Supporting Information

Synthesis of 2-acetylpyridine-N-substituted thiosemicarbazonates of copper(II) with high antimicrobial activity against methicillin resistant *S.aureus*, *K. pneumonia* 1 and *C. albicans*

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S1. Ligand details

Preparation of 2-acetylpyridine-N^1-thiosemicarbazone (HL^{3H})

The solution of thiosemicarbazide (1 g, 10.9 mmol) in methanol was refluxed for 30 minutes at 40˚C. To this solution, 2-acetylpyridine ketone (1.23 mL, 10.9 mmol) was added along with 2-3 drops of glacial acetic acid and resulting solution was refluxed for seven hours. After that, the solution was left for crystallization at room temperature. Slow evaporation of the solution yielded orange crystals in 2- 3 days. Yield : 1.95g, 92%, m.p. 108-110ºC. ^{1}H NMR data (δ, ppm; DMSO-d^6), 10.30 (s, 1H, N^{2}H); 8.54 (dq, 1H, C^{7}H); 8.39 (dt, 1H, C^{4}H); 8.12 (s, 1H, N^{1}H); 7.76 (ddd, 1H, C^{5}H); 7.35 (m, 1H, C^{6}H); 2.34 (s, 3H, CH_3).Electronic absorption spectrum, DMSO, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-5}M] 321 (8.53 × 10^4).

Preparation of 2-acetylpyridine-N^1-methyl thiosemicarbazone (HL^{3Me})

The solution of 4-methyl-3-thiosemicarbazide (1 g, 9.5 mmol) in methanol was refluxed for 30 minutes at 40˚C. To this solution, 2-acetylpyridine ketone (1.07 mL, 9.5 mmol) was added along with 2-3 drops of glacial acetic acid and resulting solution was refluxed for seven hours. After that, the solution was left for crystallization at room temperature. Slow evaporation of the solution yielded pale yellow crystalline product in 2- 3 days. Yield : 1.53g, 77%, m.p. 122-124 ºC. ^{1}H NMR data (δ, ppm; DMSO-d^6), 10.32 (s, 1H, N^{2}H); 8.59 (d, 1H, C^{7}H); 8.53 (dq, 1H, N^{1}H); 8.37 (dt, 1H, C^{4}H); 7.78 (ddd, 1H, C^{5}H); 7.35 (m, 1H, C^{6}H); 3.01 (d, 3H, N^{1}H-CH_3); 2.34 (s, 3H, CH_3).Electronic absorption spectrum, DMSO, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-5}M] 320 (9.6 × 10^4).

Preparation of 2-acetylpyridine-N^1-ethyl thiosemicarbazone (HL^{3Et})

The solution of 4-ethyl-3-thiosemicarbazide (1 g, 8.4mmol) in methanol was refluxed for 30 minutes at 40˚C. To this, 2-acetylpyridine ketone (0.94 mL, 8.4mmol) was added along with 2-3 drops of glacial acetic acid and resulting solution was refluxed for seven hours. After that, the solution was left for crystallization at room temperature. Slow evaporation of the solution yielded pale yellow crystalline product in 2- 3 days. Yield : 1.48g, 80%, m.p. 96-98 ºC. ^{1}H NMR data (δ, ppm; DMSO-d^6), 10.22 (s, 1H, N^2H); 8.65 (t, 1H, N^1H); 8.54 (dq, 1H, C^7H); 8.36 (dt, 1H, C^4H); 7.78 (ddd, 1H, C^5H); 7.35 (m, 1H, C^6H); 3.59 (p, 2H, N^1H-CH_2); 2.34 (s, 3H, CH_3); 1.12 (t, 3H, N^1H-CH_3). Electronic absorption spectrum, DMSO, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-5}M] 319 (8.21×10^4).

Preparation of 2-acetylpyridine-N^1-phenyl thiosemicarbazone (HL^{3Ph})

The solution of 4-phenyl-3-thiosemicarbazide (1 g, 5.9 mmol) in methanol was refluxed for 30 minutes at 40˚C. To this, 2-acetylpyridine ketone (0.67 mL, 5.9 mmol) was added along with 2-3 drops of glacial acetic acid and resulting solution was refluxed for seven hours. After that, the solution was left for crystallization at room temperature. Slow evaporation of the solution yielded pale yellow crystalline product in 2- 3 days. Yield : 1.27g, 79%, m.p. 98-100 ºC. ^{1}H NMR data (δ, ppm; DMSO-d^6), 10.64 (s, 1H, N^2H); 10.17 (s, 1H, N^1H); 8.56 (dq, 1H, C^7H); 8.50 (dt, 1H, C^4H); 7.78 (ddd, 1H, C^5H); 7.32-7.50 (m, 5H, N^1H-Ph); 7.19 (ddd, 1H, C^6H); 2.42 (s, 3H, CH_3).Electronic absorption spectrum, DMSO, λ_{max}/nm, ε/L mol^{-1}cm^{-1}: [10^{-5}M] 322 (9.67×10^4).

S2.*Electronic absorption spectra of ligands and complexes*

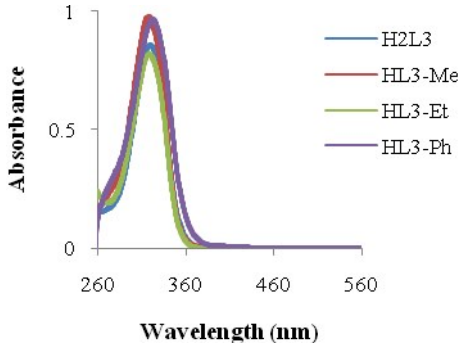


Fig S1: UV Spectra of ligands (HL^{3R}; R = H, Me, Et, Ph)

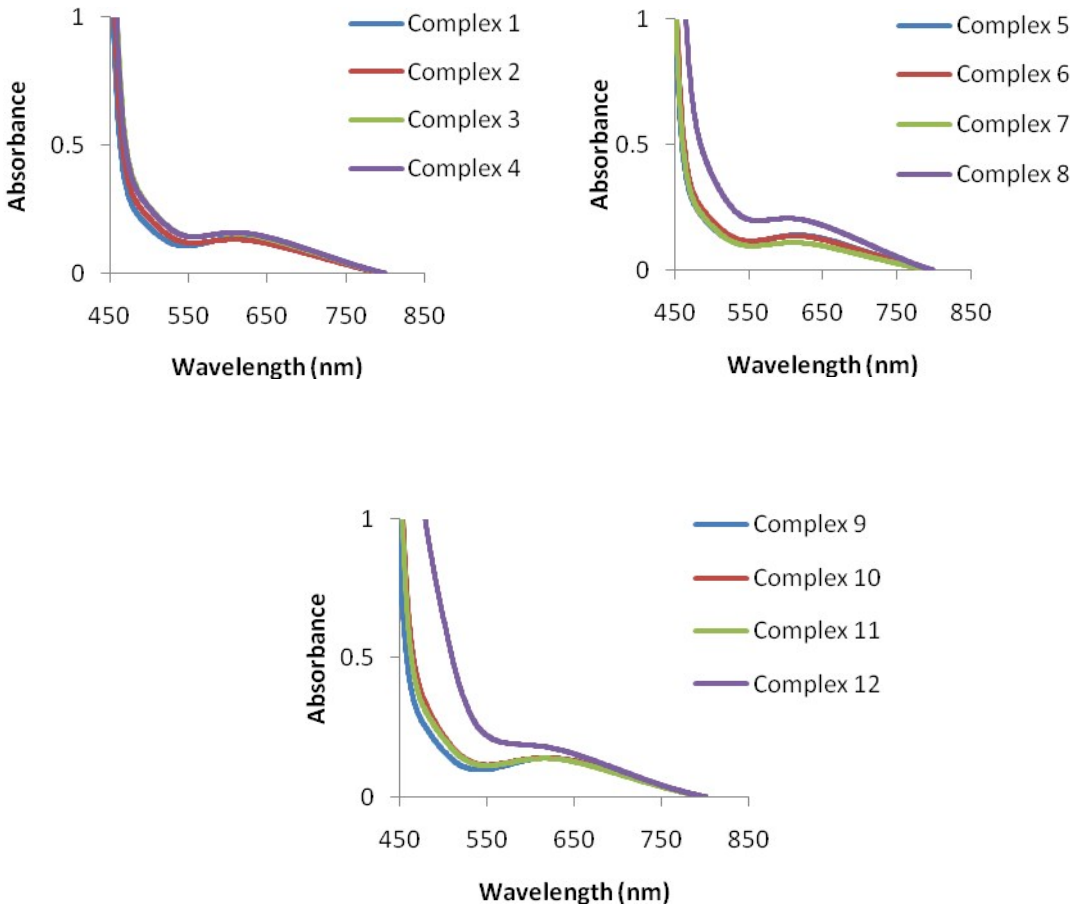
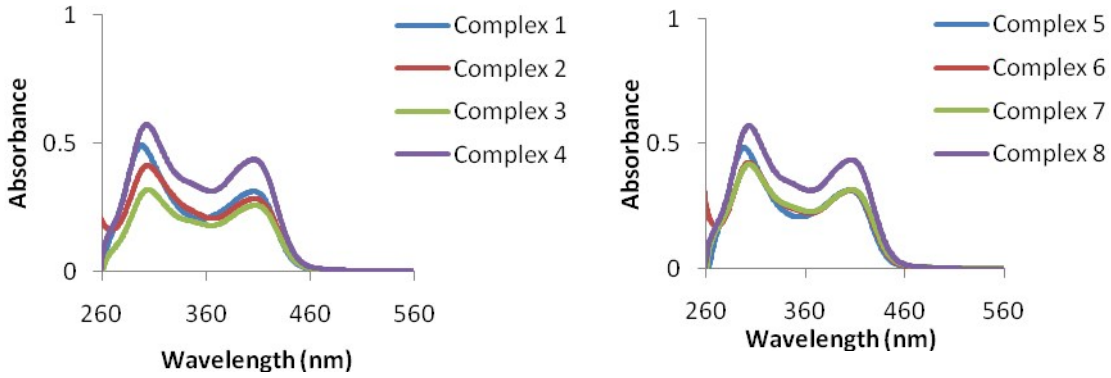


Fig S2: The electronic absorption spectra of complexes **1-12**in 10^{-3} M solution



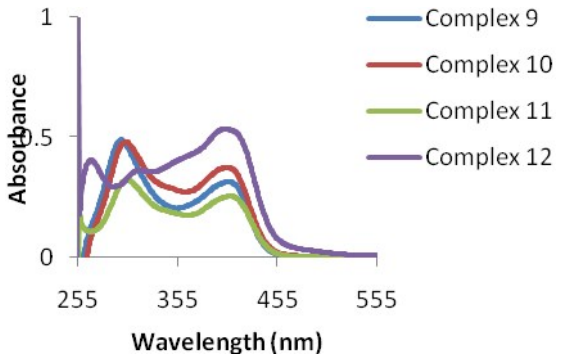


Fig S3: The electronic absorption spectra of complexes **1-12**in 10^{-5} M solution

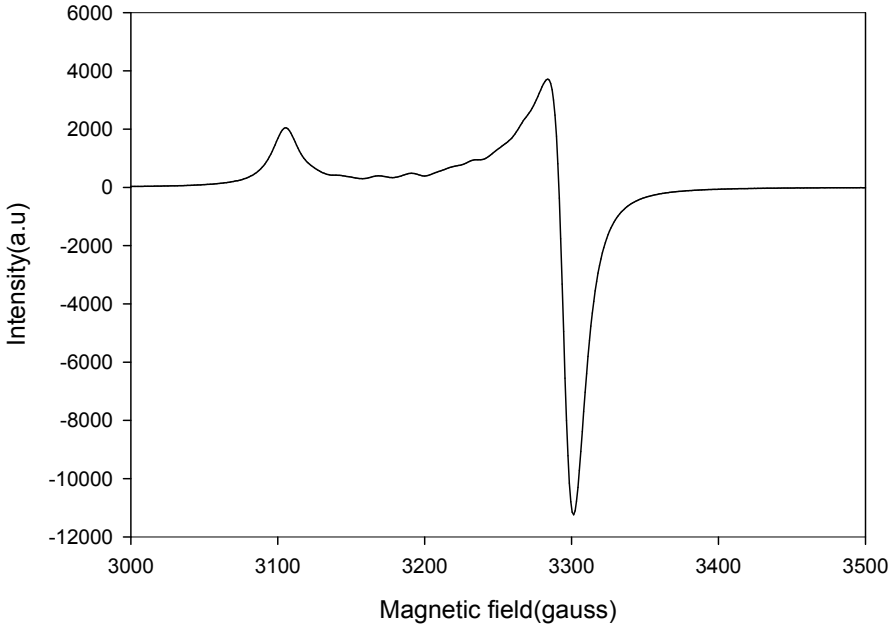


Fig. S4: EPR spectrum of [Cu^{II}(N,N,S-L^{3H})Cl] **1**

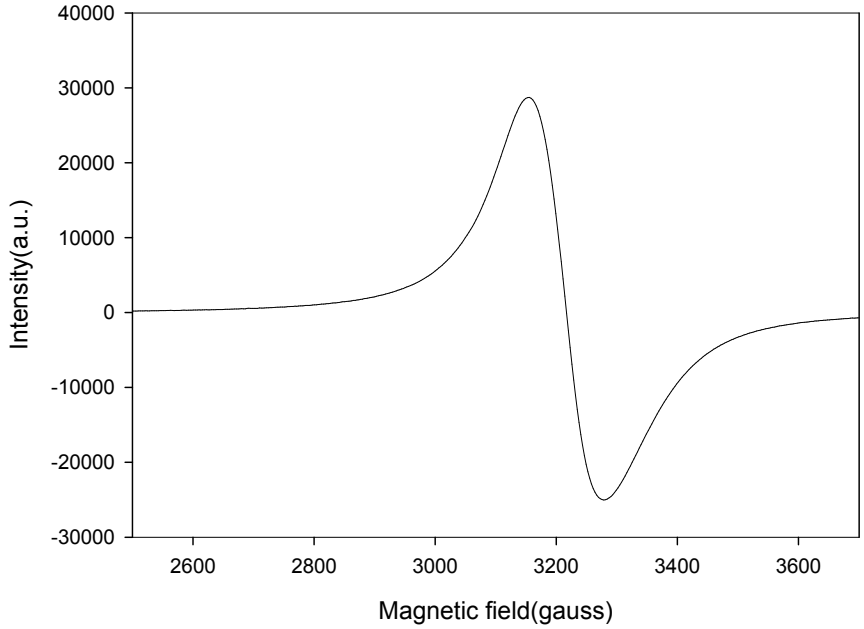


Fig. S5: EPR spectrum of [Cu^{II}(N,N,S-L^{3Me})Cl] **2**

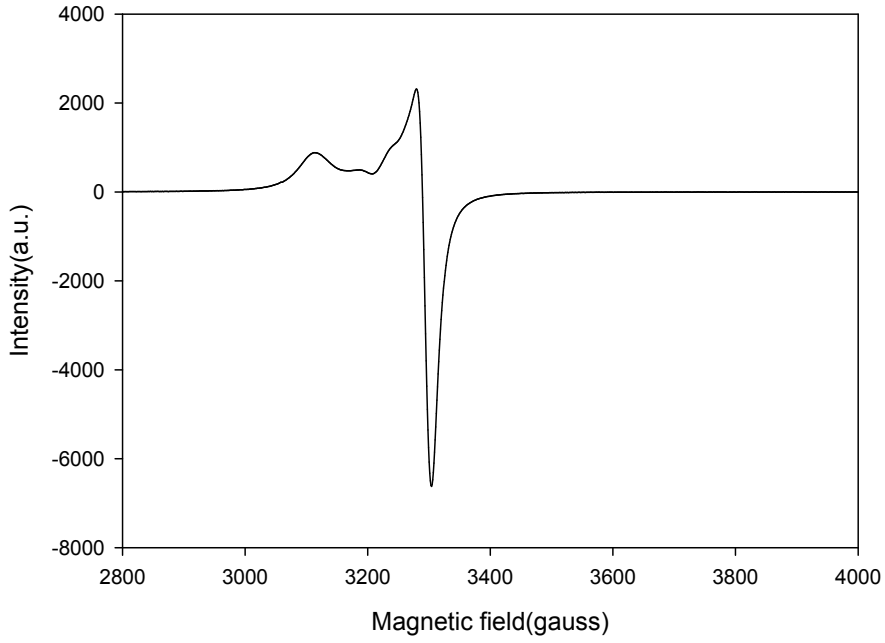


Fig. S6: EPR spectrum of [Cu^{II}(N,N,S-L^{3Ph})Cl] **4**

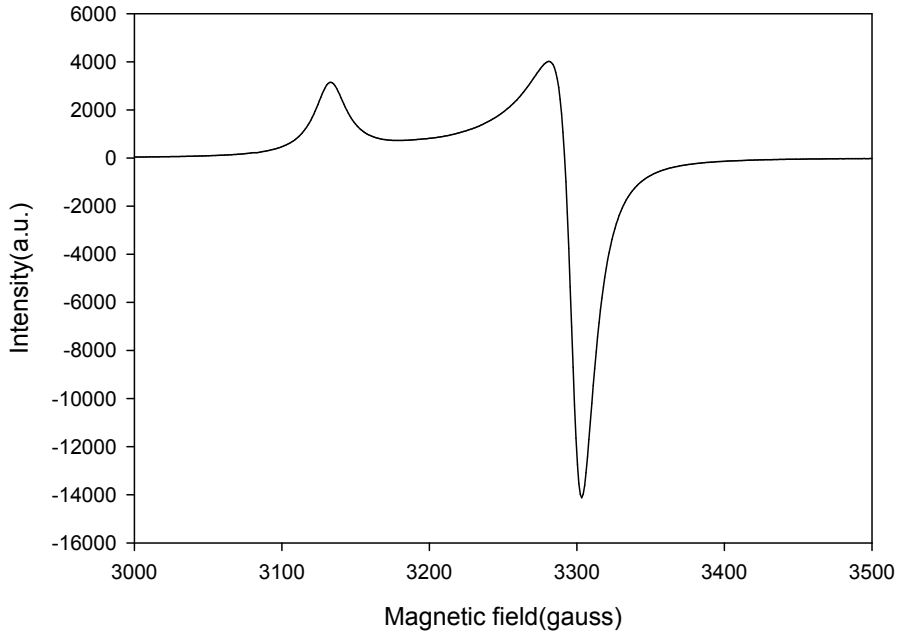


Fig. S7: EPR spectrum of [Cu^{II}(N,N,S-L^{3H})Br] **5**

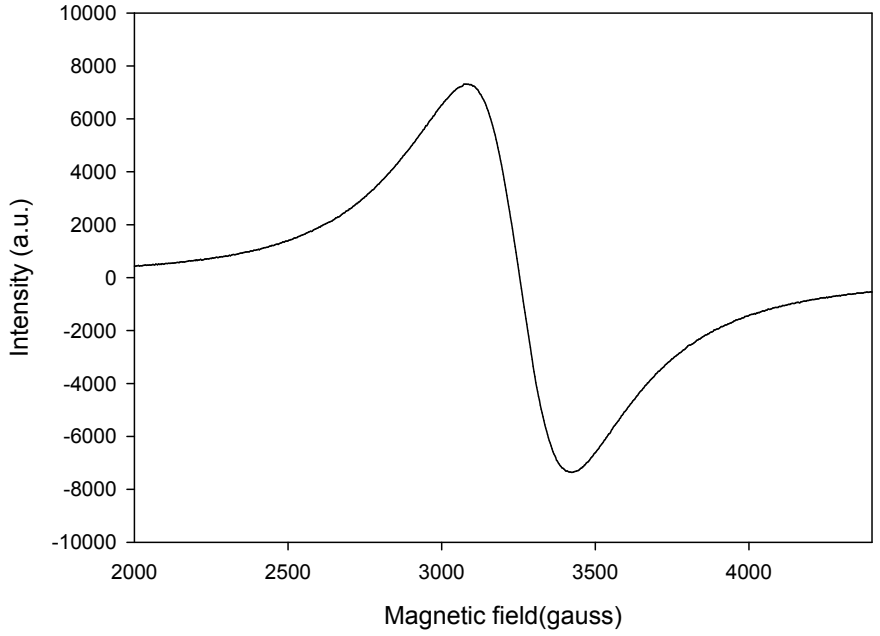


Fig. S8 EPR spectrum of [Cu^{II}(N,N,S-L^{3Me})Br] **6**

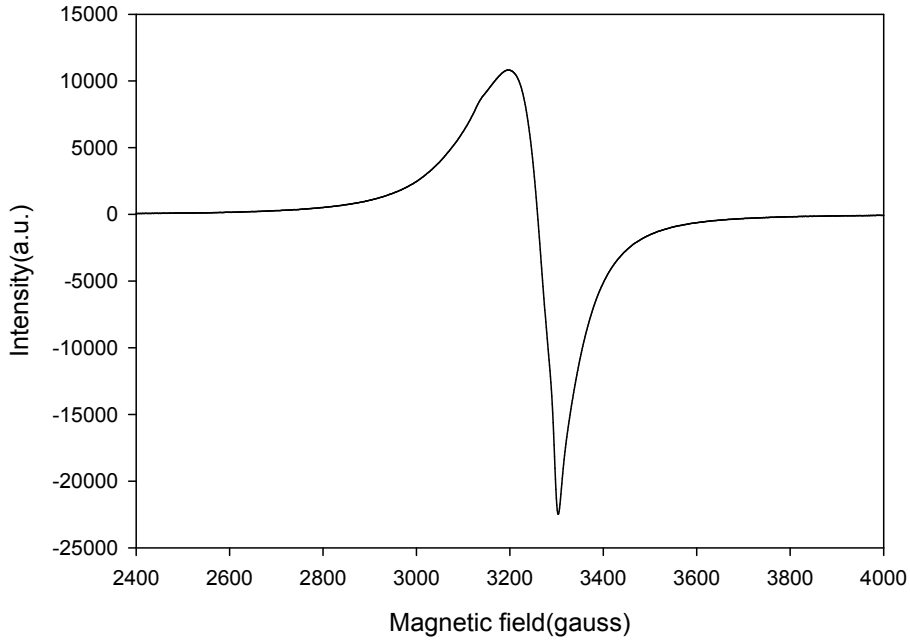


Fig. S9 EPR spectrum of [Cu^{II}(N,N,S-L^{3Ph})Br] **8**

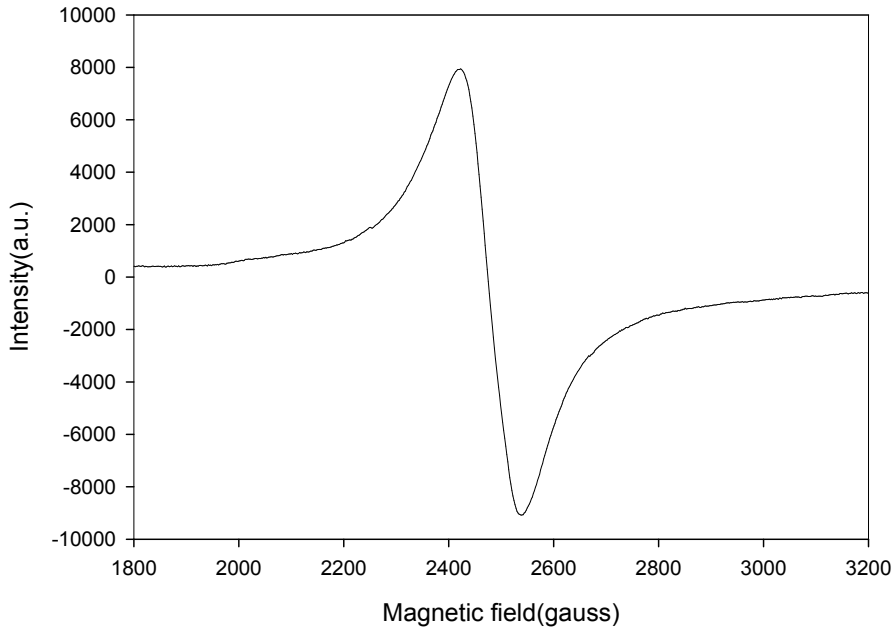


Fig. S10 EPR spectrum of [Cu^{II}(N,N,S-L^{3H})I] **9**

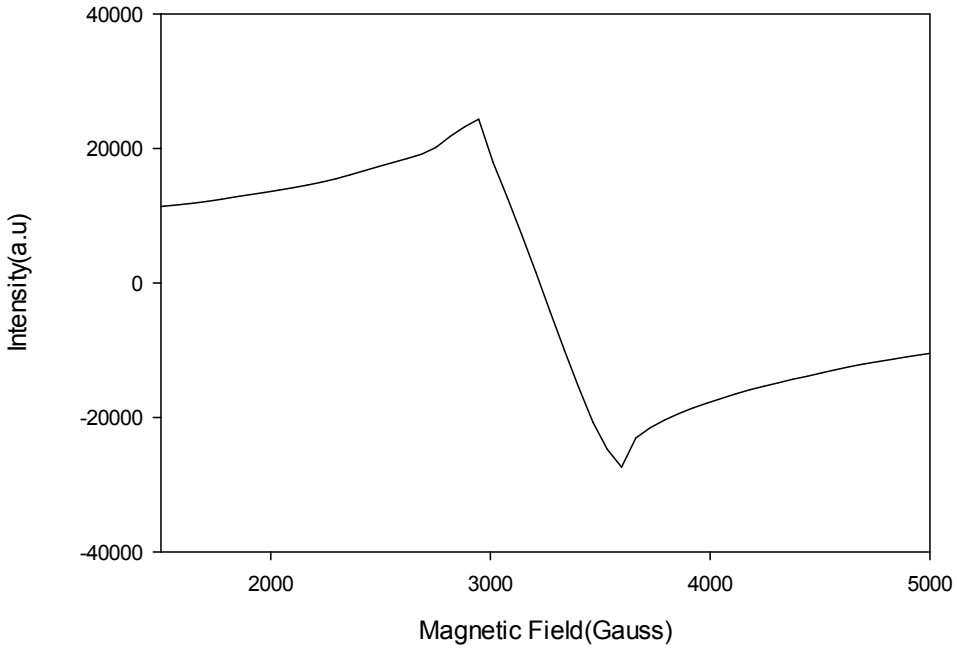


Fig. S11 EPR spectrum of [Cu^{II}(N,N,S-L^{3Me})I] **10**

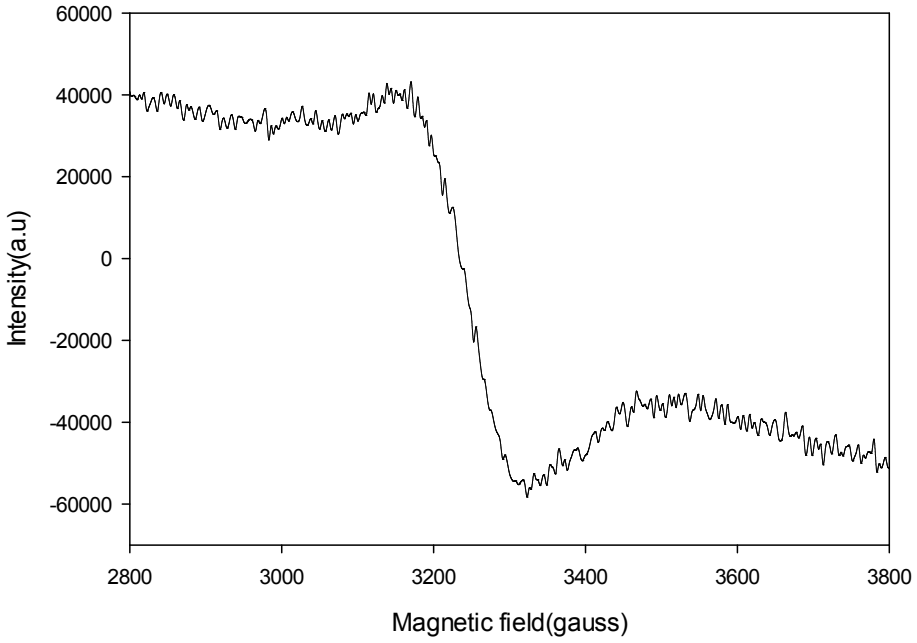


Fig. S12 EPR spectrum of [Cu^{II}(N,N,S-L^{3Et})I] **11**

S3. ESI-mass studies

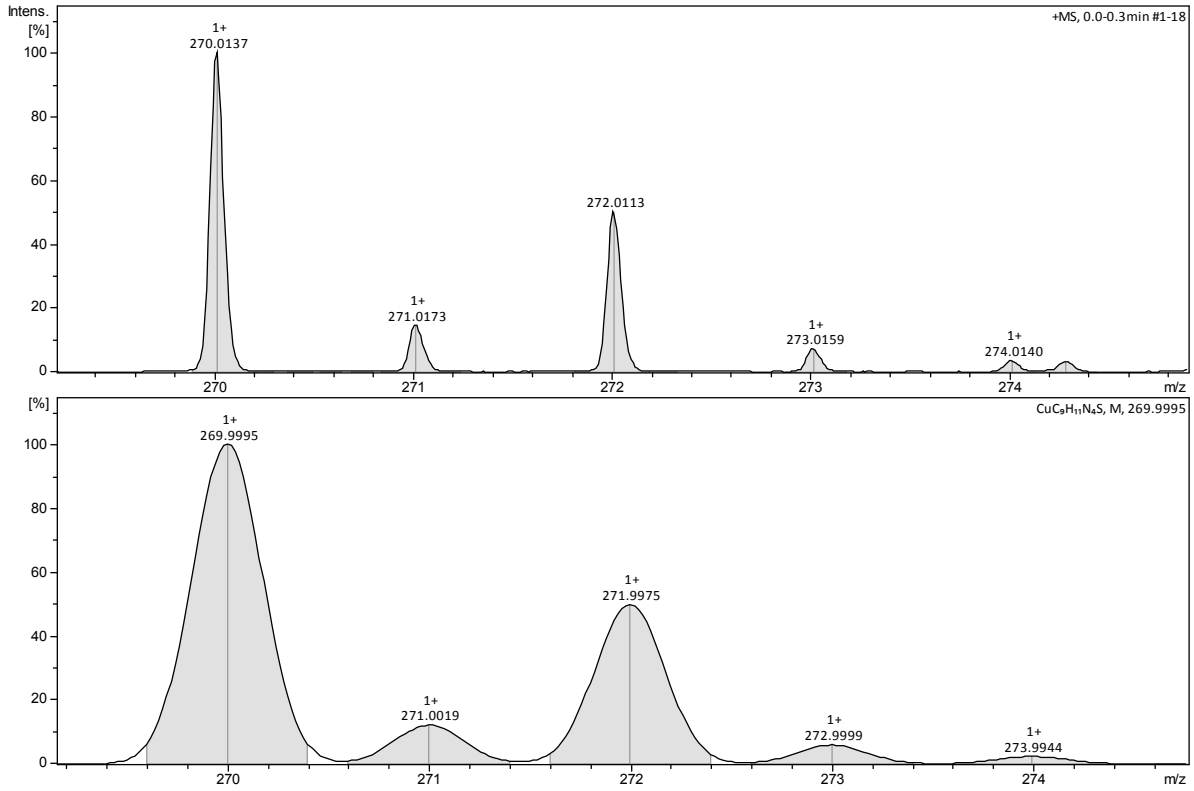


Fig S13:The mass spectrum of fragment, $[Cu(L^{3Me})]^+$ {chemical formula: $CuC_9H_{11}N_4S$; m/z = calc 269.99, obsd 270.01} with an isotopic pattern (complex **2**)

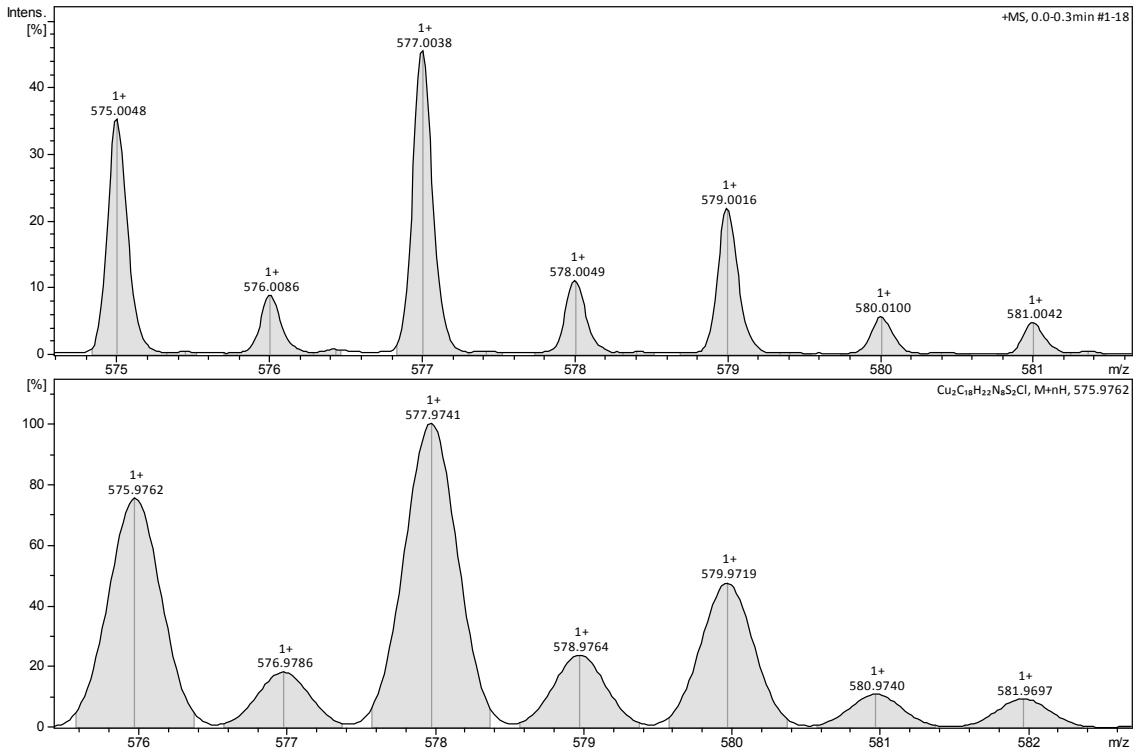


Fig S14: The mass spectrum of fragment,$[Cu(L^{3Me})_2CuCl + H]^+$ {chemical formula: $Cu_2C_{18}H_{23}N_8S_2Cl$; m/z = calc 575.97, obsd 575.00} with an isotopic pattern (complex **2**)

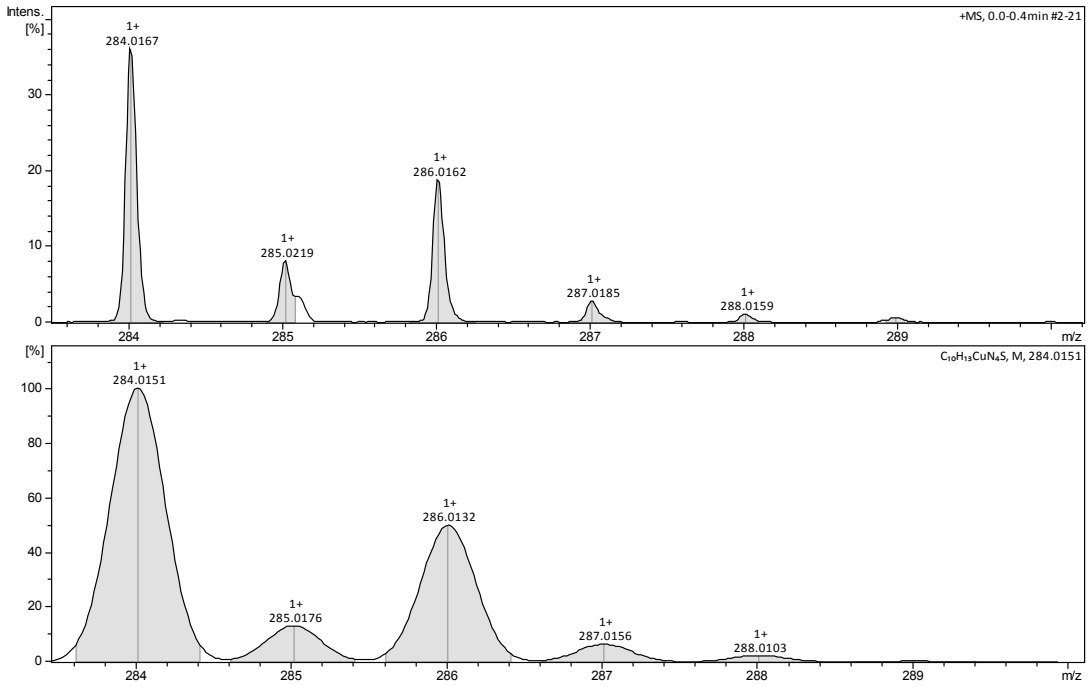


Fig S15:The mass spectrum of fragment,$[Cu(L^{3Et})]^+$ {chemical formula: $CuC_{10}H_{13}N_4S$; m/z = calc284.01, obsd284.01} with anisotopic pattern (complex **3**)

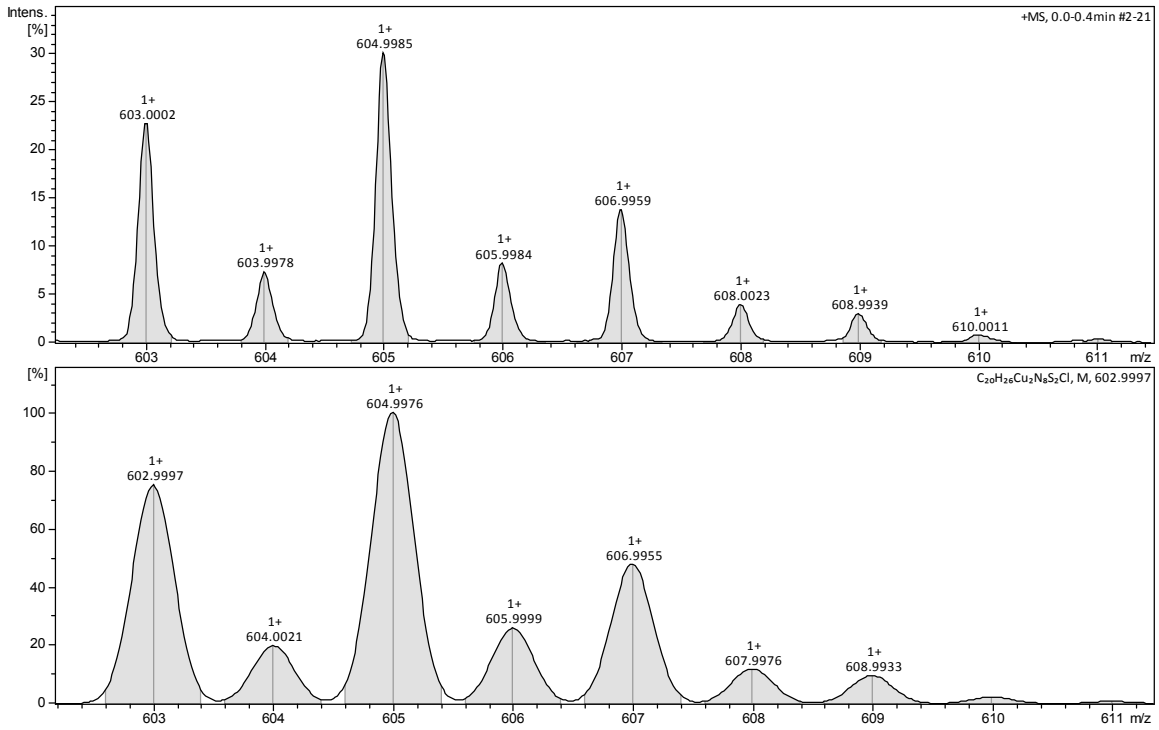


Fig S16:The mass spectrum of fragment,$[Cu(L^{3Et})_2CuCl]^+$\{chemical formula: $Cu_2C_{20}H_{26}N_8S_2Cl$; m/z = calc602.99, obsd603.00\} with an isotopic pattern (complex **3**)

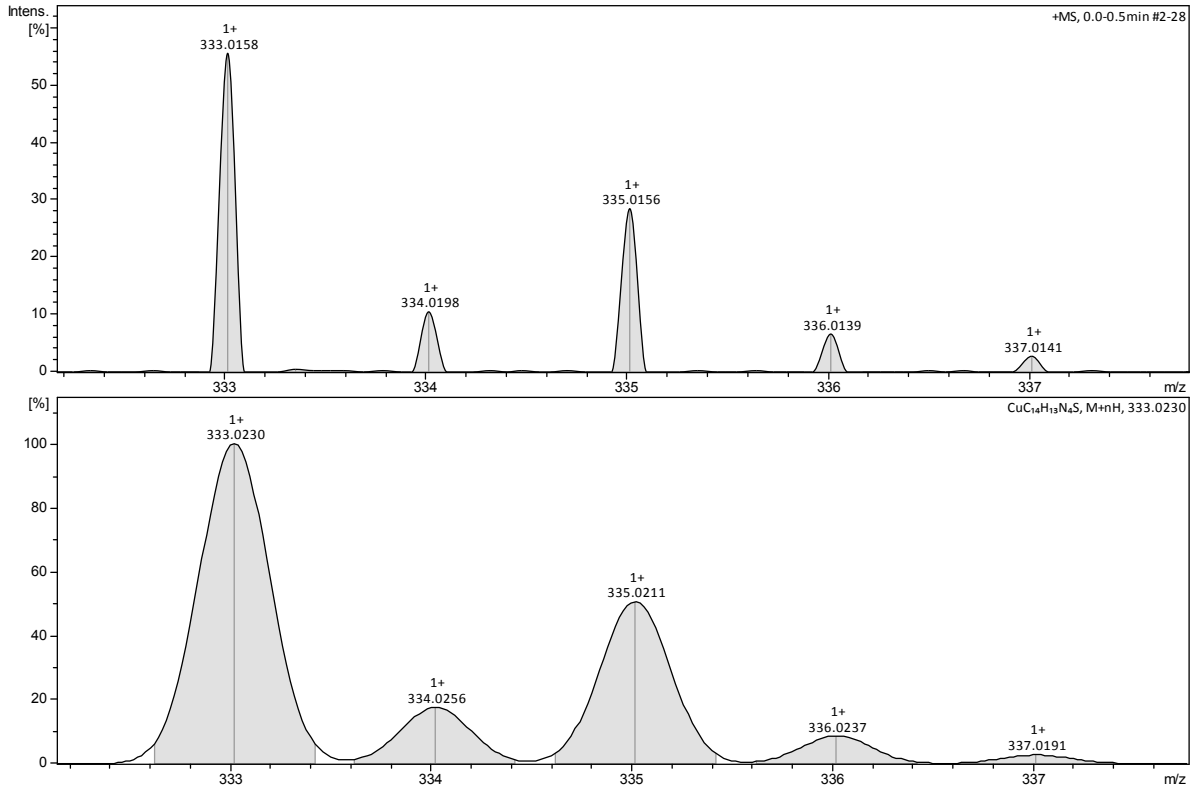


Fig S17:The mass spectrum of fragment,$[Cu(L^{3Ph}) + H]^+$\{chemical formula: $CuC_{14}H_{14}N_4S$; m/z = calc333.02,obsd333.01\} with an isotopic pattern (complex **4**)

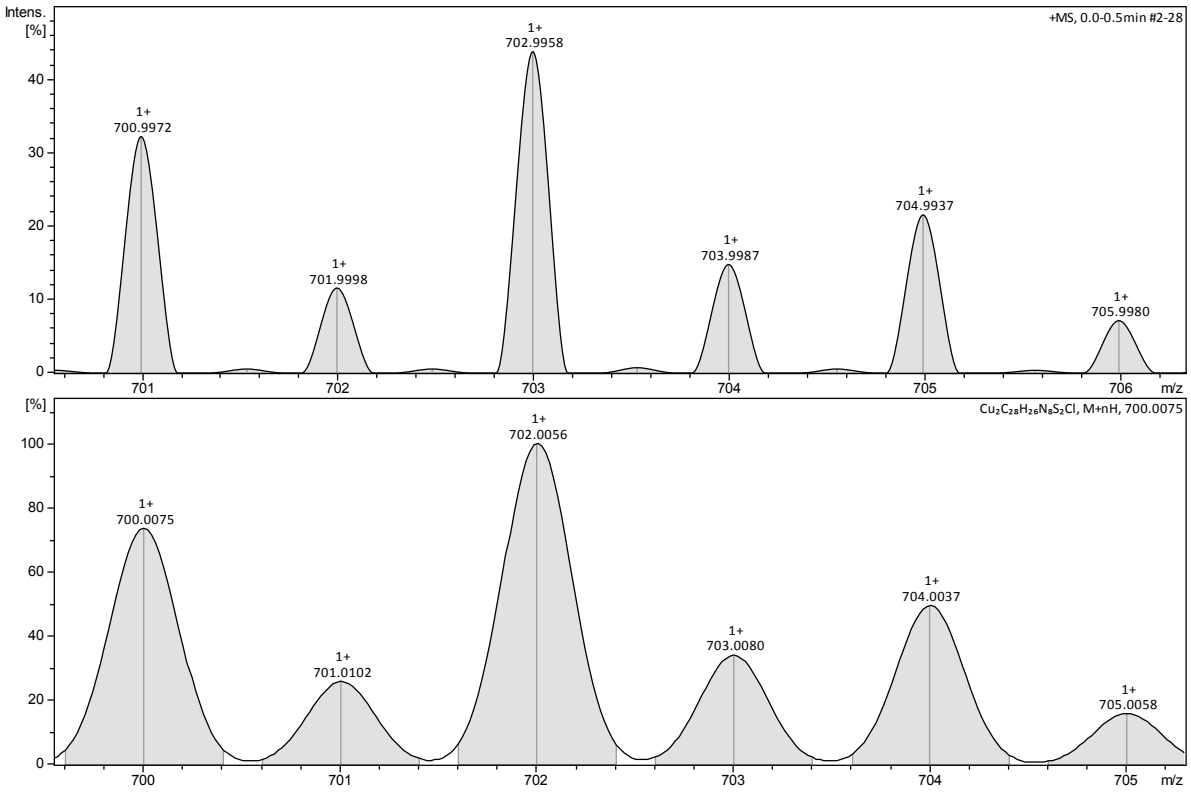


Fig S18:The mass spectrum of fragment,$[Cu(L^{3Ph})_2CuCl + H]^+$\{chemical formula: $Cu_2C_{28}H_{27}N_8S_2Cl$; m/z = calc700.00,obsd700.99\} with an isotopic pattern (complex **4**)

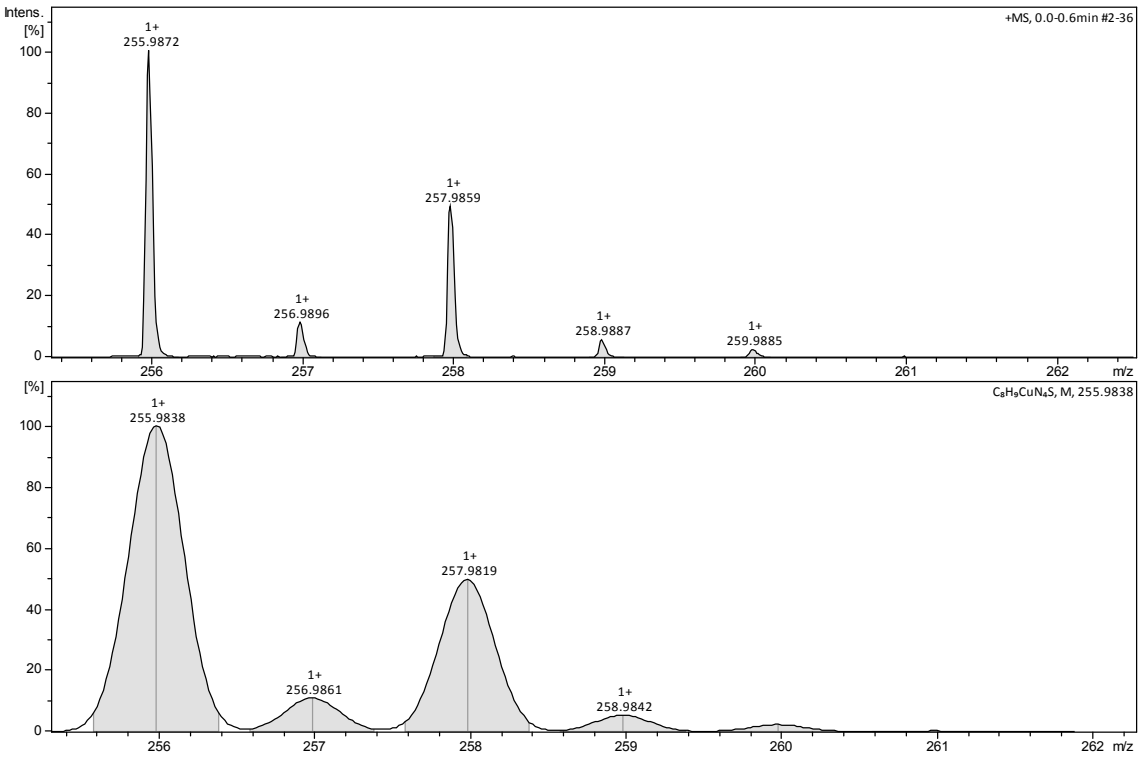


Fig S19:The mass spectrum of fragment, $[Cu(L^{3H})]^+$ {chemical formula: $CuC_8H_9N_4S$; m/z = calc255.98, obsd255.98} with an isotopic pattern (complex **5**)

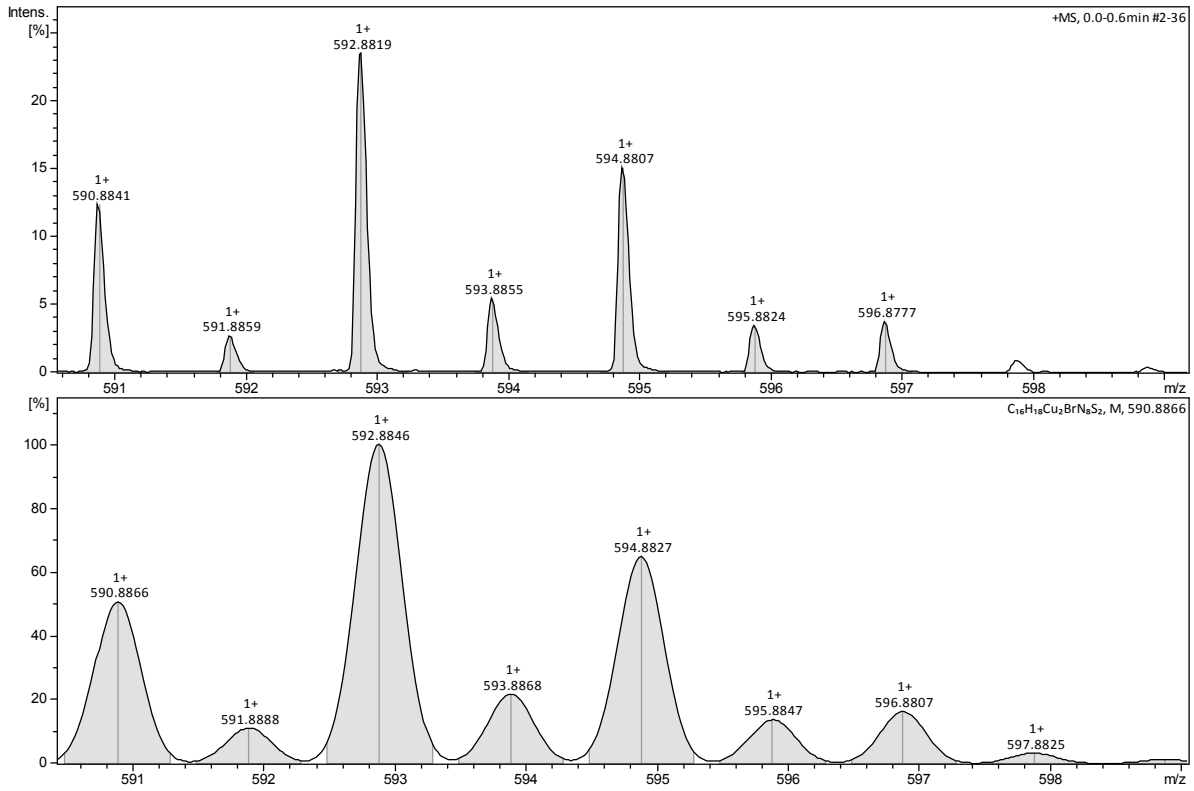
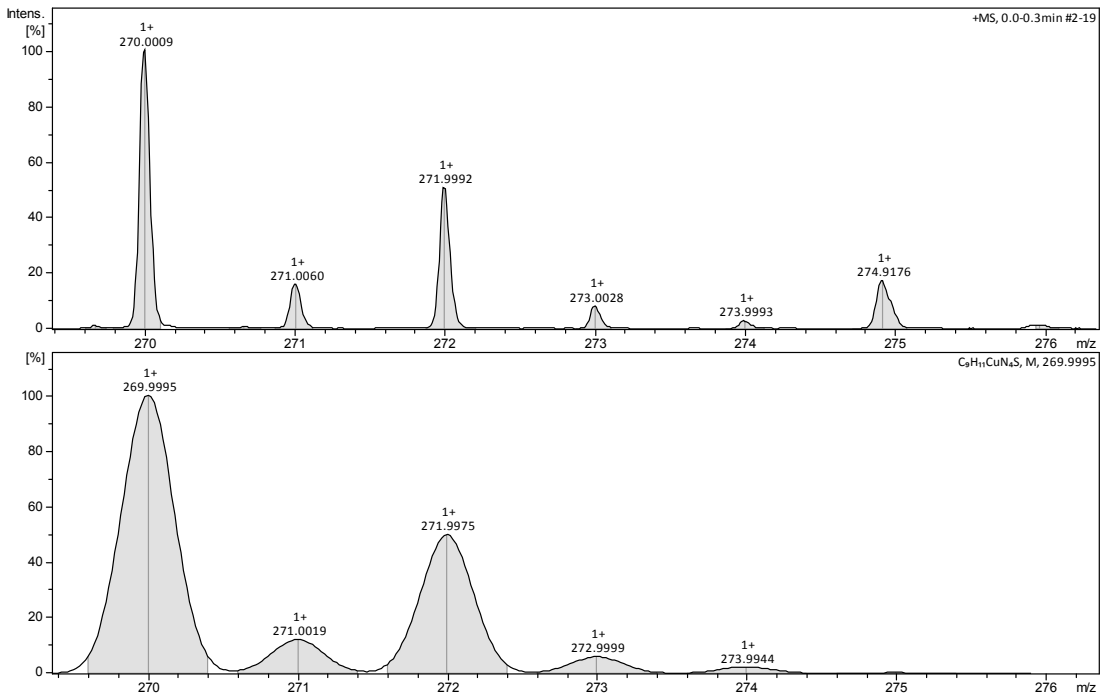


Fig S20:The mass spectrum of fragment,$[Cu(L^{3H})_2CuBr]^+$ {chemical formula: $Cu_2C_{16}H_{18}N_8S_2Br$; m/z = calc590.88, obsd590.88} with an isotopic pattern (complex **5**)



FigS21:The mass spectrum of fragment,$[Cu(L^{3Me})]^+$\{chemical formula: $CuC_9H_{11}N_4S$; m/z = calc269.99, obsd270.00\} with an isotopic pattern (complex **6**)

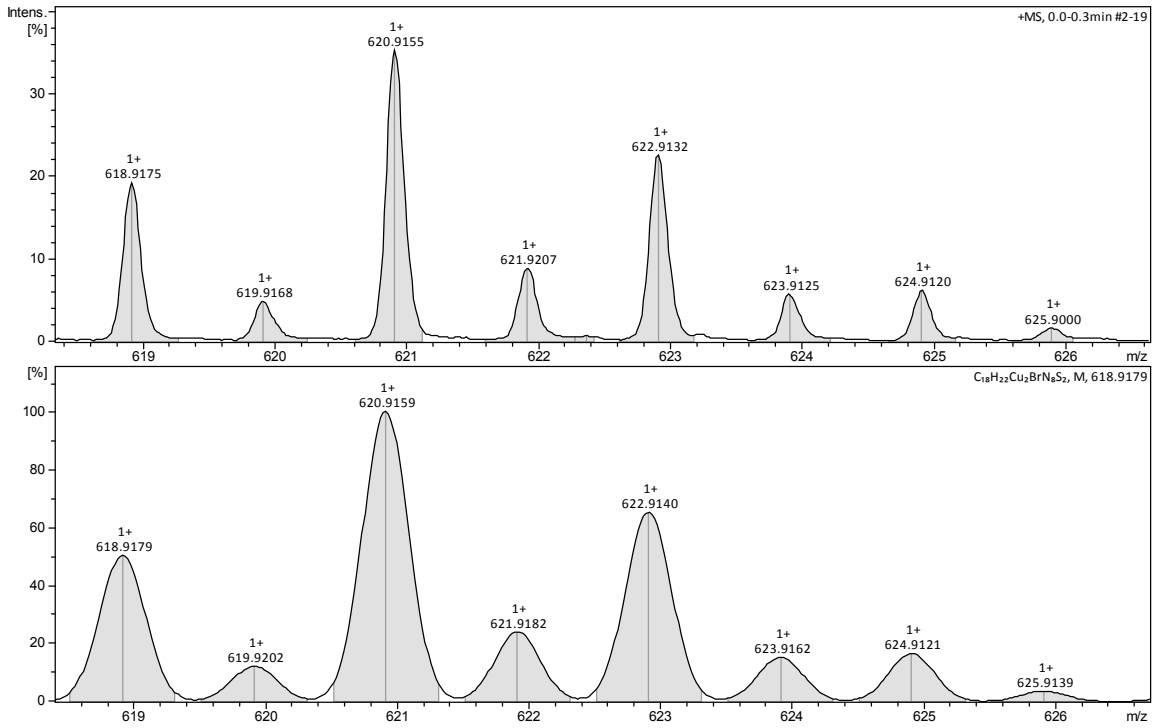
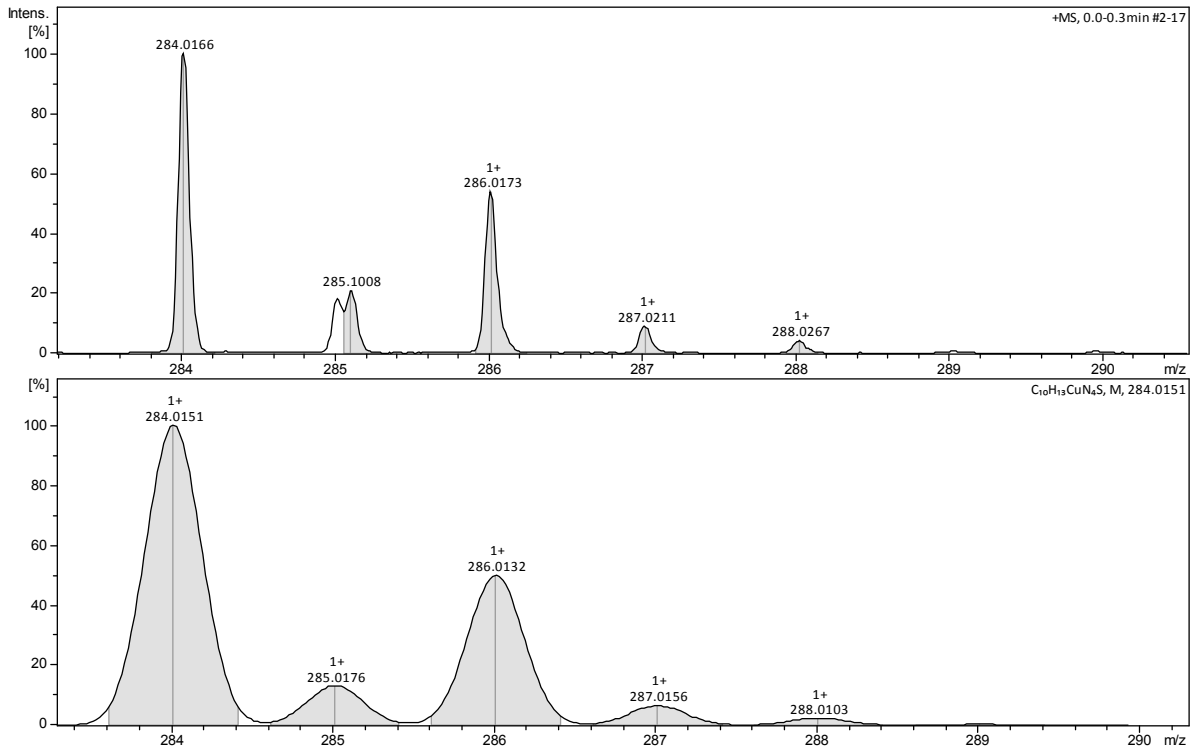


Fig S22:The mass spectrum of fragment,$[Cu(L^{3Me})_2CuBr]^+$\{chemical formula: $Cu_2C_{18}H_{22}N_8S_2Br$; m/z = calc618.91, obsd618.91\} with isotopic pattern (complex **6**)



FigS23:The mass spectrum of fragment, $[Cu(L^{3Et})]^+$ {chemical formula: $CuC_{10}H_{13}N_4S$; m/z = calc284.01, obsd284.01} with an isotopic pattern (complex **7**)

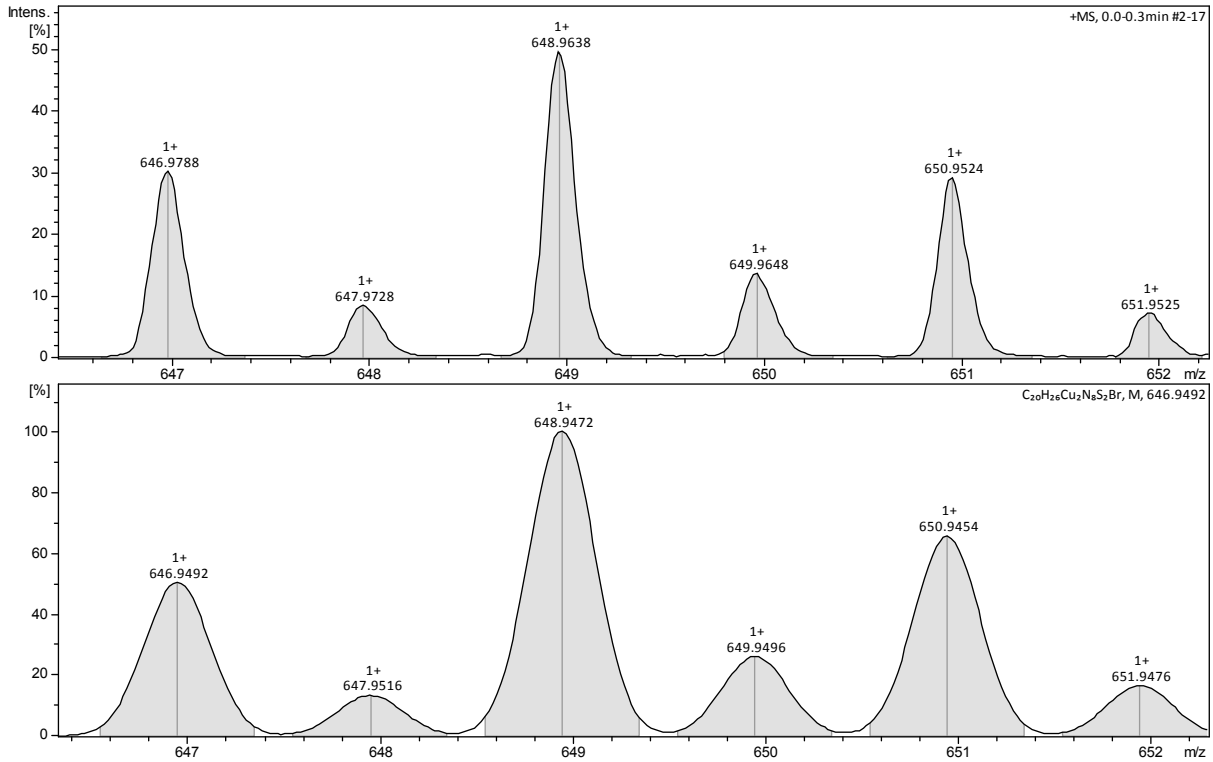


Fig S24:The mass spectrum of fragment, $[Cu(L^{3Et})_2CuBr]^+$ {chemical formula: $Cu_2C_{20}H_{26}N_8S_2Br$; m/z = calc646.94, obsd646.97} with an isotopic pattern (complex **7**)

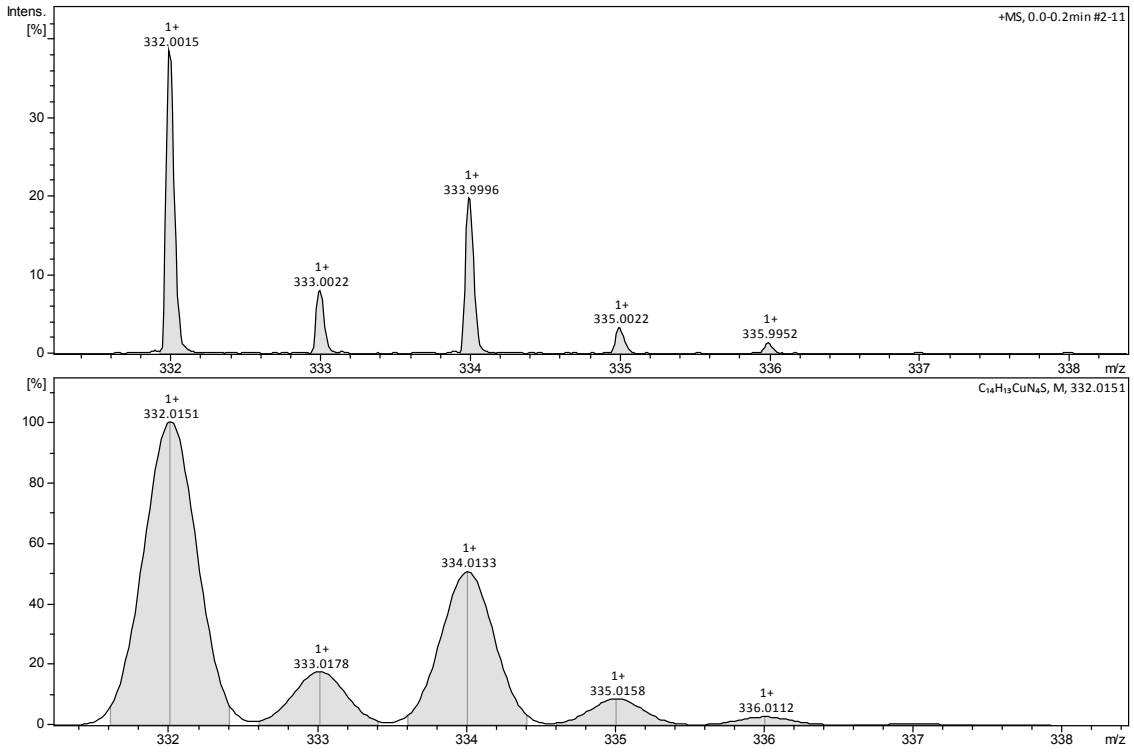


Fig S25:The mass spectrum of fragment, $[Cu(L^{3Ph})]^+$ {chemical formula: $CuC_{14}H_{13}N_4S$; m/z = calc332.01, obsd332.00} with an isotopic pattern (complex **8**)

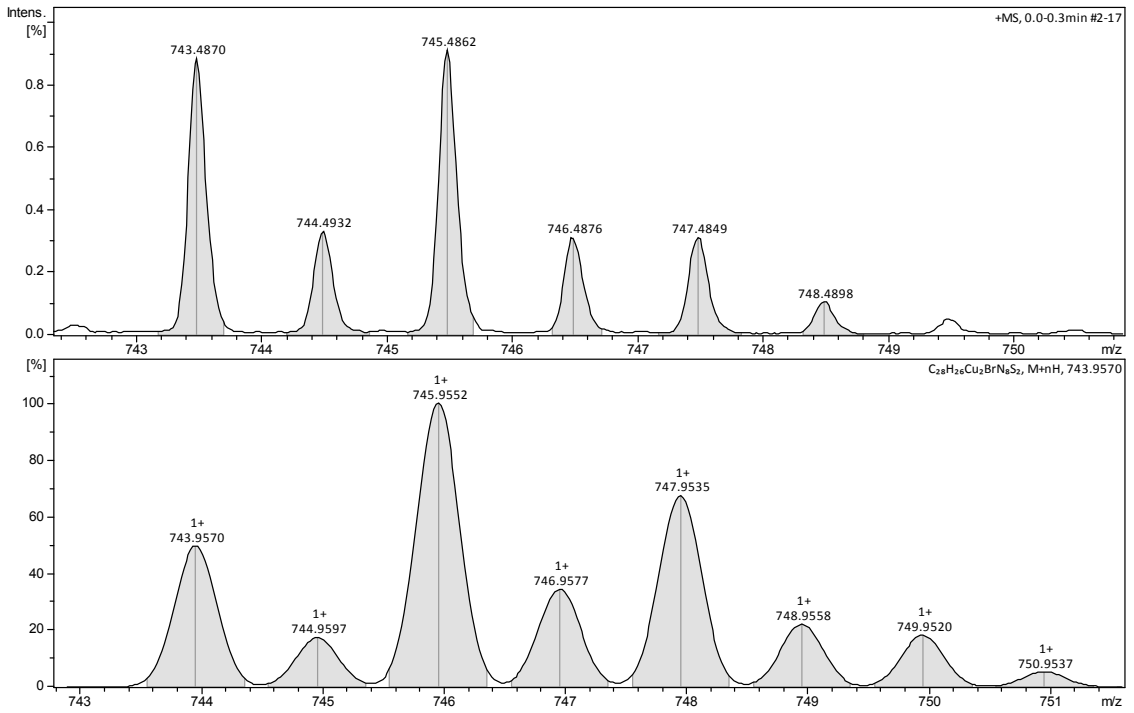


Fig S26:The mass spectrum of fragment,$[Cu(L^{3Ph})_2CuBr + H]^+$ {chemical formula: $Cu_2C_{28}H_{27}N_8S_2Br$; m/z = calc743.95, obsd743.48} with an isotopic pattern (complex **8**)

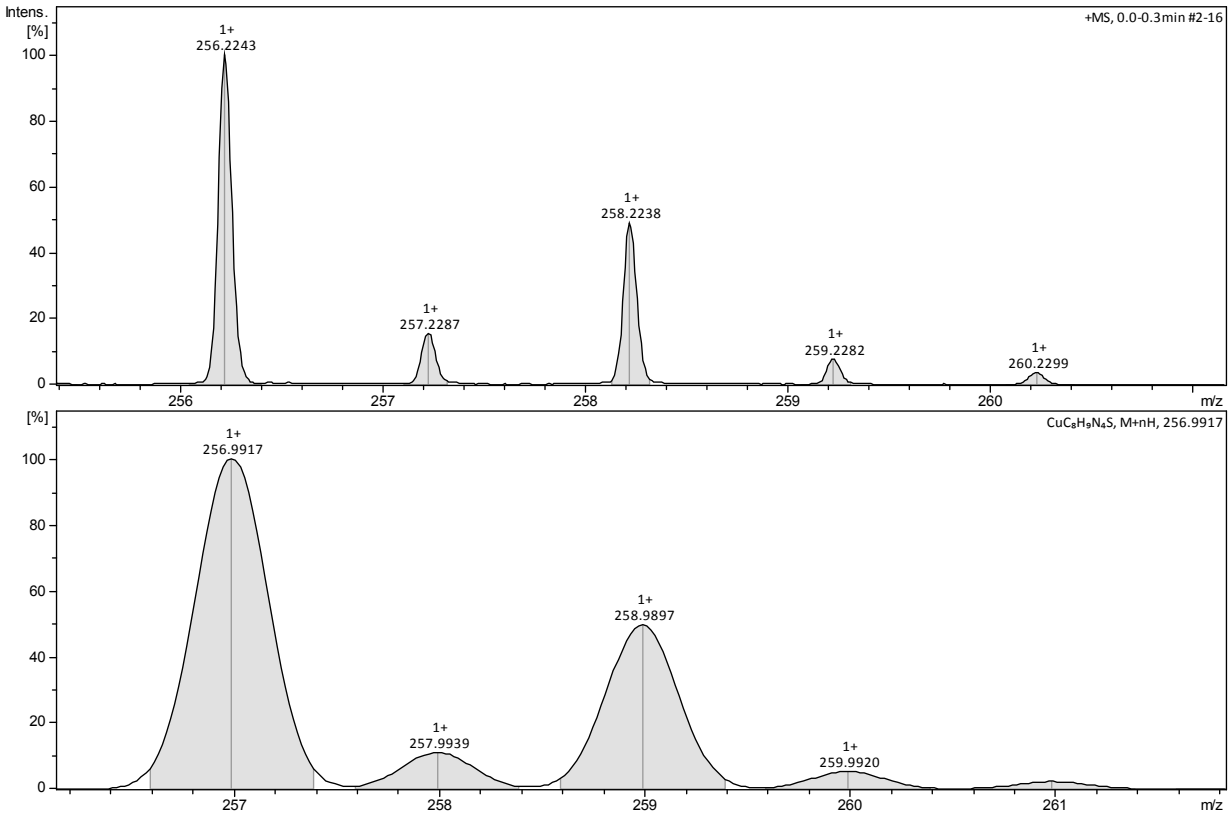
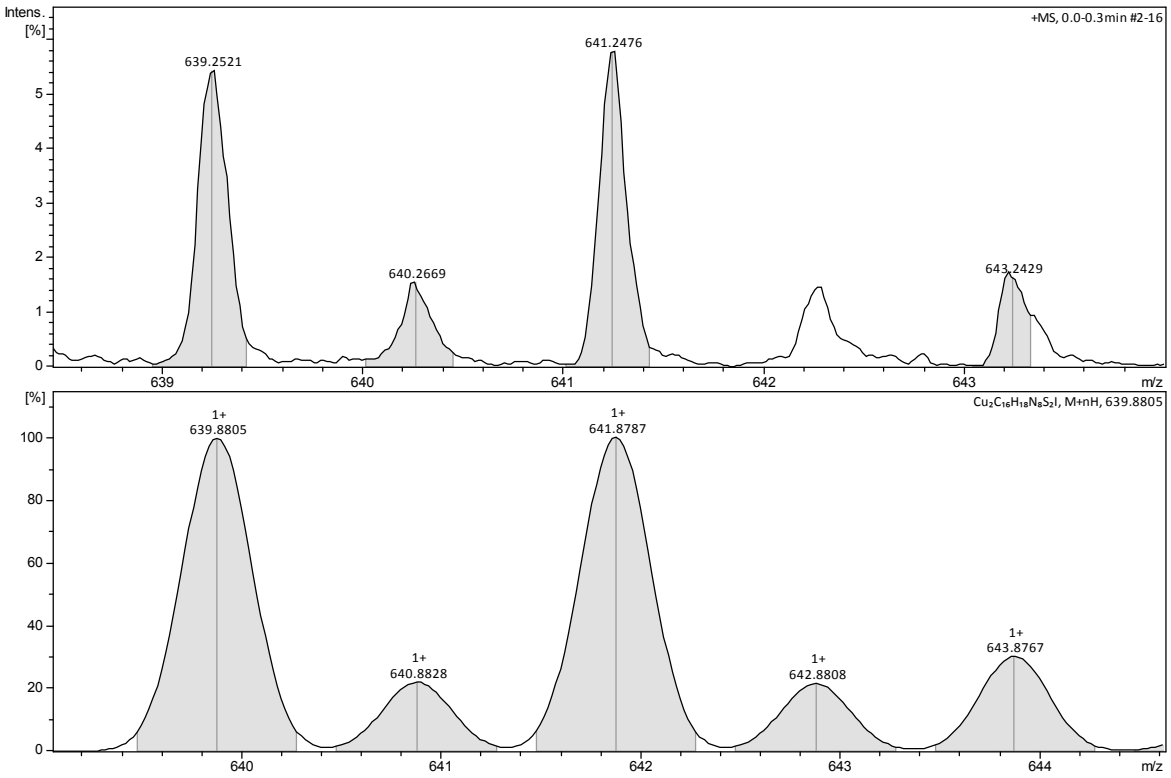
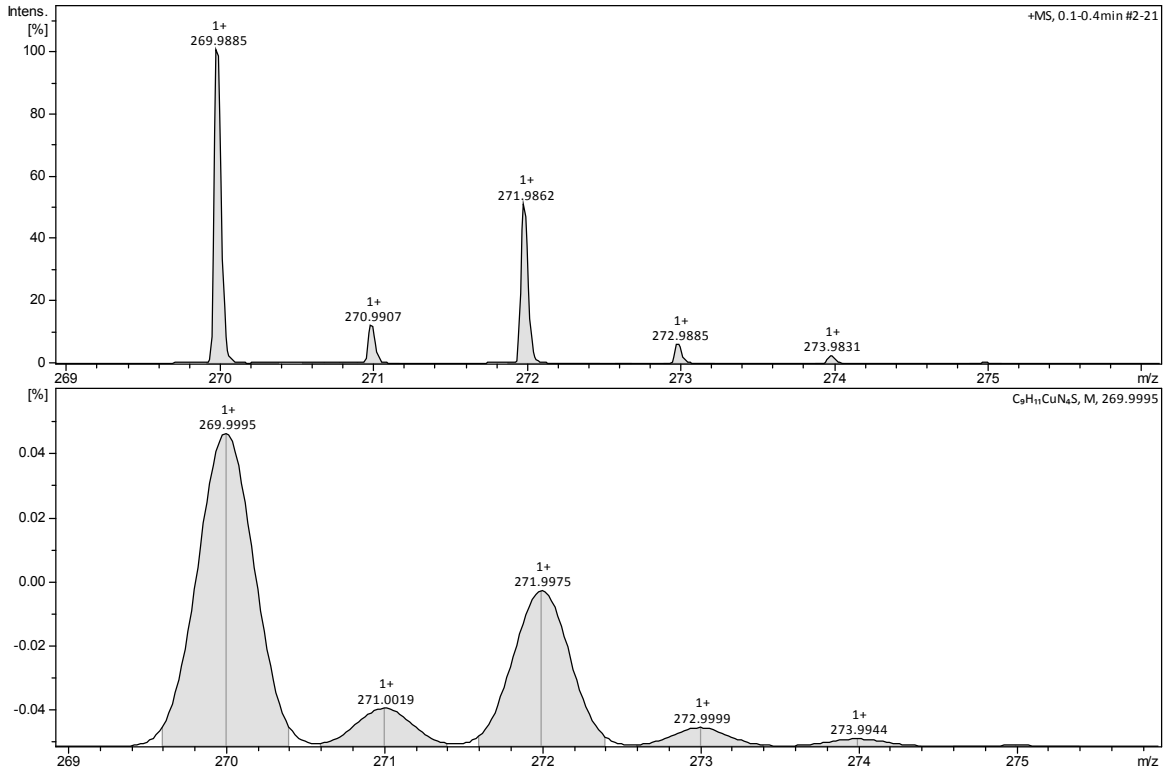


Fig S27:The mass spectrum of fragment,$[Cu(L^{3H}) + H]^+$ {chemical formula: $CuC_8H_{10}N_4S$; m/z = calc256.99, obsd256.22} with an isotopic pattern (complex **9**)

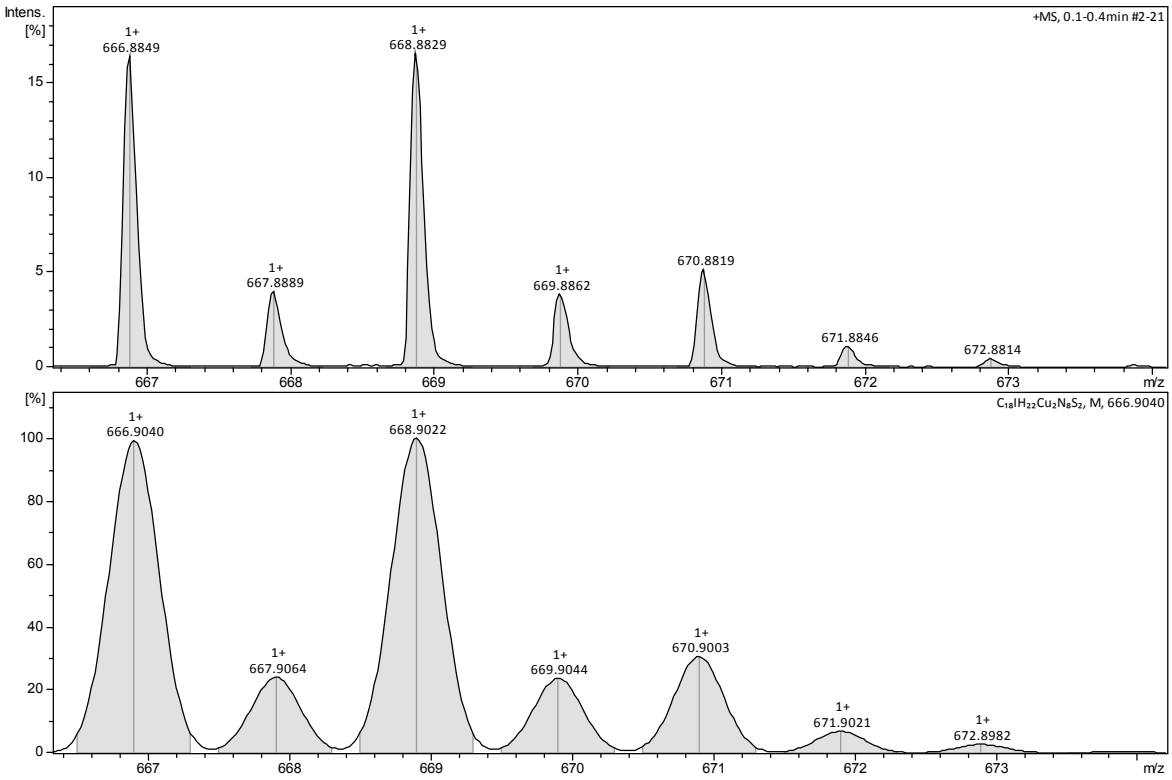


FigS28:The mass spectrum of fragment,$[Cu(L^{3H})_2CuI + H]^+$ {chemical formula:

$Cu_2C_{16}H_{19}N_8S_2I$; m/z = calc639.88, obsd639.25} with an isotopic pattern (complex **9**)



FigS29:The mass spectrum of fragment,$[Cu(L^{3Me})]^+$ {chemical formula: $CuC_9H_{11}N_4S$; m/z = calc269.99, obsd269.98} with an isotopic pattern (complex **10**)



FigS30:The mass spectrum of fragment,$[Cu(L^{3Me})_2CuI]^+$\{chemical formula: $Cu_2C_{18}H_{22}N_8S_2I$; m/z = calc666.90, obsd666.88\} with an isotopic pattern (complex **10**)

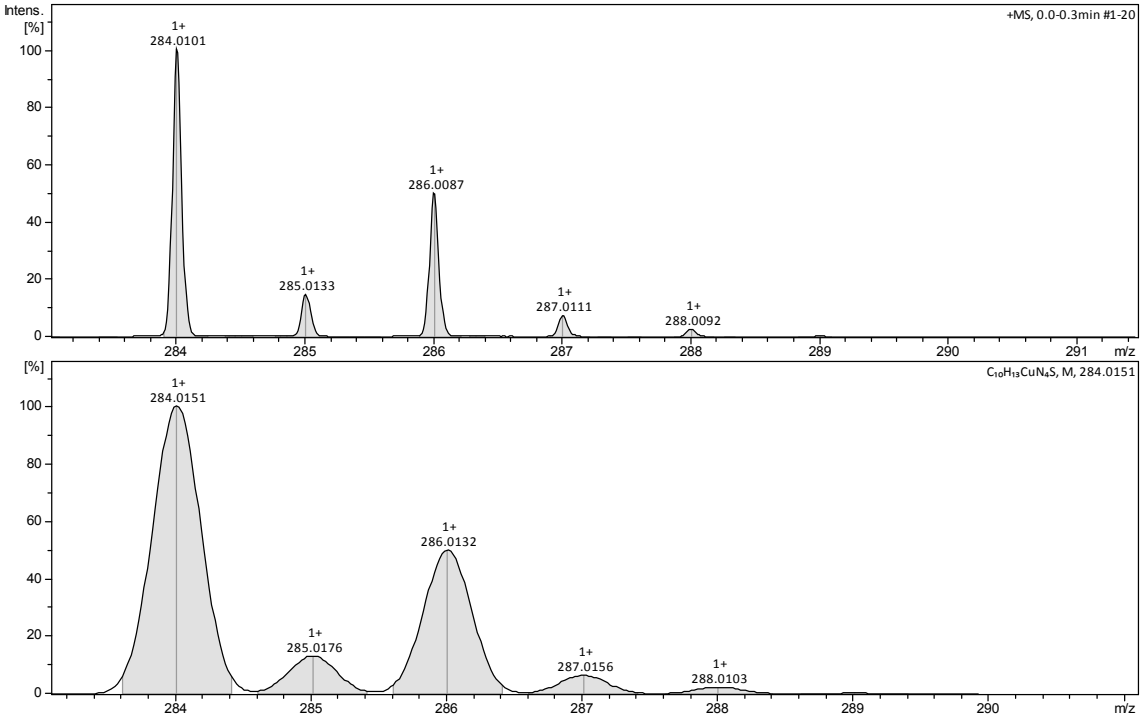
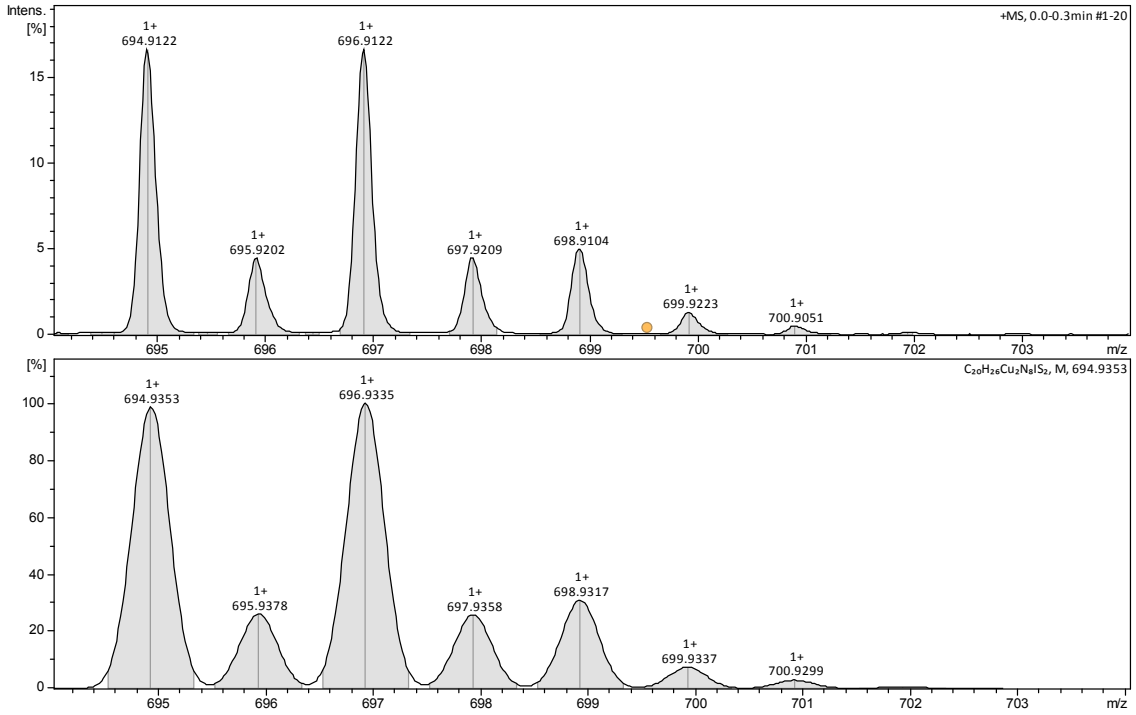


Fig S31:The mass spectrum of fragment,$[Cu(L^{3Et})]^+$\{chemical formula: $CuC_{10}H_{13}N_4S$; m/z = calc284.01, obsd284.01\} with an isotopic pattern (complex **11**)



FigS32:The mass spectrum of fragment, $[Cu(L^{3Et})_2CuI]^+$ {chemical formula: $Cu_2C_{20}H_{26}N_8S_2I$; m/z = calc694.93, obsd694.91} with an isotopic pattern (complex **11**)

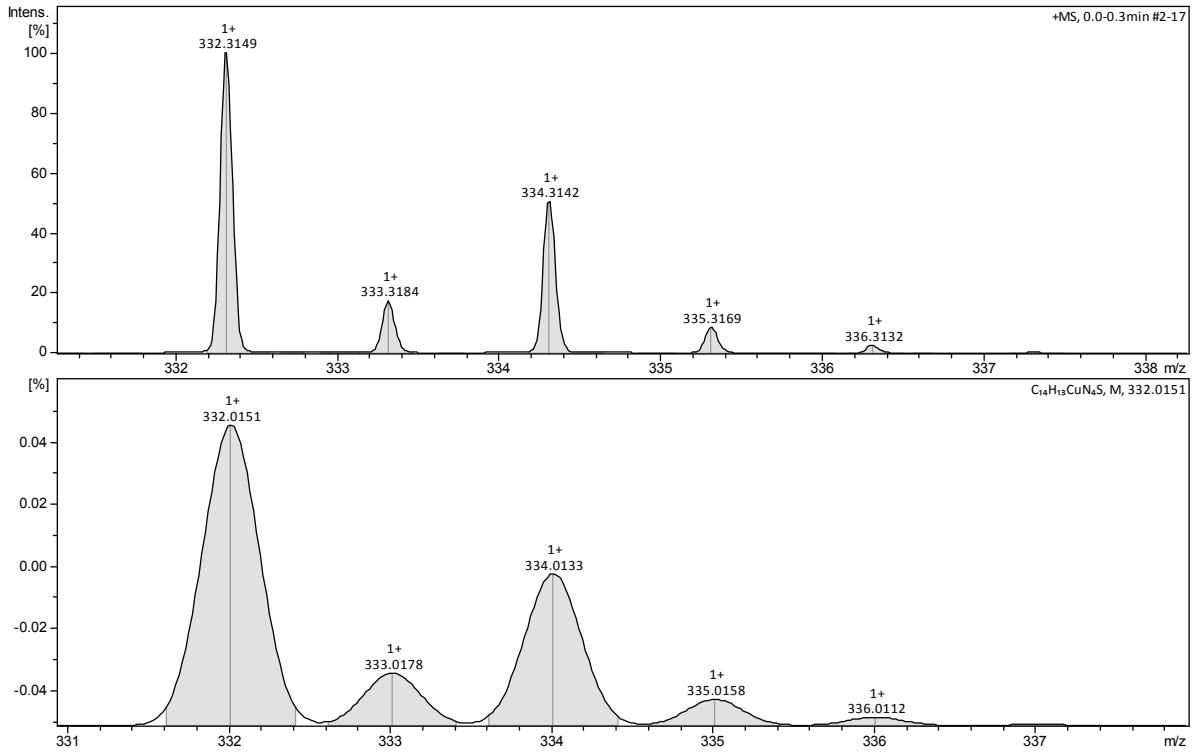


Fig. S33. The mass spectrum of fragment, $[Cu(L^{3Ph})]^+$ {chemical formula: $CuC_{14}H_{13}N_4S$; m/z = calc 332.01, obsd 332.31} with an isotopic pattern (complex **12**)

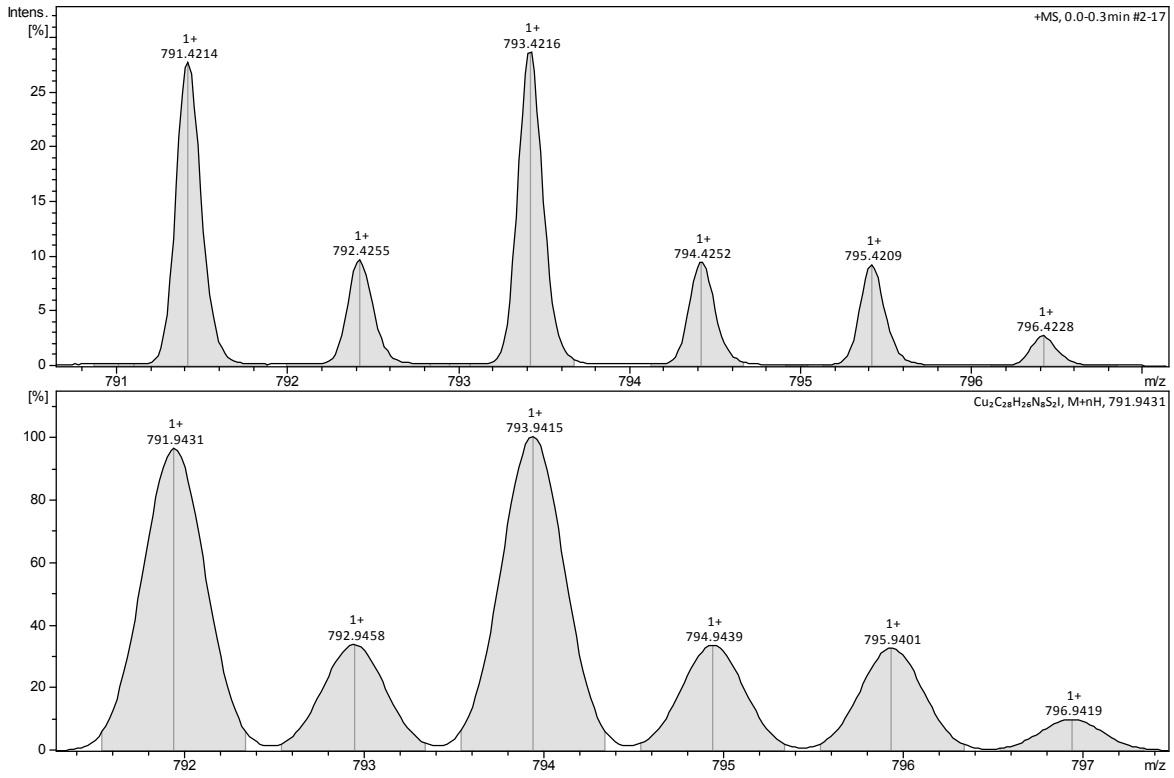


Fig. S34. The mass spectrum of fragment, $[Cu(L^{3Ph})_2CuI + H]^+$ {chemical formula: $Cu_2C_{28}H_{27}N_8S_2I$; m/z = calc 791.94, obsd 791.42} with an isotopic pattern (complex **12**)

S4.Test organisms and inoculum preparation

The reference strains of bacteria and yeasts were obtained from Microbial Type Culture Collection (MTCC), Institute of Microbial Technology (IMTECH), Chandigarh, India while the clinical isolate methicillin resistant *Staphylococcus aureus* (MRSA) was obtained from Post graduate Institute of Medical Education and Research, (PGIMER), Chandigarh, India. Reference strains included Gram positive bacteria: *Staphylococcus aureus* (MTCC-740), *Staphylococcus epidermidis* (MTCC-435), Gram negative bacteria: *Klebisella pneumoniae* (MTCC-530), *Escherichia coli* (MTCC-119), *Salmonella typhimurium* 1(MTCC-98), *Salmonella typhimurium* 2(MTCC-1251), *Shigella flexneri* (MTCC-1457), and one yeast strain: *Candida albicans* (MTCC-227). A loopful of isolated bacterial and yeast colonies were inoculated into 5 mL of their respective medium and incubated at 37 °C and 25 °C,

respectively, for 4 h. This was used as inoculums after adjusting the turbidity as per 0.5 McFarland turbidity standard. This turbidity is equivalent to approximately 1 to 2 x 10^8 colony forming units per mL (CFU mL^{-1}). The inoculums thus prepared were used for further testing.

S4.1 Antimicrobial screening

A 100 μL of activated test organism (prepared as above) was inoculated onto suitable medium plates by spread plate method. Wells measuring 8 mm in diameter were cut out in the medium using sterilized stainless steel borer. Each well was filled with 0.1 mL of test complex dissolved in DMSO and kept for incubation in an upright position for 18 – 24 h. Sensitivity was measured in terms of diameter of the resultant zone of inhibition. Any organism with a clear zone of inhibition ≤ 12mm was considered to be resistant to the compound.

S4.2 Minimum inhibitory concentration (MIC)

Minimum inhibitory concentration of the selected complex compounds dissolved in DMSO was worked out by the agar dilution method for their antimicrobial activity against the sensitive microorganisms. A stock solution of a complex under investigation of concentration (10 mg mL^{-1}) was prepared and incorporated into Muller Hinton agar medium for bacteria and yeast malt extract medium for yeast. The final concentration of the compound in the medium containing plates ranged from (0.005–1 mg mL^{-1}). These plates were then inoculated with 0.1 mL of the activated bacterial and yeast strains by streaking with a sterile tooth pick. The plates were incubated at 37ºC for bacteria and 25 ºC for yeast for 24 h each. The minimum concentration of the extract causing complete inhibition of the

microbial growth was taken as MIC. The results were compared with that of control (i.e. DMSO).

S4.3 Cellular toxicity testing using MTT assay

The biosafety of the test compounds was checked by MTT [3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyl tetrazolium bromide] assay [67]. Ten milliliter of sheep blood was taken alongwith 3 mL of Alsever's solution (anticoagulant) and transferred to sterile centrifuge tubes. The blood was centrifuged at 16,000 rpm at room temperature (25°C) for 20 min so as to separate the plasma from the cellular portion of the blood. The supernatant (plasma) was discarded and to cellular part of blood, 6 mL phosphate buffer saline (1X PBS) was added followed by centrifugation. The blood cells were washed thrice with 1X PBS by centrifugation and the cellular pellet was re-suspended in 6 mL of PBS. Various dilutions of these cells were prepared using PBS and counted with the help of a hemocytometer under a light microscope so as to obtain cellular density equivalent to 1×10^5 cells/mL. One hundred microlitre (100 µL) of this diluted suspension was added in each microtiter plate well and incubated at 37 °C for overnight. The supernatant was removed carefully (discarded) and 200 µL of the sample under study (contains 10 mg/mL) was added to each well and incubated further for 24 h. Supernatant was removed again and added 20 µL MTT solution (5 mg/mL) to each well and incubated further for 3.5 h at 37 °C on orbital shaker at 60 rpm. After this incubation, the supernatant was removed without disturbing the cells and 50 µL of DMSO was added to each well to dissolve the formazan crystals. The absorbance was measured at 590 nm using an automated microplate reader (Biorad 680-XR, Japan). The well to which DMSO in place of sample was added (untreated cells) served as control. Reduction of MTT can occur only in metabolically active cells, as MTT is converted into formazan crystals.

The the viability of the cells can be calculated as follows:

% Cell viability = (OD of Treated / OD of Control) x 100.

4.4.Time kill assay

The time kill assay for the selected purified compounds was performed by the viable cell count method (VCC). A stock solution of (1 mg mL^{-1}) was prepared. Five mL of 4 h grown inoculums was adjusted to 0.5 McFarland standards and serially diluted to 10^{-3} with the respective double strength broth medium. An equal volume of each diluted inoculums and the extract to be tested were mixed at their respective predetermined MIC values and incubated at the respective temperature of 25°C for yeast and 37°C for bacteria. At different time intervals viz. 0, 1, 2, 3, 4, upto 24 h, and 0.1 mL of the mixed suspension was spread on suitable agar plates in duplicate and incubated for 24 h at suitable temperature. The mean number of colonies was determined and compared with that of control, in which the compounds were replaced with DMSO.

Table 1S. IR Spectral bands of the complexes **1-12**

Complexes	ν(N^1-H) {ν(N^2-H)}	ν(C-H)	Bands (I, II, III, IV)	Other bands
$[Cu^{II}(L^{3H})Cl]$ **1**	3446m 3292m	3164m 3067w	1493m (I) 1320m (II) 1097sb (III) 786m (IV)	1632s, 1597m, 1560w, 1448s , 1363m, 1182s, 1160m,899vw, 810m , 736w, 647w, 615w, 567vw, 500w, 467m,
$[Cu^{II}(L^{3Me})Cl]$ **2**	3410m 3312m	3069w, 3026m, 2994w, 2936w, 2899w	1505s (I) 1301s (II) 1048m (III) 782m (IV)	1596m, 1563m, 1527s, 1458m, 1398s, 1365s, 1331m, 1244m, 1187s, 1160m, 1143m, 1105s, 1077s, 823w, 744vw, 724vw, 649w, 621w, 564w, 471m, 413w
$[Cu^{II}(L^{3Et})Cl]$ **3**	3414m	3068w, 3024w, 2969w, 2929w, 2888w	1496s (I) 1293w (II) 1082s (III) 785m (IV)	1628w, 1591w, 1562w, 1446s, 1371m, 1351w, 1328m, 1261m, 1235m, 1175m, 1159m, 832w, 806w, 745w, 720w, 663w, 648w, 614w, 565w, 466m, 412w
$[Cu^{II}(L^{3Ph})Cl]$ **4**	3320s	3124w, 3066w	1503s (I) 1295m (II) 1046m (III)	1597m, 1539m, 1458s, 1432s, 1368m, 1317m, 1249m, 1189m, 1158m, 1106m, 1086m, 898w,

			773m (IV)	852w, 825w, 796w, 751m, 691w, 648w, 609w, 587w, 567w, 507w, 472w, 413w
[$Cu^{II}(L^{3H})Br$] **5**	3447s 3292m	3164m, 3067w	1492m (I) 1318m (II) 1103s (III) 782m (IV)	1630s, 1596m, 1560w, 1444s, 1362m, 1261w, 1181s, 1159m, 808w, 734w, 646w, 613w, 567w, 498w, 465w, 430w
[$Cu^{II}(L^{3Me})Br$] **6**	3319s	3075vw, 3017vw, 2953vw	1500m (I) 1290w (II) 1084s (III) 770m (IV)	1628w, 1600w, 1564w, 1521s, 1459s, 1401s, 1371m, 1336w, 1249m, 1195s, 1162m, 827w, 739w, 646w, 614w, 562w, 469m, 440w
[$Cu^{II}(L^{3Et})Br$] **7**	3345s	3064w, 3028w, 2968w 2926w, 2867w	1504s (I) 1294w (II) 1082m (III) 779m (IV)	1635w, 1600w, 1561w, 1439s, 1384m, 1373m, 1351w, 1326m, 1269w, 1241s, 1178s, 1161m, 1128m, 1048m, 997w, 830w, 804w, 741w, 665w, 647w, 610w, 534w, 475w, 410w
[$Cu^{II}(L^{3Ph})Br$] **8**	3311s	3124w, 3067m 2912vw	1496s (I) 1316s (II) 1045w (III) 775m (IV)	1598s, 1562m, 1535s, 1456s, 1431s, 1370m, 1248m, 1192m, 1156s, 1106m, 1083m, 996w, 895w, 850w, 825w, 746m, 689m, 668w, 647w, 612w, 588w, 563w, 504w, 442w, 413w
[$Cu^{II}(L^{3H})I$] **9**	3427m 3289m	3148m, 3072m	1492s (I) 1313m (II) 1059m (III) 779m (IV)	1628s, 1596s, 1560m, 1441s, 1358m, 1259w, 1178s, 1126m, 1101m, 1038m , 890vw, 807w, 732m, 674w, 644w, 614w, 565w, 494w, 463w, 416w
[$Cu^{II}(L^{3Me})I$] **10**	3328s	3075vw, 2951w	1517s (I) 1284m (II) 1082m (III) 767m (IV)	1631w, 1598w, 1564w, 1457s, 1400s, 1370m, 1335m, 1247m, 1194s, 1161s, 884vw, 825w, 737w, 643w, 612w, 551m, 472m, 438w, 413w
[$Cu^{II}(L^{3Et})I$] **11**	3341s	3099vw, 3071vw, 2985w, 2972w, 2919w 2874w	1501s (I) 1324m (II) 1016w (III) 776m (IV)	1598m, 1559vw, 1479m, 1441s, 1390m, 1372m, 1351m, 1295m, 1276w, 1241s, 1172s, 1158s, 1130m, 1107m, 10871m, 1044m, 999w, 894w, 830m, 807m, 742w, 665w, 646w, 636w, 566w, 531wm, 488w, 410w.
[$Cu^{II}(L^{3Ph})I$] **12**	3342m 3312m	3120w, 3069w,	1498s (I) 1315m (II)	1596m, 1564w, 1534m, 1459s, 1433s, 1369m, 1251m, 1187m,

		2911vw	1018w (III) 747m (IV)	1171m, 1156m, 1109w, 1084w, 1074w, 1045w, 996w, 895w, 849w, 823w, 795w, 775w, 689w, 647w, 625w, 606w, 585w, 564w, 505w, 442w, 412w
HL^{3H}	3374s, 3261s {3185s}	3064m, 2983m	1502 s (I) 1246 s (II) 997 m (III) 783m (IV)	1609s, 1584m, 1564 m, 1467s, 1431s, 1367m, 1316 m, 1151m, 1110s, 1086s, 1052m, 969w, 898vw, 849 m, 837m, 760w, 743w, 650m, 612w, 563m, 464w, 418w
HL^{3Me}	3288s {3240s}	3064w, 3044w, 2967w, 2943w, 2900w	1498s (I) 1232s (II) 990w (III) 780m (IV)	1608vw, 1578m, 1539s, 1462s, 1434s, 1409m, 1364w, 1294m, 1149m, 1115m, 1074m, 1050m, 1038m, 967w, 904w, 834w, 743w, 683w, 644w, 622w, 575w, 542w
HL^{3Et}	3349s, 3274m {3211s}	3055w, 2978w, 2932w 2868w	1504s (I) 1221s (II) 992w (III) 783m (IV)	1614vw, 1580m, 1561w, 1534s, 1471s, 1436m, 1368w, 1343w, 1311m, 1298m, 1155m, 1103s, 1084s, 932w, 903w, 824w, 748w, 668w, 640w, 619w, 588m, 552m, 470w, 432w
HL^{3Ph}	3300s {3242m}	3050w, 2973w	1489s (I) 1262m (II) 1001w (III) 783m (IV)	1583m, 1523s, 1467s, 1440s, 1360m, 1303m, 1189s, 1149m, 1113m, 1070m, 1026m, 971w, 928w, 896w, 844vw, 800w, 764w, 740m, 690m, 654w, 637w, 619w, 584w, 555m, 489w, 468w

*Note : Band I has contributions from δNH + δC-H + υC=N; Band II has contributions from υC-N + δNH + δC-H + υC=S; Band III has contributions from υC-N + υC-S; Band IV has contributions from υC-S

Table 2S: Important bond parameters for complexes **4-7** and **9-11**

	4 (Cl)	**5** (Br)		**6** (Br)	**7** (Br)	
		5A	**5**B		**7**A	**7**B
$Cu–N_{Py}$	2.021(3)	2.022(3)	1.994(3)	2.030(4)	2.010(3)	2.004(3)

Cu–N	1.958(3)	1.978(3)	1.977(3)	1.965(3)	1.974(3)	1.973(3)
Cu–S	2.2567(11)	2.2413(9)	2.2150(9)	2.2426(13)	2.2214(11)	2.2276(11)
Cu–X	2.2058(10)	2.3587(6)	2.3855(5)	2.3652(8)	2.3829(7)	2.3742(7)
S–C	1.752(3)	1.743(4)	1.733(3)	1.747(5)	1.750(4)	1.750(4)
N_{py}-Cu-S	164.67(9)	164.97(8)	165.80(8)	164.73(12)	164.03(10)	163.81(10)
N-Cu-S	84.03(8)	84.90(8)	84.85(8)	84.70(11)	84.74(10)	84.42(10)
$N_{azomethine}$-Cu-$X_{(Cl, Br)}$	177.80(9)	172.36(8)	175.98(8)	178.40(11)	171.92(10)	178.74(10)
N_{py}-Cu-N	80.65(12)	80.27(11)	80.97(11)	80.45(15)	80.64(14)	80.74(13)
N-Cu-X	97.53(9)	95.35(3)	99.81(8)	98.68(11)	98.64(10)	98.70(10)
S-Cu-X	97.78(4)	99.02(8)	94.39(3)	96.08(4)	96.74(4)	96.26(4)

	9		**10**	**11**
	9A	**9**B		
Cu–N_{Py}	2.006(8)	2.031(8)	2.027(3)	2.027(5)
Cu–N	1.978(8)	1.977(8)	1.955(3)	1.968(4)
Cu–S	2.213(3)	2.232(3)	2.2375(12)	2.2339(14)
Cu–I	2.5730(14)	2.5481(15)	2.5598(5)	2.5682(8)
S–C	1.736(10)	1.736(11)	1.747(4)	1.748(5)
N_{py}-Cu-S	166.0(3)	164.9(2)	164.42(9)	163.65(14)
N-Cu-S	84.7(2)	85.0(2)	84.59(10)	84.36(13)
$N_{azomethine}$-Cu-I	175.0(2)	173.2(3)	179.26(10)	179.18(12)
N_{py}-Cu-N	81.4(3)	80.0(3)	80.42(13)	80.40(18)
N-Cu-I	100.8(2)	100.7(2)	100.20(9)	100.39(13)
S-Cu-I	93.14(7)	94.02(8)	94.76(3)	94.84(4)