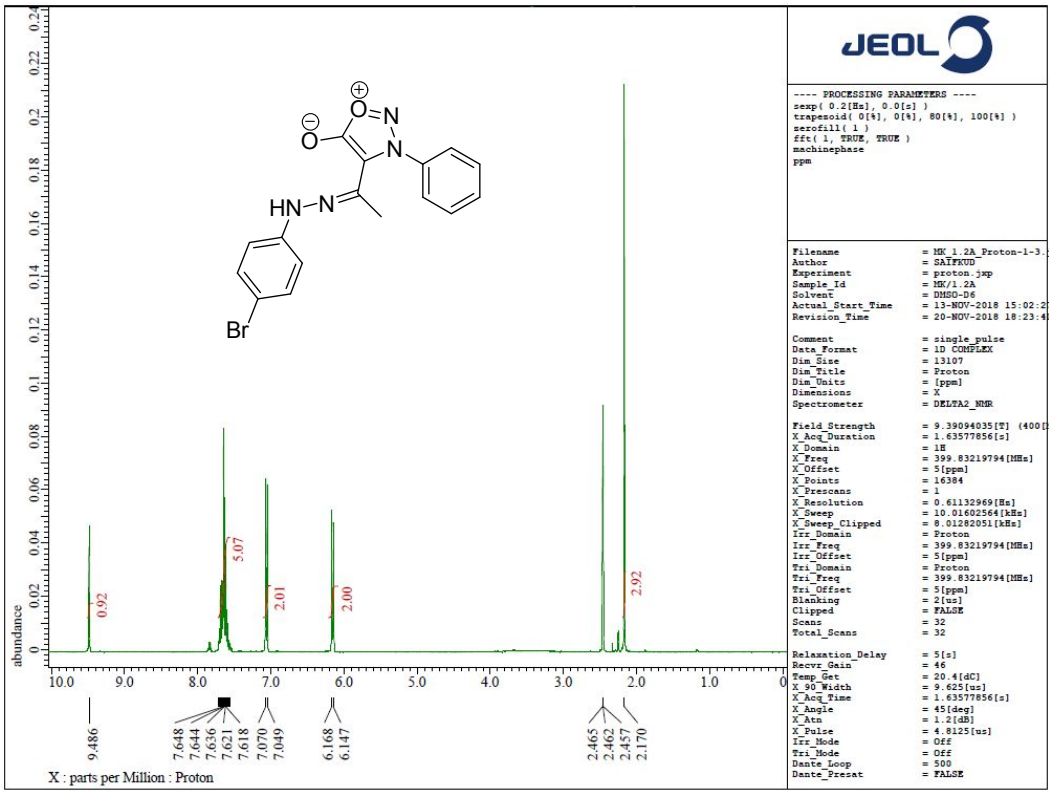


Figure S3: ^{1}H NMR Spectrum (DMSO-d$_6$) of Compound 4c

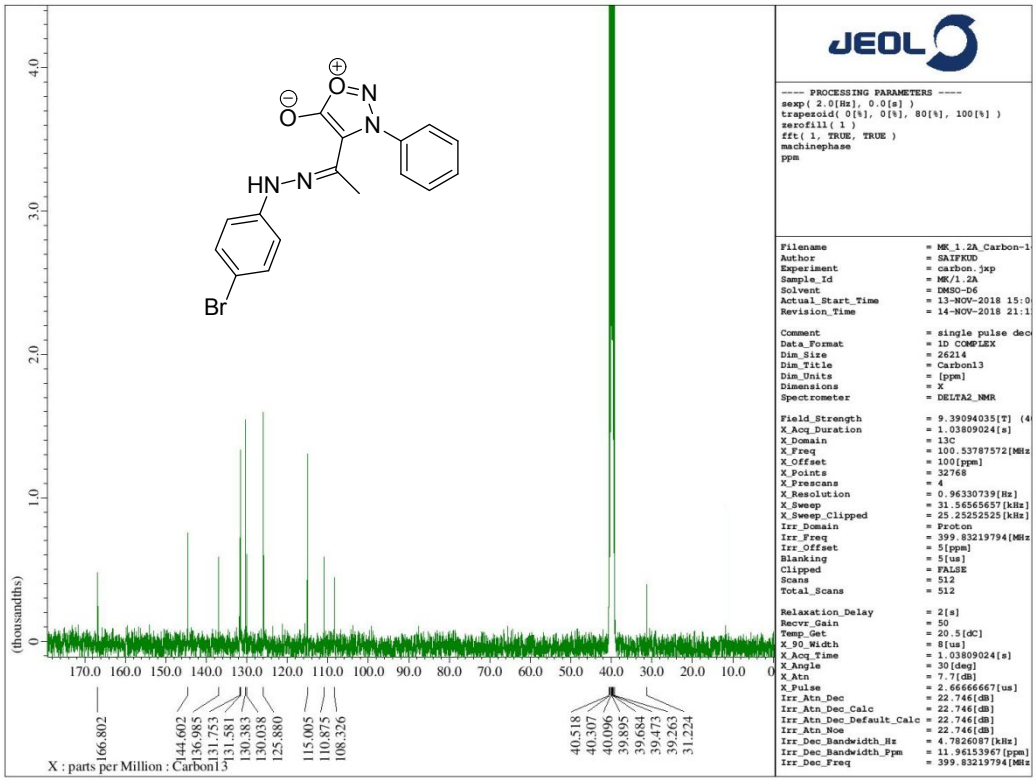


Figure S4: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 4c

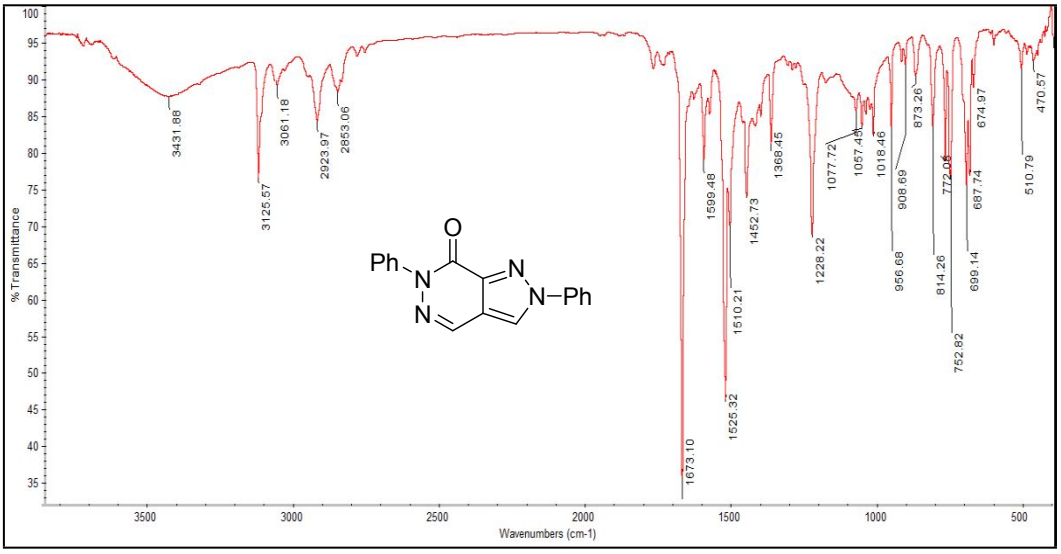


Figure S5: IR spectrum of compound 7a

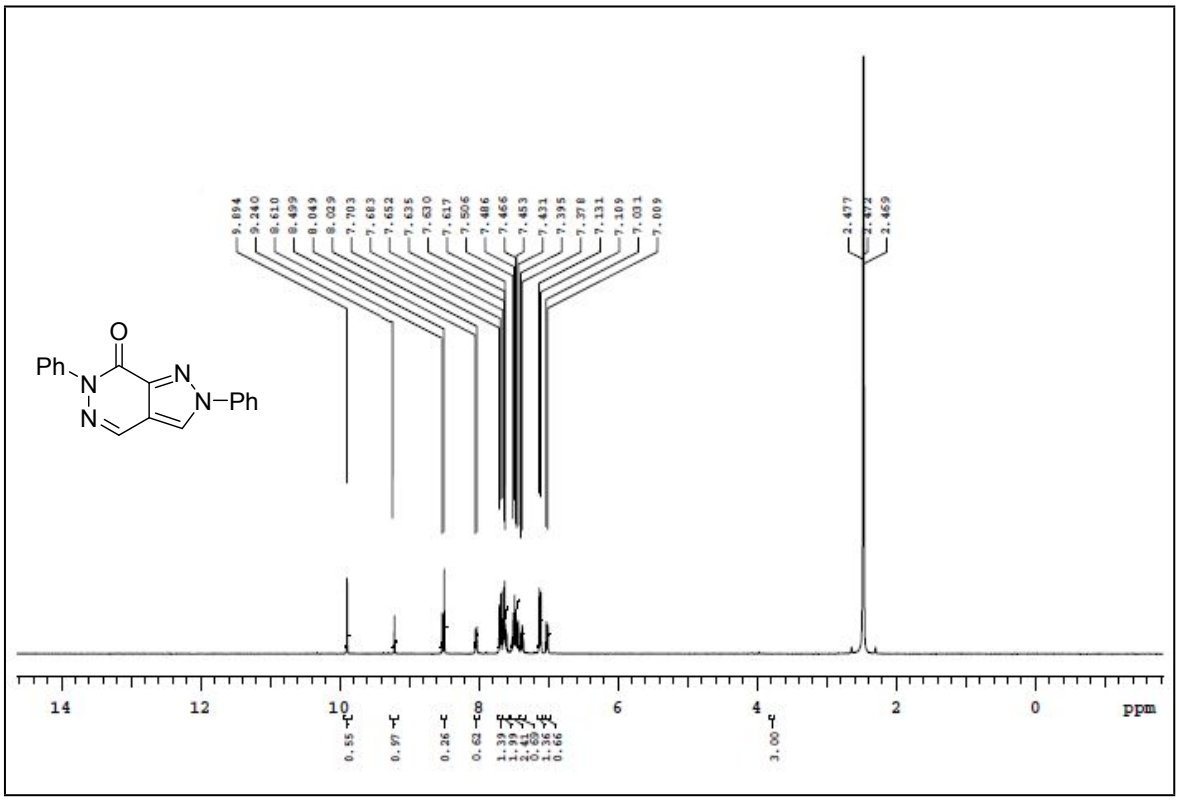


Figure S6: ^{1}H NMR Spectrum (DMSO-d_6) of Compound 7a

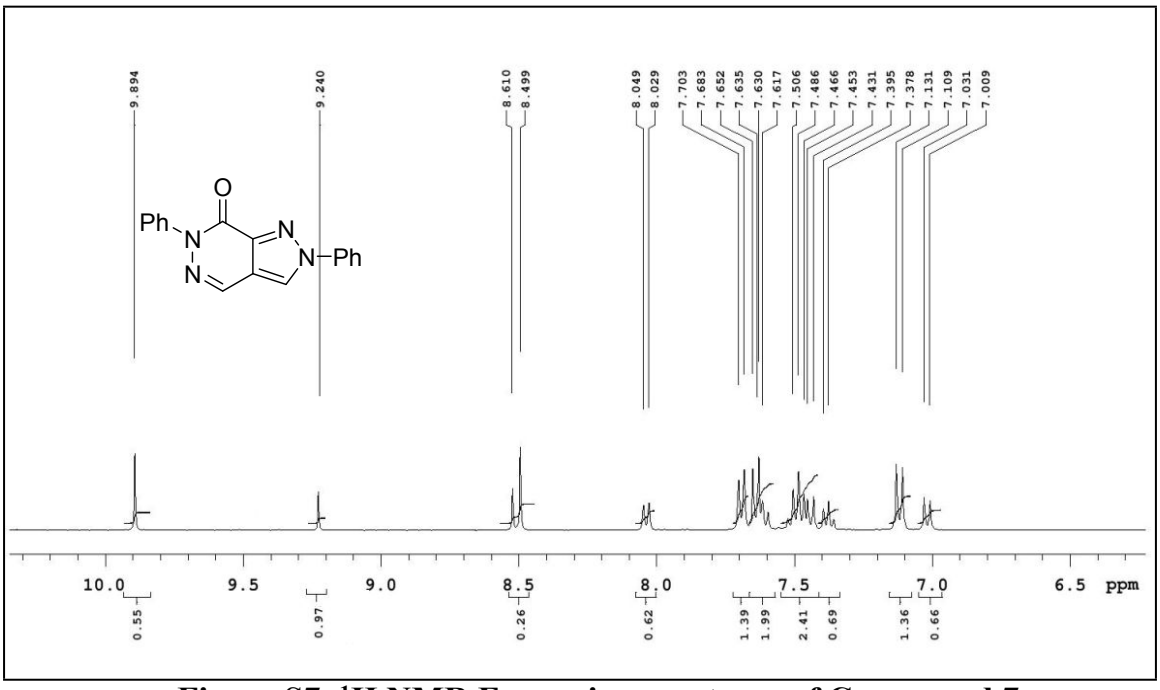


Figure S7: ^{1}H NMR Expansion spectrum of Compound 7a

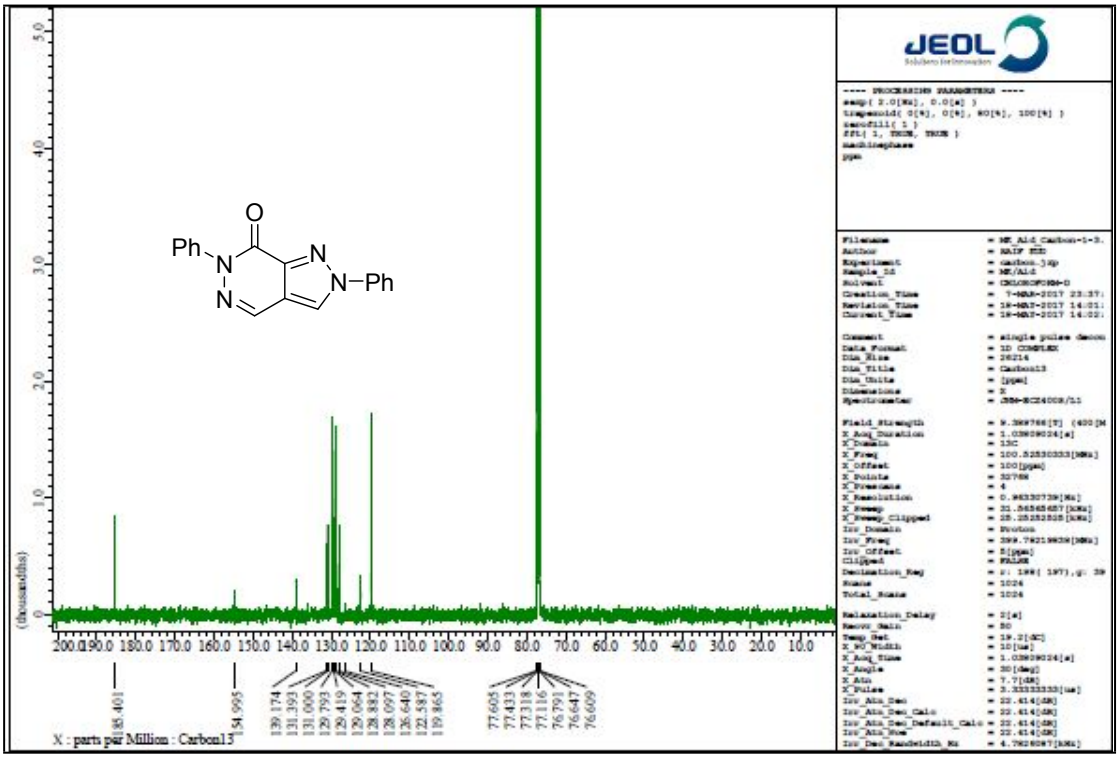


Figure S8: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7a

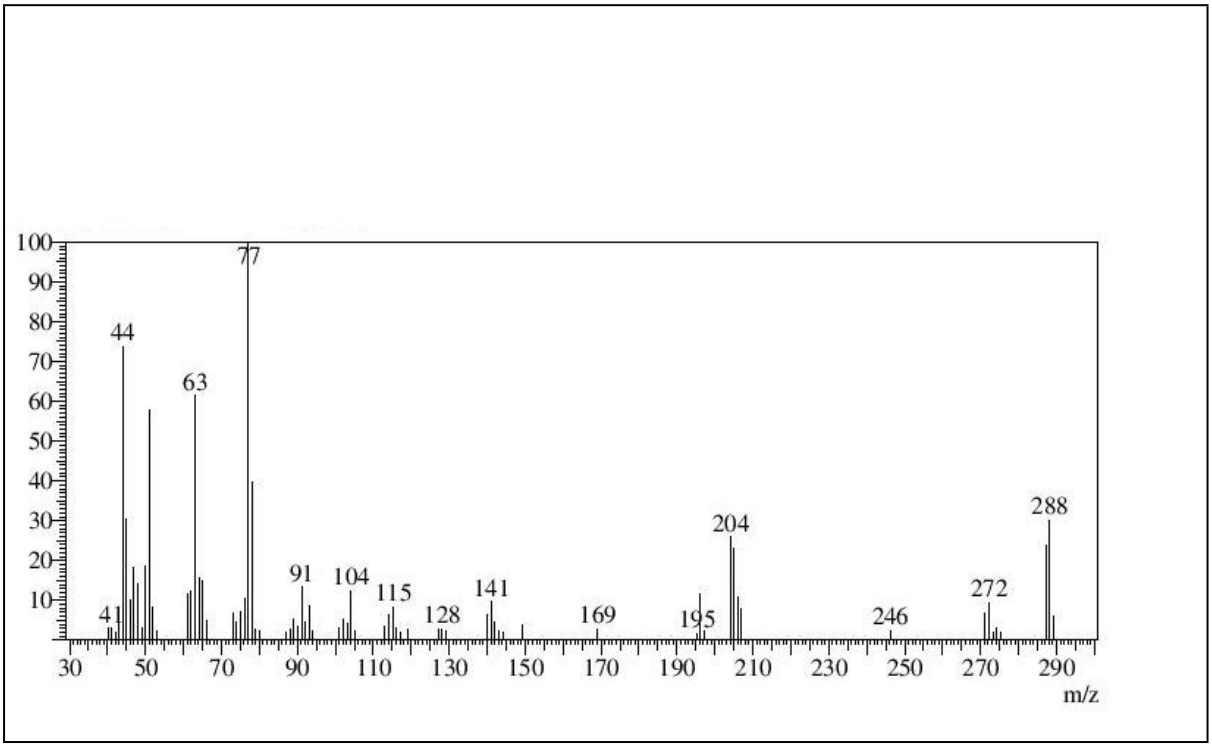


Figure S9: Mass spectrum of compound 7a

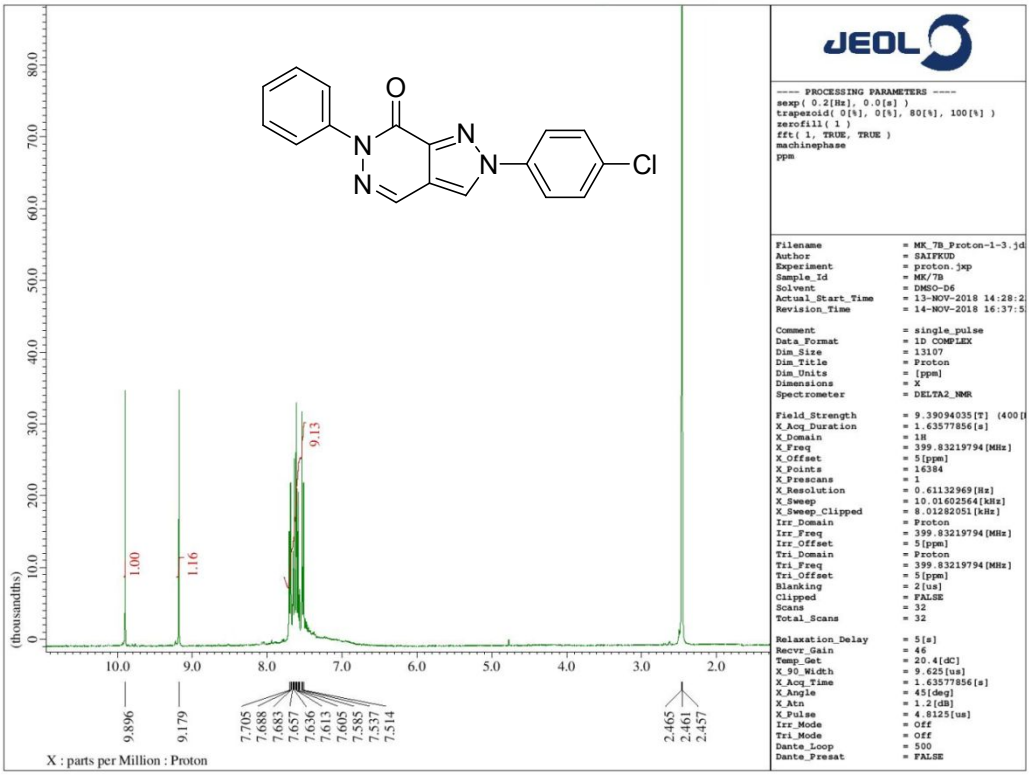


Figure S10: ^{1}H NMR Spectrum (DMSO-d_6) of Compound 7b

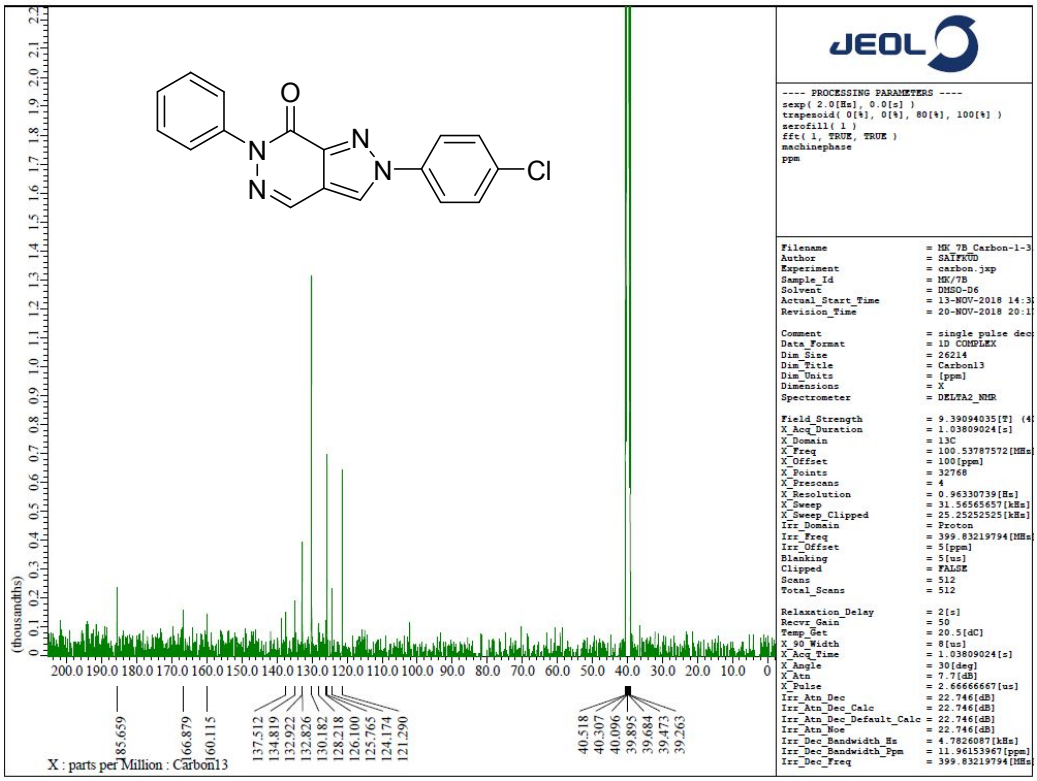


Figure S11: ^{13}C NMR Spectrum (DMSO-d$_6$) of Compound 7b

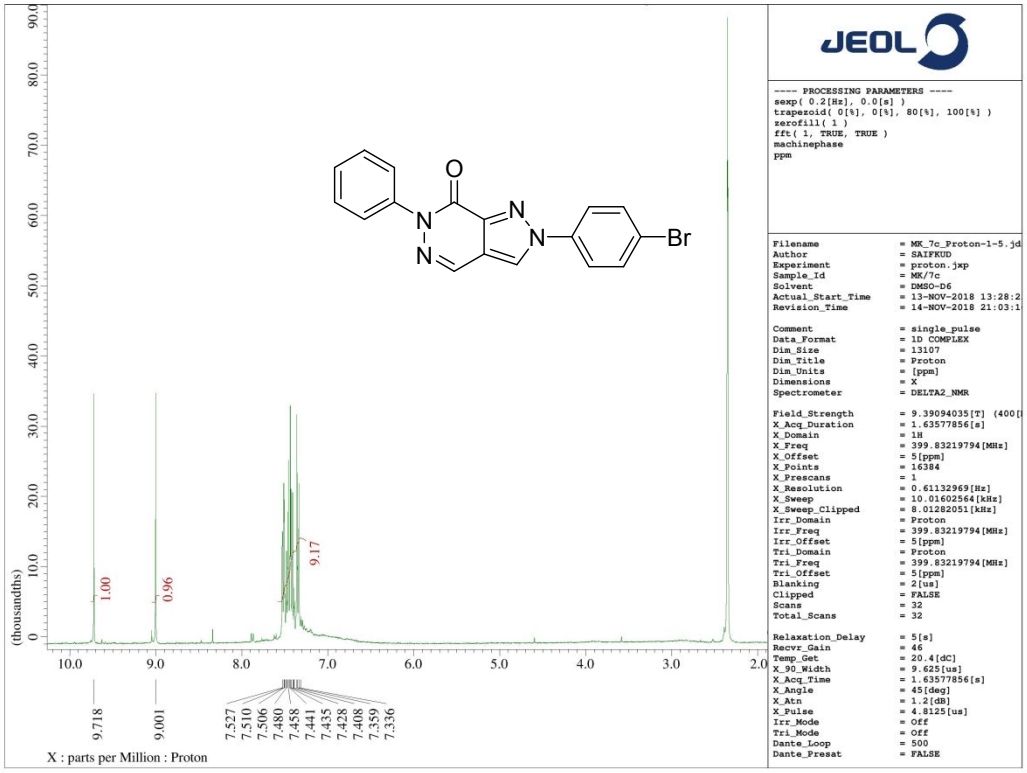


Figure S12: ^{1}H NMR Spectrum (DMSO-d$_6$) of Compound 7c

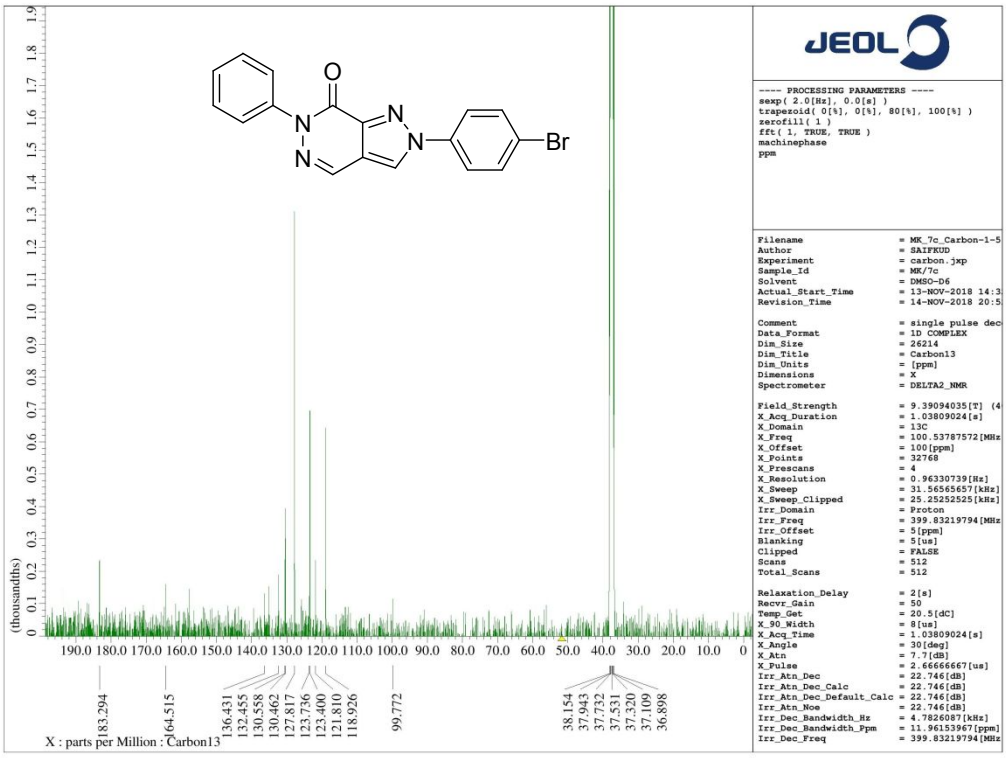


Figure S13: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7c

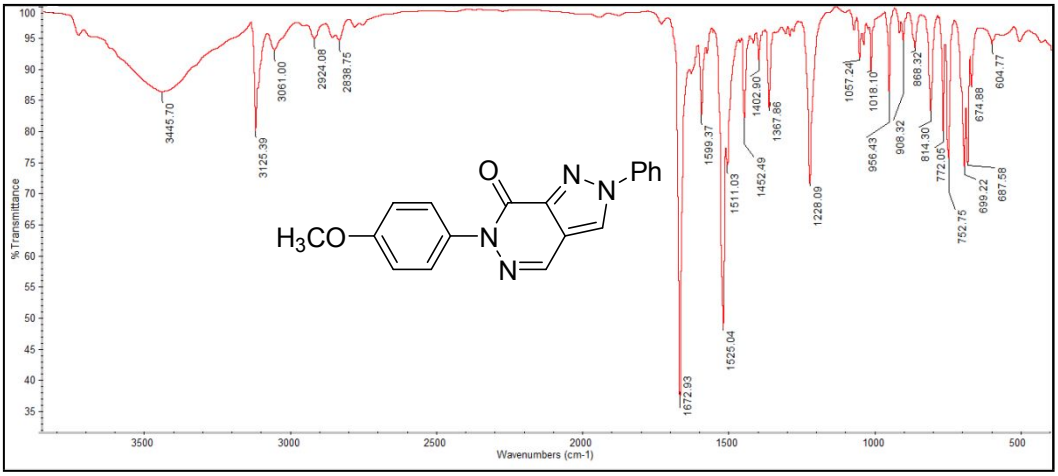


Figure S14: IR spectrum of compound 7d

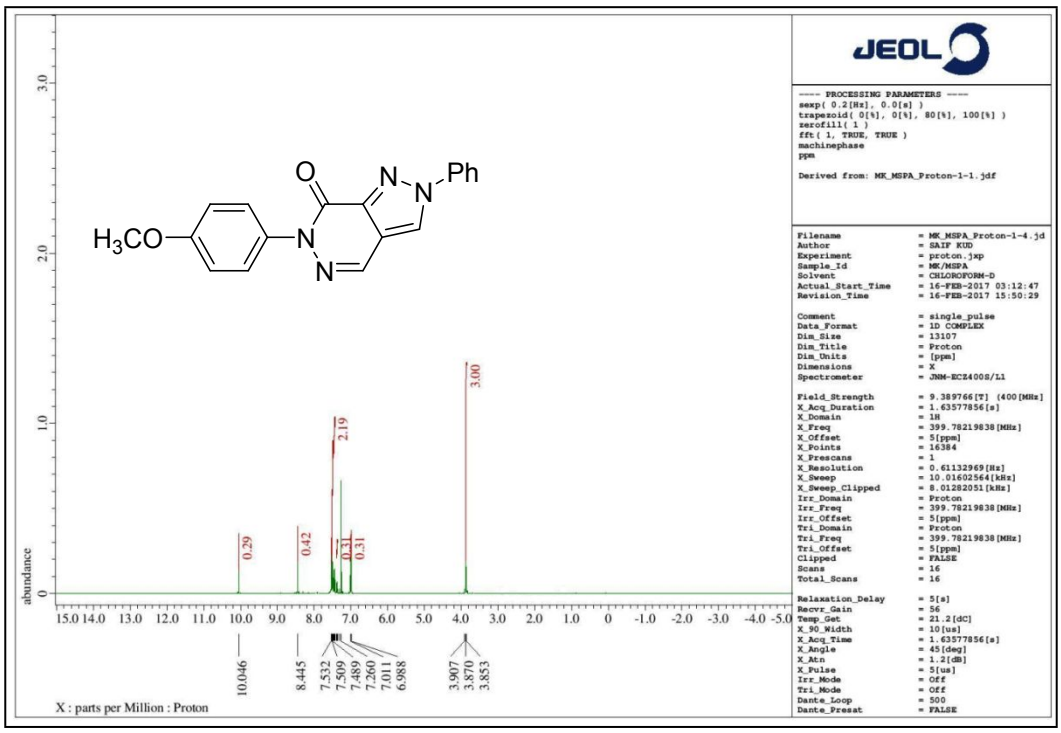


Figure S15: ^{1}H NMR Spectrum (DMSO-d_6) of Compound 7d

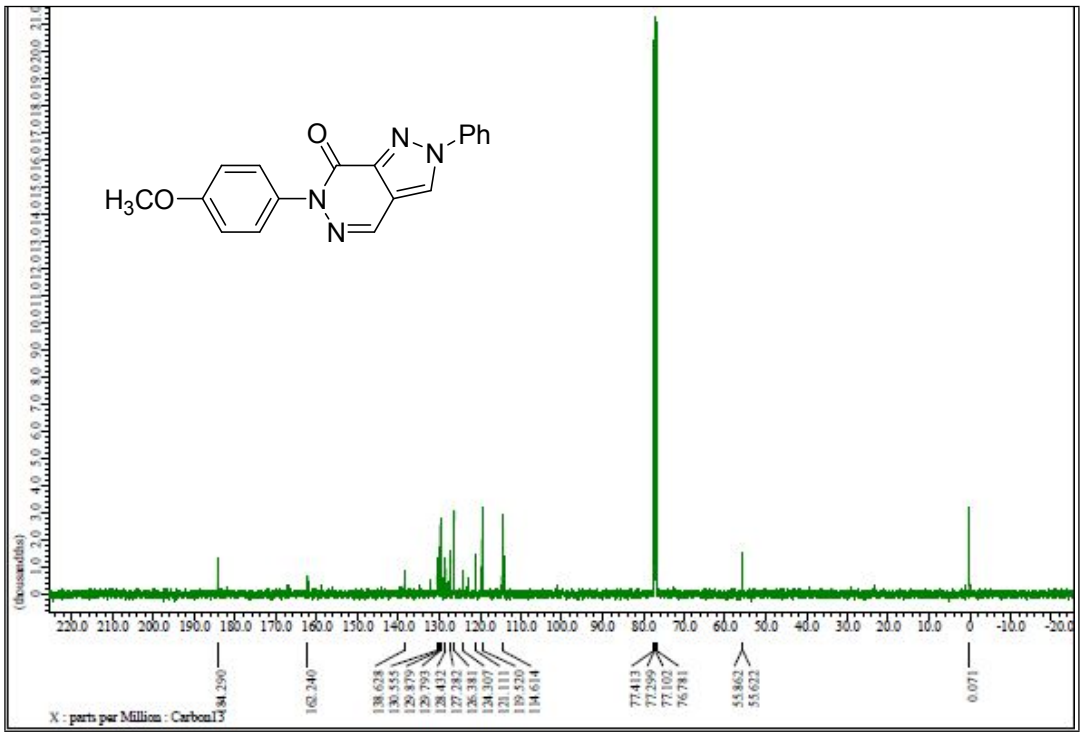


Figure S16: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7d

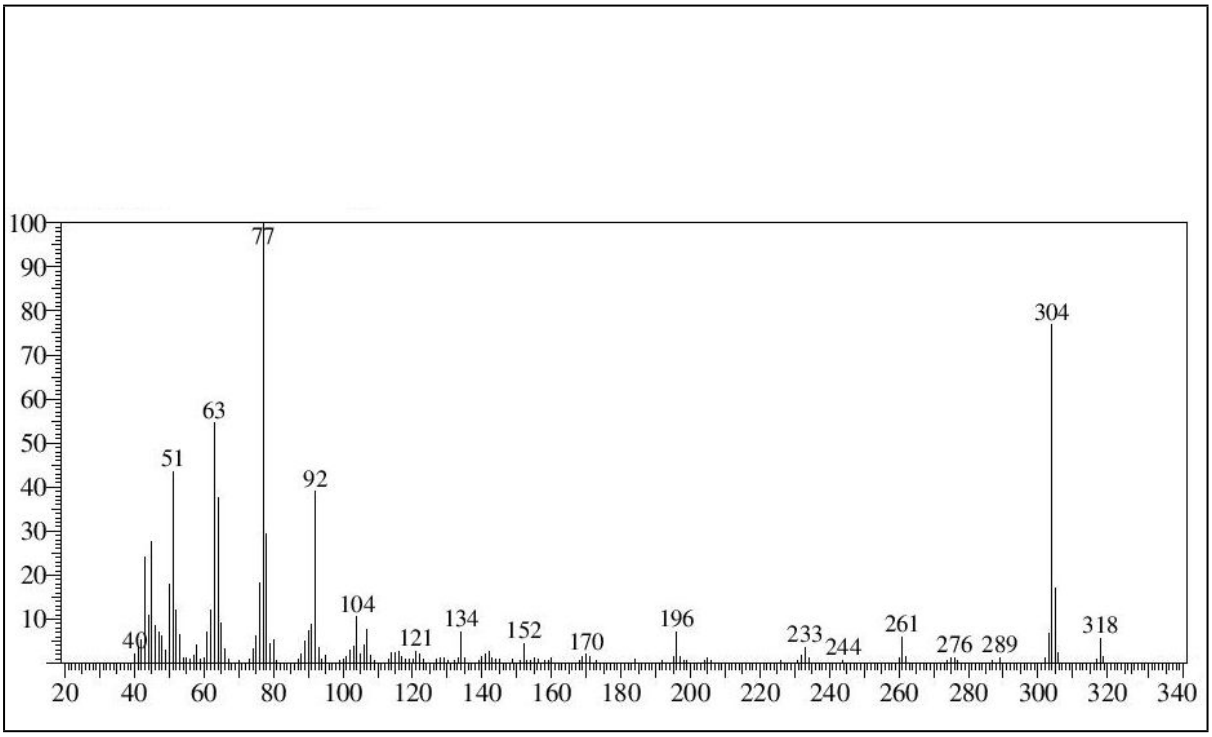


Figure S17: Mass spectrum of compound 7d

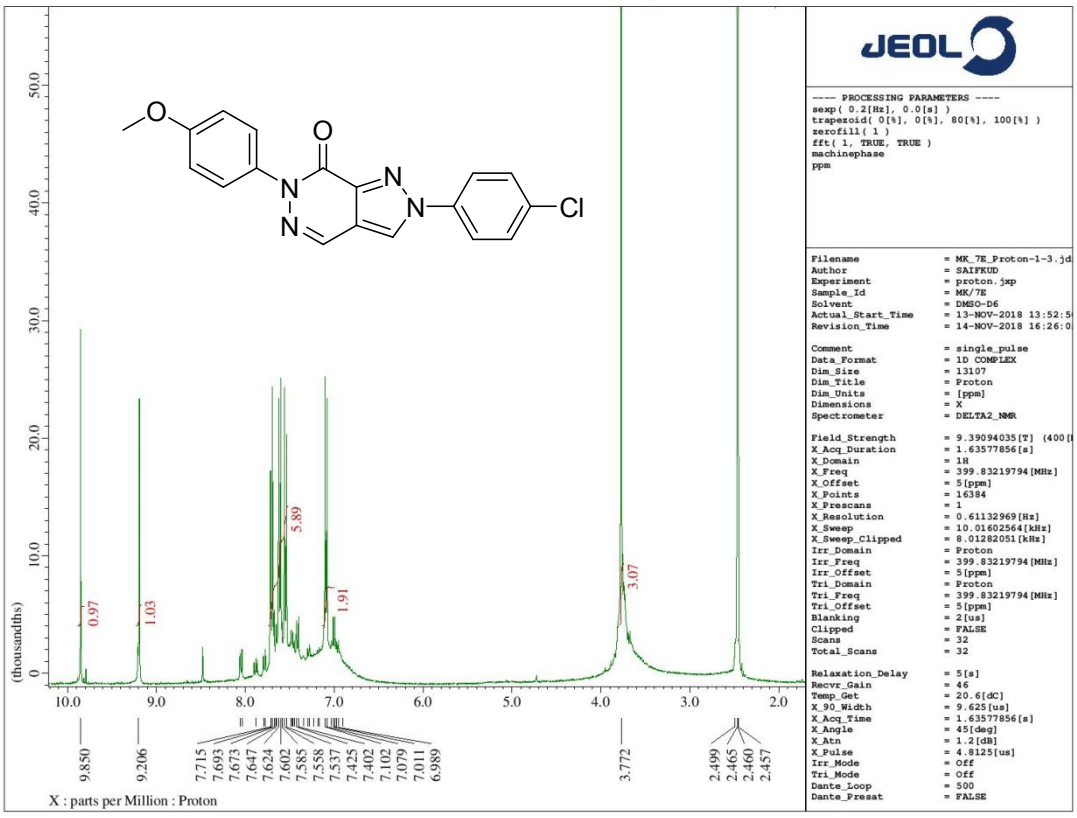


Figure S18: ^{1}H NMR Expansion Spectrum (DMSO-d_6) of Compound 7e

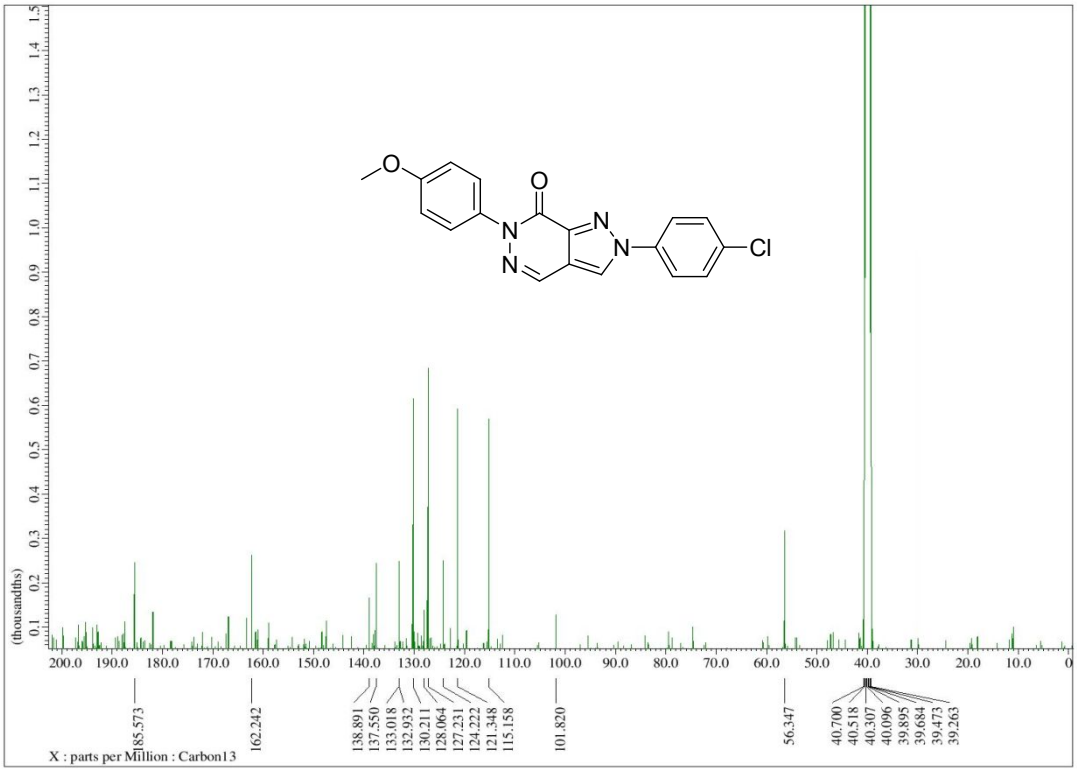


Figure S19: ^{13}C NMR Spectrum (DMSO-d$_6$) of Compound 7e

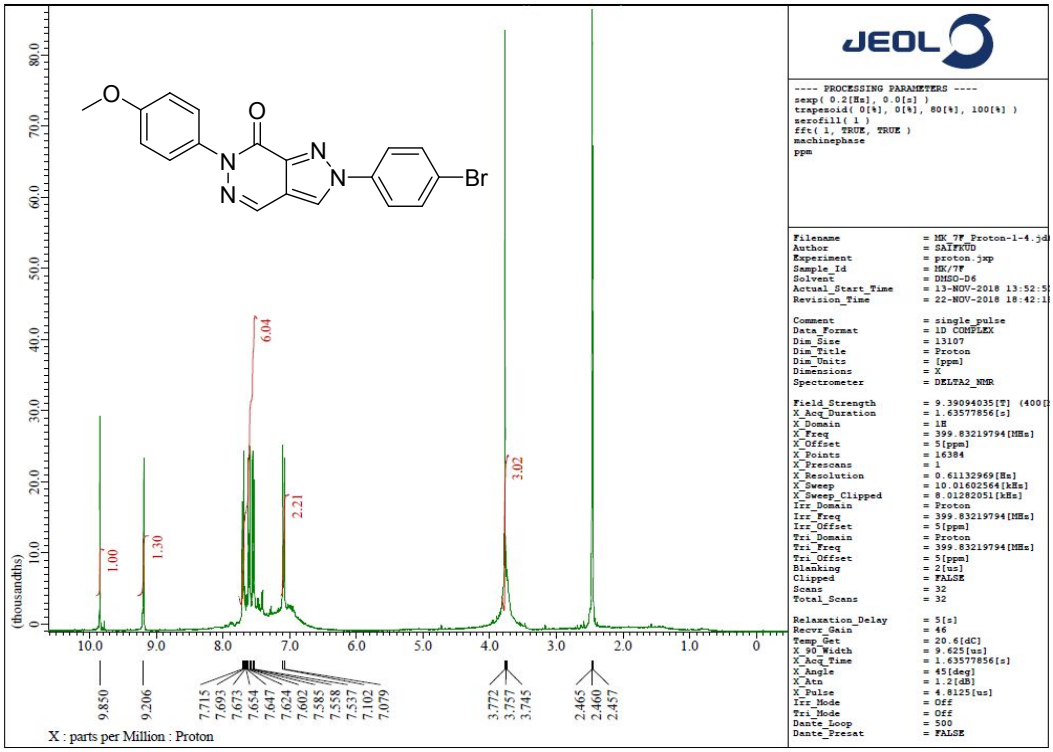


Figure S20: ^{1}H NMR Spectrum (DMSO-d$_6$) of Compound 7f

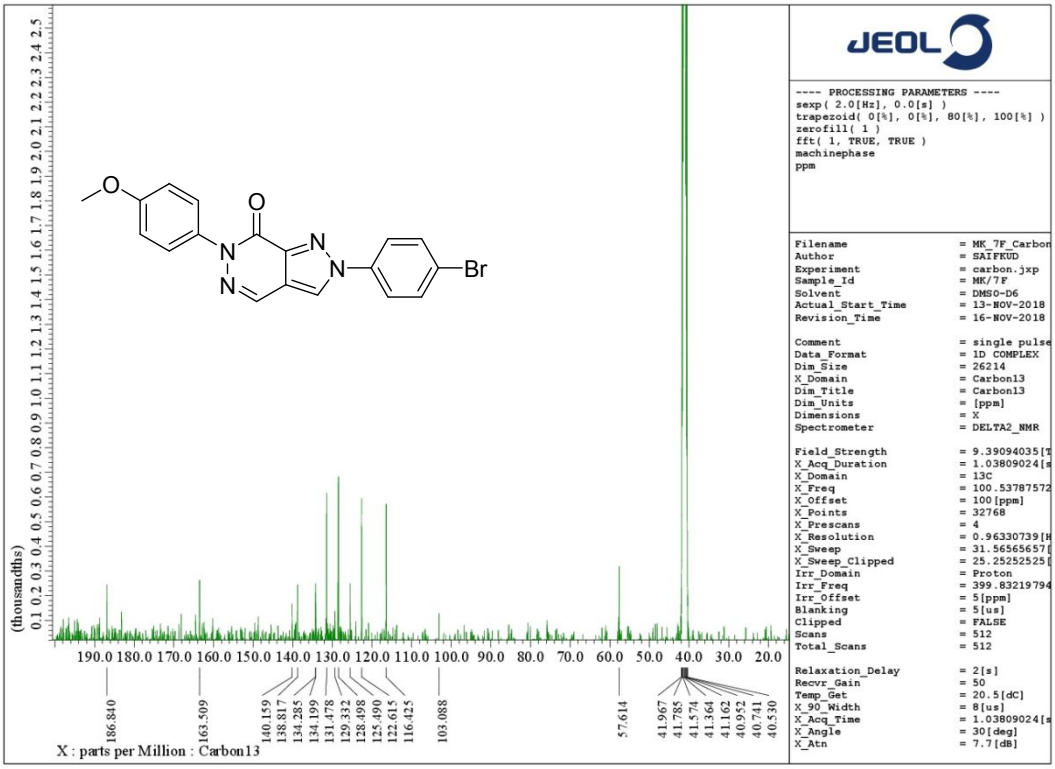


Figure S21: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7f

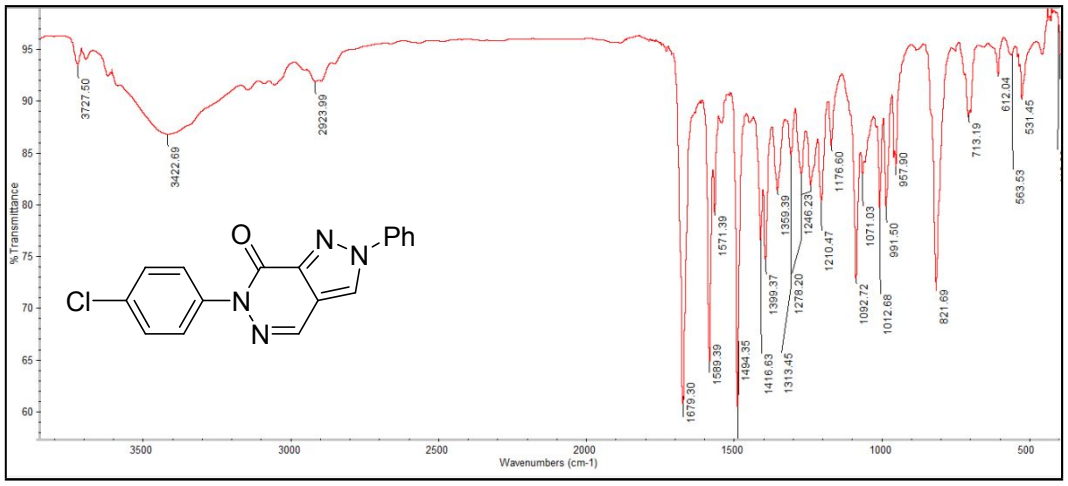


Figure S22: IR spectrum of compound 7g

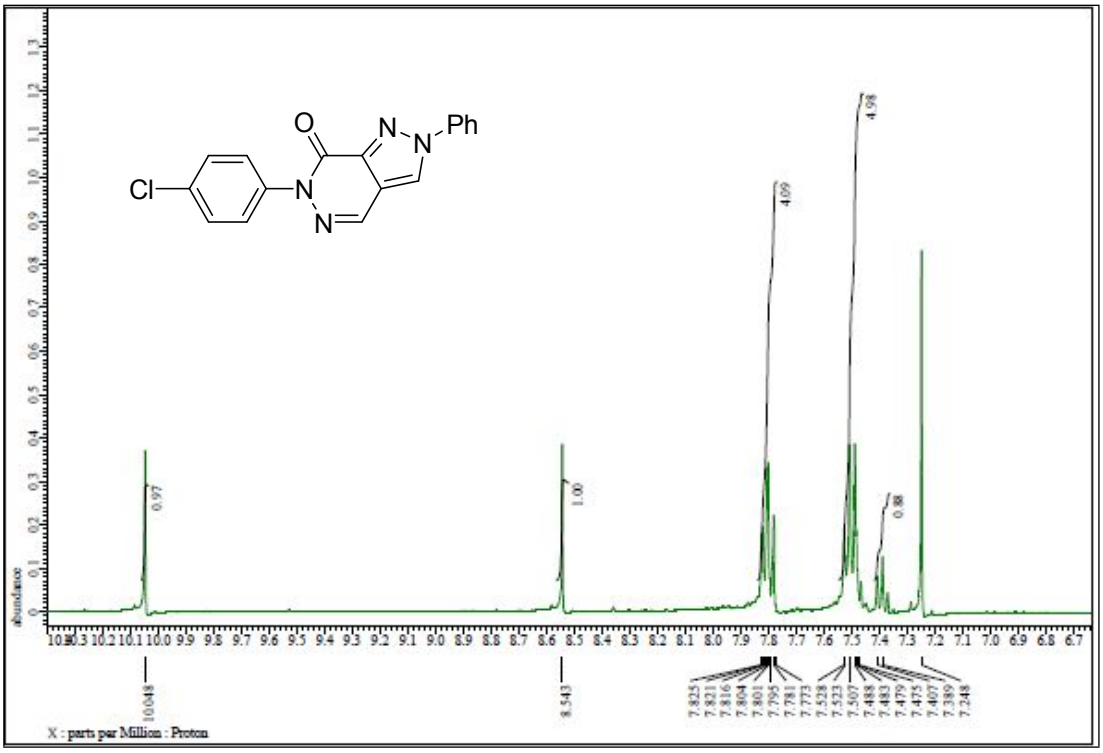


Figure S23: ^{1}H NMR Expansion spectrum (DMSO-d$_6$) of Compound 7g

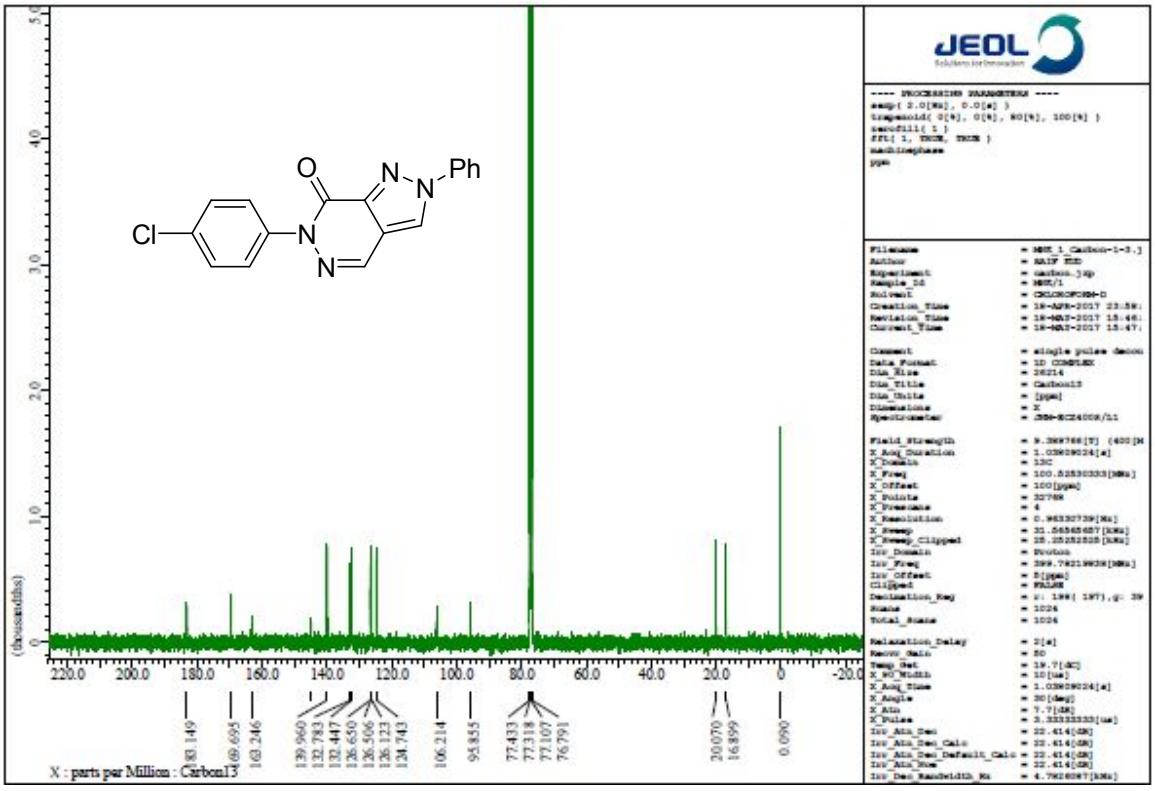


Figure S24: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7g

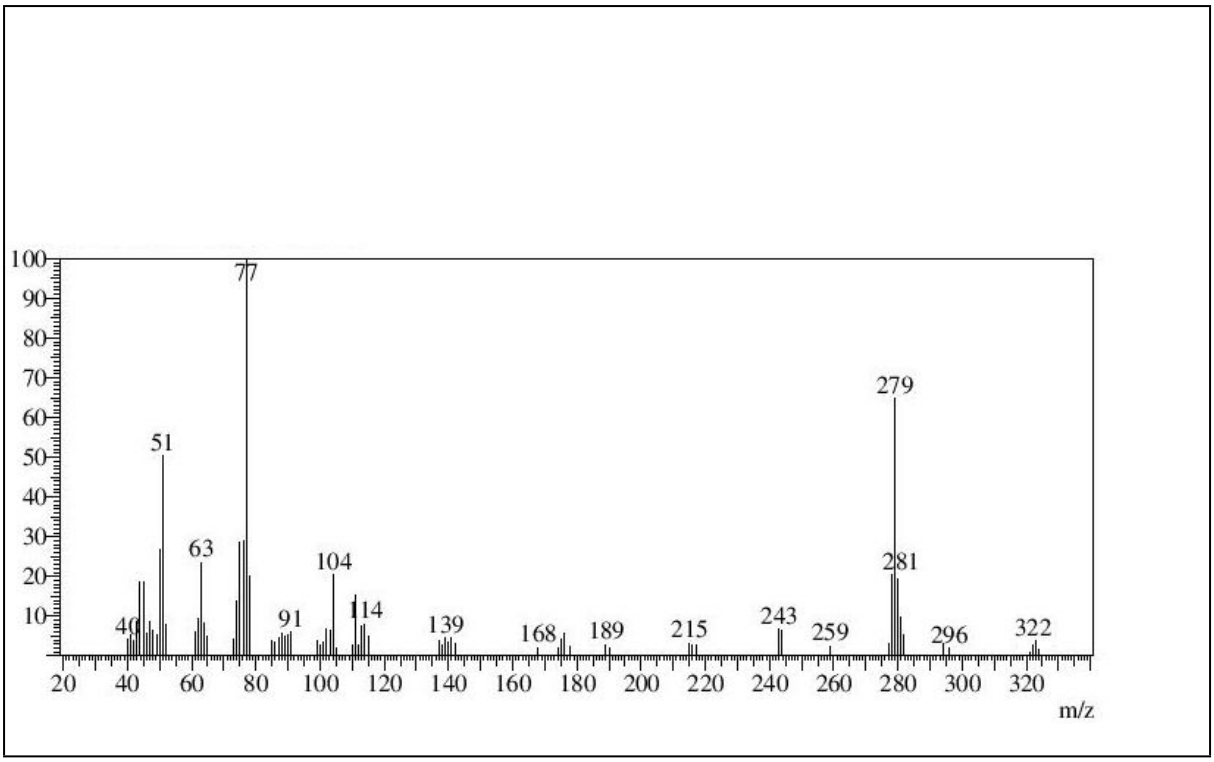
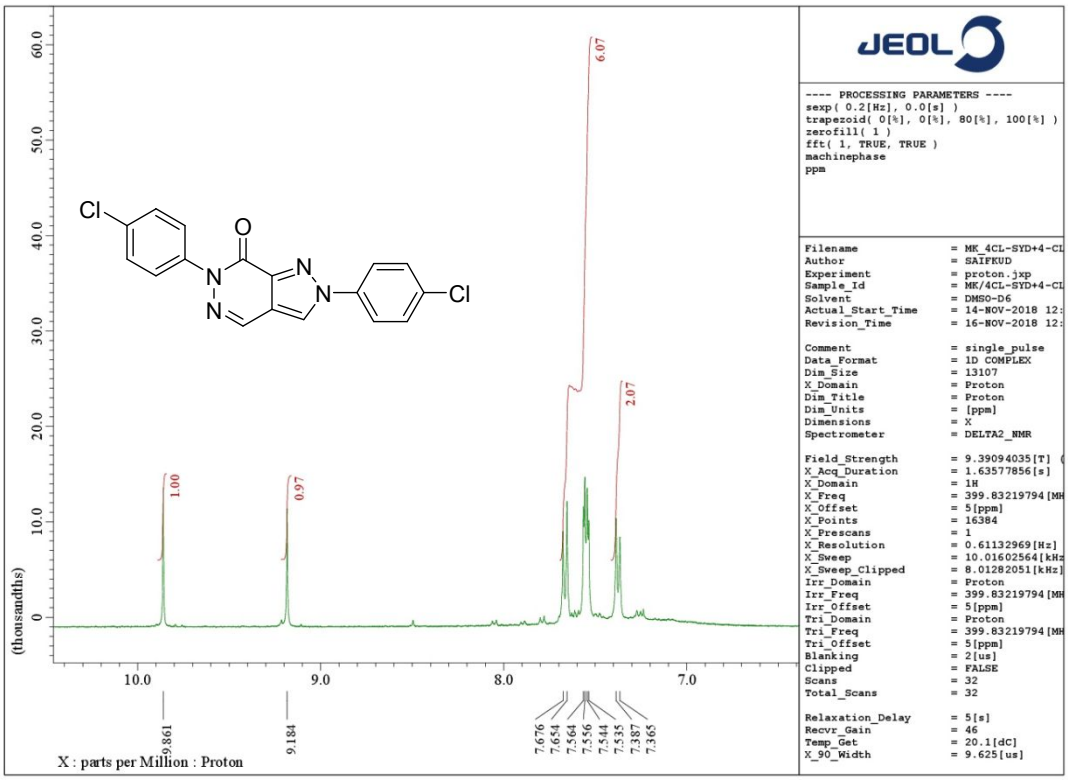


Figure S25: Mass spectrum of compound 7g



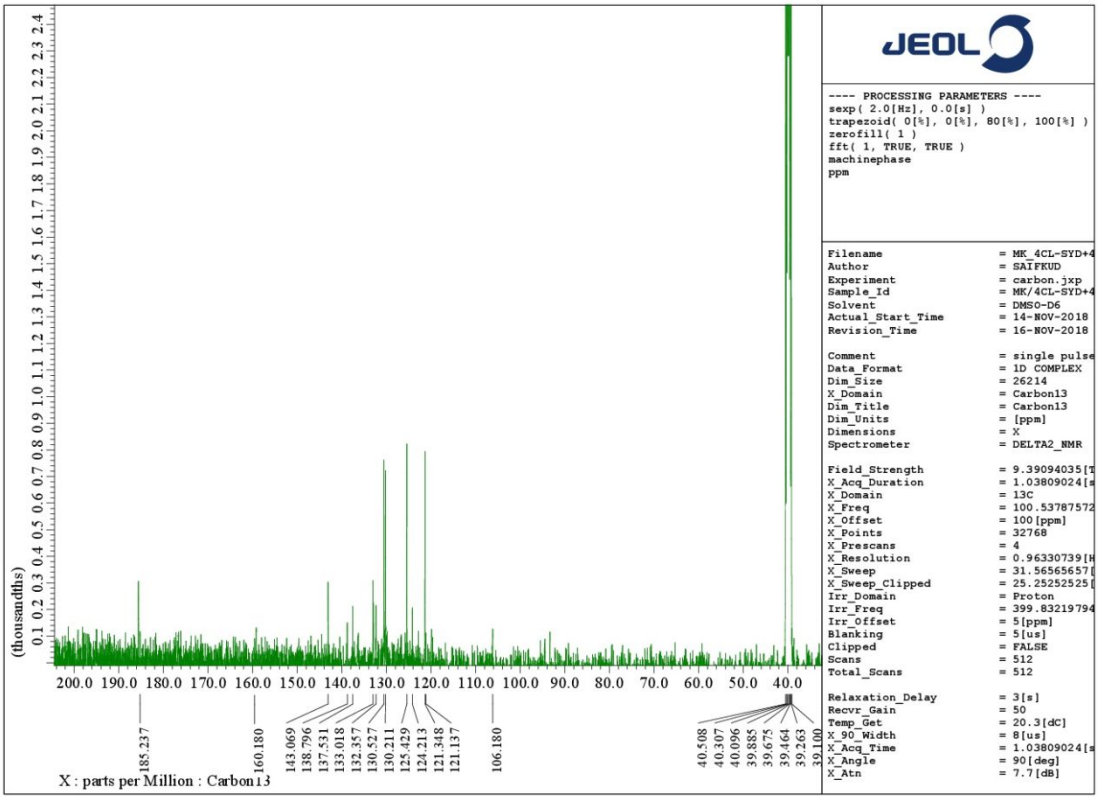


Figure S26: ^{1}H NMR Expansion spectrum (DMSO-d_6) of Compound 7h

Figure S27: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7h

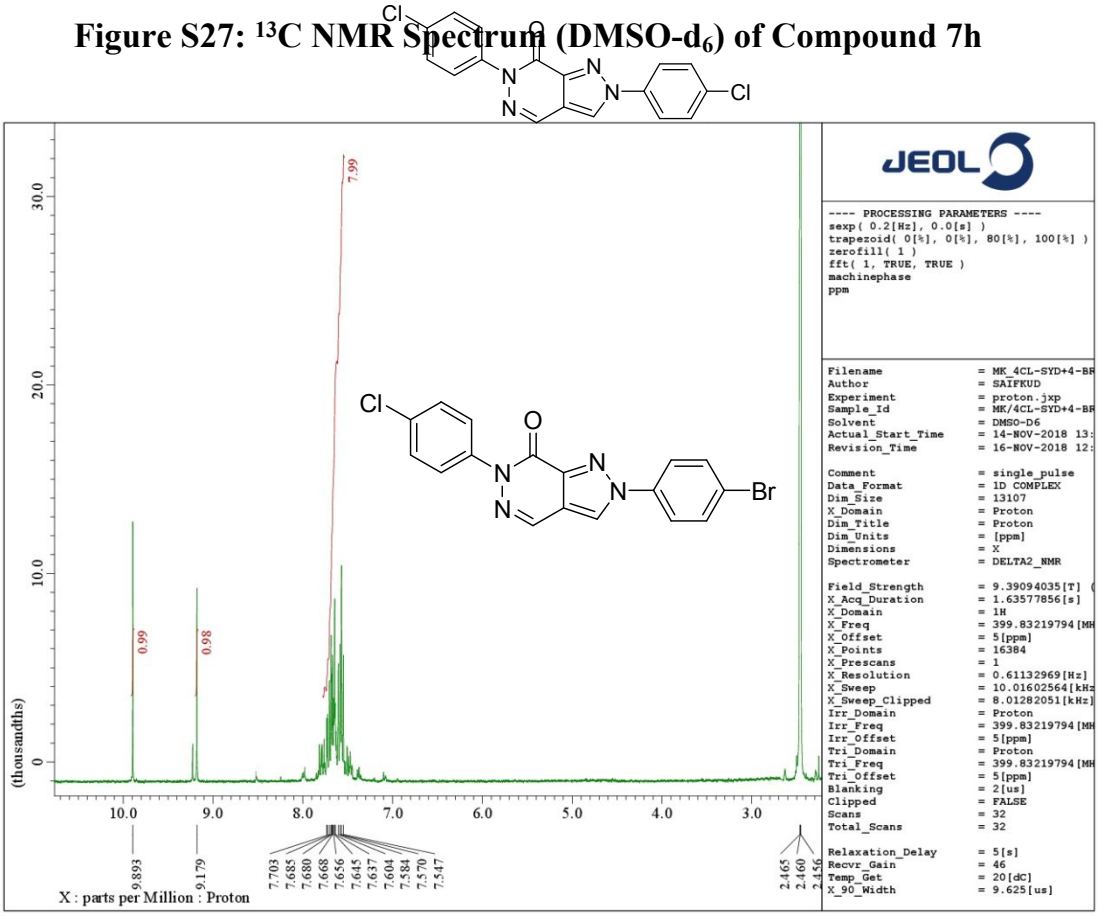


Figure S28: ^{1}H NMR Spectrum (DMSO-d_6) of Compound 7i

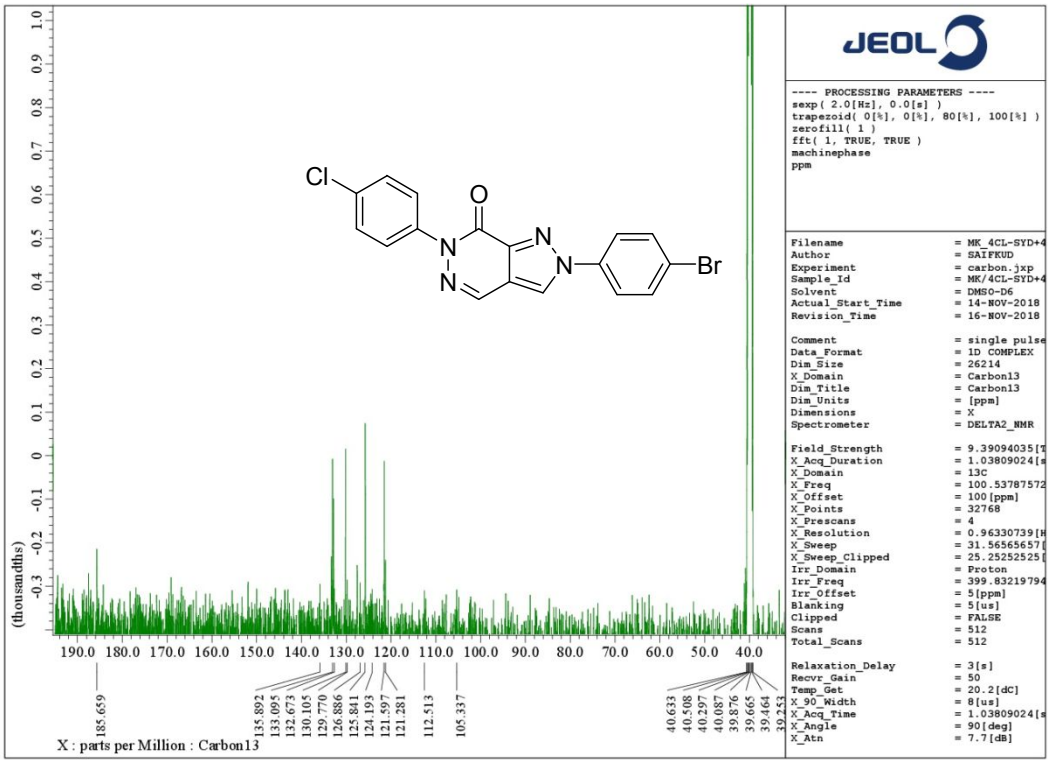


Figure S29: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7i

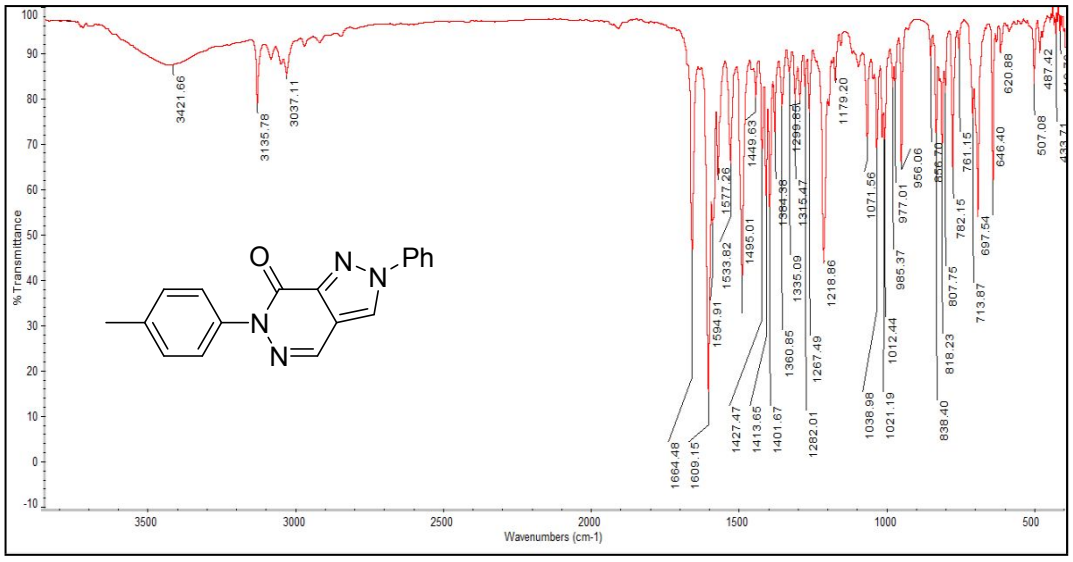


Figure S30: IR spectrum of compound 7j

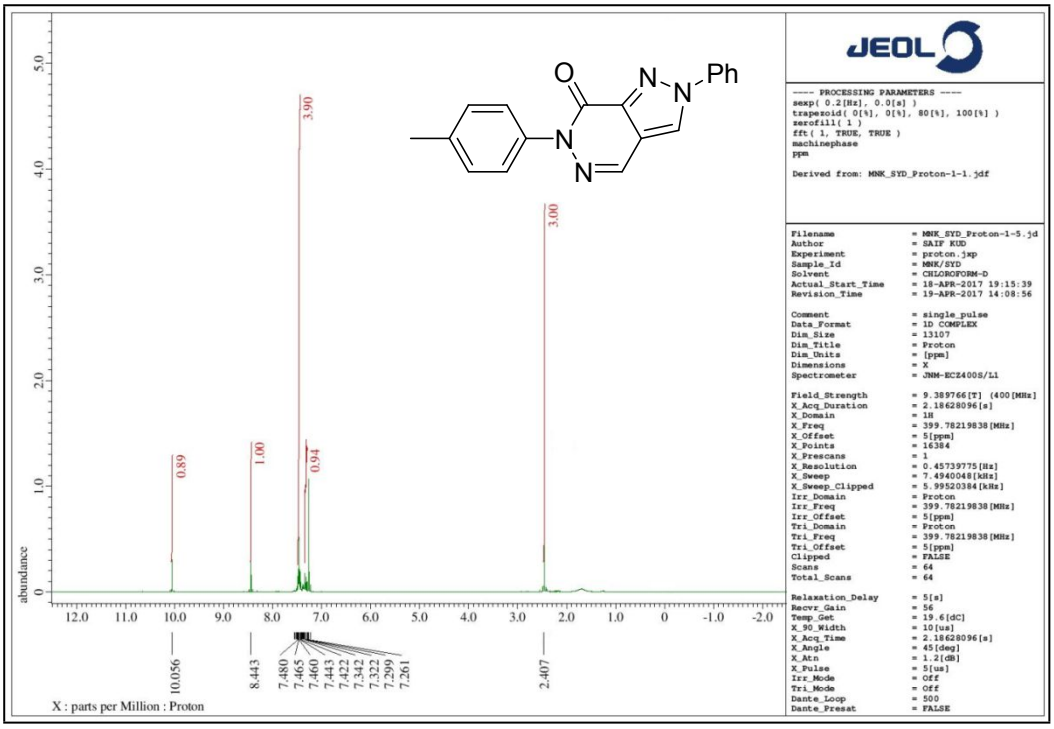


Figure S31: ^{1}H NMR Spectrum (DMSO-d_6) of Compound 7j

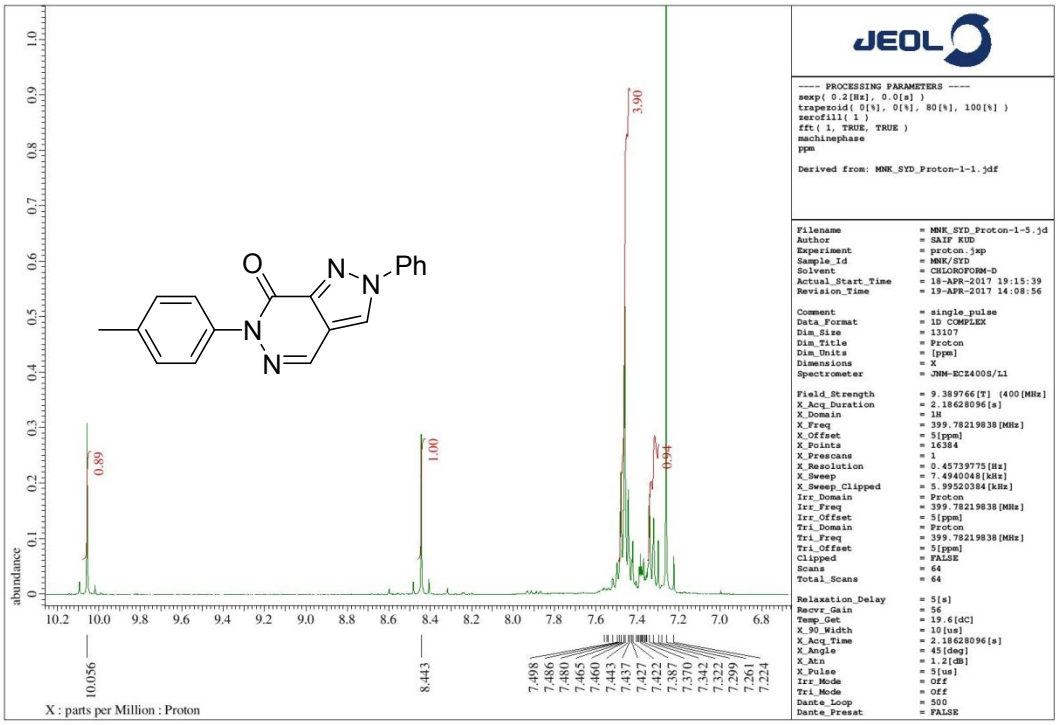


Figure S32: ^{1}H NMR Expansion Spectrum (DMSO-d_6) of Compound 7j

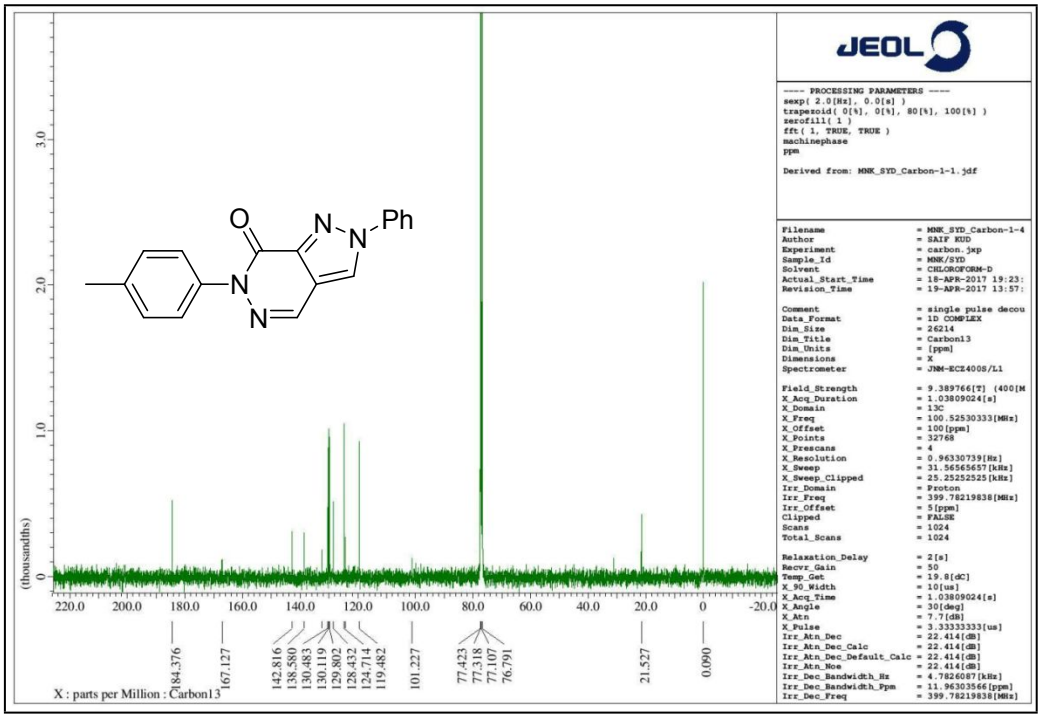


Figure S33: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7j

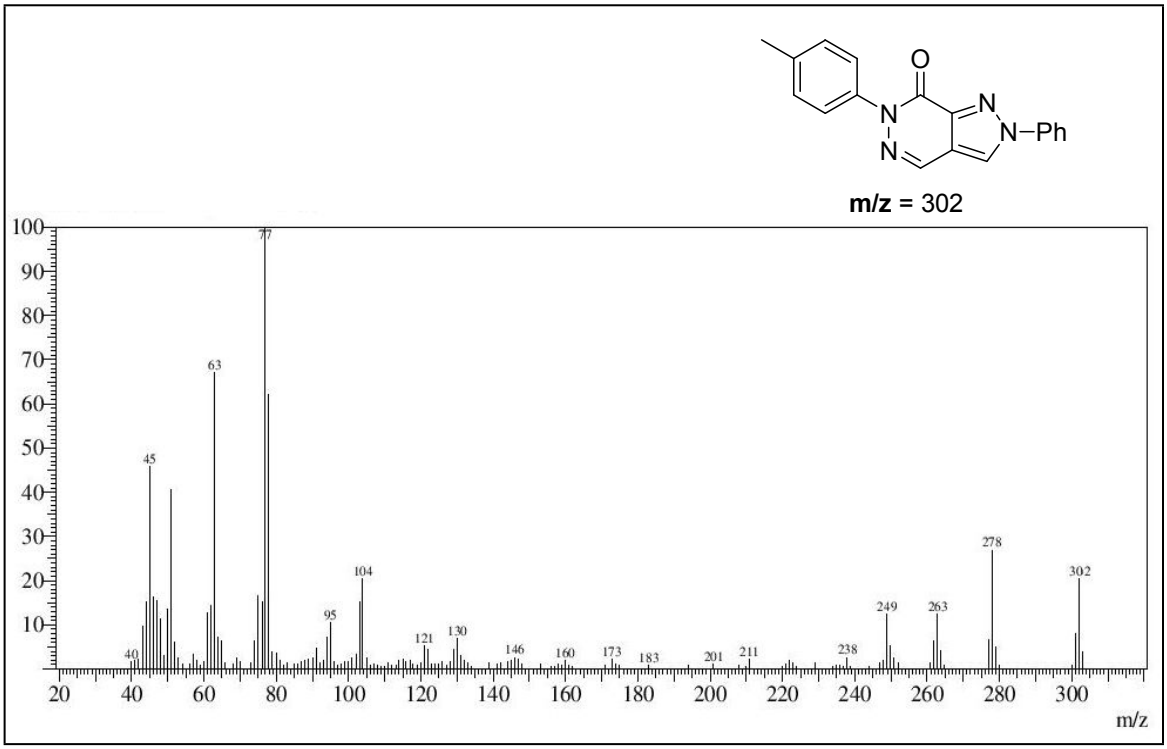


Figure S34: Mass spectrum of compound 7j

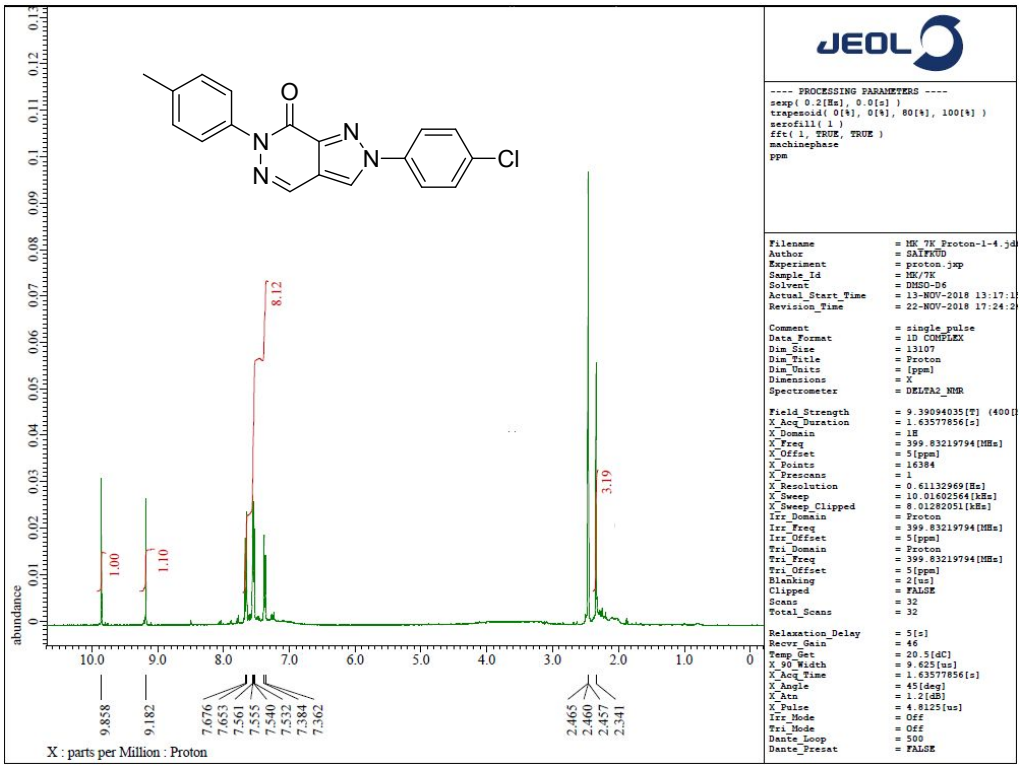


Figure S35: ^{1}H NMR Spectrum (DMSO-d_6) of Compound 7k

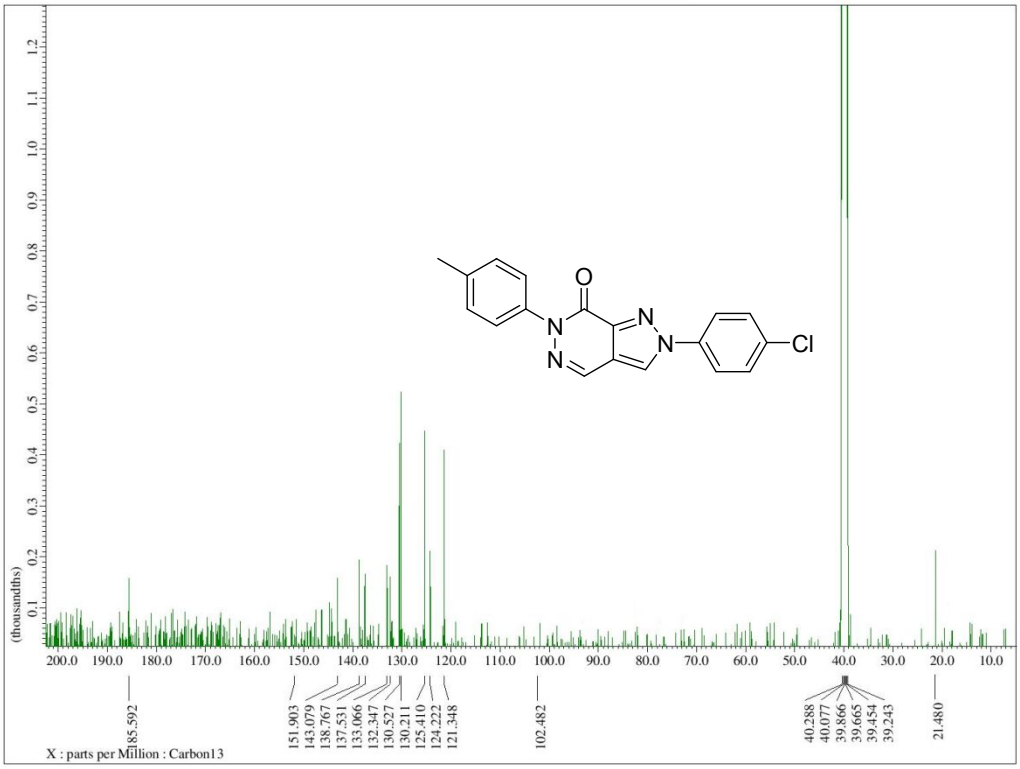


Figure S36: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7k

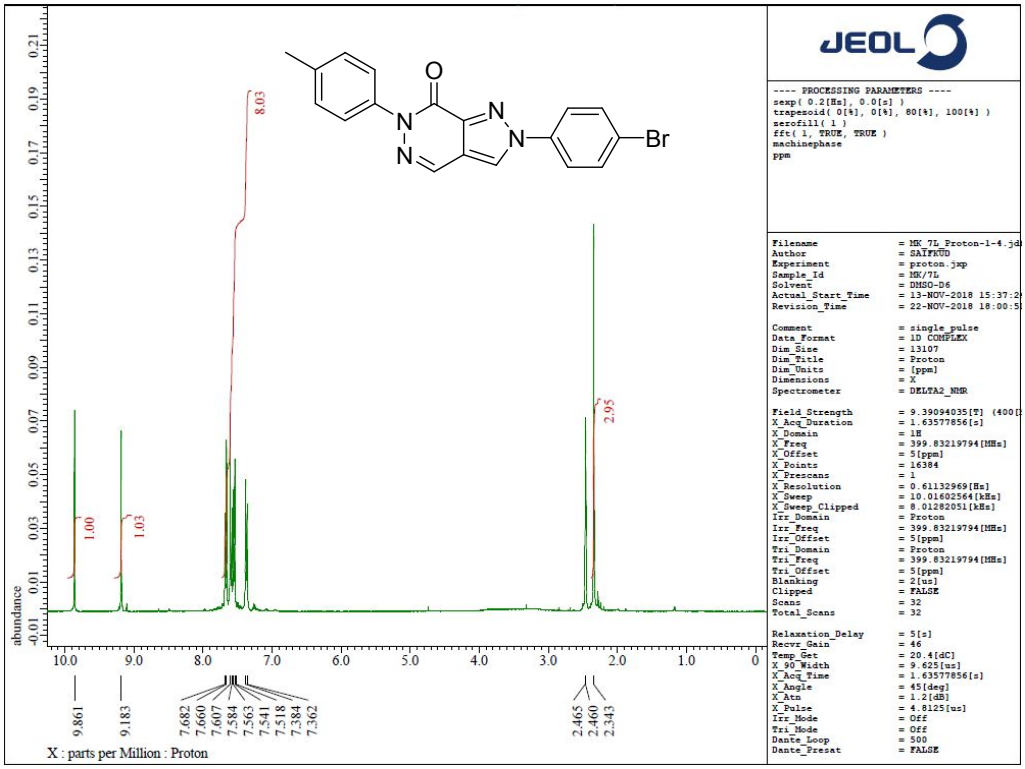


Figure S37: ^{1}H NMR Spectrum (DMSO-d_6) of Compound 7l

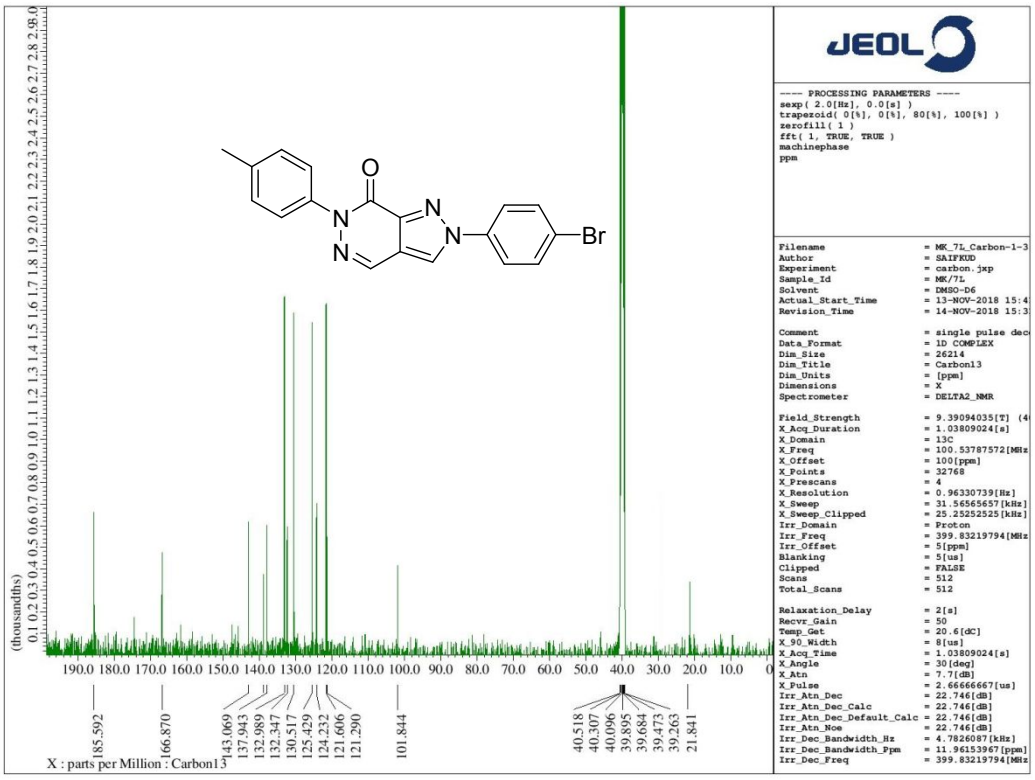


Figure S38: ^{13}C NMR Spectrum (DMSO-d_6) of Compound 7l

X-Ray data for compound 4a and 7d

The X-Ray crystals of compound **4a** and **7d** were obtained from slow evaporation of acetone (solvent) at room temperature and suitable crystal was selected. The crystal structure studies were elucidated by Bruker SMART CCD area-detector with monochromatic Mo-*K*α radiation at room temperature. The raw data frame-works was unified with the SAINT[1] program by using narrow-frame algorithm. The structures were solved by direct methods and refined by the Olex2[2] in anisotropic approximation for all non-hydrogen atoms. The structure was also solved by using charge flipping and refined with the ShelXL refinement package using least squares minimization.[3]

The crystalline nature of the compound is characterized by long range, well defined three dimensional orders. An ORTEP view of the molecule **4a** and also their packing diagram were depicted in **Figure S39**. The crystal data, refinements are represented in **Table 1**. The X-ray structure clearly suggests that it crystallizes in triclinic system with space group P-1. Asymmetric unit of this contains full molecules and there are two such molecules present in the unit cell.

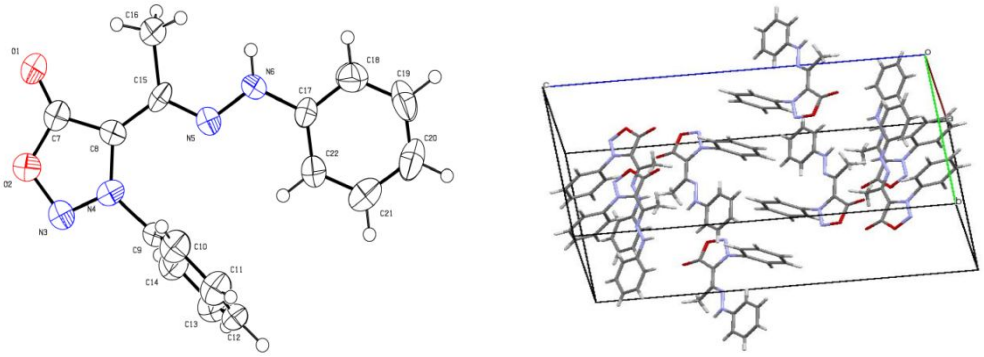


Figure S39. ORTEP and packing structure of compound **4a**

Table S1. Crystallographic parameters

Identification code	**4a**	**7d**
CCDC No.	1861797	1861799
Empirical formula	$C_{16}H_{14}N_4O_2$	$C_{18}H_{14}N_4O_2$
Formula weight	294.31	390.79
Temperature, K	296.15	296
Crystal system	monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions	a = 10.8821(12) Å	a = 7.1518 (5) Å
	b = 12.5865(15) Å	b = 9.4847 (6) Å
	c = 21.550(3) Å	c = 1.5844 (7)Å
	α = 90	α = 86.266 (4)
	β = 97.800(6)	β = 76.396 (3)
	γ = 90	γ = 88.766 (3)
Volume, Å^3	2924.3(6)	762.12 (9)
Z	8	2
Absorption coefficient (μ)	0.092	0.094 mm^{-1}
Density,ρ_{calc}, g cm^{-3}	1.337	1.387
F (000)	1232.0	332.0
Data Collection		
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD
Data collection method	ω – χ Scans	ω – χ Scans
Absorption correction	Multi-Scan	Multi-Scan
Theta range for data collection	4.98 to 50.08	0.977-28.43°
Independent reflections	1987	3850
R(reflections); wR2(reflections)	0.1236, 0.3041	0.0497, 0.1395
GOF on F^2	1.317	1.062

Table S2. Crystal data for compound 4a

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

Atom	*x*	*y*	*z*	U(eq)
N4	4952(4)	2645(4)	6352(2)	52.6(13)
O2	5778(4)	1294(3)	6826.7(18)	74.3(14)
O1	7146(4)	2049(3)	7584.2(18)	74.4(14)
N5	5285(4)	4856(3)	6680.0(18)	51.7(12)
N6	5528(4)	5894(3)	6798.9(19)	56.6(13)
C17	4707(4)	6650(4)	6511(2)	44.8(13)
C8	5794(5)	3070(4)	6821(2)	50.3(14)
N3	4899(5)	1615(4)	6337(2)	74.2(16)
C12	2480(6)	4098(4)	4966(2)	61.4(16)
C15	6049(4)	4152(4)	6945(2)	49.0(14)
C22	3668(5)	6396(4)	6103(2)	55.8(15)
C18	4963(5)	7706(5)	6638(3)	60.5(16)
C9	4100(5)	3183(4)	5881(2)	53.6(15)
C7	6355(5)	2169(5)	7135(3)	61.1(16)
C19	4219(6)	8486(5)	6344(3)	71.4(18)
C20	3189(6)	8229(5)	5933(3)	75.3(19)
C21	2927(6)	7163(5)	5819(3)	71.3(18)
C14	2888(5)	3250(5)	5953(3)	64.5(16)
C10	4530(5)	3558(5)	5350(3)	63.8(16)
C13	2067(6)	3707(5)	5487(3)	74.1(18)
C16	7204(5)	4457(5)	7395(3)	69.2(18)
C11	3686(6)	4026(5)	4891(3)	70.0(17)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$). 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}
N4	51(3)	49(3)	52(3)	1(2)	-14(2)	2(2)
O2	81(3)	46(3)	83(3)	-2(2)	-33(2)	-1(2)
O1	88(3)	47(3)	76(3)	4(2)	-32(2)	11(2)
N5	58(3)	34(3)	58(3)	-0.9(19)	-7(2)	0(2)
N6	60(3)	34(3)	68(3)	-7(2)	-22(2)	-1(2)
C17	47(3)	37(3)	48(3)	7(2)	1(2)	10(2)
C8	53(3)	39(3)	54(3)	-5(2)	-10(2)	-3(2)
N3	85(4)	38(3)	88(3)	-1(2)	-32(3)	-1(3)
C12	74(4)	42(3)	58(3)	4(3)	-27(3)	0(3)
C15	47(3)	48(3)	47(3)	14(2)	-9(2)	13(3)
C22	60(3)	37(3)	68(3)	3(3)	-3(3)	3(3)
C18	52(3)	61(4)	66(4)	-8(3)	-1(3)	-1(3)
C9	56(3)	35(3)	62(3)	-3(2)	-21(3)	-3(2)
C7	64(4)	46(3)	68(4)	6(3)	-13(3)	5(3)
C19	77(4)	32(3)	108(5)	1(3)	23(4)	-3(3)
C20	73(4)	59(4)	92(4)	24(4)	6(4)	25(4)
C21	59(4)	79(5)	71(4)	8(4)	-11(3)	11(3)
C14	54(4)	57(4)	78(4)	10(3)	-5(3)	-1(3)
C10	64(4)	60(4)	64(4)	5(3)	-2(3)	1(3)
C13	59(4)	65(4)	92(4)	7(4)	-14(3)	-4(3)
C16	69(4)	44(4)	84(4)	0(3)	-28(3)	1(3)
C11	78(4)	63(4)	64(4)	10(3)	-6(3)	3(3)

Table S4. Bond Lengths.

Atom	Atom	Length/Å	Atom	Atom	Length/Å

N4	C8	1.377(6)	C8	C7	1.415(8)
N4	N3	1.298(6)	C12	C13	1.356(8)
N4	C9	1.448(6)	C12	C11	1.347(8)
O2	N3	1.384(6)	C15	C16	1.528(7)
O2	C7	1.391(7)	C22	C21	1.351(8)
O1	C7	1.214(6)	C18	C19	1.371(8)
N5	N6	1.351(6)	C9	C14	1.351(7)
N5	C15	1.293(6)	C9	C10	1.378(7)
N6	C17	1.392(6)	C19	C20	1.370(8)
C17	C22	1.373(7)	C20	C21	1.386(9)
C17	C18	1.377(7)	C14	C13	1.377(8)
C8	C15	1.409(7)	C10	C11	1.385(7)

Table S5. Bond Angles.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C8	N4	C9	129.2(4)	C8	C15	C16	119.1(4)
N3	N4	C8	115.5(4)	C21	C22	C17	120.9(6)
N3	N4	C9	115.3(4)	C19	C18	C17	120.5(5)
N3	O2	C7	110.7(4)	C14	C9	N4	119.4(5)
C15	N5	N6	118.7(4)	C14	C9	C10	121.4(5)
N5	N6	C17	118.7(4)	C10	C9	N4	119.1(5)
C22	C17	N6	123.3(5)	O2	C7	C8	105.6(5)
C22	C17	C18	118.6(5)	O1	C7	O2	120.5(5)
C18	C17	N6	118.1(5)	O1	C7	C8	133.9(6)
N4	C8	C15	127.5(5)	C20	C19	C18	120.6(6)

N4	C8	C7	103.9(5)	C19	C20	C21	118.3(6)
C15	C8	C7	128.6(5)	C22	C21	C20	121.0(6)
N4	N3	O2	104.3(4)	C9	C14	C13	119.3(6)
C11	C12	C13	120.9(5)	C9	C10	C11	118.1(5)
N5	C15	C8	118.7(5)	C12	C13	C14	120.0(6)
N5	C15	C16	122.2(5)	C12	C11	C10	120.3(6)

Table S6. Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for

Atom	*x*	*y*	*z*	U(eq)
H6	6176	6084	7048	68
H12	1924	4419	4657	74
H22	3471	5686	6022	67
H18	5646	7891	6925	73
H19	4416	9196	6425	86
H20	2678	8755	5736	90
H21	2231	6974	5541	86
H14	2612	2989	6314	77
H10	5363	3499	5300	77
H13	1229	3749	5529	89
H16A	7567	5086	7245	104
H16B	7794	3886	7419	104
H16C	6977	4590	7803	104
H11	3954	4293	4530	84

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