

**Solution and solid behavior of mono and binuclear zinc(II)  
and nickel(II) complexes with dithiocarbazates: X-ray, mass  
spectrometry and cytotoxicity against cancer cell line**

*Supporting Information*

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## Synthesis of the ligands

**Synthesis of the ligand (HL<sup>1</sup>).** In an ice bath and under stirring, 85% potassium hydroxide (3 mmol, 198 mg) in ethanol (95%) was solubilized and added to the hydrazine monohydrate (3 mmol, 0,15 mL). After 40 minutes, the carbon disulfide (3 mmol, 0,18 mL) was added drop by drop to the solution. After 1 hour, the allyl bromide (3 mmol, 0,26 mL) was added. Finally, after 1 h, the ice bath was exchanged for an oil bath at 150 °C and 2-acetylpyridine (3 mmol, 0,34 mL) was added to complete the synthesis with a condensation reaction of 1 hour. The yellow solid obtained from the stock solution after 24 h was then filtered and washed with ice-cold 95% ethanol.

**Synthesis of the ligand (HL<sup>2</sup>).** In an ice bath under stirring, potassium hydroxide (85%) (3 mmol, 198 mg) was solubilized in ethanol (95%) and the hydrazine monohydrate (3 mmol, 0,15 mL) was added. After 40 minutes, the carbon disulfide (3 mmol, 0,18 mL) was added dropwise to the solution. After 1 hour, 1-bromo-4- (bromomethyl) benzene (3 mmol, 750 mg) was added. The solution was slightly heated. Finally, after 1 h, 2-acetylpyridine (3 mmol, 0,34 mL) was added to complete the synthesis with a condensation reaction at reflux for 1 hour. The yellow solid had already precipitated into the reaction by itself and was then filtered and washed with ice-cold 95% ethanol

**Synthesis of the ligand (HL<sup>3</sup>).** For the synthesis of the 2-acetylpyridine-S-p-nitrobenzyl dithiocarbazate (HL<sup>3</sup>), the same steps of the synthesis of the HL<sup>2</sup> ligand were also performed with a variation in the fourth step, where the 4-nitrobenzyl bromide (3 mmol, 648 mg) dissolved in 10 mL of ethanol was added to the solution. The yellow solid was filtered and washed with ice-cold ethanol.

**Table S1.** Angular strain and strain (cm<sup>-1</sup>) frequencies of the normal vibration modes selected for all compounds studied.

	HL <sup>1</sup>	HL <sup>2</sup>	HL <sup>3</sup>	(1)	(2)	(3)	(4)	(5)	(6)
$\nu(\text{C}=\text{S})$	1280	1309	1280	-	-	-	-	-	-
$\nu(\text{C}-\text{S})$	782	790	782	810	787	717	811	813	771
$\nu(\text{N}-\text{H})$	3184	2927	3167	-	-	-	-	-	-
$\nu(\text{N}-\text{N})$	1060	1067	1066	1067	1022	1037	1025	1069	1064
$\nu(\text{C}=\text{N})$	1636	1581	1603	1655	1586	1659	1680	1592	1653
$\nu(\text{C}=\text{N}_{\text{py}})$	1581	*	1564	1550	*	1520	1551	1553	1557
$\nu(\text{O}-\text{C}=\text{O})_{2 \text{ ass}}$	-	-	-	1575	1566	-	-	-	-
$\nu(\text{O}-\text{C}=\text{O})_{2 \text{ sim}}$	-	-	-	1409	1424	-	-	-	-
$\delta(\text{Py})$	687	660	637	684	623	626	623	622	623
$\nu(\text{nitro}_{\text{ass}})$	-	-	1585	-	-	1599	-	-	1599
$\nu(\text{nitro}_{\text{sim}})$	-	-	1350	-	-	1342	-	-	1342

Legend: (-) does not apply and (\*) band not observed.

**Table S2.** <sup>1</sup>H-NMR data for HL<sup>1</sup>.

$\delta$ (ppm)	Multiplicity	Integral	<i>J</i> calcd (Hz)	<i>J</i> found (Hz)	Atribution
2.46	s	3	-	-	7
3.92	d	2	<sup>3</sup> <i>J</i> <sub>H9-H10</sub> = 4-10	<sup>3</sup> <i>J</i> <sub>H9-H10</sub> = 7.1	9
5.17	dd	1	<sup>2</sup> <i>J</i> <sub>H11a-H11b</sub> = 0-5	<sup>2</sup> <i>J</i> <sub>H11a-H11b</sub> = 1.7	11b
			<sup>3</sup> <i>J</i> <sub>H10-H11b</sub> = 6-15	<sup>3</sup> <i>J</i> <sub>H10-H11b</sub> = 10.1	
5.35	dd	1	<sup>2</sup> <i>J</i> <sub>H11a-H11b</sub> = 0-5	<sup>2</sup> <i>J</i> <sub>H11a-H11b</sub> = 1.7	11a
			<sup>3</sup> <i>J</i> <sub>H10-H11a</sub> = 11-18	<sup>3</sup> <i>J</i> <sub>H10-H11a</sub> = 17.1	
5.94	ddt	1	<sup>3</sup> <i>J</i> <sub>H10-H11a</sub> = 11-18	<sup>3</sup> <i>J</i> <sub>H10-H11a</sub> = 17.1	10
			<sup>3</sup> <i>J</i> <sub>H10-H11b</sub> = 6-15	<sup>3</sup> <i>J</i> <sub>H10-H11b</sub> = 10.1	
			<sup>3</sup> <i>J</i> <sub>H9-H10</sub> = 4-10	<sup>3</sup> <i>J</i> <sub>H9-H10</sub> = 7.1	
7.46	ddd	1	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> = 4.9-5.7	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> = 4.8	2
			<sup>3</sup> <i>J</i> <sub>H2-H3</sub> = 7.2-8.5	<sup>3</sup> <i>J</i> <sub>H2-H3</sub> = 7.7	
			<sup>4</sup> <i>J</i> <sub>H2-H4</sub> = 1.4-1.9	<sup>4</sup> <i>J</i> <sub>H2-H4</sub> = 1.1	
7.89	dt	1	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> = 1.6-2.0	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> = 2.2	3
			<sup>3</sup> <i>J</i> <sub>H2-H3</sub> = 7.2-8.5	<sup>3</sup> <i>J</i> <sub>H2-H3</sub> = 7.7	
			<sup>3</sup> <i>J</i> <sub>H3-H4</sub> = 7.2-8.5	<sup>3</sup> <i>J</i> <sub>H3-H4</sub> = 7.7	
8.08	d	1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> = 0.7-1.1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> = n.o.	4
			<sup>4</sup> <i>J</i> <sub>H2-H4</sub> = 1.4-1.9	<sup>4</sup> <i>J</i> <sub>H2-H4</sub> = n.o.	
			<sup>3</sup> <i>J</i> <sub>H3-H4</sub> = 7.2-8.5	<sup>3</sup> <i>J</i> <sub>H3-H4</sub> = 7.7	
8.63	d	1	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> = 4.9-5.7	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> = 4.8	1
			<sup>4</sup> <i>J</i> <sub>H1-H3</sub> = 1.6-2.0	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> = n.o.	
			<sup>5</sup> <i>J</i> <sub>H1-H4</sub> = 0.7-1.1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> = n.o.	
12.59	s	1	-	-	3a

Legend: - (not applicable) and n.o. (not observed).

**Table S3.**  $^{13}\text{C}$ -NMR data for HL<sup>1</sup>

$\delta$ (ppm)	Atribution
12.9	7
36.1	9
118.6	11
120.3	4
124.6	2
133.0	10
136.8	3
148.8	6
152.1	1
154.1	5
198.7	8

**Table S4.** <sup>1</sup>H-NMR data for HL<sup>2</sup>.

$\delta$ (ppm)	Multiplicity	Integral	<i>J</i> calcd (Hz)	<i>J</i> found (Hz)	Atribution
2.47	s	3	-	-	7
4.48	s	2	-	-	9
7.39	m	2	n.o	n.o	11
7.46	ddd	1	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> =4.9-5.7	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> =4.9	2
			<sup>3</sup> <i>J</i> <sub>H2-H3</sub> =7.2-8.5	<sup>3</sup> <i>J</i> <sub>H2-H3</sub> =7.7	
			<sup>4</sup> <i>J</i> <sub>H2-H4</sub> =1.4-1.9	<sup>4</sup> <i>J</i> <sub>H2-H4</sub> =1.1	
7.52	m	2	n.o	n.o	12
7.86	td	1	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> =1.6-2.0	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> =1.8	3
			<sup>3</sup> <i>J</i> <sub>H2-H3</sub> =7.2-8.5	<sup>3</sup> <i>J</i> <sub>H2-H3</sub> =7.7	
			<sup>3</sup> <i>J</i> <sub>H3-H4</sub> =7.2-8.5	<sup>3</sup> <i>J</i> <sub>H3-H4</sub> =7.7	
8.03	d	1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> =0.7-1.1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> = n.o.	4
			<sup>4</sup> <i>J</i> <sub>H2-H4</sub> =1.4-1.9	<sup>4</sup> <i>J</i> <sub>H2-H4</sub> = n.o.	
			<sup>3</sup> <i>J</i> <sub>H3-H4</sub> =7.2-8.5	<sup>3</sup> <i>J</i> <sub>H3-H4</sub> =7.7	
8.62	ddd	1	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> =4.9-5.7	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> = 4.9	1
			<sup>4</sup> <i>J</i> <sub>H1-H3</sub> =1.6-2.0	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> = 1.8	
			<sup>5</sup> <i>J</i> <sub>H1-H4</sub> =0.7-1.1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> = 0.7	
12.68	s	1	-	-	3a

Legend: - (not applicable) and n.o. (not observed).

**Table S5.** <sup>13</sup>C-NMR data for HL<sup>2</sup>.

$\delta$ (ppm)	Atribution
12.9	7
36.8	9
120.2	13
120.7	4
124.6	2
131.2	11
131.3	12
135.9	3
136.8	10
148.8	6
152.3	1
154.0	5
198.5	8

**Table S6.** <sup>1</sup>H-NMR data for HL<sup>3</sup>.

$\delta$ (ppm)	Multiplicity	Integral	<i>J</i> calcd (Hz)	<i>J</i> found (Hz)	Atribution
2.47	s	3	-	-	7
4.67	s	2	-	-	9
7.46	ddd	1	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> =4.9-5.7	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> =4.9	2
			<sup>3</sup> <i>J</i> <sub>H2-H3</sub> =7.2-8.5	<sup>3</sup> <i>J</i> <sub>H2-H3</sub> =7.8	
			<sup>4</sup> <i>J</i> <sub>H2-H4</sub> =1.4-1.9	<sup>4</sup> <i>J</i> <sub>H2-H4</sub> =1.2	
7.70	m	2	n.o	n.o	11
7.86	td	1	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> =1.6-2.0	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> =1.8	3
			<sup>3</sup> <i>J</i> <sub>H2-H3</sub> =7.2-8.5	<sup>3</sup> <i>J</i> <sub>H2-H3</sub> =7.8	
			<sup>3</sup> <i>J</i> <sub>H3-H4</sub> =7.2-8.5	<sup>3</sup> <i>J</i> <sub>H3-H4</sub> =7.8	
8.05	dt	1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> =0.7-1.1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> = 1.2	4
			<sup>4</sup> <i>J</i> <sub>H2-H4</sub> =1.4-1.9	<sup>4</sup> <i>J</i> <sub>H2-H4</sub> = 1.2	
			<sup>3</sup> <i>J</i> <sub>H3-H4</sub> =7.2-8.5	<sup>3</sup> <i>J</i> <sub>H3-H4</sub> =7.8	
8.19	m	2	n.o	n.o	12
8.63	ddd	1	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> =4.9-5.7	<sup>3</sup> <i>J</i> <sub>H1-H2</sub> = 4.9	1
			<sup>4</sup> <i>J</i> <sub>H1-H3</sub> =1.6-2.0	<sup>4</sup> <i>J</i> <sub>H1-H3</sub> = 1.8	
			<sup>5</sup> <i>J</i> <sub>H1-H4</sub> =0.7-1.1	<sup>5</sup> <i>J</i> <sub>H1-H4</sub> = 1.2	
12.77	s	1	-	-	3a

Legend: - (not applicable) and n.o. (not observed).

**Table S7.** <sup>13</sup>C-NMR data for HL<sup>3</sup>.

$\delta$ (ppm)	Atribution
13.1	7
36.5	9
120.4	4
123.5	12
124.7	2
130.9	11
136.9	3
144.8	10
145.8	6
146.5	13
148.9	1
152.6	5
198.1	8



**Table S8.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR data for (1).

$^1\text{H}$			$^{13}\text{C}$	
$\delta$ (ppm)	Multiplicity	Atribution	$\delta$ (ppm)	Atribution
2.64	s	7	14.40	7
2.77	s	13	14.70	13
3.84	d	9	34.61	9
5.12	m	11b	118.07	11
5.28	dd	11a	124.30	4
6.00	m	10	127.07	2
7.50	m	2	134.69	10
7.89	d	4	140.23	3
8.04	td	3	140.93	6
8.18	d	1	146.99	1
			149.06	5
			155.47	12
			187.68	8

**Table S9.**  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR data for (2).

$^1\text{H}$			$^{13}\text{C}$	
$\delta$ (ppm)	Multiplicity	Atribution	$\delta$ (ppm)	Atribution
2.61	s	7	14.34	7
2.74	s	15	14.82	15
2.74	s	17	14.82	17
4.38	s	9	34.03	9
7.37	m	11	119.50	13
7.51	m	12	123.50	4
7.69	ddd	2	126.62	2
7.79	d	4	131.00	11
8.06	d	1	131.09	12
8.16	td	3	137.93	3
			139.87	10
			140.46	6
			146.31	1
			148.45	5
			154.69	14
			155.27	16
			186.66	8

**Table S10.** <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data for (3).

<sup>1</sup> H			<sup>13</sup> C	
δ (ppm)	Multiplicity	Atribuition	δ (ppm)	Atribuition
2.76	s	7	14.33	7
4.58	s	9	34.50	9
7.46	td	2	123.37	12
7.73	m	11	123.85	4
7.80	d	4	126.44	2
8.05	td	3	129.94	11
8.08	d	1	139.80	3
8.21	m	12	146.16	10
			146.32	6
			147.10	13
			148.25	1
			155.46	5
			186.39	8

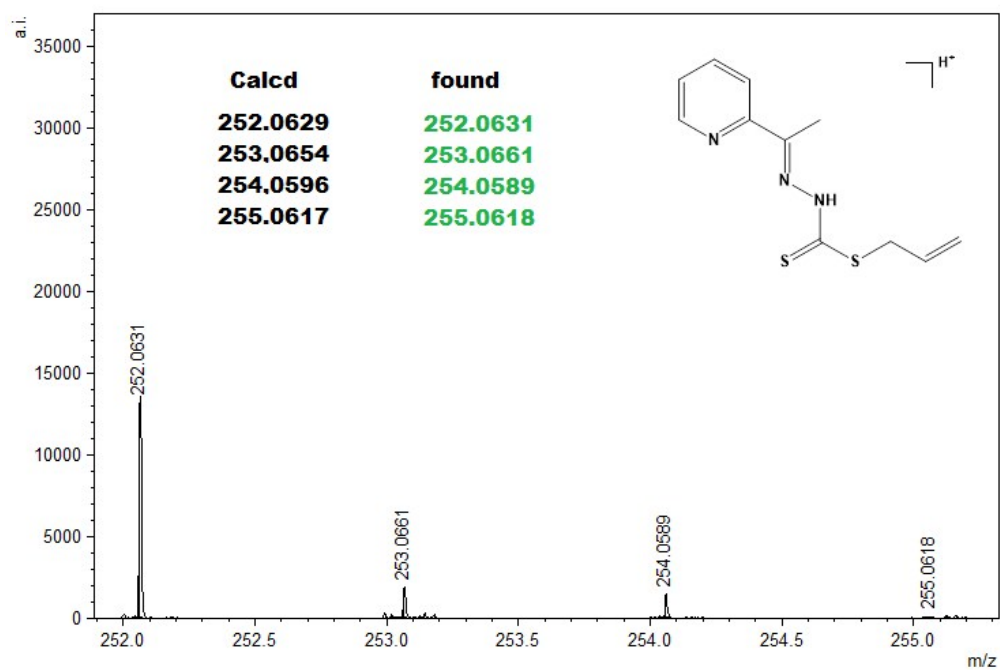
**Table S11.** Results obtained in the electron spectroscopy analysis of all the compounds obtained with wavelength values in nm.

Composto	$\pi \rightarrow \pi^*$ transition						$n \rightarrow \pi^*$ transition					
	DMF	logε	MeOH	logε	MeCN	logε	DMF	logε	MeOH	logε	MeCN	Logε
HL <sup>1</sup>	335	4.49	333	4.54	332	4.56	388	3.95	*	*	*	*
HL <sup>2</sup>	335	4.24	333	4.64	332	4.24	388	3.99	*	*	*	*
HL <sup>3</sup>	291	4.32	290	4.44	298	4.29	384	3.91	332	4.57	331	4.33
(1)	319	4.62	324	4.57	319	4.11	*	*	*	*	*	*
(2)	322	4.53	324	4.50	319	4.34	*	*	*	*	*	*
(3)	310	4.55	302	4.23	311	4.50	*	*	*	*	*	*
(4)	324	4.58	329	4.01	322	4.51	*	*	*	*	*	*
(5)	324	4.49	329	4.18	322	4.49	*	*	*	*	*	*
(6)	288	4.68	280	4.33	293	4.67	*	*	*	*	*	*

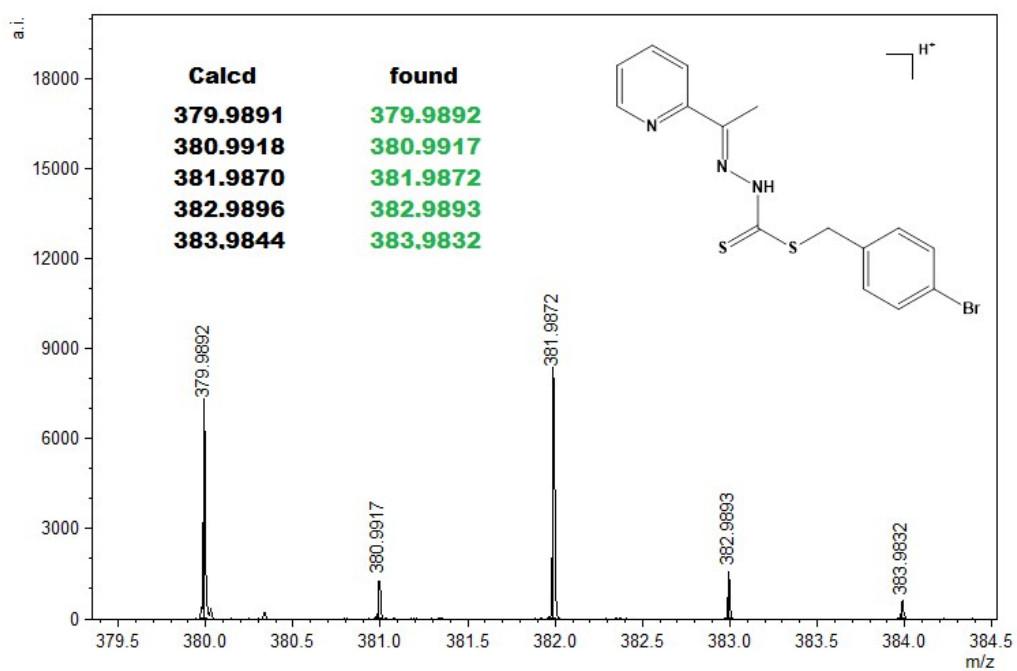
Legenda: \* não observado.

**Table S12.** Results obtained of transfer of charge in the electron spectroscopy analysis of all the compounds obtained with wavelength values in nm.

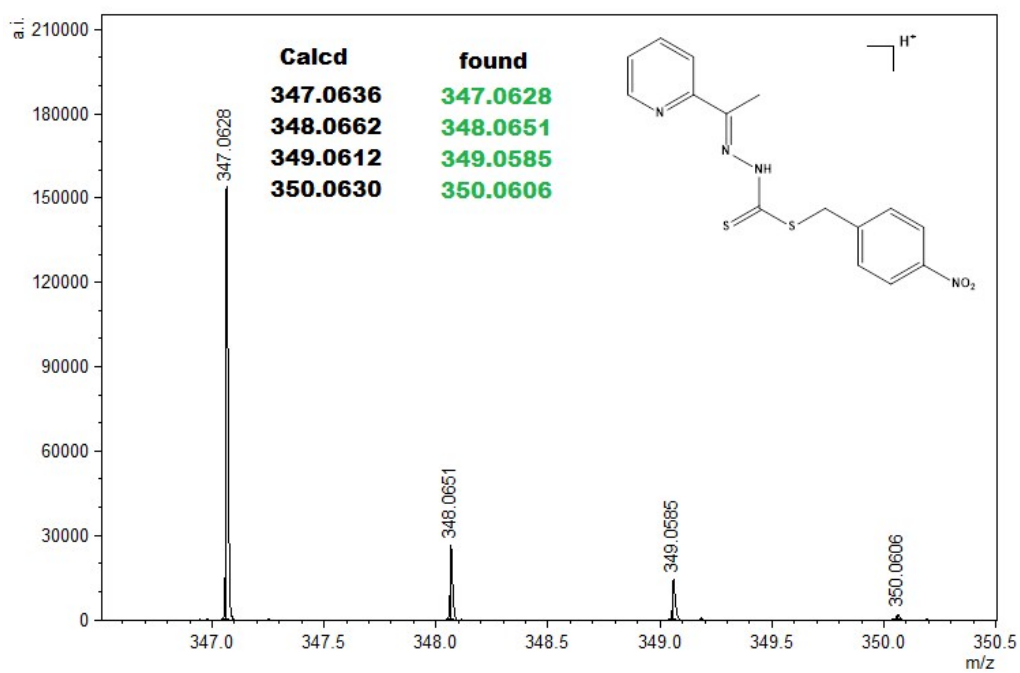
	transfer of charge transition					
	DMF	log $\epsilon$	MeOH	log $\epsilon$	MeCN	log $\epsilon$
<b>(1)</b>	385	4.46	381	4.55	385	4.03
<b>(2)</b>	386	4.47	381	4.45	387	4.20
<b>(3)</b>	388	4.26	380	4.00	386	4.25
<b>(4)</b>	430	4.35	417	3.83	426	4.24
<b>(5)</b>	430	4.23	422	3.91	426	4.18
<b>(6)</b>	430	4.26	419	3.92	423	4.27



**Figure S1.** ESI(+)-MS of HL<sup>1</sup>.



**Figure S2.** ESI(+)-MS of HL<sup>2</sup>.



**Figure S3.** ESI(+)-MS of HL<sup>3</sup>.

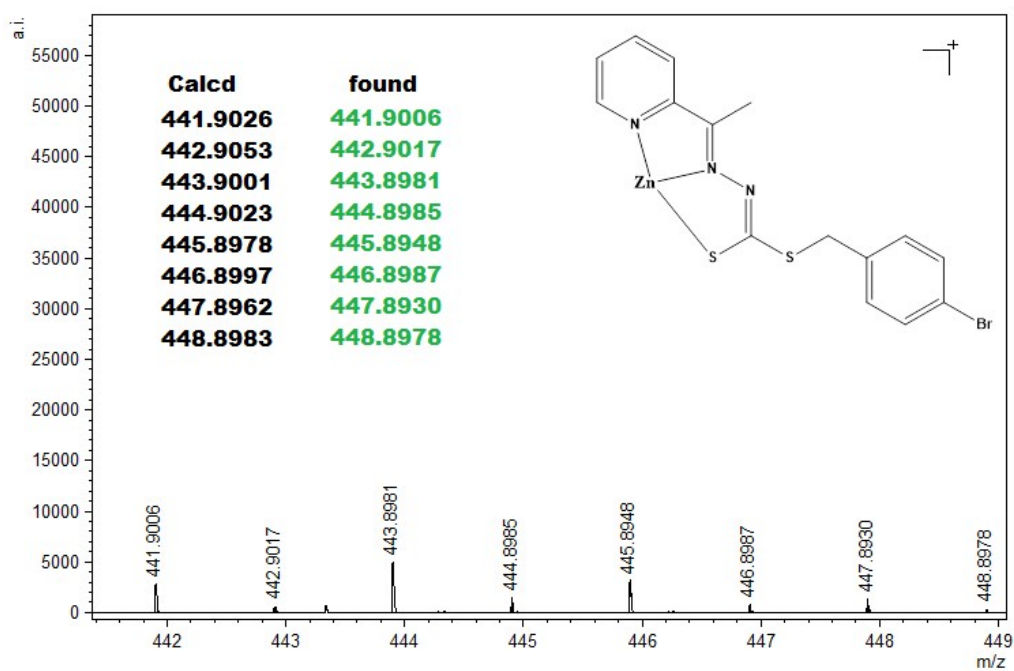


Figure S4. ESI(+)-MS of (1).

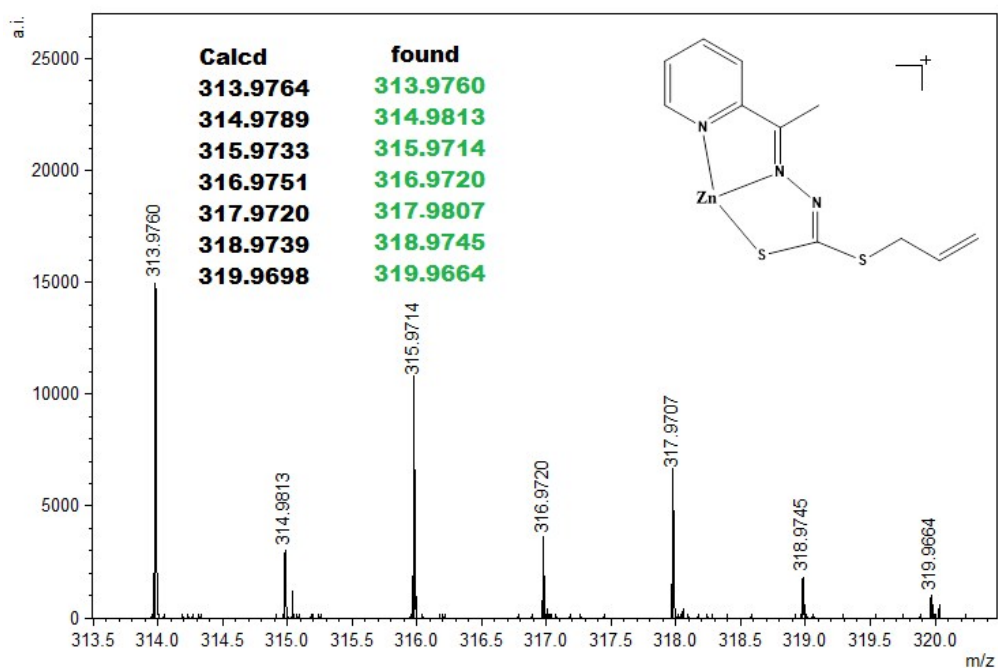
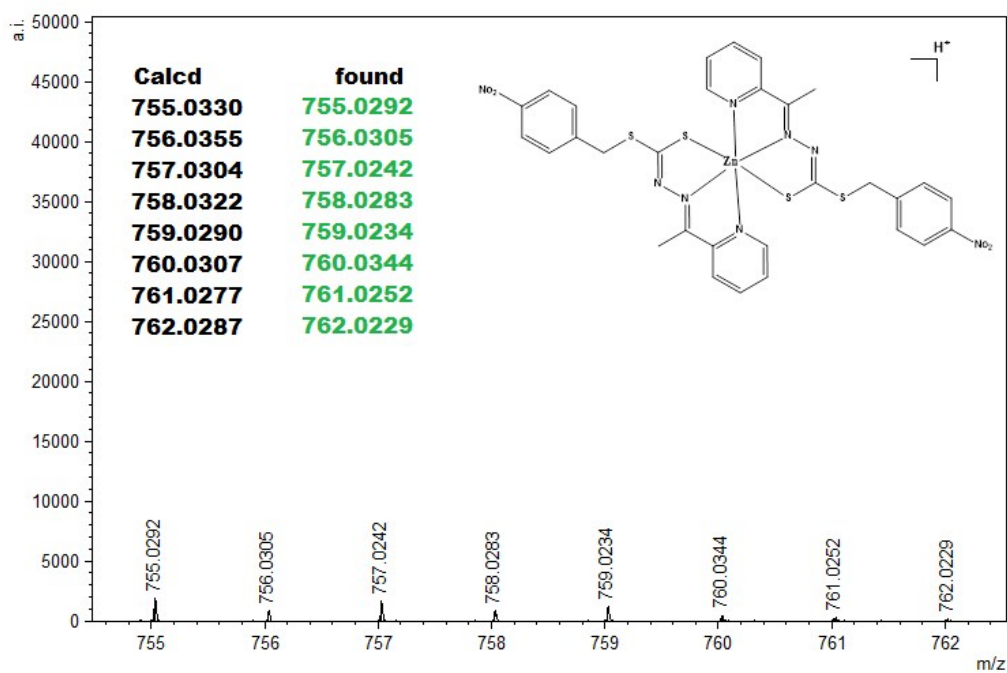
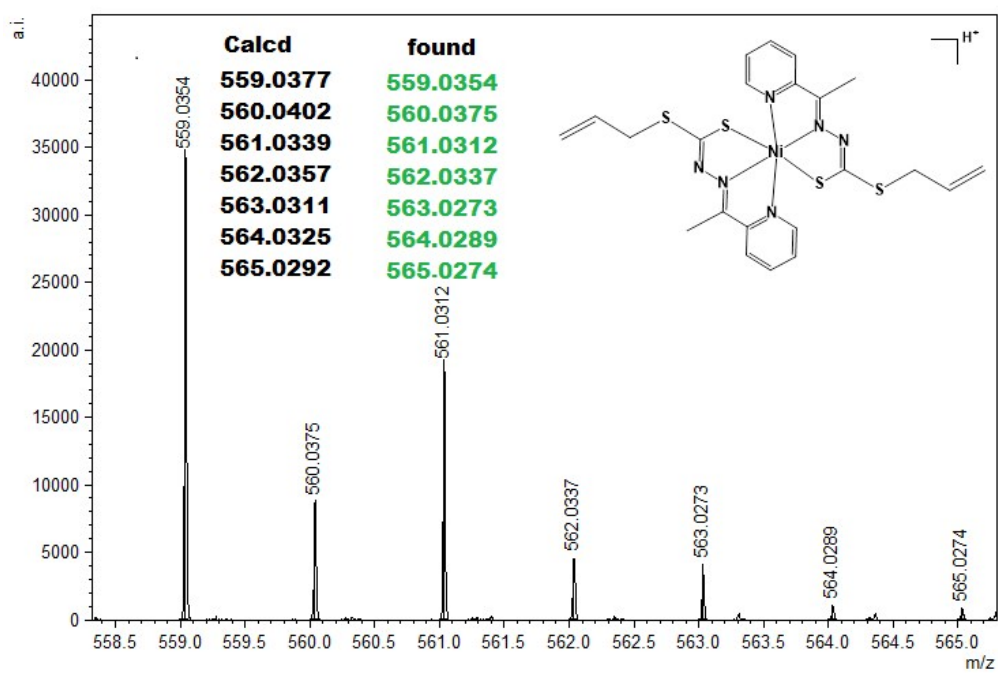


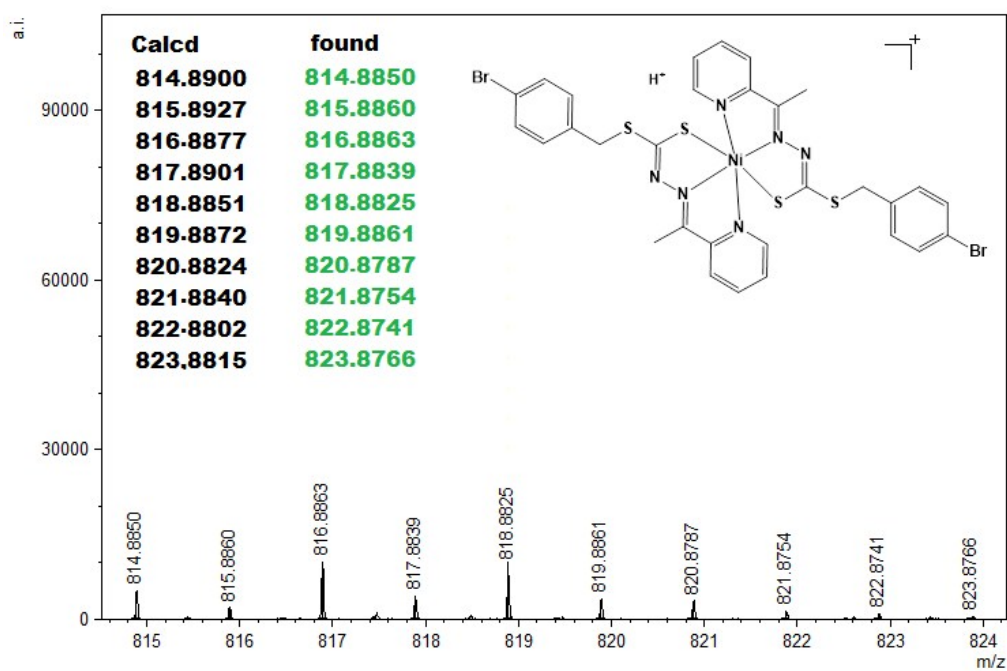
Figure S5. ESI(+)-MS of (2).



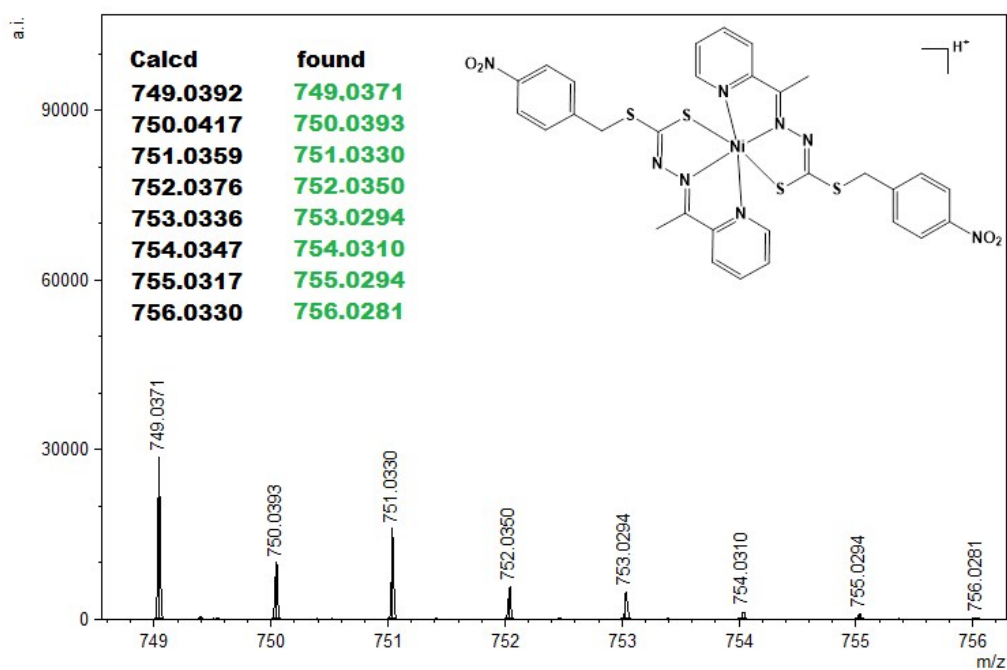
**Figure S6.** ESI(+)-MS of (3).



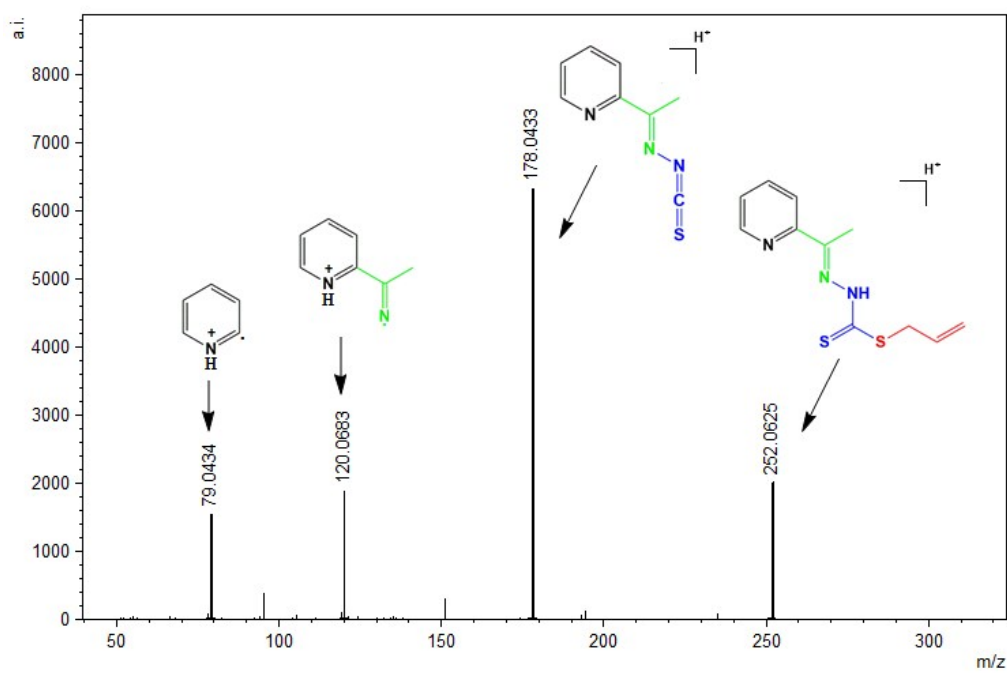
**Figure S7.** ESI(+)-MS of (4).



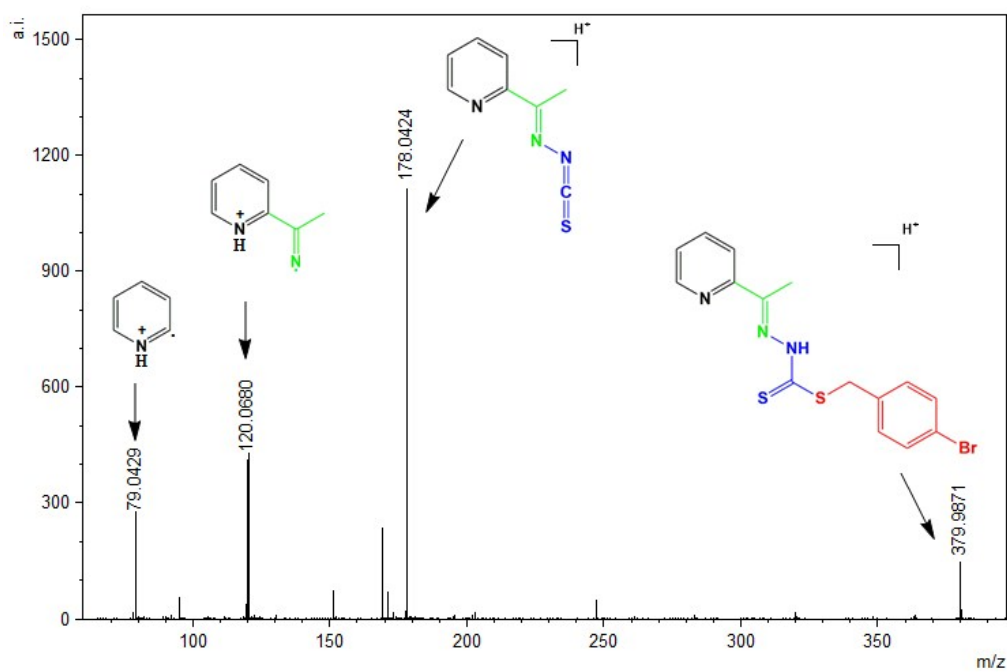
**Figure S8.** ESI(+)-MS of (5).



**Figure S9.** ESI(+)-MS of (6).

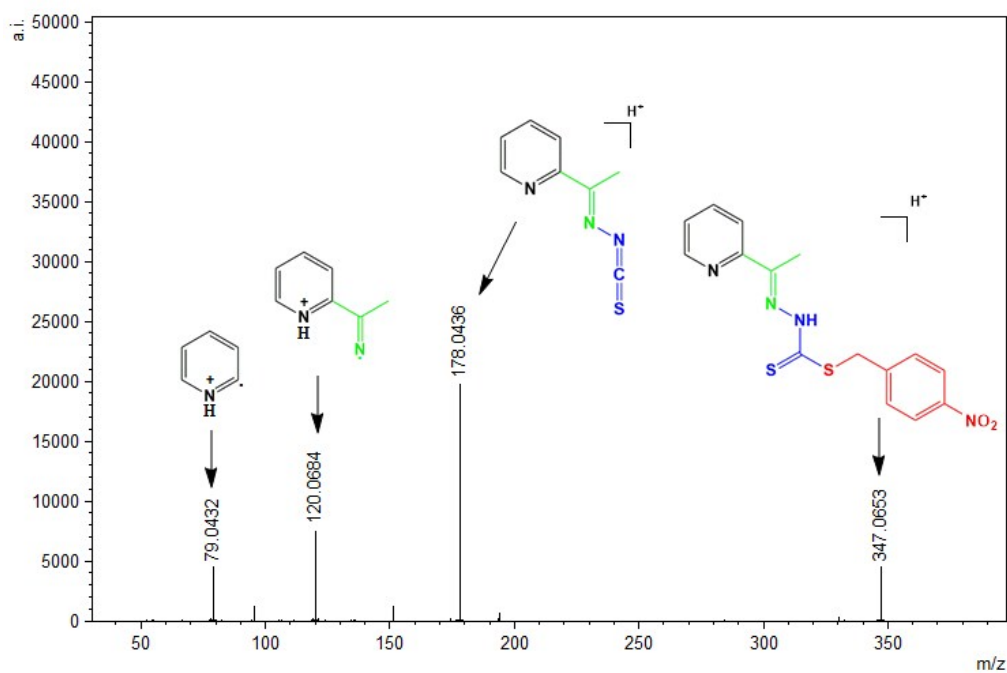


**Figure S10.** ESI(+)-MSMS of HL<sup>1</sup>.

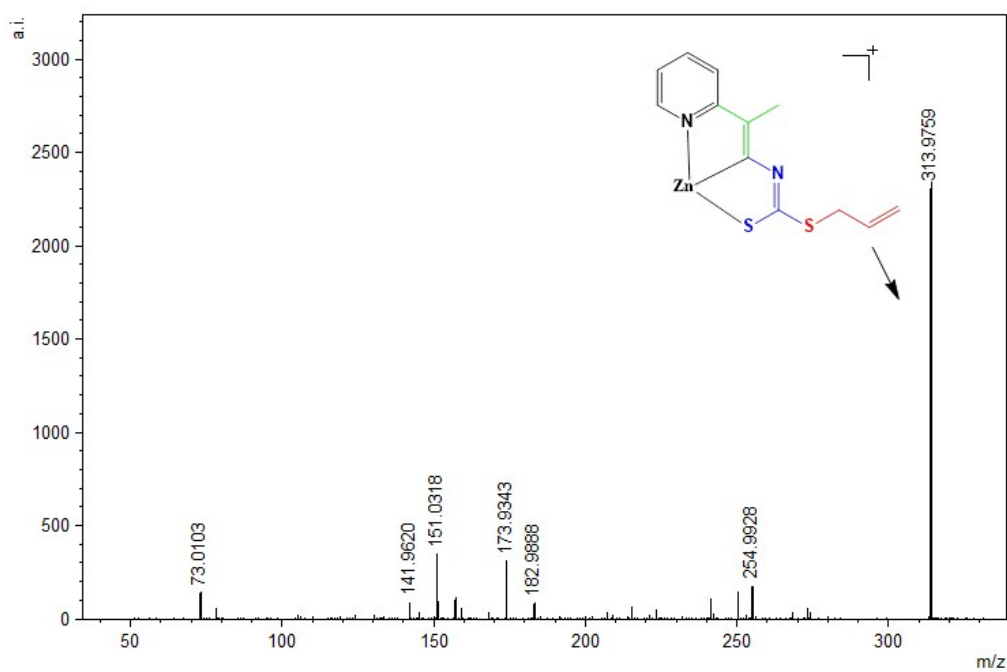


**Figure S11.** ESI(+)-MSMS of HL<sup>2</sup>.

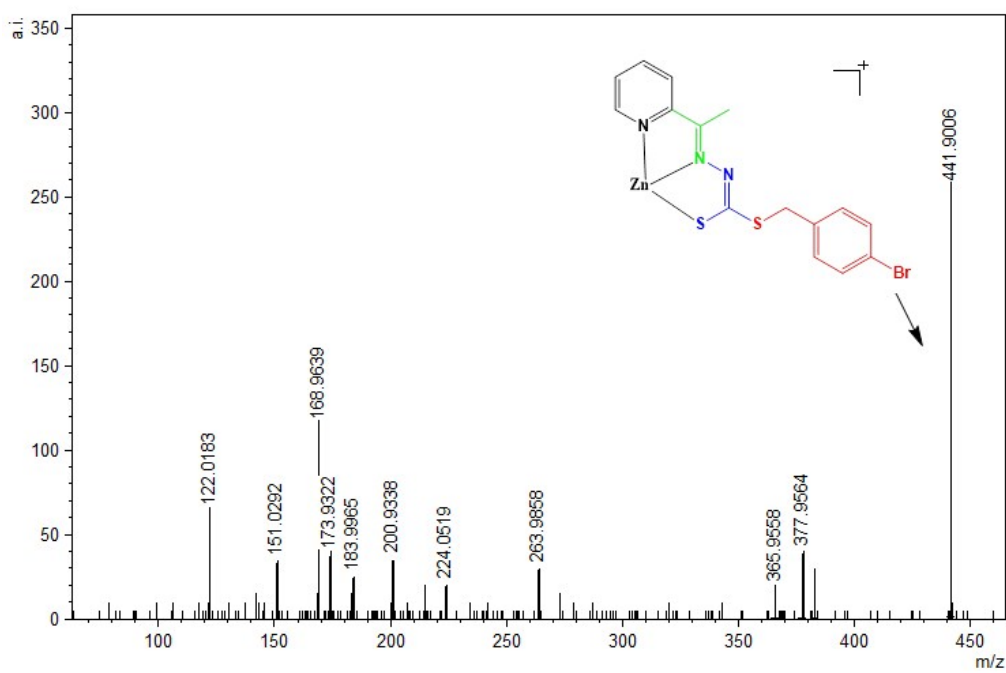




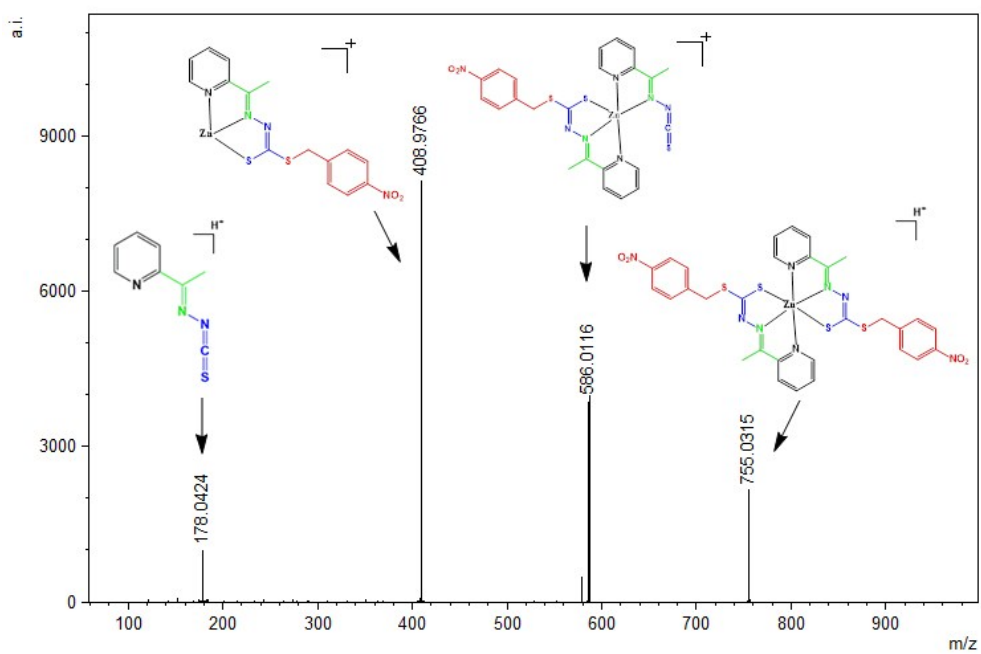
**Figure S12.** ESI(+)-MSMS of HL<sup>3</sup>.



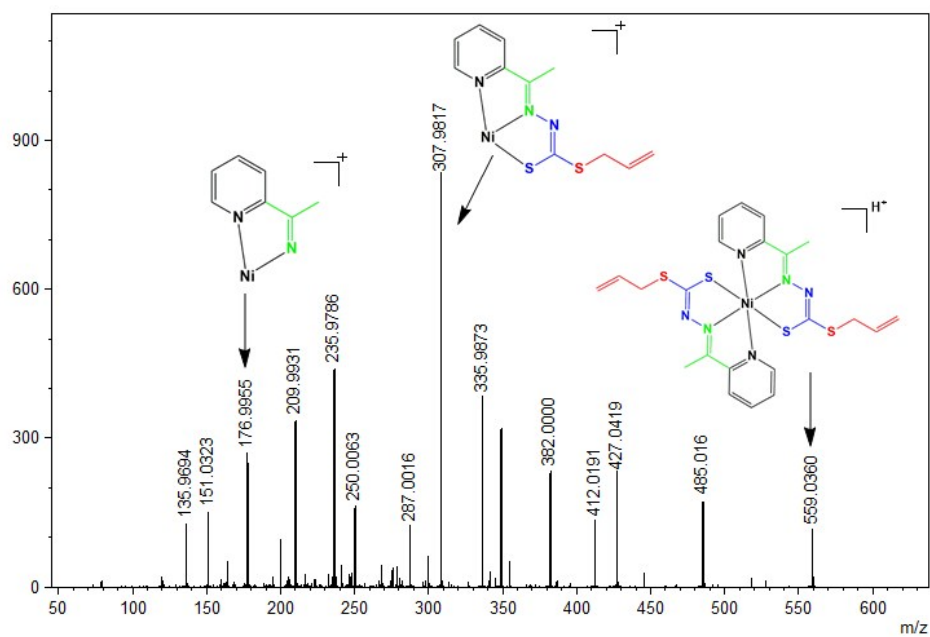
**Figure S13.** ESI(+)-MSMS of (1).



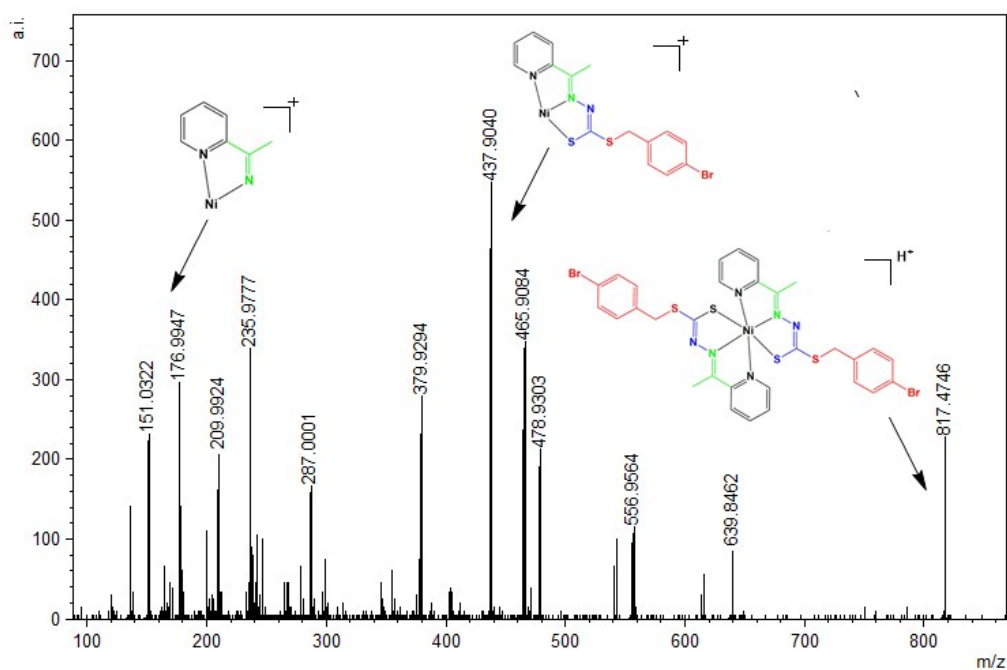
**Figure S14.** ESI(+)-MSMS of (2).



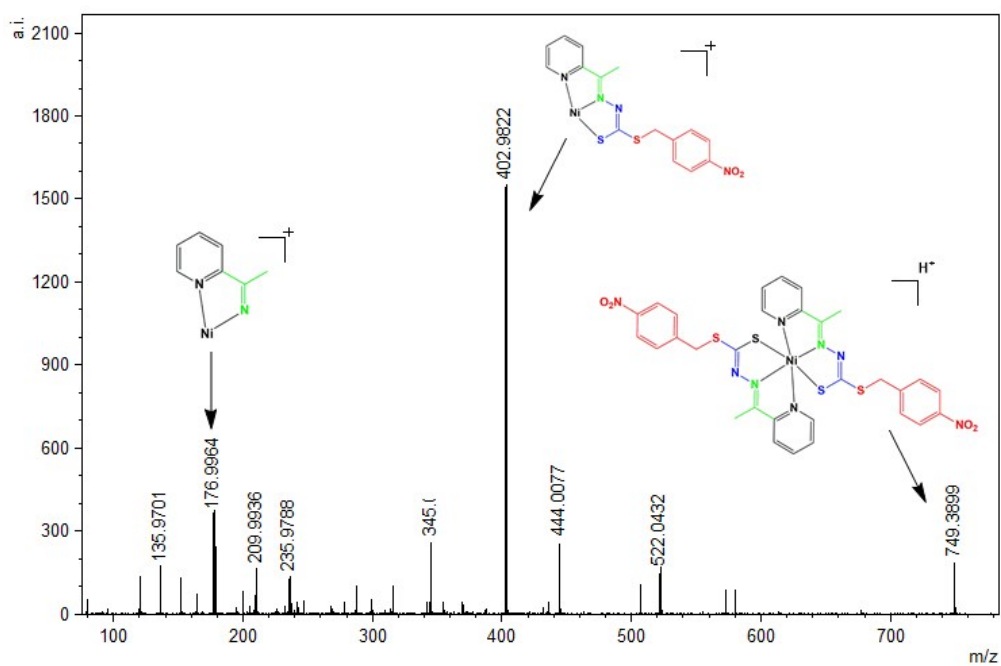
**Figure S15.** ESI(+)-MSMS of (3).



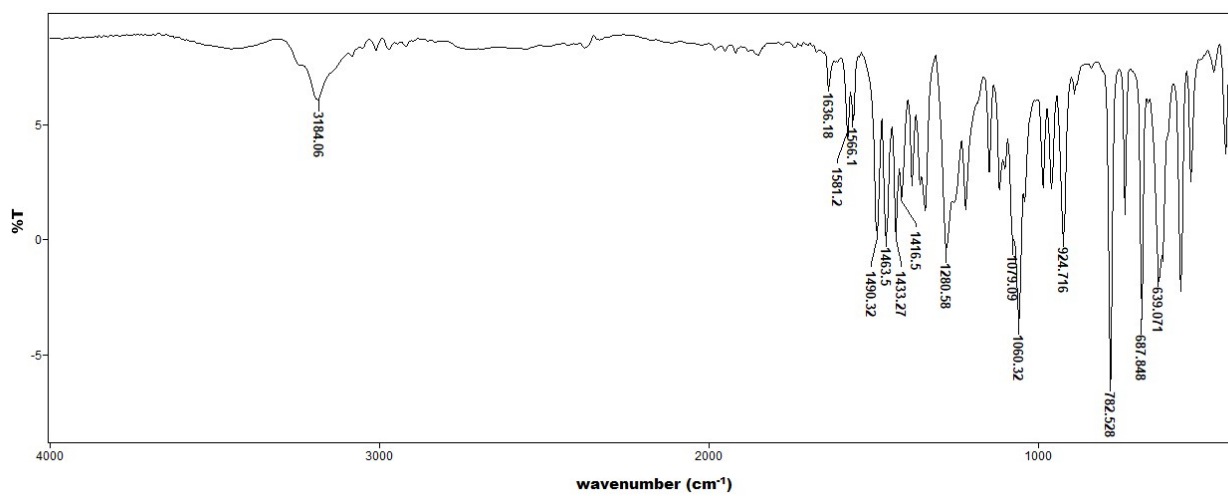
**Figure S16.** ESI(+)-MSMS of (4).



**Figure S17.** ESI(+)-MSMS of (5).



**Figure S18.** ESI(+)-MSMS of (6).



**Figure S19.** IR spectra of compound HL<sup>1</sup>.

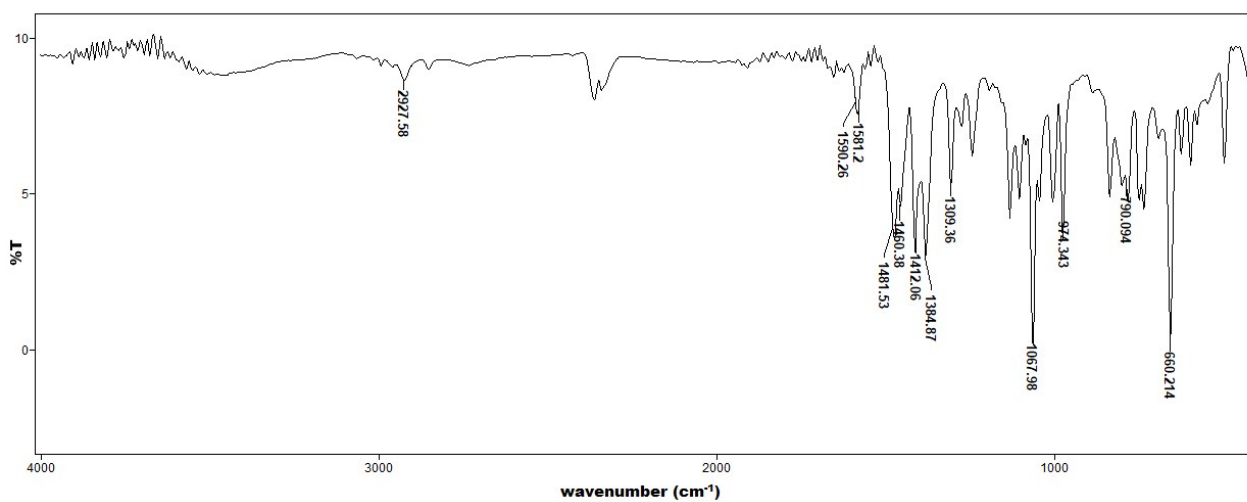


Figure S20. IR spectra of compound HL<sup>2</sup>.

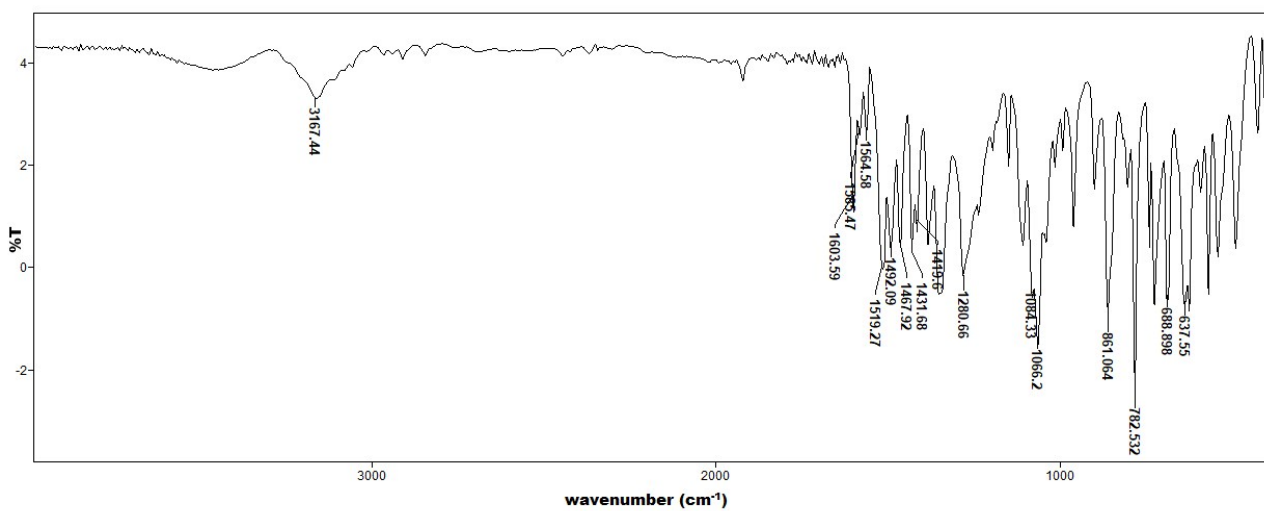


Figure S21. IR spectra of compound HL<sup>3</sup>.

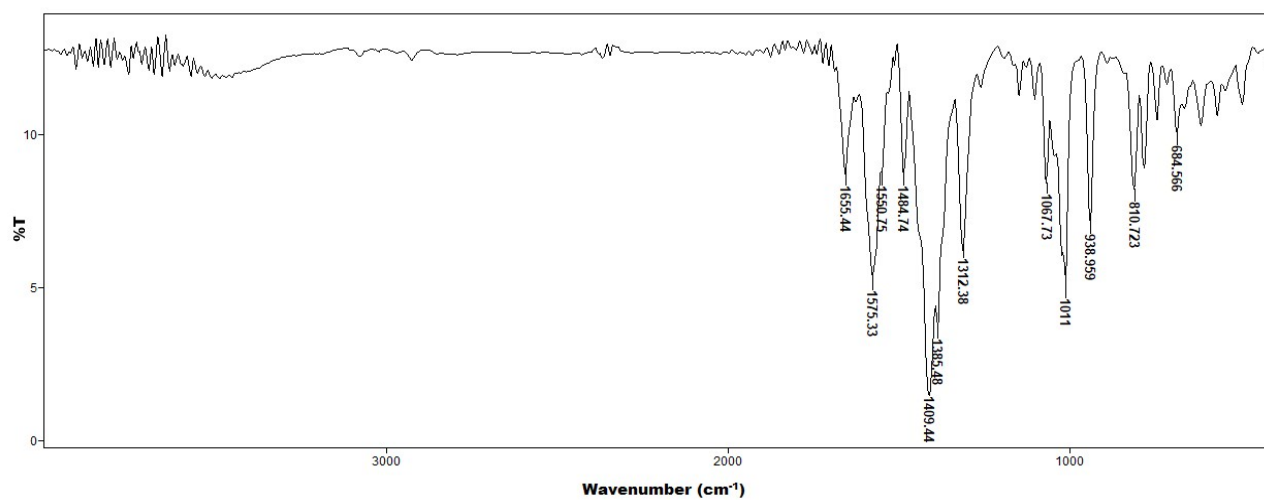
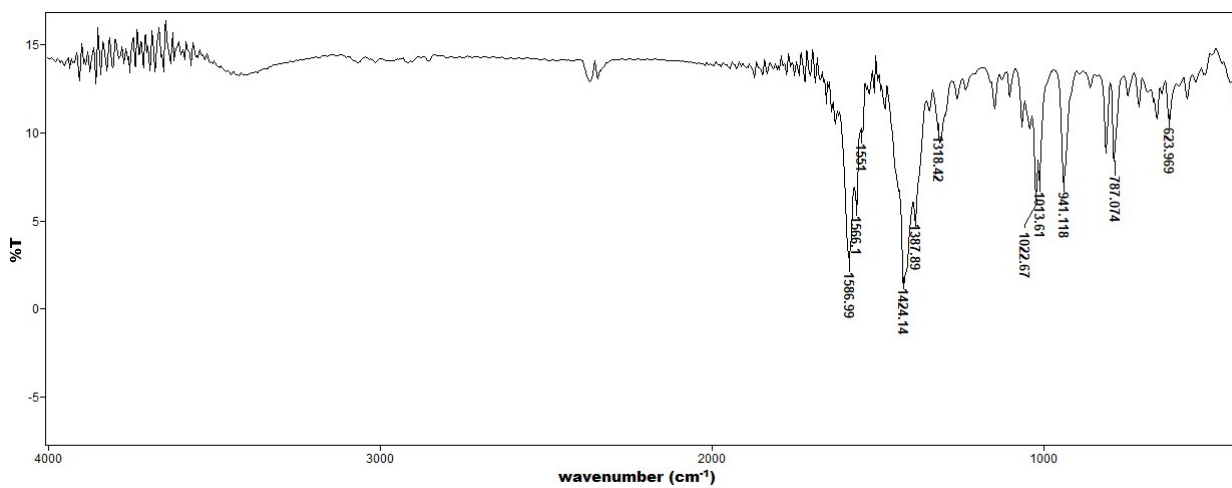
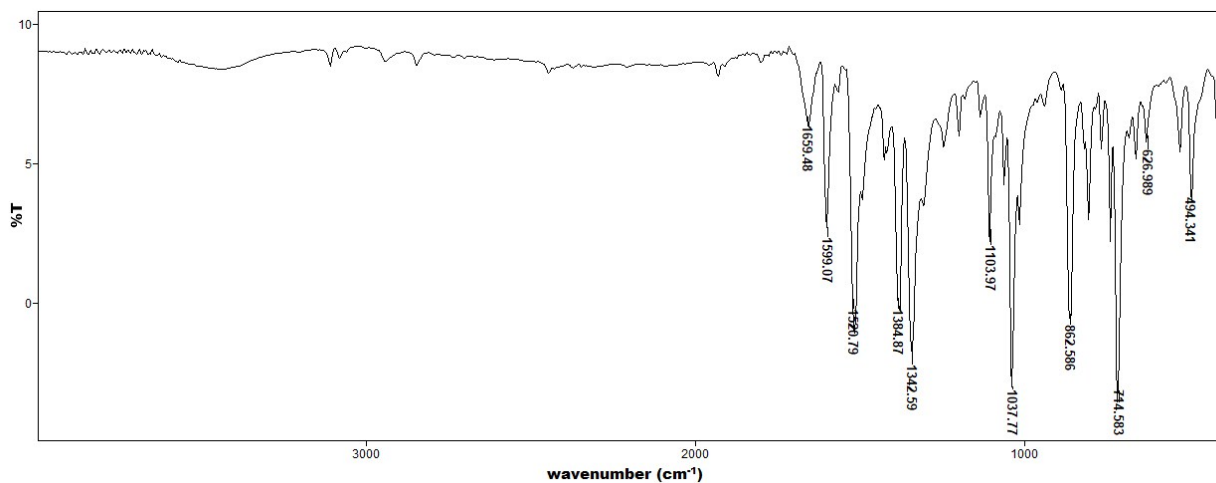


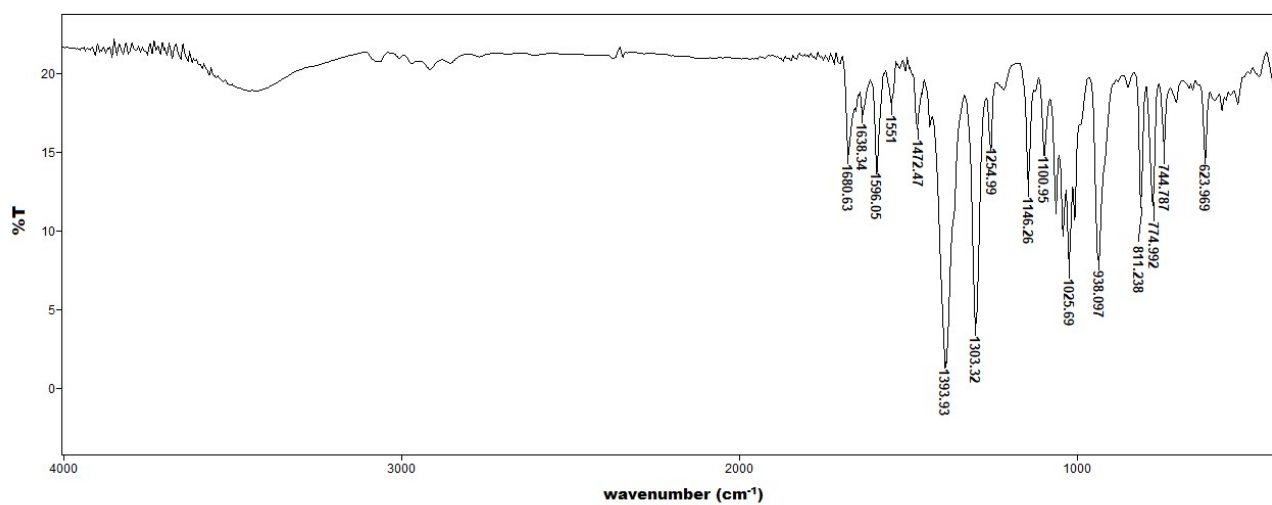
Figure S22. IR spectra of compound (1).



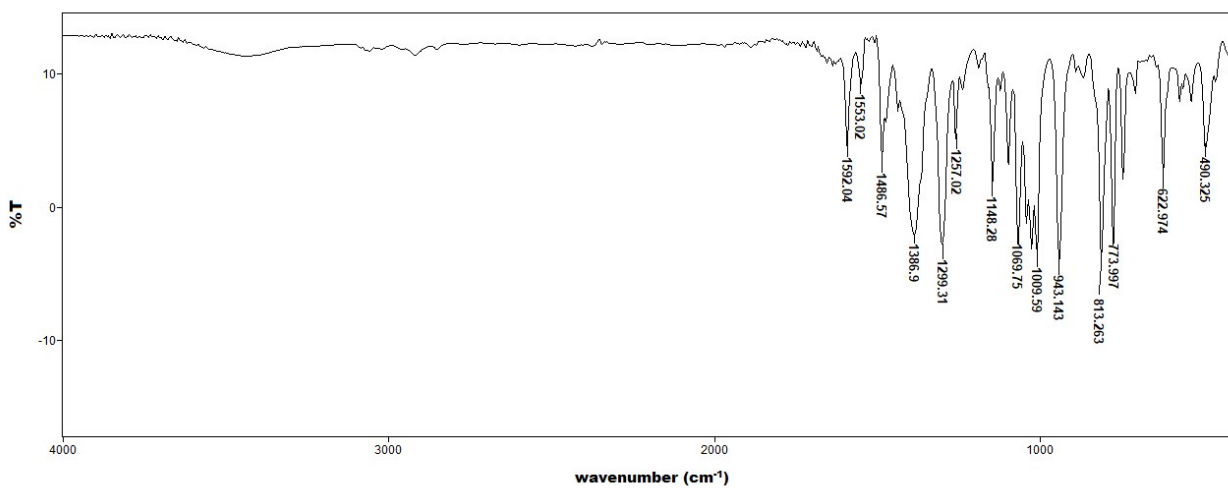
**Figure S23.** IR spectra of compound (2).



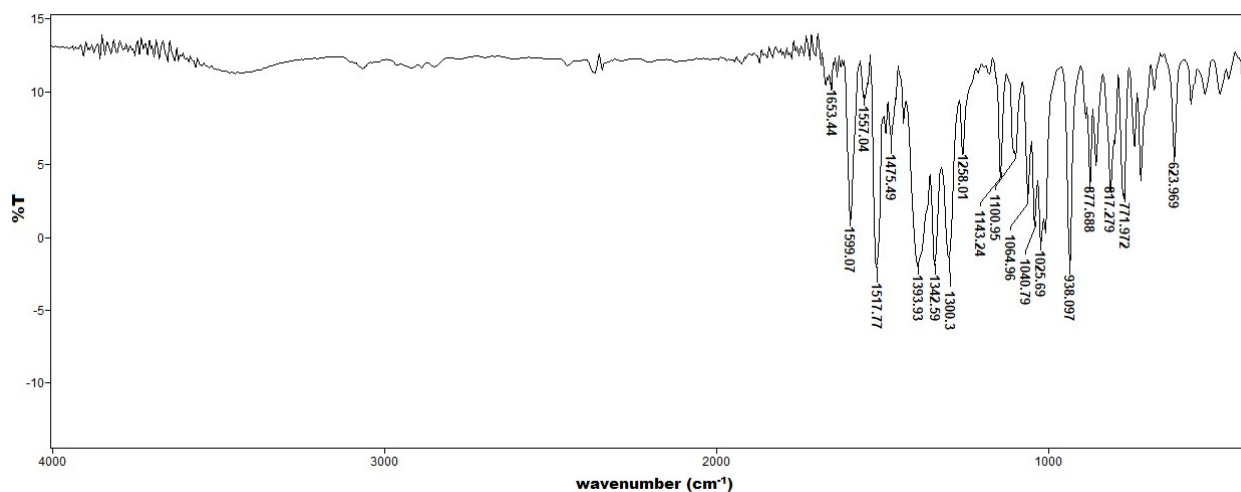
**Figure S24.** IR spectra of compound (3).



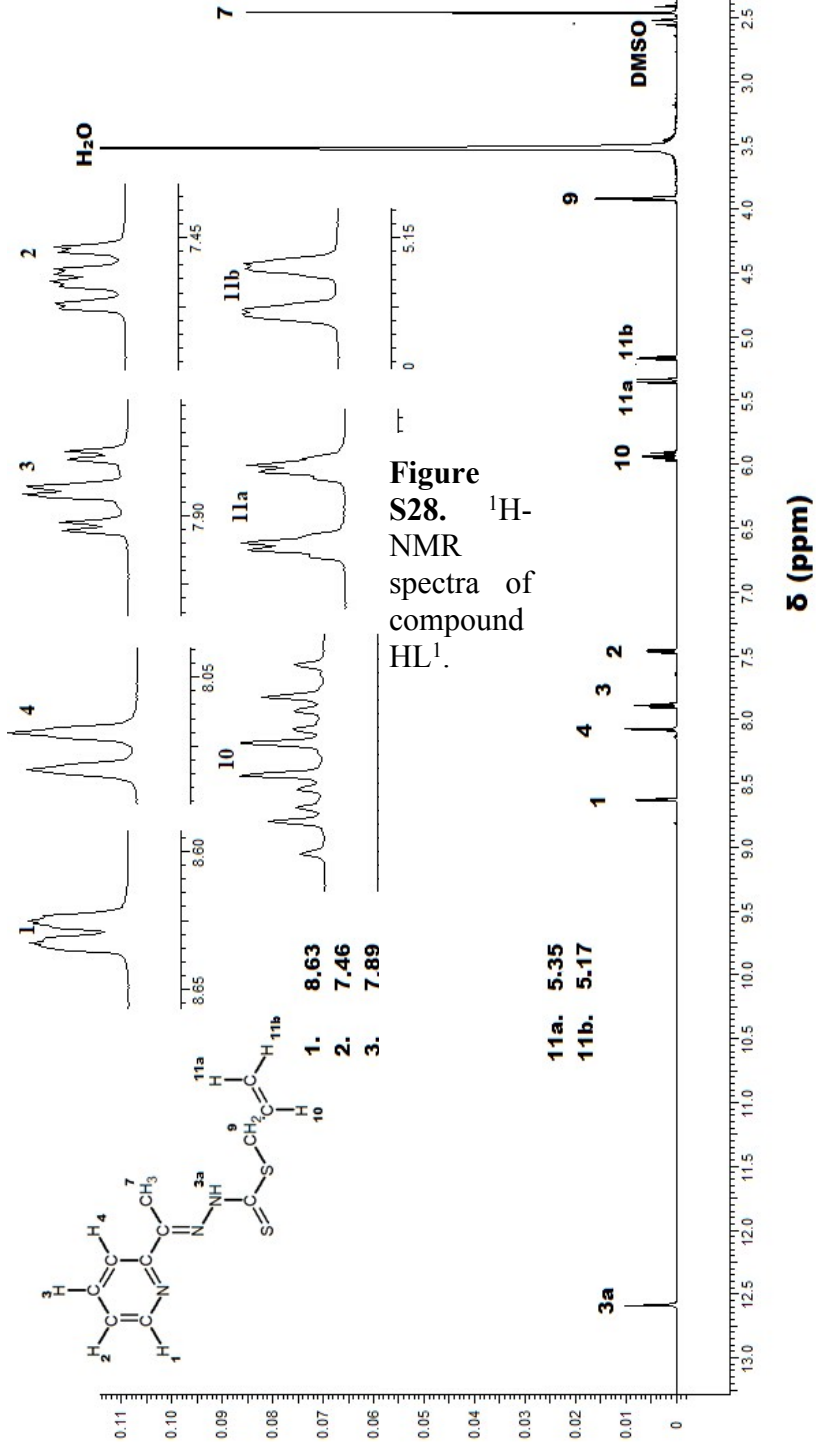
**Figure S25.** IR spectra of compound (4).



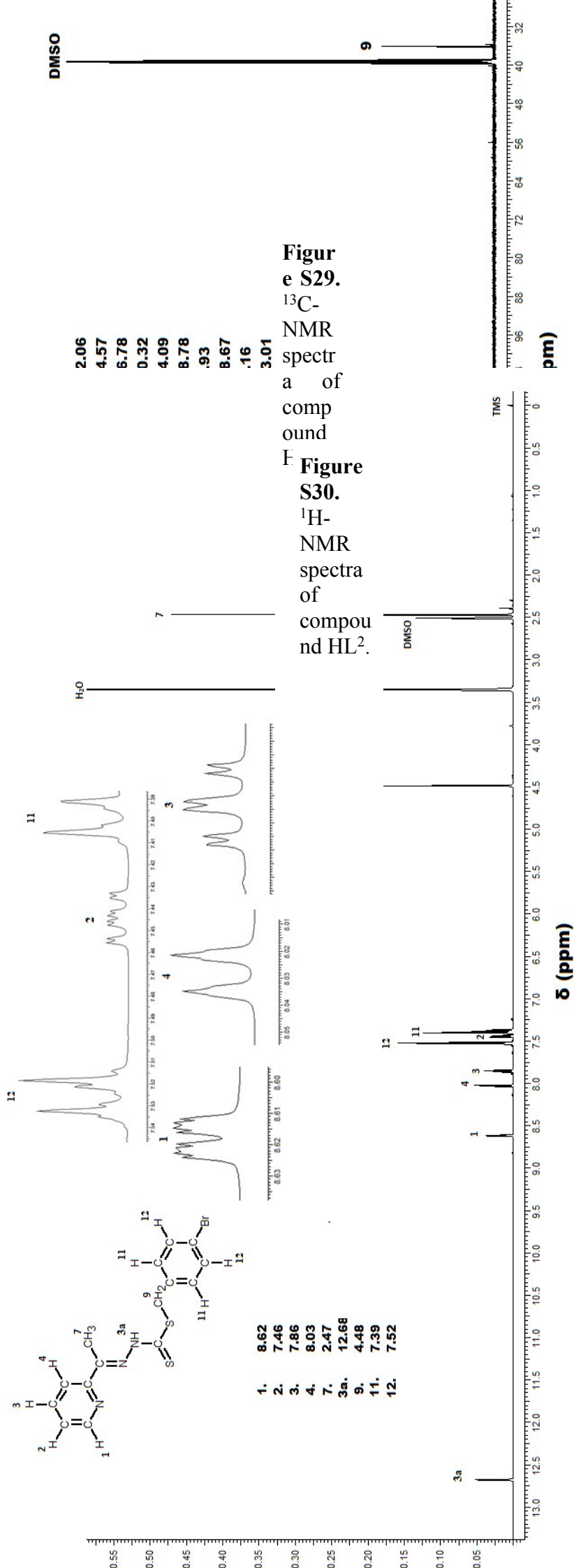
**Figure S26.** IR spectra of compound (5).

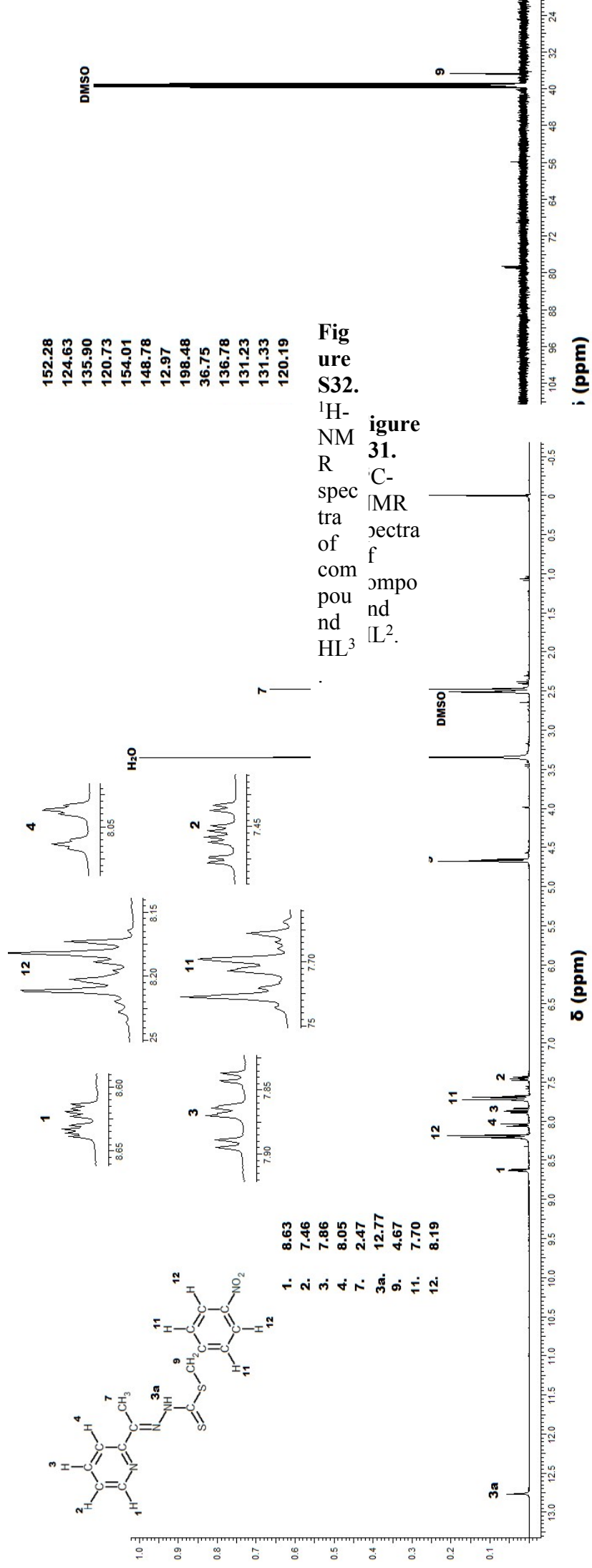


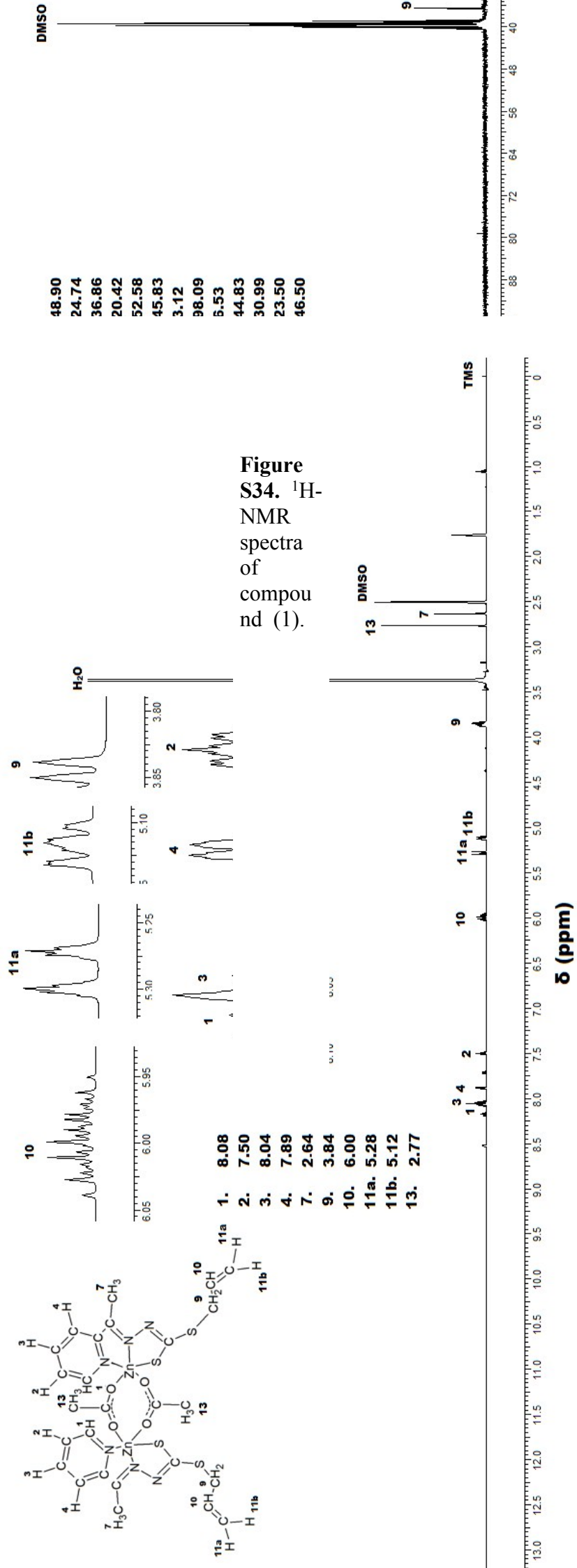
**Figure S27.** IR spectra of compound (6).

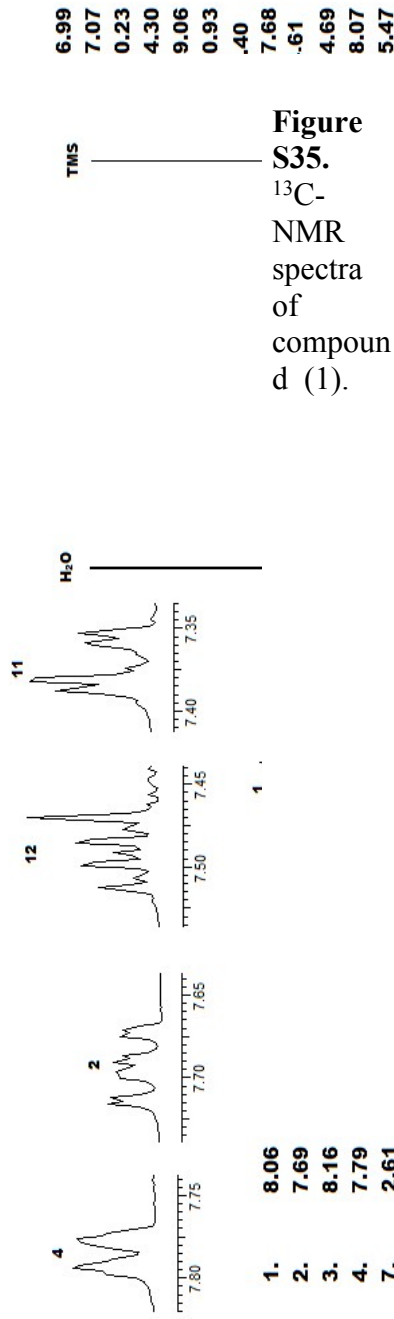
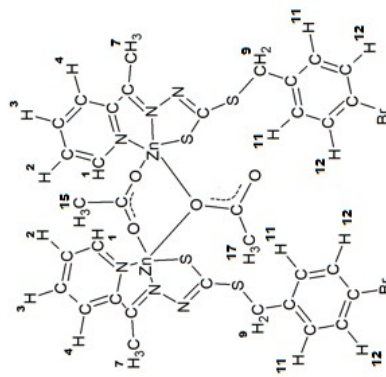






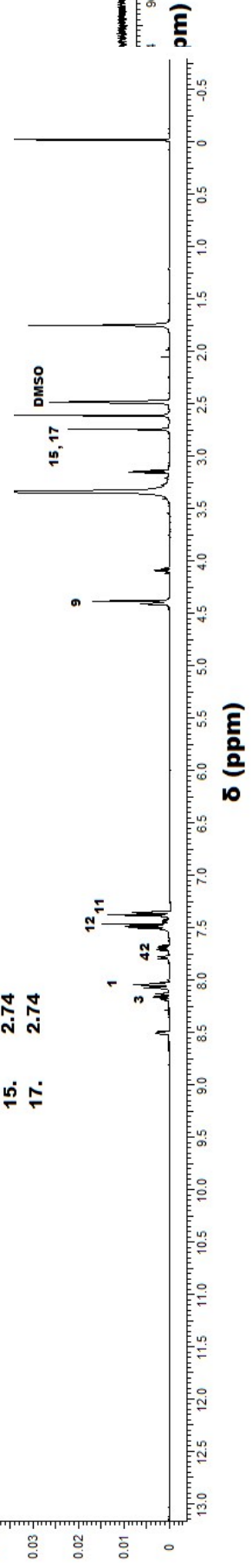


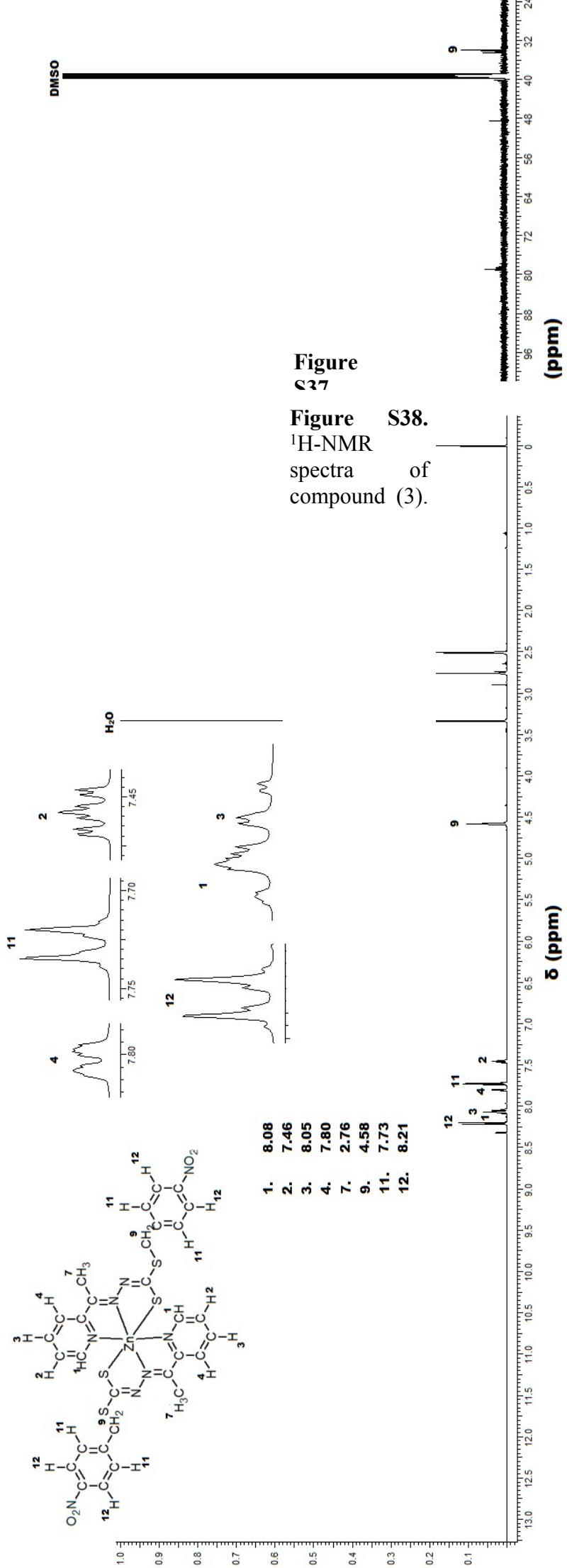


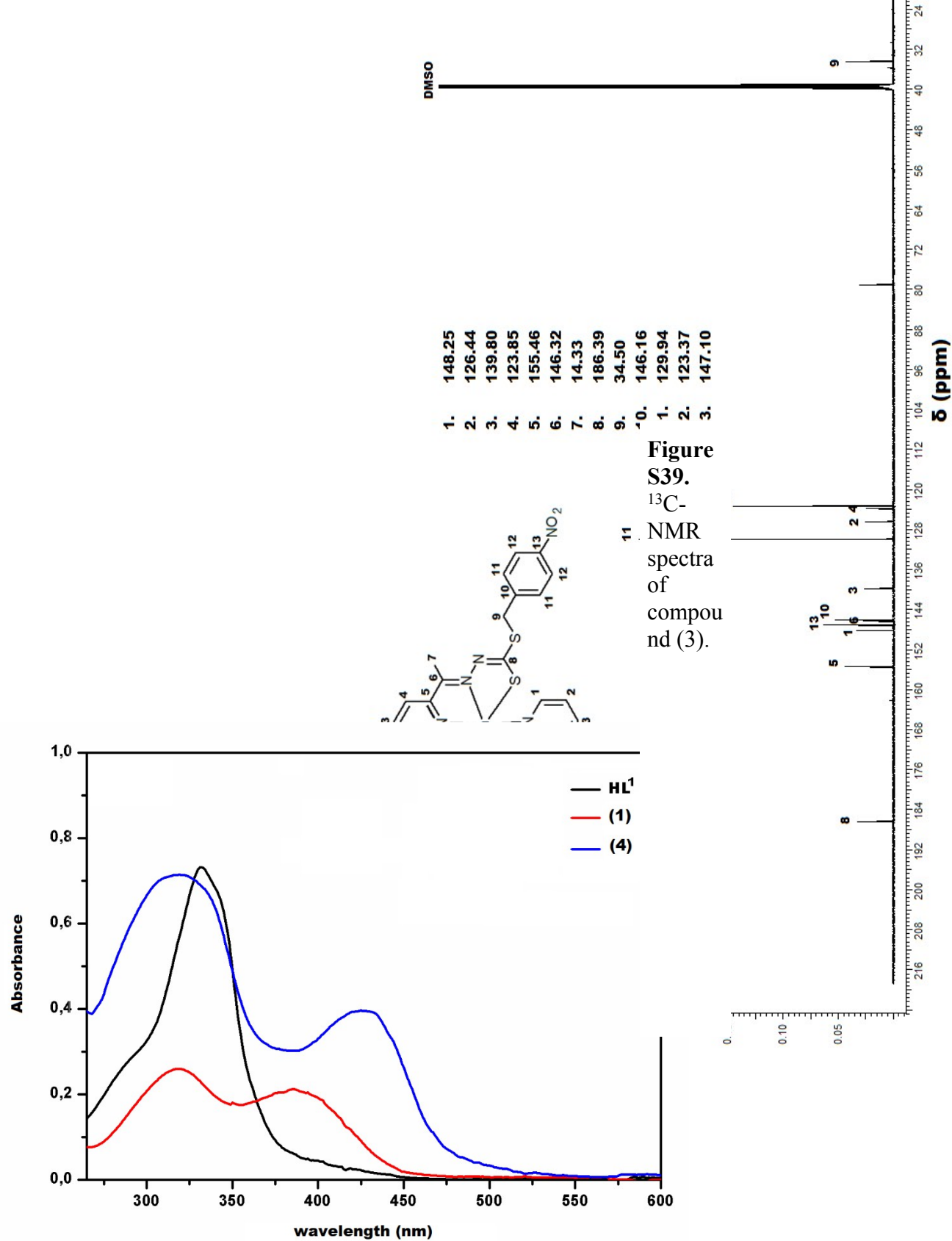


**Figure S35.**  
<sup>13</sup>C-NMR spectra of compound (1).

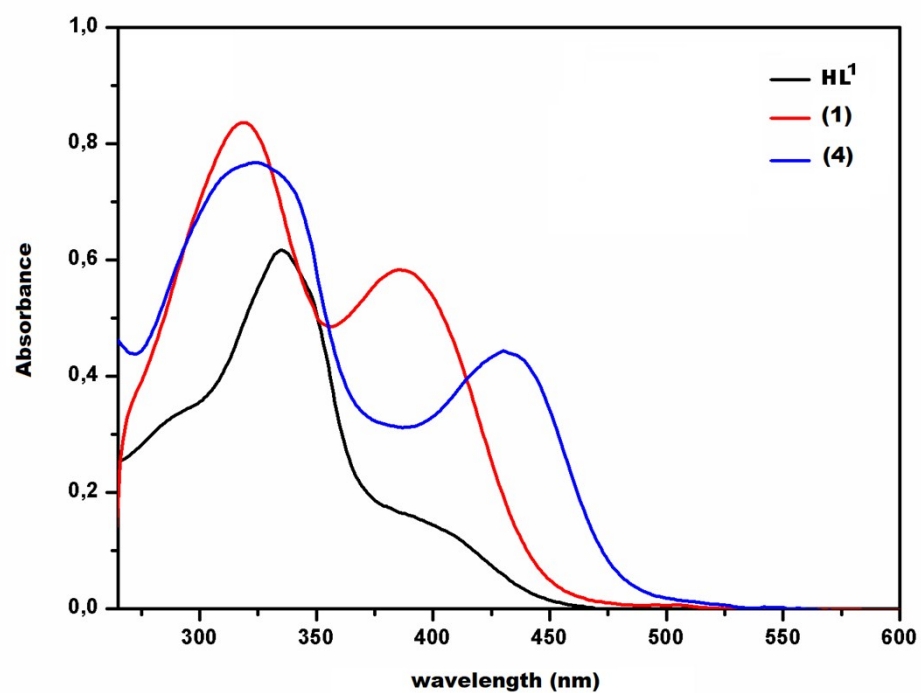
**Figure S36.**  
<sup>1</sup>H-NMR spectra of compound (2).



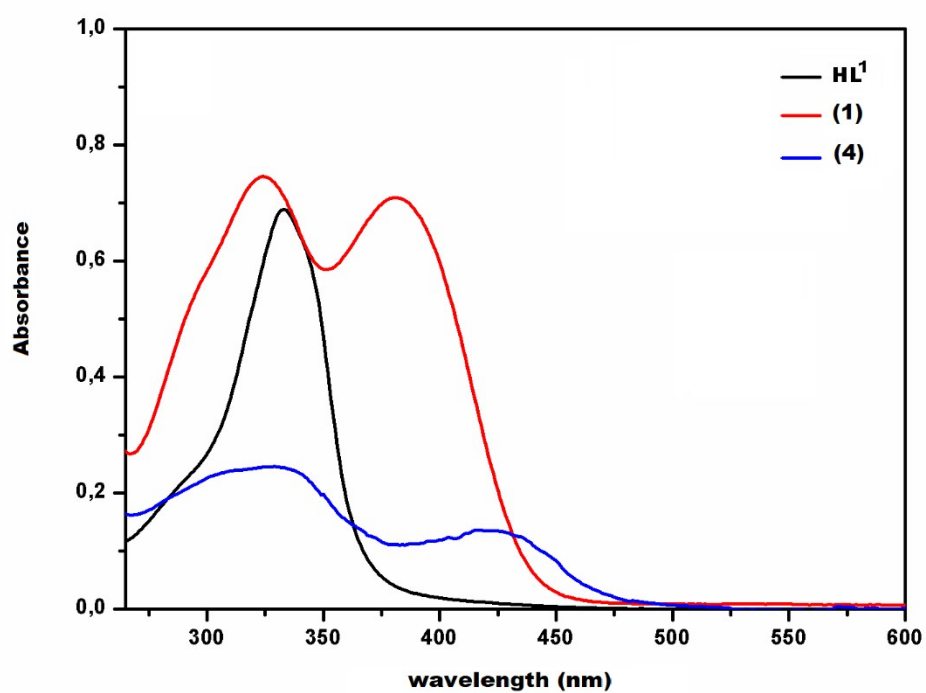




**Figure S40.** UV-vis spectra of compound  $\text{HL}^1$ , (1) and (4) in MeCN.



**Figure S41.** UV-vis spectra of compound HL<sup>1</sup>, (1) and (4) in DMF.



**Figure S42.** UV-vis spectra of compound HL<sup>1</sup>, (1) and (4) in MeOH.

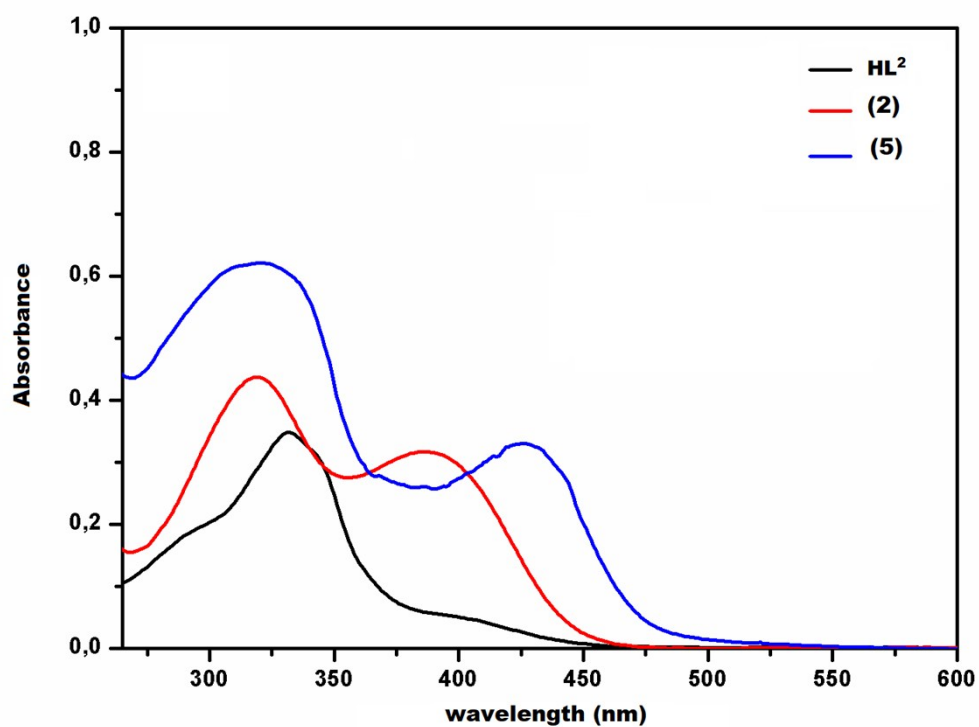


Figure S43. UV-vis spectra of compound  $HL^2$ , (2) and (5) in MeCN.

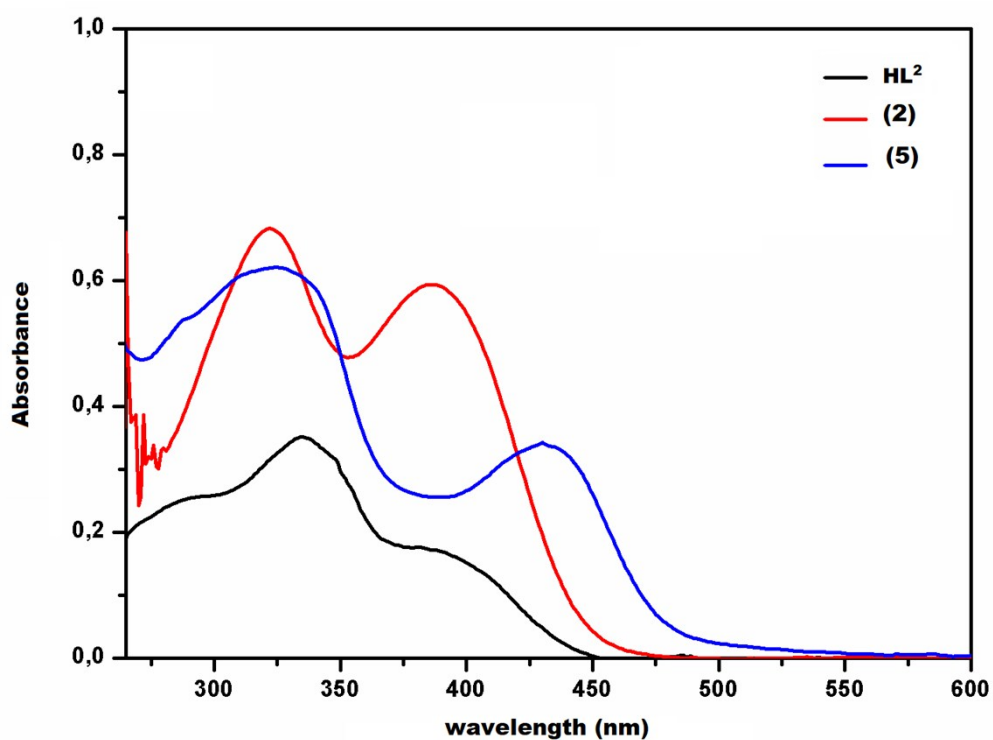
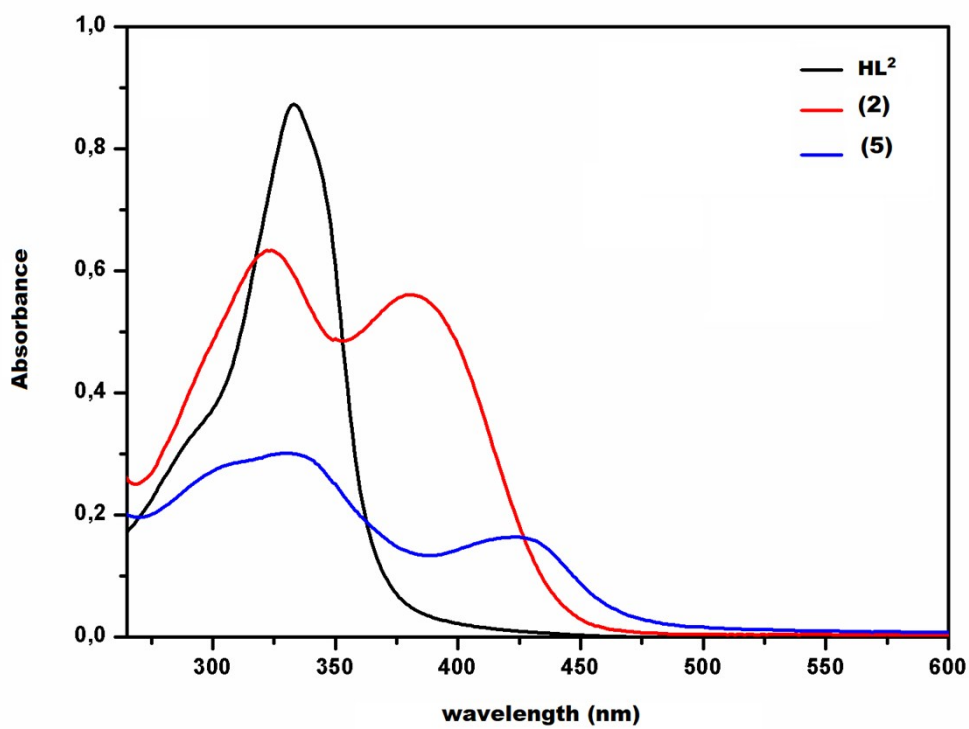
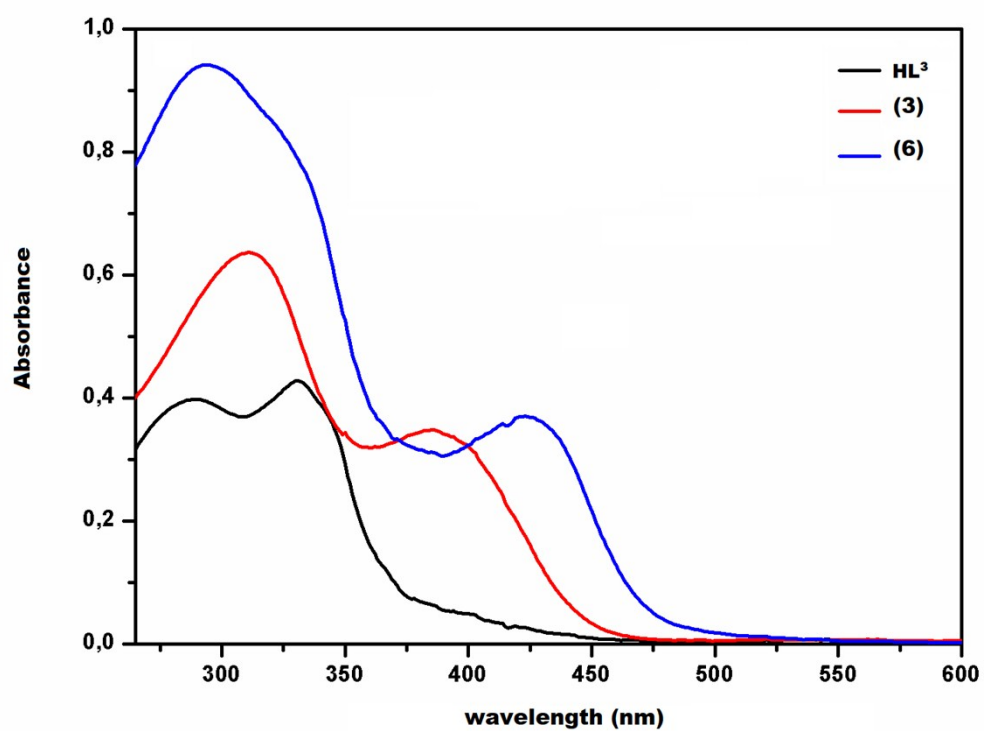


Figure S44. UV-vis spectra of compound  $HL^2$ , (2) and (5) in DMF.





**Figure S45.** UV-vis spectra of compound  $HL^2$ , (2) and (5) in MeOH..



**Figure S46.** UV-vis spectra of compound  $HL^3$ , (3) and (6) in MeCN.

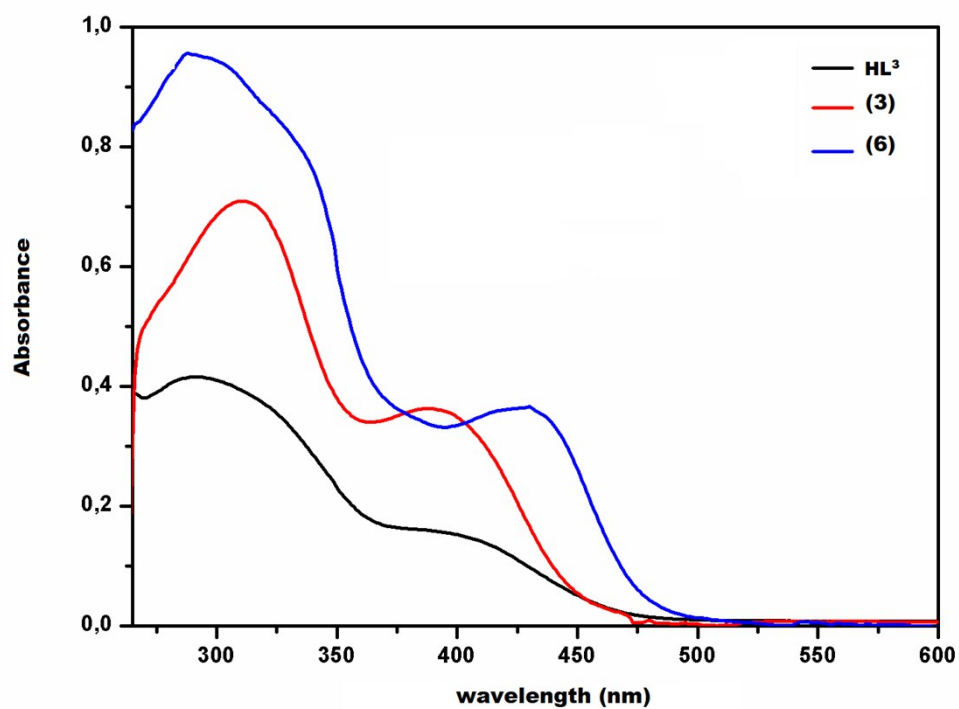


Figure S47. UV-vis spectra of compound  $HL^3$ , (3) and (6) in DMF.

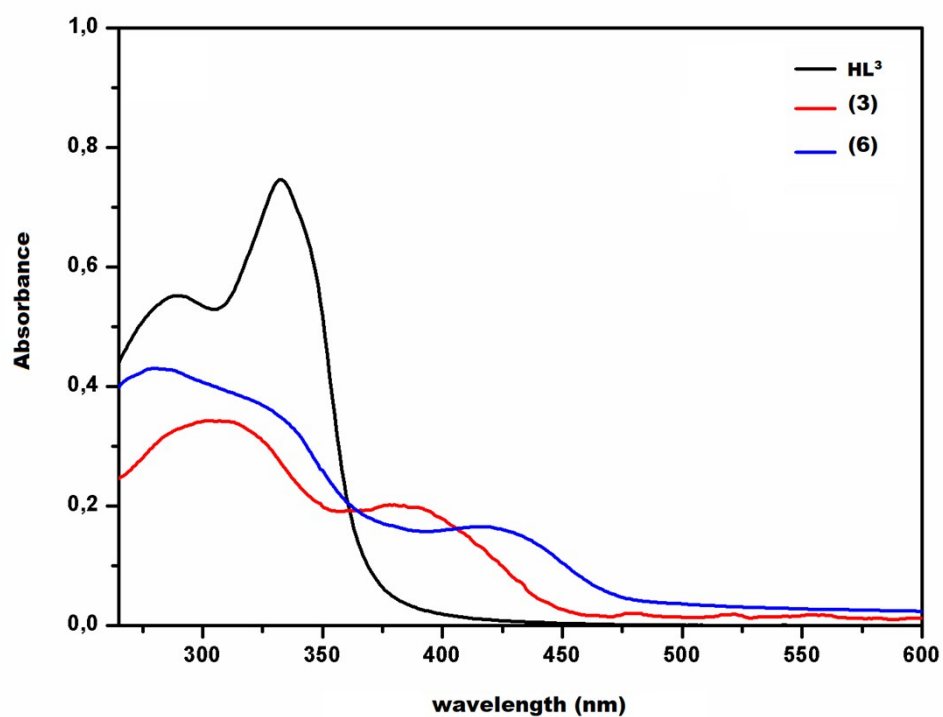
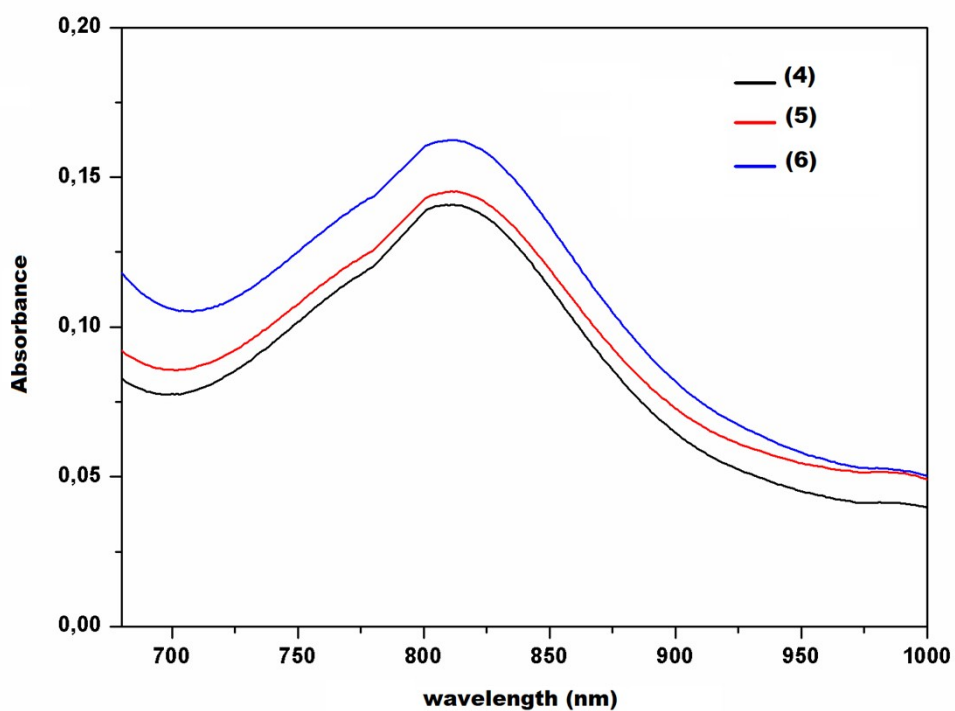
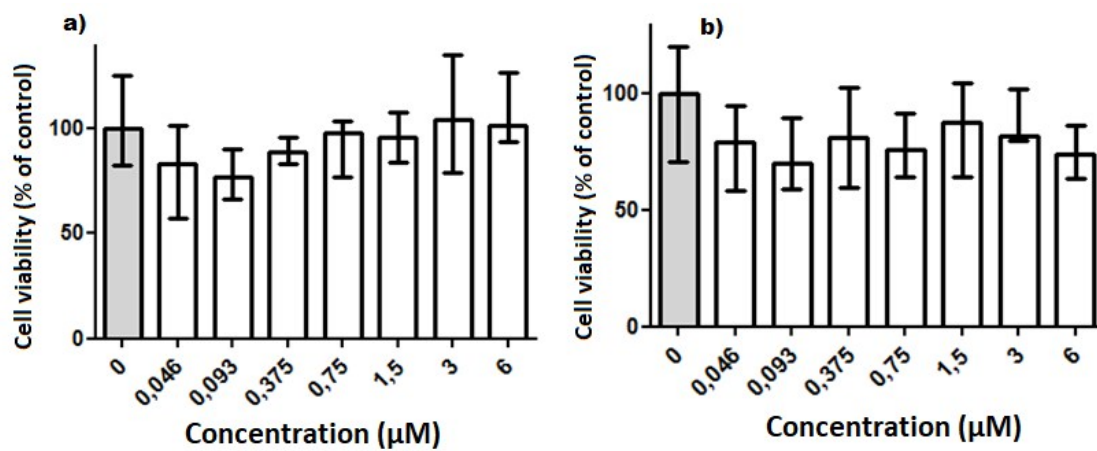


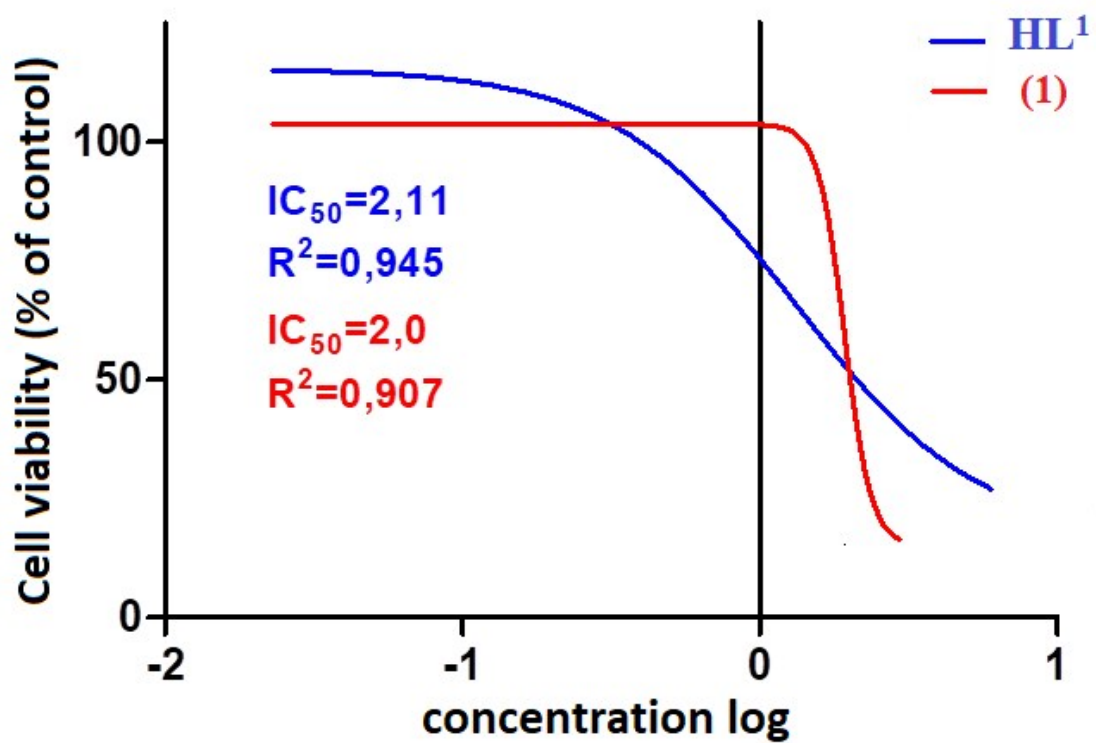
Figure S48. UV-vis spectra of compound  $HL^3$ , (3) and (6) in MeOH.



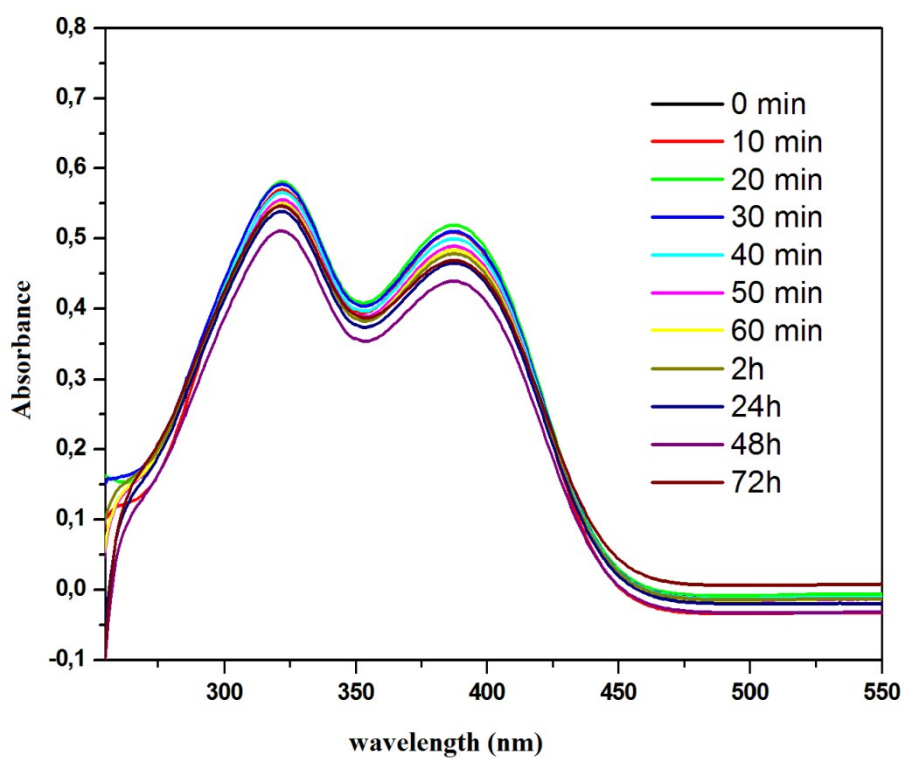
**Figure S49.** UV-vis spectra of compounds (4), (5) and (6) (d-d transition).



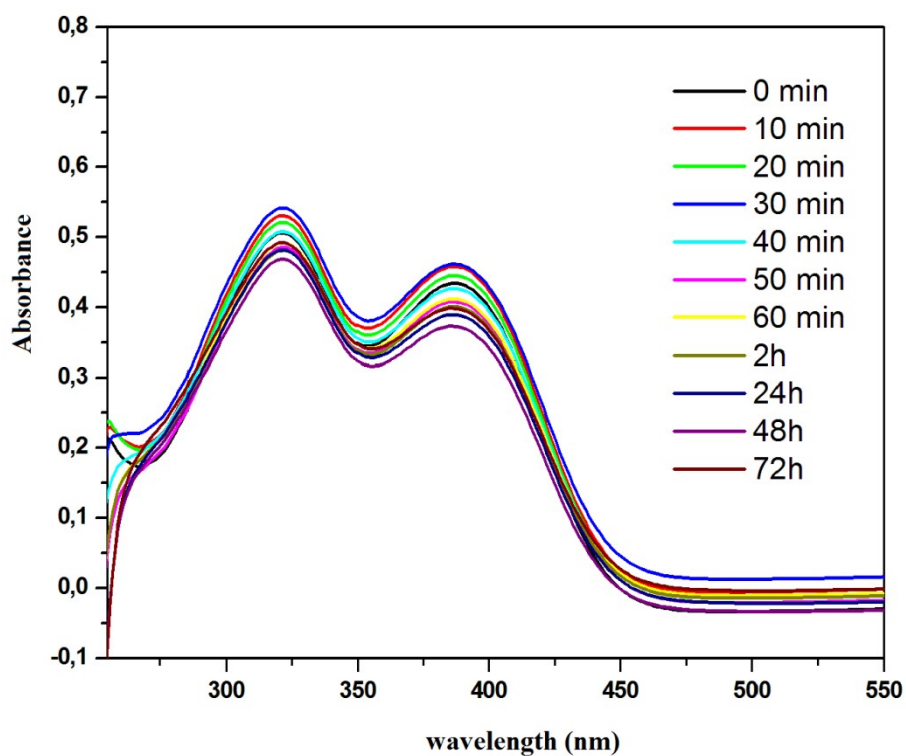
**Figure S50.** Viability of MDA-MB-231 cells after 72h of treatment with a) Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> and b) Ni(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>.



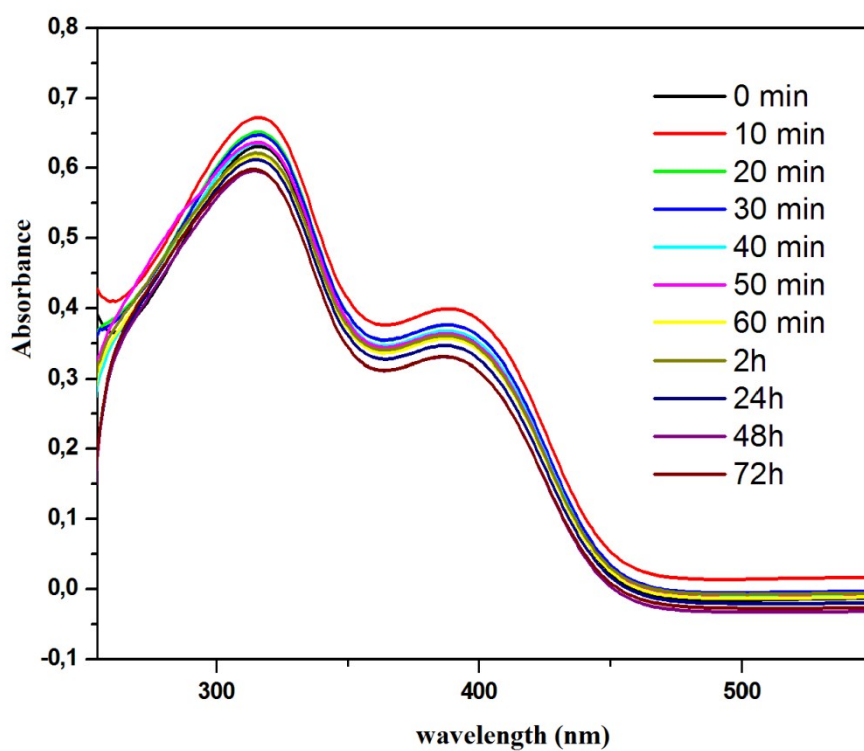
**Figure S51.** Concentration-response curves of the HL<sup>1</sup> and (1) in MDA-MB-231 cells for 72h of exposition.



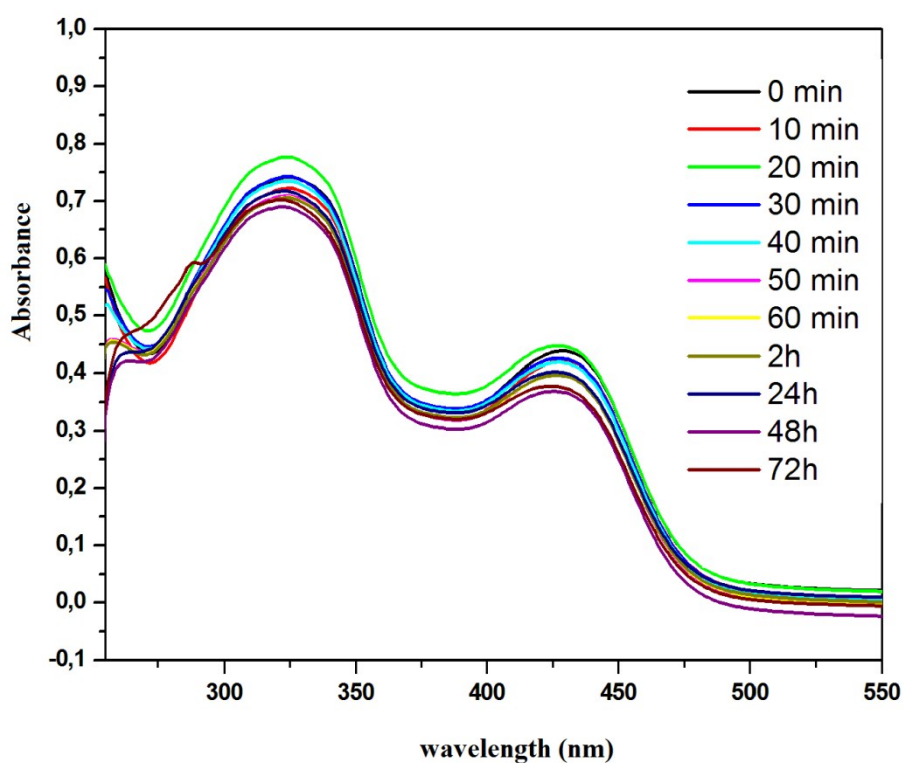
**Figure S52.** Study of the stability of the complex (1) by UV-vis up to 72h.



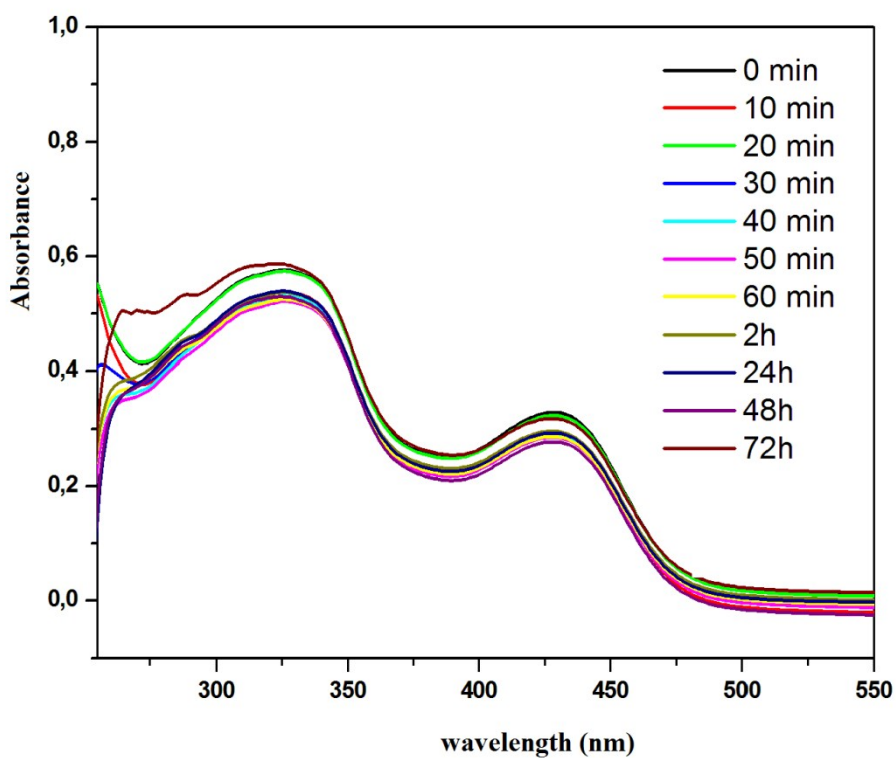
**Figure S53.** Study of the stability of the complex (2) by UV-vis up to 72h.



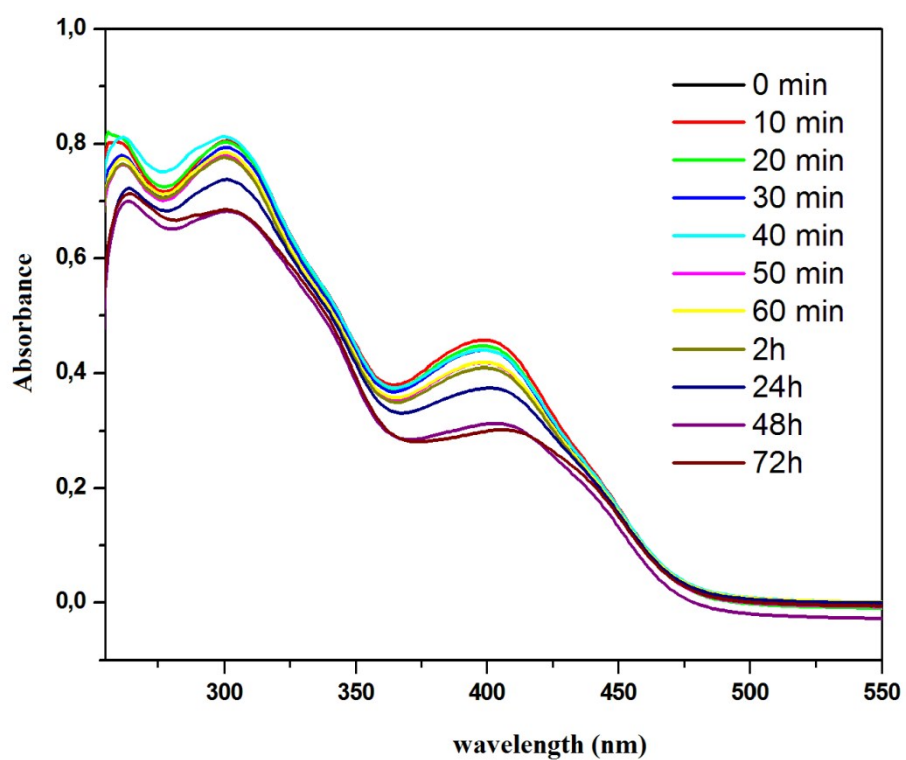
**Figure S54.** Study of the stability of the complex (3) by UV-vis up to 72h.



**Figure S55.** Study of the stability of the complex (4) by UV-vis up to 72h.



**Figure S56.** Study of the stability of the complex (5) by UV-vis up to 72h.



**Figure S57.** Study of the stability of the complex (6) by UV-vis up to 72h.