Electronic Supplementary Information (ESI)

for

Face-to-Face Stacking in Sulfonamide Based Bis-ethylene Bridged Heteroaromatic Dimers

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Contents

1- Single Crystal X-Ray Analysis:

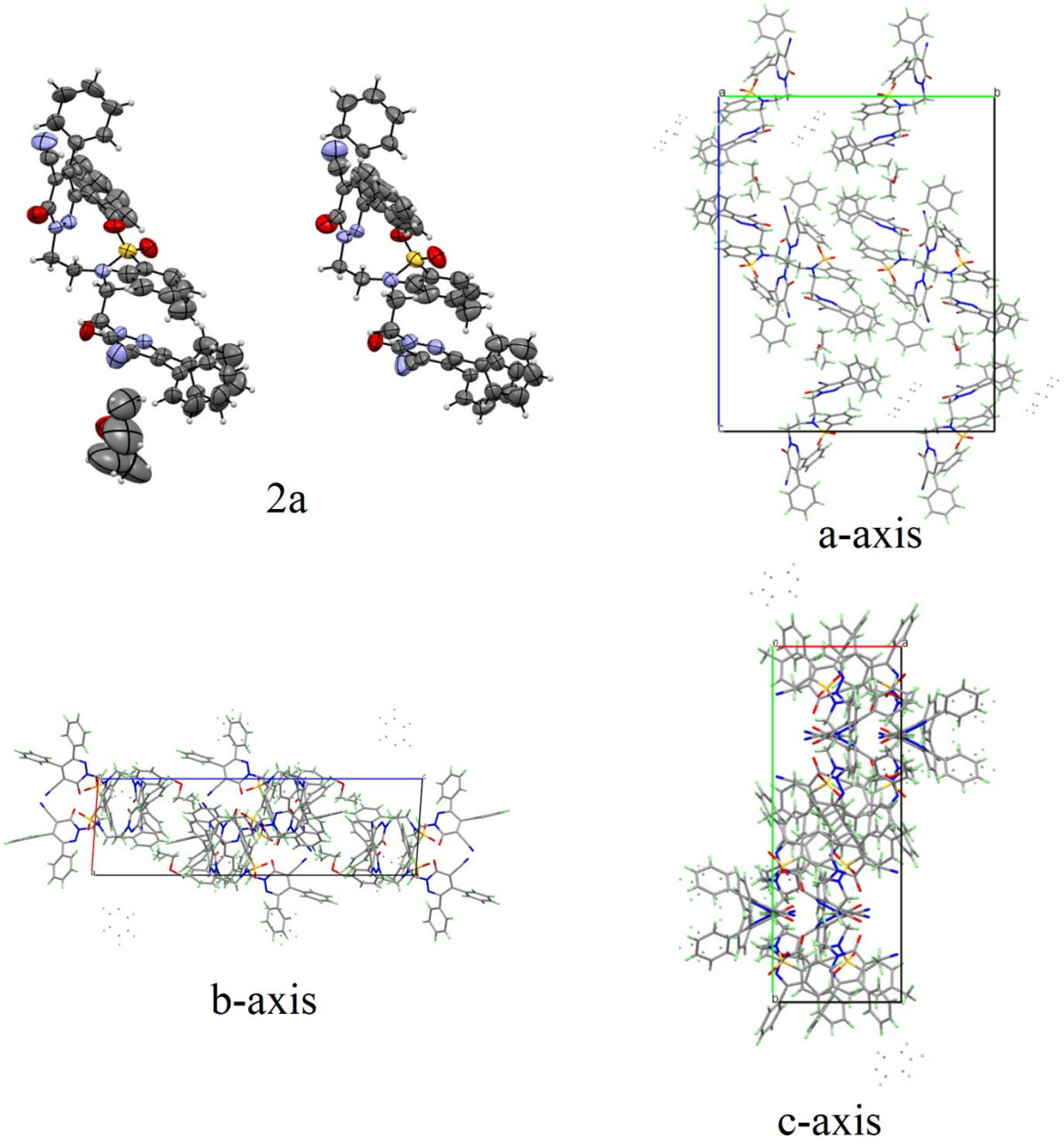


Fig. S1. ORTEP diagram and packing of compound **2a** depicted along a, b and c axis.

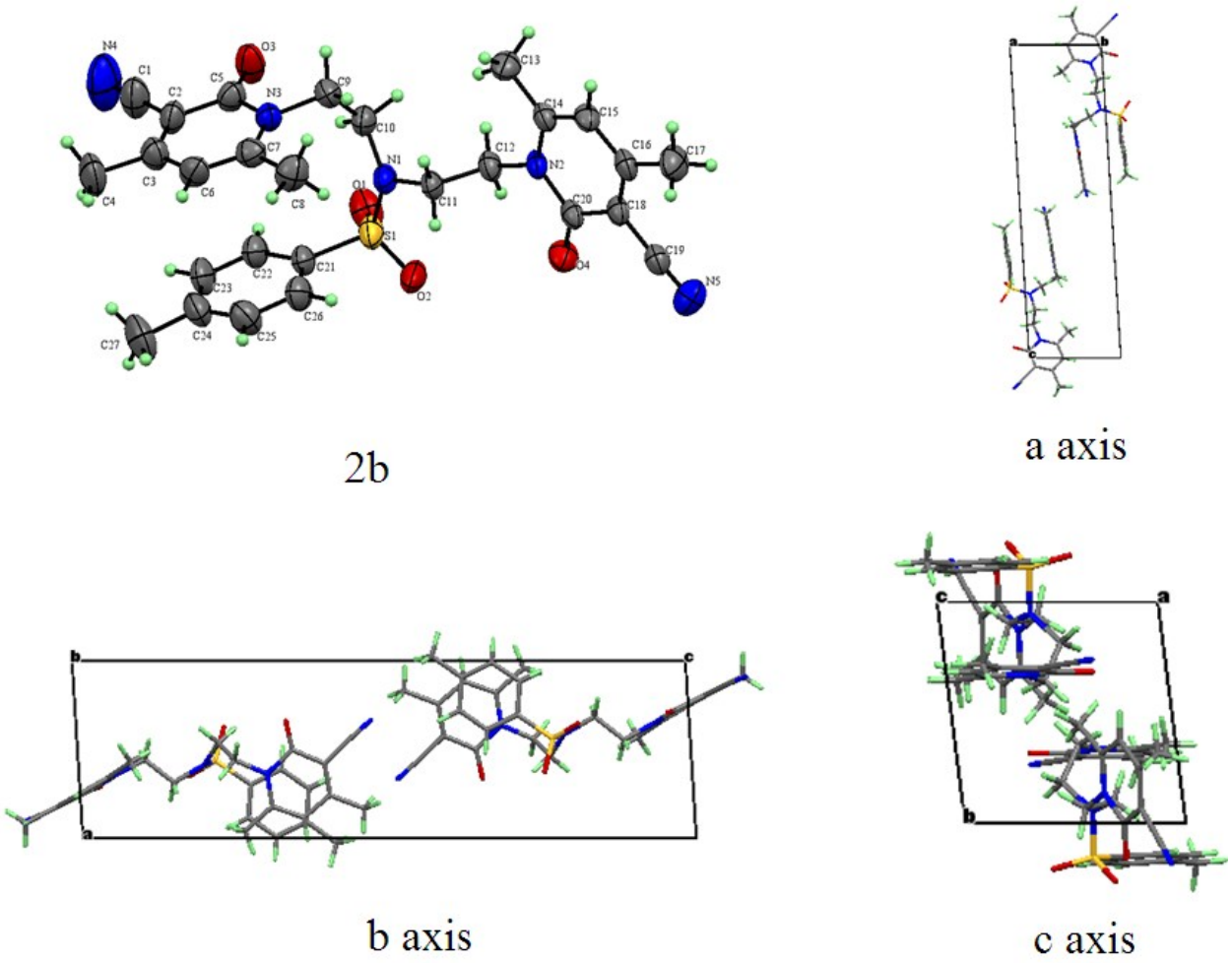


Fig. S2. ORTEP diagram and packing of compound **2b** depicted along a, b and c axis.

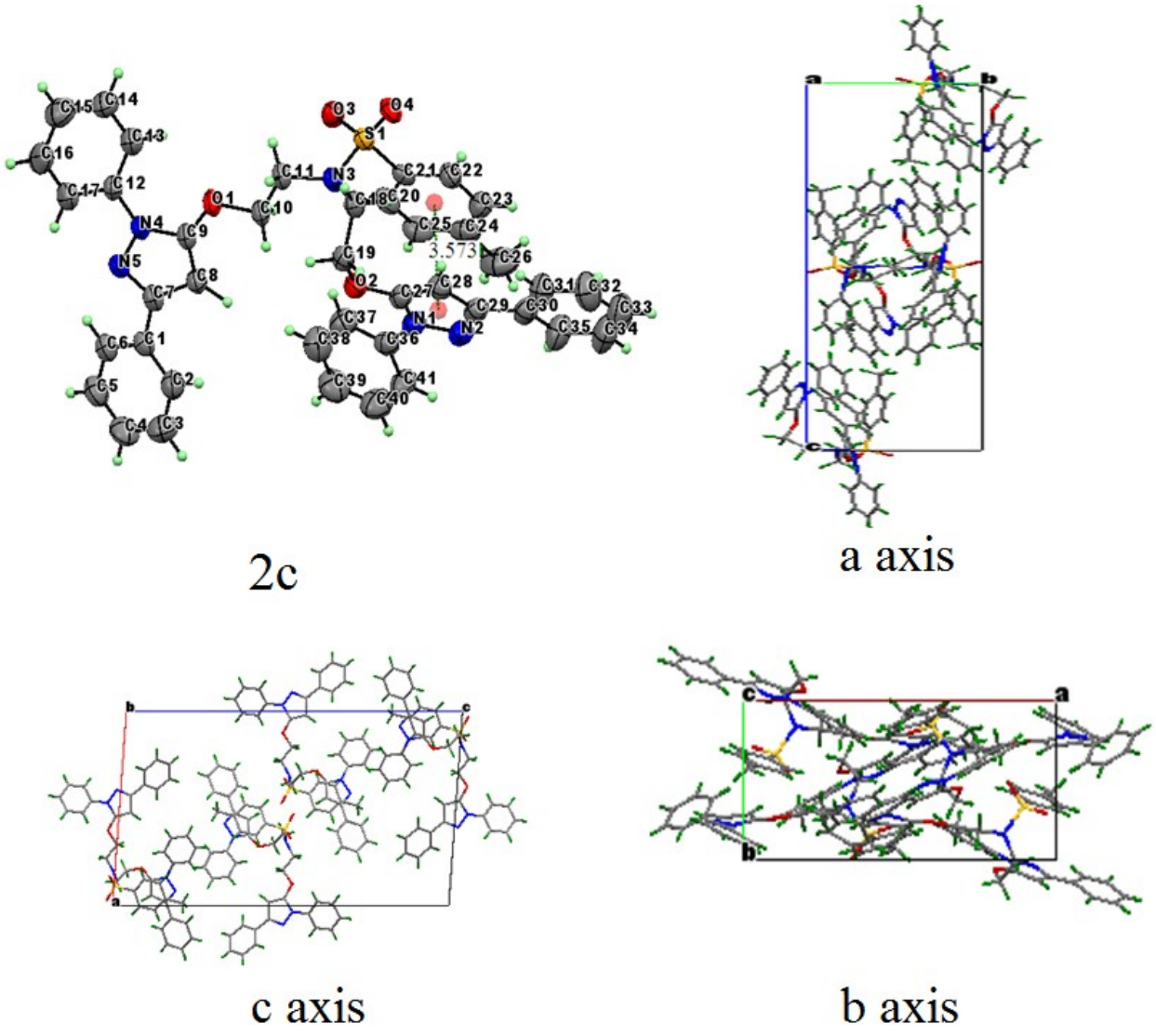


Fig. S3. ORTEP diagram and packing of compound **2c** depicted along a, b and c axis.

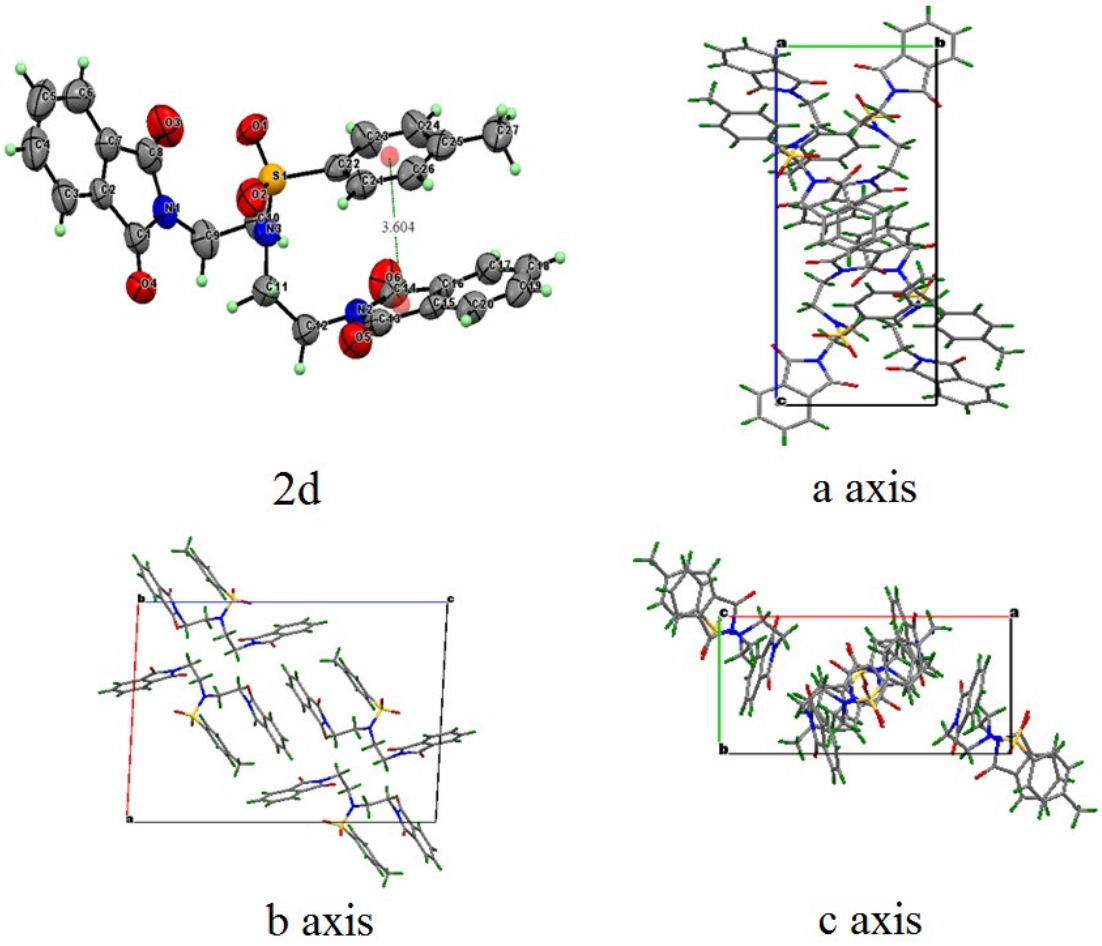


Fig. S4. ORTEP diagram and packing of compound **2d** depicted along a, b and c axis.

Responses to the Validation Reply Form

_vrf_RFACG01_2a;

PROBLEM: The value of the R factor is > 0.10

RESPONSE: Crystals diffracted extremely weakly. Multiple attempts were made to grow better diffracting crystals. Data was collected many times but all results were consistent with the model in this report. However, all yielded serious problems due to weak diffraction and disorder in the atom positions. The high weighted R factor results from the weak diffraction, and the inclusion of reflections that are essentially unobserved.

_vrf_PLAT082_2a;

PROBLEM: High R1 Value ..... 0.11 Report

RESPONSE: Crystals diffracted extremely weakly. Multiple attempts were made to grow better diffracting crystals. Data was collected many times but all results were consistent with the model in this report. However, all yielded serious problems due to weak diffraction and disorder in the atom positions. The high weighted R factor results from the weak diffraction, and the inclusion of reflections that are essentially unobserved.

_vrf_PLAT094_2a;
PROBLEM: Ratio of Maximum / Minimum Residual Density .... 2.54 Report

RESPONSE: These alerts are generated because there is a large amount of disorder in the structure.

_vrf_PLAT220_2a;
PROBLEM: Large Non-Solvent C Ueq(max)/Ueq(min) Range 3.4 Ratio

RESPONSE: C-atoms were introduced in calculated positions and refined on a riding model. Uiso(C) was calculated from U(ave) of the atom.

_vrf_PLAT234_2a;
PROBLEM: Large Hirshfeld Difference N5 -- C28 .. 0.17 Ang.

RESPONSE: RIGU restraints were applied to atoms in the disordered chains. Several of the atoms were still not ideally shaped, however, this does not indicate an incorrect atom-type assignment.

_vrf_PLAT230_2b
PROBLEM: Hirshfeld Test Diff for S1 -- O1 .. 7.5 su

RESPONSE: RIGU restraints were applied to atoms in the disordered chains. Several of the atoms were still not ideally shaped, however, this does not indicate an incorrect atom-type assignment.

Table-S1: Intermolecular interactions in **2a, 2b, 2c** and **2d**.

Crystals	Interaction	d(Å)	D(Å)	θ(d)	Symmetry Code
2a					
	C67-H67···N4	0.93	2.691	135.0	-x,-1/2+y,1/2-z
	C17A-H17A···O2	0.93	2.510	133.6	-1+x,y,z
	C72-H72A···O3	0.970	2.334	146.3	-x,1-y,1-z
	C27-H27B···O7	0.971	2.345	142.2	1-x,1-y,1-z
	C91-H91C···N14	0.96	2.55	148	2-x,1/2+y,1.5-z
	C62A-H62A···O5	0.93	2.480	133.2	-1+x,y,z
	C82-H82···O5	0.93	2.560	149.2	-x,2-y,1-z
	C94-H94B···N7	0.96	2.69	158	-1+x,y,z
	C92-H92B···N12	0.98	2.722	145	1-x,1/2+y,1.5-z
	C35-H35···π (Centroid of pyridazinone phenyl)	0.93	3.514	143.36	
	C21-H21···π (Centroid of pyridazinone phenyl)	0.93	3.659	128.51	
	C16A-H16A···π (Centroid of PTS ring)	0.93	3.252	136.84	
	C86-H86···π (Centroid of pyridazinone phenyl)	0.93	3.686	159.93	
	C63A-H63A···π (Centroid of PTS ring)	0.93	3.057	136.72	
2b					
	C11-H11A···N5	0.970	2.679	114.1	-x,-y,2-z
	C17-H17A··· N5	0.960	2.742	178.2	x,-1+y,z
	C15-H15···O4	0.931	2.707	145.2	x,1+y,z
	C13-H13B···O2	0.960	2.448	127.7	x,1+y,z
	C25-H25···O1	0.930	2.550	140.7	-1+x,y,z
	C6-H6···O3	0.931	2.431	160.2	-1+x,y,z
	C8-H8A···O3	0.960	2.650	157.1	-1+x,y,z
	C27-H27C···π (Centroid of pyridone ring)	0.960	3.759	120.78	
	C8C-H8C···π (Centroid of PTS ring)	0.960	3.421	121.36	
	C12-H12A···π (Centroid of pyridone ring)	0.970	3.461	114.87	
2c					
	π ···π (Centroid of five member ring of pyrazolone)		3.943		
	C28-H28···O4	0.928	2.454	173.2	1-x,-y,1-z
	C19H19A···O3	0.970	2.630	128.8	x,-1+y,z
	C6H6···O3	0.931	2.555	132.0	2-x,-1-y,1-z
	C26-H26B···π (Centroid of pyrazolone phenyl)	0.961	3.078	157.71	
	C16-H16···π (Centroid of pyrazolone phenyl)	0.930	3.014	122.30	
	C049-H049···π (Centroid of pyrazolone phenyl)	0.930	3.165	132.59	
	C11-H1B···π (Centroid of pyrazolone phenyl)	0.969	2.859	163.94	
	C2-H2···π (Centroid of pyrazolone phenyl)	0.930	3.356	146.07	
2d					
	C24-H24···O2	0.930	2.691	138.2	-1/2+x,1.5-y,-1/2+z
	C19-H19···O3	0.930	2.662	129.1	-1/2+x,-1/2-y,-1/2+z
	C3-H3···O3	0.930	2.579	130.0	x,-1+y,z
	C17-H17···O5	0.930	2.470	119.8	x,-1+y,z
	C20-H20···π (Centroid of PTS phenyl)	0.930	3.144	123.86	
	C19-H19··· π (Centroid of Pthalimide ring)	0.930	3.278	119.12	119.12
	C27-H27B···π (Centroid of PTS phenyl)	0.959	3.458	124.49	124.49

2. Computational studies:

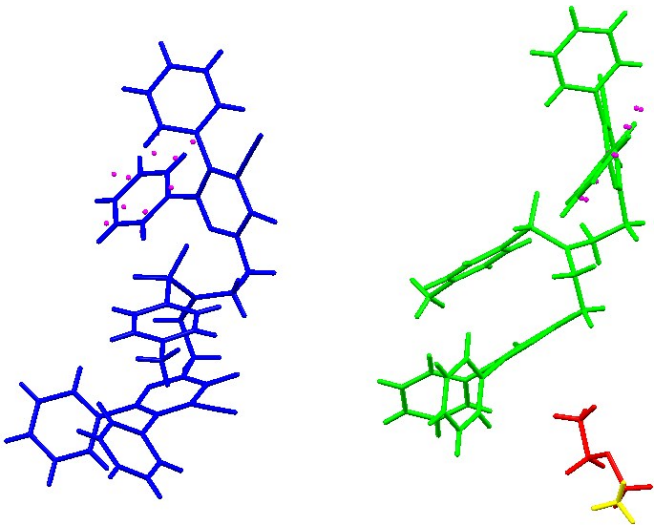


Fig. S5 Crystal structure of compound **2a** showing two molecules in asymmetric unit.

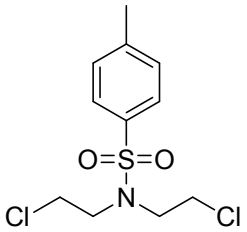
Table S2: Intramolecular interaction and geometry parameters of compounds **2a**, **2b**, **2c** and **2d** calculated at ωB97X-D /6-31G (d, p) level of theory compared with crystal structures.

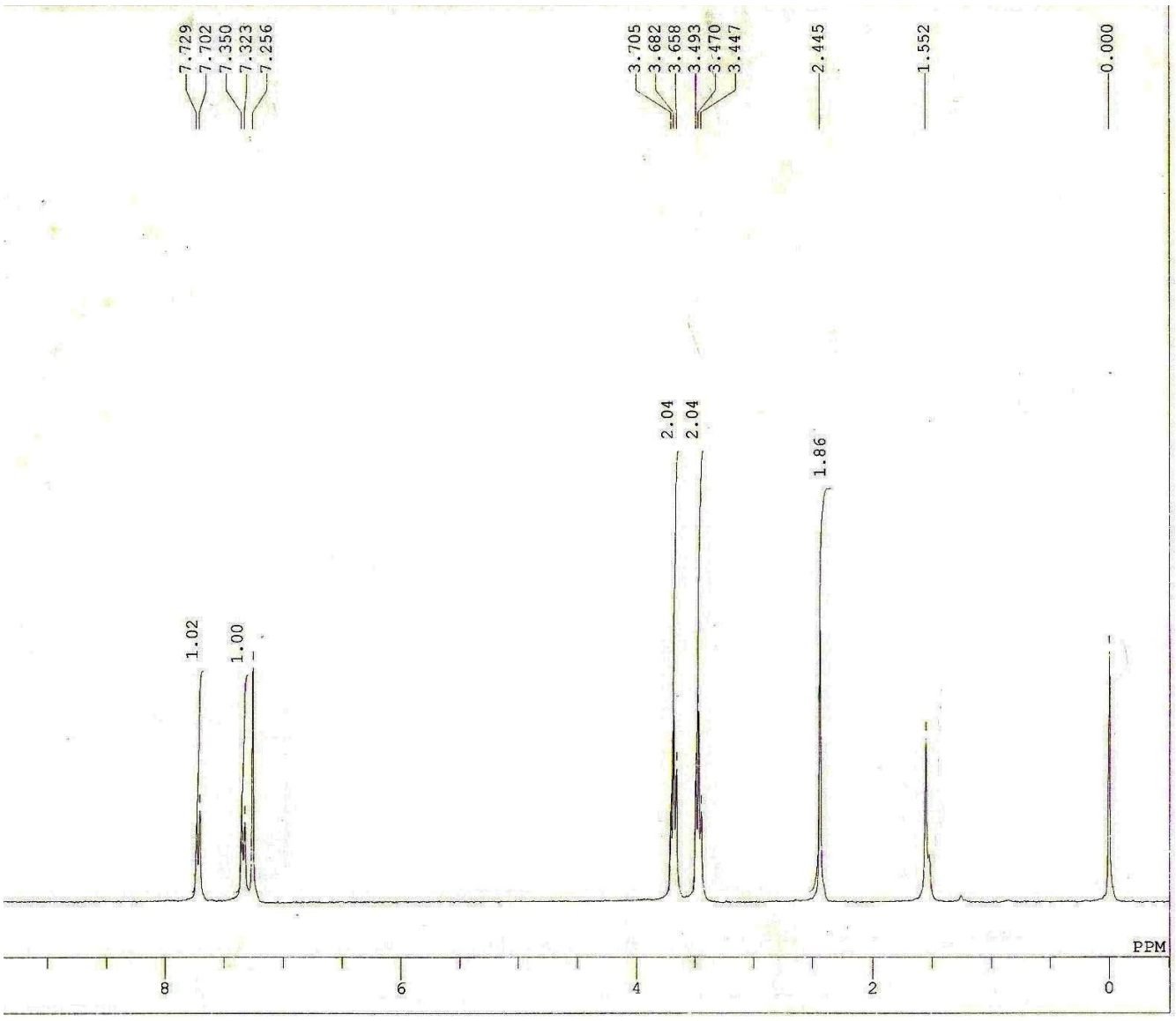
S.N.		Crystal			ωB97X-D		
	Interaction	**d(Å)**	**D(Å)**	**θ(d)**	**d(Å)**	**D(Å)**	**θ(d)**
2a (Blue)	π···π (Centroid of PTS phenyl and Centroid of Pyridazinone)	-	3.754	-	-	3.614	-
	C53-H53B···O7	0.969	2.655	114.3	1.091	2.764	109.41
	C64A-H64A···O6	0.93	2.967	165.7	1.084	2.400	152.24
	C53-H53A···O8	0.97	2.466	141.9	1.095	2.572	133.96
	C72-H72B···N12	0.968	2.656	69.8	1.090	2.624	95.73
	C50-H50···N14	0.93	3.11	106.5	1.086	2.956	108.98
2a (Green)	π···π(Centroid of PTS phenyl and Centroid of Pyridazinone)		3.789		-	3.614	-
	C8-H8A···O3	0.971	2.726	112.9	1.091	2.764	109.41
	C8-H8B···O4	0.971	2.365	142.9	1.084	2.400	152.24
	C15A-H15A···O1	0.93	2.840	163.5	1.095	2.572	133.96
	C5-H5···N7	0.931	3.15	103.5	1.090	2.624	95.73
	C27-H27A···N6	0.969	2.821	96.5	1.086	2.956	108.98
2b	π···π (Centroid of PTS phenyl and Centroid of Pyridone)	-	3.734	-	-	3.587	-
	C10-H10A···O3	0.969	2.5	114.1	1.090	2.354	114.63
	C12-H12A···O2	0.970	2.827	111.1	1.087	2.900	106.75
	C11-H11A···O4	0.970	3.094	103.13	1.088	2.225	116.90
	C11-H11B···N2	0.970	2.630	71.1	1.094	2.480	121.65
	C12-H12A···N1	0.970	2.714	65.4	-	-	-

	C12-H12B···N1	0.970	2.607	71.3	-	-	-
	C10-H10B···π (Pyridone centroid)	-	-	-	1.094	2.544	152.20
2c	π···π (Centroid of PTS phenyl and Centroid of Pyrazolone)	-	3.572	-	-	3.519	-
	C10-H10B···O2	0.970	2.843	124.5	1.094	2.511	131.94
	C26 –H26C···N2	0.960	2.963	122.8	1.093	2.773	123.33
	C032-H032···O2	0.929	2.334	116.1	1.082	2.430	107.86
	C13-H13···O1	0.929	2.358	112.9	1.081	2.374	109.79
	C17-H17···N5	0.930	2.572	98.2	1.083	2.506	95.32
	C6-H6···N5	0.931	2.610	97.9	1.085	2.527	97.09
	C35-H35···N2	0.930	2.546	99.9	1.085	2.593	94.63
	C042-H042···N2	0.930	2.498	99.7	1.084	2.563	93.51
2d	π···π (Centroid of PTS phenyl and Centroid of Pthalimide heteroaromatic)	-	3.605	-	-	3.574	-
	C27-H27C··· π (phthalimide centroide)	0.960	3.102	126.60	1.092	3.491	98.67
	C10-H10A···O6	0.970	2.832	141.9	1.092	2.842	111.35
	C11-H11B···O5	0.969	2.687	117.9	1.094	2.443	132.05
	C10-H10B···O3	0.970	2.914	111.4	1.090	2.865	110.27
	C11-H11A···O4	0.970	2.432	145.3	1.096	2.350	137.85

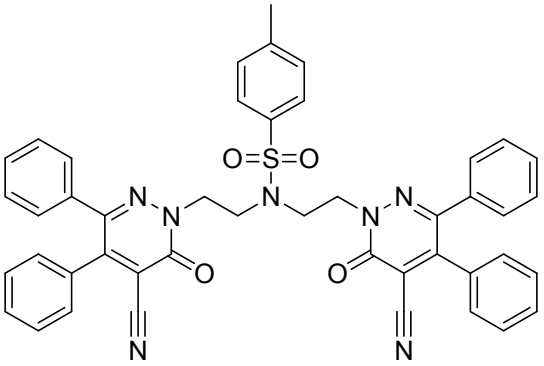
3-Copies of ^{1}H-NMR and ^{13}C-NMR spectra:

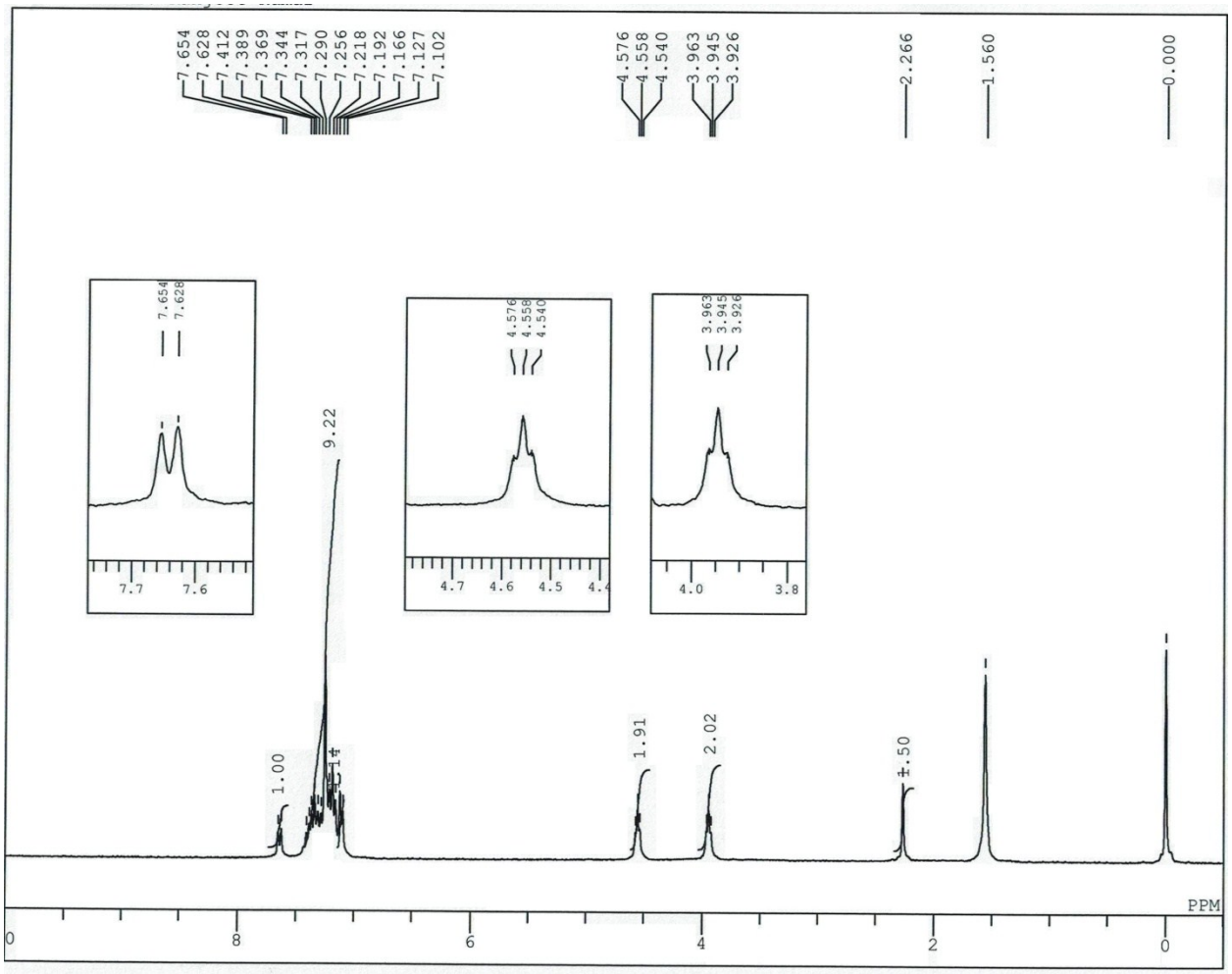
^{1}H-NMR spectra of N,N-bis(2-chloroethyl)-4-methylbenzenesulfonamide (1):

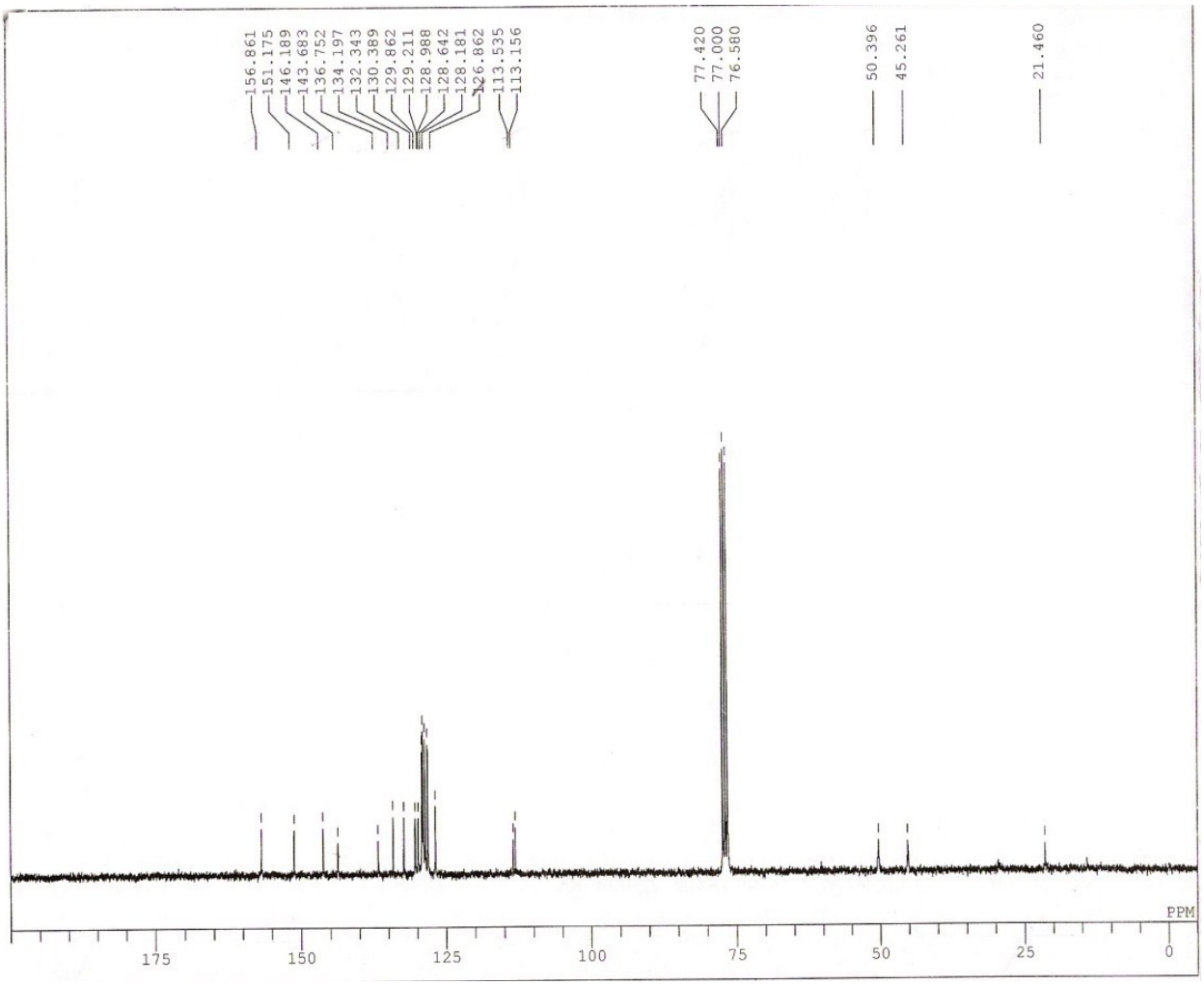




^{1}H-NMR and ^{13}C-NMR spectra of N,N-bis(2-(5-cyano-6-oxo-3,4-diphenylpyridazin-1(6H)-yl)ethyl)-4-methylbenzenesulfonamide (2a):



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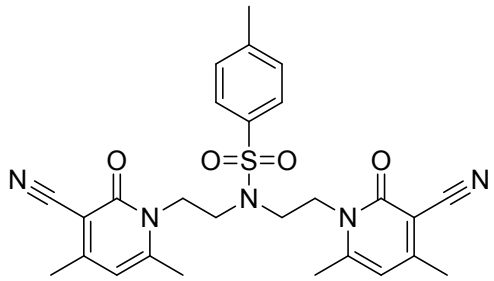
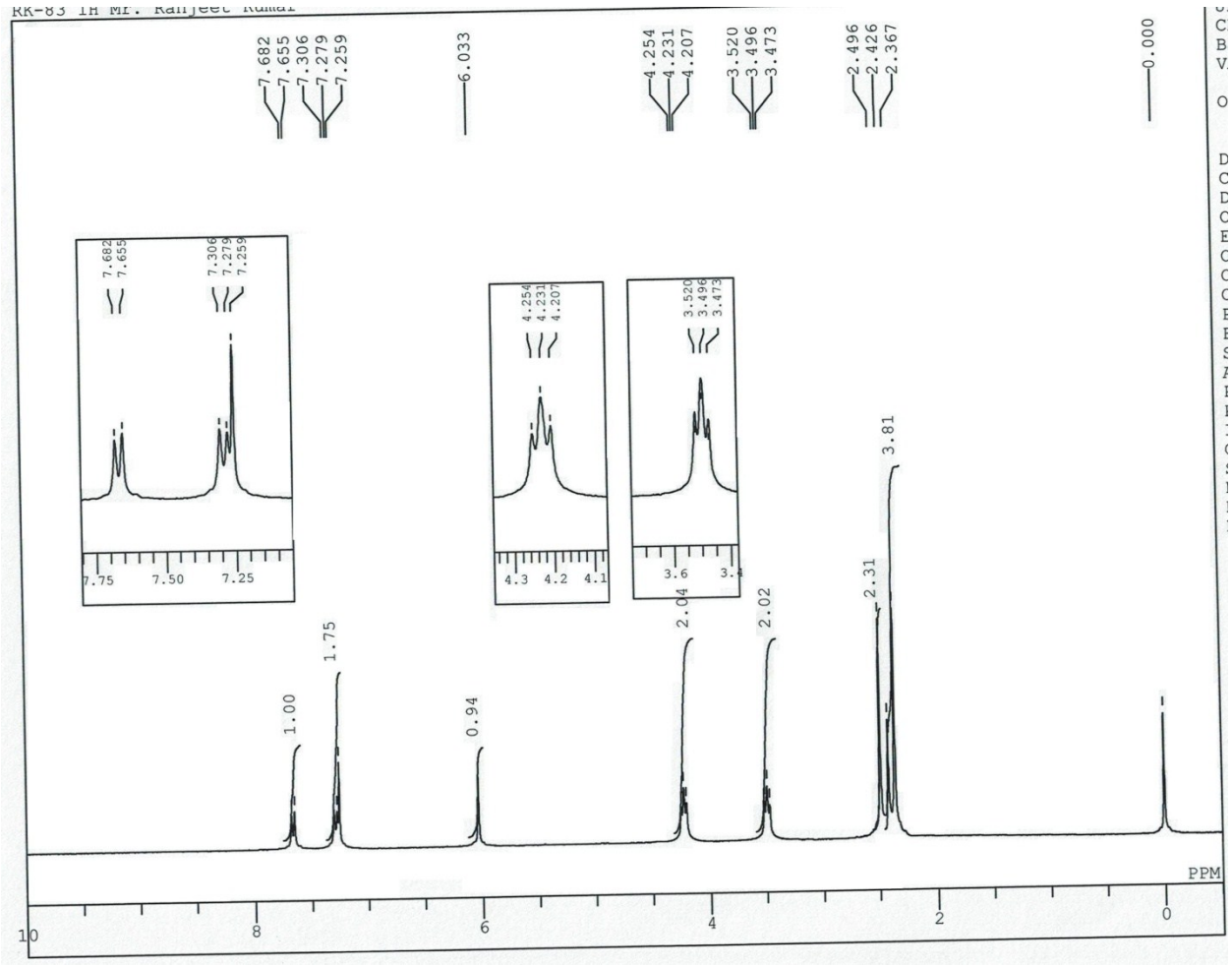
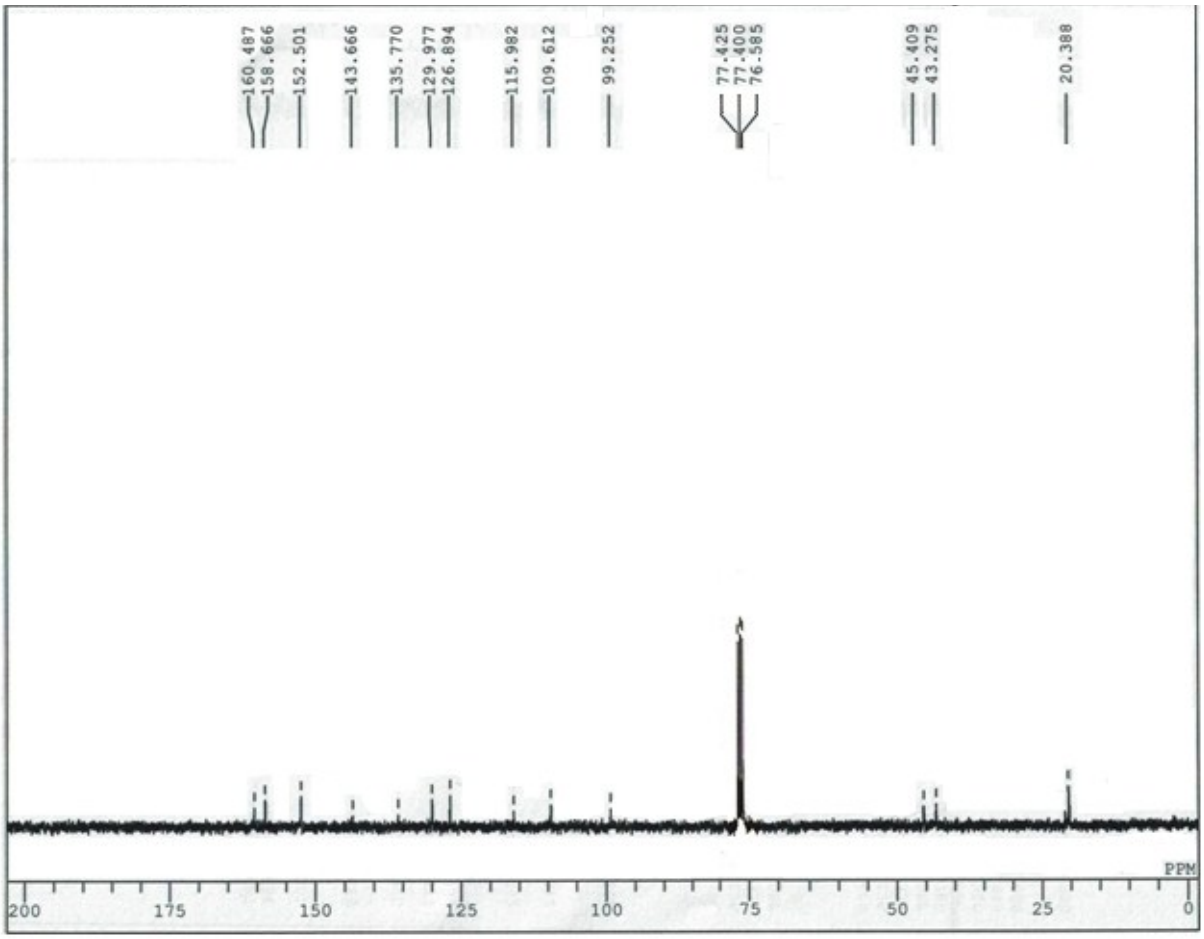
^{1}H-NMR and ^{13}C-NMR spectra of N,N-bis(2-(3-cyano-4,6-dimethyl-2-oxopyridin-1(2H)-yl)ethyl)-4-methylbenzenesulfonamide (2b):



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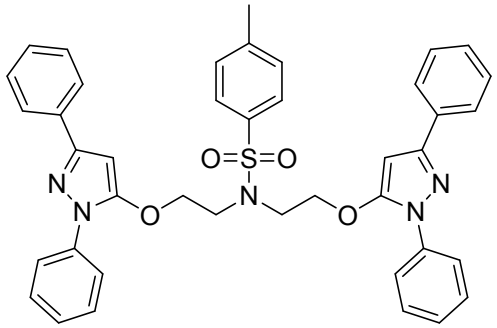
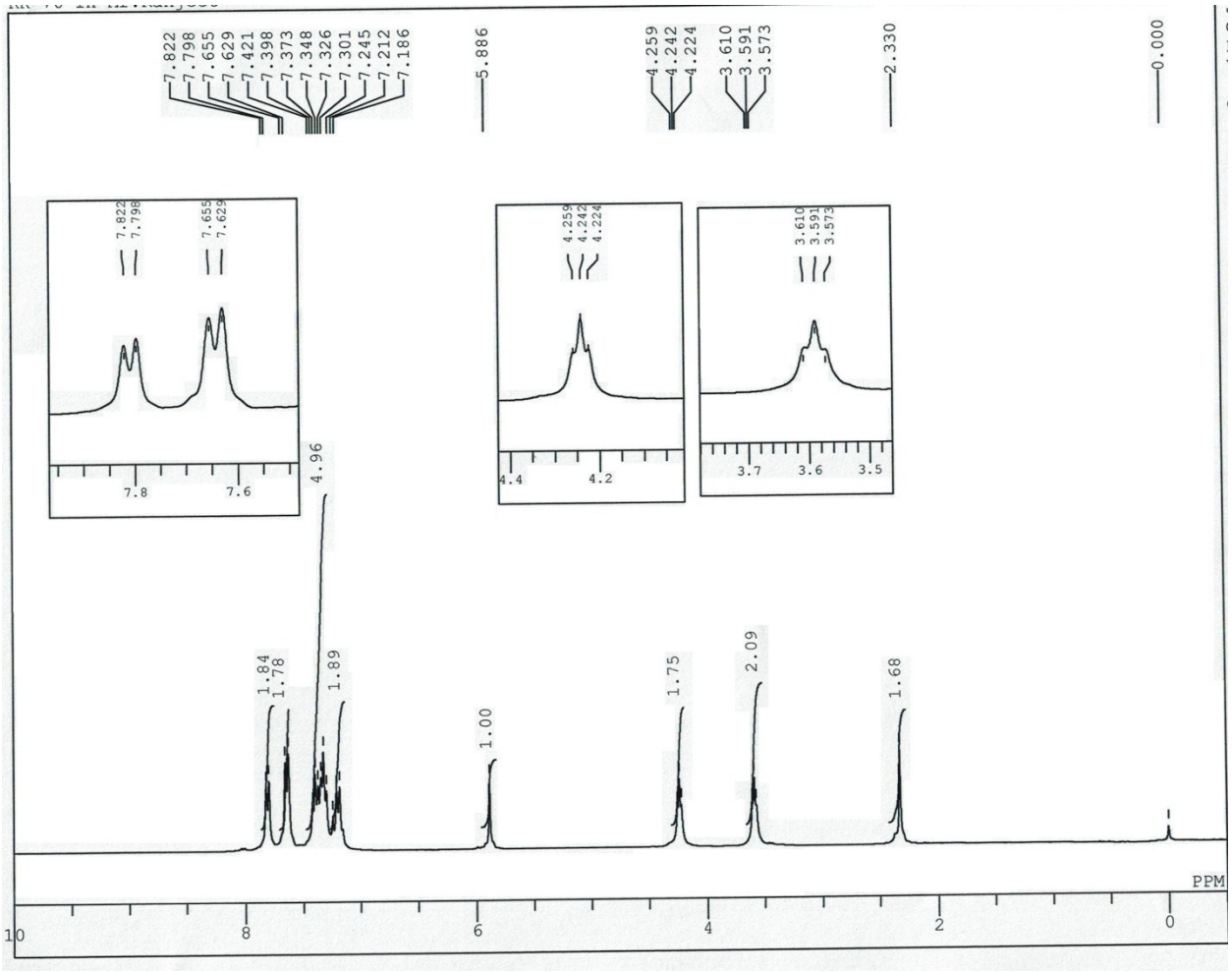
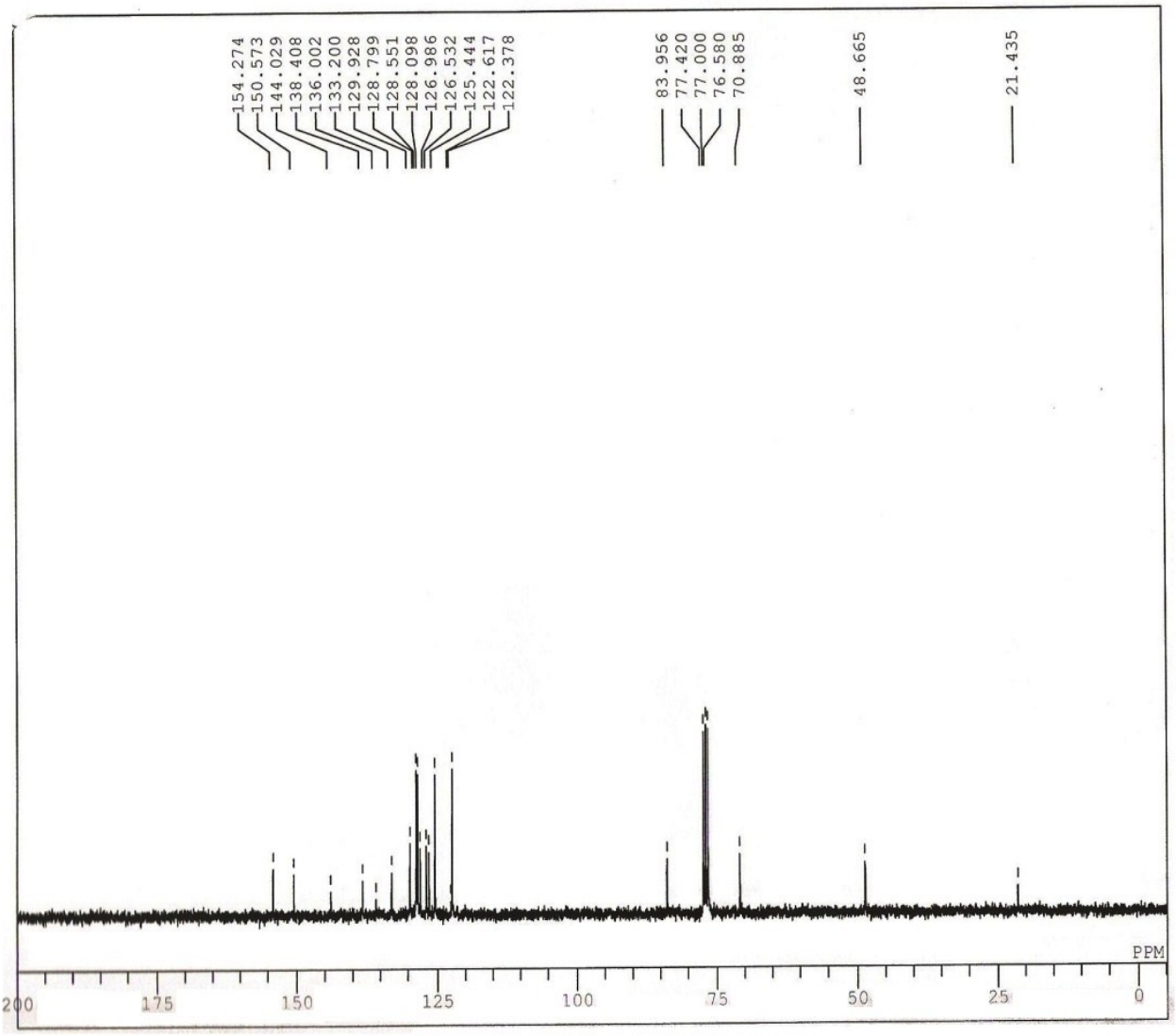
^{1}H-NMR and ^{13}C-NMR spectra of N,N-bis(2-((1,3-diphenyl-1H-pyrazol-5-yl)oxy)ethyl)-4-methylbenzenesulfonamide (2c):



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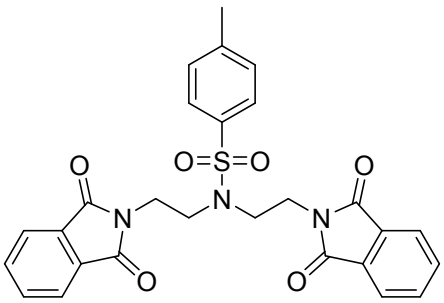
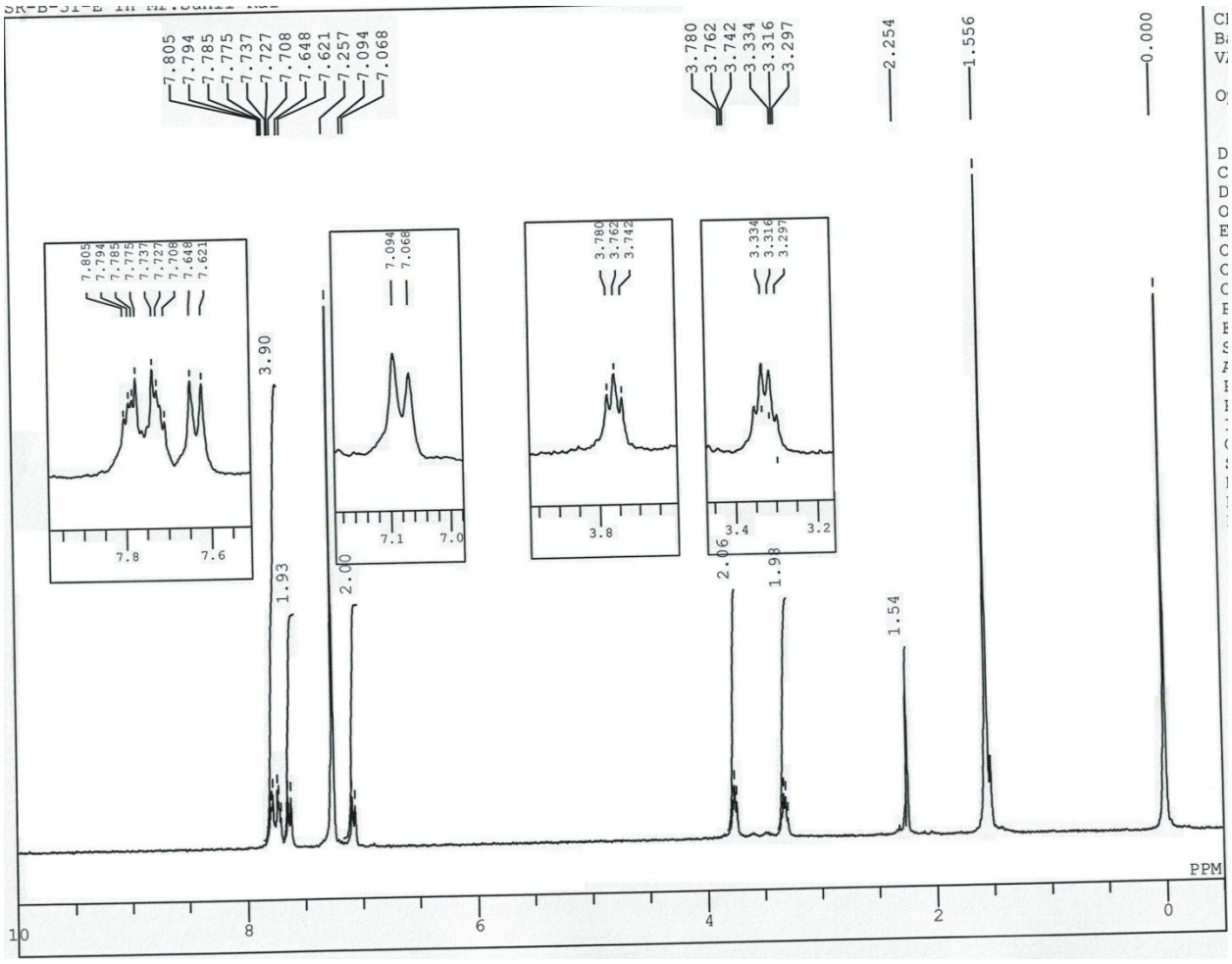
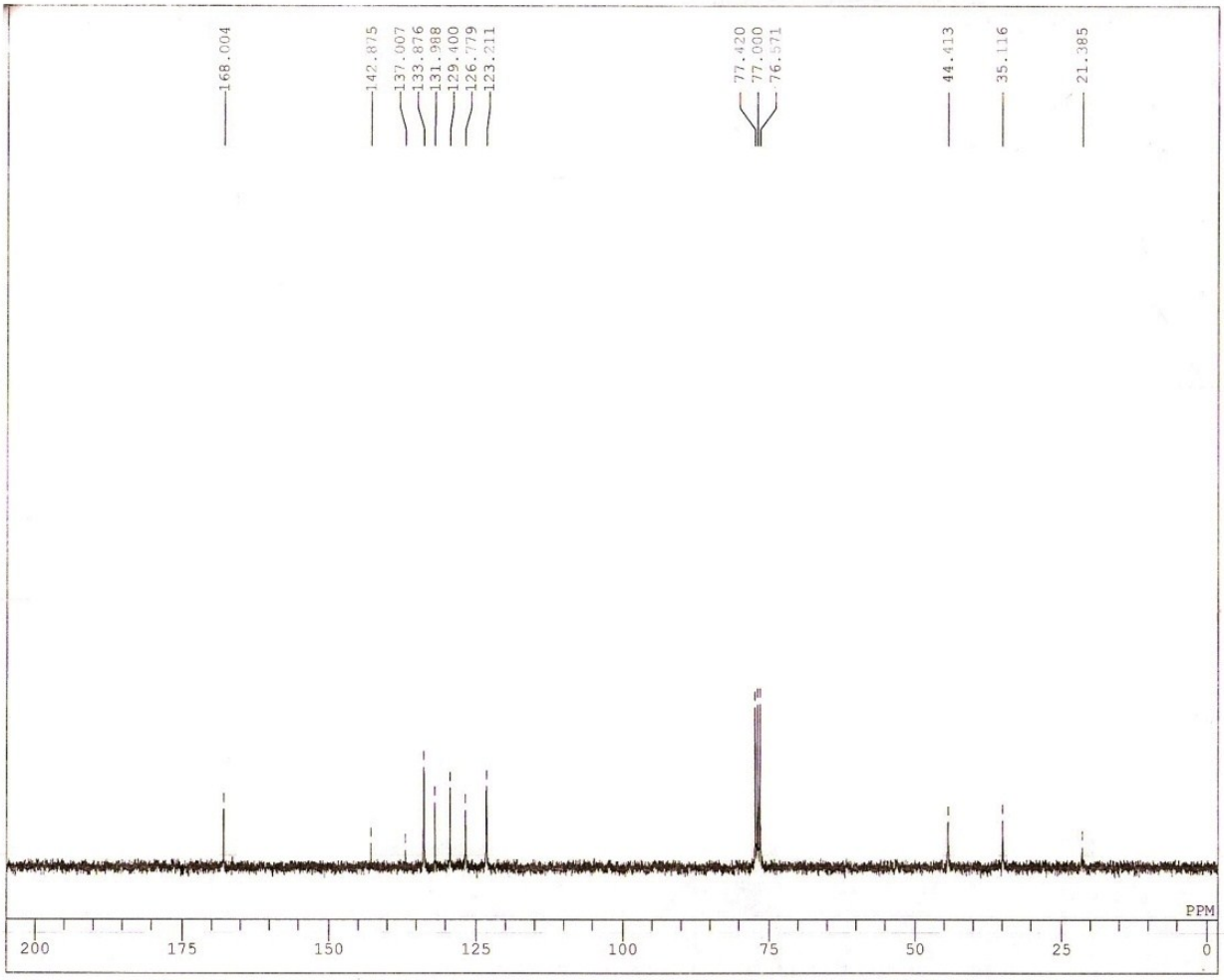
^{1}H-NMR and ^{13}C-NMR spectra of N,N-bis(2-(1,3-dioxoisoindolin-2-yl)ethyl)-4-methylbenzenesulfonamide (2d):



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