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Supplementary Materials

X-ray Single Crystal Structure, Tautomerism Aspect, DFT, NBO, and Hirshfeld Surface Analysis of a New Schiff Bases Based on 4-Amino-5-Indol-2-yl-1,2,4-Triazole-3-Thione Hybrid

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X-Ray Structure Determinations

The crystal of **3** and **4** were immersed in cryo-oil, mounted in a loop, and measured at a temperature of 120 K. The X-ray diffraction data were collected on a Rigaku Oxford Diffraction Supernova diffractometer using Cu Kα radiation. The data sets were collected by ϕ and ω omega scans with κ-offset on a κ-geometry goniometer using micro-focus sealed X-ray tube and Atlas area detector. The *CrysAlisPr* [1] software package was used for cell refinements and data reductions. A Gaussian **3**) or a multi-scan **4** absorption correction (*CrysAlisPro* [1]) was applied to the intensities before structure solution. The structure was solved by intrinsic phasing (SHELXT [2]) method. Structural refinements were carried out using *SHELXL* [3] software with SHELXLE [4] graphical user interface. In **3,** the NH and OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atoms with U_{iso} = 1.5 U_{eq}(parent atom). In **4,** the NH hydrogen atoms were located from the difference Fourier map and refined isotropically. All other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95–0.98Å and U_{iso} = 1.2-1.5·U_{eq}(parent atom).

Table S1. The calculated geometric parameters of **3**and**4**[a].

Parameter	Calc	Exp	Err.[b]	%Err.[c]	Parameter	Calc	Exp	Err.[b]	%Err.[c]
	3					**4**			
R(1-14)	1.907	1.905	0.00	0.10	R(1-9)	1.755	1.736	0.02	1.09
R(2-22)	1.673	1.685	-0.01	-0.71	R(2-12)	1.751	1.735	0.02	0.92
R(3-4)	1.377	1.387	-0.01	-0.72	R(3-20)	1.671	1.676	0.00	-0.30
R(3-20)	1.289	1.276	0.01	1.02	R(4-5)	1.373	1.387	-0.01	-1.01
R(4-22)	1.404	1.386	0.02	1.30	R(4-18)	1.289	1.264	0.02	1.98
R(4-23)	1.394	1.388	0.01	0.43	R(5-20)	1.405	1.388	0.02	1.22
R(5-7)	1.364	1.377	-0.01	-0.94	R(5-21)	1.395	1.384	0.01	0.79
R(5-22)	1.358	1.331	0.027	2.03	R(6-7)	1.364	1.374	-0.01	-0.73
R(7-23)	1.312	1.298	0.01	1.08	R(6-20)	1.358	1.339	0.019	1.42
R(8-24)	1.389	1.376	0.01	0.94	R(7-21)	1.311	1.308	0.00	0.23

R(8-36)	1.373	1.366	0.01	0.51	R(8-22)	1.389	1.384	0.01	0.36
R(10-12)	1.389	1.374	0.01	1.09	R(8-34)	1.373	1.371	0.00	0.15
R(10-19)	1.407	1.402	0.01	0.36	R(9-10)	1.394	1.381	0.01	0.94
R(12-14)	1.398	1.395	0.00	0.22	R(9-17)	1.408	1.399	0.01	0.64
R(14-15)	1.393	1.375	0.02	1.31	R(10-12)	1.392	1.385	0.01	0.51
R(15-17)	1.393	1.397	0.00	-0.29	R(12-13)	1.397	1.386	0.01	0.79
R(17-19)	1.404	1.395	0.01	0.65	R(13-15)	1.387	1.380	0.01	0.51
R(19-20)	1.464	1.454	0.01	0.69	R(15-17)	1.408	1.402	0.01	0.43
R(23-24)	1.445	1.455	-0.01	-0.69	R(17-18)	1.466	1.463	0.00	0.21
R(24-25)	1.381	1.370	0.01	0.80	R(21-22)	1.445	1.450	0.00	-0.34
R(25-27)	1.430	1.423	0.01	0.49	R(22-23)	1.381	1.372	0.01	0.66
R(27-28)	1.408	1.413	-0.01	-0.35	R(23-25)	1.430	1.428	0.00	0.14
R(27-36)	1.425	1.418	0.01	0.49	R(25-26)	1.408	1.410	0.00	-0.14
R(28-30)	1.386	1.383	0.00	0.22	R(25-34)	1.425	1.410	0.02	1.06
R(30-32)	1.413	1.407	0.01	0.43	R(26-28)	1.386	1.380	0.01	0.43
R(32-34)	1.388	1.375	0.01	0.95	R(28-30)	1.413	1.403	0.01	0.71
R(34-36)	1.400	1.403	0.00	-0.21	R(30-32)	1.388	1.384	0.00	0.29
					R(32-34)	1.400	1.397	0.00	0.21
A(1-14-12)	119.3	118.1	1.20	1.02	A(1-9-10)	117.3	117.4	-0.10	-0.09
A(1-14-15)	119.4	119.3	0.10	0.08	A(1-9-17)	121.0	120.5	0.50	0.41
A(2-22-4)	132.1	128.3	3.80	2.96	A(2-12-10)	119.1	118.3	0.80	0.68
A(2-22-5)	126.3	128.9	-2.60	-2.02	A(2-12-13)	119.6	119.4	0.20	0.17
A(4-3-20)	119.0	115.3	3.70	3.21	A(3-20-5)	131.9	131.1	0.80	0.61
A(3-4-22)	131.2	128.0	3.20	2.50	A(3-20-6)	126.5	125.8	0.70	0.56
A(3-4-23)	120.0	123.4	-3.40	-2.76	A(5-4-18)	119.3	118.4	0.90	0.76
A(3-20-19)	119.8	119.3	0.50	0.42	A(4-5-20)	131.2	131.9	-0.70	-0.53
A(22-4-23)	108.1	108.1	0.00	0.00	A(4-5-21)	120.0	120.0	0.00	0.00
A(4-22-5)	101.6	102.8	-1.20	-1.17	A(4-18-17)	118.4	119.6	-1.20	-1.00
A(4-23-7)	110.8	110.5	0.30	0.27	A(20-5-21)	108.2	108.1	0.10	0.09
A(4-23-24)	127.0	126.0	1.00	0.79	A(5-20-6)	101.6	103.0	-1.40	-1.36
A(7-5-22)	115.3	114.3	1.00	0.87	A(5-21-7)	110.7	110.6	0.10	0.09
A(5-7-23)	104.2	104.3	-0.10	-0.10	A(5-21-22)	127.0	125.4	1.60	1.28
A(7-23-24)	122.2	123.5	-1.30	-1.05	A(7-6-20)	115.3	114.0	1.30	1.14
A(24-8-36)	109.4	108.6	0.80	0.74	A(6-7-21)	104.3	104.3	0.00	0.00
A(8-24-23)	117.5	118.0	-0.50	-0.42	A(7-21-22)	122.3	124.0	-1.70	-1.37
A(8-24-25)	109.1	110.1	-1.00	-0.91	A(22-8-34)	109.4	108.6	0.80	0.74
A(8-36-27)	107.4	107.8	-0.40	-0.37	A(8-22-21)	117.5	118.5	-1.00	-0.84
A(8-36-34)	130.4	129.5	0.90	0.69	A(8-22-23)	109.1	109.5	-0.40	-0.37
A(12-10-19)	120.6	120.4	0.20	0.17	A(8-34-25)	107.4	108.1	-0.70	-0.65
A(10-12-14)	119.3	118.8	0.50	0.42	A(8-34-32)	130.5	129.4	1.10	0.85
A(10-19-17)	118.9	119.4	-0.50	-0.42	A(10-9-17)	121.7	122.1	-0.40	-0.33
A(10-19-20)	122.5	120.7	1.80	1.49	A(9-10-12)	118.9	118.0	0.90	0.76
A(12-14-15)	121.3	122.6	-1.30	-1.06	A(9-17-15)	117.3	117.6	-0.30	-0.26
A(14-15-17)	119.0	118.0	1.00	0.85	A(9-17-18)	121.7	120.3	1.40	1.16
A(15-17-19)	120.9	120.8	0.10	0.08	A(10-12-13)	121.2	122.3	-1.10	-0.90
A(17-19-20)	118.6	119.8	-1.20	-1.00	A(12-13-15)	118.8	118.5	0.30	0.25
A(23-24-25)	133.4	131.8	1.60	1.21	A(13-15-17)	122.0	121.6	0.40	0.33
A(24-25-27)	107.0	106.6	0.40	0.38	A(15-17-18)	120.9	122.0	-1.10	-0.90
A(25-27-28)	133.9	134.4	-0.50	-0.37	A(21-22-23)	133.4	131.9	1.50	1.14
A(25-27-36)	107.1	106.9	0.20	0.19	A(22-23-25)	107.0	106.9	0.10	0.09
A(28-27-36)	119.0	118.7	0.30	0.25	A(23-25-26)	133.9	134.0	-0.10	-0.07

A(27-28-30)	118.9	118.5	0.40	0.34	A(23-25-34)	107.1	106.9	0.20	0.19
A(27-36-34)	122.2	122.6	-0.40	-0.33	A(26-25-34)	119.0	119.1	-0.10	-0.08
A(28-30-31)	119.7	119.3	0.40	0.34	A(25-26-28)	118.9	118.4	0.50	0.42
A(28-30-32)	121.1	121.4	-0.30	-0.25	A(25-34-32)	122.2	122.5	-0.30	-0.24
A(30-32-34)	121.5	121.8	-0.30	-0.25					
A(32-34-36)	117.3	117.0	0.30	0.26					

[a]Atom numbering refer to **Fig. 7.**

[b] The difference between the calculated ($X_{calc.}$) and experimental ($X_{exp.}$) value ($X_{calc.}$-$X_{exp.}$).

[c] Percentage relative error.

Table S2. The calculated natural charges of **3**and**4**[a].

Atom	Charge	Atom	Charge
	3		**4**
Br1	0.0724	Cl 1	0.02396
S2	-0.2182	Cl 2	0.01952
N3	-0.28757	S 3	-0.20247
N4	-0.2253	N 4	-0.28372
N5	-0.3925	N 5	-0.22405
H6	0.46062	N 6	-0.39317
N7	-0.30345	N 7	-0.30209
N8	-0.54673	N 8	-0.54655
H9	0.45155	C 9	-0.00384
C10	-0.18601	C10	-0.26532
H11	0.26043	H11	0.27582
C12	-0.24749	C12	-0.02404
H13	0.26158	C13	-0.25304
C14	-0.09829	H14	0.26413
C15	-0.24955	C15	-0.17679
H16	0.26227	H16	0.26712
C17	-0.1895	C17	-0.1282
H18	0.25179	C18	0.07898
C19	-0.11281	H19	0.25164
C20	0.08633	C20	0.16683
H21	0.23802	C21	0.37065
C22	0.17028	C22	0.09575
C23	0.37069	C23	-0.24913
C24	0.0962	H24	0.26212
C25	-0.24845	C25	-0.10226
H26	0.26216	C26	-0.21113
C27	-0.10219	H27	0.24092
C28	-0.2111	C28	-0.25999
H29	0.24091	H29	0.24113
C30	-0.26026	C30	-0.23062
H31	0.2409	H31	0.24157
C32	-0.23103	C32	-0.27099
H33	0.2413	H33	0.24169
C34	-0.27114	C34	0.17287
H35	0.24142	H35	0.45176
C36	0.1727	H36	0.46096

[a]Atom numbering refer to **Fig. 7.**

^{1}H NMR and ^{13}C NMR of the Schiff bases 3–6

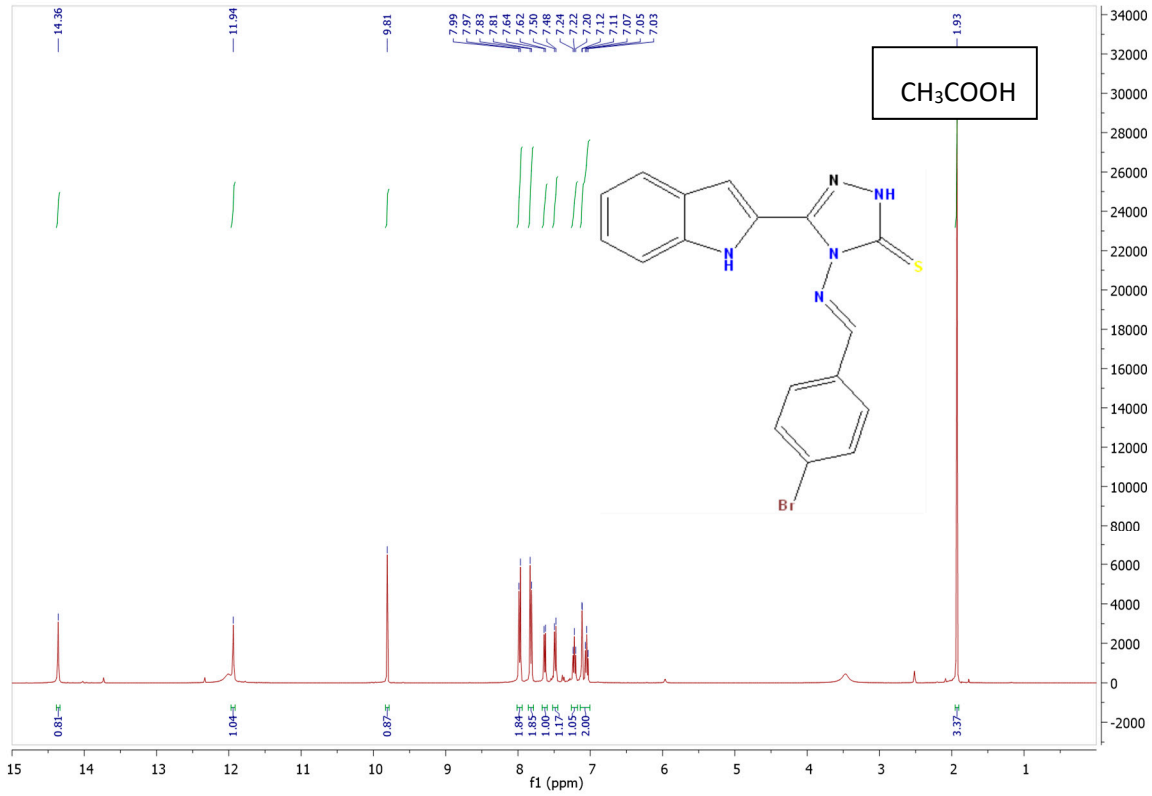

Figure S1. ^{1}H NMR of 3 in DMSO-*d*$_6$.

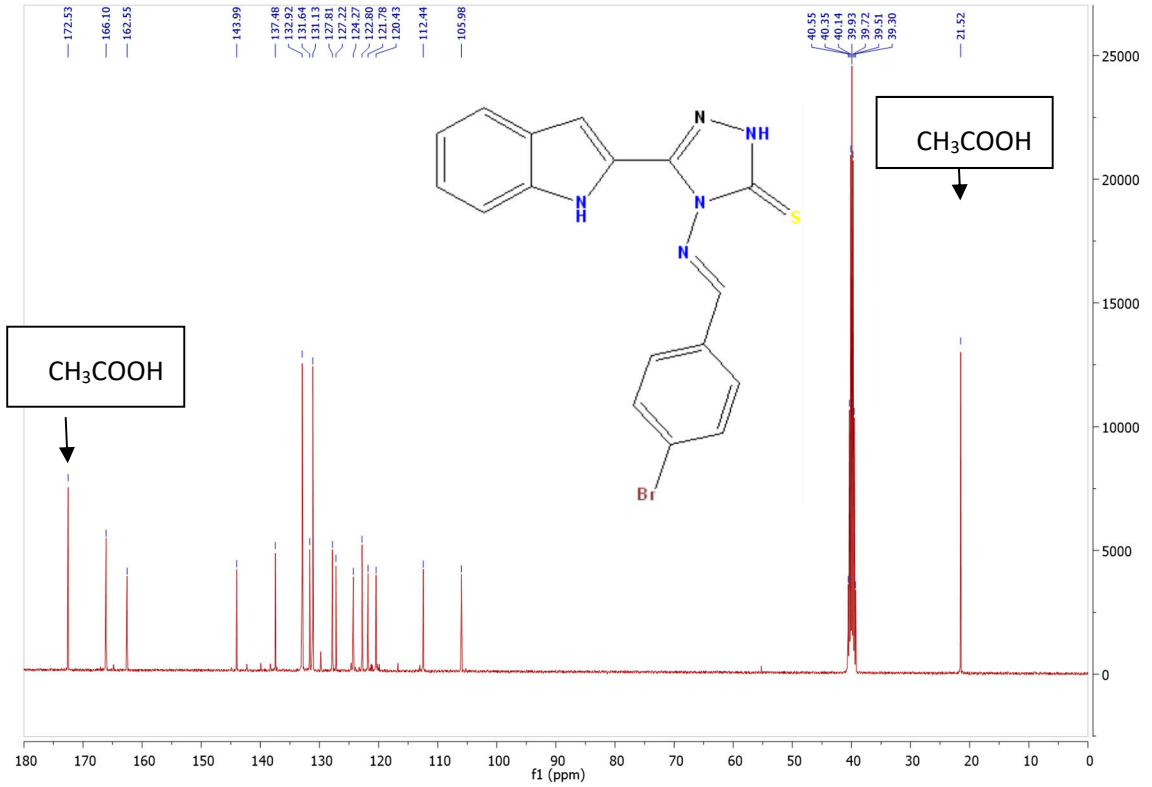

Figure S2. ^{13}C NMR of 3 in DMSO-*d*$_6$.

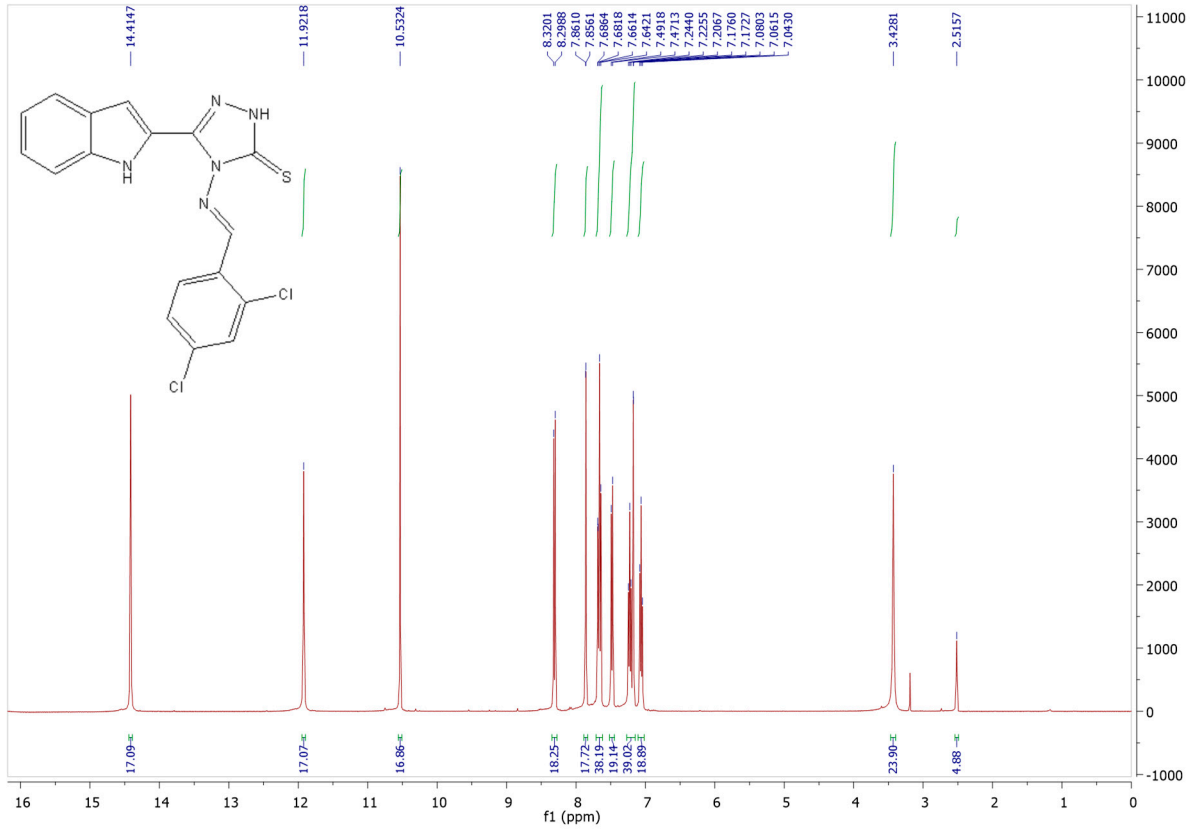

Figure S3. [1]H NMR of 4 in DMSO-*d*6.

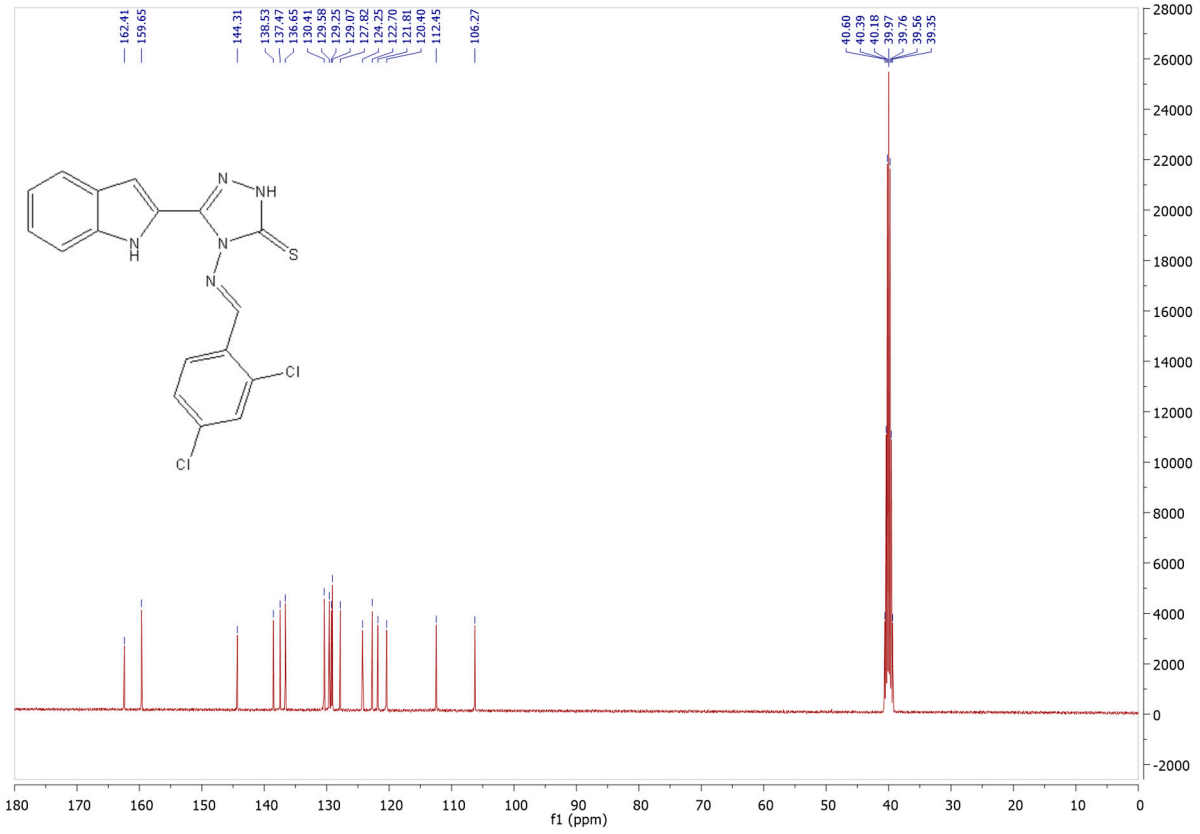

Figure S4. [13]C NMR of 4 in DMSO-*d*6.

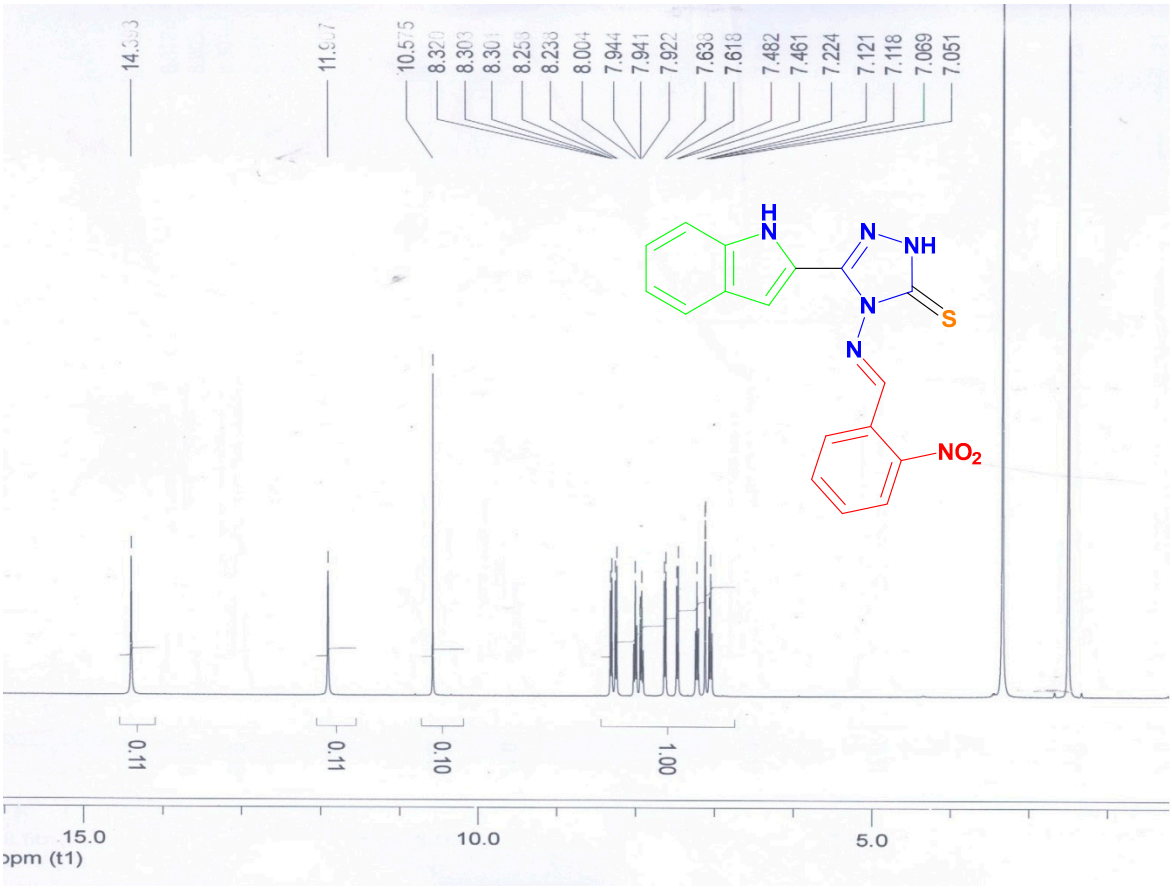

Figure S5. ^{1}H NMR of 5 in DMSO-*d*$_6$.

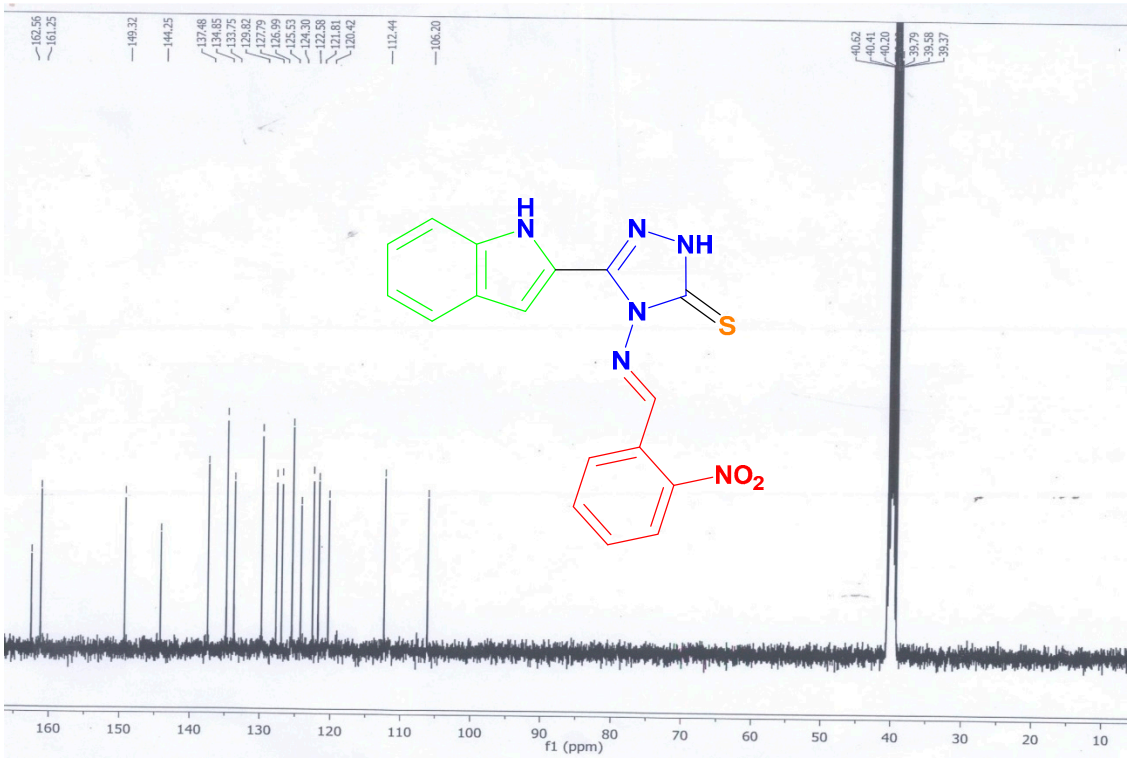

Figure S6. ^{13}C NMR of 5 in DMSO-*d*$_6$.

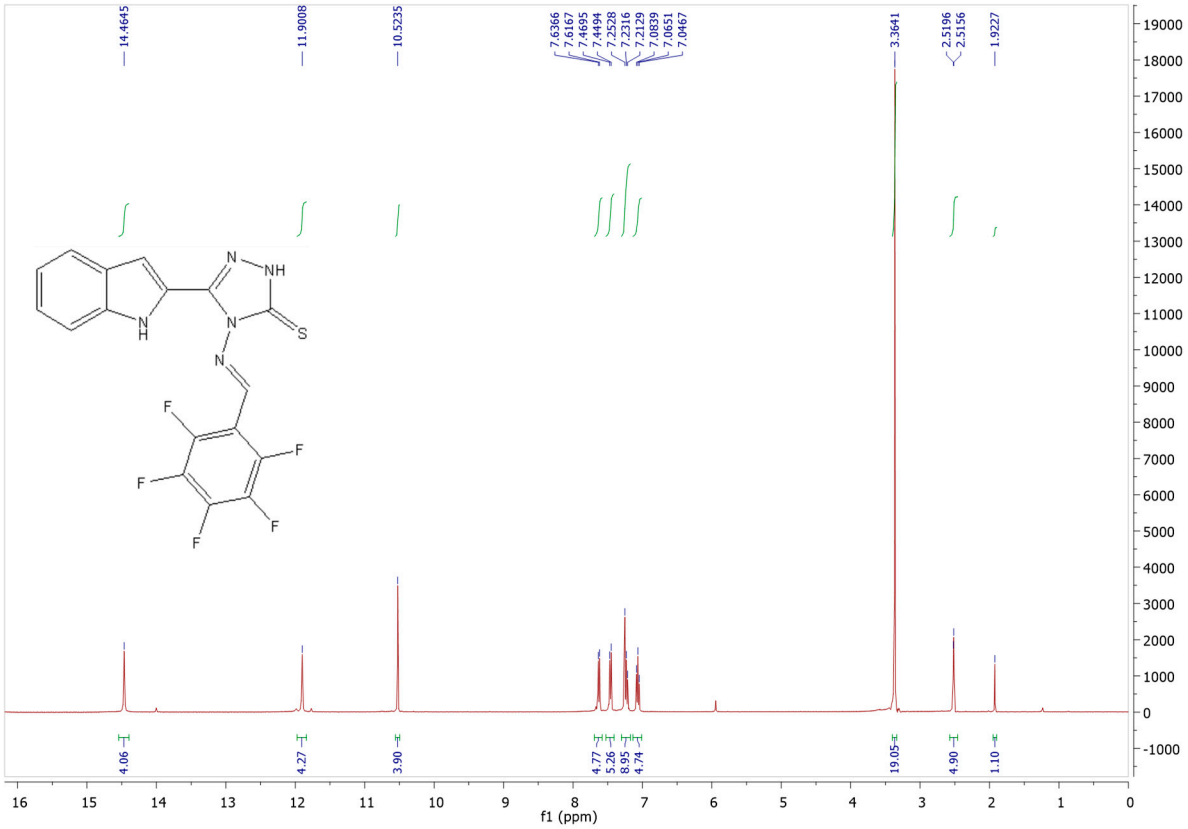

Figure S7. ^{1}H NMR of 6 in DMSO-d_6.

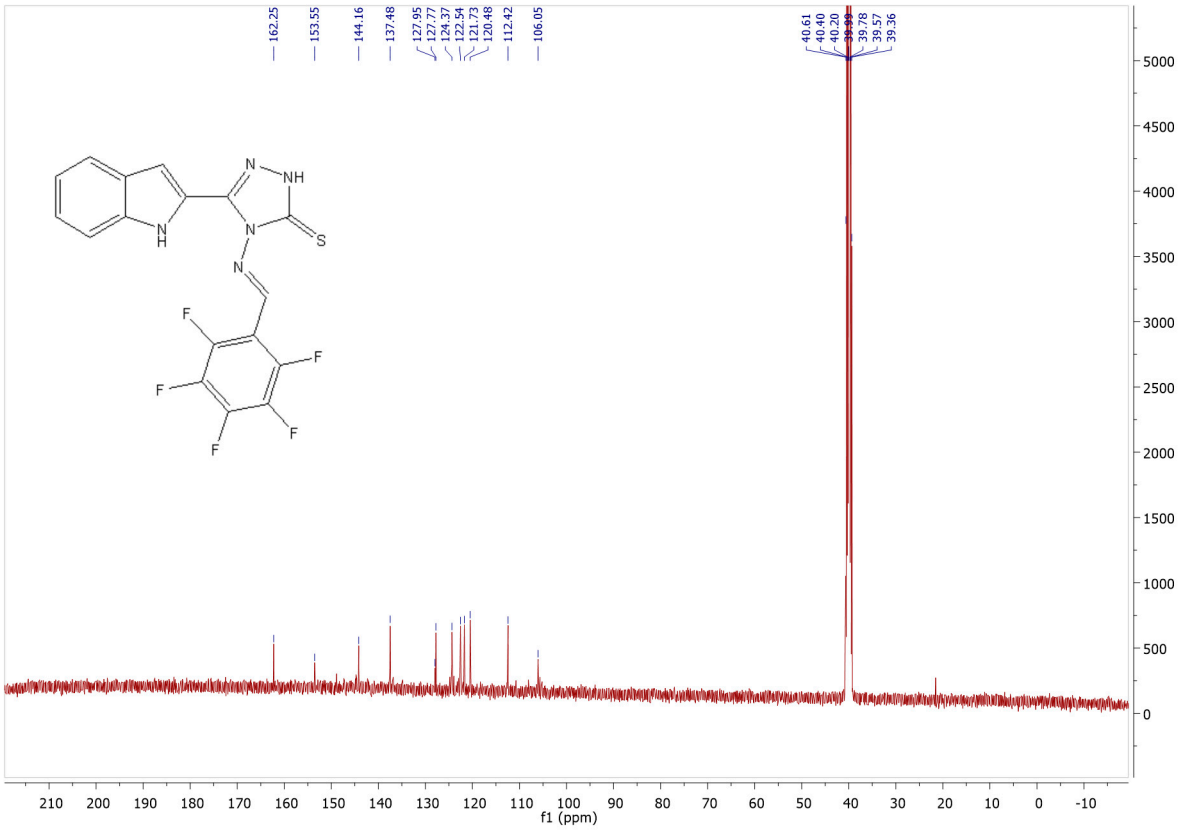

Figure S8. ^{13}C NMR of 6 in DMSO-d_6.

References

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1. Sheldrick, G. M. SHELXT–Integrated space-group and crystal-structure determination,*Acta Cryst.* **2015**, *A71*, 3–8.
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3. Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL, *J. Appl. Cryst.***2011**, *44*, 1281–1284.