SUPPLEMENTARY MATERIAL

Synthesis, structures and electronic properties of Co(III) complexes with 2-quinolinecarboxaldehyde thio- and selenosemicarbazone: a combined experimental and theoretical study

IVANA S. DJORDJEVIĆ[1]**, JELENA VUKAŠINOVIĆ[2], TAMARA R. TODOROVIĆ[3#], NENAD R. FILIPOVIĆ[4#], MARKO V. RODIĆ[5], ALEKANDAR LOLIĆ[3], GUSTAVO PORTALONE[6], MARIO ZLATOVIĆ[3#] and SONJA GRUBIŠIĆ[1]*

[1] *Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11001 Belgrade, Serbia*

[2] *Institute for multidisciplinary research, University of Belgrade, Volgina 15, 11060 Belgrade, Serbia*

[3] *Faculty of Chemistry, University of Belgrade, Studentski trg 12–16, 11001 Belgrade, Serbia*

[4] *Faculty of Agriculture, University of Belgrade, Nemanjina 6, Belgrade, Serbia*

[5] *Department of Chemistry, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 4, Novi Sad, Serbia*

[6] *Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy*

*,**Corresponding authors. E-mail: (*)grubisic@chem.bg.ac.rs; (**)ivana.djordjevic@chem.bg.ac.rs
Serbian Chemical Society member.

TABLE S-I. Crystal data and structure refinement for complexes **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{22}H_{18}CoN_8S_2^+ \times ClO_4^- \times OH_2$	$C_{22}H_{18}CoN_8Se_2^+ \times ClO_4^- \times OH_2$
Formula weight	634.96	726.74
Temperature, K	293(2)	293(2)
Wavelength , Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	*P* –1	*P* –1
Unit cell dimensions		
a / Å	9.4673(4)	9.5870(5)
b / Å	10.9731(3)	11.2021(6)
c / Å	13.9826(4)	13.9356(6)
α / °	70.668(3)	71.128(4)
β / °	87.653(3)	87.977(4)
γ / °	72.439(3)	72.076(5)
Volume, Å^3	1304.01(8)	1343.99(13)
Z	2	2
Density (calculated), Mg m^{-3}	1.617	1.801
Absorption coefficient, mm^{-1}	0.97	3.50
F(000)	648	720
Theta range for data collection, °	2.6 to 29.1	2.5 to 29.0
Reflections collected	28698	20644
Independent reflections	6312 [*R*(int) = 0.0250]	6379 [*R*(int) = 0.0243]
Completeness to theta = 26.320°	99.9 %	99.9 %
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6312 / 4 / 364	6379 / 4 / 366
Goodness-of-fit on F^2	1.05	1.007
Final *R* indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0359$, $wR_2 = 0.0916$	$R_1 = 0.0370$, $wR_2 = 0.0976$
R indices (all data)	$R_1 = 0.0430$, $wR_2 = 0.0963$	$R_1 = 0.0475$, $wR_2 = 0.1037$
Largest diff. peak and hole, e Å^{-3}	0.48 and –0.41	0.91 and –0.51

TABLE S–II. Hydrogen bond (Å) and π–π stacking interaction parameters (angle, ° and distance, Å) in the crystal structure of complexes **1** and **2**.

H–bond parameters					
D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / °	symmetry operation on A
complex **1**					
N4A–H41A···N3A	0.845(17)	2.357(18)	3.166(2)	161(2)	$1-x, 1-y, 1-z$
N4A–H42A···N3B	0.857(17)	2.441(19)	3.252(3)	158(2)	$1-x, -y, 1-z$
N4B–H41B···O5	0.862(17)	2.28(2)	3.054(4)	150(3)	$1-x, -y, 1-z$
N4B–H42B···O4	0.872(18)	2.302(19)	3.158(4)	167(3)	$2-x, -y, 1-z$
complex **2**					
N4A–H41A···N3A	0.849(19)	2.32(2)	3.122(4)	157(4)	$1-x, 1-y, 1-z$
N4A–H42A···N3B	0.860(18)	2.59(2)	3.408(4)	158(4)	$1-x, -y, 1-z$
N4B–H41B···O5	0.871(19)	2.23(3)	3.041(6)	154(4)	$1-x, -y, 1-z$
N4B–H42B···O4	0.870(19)	2.35(2)	3.212(8)	169(4)	$2-x, -y, 1-z$
π–π interaction parameters					
Cg(I),Cg(J)[a] Cg–Cg[b] / Å	α[c] / °	β[d] / °	γ[e] / °	slippage[f] /Å	symmetry operation on J
complex **1**					
Cg1, Cg1 4.184(16)	0.00(13)	21.9	21.9	1.560	$1-x, 1-y, -z$
Cg2, Cg2 3.7319(17)	0.02(14)	17.9	17.9	1.150	$-x, 1-y, -z$
Cg3, Cg3 3.6062(14)	0.03(11)	18.3	18.3	1.132	$-x, 1-y, 1-z$
complex **2**					
Cg1, Cg1 4.506(3)	0.0(2)	21.8	21.8	1.673	$1-x, 1-y, -z$
Cg2, Cg2 3.759(3)	0.0(2)	20.0	20.0	1.285	$-x, 1-y, -z$
Cg3, Cg3 3.630(2)	0.03(17)	19.9	19.9	1.233	$-x, 1-y, 1-z$

[a] Planes of the rings I/J: ring (1) = N(1A),C(3A),C(4A),C(5A),C(6A),C(7A); ring (2) = C(6A),C(7A),C(8A),C(9A),C(10A),C(11A); ring (3) = C(6B),C(7B),C(8B),C(9B),C(10B),C(11B); [b] Cg–Cg = distance between ring centroids (Å); [c] α = dihedral angle between planes I and J (°); [d] β = angle between Cg(I),Cg(J) vector and normal to plane I (°); [e] γ = angle between Cg(I), Cg(J) vector and normal to plane J (°); [f] Slippage = distance between Cg(I) and perpendicular projection of Cg(J) on ring I (Å).

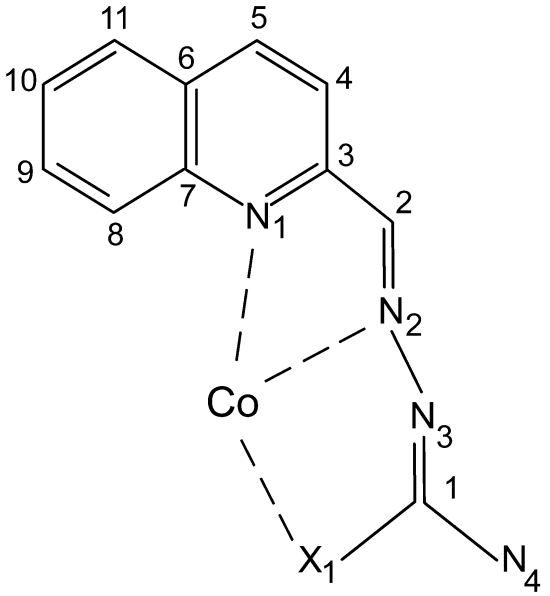

Fig. S-1. Atomic numbering for investigated molecules (X=S for **1** and X=Se for **2**).

TABLE S-III. Comparison of average values of the theoretically calculated Co–N and Co-Se bond lengths (Å) obtained for the complex **2**, using two DFT/B3LYP with two basis sets and experimental measured values.

Basis sets / Bond	Co–N_2	Co–N_1	Co–Se_1
6-311g(d,p)[a]	1.925	2.099	2.380
cc-pVTZ / 6-311g(d)[b]	1.940	2.120	2.398
Measured[c]	1.913	2.056	2.335

[a] B3LYP functional with 6-311g(d,p) on all atoms; [b]B3LYP functional with cc–pVTZ on Co and 6-311g(d) on all others atoms; [c] Experimental measured bond lengths

TABLE S-IV. Comparison average values of the experimental and the theoretical calculated Co-N, Co-S and Co-Se bond lengths (Å) obtained for the complexes **1** and **2**.

Compound / Bond, Å	Co–N_2		Co–N_1		Co–S_1	
1	1.901[a]	1.914[b]	2.058[a]	2.081[b]	2.224[a]	2.267[b]
	Co–N_2		Co–N_1		Co–Se_1	
2	1.913[a]	1.925[b]	2.056[a]	2.099[b]	2.335[a]	2.380[b]

[a] Crystal structure data obtained by XRD in the presentwork; [b] Optimized geometries parameters obtained by the use of DFT/B3LYP/6-311G(d,p)

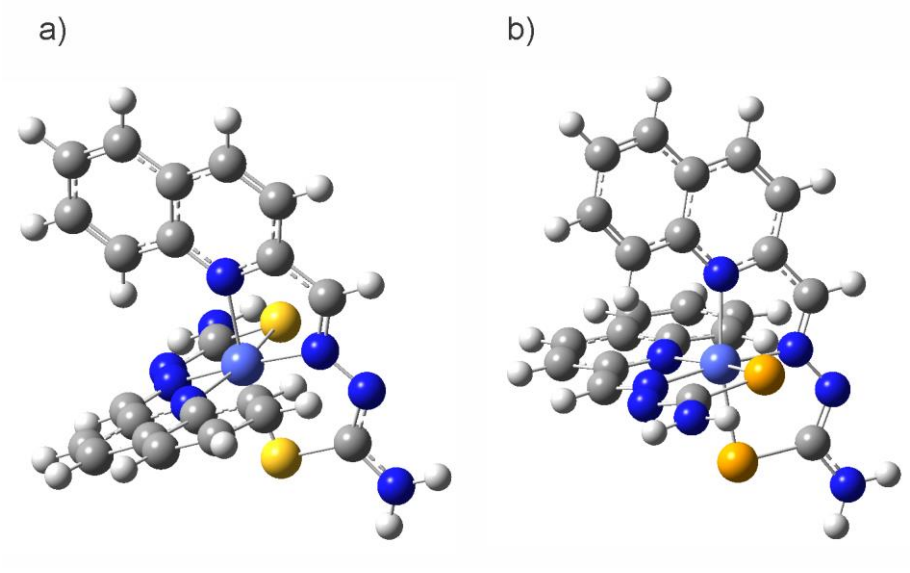

Fig. S-2. The ground state geometries of a) complex **1** and b) complex **2**.

TABLE S-V. TD–DFT electronic transitions (absorption maxima, nm), oscillator strengths (*f*) and major MO contributors in percent of complexes **1** in DMSO.

Complex	No.	λ / nm	*f*	MO major contributors, %					
1				Transition	%	Transition	%	Transition	%
	1	715	0.0004	H–1→L+2	33	H–5→L+2	25	H–13→L+2	14
	2	526	0.0017	HOMO→L+2	46	HOMO→L+1	28		
	3	507	0.0000	H–1→L+3	32	HOMO→L+1	13	H–1→LUMO	11
	4	**500**	**0.0318**	HOMO→LUMO	91	H–1→L+1	3		
	5	493	0.0081	H–12→L+3	23	HOMO→L+3	12	H–11→L+2	11
	6	476	0.0008	HOMO→L+1	39	HOMO→L+2	30	H–1→LUMO	21
	7	**453**	**0.1186**	H–1→LUMO	45	HOMO→L+1	16		
	8	**444**	**0.1238**	H–1→L+1	73	H–1→L+2	12		
	9	439	0.0250	HOMO→L+3	52	H–1→L+1	13	H–1→L+2	11
	10	438	0.0416	H–1→L+3	23	H–1→LUMO	13	H–5→L+3	11
	11	411	0.0003	H–1→L+2	28	HOMO→L+3	27	H–12→L+3	12
	12	394	0.0153	H–2→L+2	48	H–2→L+1	24	H–5→LUMO	6
	13	**390**	**0.0523**	H–2→LUMO	87	H–5→L+1	4		
	14	381	0.0488	H–2→L+2	23	H–3→LUMO	17	H–5→LUMO	12
	15	379	0.0128	H–2→L+1	34	H–3→LUMO	26	H–2→L+2	19
	16	376	0.0167	H–3→L+1	52	H–3→L+2	11	H–5→L+2	10

	17	371	0.0008	H–3→LUMO	54	H–2→L+1	14	H–11→L+3	6
	18	368	0.0695	H–4→LUMO	82	H–3→L+1	6		
	19	360	0.0038	H–3→L+1	31	H–5→L+1	18	H–4→LUMO	12
	20	**359**	**0.1652**	H–5→LUMO	53	H–2→L+1	22	H–2→L+2	5
	21	357	0.0339	H–4→L+1	88	H–6→L+2	2		
	22	**354**	**0.1253**	H–5→L+1	48	H–3→L+2	11	H–13→L+2	9
	23	349	0.0493	H–3→L+2	41	H–2→L+3	26	H–5→L+1	10
	24	346	0.0312	H–5→L+3	42	H–1→L+3	30	H–13→L+3	10
	25	343	0.0403	H–2→L+3	68	H–3→L+2	20	H–5→L+1	3
	26	337	0.0067	H–4→L+2	84	H–6→L+1	5	H–6→L+2	3
	27	330	0.0028	H–6→LUMO	86	H–7→L+1	3		
	28	324	0.0008	H–6→L+1	58	H–7→LUMO	20	H–9→LUMO	5
	29	316	0.0012	H–3→L+3	72	HOMO→L+4	6	H–13→L+3	5
	30	312	0.0176	HOMO→L+5	66	H–7→L+1	9	H–13→L+2	7
	31	312	0.0445	HOMO→L+4	50	H–7→LUMO	17	H–7→LUMO+3	14
	32	**309**	**0.1095**	HOMO→L+5	26	H–13→L+2	20	H–5→L+2	18
	33	308	0.0204	H–7→LUMO	38	HOMO→L+4	29	H–6→L+1	13
	34	303	0.0020	H–4→L+3	81	H–7→L+1	6	H–12→L+3	4
	35	301	0.0403	H–6→L+2	56	H–10→L+2	16	H–12→L+2	6
	36	298	0.0994	H–1→L+4	89				
	37	**296**	**0.1203**	H–1→L+5	84	H–7→LUMO	4	HOMO→L+4	4

TABLE S-VI. TD–DFT electronic transitions (absorption maxima, nm), oscillator strengths (*f)* and major MO contributors in percent of complexes **2** in DMSO.

Complex	No.	λ / nm	*f*	MO major contributors, %					
2				Transition	%	Transition	%	Transition	%
	1	748	0.0003	H–1→L+2	39	H–13→L+2	13	H–4→L+2	10
	2	590	0.0008	HOMO→L+1	54	HOMO→L+2	44		
	3	**570**	**0.0189**	HOMO→LUMO	97				
	4	535	0.0001	H–1→L+3	24	H–1→LUMO	19	H–13→L+3	15
	5	530	0.0089	HOMO→L+2	39	HOMO→L+1	29	H–1→L+3	16
	6	513	0.0053	H–12→L+3	33	HOMO→L+3	20	H–14→L+2	7
	7	482	0.0609	H–1→LUMO	60	H–14→L+3	5		
	8	478	0.0005	HOMO→L+3	71	H–14→L+2	3	H–11→L+2	4
	9	**466**	**0.0914**	H–1→L+1	80	H–1→L+2	10		

10	460	0.0302	H–1→L+3	28	H–1→LUMO	14	H–12→L+2	11
11	429	0.0010	H–1→L+2	26	H–12→L+3	18	H–4→L+2	6
12	417	0.0082	H–2→L+2	38	H–2→L+1	32		
13	**408**	**0.0790**	H–2→LUMO	84	H–3→L+2	4	H–3→L+1	3
14	396	0.0083	H–2→L+2	37	H–2→L+1	34	H–3→LUMO	24
15	389	0.0588	H–12→L+2	17	H–4→LUMO	14	H–2→L+2	12
16	386	0.0147	H–3→L+1	50	H–3→L+2	24	H–4→L+1	10
17	376	0.0448	H–3→LUMO	48	H–4→LUMO	31	H–2→L+1	14
18	**371**	**0.1849**	H–3→LUMO	48	H–4→LUMO	18		
19	370	0.0440	H–5→LUMO	59	H–13→L+2	9	H–4→L+1	8
20	**367**	**0.1496**	H–4→L+1	44	H–3→L+1	24	H–4→L+2	8
21	366	0.0180	H–5→LUMO	31	H–13→L+2	16	H–2→L+3	14
22	360	0.0370	H–5→L+1	88	HOMO→L+4	3		
23	359	0.0431	H–2→L+3	35	H–3→L+2	21	H–4→L+1	13
24	352	0.0630	H–2→L+3	42	H–3→L+	24	H–4→L+2	12
25	348	0.0175	H–3→L+3	38	H–1→L+3	24	H–13→L+3	15
26	339	0.0115	H–6→LUMO	81				
27	339	0.0006	H–5→L+2	61	H–6→L+1	19		
28	335	0.0252	HOMO→L+4	62	H–6→L+1	13	H–7→LUMO	12
29	335	0.0296	HOMO→L+5	92				
30	331	0.0372	H–6→L+1	33	H–5→L+2	27	HOMO→L+4	15
31	325	0.0038	H–3→L+3	42	H–4→L+3	28	H–13→L+3	13
32	324	0.0501	H–4→L+2	38	H–7→L+1	18	H–13→L+2	18
33	320	0.0019	H–7→LUMO	65	H–6→L+1	20		
34	313	0.0033	H–7→L+1	62				
35	311	0.0020	H–5→L+3	28	H–6→L+3	25	H–12→L+3	22
36	**309**	**0.0574**	H–6→L+2	57	H–12→L+1	9	H–12→L+2	9
37	**306**	**0.0543**	H–1→L+4	92				

NMR spectra

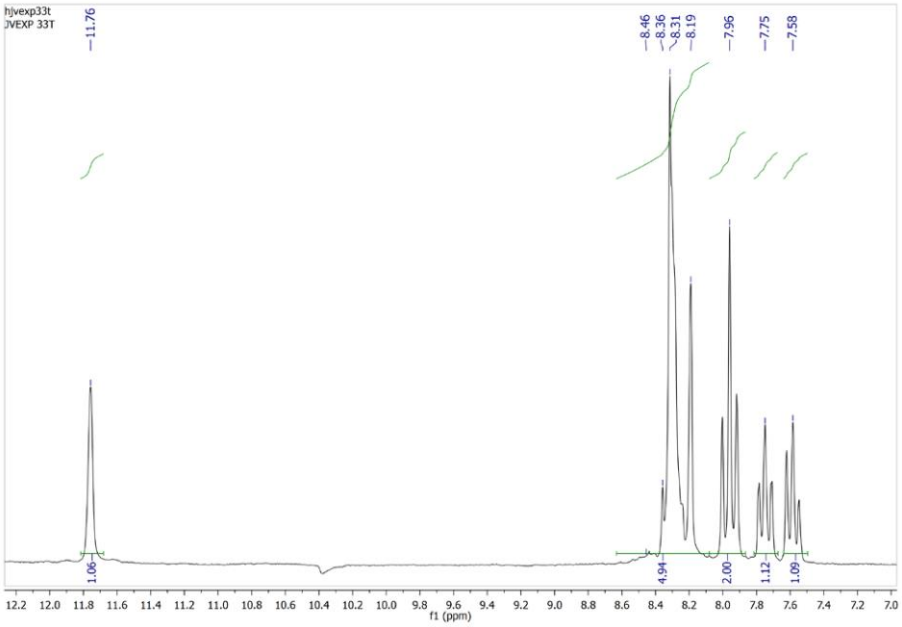

Fig. S-3. ^{1}H NMR spectrum of H2qatsc in DMSO-d_6.

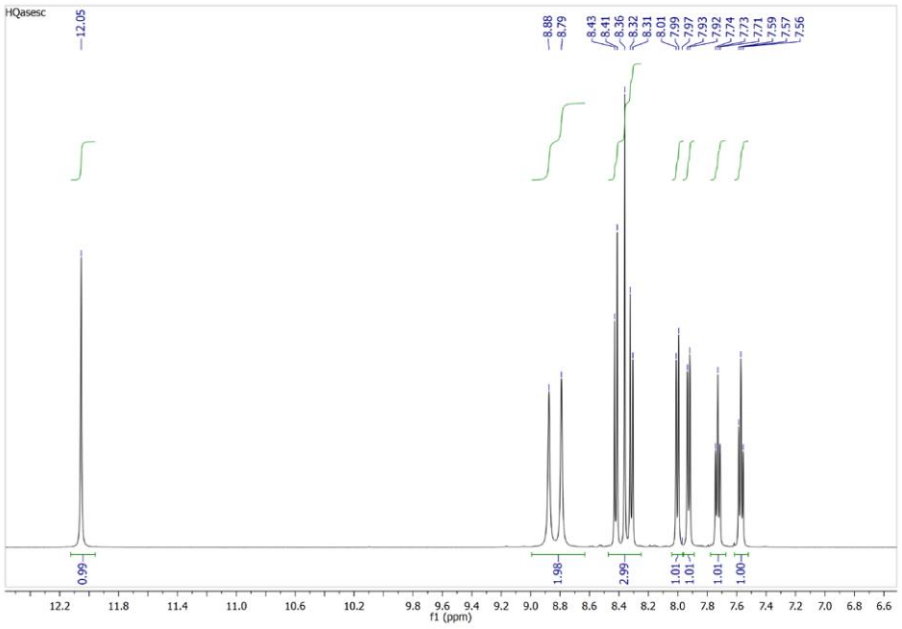

Fig. S-4.^{1}H NMR spectrum of H2qasesc in DMSO-d_6.

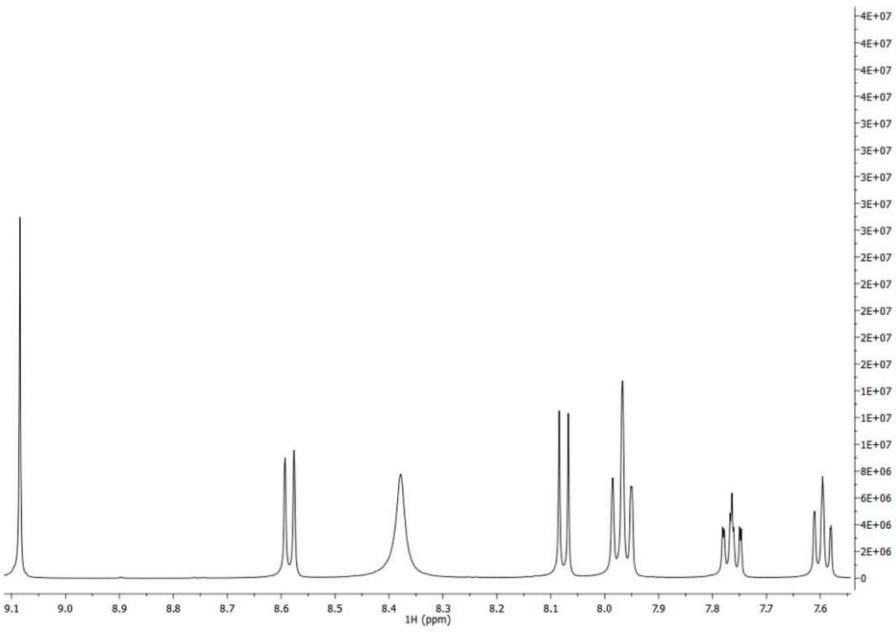

Fig. S-5. ^{1}H NMR spectrum of **1** in DMSO-d_6.

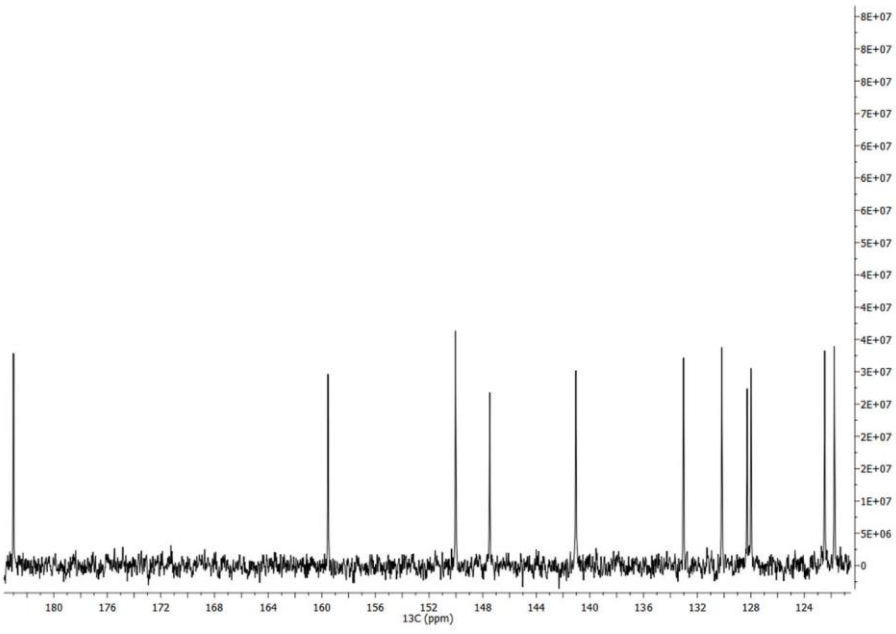

Fig. S-6. ^{13}C NMR spectrum of **1** in DMSO-d_6.

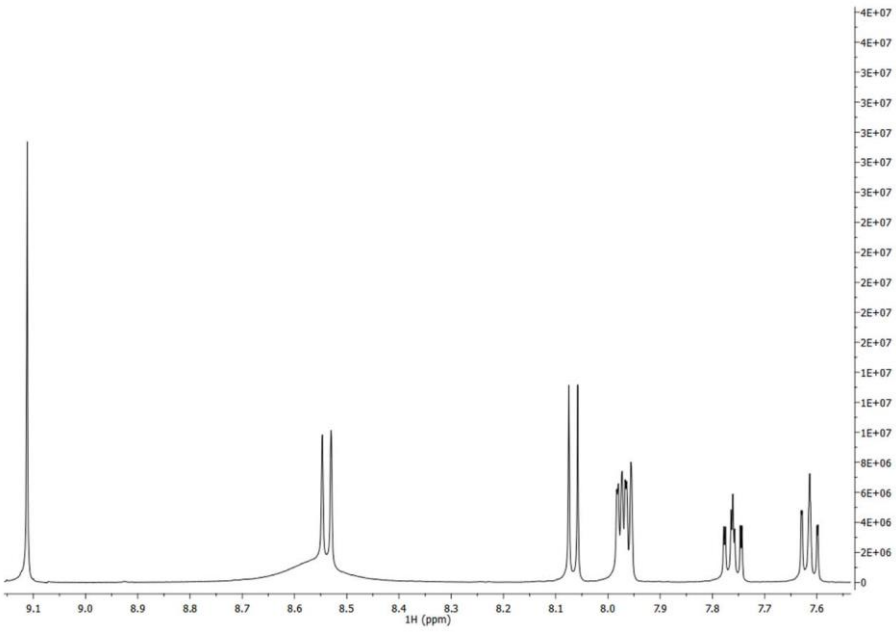

Fig. S-7. ^{1}H NMR spectrum of **2** in DMSO-d_6.

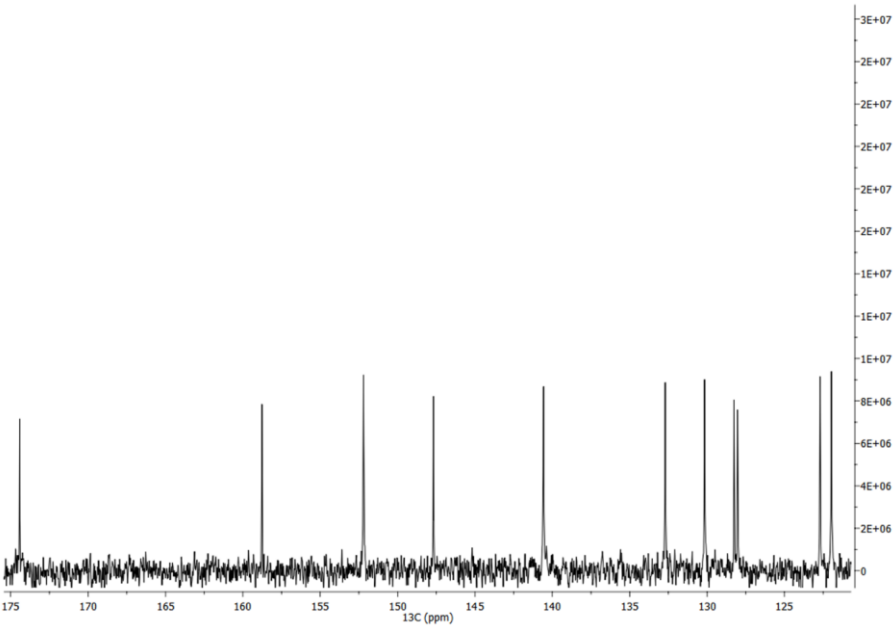

Fig. S-8. ^{13}C NMR spectrum of **2** in DMSO-d_6.