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Supplementary material

SUPPLEMENTARY MATERIAL TO

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

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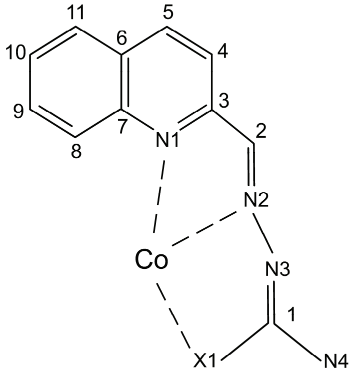

Fig. S-1. Atom numbering for the investigated molecules (X = S for **1** and X = Se for **2**).

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

Complex	**1**	**2**
Empirical formula	$C_{22}H_{18}CoN_8S_2^{+}\cdot ClO_4^{-}\cdot OH_2$	$C_{22}H_{18}CoN_8Se_2^{+}\cdot ClO_4^{-}\cdot OH_2$
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 difference 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

TABLE S-II. Continued

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 the normal to plane I (°); [e] γ = angle between Cg(I), Cg(J) vector and the normal to plane J (°); [f] slippage = distance between Cg(I) and perpendicular projection of Cg(J) on ring I (Å)

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

Basis sets / Bond	Co–N2	Co–N1	Co–Se1
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] experimentally measured bond lengths

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

Complex	Co–N2		Co–N1		Co–S1	
1	1.901[a]	1.914[b]	2.058[a]	2.081[b]	2.224[a]	2.267[b]
	Co–N2		Co–N1		Co–Se1	
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 present work; [b] optimized geometries parameters obtained using of DFT/B3LYP/6-311G(d,p)

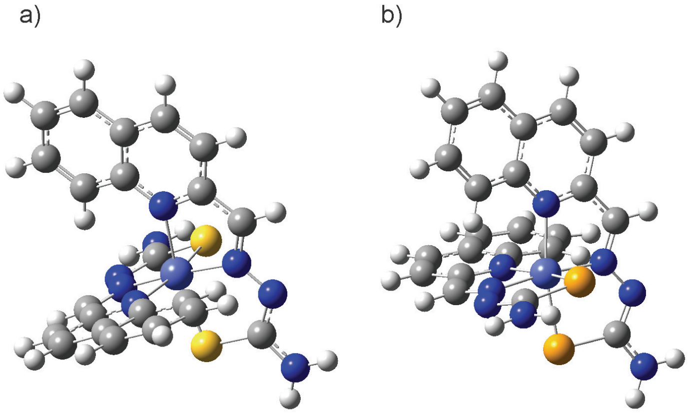

Fig. S-2. The ground state geometries of a) complex **1** and b) complex **2**.

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

No.	λ / nm	*f*	MO major contributors					
			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		

TABLE S-V. Continued

No.	λ / nm	*f*	MO major contributors					
			Transition	%	Transition	%	Transition	%
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 complex **2** in DMSO

No.	λ / nm	*f*	MO major contributors, %					
			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				

TABLE S-VI. Continued

No.	λ / nm	f	MO major contributors, %					
			Transition	%	Transition	%	Transition	%
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				

PHYSICAL AND SPECTRAL DATA FOR COMPLEXES **1** AND **2**

*Complex **1***. Yield: 80 %; IR (ATR, cm^{-1}): 3275*m*, 3152*m*, 1619*s*, 1580*m*, 1546*m*, 1472*vs*, 1439*vs*, 1325*m*, 1292*w*, 1211*w*, 1125*m*, 1076*vs*, 882*w*, 820*w*, 622*m*; ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 7.60 (1H, *t*, J = 7.8 Hz, H10), 7.76 (1H, *ddd*, J = 8.7 Hz, J = 7.0 Hz & J = 1.5 Hz, H9), 7.96 (2H, *dd*, overlap, J = 12.8 Hz & J = 5.0 Hz, H8 & H11), 8.08 (1H, *d*, J = 8.5 Hz, H4), 8.38 (2H, *s*, N1H$_2$), 8.58 (1H, *d*, J = 8.4 Hz, H5), 9.08 (1H, *s*, H2); ^{13}C-NMR (126 MHz, DMSO-d_6, δ / ppm): 121.77 (C8), 122.49 (C4), 127.98 (C6), 128.28 (C10), 130.17 (C11), 133.02 (C9), 141.05 (C5), 147.48 (C7), 150.02 (C2), 159.54 (C3), 183.0 (C1); Λ_M (DMSO (1×10^{-3} M), Ω^{-1} cm^2 mol^{-1}): 28.40.

*Complex **2***. Yield: 57 %; IR (ATR, cm^{-1}): 3623*m*, 3275*s*, 3149*s*, 1619*vs*, 1579*w*, 1475*vs*, 1445*vs*, 1389*w*, 1320*m*, 1290*w*, 1211*w*, 1071*vs*, 988*w*, 897*m*, 822*m*, 752*w*, 700*w*, 622*m*; ^{1}H-NMR (500 MHz, DMSO-d_6, δ / ppm): 7.61 (1H, *m*, H10), 7.76 (1H, *ddd*, J = 8.8 Hz, J = 7.0 Hz & J = 1.5 Hz, H9), 7.97 (2H, *m*, overlap, H11 & H8), 8.07 (1H, *d*, $^3J_{3,4}$ = 8.5, H4), 8.54 (3H, *d*, J = 8.3 Hz, H5 & N1H$_2$), 9.11 (1H, *s*, H2); ^{13}C-NMR (126 MHz, DMSO-d_6, δ / ppm): 121.97 (C8), 122.70 (C4), 128.03 (C6), 128.25 (C10), 130.16 (C11), 132.70 (C9), 140.57 (C5), 147.68 (C7), 152.20 (C2), 158.76 (C3), 174.43 (C1); Λ_M (DMSO (1 × 10^{-3} M), Ω^{-1} cm^2 mol^{-1}): 29.30.

Abbreviations and atomic numbering

IR spectra. Intensity: *vs* – very strong, *s* – strong; *m* – medium and *w* – weak.

NMR spectra. The atomic numbering used for the assignments is given in Fig. S-1. Multiplicity: *s* – singlet, *d* – doublet, *t* – triplet, *dd* – doublet of doublets, *ddd* – doublet of doublet of doublets, *m* – multiplet.

IR AND ^{1}H-NMR SPECTRA OF THE LIGANDS

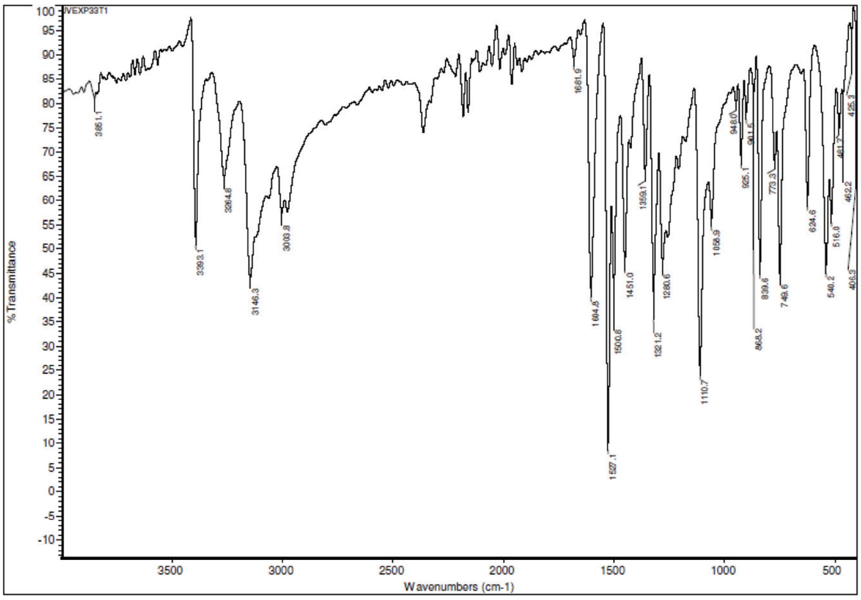

Fig. S-3. IR spectrum of Hqatsc.

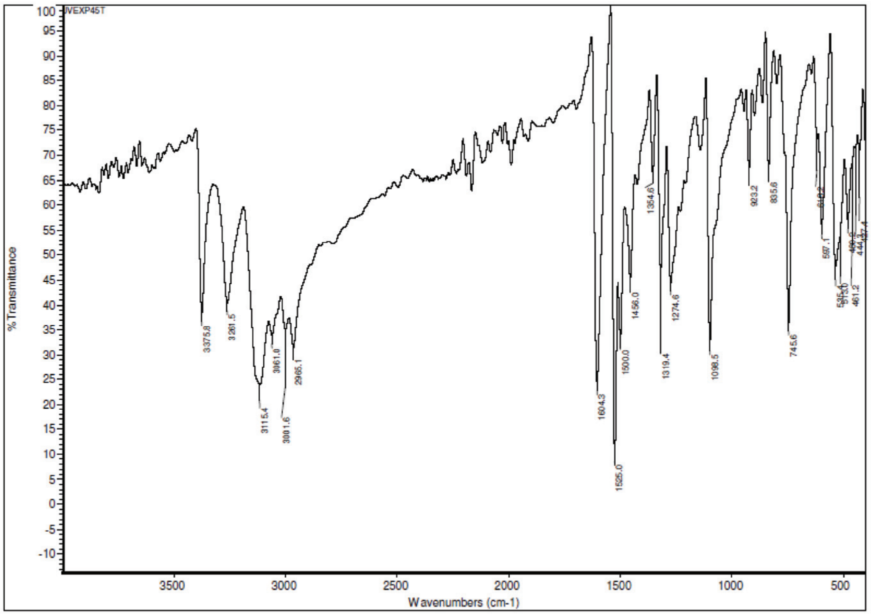

Fig. S-4. IR spectrum of Hqasesc.

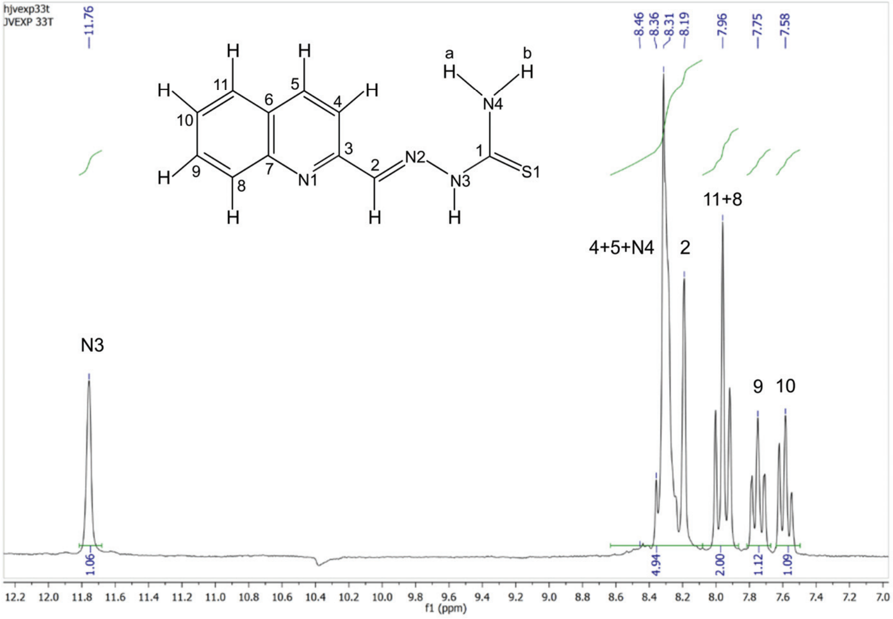

Fig. S-5. ^{1}H-NMR spectrum of Hqatsc in DMSO-d_6.

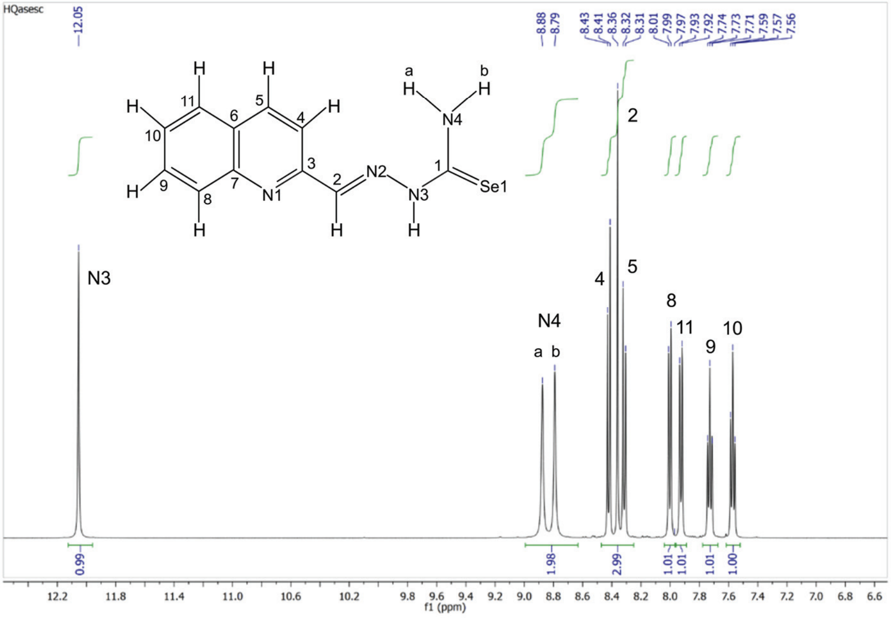

Fig. S-6. ^{1}H-NMR spectrum of Hqasesc in DMSO-d_6.

^{1}H- AND ^{13}C-NMR SPECTRA OF **1** AND **2**

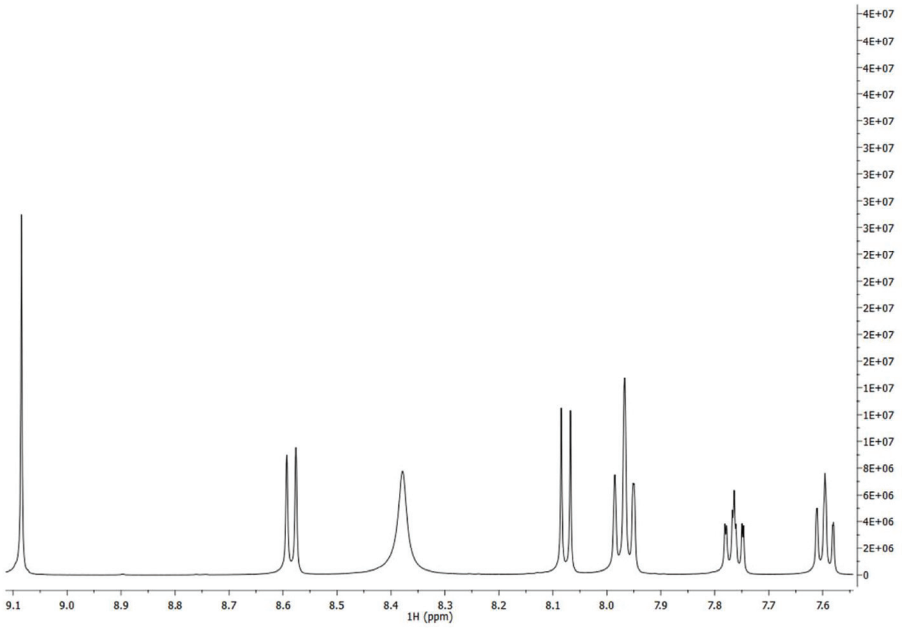

Fig. S-7. ^{1}H-NMR spectrum of **1** in DMSO-d_6.

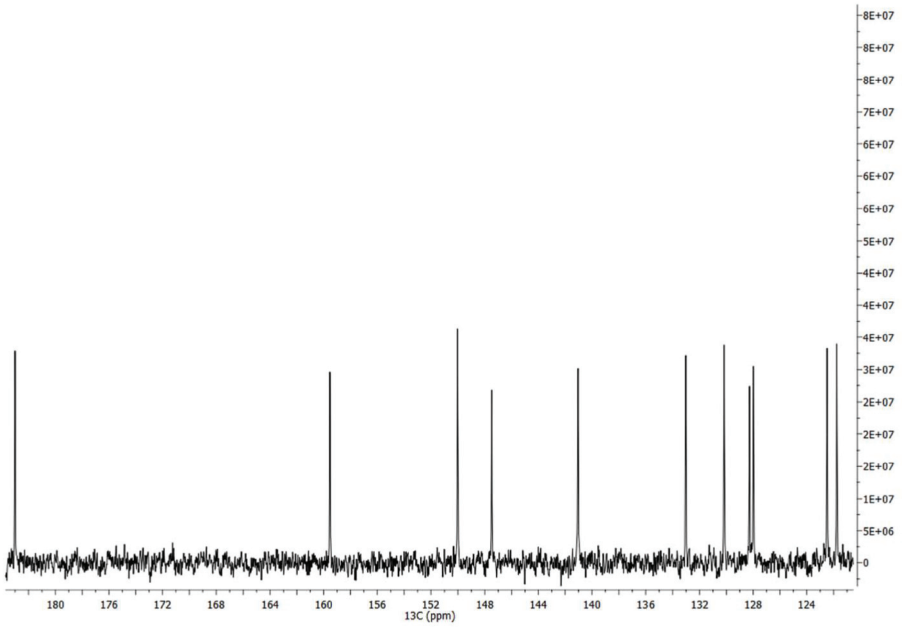

Fig. S-8. ^{13}C-NMR spectrum of **1** in DMSO-d_6.

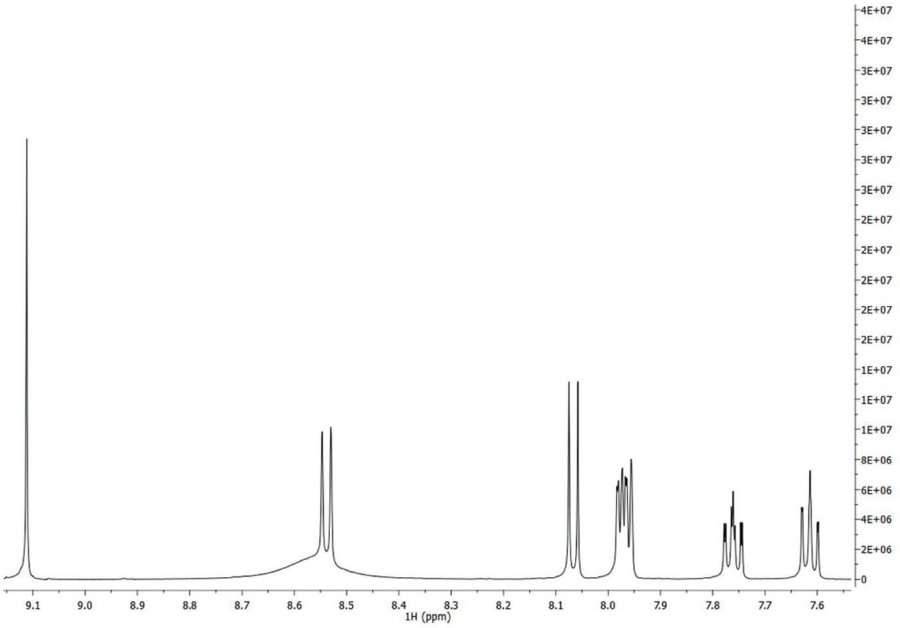

Fig. S-9. ^{1}H NMR spectrum of **2** in DMSO-d_6.

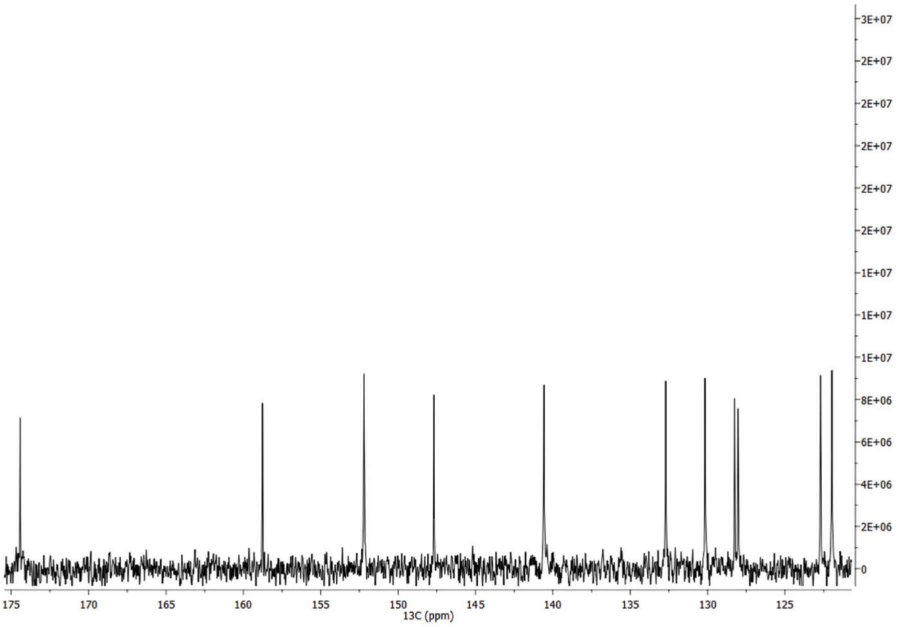

Fig. S-10. ^{13}C NMR spectrum of **2** in DMSO-d_6.