Impact of Complementary Electronic Nature of C−X and M−X Halogens and Intramolecular X···O Interaction in Supramolecular Assemblies of Zn(II) Complexes of *O*-Halophenyl Substituted Hydrazides

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Materials: 2-Fluorobenzhydrazide, 2-chlorobenzhydrazide, 2-bromobenzhydrazide (Alfa Aeser), 2-cyanopyridine (Aldrich, USA), anhydrous $ZnCl_2$ (Merck India) and solvents were used as received without further purification. Single crystals of complexes **1-3** and ligands **hyd-Cl** and **hyd-Br** were grown by slow evaporation from common organic solvents

(methanol and DMF) at room temperature. X-ray crystallographic data were collected using a Bruker SMART APEX-CCD diffractometer and Agilent Supernova diffractometer with Mo-Kα radiation (λ= 0.71073 Å). The intensity data were corrected by Lorentz and polarization effects and empirical absorption corrections were made using multi-scan method. All structures were solved by direct methods using SHELX-97. Non hydrogen atoms were refined anisotropically by full matrix least-squares on F^2, using SHEXL-97 and further refined using PLATON. All hydrogen atoms were included in the calculated positions and refined isotropically using a riding model. Useful parameters for hydrogen bond and other non-covalent interactions were calculated using PARST program implemented in PLATON.

Syntheses procedure and characterization data

2-[5-(2-Fluoro-phenyl)-1H-[1,2,4]triazol-3-yl]-pyridine (**trz-F**): 2-Fluorobenzhydrazide (0.925 g, 6 mmol) and 2-cyanopyridine (0.677 g, 6.5 mmol) were taken together in 1.5 mL of PEG-400 in a 25 mL round bottom flask and heated at 100 °C for 12 h. The resulting gummy yellow liquid was then added to a beaker containing 50 mL of water and stirred for 1 hour from which a pale yellow solid precipitate out. It was filtered, dried and subjected to column chromatography on a basic alumina column by eluting it with EtOAc:hexane (2:1) to obtain pure **trz-F** as a white solid. Yield 1.155 g, 80%; IR (KBr, cm^{-1}): 3564, 3344, 3135, 1691, 1641, 1615, 1590, 1543, 1495, 1384, 1334, 1286, 1232, 1102, 1026, 985, 823, 790, 759; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 8.59 (d, *J* = 4.5 Hz, 1H), 8.12 (d, *J* = 7.9 Hz, 1H), 8.04 (dd, *J* = 10.6, 4.5 Hz, 1H), 7.87 (td, *J* = 7.8, 1.6 Hz, 1H), 7.47-7.41 (m, 1H), 7.40-7.36 (m, 1H), 7.26 (dd, *J* = 11.0, 4.1 Hz, 1H), 7.21 (dd, *J* = 10.5, 8.8 Hz, 1H);^{13}C NMR (DMSO-d_6, 150 MHz) δ 161.11, 159.45, 149.53, 148.17, 137.58, 131.82, 131.77, 130.19, 124.67, 121.74, 116.23, 116.08; ESI MS calcd for $C_{13}H_{10}N_4F^+$ $(M+H)^+$ 241.089, found 241.088.

2-Chlorobenzoic acid(amino-pyridin-2-yl-methylene)hydrazide (**hyd-Cl**): Ligand **hyd-Cl** was synthesized by heating 2-chlorobenzhydrazide (0.925 g, 6 mmol) with 2-cyanopyridine (0.677 g, 6.5 mmol) in 1.2 g of PEG 400 under an identical reaction conditions as described for **trz-F**. The crude product so obtained was purified over a column of basic alumina by eluting it with EtOAc:hexane (1:1) to give product as a white solid. Yield 1.233 g, 75%; IR (KBr, cm^{-1}): 3416, 3201, 1667, 1639, 1603, 1591, 1580, 1545, 1505, 1467, 1443, 1422, 1399, 1366, 1309 (s), 1262, 1250, 1171, 1148, 1128, 1054, 1036, 1012, 910, 797, 776, 747, 738; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 8.72 (s, 1H), 8.13 (d, J = 7.7 Hz, 1H), 8.01 (s, 1H), 7.92 (s, 1H), 7.64-7.40 (m, 5H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 160.92, 154.79, 150.30, 146.75, 138.55, 137.72, 132.31, 132.06, 131.13, 127.87, 125.86, 122.14; ESI MS calcd for $C_{13}H_{12}N_4{}^{35}Cl^+$ $(M+H)^+$ 275.070 found 275.063.

2-Bromobenzoic acid(amino-pyridin-2-yl-methylene)hydrazide (**hyd-Br**): Solid **hyd-Br** was obtained by heating a mixture of 2-bromobenzhydrazide (1.290 g, 6 mmol) and 2-cyanopyridine (0.677 g, 6.5 mmol) in PEG 400 under an identical reaction conditions as described for **trz-F**. The crude product so obtained was purified over a column of basic alumina by eluting it with EtOAc:hexane (2:3) to give product as a white solid. Yield 1.145 g, 60%; IR (KBr, cm^{-1}): 3443 (s), 3318 (m), 3191 (m), 3043 (m), 3008 (m), 2925 (w), 2852 (w), 1670 (s), 1642 (s), 1588 (m), 1550 (s), 1473 (s), 1440 (m), 1397 (s), 1313 (s), 1269 (m), 1168 (s), 1089 (w), 1050 (s), 1030 (s), 996 (m), 971 (w), 952 (m), 904 (s), 866 (w), 795 (s), 777 (m), 742 (s); ^{1}H NMR (DMSO d_6, 400 MHz) δ 8.71 (d, J = 3.8 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H), 7.99 (t, J = 7.9 Hz, 1H), 7.89 (s, 1H), 7.62- 7.40 (m, 5H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 160.73, 158.22, 149.62, 147.15, 137.74, 131.08, 131.00, 129.98, 124.81, 124.64, 121.43, 116.67, 116.46; ESI MS calcd for $C_{13}H_{11}N_4{}^{79}Br^+$ $(M+H)^+$ 319.019, found 318.990.

Synthesis of [Zn(hyd-F)Cl_2] (1): To a solution of ligand **trz-F** (48 mg, 0.20 mmol) in DMF (2.5 mL), solid anhydrous $ZnCl_2$ (34 mg, 0.25 mmol) was added and stirred for five hours. The golden yellow coloured clear solution so obtained was left undisturbed in a 5 mL conical flask for crystallization from which prismatic colourless crystals of **1** was obtained after two weeks. Isolated yield: 55 mg, 70%. Anal. Calcd. for $C_{13}H_{11}N_4OFCl_2Zn$: C, 39.57%; H, 2.81%; N, 14.20%. Found: C, 39.85%; H, 2.85%; N, 14.05%. IR (KBr, cm^{-1}): 3195 (b), 3115 (m), 1622 (s), 1588 (w), 1562 (s), 1497 (s), 1453 (s), 1387 (s), 1282 (s), 1263 (w), 1229 (s), 1181 (s), 1151 (s), 1127 (w), 1094 (s), 1046 (s), 1025 (s), 1006 (m), 985 (s), 945 (w), 865 (w), 824 (s), 792 (s), 771 (s), 746 (s), 716 (m), 695 (w), 664 (w), 644 (m), 496 (m); UV-Vis [λ_{max} (nm), (ε, $M^{-1}cm^{-1}$), DMSO solution]: 270 (21490), 314 (38515), 327 (29850). ESI MS *m/z* calcd [^{64}Zn(**hyd-F**)(^{35}Cl)]$^+$ 356.99, found 357.65.

*Synthesis of [Zn(**hyd-Cl**)Cl_2]·DMF (**2**):* To a stirred solution of ligand **hyd-Cl** (69 mg, 0.25 mmol) in DMF (2.5 mL) was added anhydrous $ZnCl_2$ (41 mg, 0.30 mmol). The light yellow colured solution so obtained was left undisturbed in a 5 mL conical flask. A white prismatic crystal deposited after two weeks were collected and washed with cold methanol (2 x 1 mL). Yield 89 mg, 74%. Anal. Calcd. for $C_{16}H_{18}N_5O_2Cl_3Zn$: C, 39.70%; H, 3.75%; N, 14.47%. Found: C, 39.81%; H, 3.68%; N, 14.55%. IR (KBr, cm^{-1}): 3627 (m), 3419 (b), 1703 (s), 1655 (w), 1613 (s), 1556 (s), 1476 (s), 1385 (s), 1320 (s), 1282 (s), 1182 (s), 1155 (s), 1130 (w), 1113 (w), 1091 (m), 1067 (s), 1049 (m), 1031 (m), 1002 (m), 984 (m), 876 (w), 845 (s), 802 (s), 775 (s), 757 (m), 737 (m), 712 (s), 655 (m), 637 (m), 570 (m), 452 (s). UV-Vis [λ_{max} (nm), (ε, $M^{-1}cm^{-1}$), DMSO] 269 (7800), 313 (15840), 377 (2520). ESI MS *m/z* calcd [**hyd-**^{35}**Cl**+H]$^+$ 275.07, found 275.14; cald [^{64}Zn(**hyd-**^{35}**Cl**)^{35}Cl]$^+$ 372.96, found 373.05.

*Synthesis of [Zn(**hyd-Br**)Cl_2]·DMF (**3**)*: The procedure adopted for the synthesis of complex **2**, was applied for the synthesis of complex (**3**). Yield 84 mg, 64%. Anal. Calc. for

$C_{16}H_{18}N_5O_2Cl_2BrZn$: C, 36.36%; H, 3.43%; N, 13.25%. Found: C, 36.43%; H, 3.32%; N, 13.19%. IR (KBr, cm^{-1}): 3653 (s), 3473 (b), 3182 (b), 3049 (w), 1704 (s), 1656 (m), 1616 (m), 1533 (s), 1486 (m), 1473(m), 1445(m), 1426(s), 1318(s), 1275(s), 1198(m), 1173 (m), 1157 (w), 1141 (w), 1121 (m), 1094 (s), 1044 (m), 1030 (m), 1017 (s), 970 (w), 915 (m), 897 (w), 825 (w), 793 (s), 763 (w), 750 (m), 724 (m), 687 (s), 641 (m), 570 (m); UV-Vis [λ_{max}(nm), (ε, $M^{-1}cm^{-1}$), DMSO]: 265 (9750), 312 (26180), 329 (19870); ESI MS *m/z* calcd [^{64}Zn(^{79}**hyd-Br**)(^{35}Cl)$^+$] 416.91, found 416.99.

Table S1. Relevant bond lengths (Å) and bond angles (°) in metal complex **1**

Zn1–O1	2.212(2)	N1–Zn1–N2	74.43(6)
Zn1–N1	2.159(2)	N2–Zn1–O1	72.97(6)
Zn1–N2	2.079(2)	N1–Zn1–O1	147.40(6)
Zn1–Cl1	2.250(6)	O1–Zn1–Cl1	97.86(4)
Zn1–Cl2	2.258(6)	O1–Zn1–Cl2	100.64(4)
		N1–Zn1–Cl1	99.29(5)
N1–Zn1–Cl2	97.27(5)	N2–Zn1–Cl2	122.69(5)
N2–Zn1–Cl1	123.08(5)	Cl1–Zn1–Cl2	114.23(2)

Table S2. Relevant bond lengths (Å) and bond angles (°) in metal complexes **2** and **3**

Complex **2**		Complex **3**	
Zn1−N1	2.222(3)	Zn1−N1	2.189(4)
Zn1−N2	2.070(3)	Zn1−N2	2.079(3)
Zn1−O1	2.250(3)	Zn1−O1	2.241(4)
Zn1−Cl2	2.231(9)	Zn1−Cl1	2.249(1)
Zn1−Cl3	2.262(9)	Zn1−Cl2	2.218(1)
Zn2−N5	2.198(3)	Zn2−N5	2.225(3)
Zn2−N6	2.078 (2)	Zn2−N6	2.086(4)
Zn2−O2	2.250(3)	Zn2−O2	2.256(4)
Zn2−Cl5	2.228(9)	Zn2−Cl3	2.260(1)
Zn2−Cl6	2.249(9)	Zn2−Cl4	2.221(1)
N1−Zn1−N2	73.71(9)	N1−Zn1−N2	73.5(1)
N1−Zn1−O1	147.25(9)	N1−Zn1−O1	145.5(1)
N2−Zn1−O1	73.60(9)	N2−Zn1−O1	73.1(1)
N1−Zn1−Cl2	98.78(7)	N1−Zn1−Cl1	99.9(1)

N1−Zn1−Cl3	99.40(7)	N1−Zn1−Cl2	100.1(1)
N2−Zn1−Cl2	125.33(7)	N2−Zn1−Cl1	132.4(1)
N2−Zn1−Cl3	116.31(7)	O1−Zn1−Cl1	96.1(1)
O1−Zn1−Cl2	98.42(6)	O1−Zn1−Cl2	98.6(1)
O1−Zn1−Cl3	96.62(6)	N2−Zn1−Cl1	132.4(1)
Cl2−Zn1−Cl3	118.33(4)	N2−Zn1−Cl2	108.9(1)
N5−Zn2−N6	73.8(1)	N5−Zn2−N6	73.7(1)
N5−Zn2−O2	146.1(1)	N5−Zn2−O2	146.8(1)
N6−Zn2−O2	73.29(9)	N6−Zn2−O2	73.3(1)
Cl5−Zn2−Cl6	118.84(4)	Cl3−Zn2−Cl4	118.03(5)
N5−Zn2−Cl5	100.08(8)	N5−Zn2−Cl3	100.09(9)
N6−Zn2−Cl5	108.83(7)	N6−Zn2−Cl3	115.2(1)
N5−Zn2−Cl6	99.27(7)	N5−Zn2−Cl4	98.47(9)
N6−Zn2−Cl6	132.26(7)	N6−Zn2−Cl4	126.7(1)
O2−Zn2−Cl5	98.03(7)	O2−Zn2−Cl3	96.66(9)
O2−Zn2−Cl6	96.68(7)	O2−Zn2−Cl4	98.58(9)

Table S3. Hydrogen bonding interactions in ligand **hyd-Cl** and **hyd-Br**

Compound	D−H···A	D···A (Å)	H···A (Å)	D−H···A(°)	Symmetry
hyd-Cl	N4−H4A···O1	2.886(3)	2.01	178	-x+1/2, y+1/2, z
	N3−H3···O1	2.932(3)	2.11	160	-x+1/2, y+1/2, z
	C9−H9···N2	3.414(4)	2.61	145	-x+1/2, y+1/2, z
hyd-Br	N4−H4A···O1	2.887(1)	2.03	180	-x+1/2, y+1/2, z
	N3−H3···O1	2.968(1)	2.14	161	-x+1/2, y+1/2, z
	C9−H9···N2	3.376(1)	2.86	143	-x+1/2, y+1/2, z

Table S4. Hydrogen bonding interactions in metal complexes **2** and **3**

Compound	D−H···A	D···A (Å)	H···A (Å)	D−H···A(°)	Symmetry
2	N4−H4A···O3	2.793(4)	1.94	170	x,-y+1/2,z+1/2
	N3−H3A···O3	2.737(4)	1.88	171	x,-y+1/2,z+1/2
	N7−H7A···O4	2.776(3)	1.92	171	x,y-1,z
	N8−H8A···O4	2.881(5)	2.04	167	x,y-1,z
	N3−H3···O3	2.781(2)	1.93	169	x,y,z

3	N4−H4A···O3	2.868(4)	2.02	167	x,y,z
	N7−H7A···O4	2.729(2)	1.87	173	x,-y+1/2+1,z+1/2
	N8−H8A···O4	2.794(3)	1.94	172	x,-y+1/2+1,z+1/2

Table S5. NBO charge on halogen atoms calculated at dispersion corrected B3LYP/6-31G(d,p) level of theory

Molecule	Halogen atom	NBO charge
hyd-Cl	Cl	0.0264
% of *s* character in C hybrid orbital of C−X		22.59
hyd-Br	Br	0.0910
% of *s* character in C hybrid orbital of C−X		22.25
1	F	-0.3515
% of *s* character in C hybrid orbital of C−X		21.01
2-closed	Cl	0.0602
% of *s* character in C hybrid orbital of C−X		23.15
2-open	Cl	0.0049
% of *s* character in C hybrid orbital of C−X		22.26
3-closed	Br	0.1454
% of *s* character in C hybrid orbital of C−X		22.79
3-open	Br	0.0667
% of *s* character in C hybrid orbital of C−X		21.22

Table S6. Energy of 'closed' and 'open' molecules in complex **2** and **3** determined at M06-2X/6-31G(d,p) and B3LYP-D3/6-31G(d,p) level

E ('closed' molecule of complex **2**, at M06-2X/6-31G(d,p)) = -3955.38534 a.u.
E ('closed' molecule of complex **2**, at B3LYP-D3/6-31G(d,p)) = -3955.88634 a.u.
E ('open' molecule of complex **2**, at M06-2X/6-31G(d,p)) = -3955.38843 a.u.
E ('open' molecule of complex **2**, at B3LYP-D3/6-31G(d,p)) = -3955.89017 a.u.
E ('closed' molecule of complex **3**, at M06-2X/6-31G(d,p)) = -6067.00176 a.u.
E ('closed' molecule of complex **3**, at B3LYP-D3/6-31G(d,p)) = -6067.00278 a.u.
E ('open' molecule of complex **3**, at M06-2X/6-31G(d,p)) = -6067.00278 a.u.
E ('open' molecule of complex **3**, at B3LYP-D3/6-31G(d,p)) = -6067.40137 a.u.

Table S7A. Coordinates of optimized geometry of ligand **hyd-Cl** determined at M06-2X/6-31G(d,p) level

Cl	-3.58051200	2.00457300	0.90220700
O	-1.11583400	1.64172900	-0.97489600
N	-0.17680800	-0.19165500	0.01707100
H	-0.34268600	-1.14071500	0.33803500
N	1.11262200	0.18661200	-0.25492400
N	4.32280200	-0.78708700	0.89822200
N	1.74167800	-1.39183800	1.39356700
H	0.98689600	-1.14626200	2.02328500
H	2.58919900	-1.67689700	1.87221900
C	-1.22706500	0.54008400	-0.49184400
C	2.00373900	-0.43712900	0.42768600
C	-3.67113800	0.41634000	0.19964100
C	-2.54419500	-0.18512300	-0.36733500
C	3.43359800	-0.15853200	0.12477300
C	6.07777800	0.28965100	-0.32964500
H	7.14200000	0.43722400	-0.47329600
C	-2.67083300	-1.47643200	-0.88723500
H	-1.80544600	-1.94080000	-1.35201400
C	5.61760300	-0.56379000	0.66646500
H	6.31662900	-1.09152600	1.31014500
C	3.79058400	0.71318600	-0.90697200
H	3.01174800	1.18423800	-1.49450600
C	5.14003800	0.94108400	-1.12874600

H	5.45946100	1.61591200	-1.91623200
C	-4.99445000	-1.53764300	-0.27785500
H	-5.94820900	-2.05322700	-0.24007000
C	-4.88835800	-0.25551200	0.25123200
H	-5.74214200	0.23255400	0.70738200
C	-3.88544300	-2.15210000	-0.85030100
H	-3.96529800	-3.14880200	-1.27003600

Table S7B. Coordinates of optimized geometry of ligand **hyd-Cl** determined at B3LYP-D3/6-31G(d,p) level

Cl	0.51830900	-0.11230500	-0.11675800
O	-0.26379900	0.17805800	2.97201900
N	1.89264800	0.13522800	3.76564900
H	2.81586600	0.55150800	3.67826000
N	1.58927800	-0.56772500	4.90633800
N	3.42252200	-2.38147200	7.35987000
N	3.91832000	-1.04167600	5.07809400
H	4.04587900	-1.20792700	4.08640300
H	4.52030200	-1.61485300	5.66215700
C	0.88883700	0.55988400	2.91654000
C	2.60136000	-1.10031500	5.50989400
C	1.21340000	1.37026700	0.51593200
C	1.38706800	1.55605000	1.89530200
C	2.35243700	-1.78997200	6.80273100
C	2.02250900	-3.11132000	9.17318500
H	1.93834500	-3.64725100	10.11276300
C	1.98577600	2.74714600	2.33200600
H	2.10817400	2.90855200	3.39936700
C	3.25147200	-3.02254800	8.52155800
H	4.13851300	-3.48730500	8.94656200
C	1.07674400	-1.81499500	7.38411900
H	0.25615300	-1.31362800	6.88536000
C	0.91481200	-2.49408100	8.58564300
H	-0.06036800	-2.54007100	9.06096200
C	2.20982200	3.52199800	0.06200400
H	2.52216900	4.27628600	-0.65362800
C	1.62538500	2.34159900	-0.39664500
H	1.48816900	2.16537900	-1.45761900
C	2.39182500	3.72808200	1.42914000
H	2.84248700	4.64651000	1.79152600

Table S8A. Coordinates of optimized geometry of ligand **hyd-Br** determined at B3LYP-D3/6-31G(d,p) level

Br	3.28138900	-1.80008100	-0.42195900
O	0.78164100	-1.00651900	1.48437500
N	-0.24508300	0.45512000	0.03914900
H	-0.11485400	1.28775400	-0.52921000
N	-1.52367900	0.06553300	0.35747400
N	-2.20512100	1.10799300	-1.67368300
H	-1.41253000	0.77507400	-2.21060600
H	-3.05713600	1.18781800	-2.22107000
C	3.27586400	0.06470700	-0.00826200
C	-2.43289200	0.42011700	-0.49110100
C	0.83595900	-0.05308300	0.73178500
C	2.11131400	0.70242600	0.44046800
N	-4.75057500	0.44855400	-1.09590900
C	-6.03994700	0.19346900	-0.84626100
H	-6.74327700	0.47580200	-1.62669400
C	-3.84906800	0.11850100	-0.15583100
C	-4.20077300	-0.47475400	1.06497300
H	-3.42509800	-0.71201100	1.78297800
C	2.16518900	2.08212900	0.68798700
H	1.27318200	2.58305300	1.05374400
C	-6.48841300	-0.40072500	0.33214500
H	-7.54633000	-0.58862500	0.48254700
C	4.45637100	0.78007000	-0.20508400
H	5.33965600	0.26365600	-0.56322000
C	4.48921200	2.15013000	0.05583300
H	5.41332200	2.70013200	-0.09348900
C	3.34238200	2.80519800	0.50341100
H	3.36366500	3.87015600	0.71184100
C	-5.54344900	-0.74179300	1.30363600
H	-5.85164700	-1.20658000	2.23531300

Table S8B. Coordinates of optimized geometry of ligand **hyd-Br** determined at M06-2X/6-31G(d,p) level

Br	3.30603600	-1.76887900	-0.44511100
O	0.77717000	-1.10659500	1.33745400
N	-0.25660700	0.45156200	0.02295500
H	-0.14774900	1.33871000	-0.45900000

N	-1.52392700	0.03069300	0.33385900
N	-2.21116000	1.23854200	-1.58296400
H	-1.41946300	0.94550600	-2.14312100
H	-3.06074200	1.36730700	-2.12172500
C	3.27185600	0.06659800	-0.00337000
C	-2.43472400	0.45325400	-0.46678200
C	0.82607300	-0.10110900	0.66897800
C	2.09585400	0.67936600	0.43476400
N	-4.75613000	0.53262300	-1.03828000
C	-6.03810400	0.25313400	-0.79638400
H	-6.75191300	0.60191300	-1.53821600
C	-3.84981300	0.12257700	-0.14704100
C	-4.17637200	-0.57767200	1.01699000
H	-3.38526000	-0.87459000	1.69497100
C	2.12457200	2.04783800	0.71811300
H	1.22019700	2.52725600	1.08267000
C	-6.46766000	-0.44396400	0.32692700
H	-7.52234200	-0.64705500	0.47306400
C	4.44330400	0.79958700	-0.16033800
H	5.33811400	0.29965900	-0.51270300
C	4.45294500	2.15963400	0.13305500
H	5.37162600	2.72452500	0.01483700
C	3.29309700	2.78787600	0.57475100
H	3.29785500	3.84621200	0.81137700
C	-5.51213400	-0.86785900	1.24872000
H	-5.80752800	-1.41541400	2.13783500

Table S9A. Coordinates of optimized geometry of complex **1** determined at M06-2X/6-31G(d,p) level

Zn	-0.95867000	-1.17023200	0.17833400
Cl	-0.92331200	-0.52241900	2.36729800
Cl	-1.65468300	-3.01923100	-0.85182500
C	-2.57468300	1.34621300	-0.23476900
C	1.75256100	-0.10171200	-0.20272100
C	-3.59768800	2.27601200	-0.34640600
H	-3.38850800	3.34000500	-0.31495100
C	-5.10440900	0.42487200	-0.61475800
H	-6.09700200	0.01771000	-0.76566700
C	3.23862100	-0.02415300	-0.19672000
C	3.99183100	1.14118400	-0.32889200
C	-1.14187200	1.70650900	-0.03811500
C	-4.89310500	1.79427100	-0.53717500

H	-5.72264800	2.48666400	-0.63312000
C	5.32173000	-1.25432700	-0.02486400
H	5.84235800	-2.19708000	0.09648000
C	-4.00920300	-0.43320700	-0.49557200
H	-4.09672700	-1.51517800	-0.55271200
C	3.93467100	-1.22890500	-0.04214900
H	3.34784000	-2.13457100	0.06400000
C	5.37484500	1.14326300	-0.31499100
H	5.89956500	2.08503000	-0.42322900
C	6.04106700	-0.06790100	-0.16099300
H	7.12559500	-0.08137600	-0.14726400
N	-0.31612500	0.85116100	-0.53555200
N	-2.77901100	0.02656800	-0.30248400
N	1.03077900	1.05480000	-0.28621300
H	1.47373700	1.89409400	-0.63973500
N	-0.81737500	2.85515200	0.60702000
H	0.11167300	2.85495600	1.01399600
H	-1.52509400	3.20621800	1.23816800
O	1.18122300	-1.18669900	-0.10908300
F	3.37015200	2.33396100	-0.48078100

Table S9B. Coordinates of optimized geometry of complex **1** determined at B3LYP-D3/6-31G(d,p) level

Zn	-0.99681000	-1.19987700	0.16047600
Cl	-1.04308300	-0.97864000	2.40024200
Cl	-1.61214900	-2.83558900	-1.20138000
C	-2.56787300	1.40356300	-0.18004600
C	1.79219000	-0.13557400	-0.11542800
C	-3.58960400	2.34153700	-0.31802700
H	-3.37946400	3.40659000	-0.31594300
C	-5.12176600	0.50027900	-0.55893200
H	-6.11937200	0.10107600	-0.70821000
C	3.27511600	-0.01733600	-0.15287300
C	4.00152000	1.17378400	-0.26595100
C	-1.13588800	1.75499000	0.01732900
C	-4.89290400	1.87249300	-0.50434600
H	-5.71283900	2.57554100	-0.61729400
C	5.40361700	-1.20007600	-0.09560500
H	5.95110400	-2.13459600	-0.02702000
C	-4.03203300	-0.36623600	-0.42547700
H	-4.12844100	-1.44677900	-0.48032500

C	4.01343300	-1.21062400	-0.06759700
H	3.45786900	-2.13770100	0.02175000
C	5.38649500	1.21205400	-0.29671200
H	5.88460300	2.17111600	-0.38759200
C	6.09151400	0.01152400	-0.20959700
H	7.17711000	0.02659400	-0.23158800
N	-0.30912600	0.81429300	-0.30437400
N	-2.79347500	0.08025800	-0.23034000
N	1.04091300	1.01952200	-0.12182600
H	1.46203800	1.88166300	-0.44961700
N	-0.78207100	2.99818200	0.47530300
H	0.11585500	3.03462000	0.94852500
H	-1.50019000	3.49258100	0.99024400
O	1.23636500	-1.23423200	-0.05225100
F	3.34527400	2.36814400	-0.35684500

Table S10A. Coordinates of optimized geometry of complex **2** determined at M06-2X/6-31G(d,p) level

Zn	-0.96210400	-1.03466100	-0.07957400
N	-2.93335900	-0.00150100	0.00315200
N	0.71436500	1.42977400	-0.29749000
H	0.99907100	1.95522400	0.52874100
N	-1.33841300	3.19946200	0.40679600
H	-0.42430900	3.61644100	0.33835000
H	-1.97205900	3.60712800	1.07542900
N	-0.61428500	1.09074800	-0.37150600
C	1.54223800	0.33642600	-0.57190600
C	-2.89690100	1.33557100	0.03936200
C	-1.51957600	1.90635700	0.02668000
C	2.99278200	0.61263900	-0.40513900
C	-4.04493400	2.11681400	0.05791200
H	-3.98219900	3.19908200	0.03813800
C	-5.31423200	0.08001600	0.01383100
H	-6.25406500	-0.45862400	0.00203100
C	4.84354300	2.16088600	-0.66398200
H	5.21737000	3.13003400	-0.97440900
C	5.23167500	-0.04861900	0.22863500
H	5.89853700	-0.80150700	0.63261100
C	3.49245900	1.86539300	-0.78095900
H	2.80642000	2.59435400	-1.20009500
C	-5.27802400	1.46667700	0.05513100
H	-6.19696800	2.04300400	0.06922200

C	-4.10871400	-0.62139500	-0.02612400
H	-4.06203800	-1.70480200	-0.09549200
C	5.71109300	1.19843700	-0.15513300
H	6.76964600	1.41471500	-0.05651500
C	3.87795500	-0.35035400	0.10111300
Cl	3.33622200	-1.90490800	0.62583600
O	1.07501000	-0.71624000	-0.96517900
Cl	-1.72024800	-2.74869400	-1.28062000
Cl	-0.23425100	-0.88803200	2.06934100

Table S10B. Coordinates of optimized geometry of complex **2** determined at B3LYP-D3/6-31G(d,p) level

Zn	1.01628800	-1.04011900	0.06393600
N	2.95538400	0.00836800	-0.04645300
N	-0.72130400	1.40131400	0.25298500
H	-1.01048700	1.92163900	-0.57439700
N	1.31978500	3.21522800	-0.35511000
H	0.40114000	3.61743300	-0.26199200
H	1.95342000	3.67847000	-0.98631900
N	0.61109900	1.05540900	0.31290600
C	-1.56957800	0.32751800	0.57274300
C	2.90176100	1.35173700	-0.05425900
C	1.52070300	1.90413200	-0.03497700
C	-3.01649500	0.62170100	0.39105800
C	4.05093600	2.14200600	-0.05121700
H	3.98387900	3.22328700	-0.00486900
C	5.34238900	0.11163100	-0.05127100
H	6.28805300	-0.41853900	-0.05119200
C	-4.84620600	2.22093600	0.59079200
H	-5.19925000	3.20941100	0.86573200
C	-5.27981800	-0.01538100	-0.22216300
H	-5.96417900	-0.76674800	-0.59926300
C	-3.49906000	1.90032900	0.72072600
H	-2.80176700	2.63241700	1.11511000
C	5.29238300	1.50308200	-0.06119100
H	6.20583800	2.08934600	-0.05996200
C	4.14100100	-0.60099900	-0.02716400
H	4.10071300	-1.68466900	0.02448900
C	-5.73612500	1.25716900	0.11520800
H	-6.79075600	1.49098200	0.00712600
C	-3.92896800	-0.34231000	-0.08213600
Cl	-3.42710300	-1.94130000	-0.55783200
O	-1.11357400	-0.71814500	1.00893600

Cl	1.75264100	-2.67853900	1.35355700
Cl	0.25452400	-1.03285800	-2.05756200

Table S11A. Coordinates of optimized geometry of complex **3** determined at M06-2X/6-31G(d,p) level

Zn	-1.08599300	-0.90936900	0.14462100
Br	3.01404700	-1.67578200	-0.42467200
Cl	-0.27685600	-0.59525300	-1.96595300
Cl	-1.66840400	-2.76474800	1.22464400
O	0.80537800	-0.35634900	1.19271400
N	-3.15222700	-0.10286300	-0.00132600
N	-0.99243000	1.25360800	0.44951300
N	0.30383500	1.70965800	0.38215100
H	0.55737300	2.18200200	-0.48644600
N	-1.89631400	3.23147800	-0.47616800
H	-1.02685600	3.73644600	-0.41309600
H	-2.53616200	3.52640300	-1.19664700
C	-4.25305200	-0.84809400	0.00518800
H	-4.08892200	-1.91855700	0.09592700
C	-5.52621400	-0.28455600	-0.08637000
H	-6.40107300	-0.92346700	-0.09093500
C	-5.64131200	1.09651300	-0.15972600
H	-6.61710600	1.56717100	-0.21569600
C	-4.48746600	1.87864800	-0.14146600
H	-4.54215700	2.96157300	-0.14852800
C	-3.26214300	1.22985100	-0.06718100
C	-1.95641000	1.94880700	-0.02910500
C	1.20374900	0.69498900	0.72325200
C	2.63169900	1.02778300	0.49771200
C	3.53921000	0.07288800	0.01767300
C	4.87066500	0.42763800	-0.18385700
H	5.55878500	-0.31646600	-0.56724200
C	5.30399800	1.71762100	0.10134000
H	6.34662200	1.97444900	-0.05413800
C	4.41190500	2.67179400	0.58318600
H	4.75114100	3.67504200	0.81522400
C	3.08154500	2.32420200	0.77264300
H	2.37579300	3.04798400	1.16807200

Table S11B. Coordinates of optimized geometry of complex **3** determined at B3LYP-D3/6-31G(d,p) level

Zn	-1.13554700	-0.91881000	0.13246700
Br	3.09639800	-1.68668400	-0.40739000
Cl	-0.33197900	-0.76876600	-1.97611300
Cl	-1.70160000	-2.68621800	1.33367900
O	0.83401500	-0.34625900	1.20986900
N	-3.17918700	-0.09673500	-0.02848800
N	-0.98852100	1.22357800	0.37170800
N	0.30918700	1.68869100	0.32029300
H	0.57197100	2.16960500	-0.53968200
N	-1.90221900	3.25669600	-0.43993500
H	-1.02736100	3.75132600	-0.36845100
H	-2.55387900	3.60017000	-1.12761700
C	-4.28914200	-0.83541400	-0.01882200
H	-4.12778100	-1.90541600	0.07075100
C	-5.56167000	-0.26438800	-0.10157200
H	-6.44141000	-0.89797200	-0.10713800
C	-5.66793000	1.12249000	-0.16409500
H	-6.64100500	1.60110200	-0.21100300
C	-4.50683000	1.89792300	-0.14530300
H	-4.56151100	2.98091400	-0.14065800
C	-3.27698900	1.24359800	-0.08515400
C	-1.96749600	1.94993600	-0.05191800
C	1.22570600	0.69703300	0.70551700
C	2.65085200	1.04593200	0.47974600
C	3.58549900	0.09643100	0.02306600
C	4.91636400	0.47097100	-0.17214600
H	5.62271300	-0.26583200	-0.53648000
C	5.32836800	1.77565100	0.09434200
H	6.36909500	2.04626500	-0.05556100
C	4.41333600	2.72517000	0.55109600
H	4.73328300	3.73891200	0.76873500
C	3.08427900	2.35781100	0.73485100
H	2.36617300	3.07948800	1.11147500

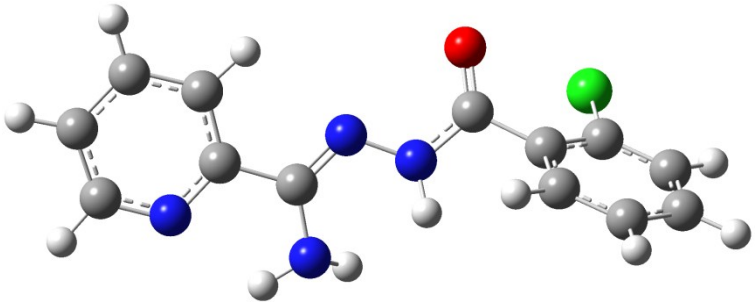

Figure S1. Optimized geometry of 'closed' molecule in asymmetric unit of ligand **hyd-Cl** calculated at dispersion corrected B3LYP/6-31G(d,p) level of theory

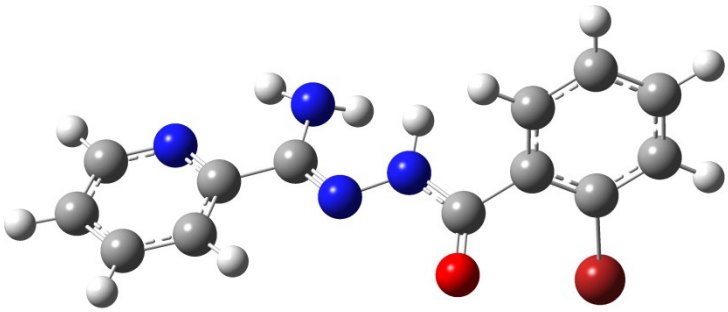

Figure S2. Optimized geometry of 'closed' molecule in asymmetric unit of ligand **hyd-Br** calculated at dispersion corrected B3LYP/6-31G(d,p) level of theory

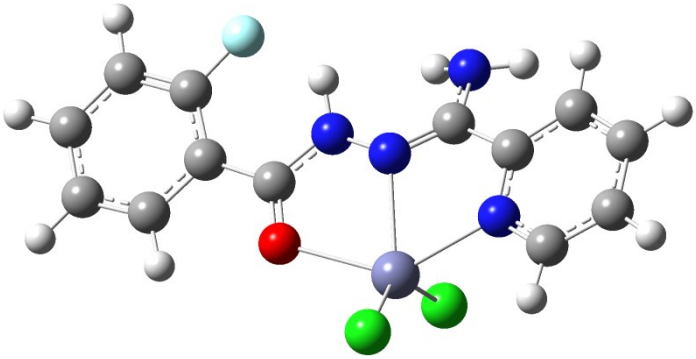

Figure S3. Optimized geometry of 'closed' molecule in asymmetric unit of complex **1** calculated at dispersion corrected B3LYP/6-31G(d,p) level of theory

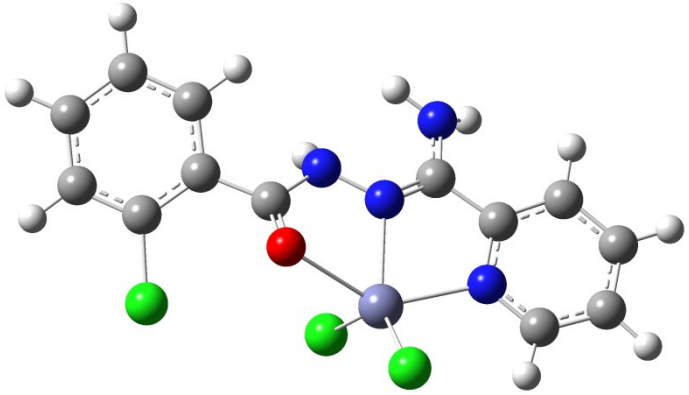

Figure S4. Optimized geometry of 'closed' molecule in asymmetric unit of complex **2** calculated at dispersion corrected B3LYP/6-31G(d,p) level of theory

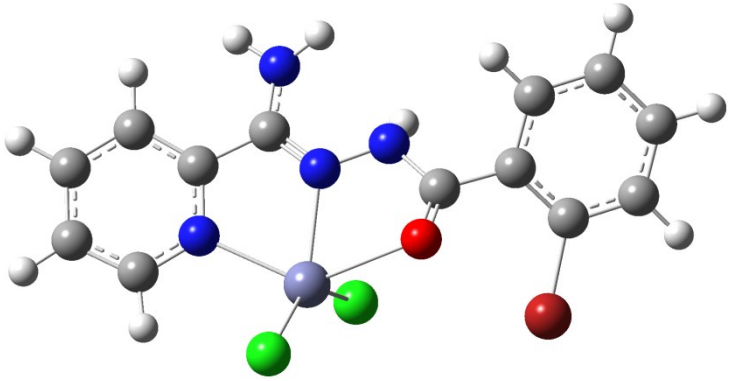

Figure S5. Optimized geometry of 'closed' molecule in asymmetric unit of complex **3** calculated at dispersion corrected B3LYP/6-31G(d,p) level of theory

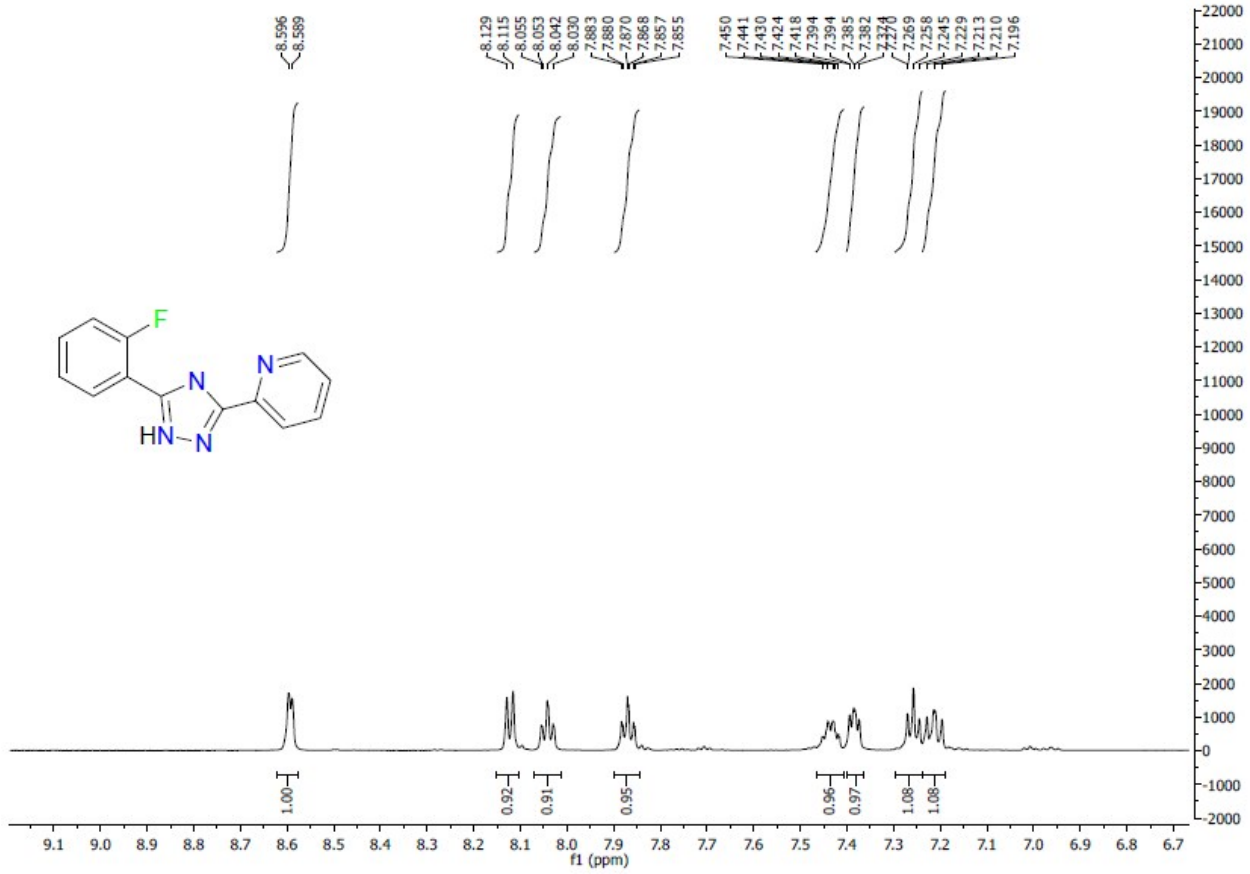

Figure S6. ^{1}H NMR spectrum of ligand **trz-F** (600 MHz, DMSO d_6)

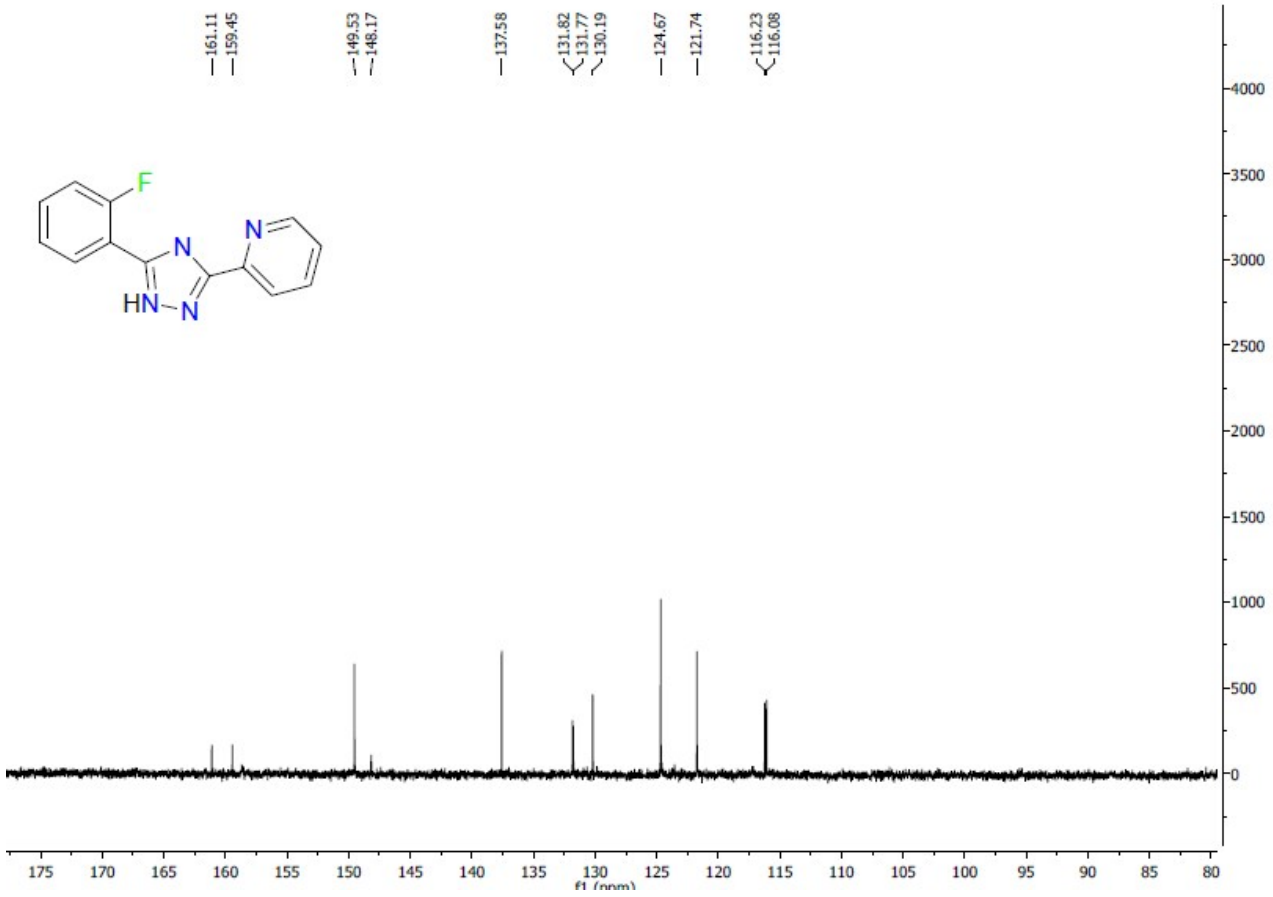

Figure S7. ^{13}C NMR spectrum of ligand **trz-F** (150 MHz, DMSO d_6)

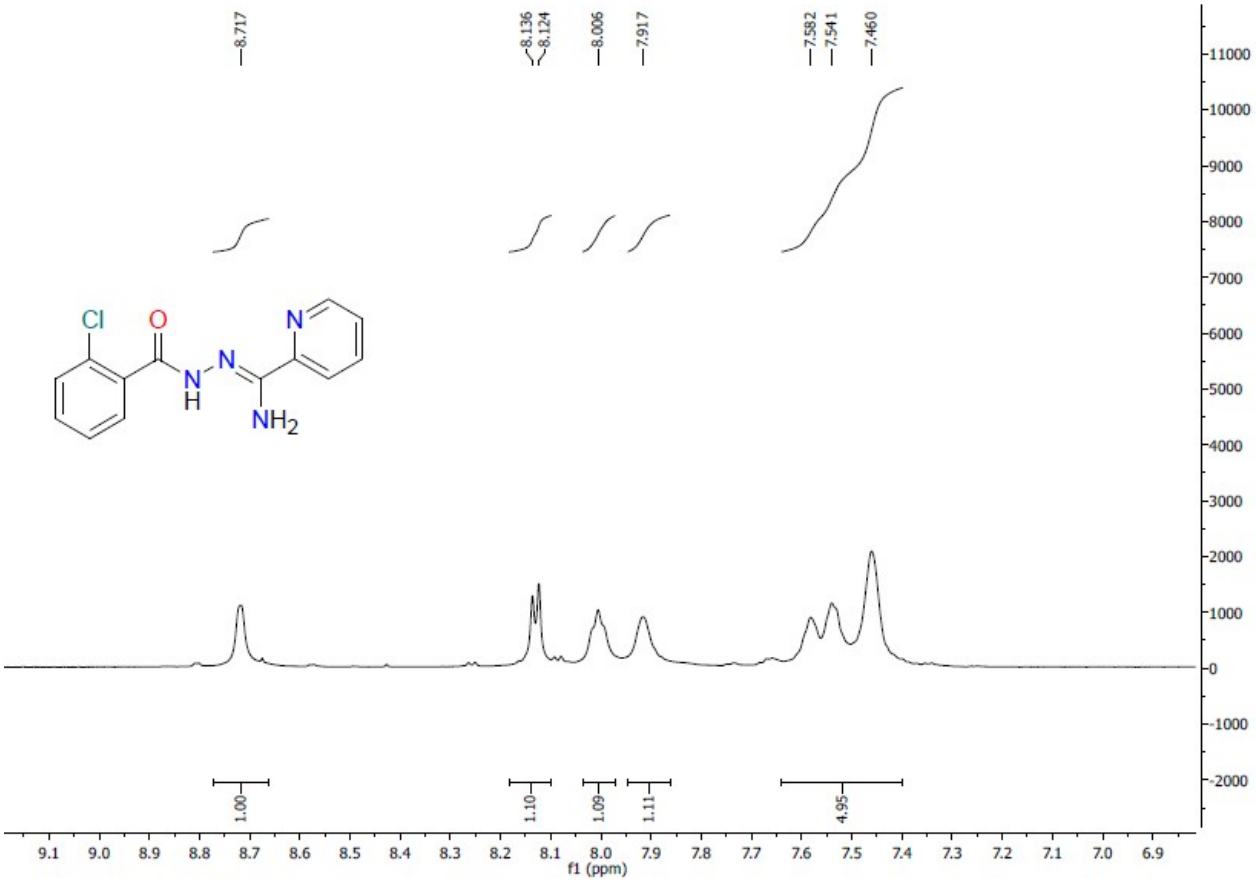

Figure S8. ^{1}H NMR spectrum of ligand **hyd-Cl** (600 MHz, DMSO d_6)

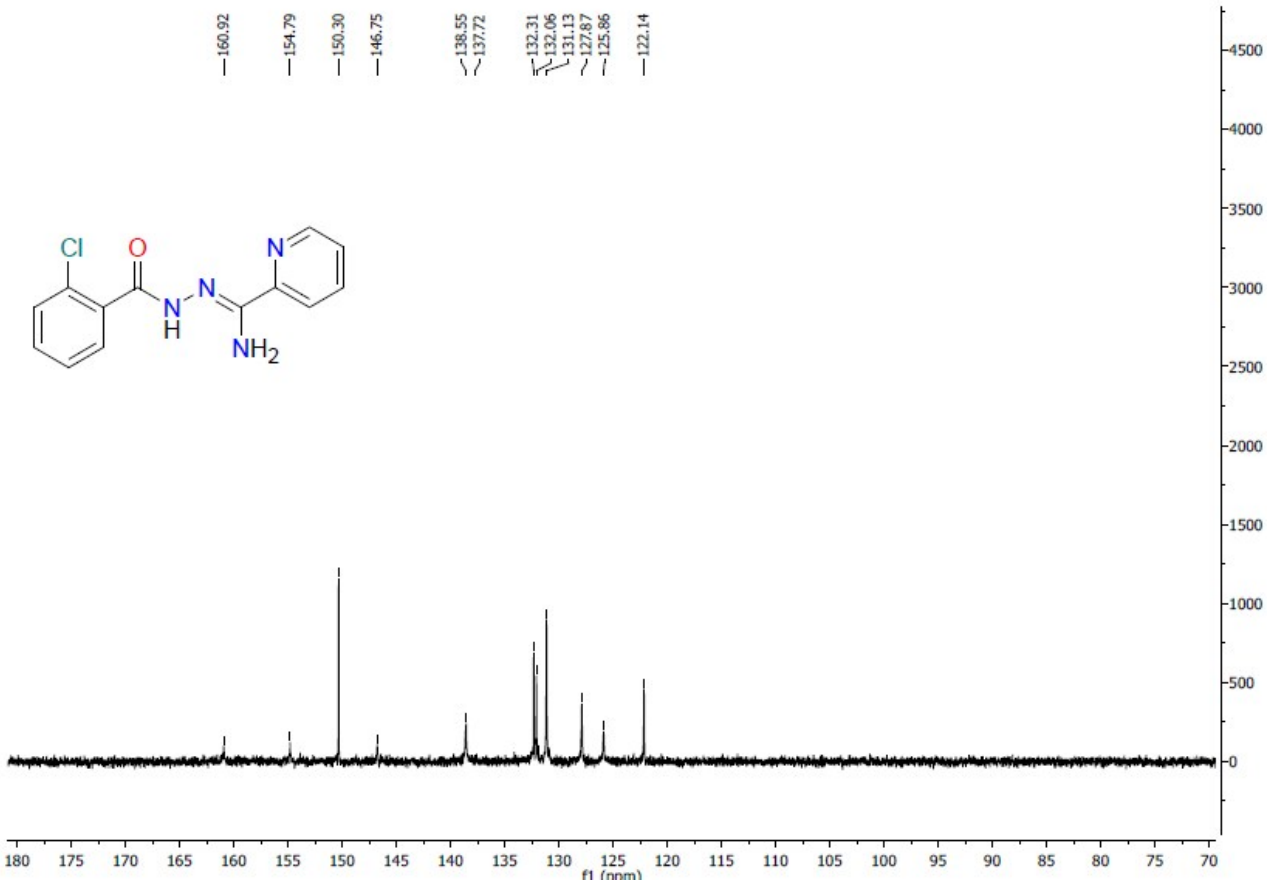

Figure S9. ^{13}C NMR spectrum of ligand **hyd-Cl** (150 MHz, DMSO d_6)

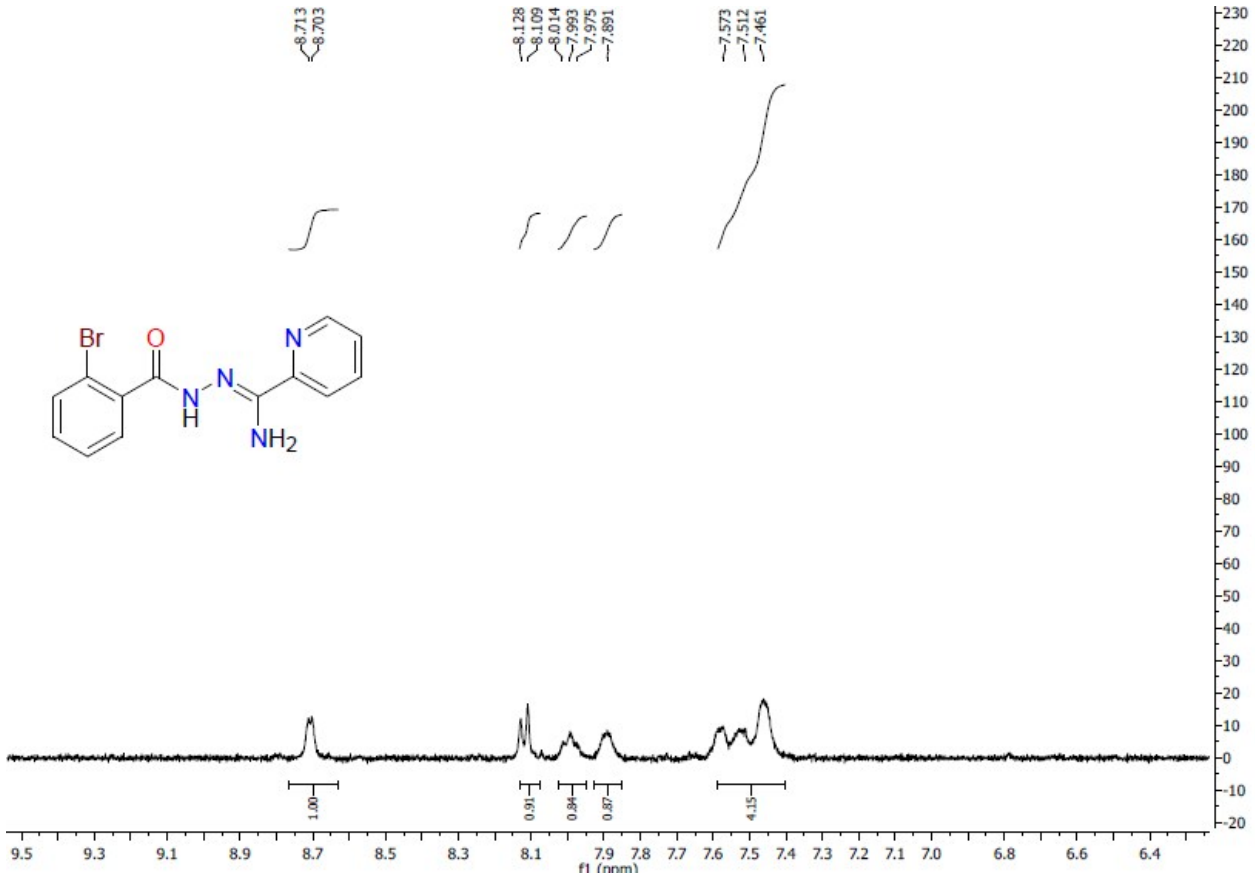

Figure S10. ^{1}H NMR spectrum of ligand **hyd-Br** (400 MHz, DMSO d_6)

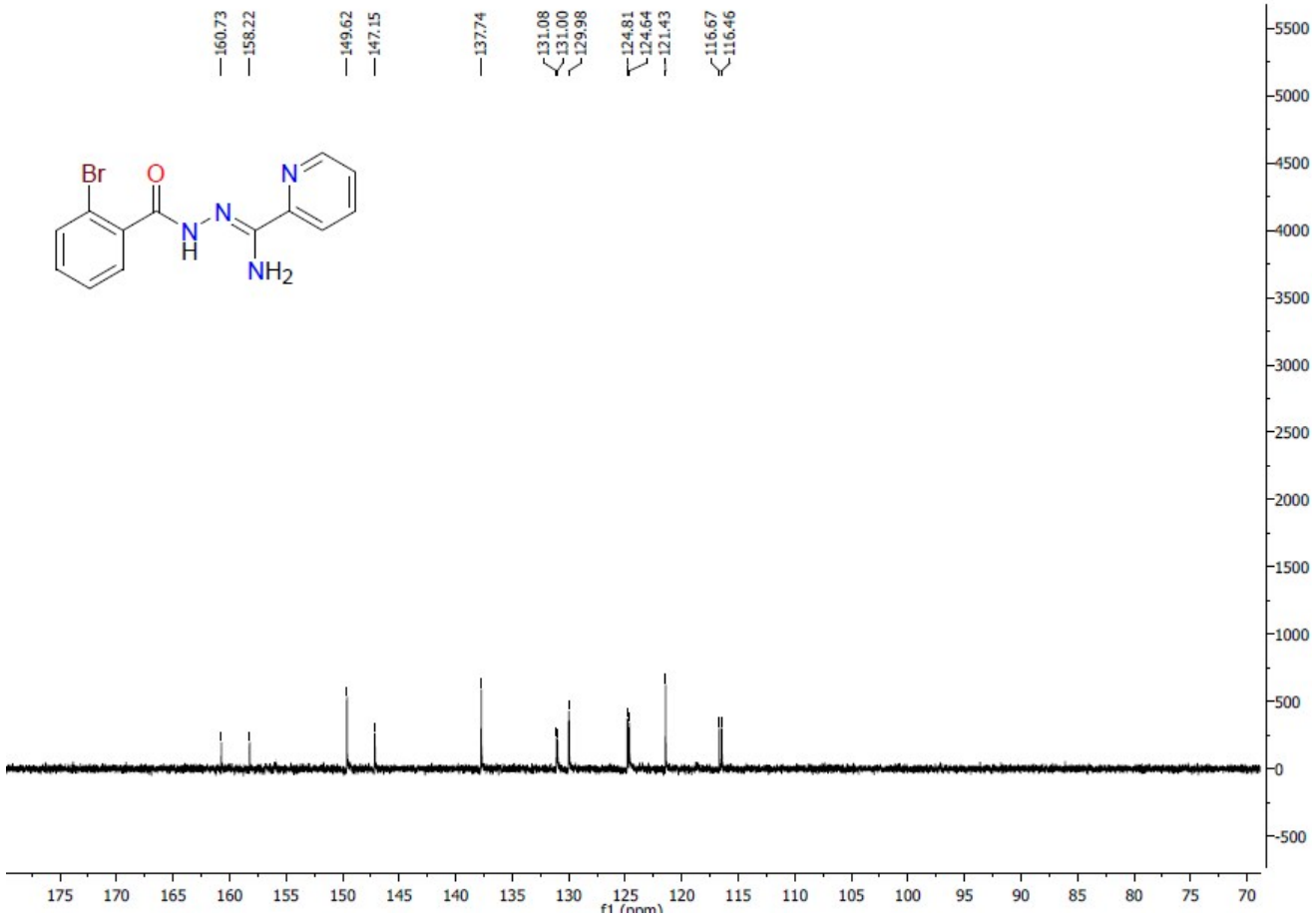

Figure S11. ^{13}C NMR spectrum of ligand **hyd-Br** (150 MHz, DMSO d_6)

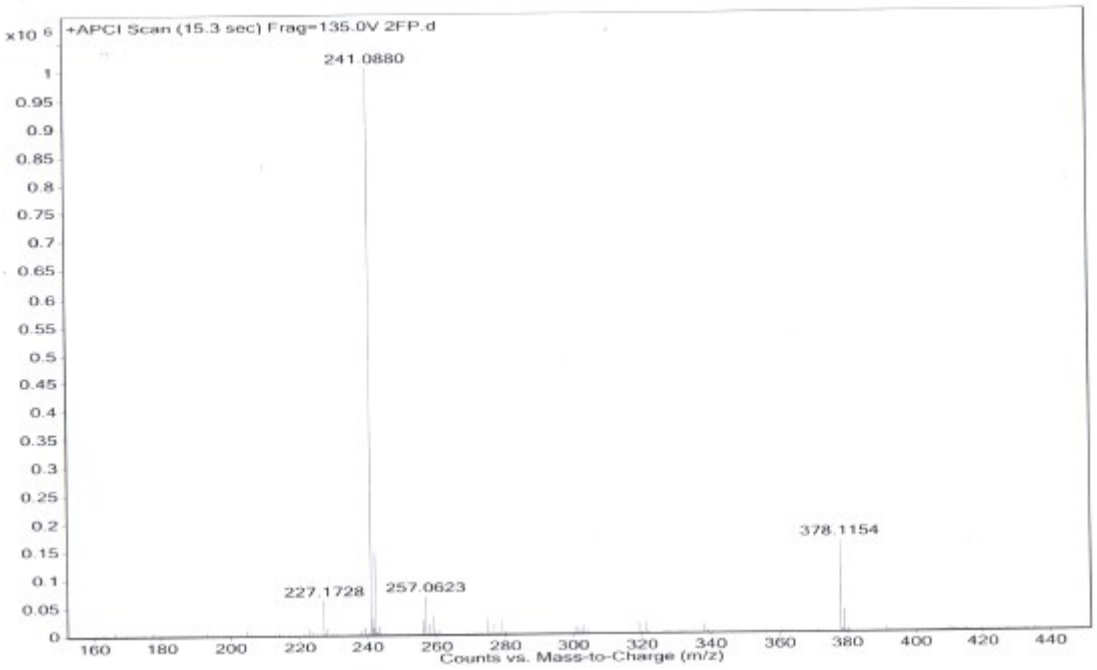

Figure S12. ESI MS of ligand **trz-F**

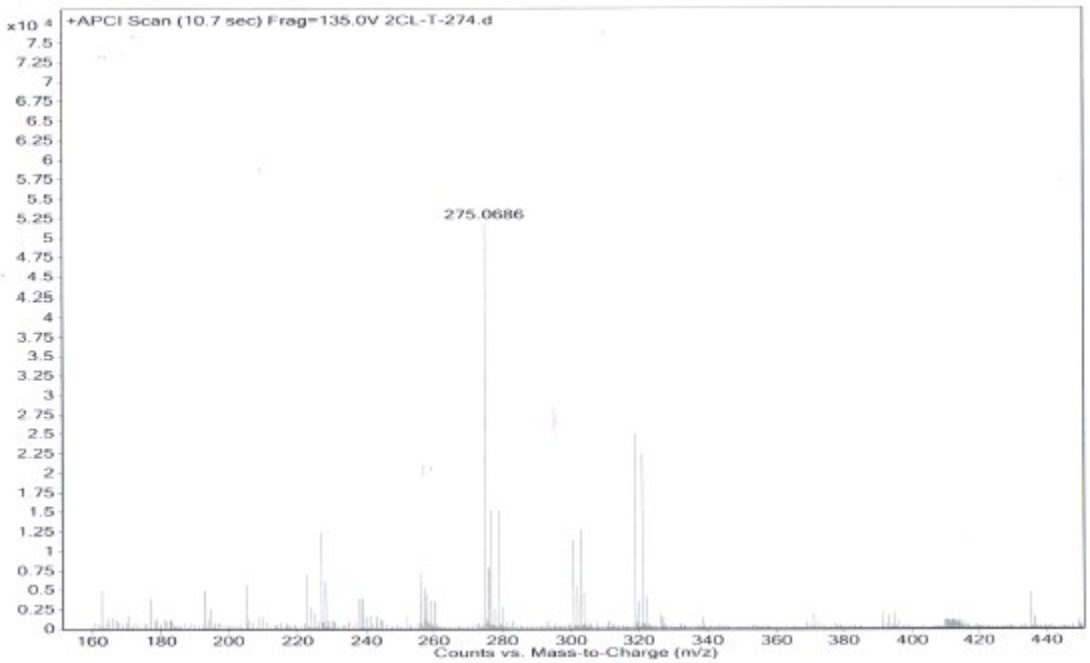

Figure S13. ESI MS of ligand **hyd-Cl**

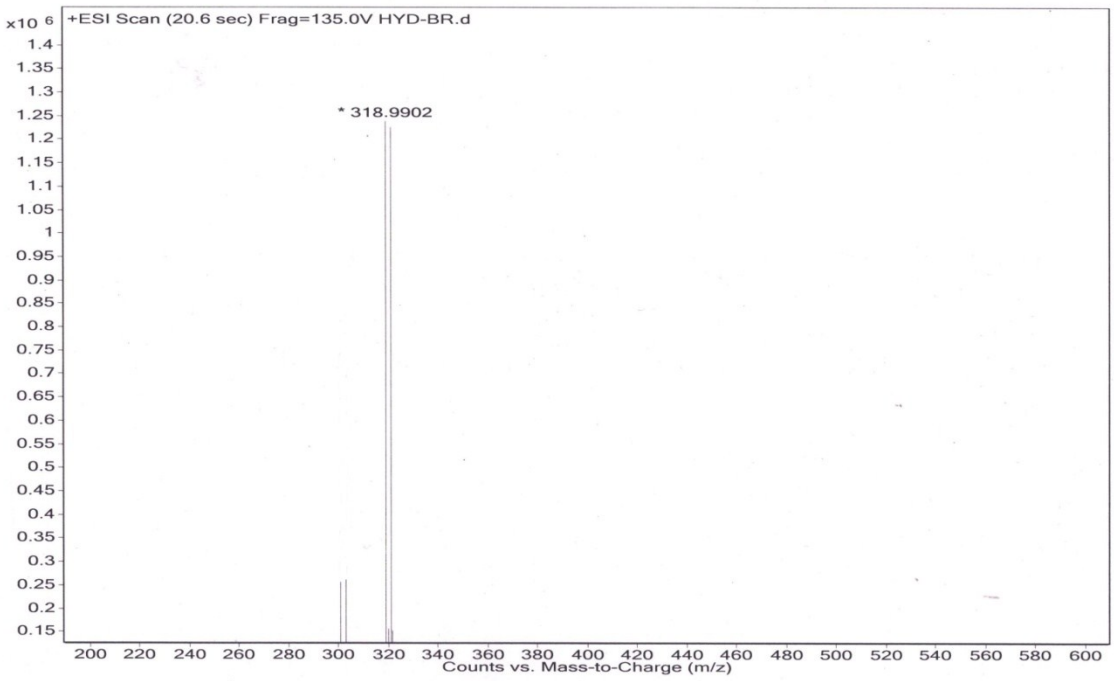

Figure S14. ESI MS of ligand **hyd-Br**

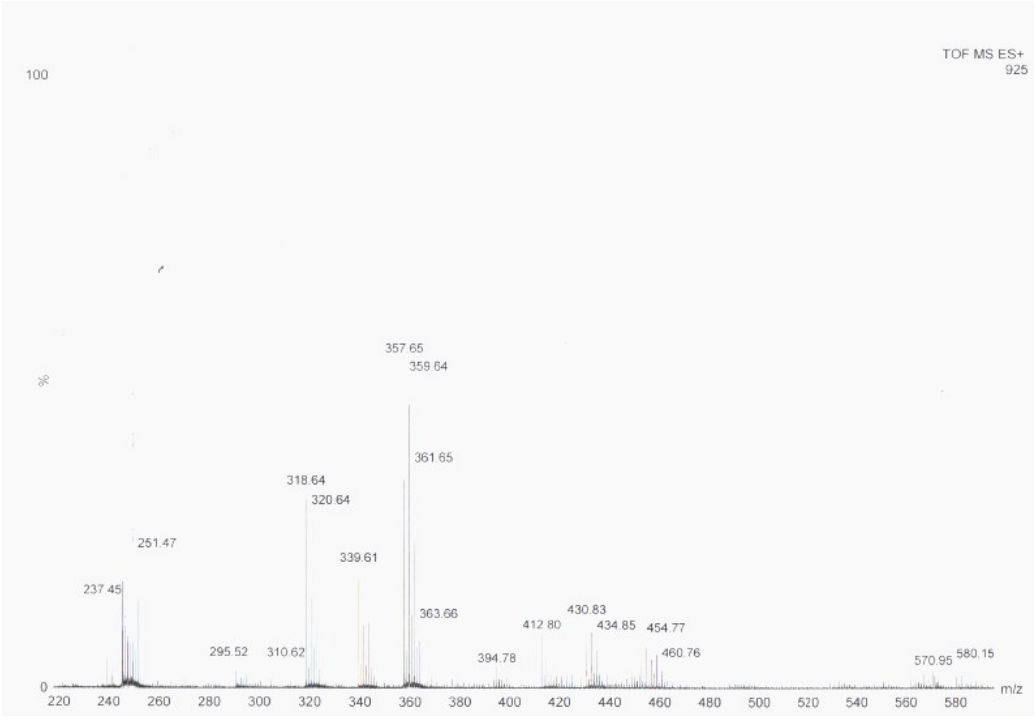

Figure S15. ESI MS of complex **1**

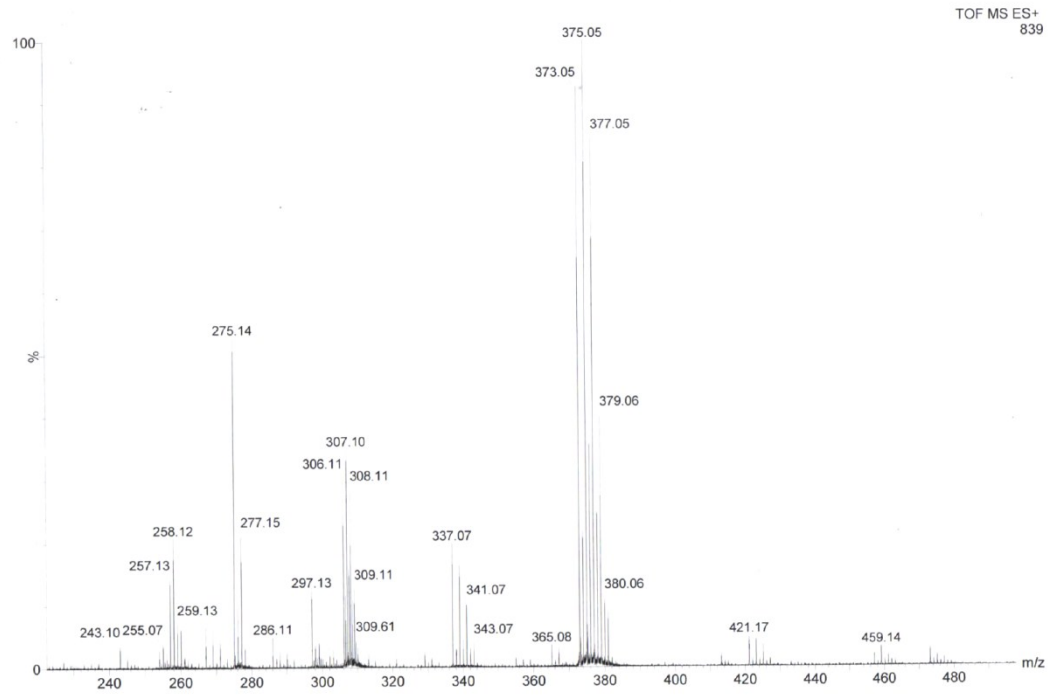

Figure S16. ESI MS of complex **2**

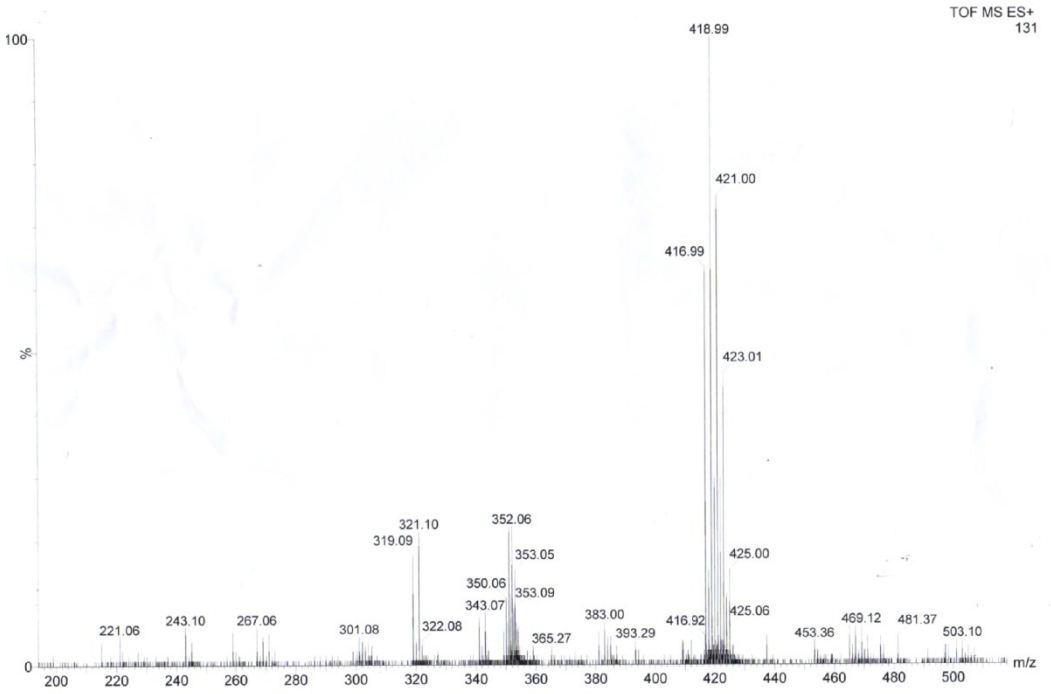

Figure S17. ESI MS of complex **3**