Supporting information

Effect of pyridyl substituents on dithiocarbamates leading to the formation of green luminescent mercury(II) coordination polymers, zinc(II) dimers and a monomer

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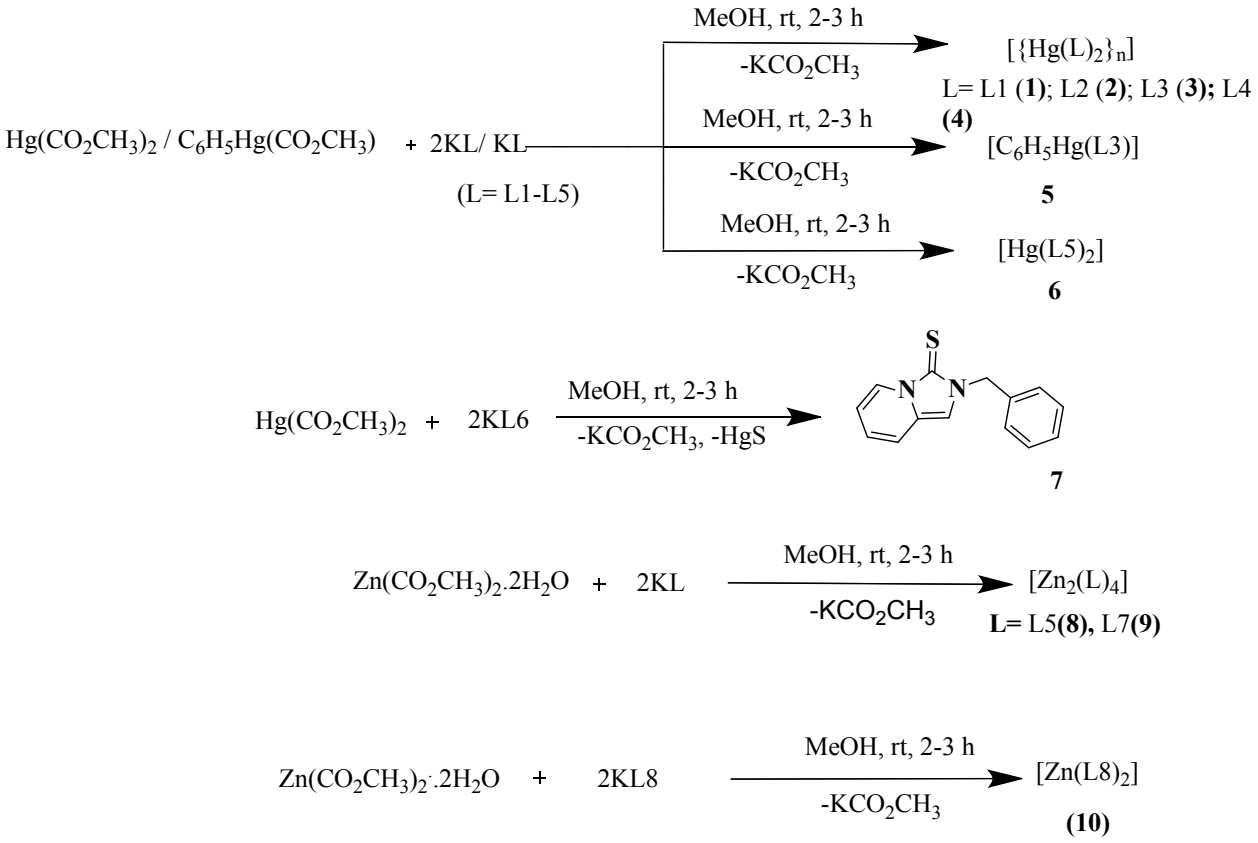


Scheme S1. General methodology for the synthesis of compounds (**1-10**).

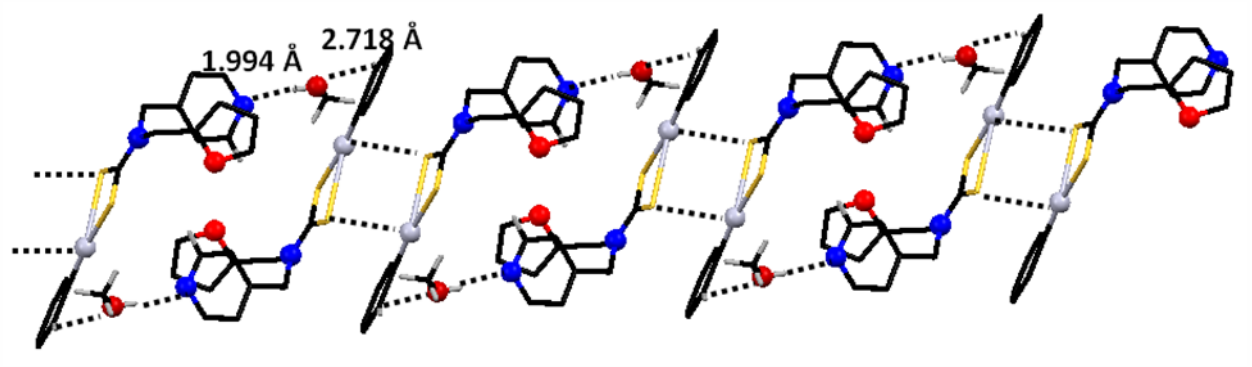


Figure S2. Solvate methanol stabilizing 1-D layer structure via O-H···N and C-H···O hydrogen bonding connecting Hg···S dimeric units in **5.**

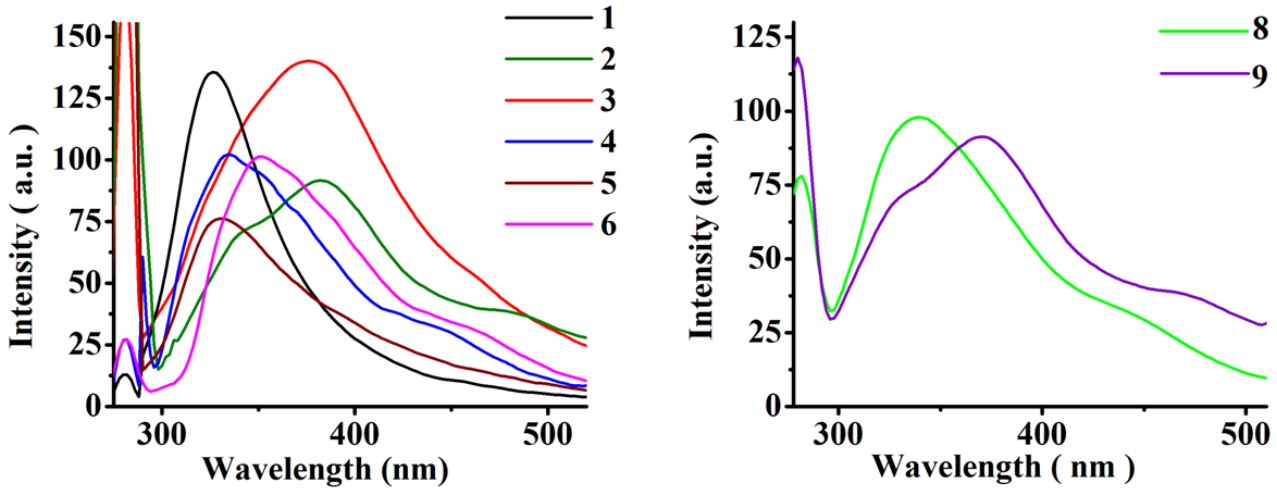


Figure S3. Emission spectra of the complexes in CH_2Cl_2 solution when excited at λ_{ex} 280 nm.

Table S1

Dimensions (distances, Å angles, deg) in the metal coordination spheres.

Structures **1, 2, 3**

	1	**2**	**3**
Hg-S11	2.658(2)	2.507(2)	2.479(1)
Hg-S13	2.513(2)	2.836(3)	2.820(1)
Hg-S41	2.389(2)	2.605(2)	
Hg-S43	3.112(2)	2.657(3)	
Hg-N6*	2.544(7)	2.586(5)	2.646(4)
S11-Hg-S13	69.89(7)	67.11(6)	67.95(4)
S41-Hg-S43	64.46(6)	68.20(6)	
S11-Hg-S43	98.10(7)	116.88(7)	
S13-Hg-S43	161.62(7)	172.10(6)	
S11-Hg-S41	132.40(7)	167.93(7)	
S13-Hg-S41	149.35(8)	106.54(6)	
S11-Hg-N6*	86.66(16)	92.81(13)	89.65(12)
S13-Hg-N6*	102.85(17)	87.91(14)	83.08(10)
S41-Hg-N6*	99.64(16)	97.27(13)	
S43-Hg-N6*	82.47(16)	98.48(13)	

* N6 = N66 (x, 1/2-y, z-1/2) in **1**, N65 (x,y-1,z) in **2**, N65 (1.5-x, y+1/2, -z-1/2) in **3**.

Table S2

Structure **4**

Hg(1)-S(11) 2.410(5)	Hg(2)-S(71) 2.432(4)
Hg(1)-S(41) 2.825(5)	Hg(2)-S(13) 2.904(4)
Hg(1)-S(13) 3.006(5)	Hg(2)-S(103) $1 3.009(5)
Hg(1)-S(43) 2.429(4)	Hg(2)-S(101) $1 2.423(5)
Hg(1)-S(103) 2.916(5)	Hg(2)-S(73) 2.828(5)
S(11)-Hg(1)-S(43) 167.84(17)	S(11)-Hg(1)-S(41) 116.31(16)
S(43)-Hg(1)-S(41) 68.71(14)	S(11)-Hg(1)-S(103) 94.47(15)
S(43)-Hg(1)-S(103) 95.44(15)	S(41) – Hg(1) - S(103) 100.15(14)
S(11) – Hg(1) - S(13) 65.95(15)	S(43) – Hg(1) - S(13) 102.36(15)
S(103) – Hg(1) - S(13) 126.39(12)	S(41)-Hg(1)-S(13) 133.49(14)
S(101)$1- Hg(2) – S(73) 117.81(16)	S(71) – Hg(2) – S(73) 68.37(14)
S(101)$1 - Hg2- S(13) 94.15(14)	S(71)-Hg(2)-S(13) 95.76(14)
S(73)-Hg(2)-S(13) 98.34(15)	S(101)$1- Hg2 – S(103)$1 65.71(13)
S(71) - Hg2- S(103)$1 101.88(14)	S(73) - Hg2 – S(103)$1 133.13(14)
S(13) - Hg2 – S(103)$1 126.39(12)	S(101)$1- Hg(2) – S(71) 167.38(15)
Symmetry element $1 = 1+x,y,z	

Table S3

Structure **5**

Hg(1) - C(41) 2.127(14)	Hg(1)- S(11) 2.389(4)
Hg(1)- S(13) 3.020(5)	Hg(1) - S(13)$1 3.191(4)
Hg(1) - O(1) 3.26(2)	C(41)- Hg(1)- S(11) 174.2(4)
C(41)- Hg(1)- S(13) 115.7(4)	C(41) - Hg(1) - S(13)$1 92.1(4)
C(41) - Hg(1) - O(1) 95.0(5)	S(11)- Hg(1)- S(13) 66.1(1)
S(11) - Hg(1) - S(13)$1 92.9(2)	S(11) - Hg(1) - O(1) 81.5(3)
S(13) - Hg(1) - S(13)$1 102.3(1)	S(13) - Hg(1) - O(1) 143.1(3)
S(13)$1-Hg(1) - O(1)$1 96.2(3)	

$1 Symmetry element $1 1-x, -y, -z

Table S4

Structure **6**

Hg(1) - S(11) 2.399(2)	S(11) - Hg(1) - S(13) 66.9(1)
Hg(1) - S(13) 2.952(2)	S(11) - Hg(1) - S(13)$1 89.5(1)
Hg(1) - S(13)$1 3.218(2)	S(13) - Hg(1) - S(13)$1 83.2(1)
$1 Symmetry element x,-1+y,z	

Table S5
Structure **8**

Zn(1)- N(37)$1 2.080(5)	Zn(1)- S(13) 2.404(2)
Zn(1)- S(11) 2.504(2)	Zn(1)- S(43) 2.521(2)
Zn(1)-S(41) 2.420(2)	
N(37)$1- Zn(1)- S(13) 107.06(17)	N(37)$1- Zn(1)- S(41) 110.07(18)
S(13) - Zn(1)- S(41) 142.87(8)	N(37)$1- Zn(1)- S(11) 104.18(16)
S(13) - Zn(1)- S(11) 73.25(7)	S(41) - Zn(1)- S(11) 97.91(8)
N(37)$1- Zn(1)- S(43) 101.17(17)	S(13) - Zn(1)- S(43) 99.81(8)
S(41) - Zn(1)- S(43) 72.61(8)	S(11) - Zn(1)- S(43) 154.65(7)
$1 Symmetry element 1-x, 1-y, 1-z	

Table S6
Structure **9**

Zn(1)- S(13) 2.340(1)	Zn(1)- S(41) 2.340(1)
Zn(1)- S(43)$1 2.375(1)	Zn(1)- S(11) 2.448(1)
Zn(1)- S(43) 2.814(1)	S(13)- Zn(1)-S(41) 134.3(1)
S(13)- Zn(1)-S(43)$1 117.9(1)	S(41)- Zn(1)-S(43)$1 104.8(1)
S(13)- Zn(1)-S(11) 75.8(1)	S(41)- Zn(1)-S(11)107.1(1)
S(11)- Zn(1)-S(43)$1 107.6(1)	S(13)- Zn(1)-S(43) 95.5(1)
S(41)- Zn(1)-S(43) 69.3(1)	S(43)- Zn(1)-S(43)$1 88.2(1)
S(11)- Zn(1)-S(43) 164.1(1)	
$1 Symmetry element 1-x, 1-y, 1-z	

Table S7
Structure **10**

Zn(1)- S(11) 2.334(2)	Zn(1)- S(41) 2.337(2)
Zn(1)- S(13) 2.350(2)	Zn(1)- S(43) 2.366(2)
S(11)- Zn1 - S(41) 129.7(1)	S(11)- Zn1 - S(13) 77.7(1)
S(41)- Zn1 - S(13) 123.1(1)	S(11)- Zn1 - S(43) 127.3(1)
S(41)- Zn1 - S(43)77.5(1)	S(13)- Zn1 - S(43) 129.6(1)

Table S8. Solvent assisted hydrogen bonding parameters in structures **5** and **8**.

	D-H···A	D-H/ Å	H···A/Å	D···A/Å	D-H···A/°	Symmetry elements
5	C(31)-H(31B)···O(1)	0.96	2.72	3.65(1)	161	x, 1+y, z
	O(1)-H(1)···N(35)	0.82	2.01	2.81(1)	165	1-x, 2-y, -z
8	C(64)-H(64)···O(91)	0.93	2.38	3.21(1)	149	

Table S9. Photophysical data of the complexes **1-9.**

complexes	λ_{max} excitation (nm)	λ_{max} emission (Solution) nm	λ_{max} emission (Solid) nm	Quantum yield Φ	Stoke's Shift (cm^{-1})	
					Solution	Solid
1	283	326	455	0.120	4660	13360
2	257	369	424	0.142	11810	15325
3	255	377	470	0.173	12690	17939
4	256	334	354	0.132	9122	10813
5	266	330	384	0.119	7290	11552
6	259	342	355	0.131	9370	10441
8	266	338	363	0.139	8008	10045
9	266	366	397	0.141	10271	12405
Solution Quantum yield of the complexes were recorded as pyridyl-2-amine (0.1 M H_2SO_4, quantum yield 0.6) as reference.						

Synthesis of Complexes

$[Hg(L)_2]$ [L = L1 **(1)**, L2 **(2)**, L3 **(3)**, L4 **(4),** L**5, 6**]

To a 10 mL methanolic solution of KL1 (0.356 g, 1 mmol), KL2 (0.236 g, 1 mmol), KL3 (0.302 g, 1 mmol), or KL4 (0.326 g, 1 mmol) was added slowly a (5 mL) solution of $Hg(CO_2CH_3)_2$ (0.159 g, 0.5 mmol) in the same solvent mixture. The reaction mixture was allowed to stir for 2 h yielding yellow to yellowish coloured precipitate. In each case the solid product thus formed was filtered off washed with methanol followed by diethylether. The compound was recrystallized in dichloromethane-methanol (70:30) solvent mixture. Yellowish crystals were obtained.

$[C_6H_5Hg(L3)]$ (**5**)

The orange compound **5** was synthesized and isolated adopting the method described for **1-6,** but using KL3 (0.302 g, 1 mmol) and $C_6H_5Hg(CO_2CH_3)_2$ (0.337 g, 1 mmol). Yellowish crystals were obtained.

2-Benzyl-2H-imidazo[1,5-a] pyridine-3-thione ($C_{14}H_{12}N_2S$) (**7**)

To a 5 mL methanolic solution of the ligand KL6, Potassium benzyl(pyridin-2-ylmethyl) dithiocarbamate (0.312 g, 1 mmol) was added slowly a 5 mL solution of the $Hg(CO_2CH_3)_2$ (0.159 g, 0.5 mmol) in the same solvent. The reaction mixture was stirred which produced the light blue solution along with the formation of black HgS, which was filtered off and the filtrate was kept for crystallization in methanol-dichloromethane mixture (1:1). Light blue coloured crystals were obtained.

Characterization details

(**1**) Yellow green solid, yield: 0.303 g, 72%. m.p. 180-184 ˚C. Elemental analysis calcd (%) for $C_{30}H_{26}O_4N_4S_4Hg$: C 43.13, H 3.13, N 6.70; found(%): C 42.85, H 3.18, N 6.42. ^1H NMR (300.40 MHz, $CDCl_3$, ppm): δ 8.60-8.51 (m, 4H, $-C_5H_4N$), 7.36-7.32 (m, 4H, C_5H_4N), 6.82-6.74 (s, 6H, $C_6H_3CH_2O_2$), 5.99 (s, 4H, $-CH_2C_6H_3O_2$), 5.01-4.91 (s, 4H, $-CH_2C_6H_3CH_2O_2$, $-CH_2C_5H_4N$), $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, ppm): δ 206.7 (CS_2), 149.12, 149.05, 148.97 (NC_5H_4), 135.07, 129.95, 127.30, 123.30, 121.15 ($-C_6H_3CH_2O_2$), 107.97 ($-CH_2C_6H_3CH_2O_2$), 58.12 ($-CH_2C_5H_4N$), 54.66 ($-CH_2C_7H_5O_2$). IR (KBr, cm^{-1}): 1370 υ(C=N), 1039, 972 υ(C-S). UV-vis.(CH_2Cl_2, λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 283 (1.63).

(2) Yellow solid, yield: 0.225 g, 76 %. m.p. 170-174 ˚C. Elemental analysis calcd (%) for $C_{16}H_{18}N_4S_4Hg$: C 32.29, H 3.05, N 9.42; found(%): C 32.15, H 2.94, N 9.37. ^{1}H NMR (300.40 MHz, $CDCl_3$, ppm): δ 8.63-8.57 (s, 4H, C_5H_4N), 7.25 (s, 3H, C_5H_4N), 5.07 (s, 2H, -$CH_2C_5H_4N$), 3.39 (s, 6H, -CH_3), $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, ppm): δ 205.7 (CS_2), 149.8, 149.3 (NC_5H_4), 58.0 (-$CH_2C_5H_4N$), 52.0 (-CH_3). IR (KBr, cm^{-1}): 1390 υ(C=N), 1026, 969 υ(C-S). UV-vis. (CH_2Cl_2, λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 275 (1.12), 258 (1.42).

(3) Yellow solid, yield: 0.295 g, 81%. m.p. 182-186 ˚C. Elemental analysis calcd (%) for $C_{24}H_{22}N_4O_2S_4Hg$: C 39.63, H 3.05, N 7.70; found(%): C 39.52, H 2.94, N 7.55. ^{1}H NMR (300.40 MHz, $CDCl_3$, ppm): δ 8.63-8.59 (s, 4H, C_5H_4N), 7.85-7.25 (s, 4H, C_5H_4N), 7.41 (d, 2H, C_4H_3O), 6.30 (m, 4H, C_4H_3O), 5.29-5.08 (s, 2H, -$CH_2C_5H_4N$, -$CH_2C_4H_3O$), $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, ppm): δ 202.1 (CS_2), 149.6, 149.5 (NC_5H_4), 141.4 (-C_4H_3O), 137.6, 137.0, 134.4 (C_5H_4N), 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 127.8, 122.2 (-C_6H_5), 56.0 (-$CH_2C_5H_4N$), 54.0 (-$CH_2C_4H_3O$). IR (KBr, cm^{-1}): 1415 υ(C=N), 1065, 932, υ(C-S). UV-vis.(CH_2Cl_2, λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 280(1.06), 252(1.42).

(4) Light yellow solid yield: 0.290 g, 76 %. m.p. 194-198 °C. Elemental analysis calcd (%) for $C_{30}H_{30}N_4S_4Hg$: C 46.46, H 3.89, N 7.52; found(%): C 46.28, H 3.84, N 7.95. ^{1}H NMR (300.40 MHz, $CDCl_3$, ppm): δ 8.59-8.50 (d, 4H, C_5H_4N), 7.81-7.78 (m, 4H, C_5H_4N), 7.19 (m, 10H,-C_6H_5), 5.26 (s, 4H, -$CH_2C_4H_3O$), 4.90 (s, 4H, -$CH_2C_5H_4N$), 3.92-3.87, 3.14-3.09 (t, t, -CH_2-CH_2-C_6H_5). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, ppm): δ 206.57 (CS_2), 149.80-149.08 (-C_5H_4N), 137.63-135.45 (-C_5H_4N), 137.63-123.79 (-C_6H_5), 57.59 (-$CH_2C_5H_4N$), 58.4-58.1 (-$CH_2CH_2C_6H_5$). IR (KBr, cm^{-1}): 1422 υ(C=N), 1084, 1026 υ(C-S). UV-vis.(CH_2Cl_2, λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 290(1.18), 251(1.41).

(5) Orange solid, yield: 0.225 g, 83 %. m.p. 162-166 °C. Elemental analysis calcd (%) for $C_{18}H_{16}N_2OS_2Hg$: C 39.96, H 2.98, N 5.18; found(%): C 39.82, H 2.86, N 5.08; ^{1}H NMR (300.40 MHz, $CDCl_3$, ppm): δ 8.63-8.57 (s, 4H, C_5H_4N), 7.85-7.67 (s, 4H, C_5H_4N), 7.41 (m, 10H, -C_6H_5), 6.30 (m, 6H, C_4H_3O), 5.27 (s, 4H, -$CH_2C_5H_4N$), 5.07 (-$CH_2C_4H_3O$). 2.35(-CH_3), 3.51(-CH_3OH). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, ppm): δ 204.1 (CS_2), 149.73, 149.08, (NC_5H_4), 141.4 (-C_4H_3O), 137.6, 137.0,

134.4 (C_5H_4N), 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 127.8, 122.2 (-C_6H_5), 56.0, 54.0 (-$CH_2C_5H_4N$, -$CH_2C_4H_3O$). IR (KBr, cm^{-1}): 1419 υ(C=N), 1064, 956 υ(C-S), 460 υ(C-Hg). UV-vis.(CH_2Cl_2, λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 280(1.41), 266(1.64).

(**6**) Yellow solid, Yield: 0.298 g, 80 % yield, m.p. 140-142 ˚C. Elemental analysis calc(%) for $C_{28}H_{26}N_4S_4Hg$: C, 45.00 ; H, 3.51; N, 7.50; found(%): C, 44.88; H, 3.38; N, 7.37; ^{1}H NMR(300.40 MHz, $CDCl_3$, ppm): δ 8.32 (m, 4H, C_5H_5N), δ 7.27-7.16 (m, 10 H, -C_6H_5), δ 7.36 (m, 4H, C_5H_4N), δ 5.09 (s, 4H, -CH_2Ar), δ 5.02 (s, 4H, -$CH_2C_6H_5$). ^{13}C NMR (75.45 MHz $CDCl_3$): δ 205.60 (CS_2), 149.56, 142.32, 136.23, 135.38 (NC_5H_4), 127.45, 126.32, 124.65, 122.09 (-C_6H_5), 59.67 (-$CH_2C_5H_4N$), 57.69 (-CH_2Ar). IR (KBr, cm^{-1}): 1420 υ(C=N), 1028 and 1076 υ(C-S). λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 301(1.04), 258 (1.51).

(**7**) Light bluish solid, Yield: 0.199 g, 82 %. m.p. 172-174 °C. Elemental analysis calc(%) for $C_{14}H_{12}N_2S$: C, 69.98; H, 5.04; N, 11.67; found(%): C, 69.85; H, 4.95; N, 11.75. ^{1}H NMR (300.40 MHz, $CDCl_3$, ppm): δ 8.33 (d, ^{1}H, C_5H_4N), δ 7.35-7.25 (m, 3H, -C_6H_5), 7.36 (m, 4H, C_5H_4N), 5.52 (s, 2H, -CH_2Ar). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$): δ 205.60 (CS_2), 149.56, 142.32, 136.23, 135.38 (NC_5H_4), 127.45, 126.32, 124.65, 122.09 (-C_6H_5), δ 57.69 (-CH_2Ar). IR (KBr, cm^{-1}): 1420 υ(C=N), 1028 and 1076 υ(C-S),

[$Zn(L)_2$], [L = L5 (**8**), L7 (**9**), L8 (**10**)]

To a 10 mL stirred methanolic solution of the ligand KL5 (0.315 g, 1 mmol), KL7 (0.256 g, 1 mmol), or KL8 (0.314 g, 1 mmol) was added separately a 5 mL solution of $Zn(CO_2CH_3)_2{\cdot}2H_2O$ (0.110 g, 0.05 mmol) in the same solvent. The reaction mixture was stirred for 6 h yielding white precipitate. In each case the solid product thus formed was washed thrice with methanol and diethylether. The compound was recrystallized in dichloromethane/ ethanol (70:30, v/v) mixture.

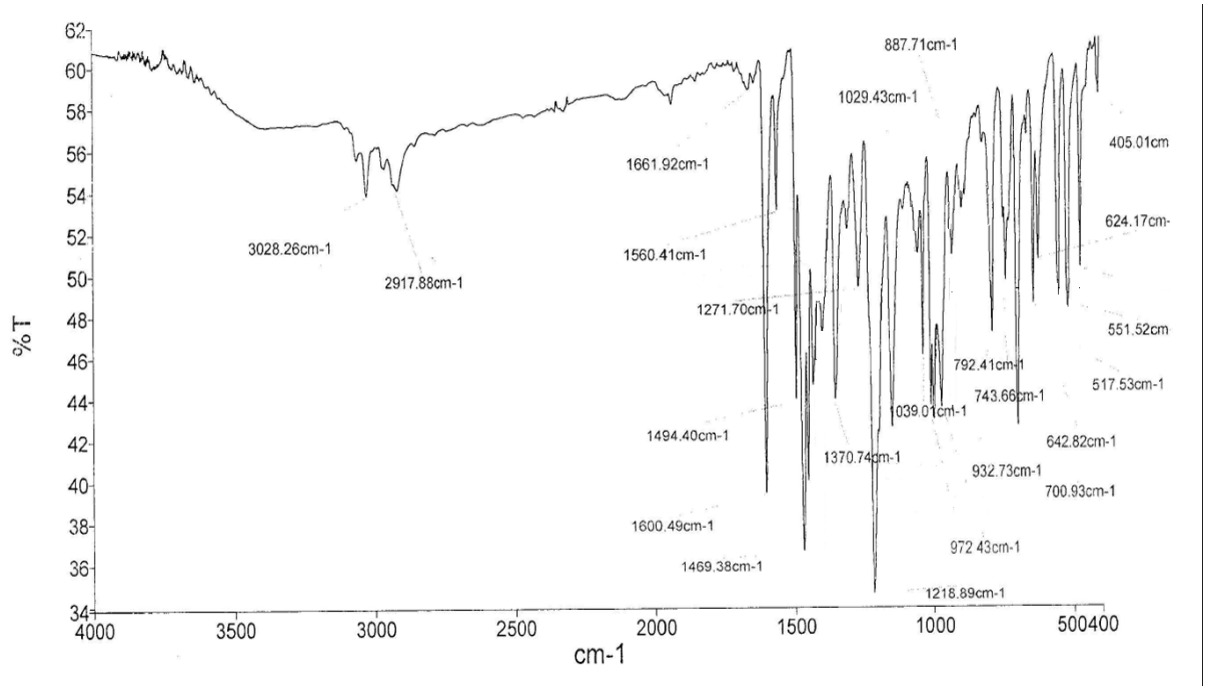
(8) Pale yellow solid, yield: 0.256 g, 83 %. m.p. 180-184 °C. Elemental analysis calcd (%) for $C_{56}H_{52}N_8S_8Zn_2$: C 55.04, H 4.30, N 9.18; found(%): C 54.92, H 4.18, N 9.08. ^{1}H NMR (300.40 MHz,

$CDCl_3$, ppm): δ 8.92-8.84 (d, 4H, C_5H_4N), 7.79-7.42 (m, 4H, C_5H_4N), 7.25-6.77 (m, 10H, $-C_6H_5$), 5.26 (s, 4H, $-CH_2C_5H_4N$), 5.13 (s, 4H, $-CH_2C_6H_5$). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, ppm): δ 204.12 (CS_2), 148.63-147.51 ($-C_5H_4N$), 137.40 ($-C_5H_4N$), 121.89 ($-C_6H_5$), 56.79 ($-CH_2C_5H_4N$), 43.87 ($-CH_2C_6H_6$); IR (KBr, cm^{-1}): 1432 υ(C=N), 1049, 940 υ(C-S); UV-vis. (CH_2Cl_2, λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 285(1.18), 266(1.37).

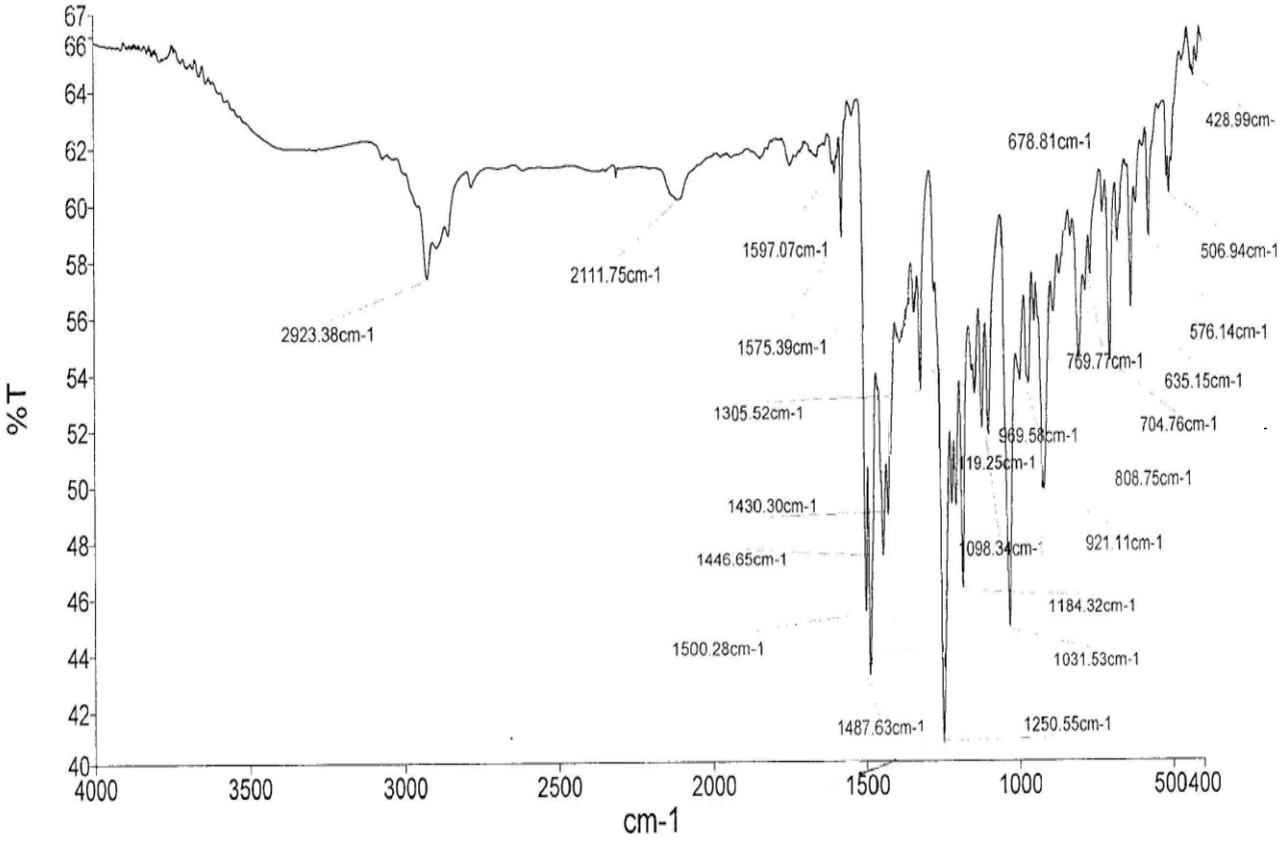
(9) White solid, yield: 0.213 g, 84 %, m.p. 165-170 °C. Elemental analysis calcd (%) for $C_{36}H_{56}N_4S_8O_8Zn_2$: C 40.91, H 5.32, N 5.29; found(%): C 40.8, H 5.24, N 5.12. ^1H NMR (300.40 MHz, $CDCl_3$, ppm): δ 1.29-1.24 (t, 6H, CH_3), 1.90-1.82 (m, 2H, $-CH-(CH_2)_4N$). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, ppm): δ 202.32 (CS_2), 65.13, 70.12 ($-CH_2$), 55 ($-OCH_2$), 35 ($-CH_3$). IR (KBr, cm^{-1}): 1435 υ(C=N), 1067-945 υ(C-S). UV-vis.(CH_2Cl_2, λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 266(1.54).

(10) White solid**,** yield: 0.240 g, 77 %, m.p. 142-146 °C. Elemental analysis calcd (%) for $C_{28}H_{30}N_4S_4Zn$: C 54.58, H 4.91, N 9.09; found(%): C 54.47, H 4.84, N 9.17. ^1H NMR (300.40 MHz, $CDCl_3$, ppm): δ 7.39-7.29 (m, 10H, C_6H_5), 6.08-6.07 (m, 6H, $-C_4H_3NCH_3$), 5.29 (s, 4H-$CH_2C_4H_3NCH_3$), 5.03 (s, 4H, $-CH_2C_6H_5$,), 3.61 (s, 6H, $-CH_3C_4H_3N$), ^{13}C NMR (300.40 MHz, $CDCl_3$, ppm): δ 205.1 (CS_2), 134.7-124.2 (C_6H_5), 111.8-107.4 ($C_4H_3NCH_3$), 54.2 ($-CH_2C_6H_5$), 48.4 ($-CH_2C_4H_3NCH_3$), IR (KBr, cm^{-1}): 1430 υ(C=N), 1072, 978 υ(C-S). UV-vis.(CH_2Cl_2, λ_{max}, nm, 10^4 ε/ $M^{-1}cm^{-1}$): 285(1.45).

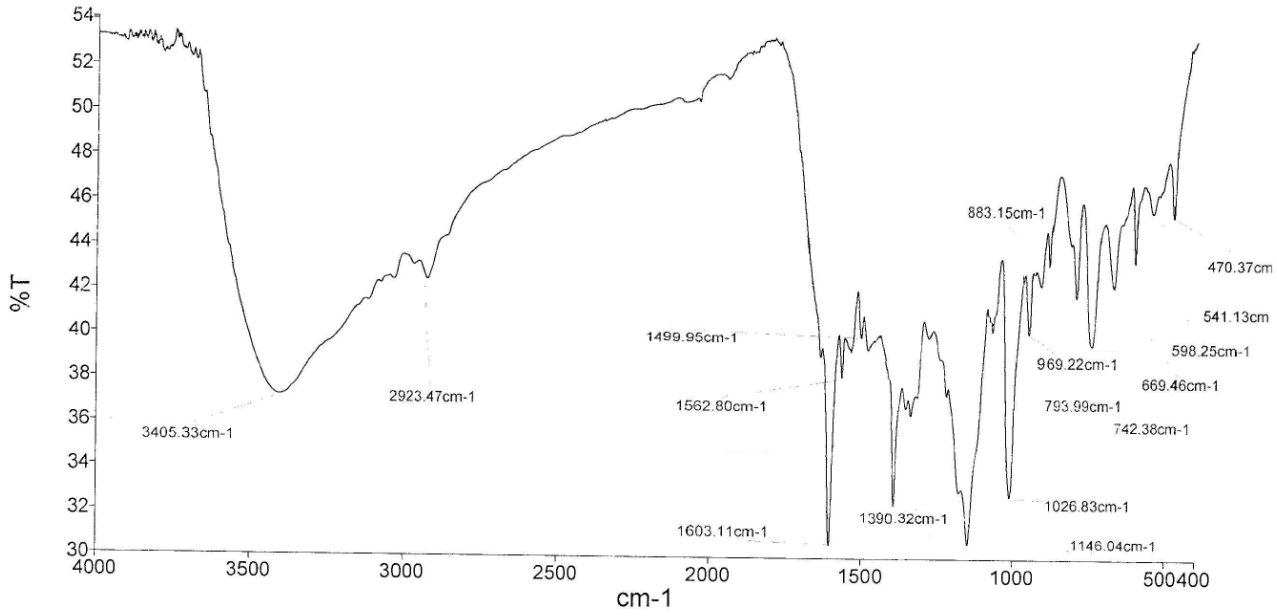
Figure S4. IR Spectra of complexes and their corresponding Ligands.



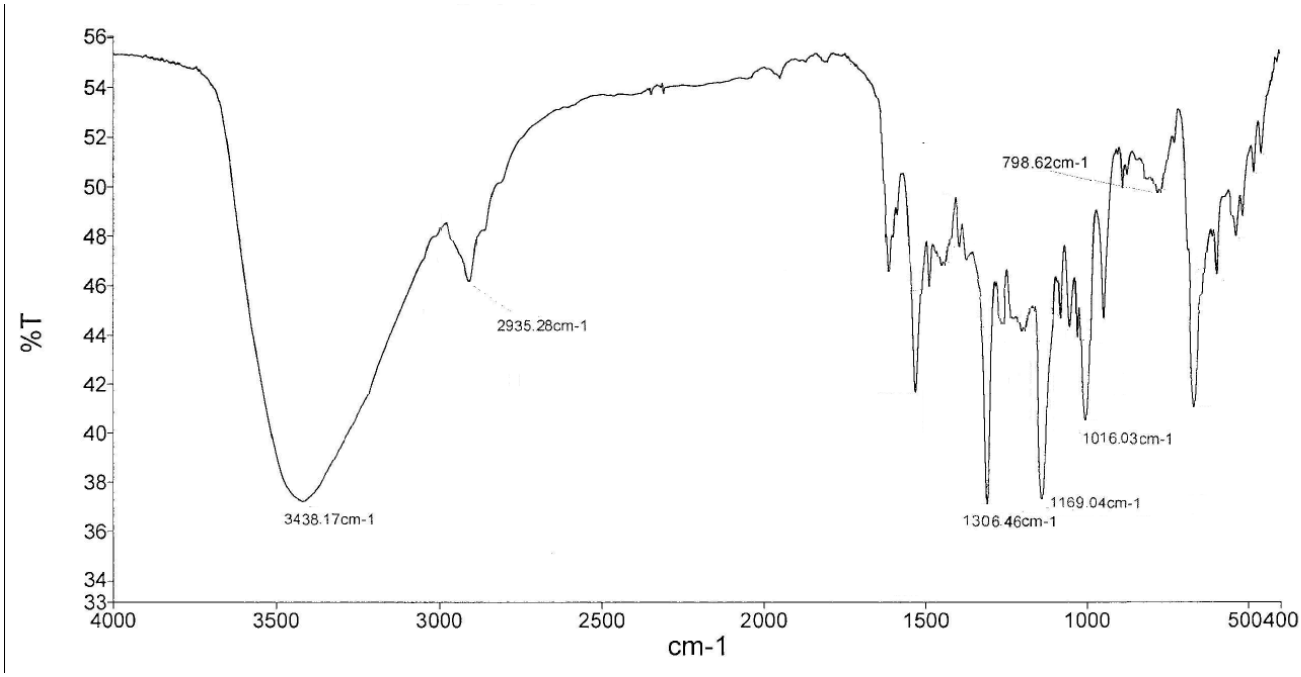
IR Spectra of Complex **1**



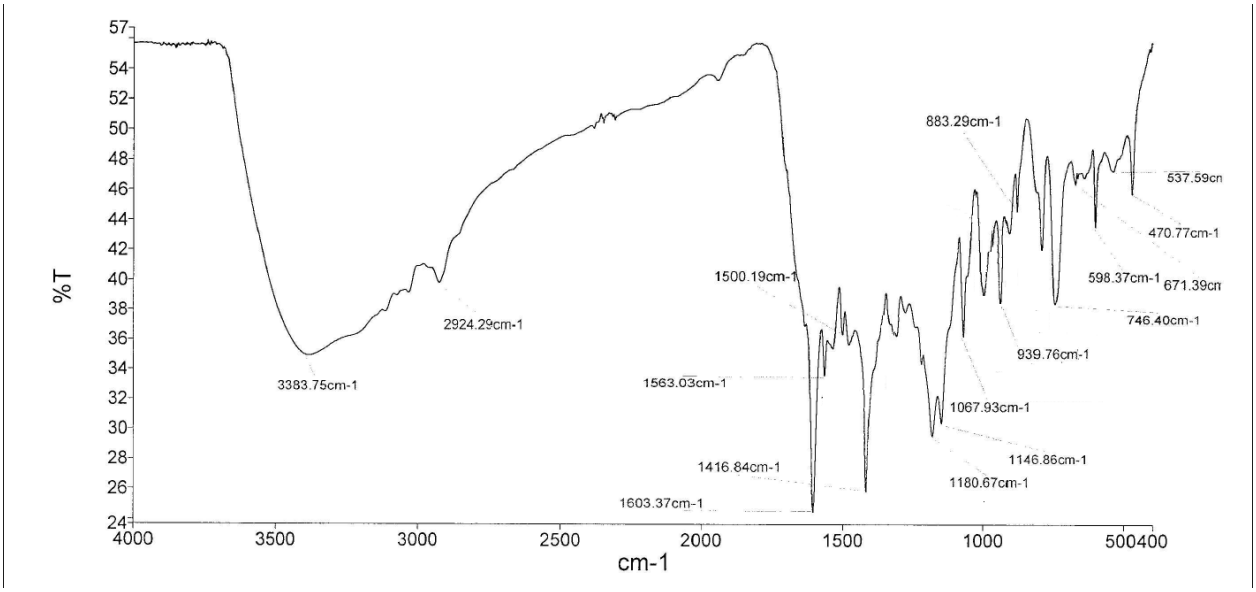
IR Spectra of KL1



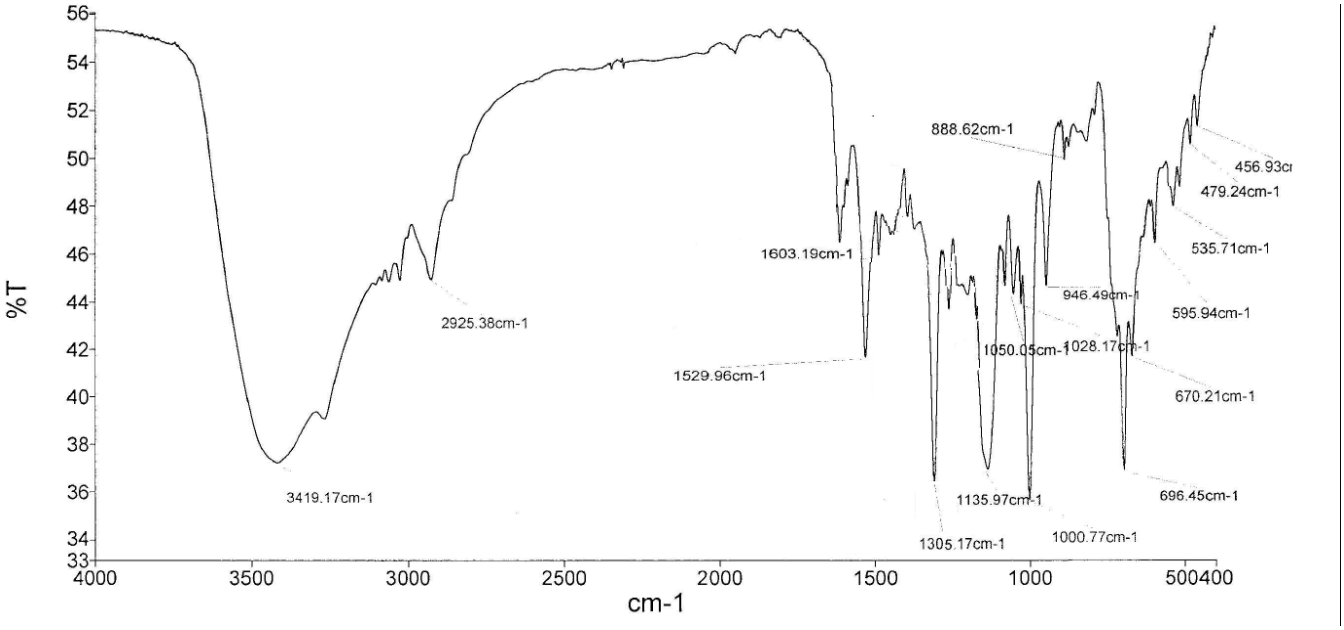
IR Spectra of **2**



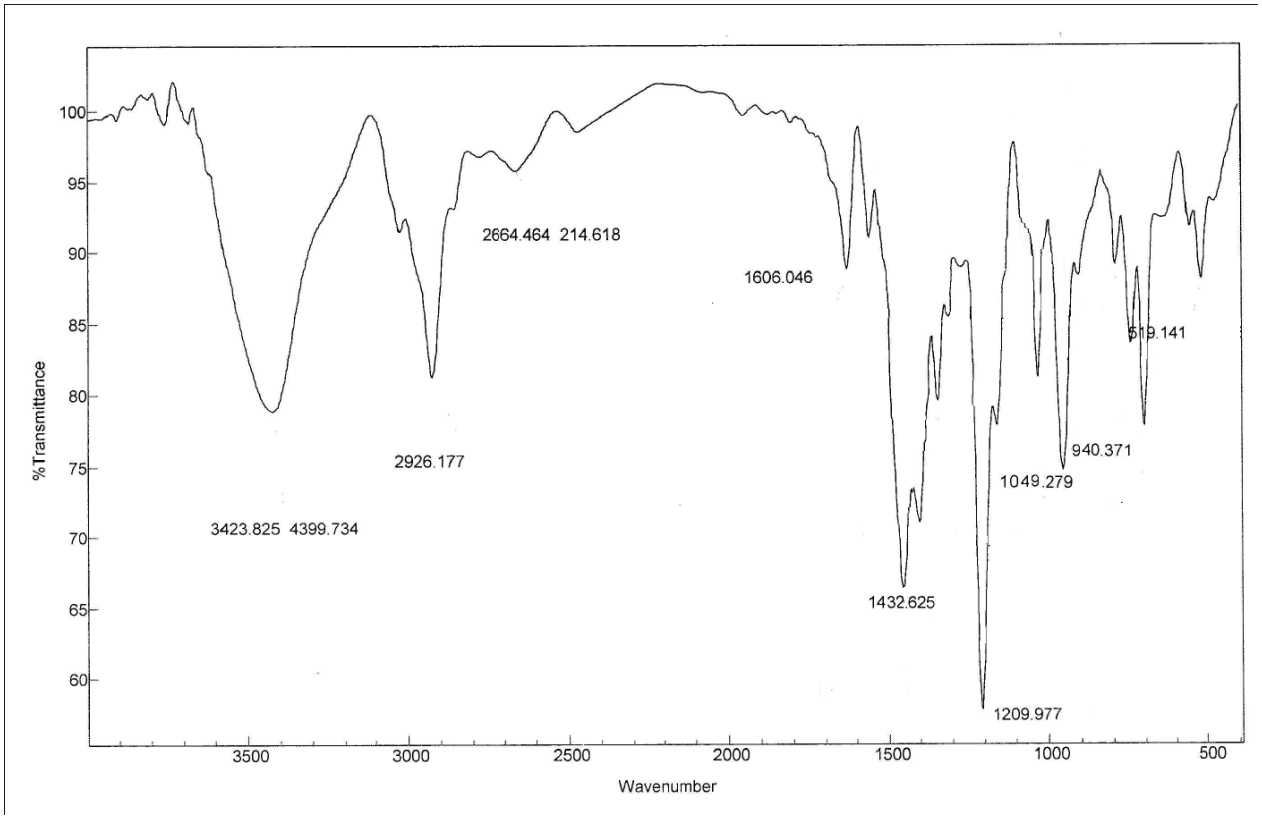
IR Spectra of KL2



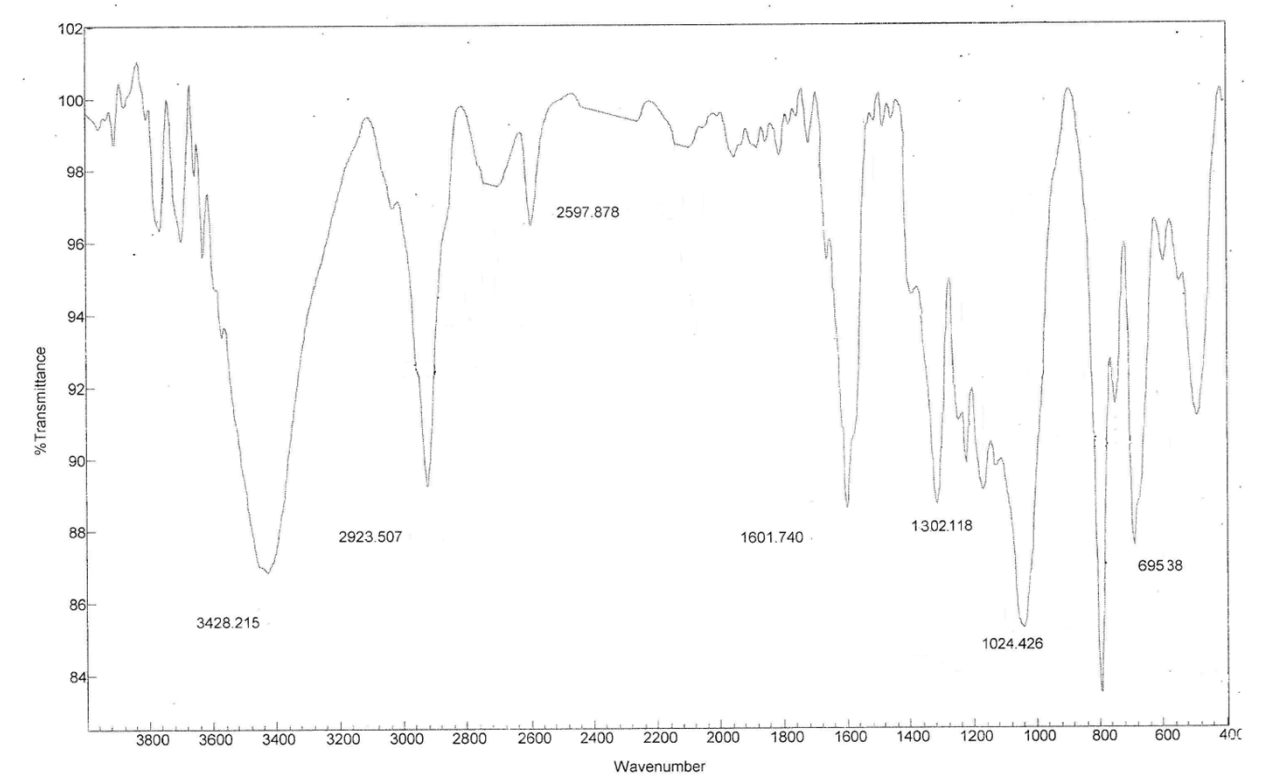
IR Spectra of **3**



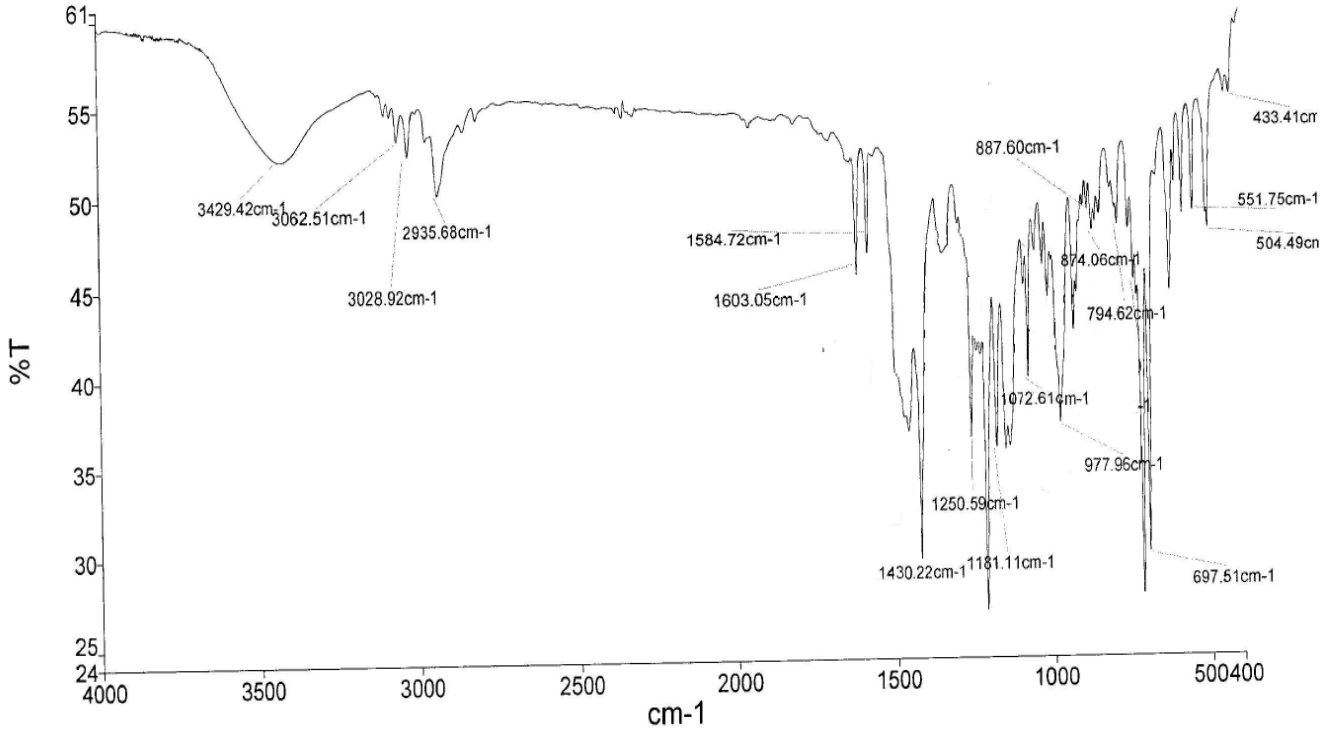
IR Spectra of **KL3**



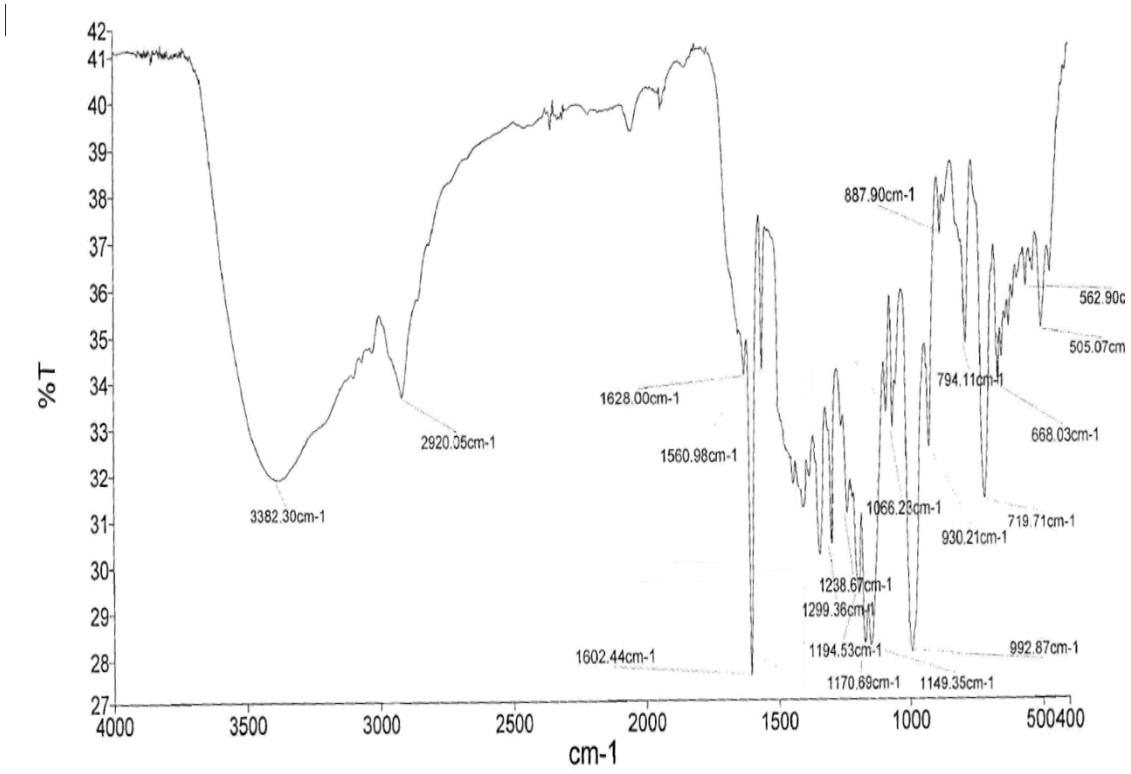
IR Spectra of **8**



IR Spectra of **KL5**



IR Spectra of **10**



IR Spectra of **KL8**