SUPPLEMENTARY INFORMATION

Comparative solution study of imidazole-derived thiosemicarbazone complexes: effects of methylation and aromatic conjugation on the redox properties, anticancer, and antibacterial activity

Tatsiana V. Petrasheuskaya,[a] Márton A. Kiss,[a] Peter Rapta,[b] Csenge Fonay,[c] Nóra V. May,[c] Gabriella Spengler,[d] Éva Frank,[a] Éva A. Enyedy[a*]

[a]Department of Molecular and Analytical Chemistry, University of Szeged, Dóm tér 7-8, H-6720 Szeged, Hungary
[b]Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Radlinského 9, SK-81237 Bratislava, Slovakia
[c]Centre for Structural Science, Research Centre for Natural Sciences, Magyar tudósok körútja 2, H-1117 Budapest, Hungary
[d]Department of Medical Microbiology, Albert Szent-Györgyi Medical School, University of Szeged, Semmelweis utca 6, H-6725 Szeged, Hungary

Table of contents

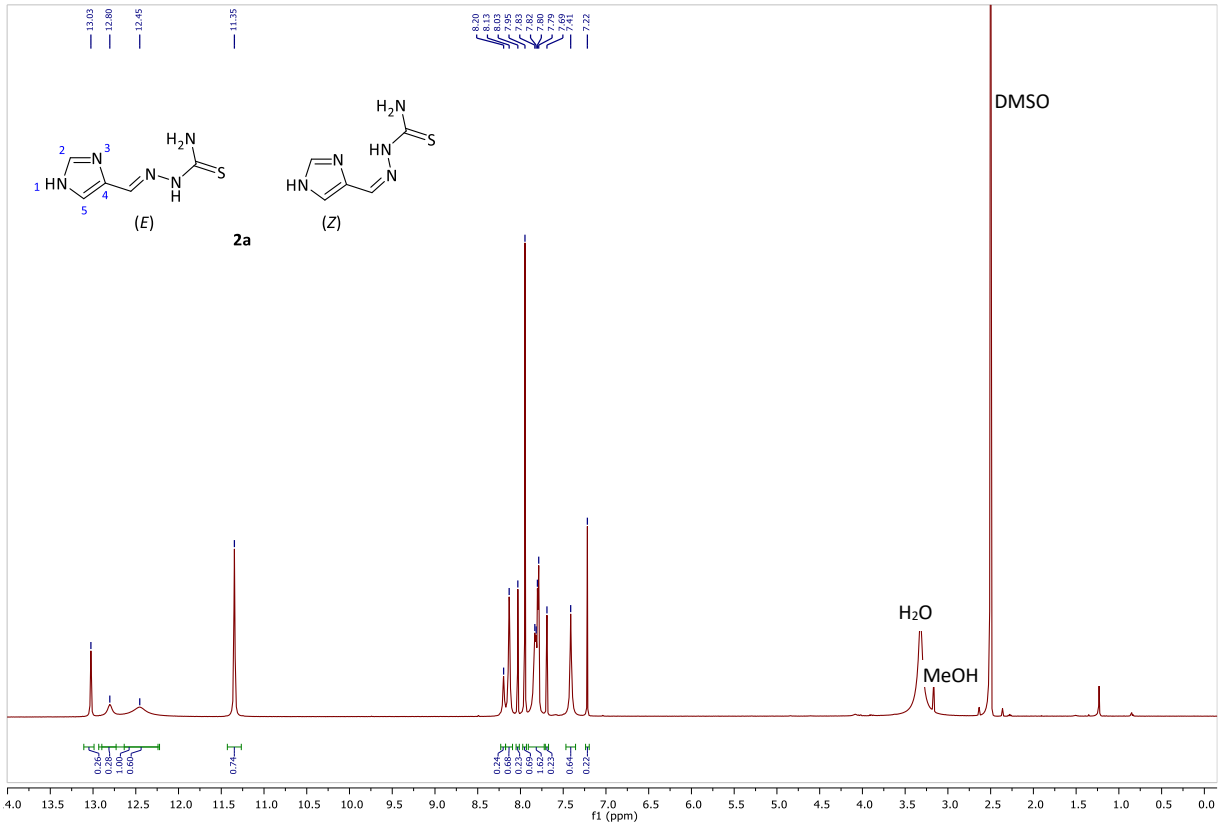


Figure S1. ^{1}H NMR spectrum of **imidazole-TSC** (500 MHz, DMSO-d_6).

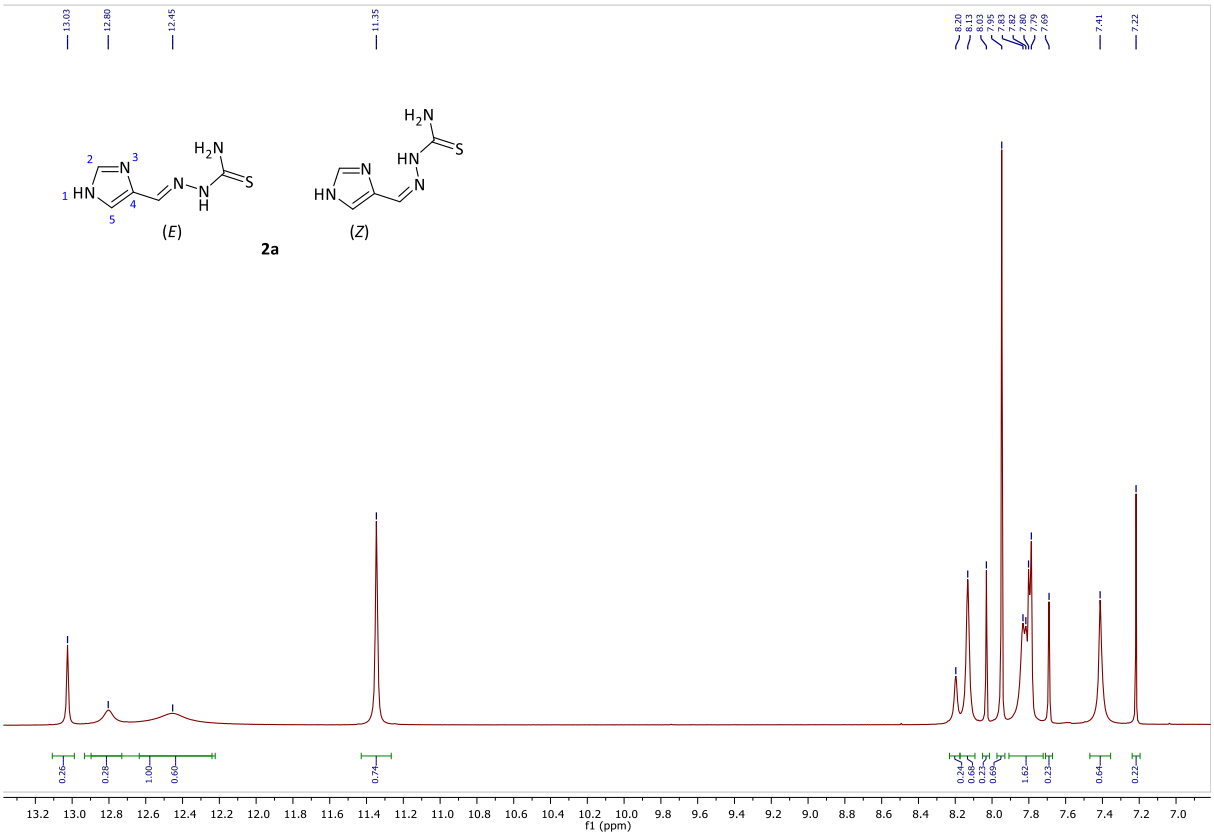


Figure S2. Partial ^{1}H NMR spectrum of **imidazole-TSC** (7.0-13.5 ppm).

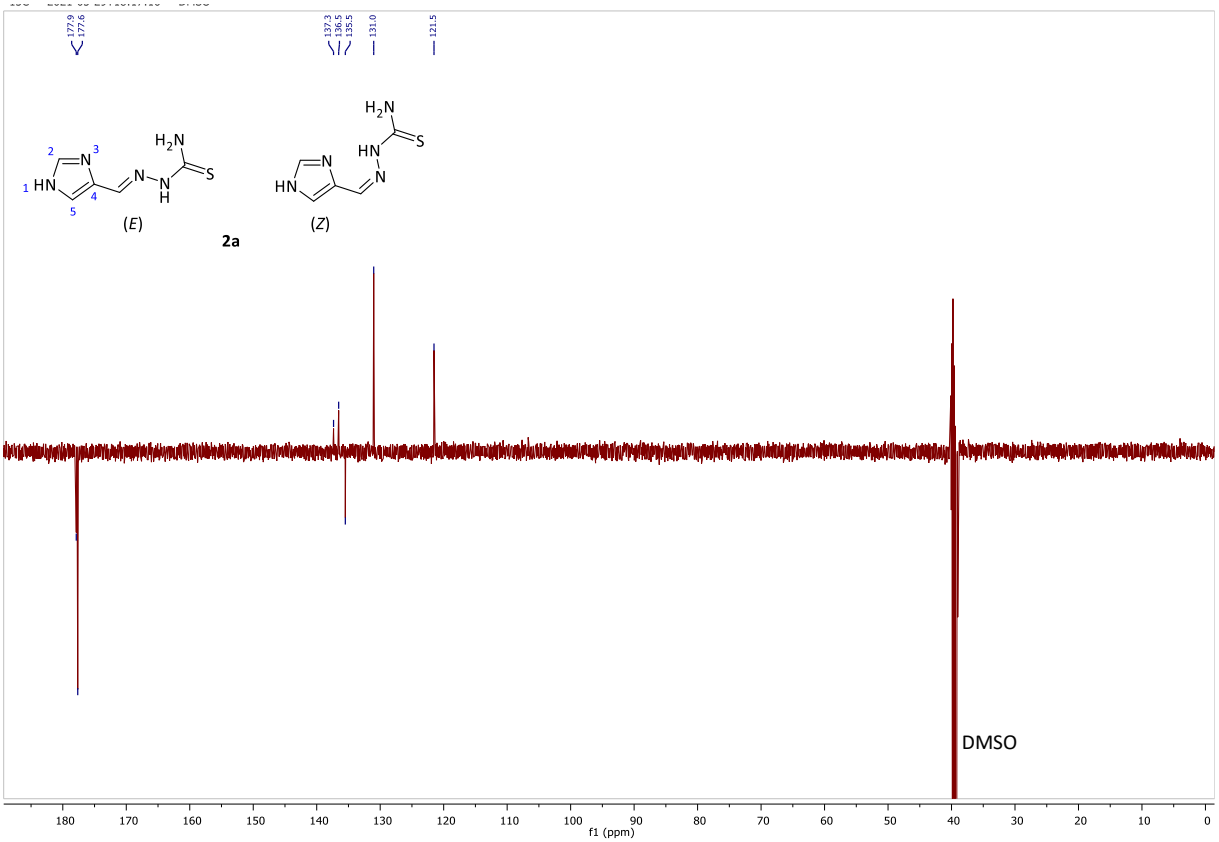


Figure S3. ^{13}C NMR spectrum (J-MOD) of **imidazole-TSC** (125 MHz, DMSO-d_6).

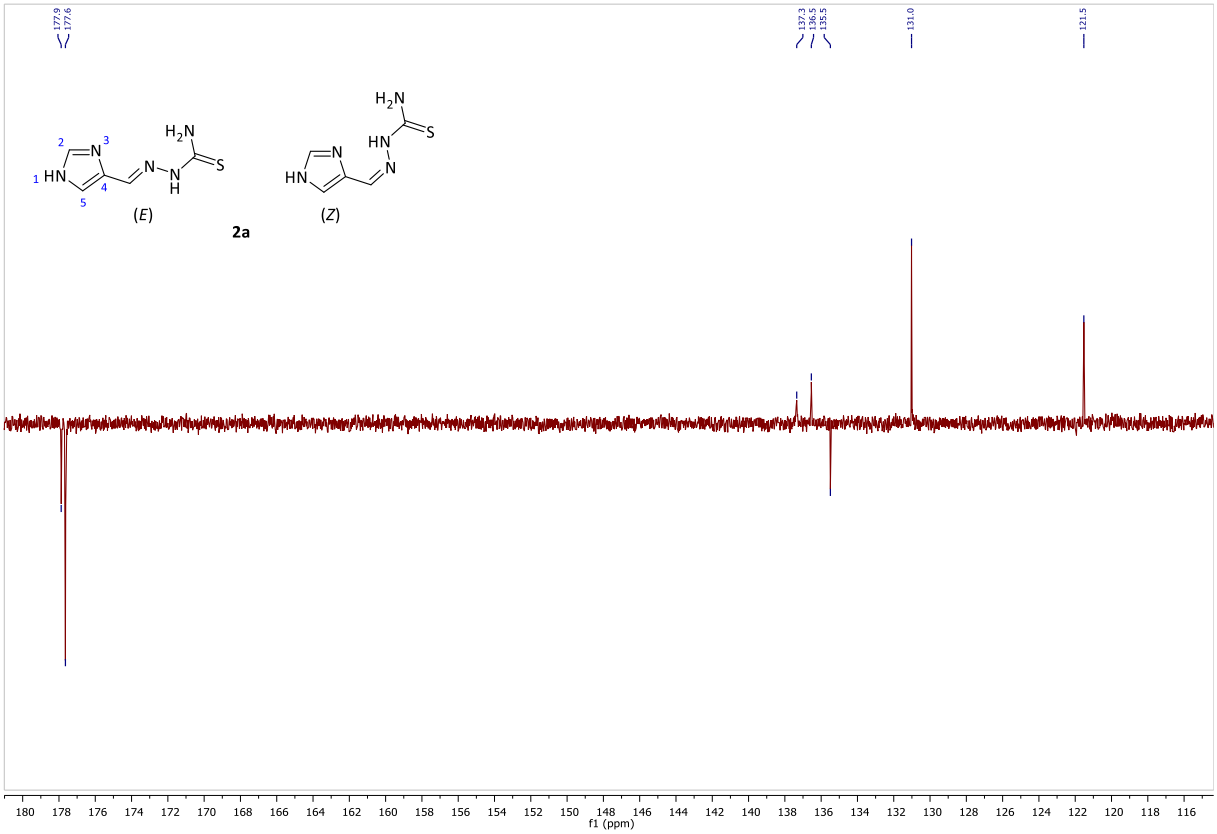


Figure S4. Partial ^{13}C NMR spectrum (J-MOD) of **imidazole-TSC** (115-180 ppm).

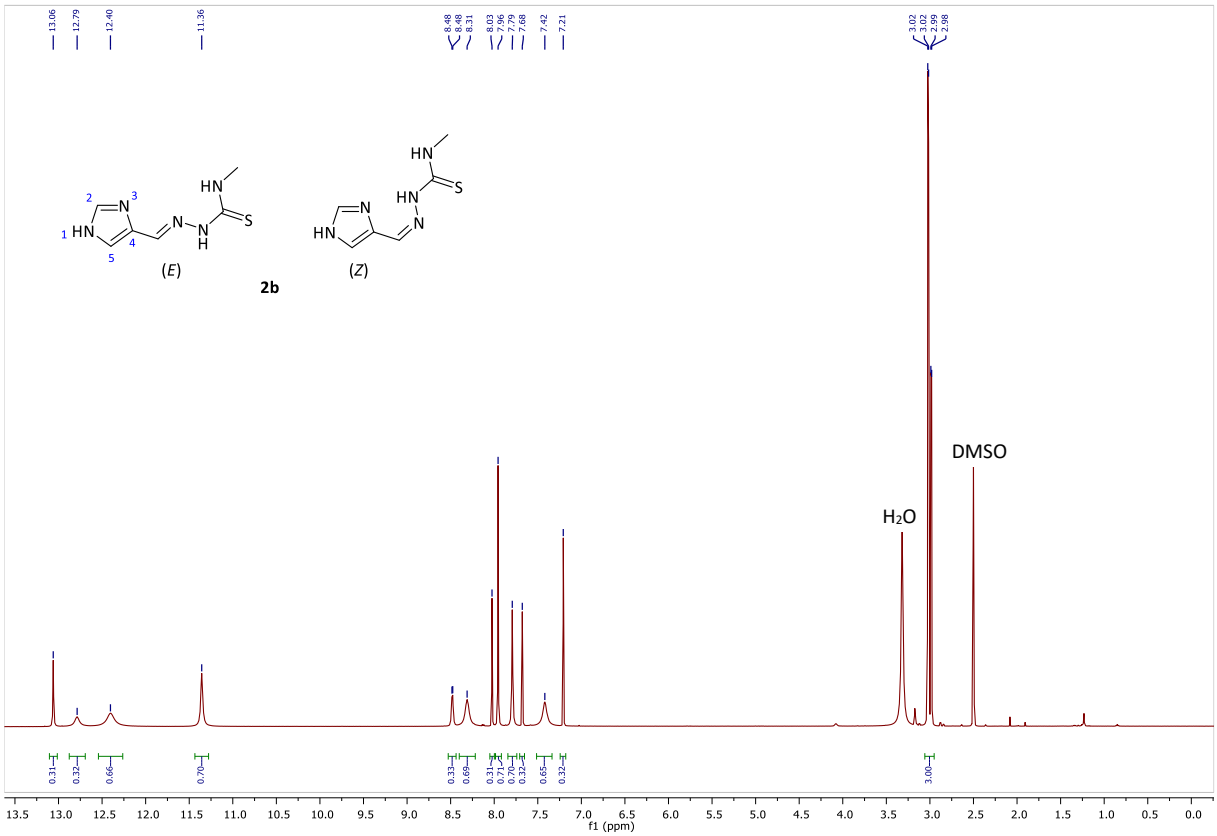


Figure S5. ^{1}H NMR spectrum of **imidazole-Me-TSC** (500 MHz, DMSO-d_6).

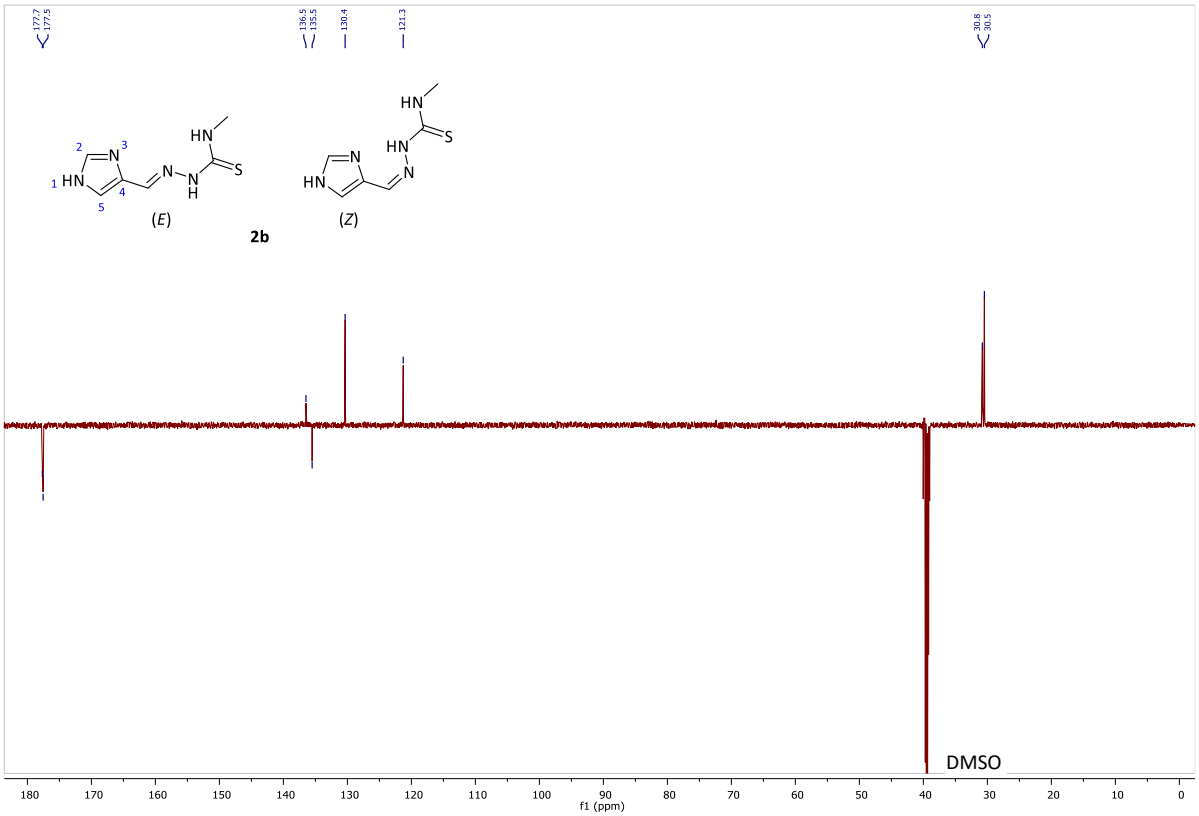


Figure S6. ^{13}C NMR spectrum (J-MOD) of **imidazole-Me-TSC** (125 MHz, DMSO-d_6).

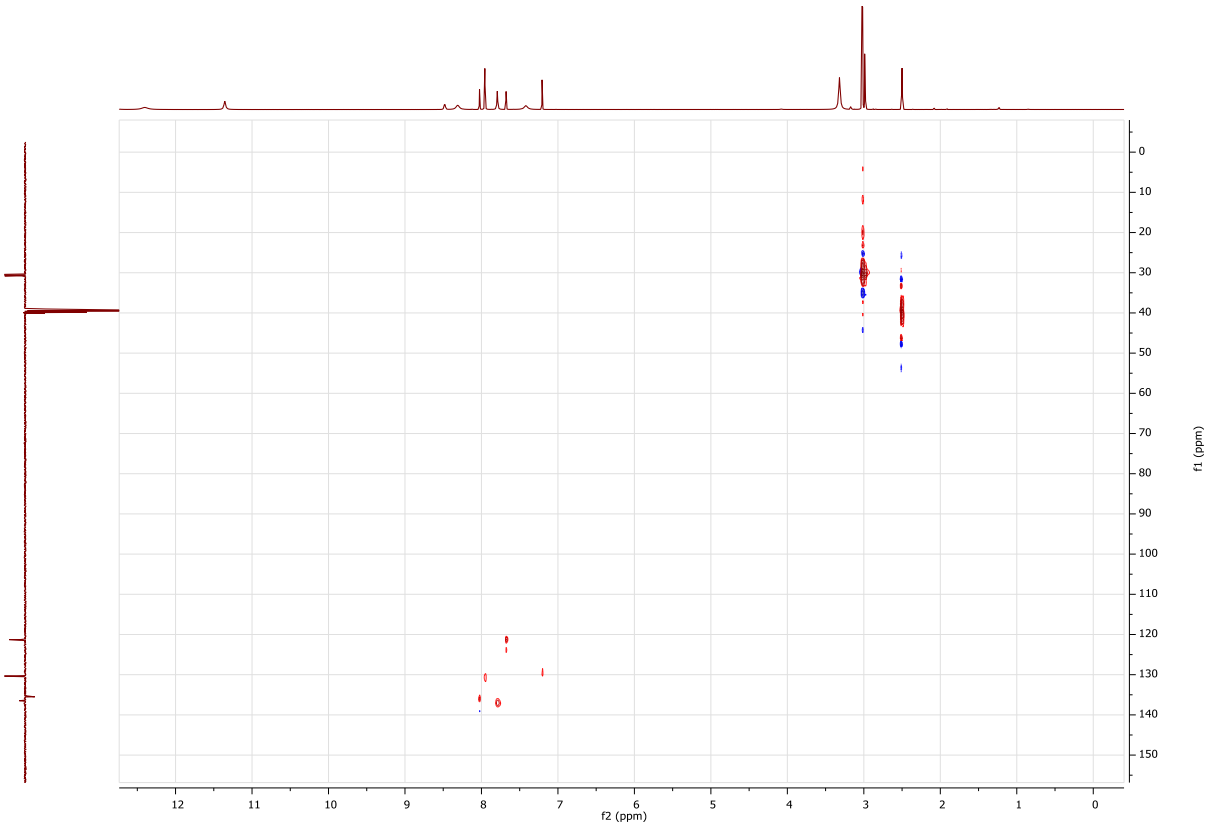


Figure S7. HSQC spectrum of **imidazole-Me-TSC**.

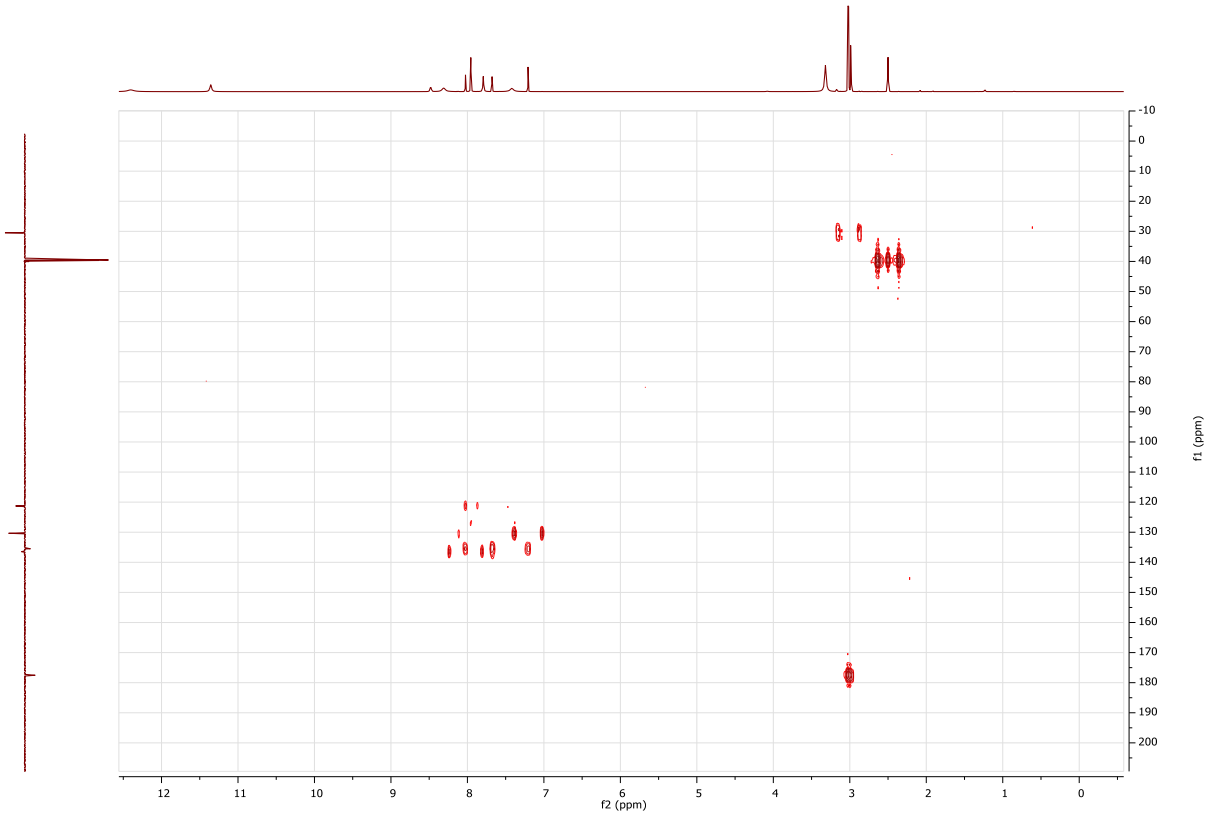


Figure S8. HMBC spectrum of **imidazole-Me-TSC**.

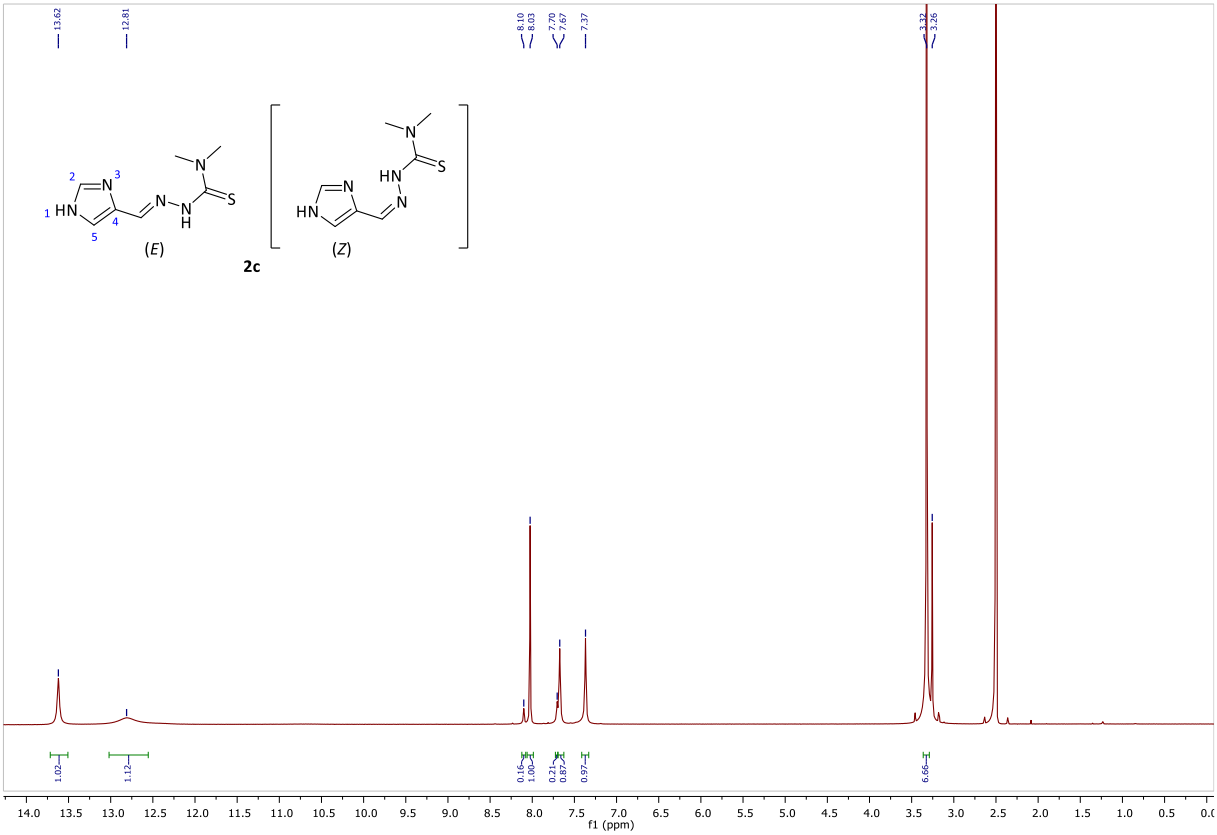


Figure S9. ^{1}H NMR spectrum of **imidazole-Me$_2$-TSC** (500 MHz, DMSO-d_6).

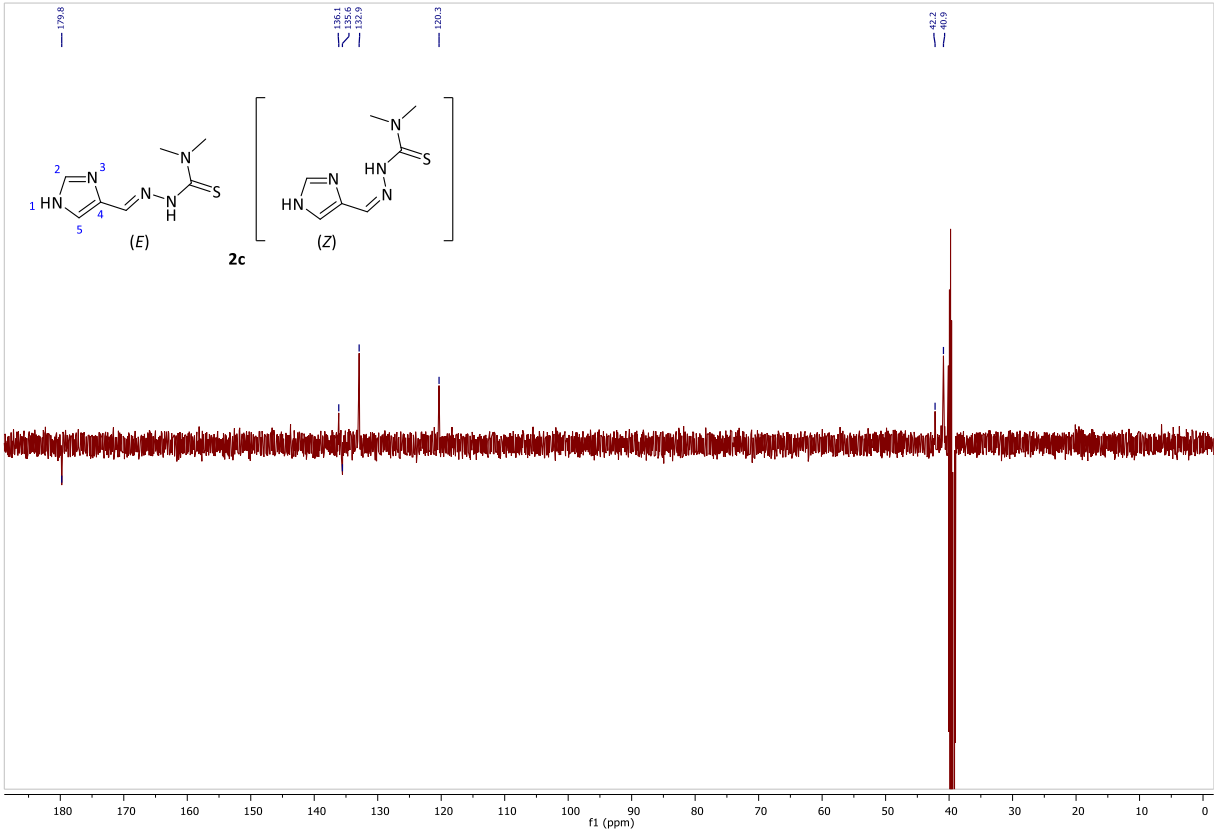


Figure S10. ^{13}C NMR spectrum of **imidazole-Me$_2$-TSC** (125 MHz, DMSO-d_6).

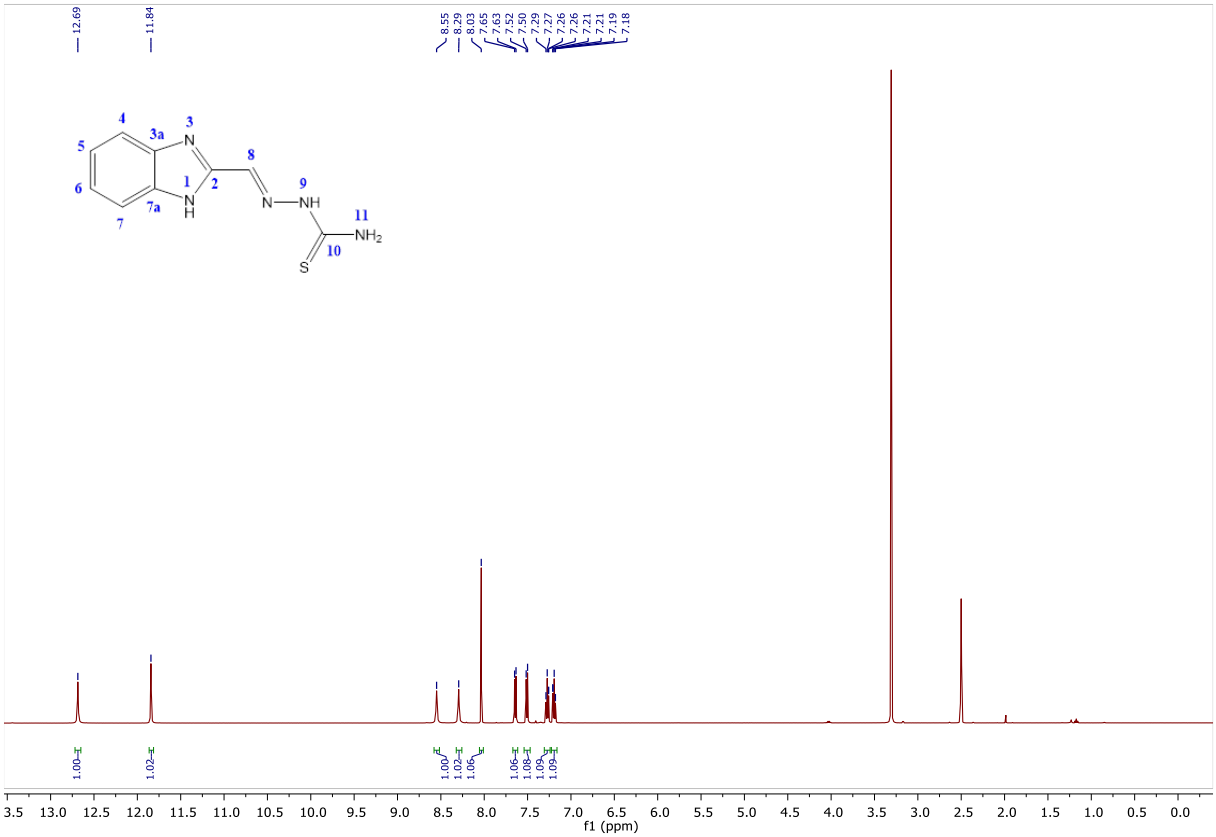


Figure S11. ^{1}H NMR spectrum of **benzimidazole-TSC** (DMSO-d_6, 500 MHz).

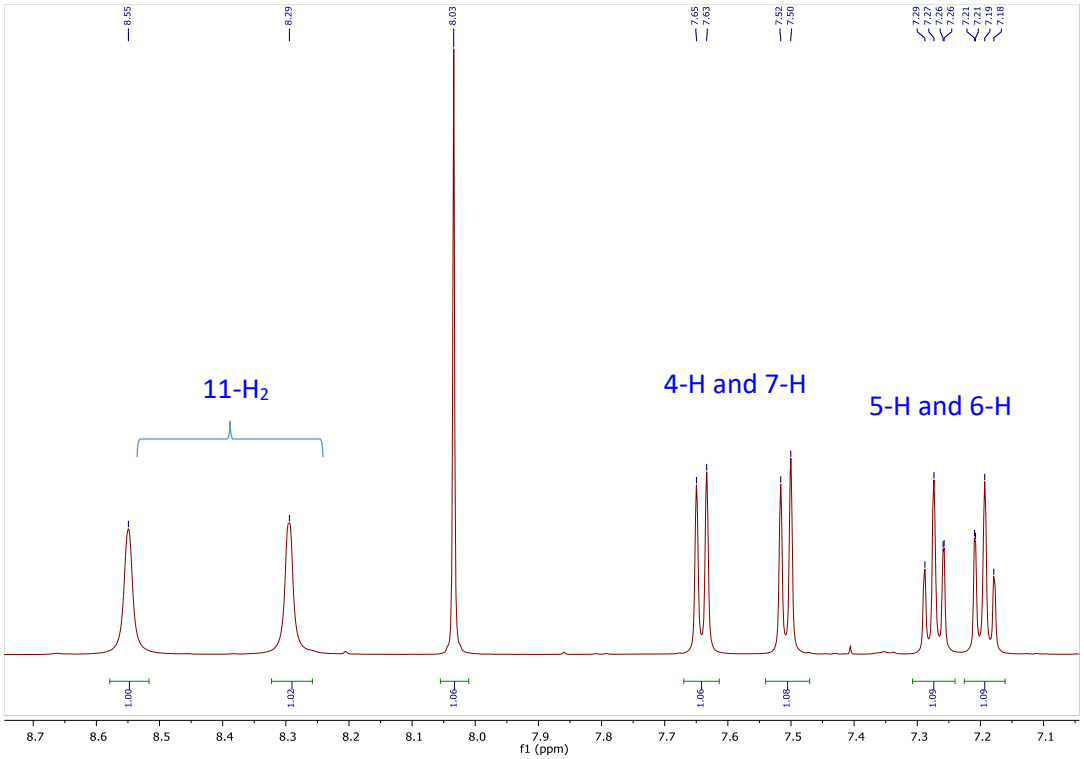


Figure S12. Enlarged ^{1}H NMR spectrum of **benzimidazole-TSC** between 7.1-8.7 ppm.

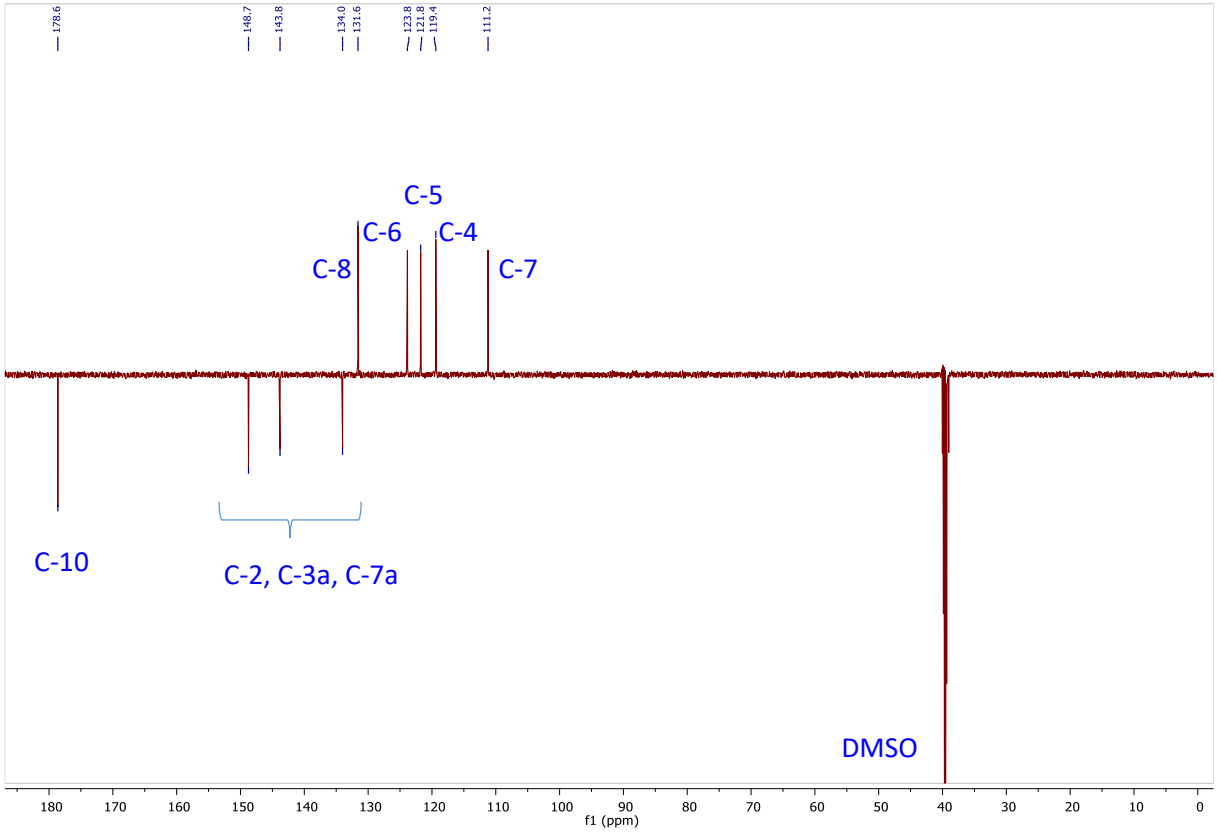


Figure S13. ^{13}C NMR spectrum of **benzimidazole-TSC** (DMSO-d_6, 125 MHz).

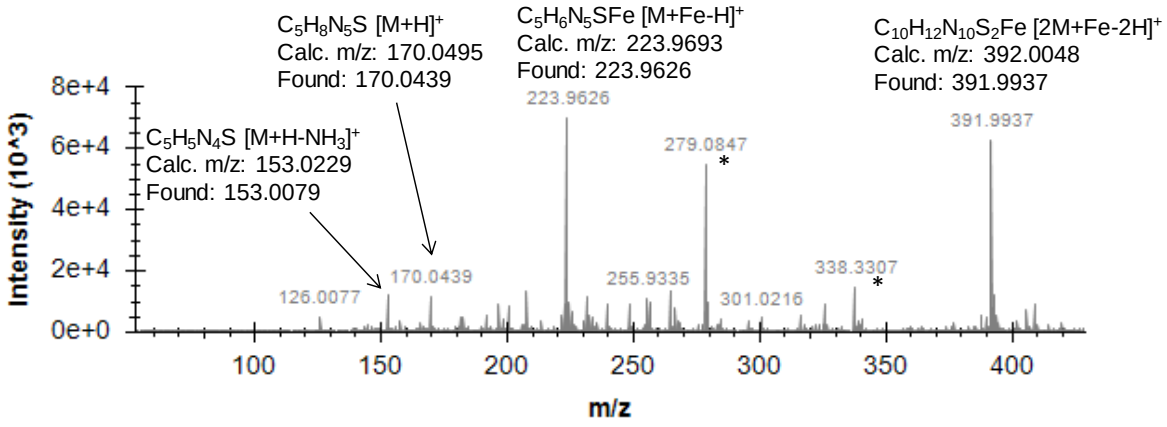


Figure S14. ESI-MS spectra of **imidazole-TSC**. Samples were prepared in methanol. (*background)

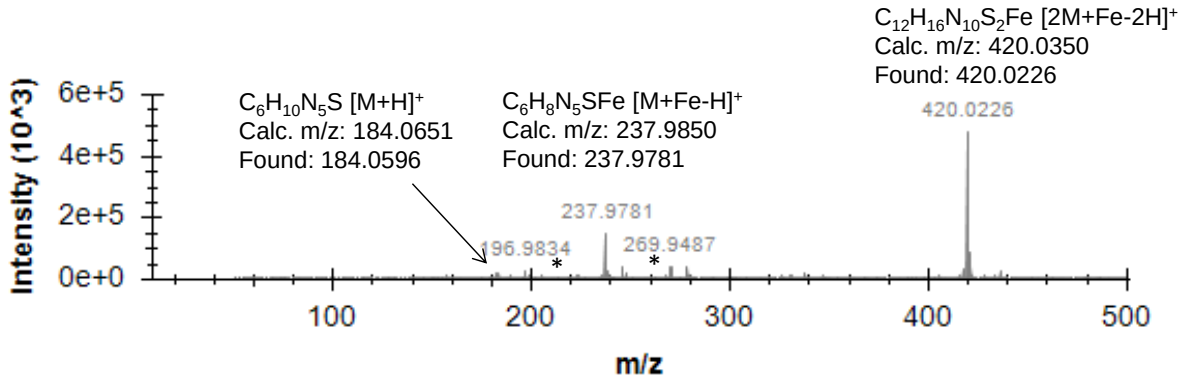


Figure S15. ESI-MS spectra of **imidazole-Me-TSC**. Samples were prepared in methanol. (*background)

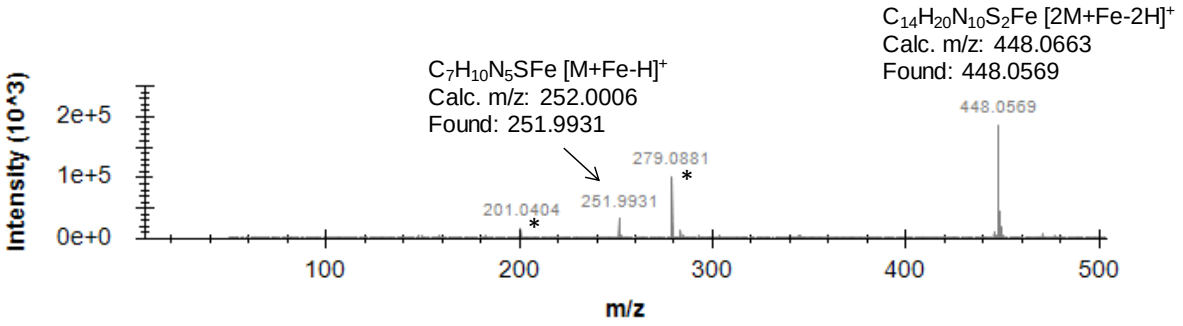


Figure S16. ESI-MS spectra of **imidazole-Me$_2$-TSC**. Samples were prepared in methanol. (*background)

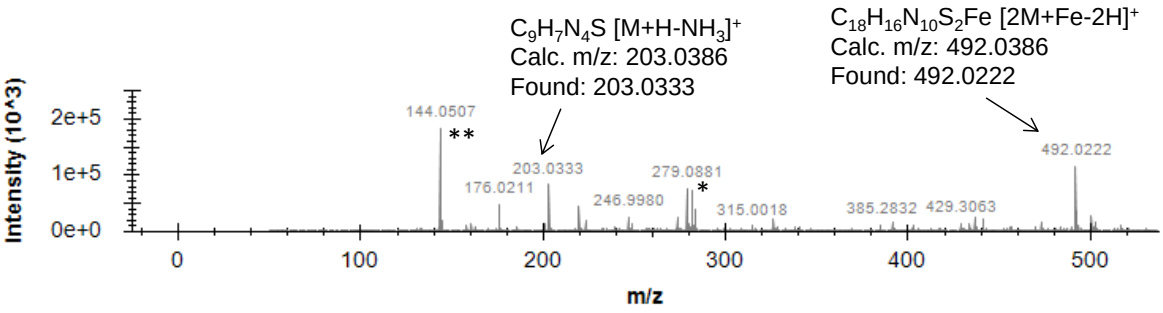


Figure S17. ESI-MS spectra of **benzimidazole-TSC**. Samples were prepared in methanol. (*background; ** hydrolysis product most likely)

Table S1. MIC values determined for the ligands in the absence and presence of one equivalent of Cu(II) and Ni(II) on various bacterial strains.

	MIC (μM)			
	***E. coli* ATCC 25922**	***S. aureus* ATCC 25928**	***S. aureus* MRSA 272123**	***Klebsiella quasipneumoniae* ATCC 700603**
imidazole-TSC	>100	>100	>100	>100
imidazole-Me-TSC	>100	>100	>100	>100
imidazole-Me_2-TSC	>100	**50**	>100	>100
benzimidazole-TSC	>100	**100**	>100	>100
imidazole-TSC + $CuCl_2$	>100	**100**	>100	>100
imidazole-Me-TSC + $CuCl_2$	>100	**100**	>100	>100
imidazole-Me_2-TSC + $CuCl_2$	>100	**50**	>100	>100
benzimidazole-TSC + $CuCl_2$	**100**	**50**	**100**	>100
imidazole-TSC + $NiCl_2$	>100	>100	>100	>100
imidazole-Me-TSC + $NiCl_2$	>100	>100	>100	>100
imidazole-Me_2-TSC + $NiCl_2$	>100	100	>100	>100
benzimidazole-TSC + $NiCl_2$	>100	>100	>100	>100
$CuCl_2$	>100	>100	>100	>100
$NiCl_2$	>100	>100	>100	>100
blank (DMSO)	>2%	>2%	>2%	>2%

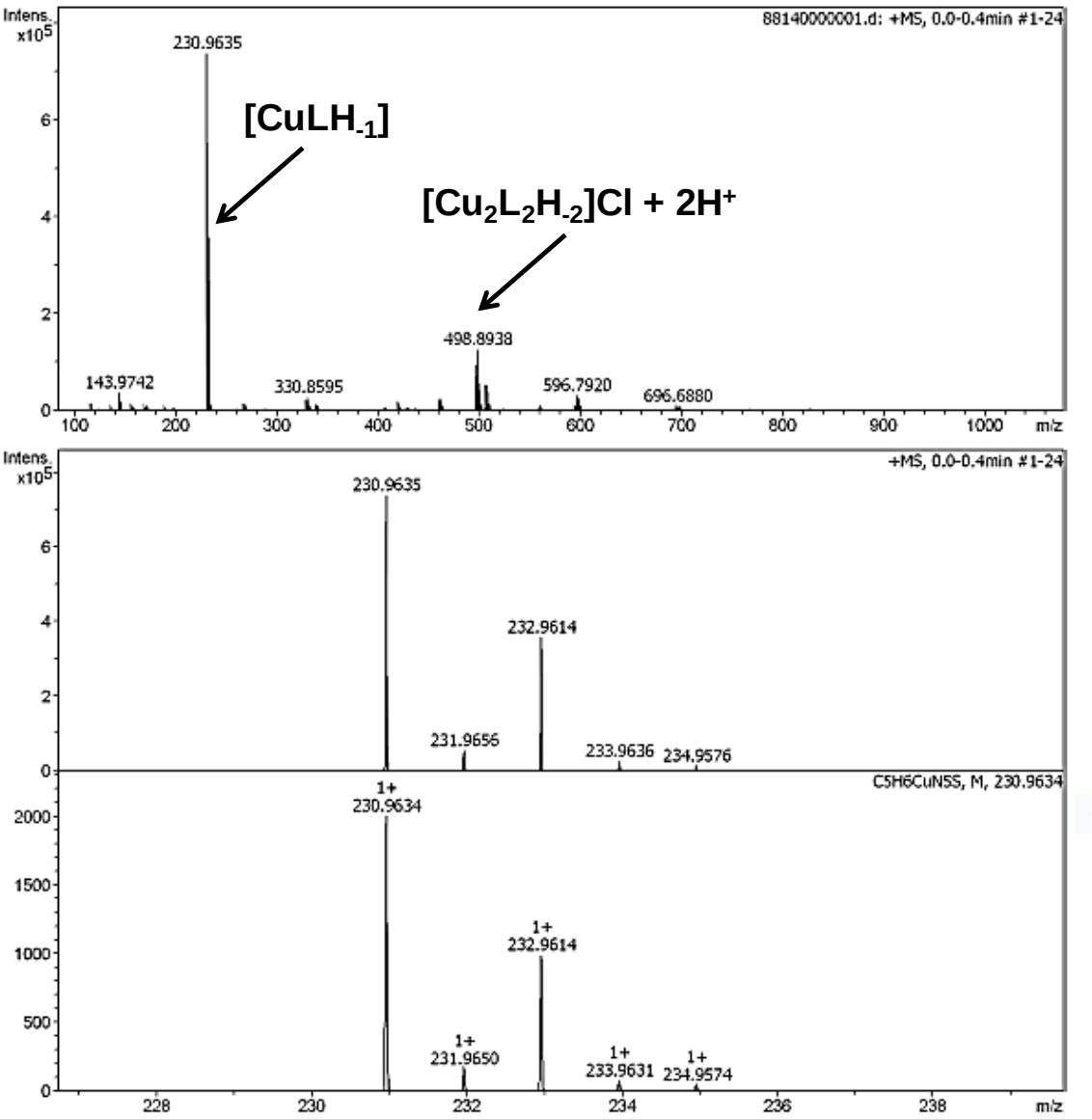


Figure S18. ESI-MS spectra of the indicated Cu(II) complexes of the imidazole-TSC. Samples were prepared in methanol.

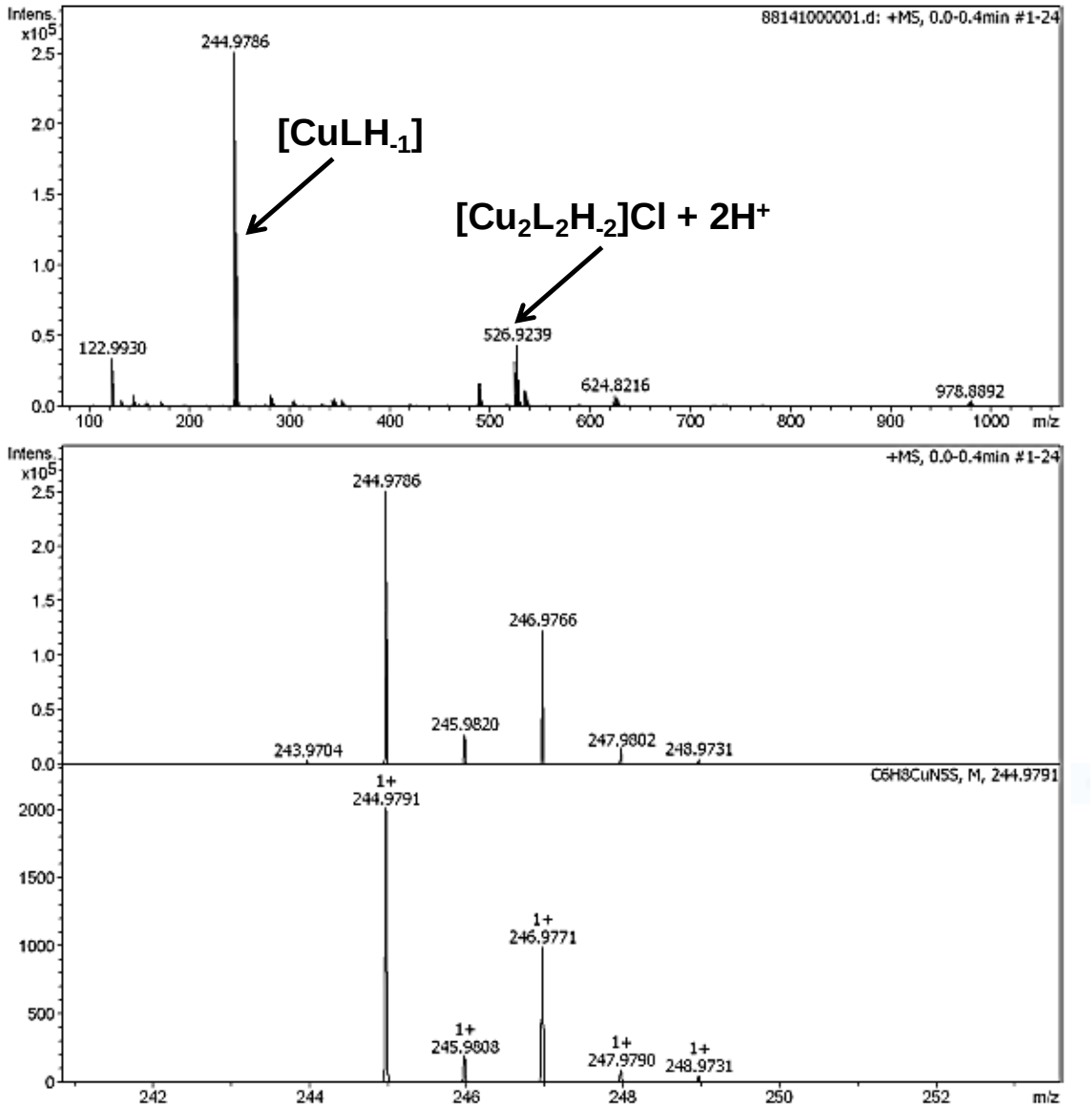


Figure S19. ESI-MS spectra of the indicated Cu(II) complexes of the imidazole-Me-TSC. Samples were prepared in methanol.

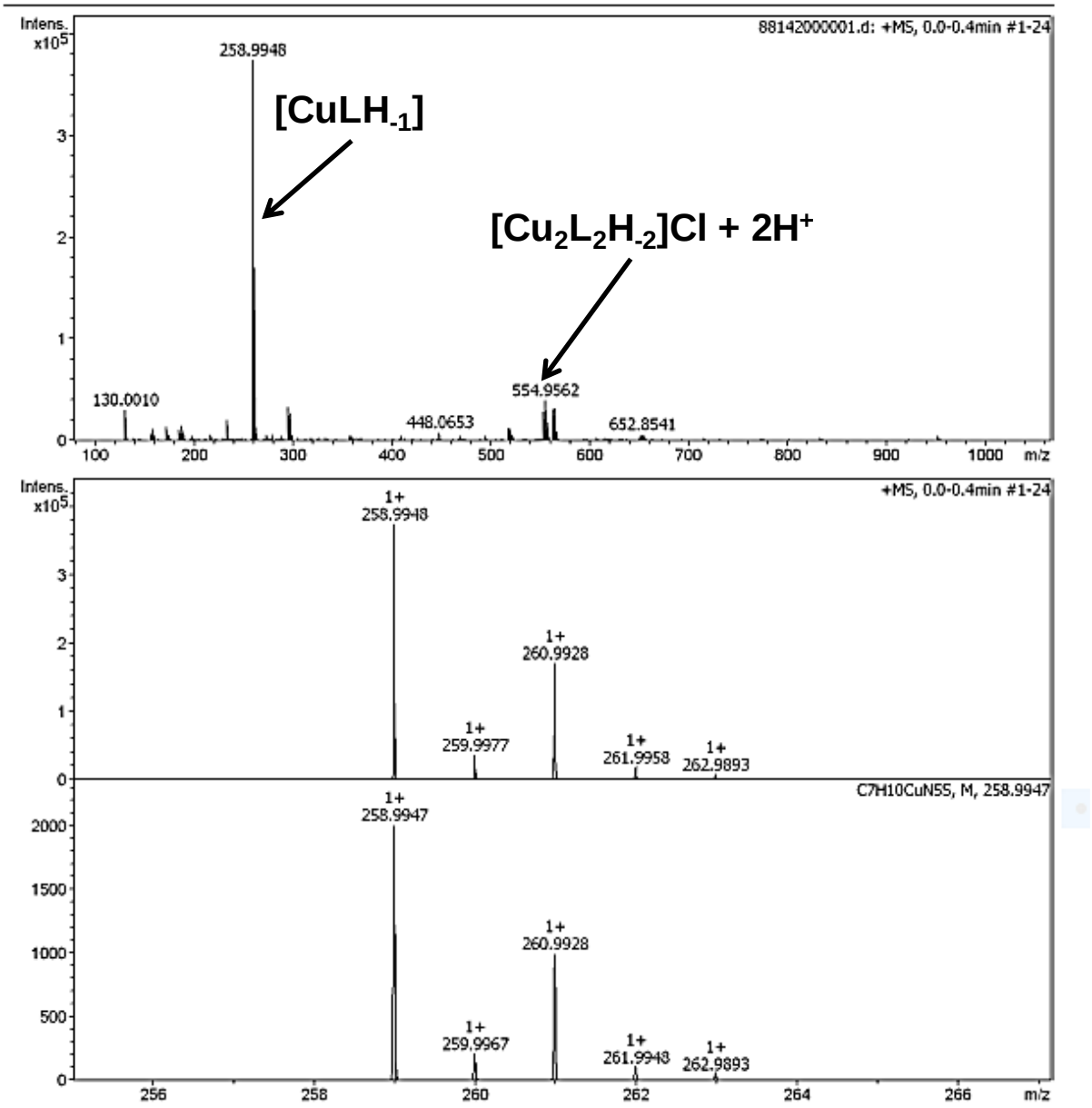


Figure S20. ESI-MS spectra of the indicated Cu(II) complexes of the imidazole-Me_2-TSC. Samples were prepared in methanol.

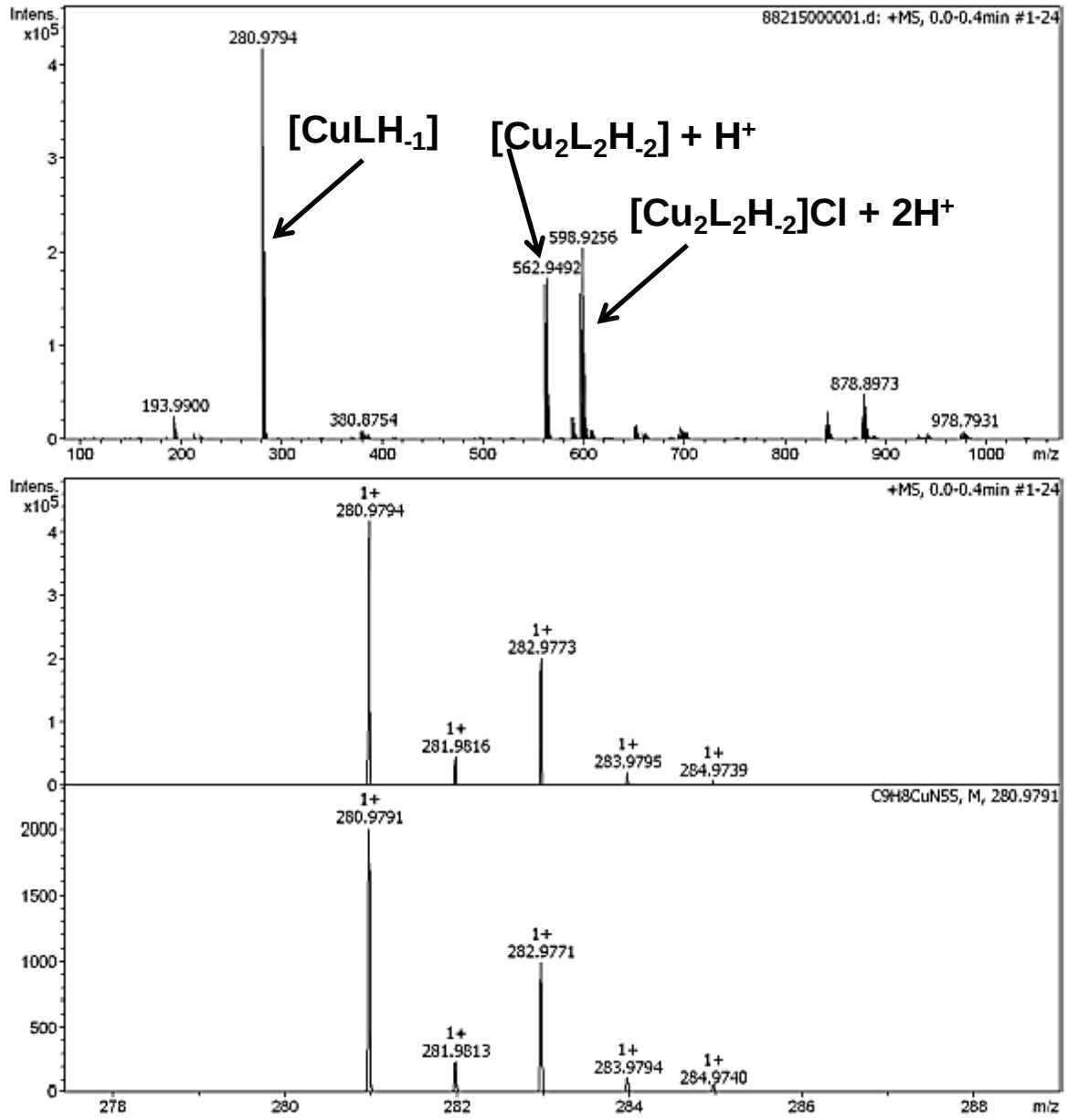


Figure S21. ESI-MS spectra of the indicated Cu(II) complexes of the benzimidazole-TSC. Samples were prepared in methanol.

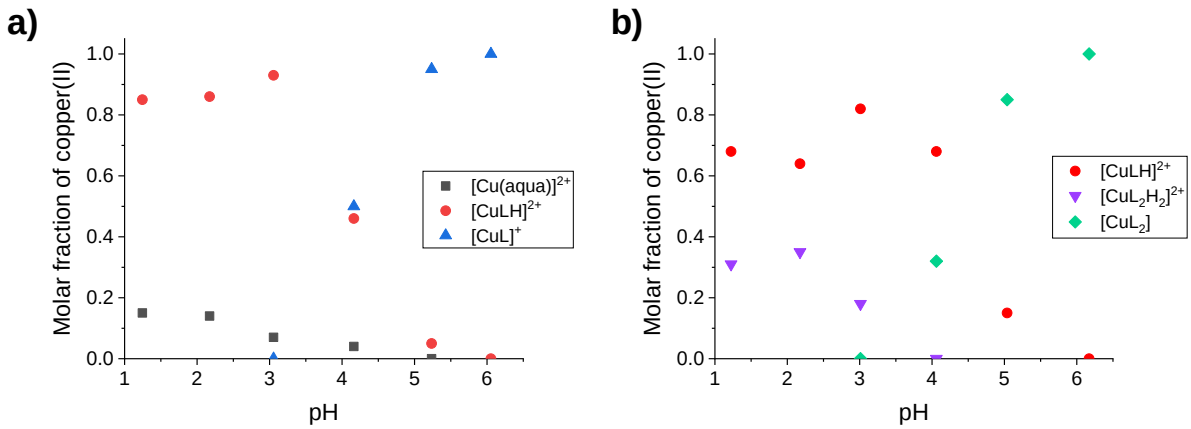


Figure S22. The ratio of the components at different pH values obtained by the simulation of the anisotropic EPR spectra for Cu-imidazole-TSC complexes: a) Cu(II):L = 1:1 molar ratio; b) Cu(II):L = 1:2 molar ratio.

Table S2. Isotropic EPR parameters and component ratios obtained by the simulation of room temperature DMSO solution (with ~1% (*v*/*v*) H_2O) EPR spectra of Cu(II) with imidazole-TSC, imidazole-Me-TSC and imidazole-Me_2-TSC complexes shown in Fig. 9.

Coupling values are shown in 10^{-4} cm^{-1} units.

complexes	g_0	A_0	a_0^{N1}	a_0^{N2}	**α**	**β**	**γ**	**ratio (%)**
imidazole-TSC								
$[CuL]^+$	2.081	81	10	15	26	-14	2	47
$[CuLH]^{2+}$	2.091	67	18	17	29	-12	3	53
imidazole-Me-TSC								
$[CuL]^+$	2.081	81	10	15	26	-13	2	52
$[CuLH]^{2+}$	2.092	67	19	17	30	-11	1	48
imidazole-Me_2-TSC								
$[CuL]^+$	2.081	80	10	15	23	-12	2	60
$[CuLH]^{2+}$	2.092	67	18	15	26	-11	1	40

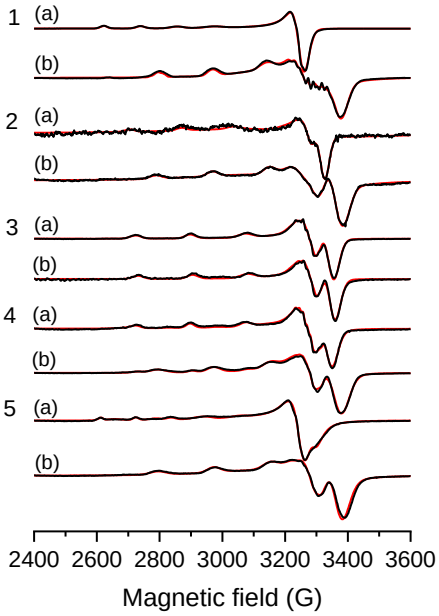


Figure S23. Frozen solution EPR spectra (black) together with simulated curves (red) recorded for (a) $CuCl_2$ and (b) [Cu(imidazole-TSC)] powder dissolved in (1) DMSO/MeOH solvent, (2) HEPES solvent and (3) EMEM medium (4) RPMI 1640 medium and (5) serum. The simulation parameters are collected in Table S3.

Table S3. Anisotropic EPR parameters obtained by the simulation of EPR spectra recorded by dissolution of (a) $CuCl_2$ and (b) Cu-imidazole-TSC complex powder in (1) DMSO/MeOH solvent, (2) HEPES solvent and (3) EMEM medium, (4) RPMI 1640 medium and (5) blood serum shown in Fig. S18. Coupling values are shown in 10^{-4} cm^{-1} units.

Samples	Complexes	g_x	g_y	g_z	A_x	A_y	A_z	a_0^N	%
DMSO/MeOH									
1a	[Cu(aqua)]	2.081	2.081	2.420	14	14	129		100
1b	$[CuLH]^{2+}$	2.036	2.067	2.207	32	16	173	17, 13	100
HEPES									
2a	$[Cu(aqua)L^1]$	2.058	2.058	2.283	12	12	173		100
2b	$[CuL]^+$	2.040	2.050	2.203	28	28	182	13, 13	100
EMEM									
3a	$[CuL^2]$	2.046	2.056	2.259	28	0	180	11, 13	100
3b	$[CuL^2]$	2.044	2.054	2.253	28	0	180	11, 13	100
RPMI 1640									
4a	$[CuL^2]$	2.046	2.056	2.259	28	0	180	11, 13	70
	$[CuL^3]$	2.065	2.065	2.320	17	17	162		30
4b	$[CuL^2]$	2.046	2.056	2.259	28	0	180	11, 13	20
	$[CuL]^+$	2.034	2.060	2.201	28	20	178	11, 13	80
Blood serum									
5a	Cu(aqua)	2.081	2.081	2.420	14	14	129		30
	$[CuL^4]_4$	2.065	2.065	2.361	16	16	142		70
5b	$[CuL]^+$	2.034	2.060	2.201	28	20	178	11, 13	100

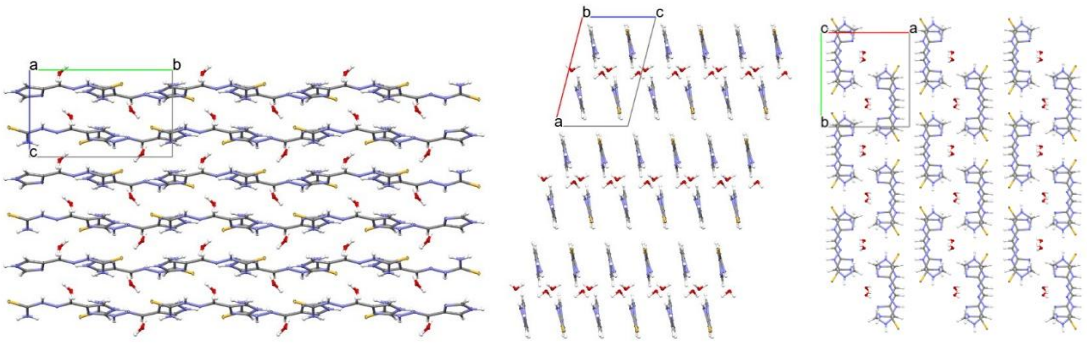


Figure S24. Packing arrangements in crystal imidazole-TSC×H_2O (**I**) viewed from the crystallographic directions 'a', 'b' and 'c'.

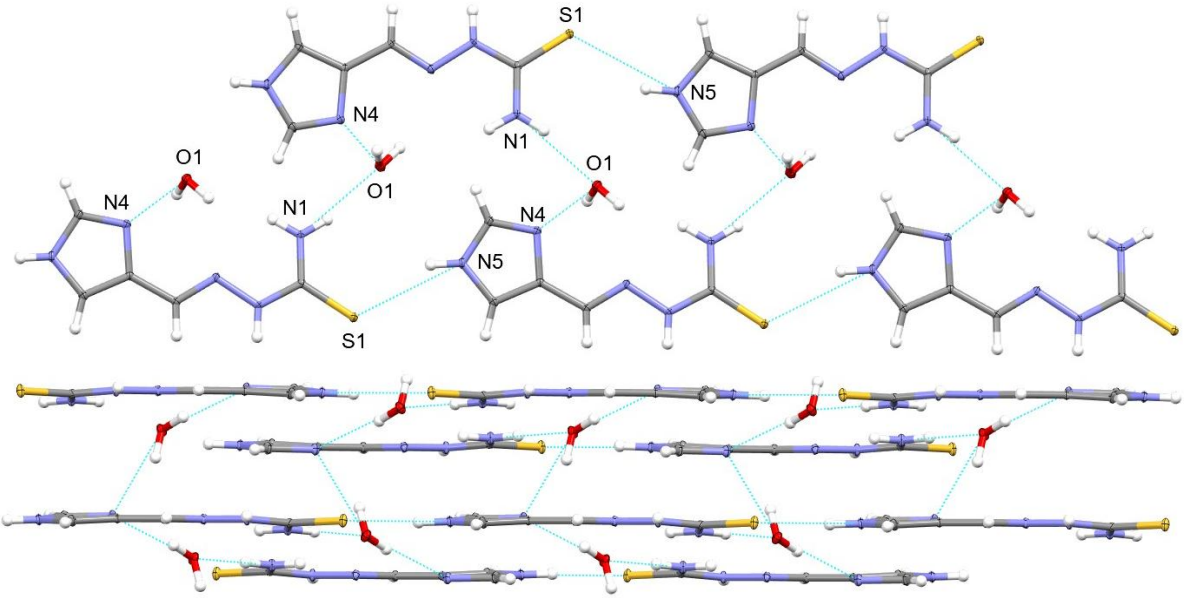


Figure S25. Packing arrangements showing the H-bond interactions in crystal imidazole-TSC×H_2O (**I**) from two different views.

Table S4. Hydrogen-bond geometry of crystal imidazole-TSC×H_2O (**I**).

D-H…A	**D-H** (Å)	**H…A**(Å)	**D…A**(Å)	**D-H…A** (°)	**symmetry codes**
N1-H1A…N2	0.86	2.28	2.6334(18)	105	Intramolecular
N1-H1A…O1	0.86	2.40	3.2231(17)	161	x,1/2-y,1/2+z
N1-H1B…O1	0.86	2.08	2.9205(17)	165	1-x,1/2+y,1/2-z
O1-H1C…N5	0.85	2.12	2.9262(18)	158	A.U.
O1-H1D…N5	0.85	2.20	3.0366(17)	170	x,1/2-y,1/2+z
N3-H3…S1	0.86	2.58	3.3926(14)	157	-x,1-y,-z
N4-H4…S1	0.86	2.56	3.3244(13)	149	x,-1+y,z

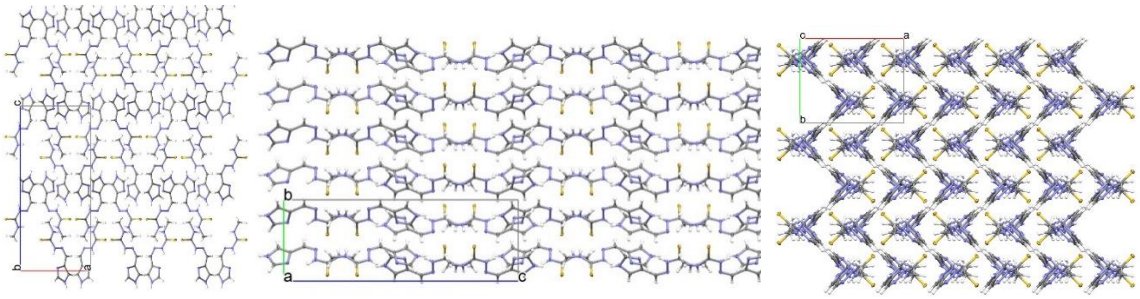


Figure S26. Packing arrangements in crystal imidazole-Me-TSC (**II**) viewed from the crystallographic directions 'a', 'b' and 'c'.

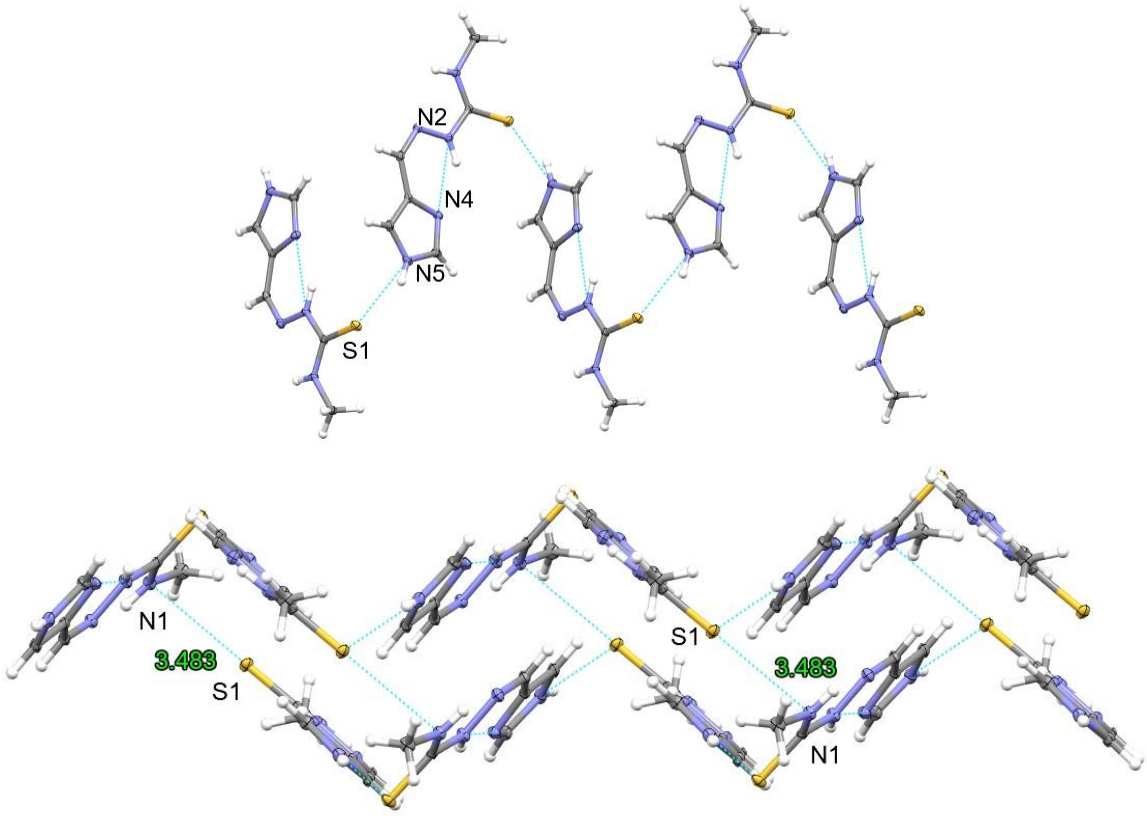


Figure S27. Packing arrangements showing the H-bond interactions in crystal imidazole-Me-TSC (**II**) from two different views.

Table S5. Hydrogen-bond geometry of crystal imidazole-Me-TSC (**II**).

D-H…A	**D-H** (Å)	**H…A**(Å)	**D…A**(Å)	**D-H…A** (°)	**Symmetry codes**
N1-H1A…N3	0.83	2.24	2.624(2)	108	Intramolecular
N2-H2N…N4	0.85	2.06	2.7411(19)	137	Intramolecular
N5-H5N…S1	0.80	2.55	3.2823(16)	152	1/2+x,1/2-y,-z
C6-H6C…N3	0.96	2.59	3.530(3)	168	1-x,-1/2+x,1/2-z

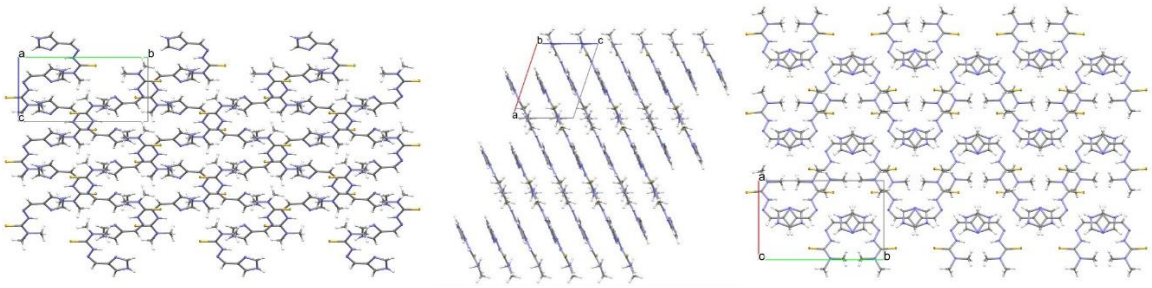


Figure 28. Packing arrangements in crystal imidazole-Me_2-TSC (**III**) viewed from the crystallographic directions 'a', 'b' and 'c'.

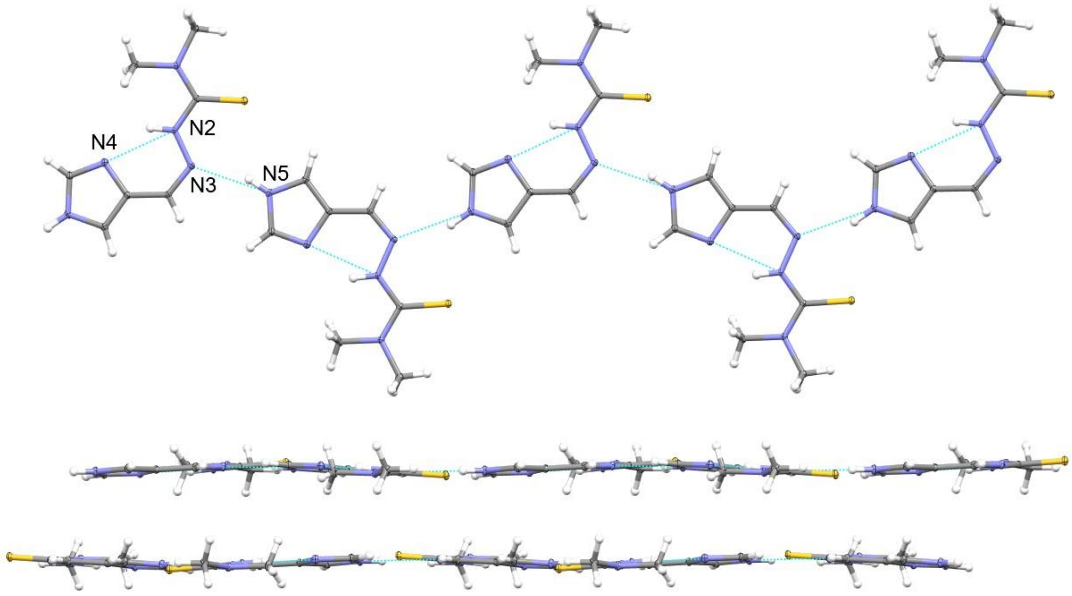


Figure S29. Packing arrangements showing the H-bond interactions in crystal imidazole-Me_2-TSC (**III**) from two different views.

Table S6. Hydrogen-bond geometry of crystal imidazole-Me_2-TSC (**III**)

D-H…A	**D-H** (Å)	**H…A**(Å)	**D…A**(Å)	**D-H…A** (°)	**Symmetry codes**
N2-H2N…N4	0.86	2.02	2.717(2)	138	Intramolecular
N5-H5N…S1	0.86	2.78	3.3660(16)	127	1-x,1/2+y,1/2-z
N5-H5N…N3	0.86	2.09	2.912(2)	160	1-x,1/2+y,1/2-z
C7-H7A…S1	0.98	2.55	3.073(2)	115	Intramolecular

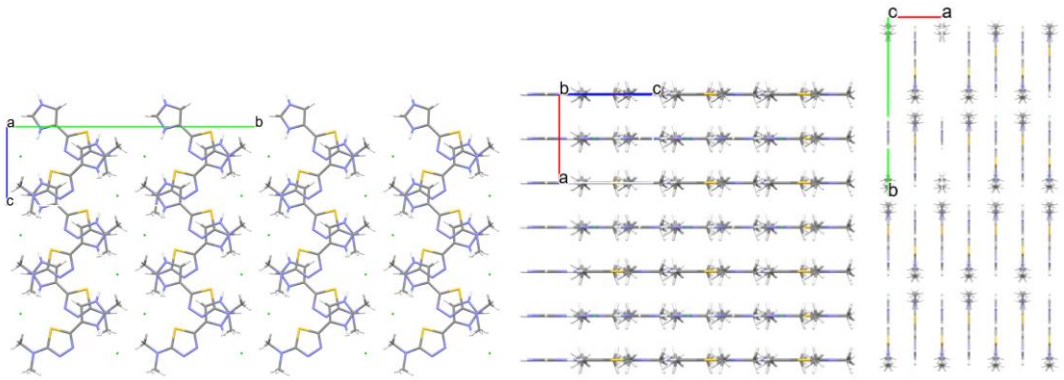


Figure S30. Packing arrangements in crystal imidazole-Me_2-TF×Cl (**IV**) viewed from the crystallographic directions 'a', 'b' and 'c'. The planar molecule lays in a mirror plane so that the CH3 hydrogen atoms are doubled and are treated with half occupancy in the refinement procedure. The imidazole-N is protonated and the positive charge of the molecule is neutralized by a chloride counter ion. The molecules are arranged in planes and beside the hydrogen bonds between chloride ion and imidazole hydrogens offset parallel stacking interactions are the main secondary interactions in the crystal.

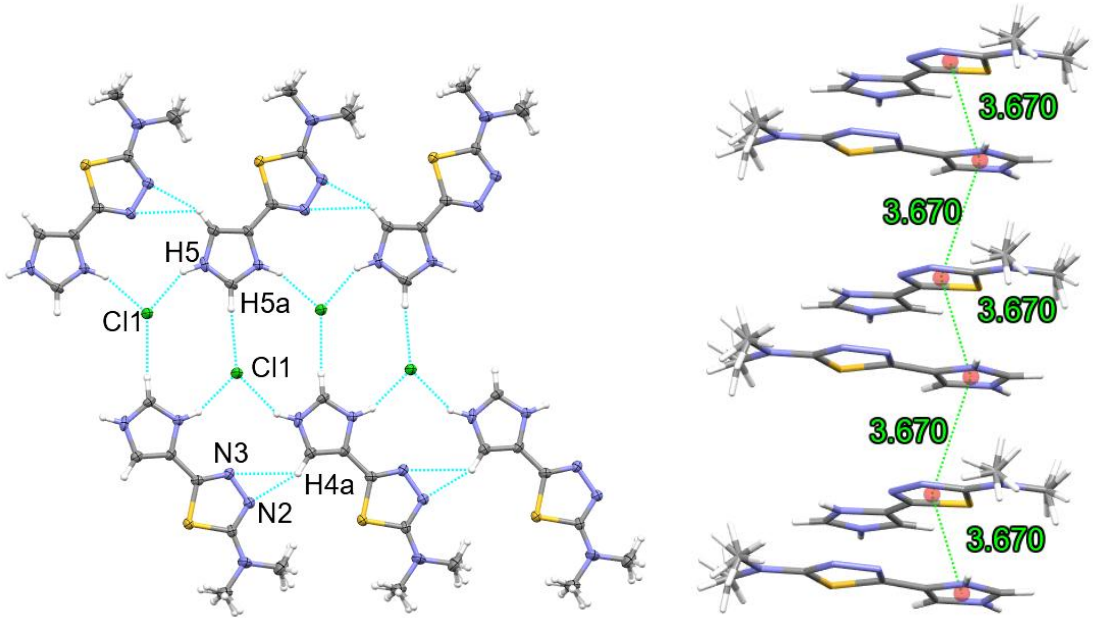


Figure S31. Packing arrangements showing the H-bond interactions (left) and parallel stacking interactions (right) in crystal imidazole-Me_2-TF×Cl (**IV**).

Table S7. Hydrogen-bond geometry of crystal imidazole-Me_2-TF×Cl (**IV**).

D-H…A	**D-H** (Å)	**H…A**(Å)	**D…A**(Å)	**D-H…A** (°)	**Symmetry codes**
N4-H4…Cl1	0.88	2.20	3.033(5)	158	A.U.
N5-H5…Cl1	0.88	2.23	3.024(5)	150	x,y,-1+z
C4-H4A…N2	0.95	2.30	3.179(8)	154	x,y,-1+z
C5-H5A…Cl1	0.95	2.53	3.477(5)	175	1-x,-y,-1/2+z
C6-H6B…N2	0.98	2.40	2.810(8)	105	Intramolecular
C7-H7A…S1	0.98	2.63	3.035(7)	105	Intramolecular

Table S8. Comparison of selected bond distances and angles of imidazole-TSC, imidazole-Me-TSC and imidazole-Me_2-TSC in crystals **I**, **II** and **III**, respectively.

Atoms	Bond distances (Å)		
	imidazole-TSC	imidazole-Me-TSC	imidazole-Me_2-TSC
N1-C1	1.329(2)	1.319(2)	1.344(2)
C1-S1	1.696(2)	1.693(2)	1.691(2)
C1-N2	1.345(2)	1.362(2)	1.369(2)
N2-N3	1.381(2)	1.373(2)	1.378(2)
N3-C2	1.280(2)	1.287(2)	1.290(2)
C2-C3	1.445(2)	1.445(2)	1.440(2)
N1-C6	-	1.449(2)	1.467(2)
N1-C7	-	-	1.461(2)
Atoms	Torsion angles (°)		
C3-C2-N3-N2	179.9(3)	0.1(3)	0.0(3)
N3-N2-C1-S1	177.71(10)	177.72(12)	2.8(2)

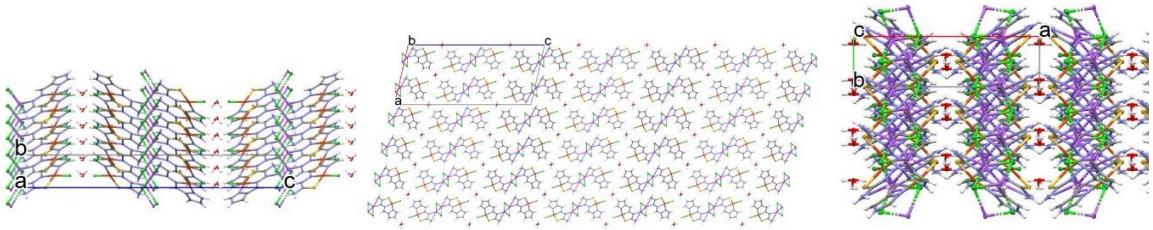


Figure 32. Packing arrangements in crystal [Cu(imidazole-TSCH$_{-1}$)Cl]×NaCl×H_2O (**V**) viewed from the crystallographic directions 'a', 'b' and 'c'.

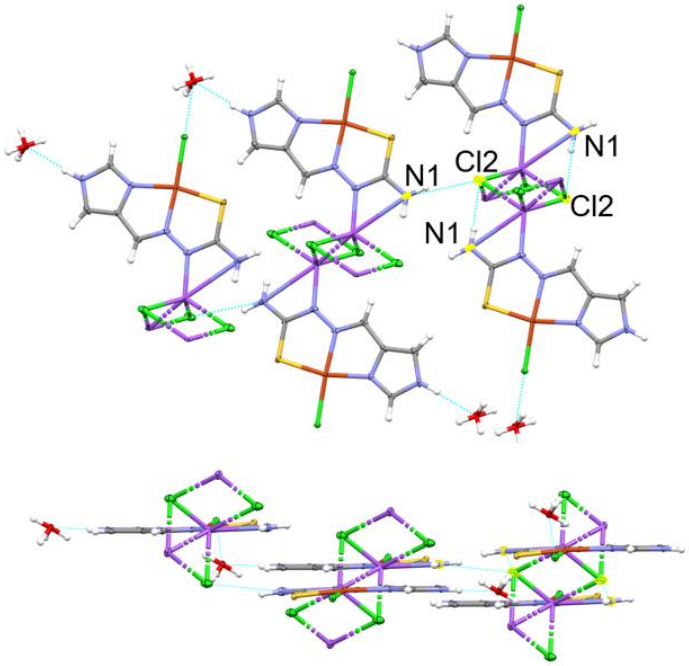
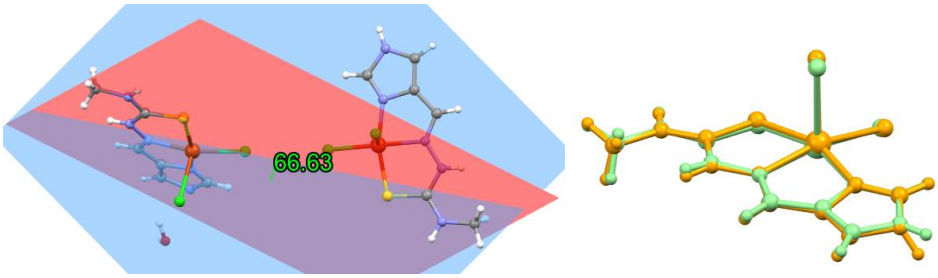


Figure S33. Packing arrangements showing the H-bond interactions in crystal [Cu(imidazole-TSCH$_{-1}$)Cl]×NaCl×H_2O (**V**) from two different views. The planar complexes are positioned slightly offset above and below each other, so that one apical position above the copper ion is 3.04 Å away from the sulfur atom of an adjacent complex.

Table S9. Hydrogen-bond geometry of crystal [Cu(imidazole-TSCH$_{-1}$)Cl]×NaCl×H_2O (**V**).

D-H…A	**D-H** (Å)	**H…A**(Å)	**D…A**(Å)	**D-H…A** (°)	**Symmetry operation**
N1-H1B…Cl2	0.91	2.40	3.260(9)	157	-1/2+x,-1/2+y,z
O1-H1C…N5	0.85	2.57	2.925(7)	107	1-x,-1+y,1/2-z
O1-H1D…Cl1	0.86	2.49	3.275(5)	153	1/2-x,1+y,1/2-z
N5-H5…O1	0.88	2.048	2.925(7)	174.9	x,1+y,z
C2-H2…Cl2	0.951	2.787	3.523(7)	134.9	x,1+y,z
C4-H4…S1	0.950	2.823	3.488(8)	127.8	1/2+x,1/2+y,z
C5-H5A…Cl1	0.950	2.757	3.381(7)	124.0	1/2-x,1+y,1/2-z



(a) (b)

Figure S34. Asymmetrical unit of crystal [Cu(imidazole-Me-TSC)Cl_2]×0.5H_2O (**VI**) showing (a) the ligand planes and angle closed between them and (b) comparison of the conformation of the two complexes by overlay (green Cu1, yellow Cu2 complex).

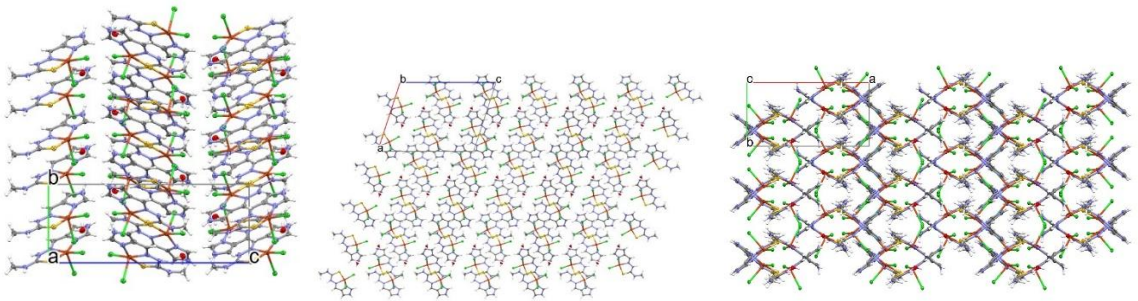


Figure S35. Packing arrangements in crystal [Cu(imidazole-Me-TSC)Cl_2]×0.5H_2O (**VI**) viewed from the crystallographic directions ’a’, ’b’ and ’c’.

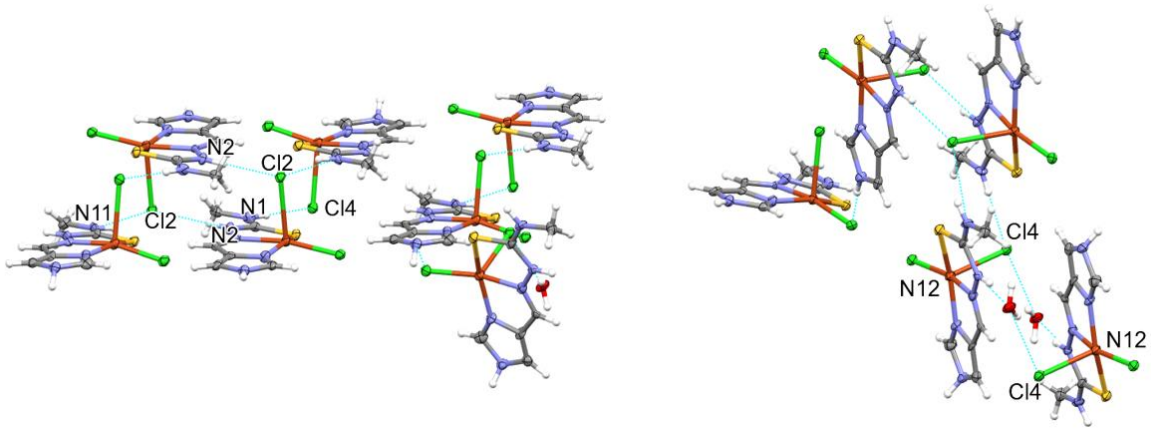


Figure S36. Packing arrangements showing the H-bond interactions in crystal **VI** from two different views.

Table 10. Hydrogen-bond geometry of crystal **VI.**

D-H…A	D-H (Å)	H…A(Å)	D…A(Å)	D-H…A (°)	Symmetry operation
N1-H1...Cl4	0.86	2.354	3.214(15)	180	x,1/2-y,1/2+z
O1-H1A...N12	0.85	2.5	2.79(2)	101	1-x,1-y,-z
O1-H1B...Cl4	0.85	2.46	3.015(14)	123	A.U.
N2-H2...Cl2	0.859	2.359	3.159(14)	155.2	x,1-y,1-z
N5-H5...Cl1	0.86	2.334	3.184(16)	169.8	-x,1/2+y,1/2-z
N11-H11...Cl2	0.86	2.424	3.223(15)	155.1	x,1/2-y,-1/2+z
N12-H12...O1	0.860	1.94	2.79(2)	168.5	1-x,1-y,-z
N15-H15...Cl3	0.87	2.728	3.286(16)	123.4	1-x,1/2+y,1/2-z
C4-H4...Cl3	0.93	2.822	3.491(19)	129.5	-x,1/2+y,1/2-z
C4-H4...S2	0.93	2.676	3.454(18)	141	-x,1/2+y,1/2-z
C5-H5A...Cl2	0.93	2.735	3.560(18)	148.1	-x,1/2+y,1/2-z
C6-H6C...Cl3	0.96	2.76	3.598(16)	147	x,3/2-y,1/2+z
C16-H16B...O1	0.96(4)	2.43	3.08(2)	126	1-x,1-y,-z

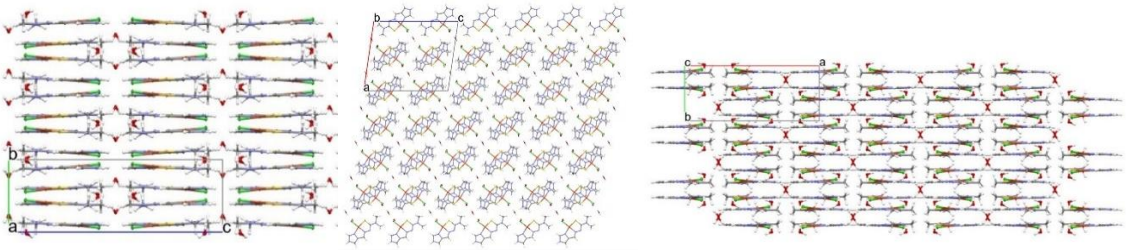


Figure S37. Packing arrangements in crystal [Cu(imidazole-Me_2-TSCH$_{-1}$)Cl]×1.5H_2O (**VII**) viewed from the crystallographic directions 'a', 'b' and 'c'.

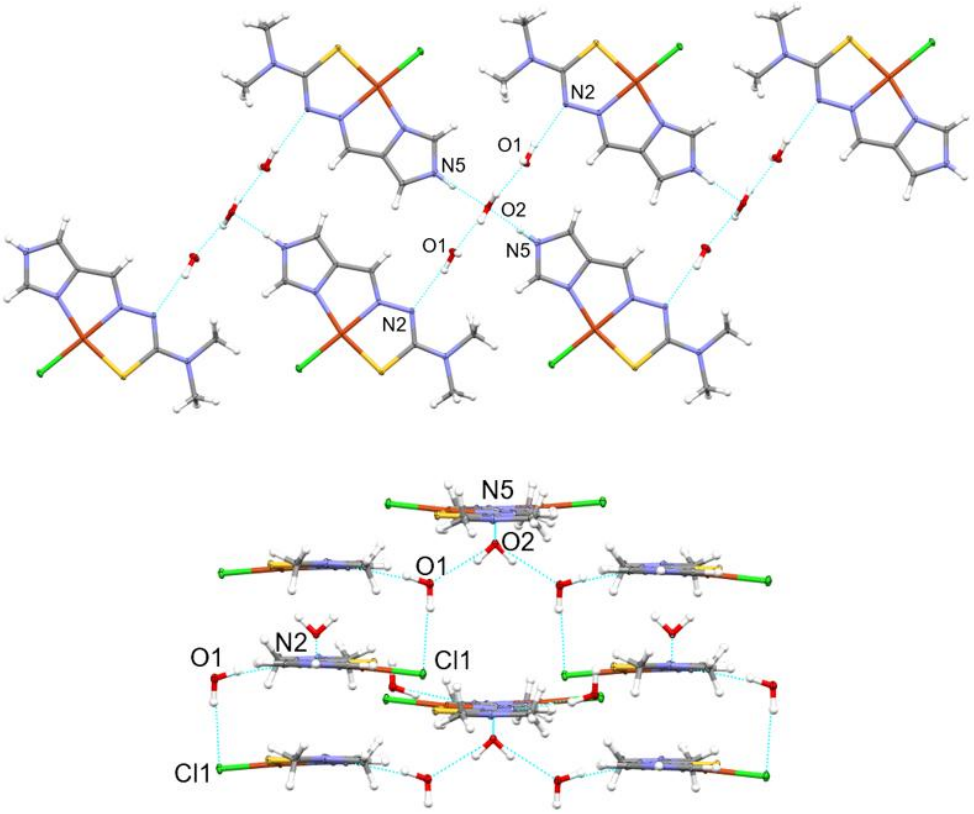


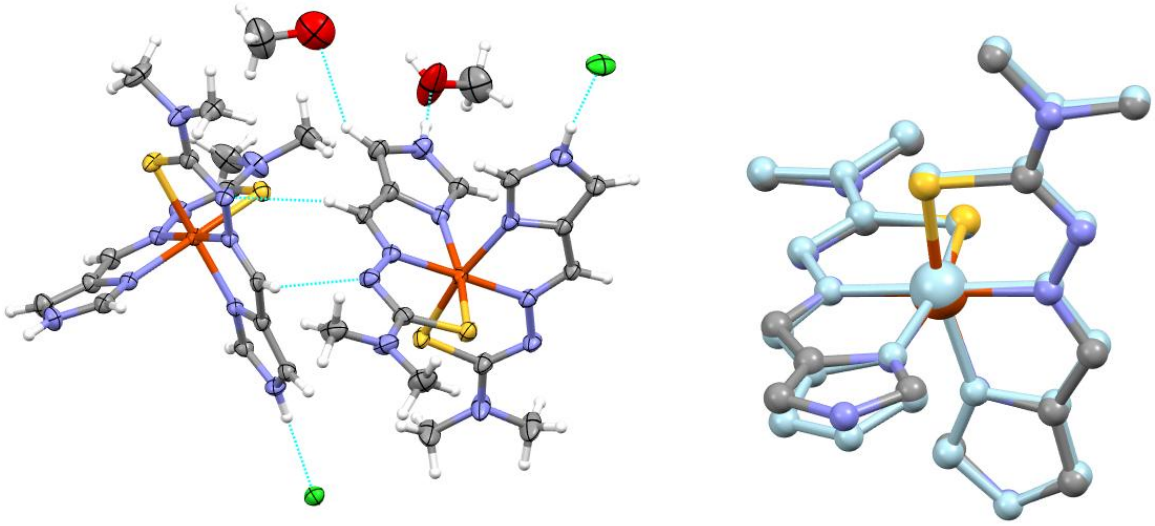
Figure S38. Packing arrangements showing the H-bond interactions in crystal [Cu(imidazole-Me_2-$TSCH_{-1}$)Cl]×1.5H_2O (**VII**) from two different views.

Table S11. Hydrogen-bond geometry of crystal [Cu(imidazole-Me_2-$TSCH_{-1}$)Cl]×1.5H_2O (**VII**)

D-H…A	**D-H** (Å)	**H…A**(Å)	**D…A**(Å)	**D-H…A** (°)	**Symmetry operation**
O1-H1A...N2	0.850	2.123	1.955(3)	166.1	1/2-x,3/2-y,1/2-z
O1-H1B...Cl1	0.850	2.364	3.207(2)	171.8	1/2+x,2-y,z
O2-H2A...O1	0.850	1.900	2.716(2)	160.45	1/2-x,y,-z
N5-H5...O2	0.880	1.951	2.735(2)	147.8	A.U.
C4-H4...S1	0.950	2.781	3.588(3)	143.4	1/2+x,1-y,z
C7-H7A...S1	0.978	2.545	2.993(3)	107.9	Intramolecular

Table S12. Comparison of selected bond distances and angles of complexes [Cu(imidazole-TSCH$_{-1}$)Cl], [Cu(imidazole-Me-TSC)Cl$_2$] and [Cu(imidazole-Me$_2$-TSCH$_{-1}$)Cl] in crystals **V**, **VI** and **VII**, respectively.

Atoms	Bond distances (Å)		
	[Cu(imidazole-TSCH$_{-1}$)Cl]	[Cu(imidazole-Me-TSC)Cl$_2$]	[Cu(imidazole-Me$_2$-TSCH$_{-1}$)Cl]
N1-C1	1.323(9)	1.32(2)	1.342(3)
C1-S1	1.726(7)	1.718(16)	1.748(2)
C1-N2	1.345(9)	1.33(2)	1.327(3)
N2-N3	1.372(8)	1.380(18)	1.376(3)
N3-C2	1.285(9)	1.287(18)	1.287(3)
C2-C3	1.436(10)	1.41(2)	1.441(3)
N1-C6	-	1.42(2)	1.459(3)
N1-C7	-	-	1.457(3)
S1-Cu1	2.2589(19)	2.234(5)	2.2251(7)
Cu1-Cl1	2.2300(17)	2.253(5)	2.2405(8)
Cu1-N3	1.992(5)	2.017(12)	1.9742(19)
Cu1-N4	1.990(6)	1.979(13)	1.975(2)
Atomok	Torsion angle (°)		
C3-C2-N3-N2	179.8(6)	176.8(15)	-178.27(19)
N3-N2-C1-S1	-2.4(9)	3.3(19)	1.1(3)



(a) (b)

Figure S39. Asymmetrical unit of crystal [Fe(imidazole-Me$_2$-TSCH$_{-1}$)$_2$]×Cl×MeOH (**VIII**) showing (a) the two Fe(III) complexes with the two methanol and chloride counter ions and (b) comparison of the conformation of the two complexes by overlay (colored by element for Fe1 and blue for Fe2 complex).

Table S13 Selected bond distances in crystal [Fe(imidazole-Me_2-$TSCH_{-1}$)$_2$]×Cl×MeOH (**VIII**).

Atom	Bond distances (Å)	Atom	Bond distances (Å)
Fe1-S1	2.2153(9)	Fe2-S4	2.2146(9)
Fe1-S2	2.2240(8)	Fe2-N13	1.937(3)
Fe1-N8	1.933(2)	Fe2-N18	1.935(3)
Fe1-N2	1.987(3)	Fe2-N12	1.987(3)
Fe1-N3	1.932(2)	Fe2-N17	1.981(3)
Fe1-N7	1.976(2)	Fe2-S3	2.2143(9)

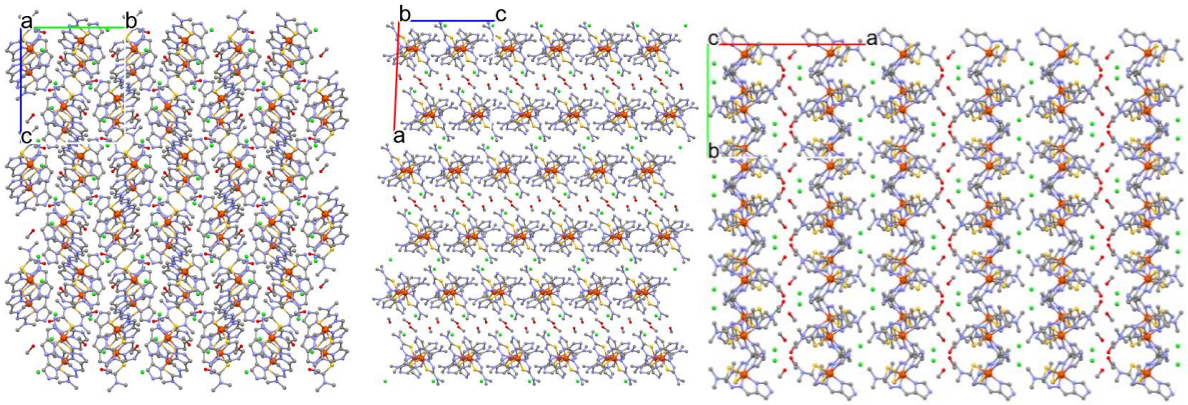


Figure S40. Packing arrangements in crystal [Fe(imidazole-Me_2-$TSCH_{-1}$)$_2$]×Cl×MeOH (**VIII**) viewed from the crystallographic directions 'a', 'b' and 'c'.

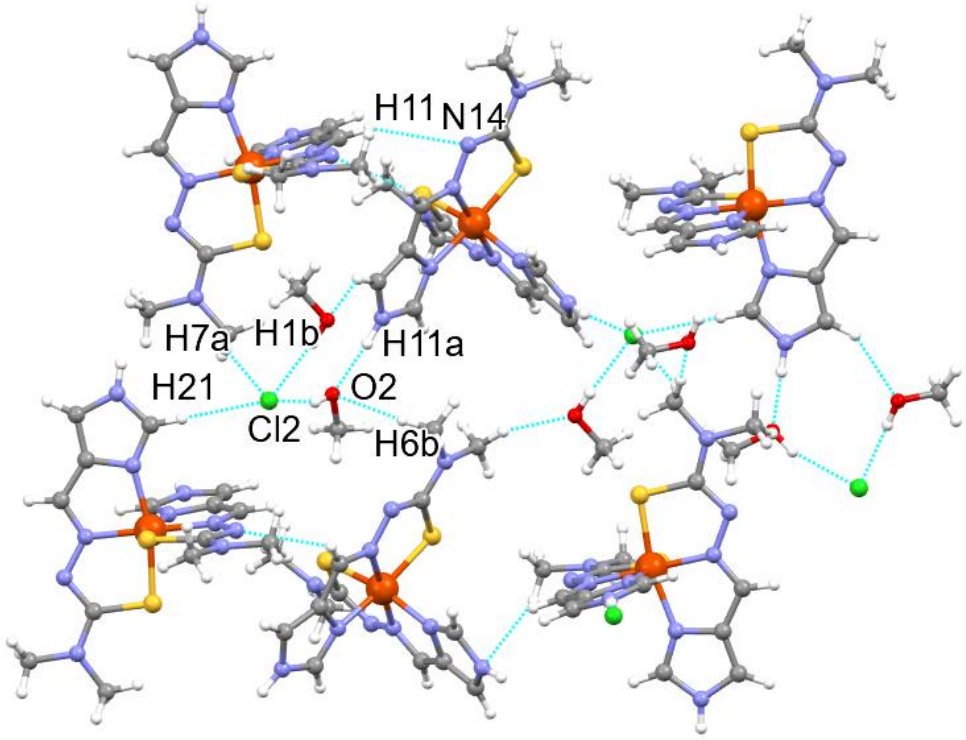


Figure S41. Packing arrangements showing the H-bond interactions in crystal [Fe(imidazole-Me_2-$TSCH_{-1}$)$_2$]×Cl×MeOH (**VIII**).

Table S14. Hydrogen-bond geometry of crystal [Fe(imidazole-Me_2-$TSCH_{-1})_2$]×Cl×MeOH (**VIII**).

D-H…A	**D-H** (Å)	**H…A**(Å)	**D…A**(Å)	**D-H…A** (°)	**Symmetry operation**
N1-H1…Cl1	0.88	2.192	3.054(1)	166.3	-x,-1/2+y,1/2-z
O1-H1B…Cl2	0.84	2.290	3.127(5)	176.0	A.U.
O2-H1A…Cl2	0.84	2.250	3.063(4)	164.0	A.U.
N6-H6…Cl1	0.88	2.232	3.111(3)	177.5	A.U.
N11-H11A…O2	0.88	1.811	2.688(5)	174.3	A.U.
N16-H16…Cl2	0.88	2.228	3.100(3)	171.2	1-x,1-y,-z
C1-H1A…Cl1	0.95	2.611	3.554(3)	172.3	x,1/2-y,-1/2+z
C7-H7A…Cl2	0.98	2.790	3.652(4)	147.7	A.U.
C7-H7B…S1	0.98	2.503	3.000(4)	111.2	Intra
C7-H7C…O1	0.98	2.560	3.510(7)	163.1	x,1/2-y,1/2+z
C8-H8…N14	0.95	2.420	3.317(4)	157.4	x,1/2-y,1/2+z
C14-H14B…S2	0.98	2.468	2.989(3)	113.0	Intra
C21-H21…Cl2	0.95	2.637	3.578(3)	171.0	1-x,1/2+y,1/2-z
C22-H22…O1	0.95	2.497	3.308(5)	143.4	A.U.
C27-H27A…S3	0.98	2.469	3.012(4)	114.7	Intra
C27-27A…Cl1	0.98	2.786	3.473(4)	127.7	-x,1/2+y,1/2-z
C28-H28…N4	0.95	2.324	3.263(4)	169.1	x,1/2-y,-1/2+z
C33-H33A…S4	0.98	2.512	2.998(5)	110.4	Intra

Table S15 Crystal data and structure refinement for crystals (**I**)-(**IV**).

Identification code	imidazole-TSC×H_2O (**I**)	imidazole-Me-TSC (**II**)	imidazole-Me_2-TSC (**III**)	imidazole-Me_2-TF×Cl (**IV**)
Empirical formula	$C_5H_9N_5SO$	$C_6H_9N_5S$	$C_7H_{11}N_5S$	$C_7H_{10}ClN_5S$
Formula weight	187.23	183.24	197.27	231.710
Temperature/K	111(2)	153(2)	103(2)	125(2)
Crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pbca$	$P2_1/c$	$Cmc2_1$
a/Å	10.8579(5)	9.6485(4)	9.4428(8)	6.6090(9)
b/Å	11.2199(4)	7.8052(3)	14.1585(11)	21.973(3)
c/Å	7.0701(3)	22.5205(8)	7.3587(7)	6.9687(8)
β/°	104.371(7)	90	108.425(8)	90
Volume/$Å^3$	834.36(7)	1695.98(11)	933.39(15)	1012.0(2)
Z	4	8	4	4
$\rho_{calc}g/cm^3$	1.491	1.435	1.404	1.521
μ/mm^{-1}	0.348	0.332	0.307	0.551
F(000)	392.0	768.0	416.0	481.3
Crystal size/mm^3	0.5 × 0.4 × 0.3	0.6 × 0.6 × 0.6	0.5 × 0.4 × 0.3	0.6 × 0.15 × 0.11
Radiation (λ)	MoKα (0.71075)	MoKα (0.71073)	MoKα (0.71073)	Mo Kα (0.71073)
2Θ range for data collection/°	6.97 to 54.96	6.954 to 54.966	6.506 to 54.924	6.44 to 54.92
Index ranges	$-14 \le h \le 14$, $-13 \le k \le 14$, $-9 \le l \le 9$	$-12 \le h \le 12$, $-10 \le k \le 10$, $-29 \le l \le 29$	$-12 \le h \le 12$, $-18 \le k \le 18$, $-9 \le l \le 9$	$-8 \le h \le 8$, $-28 \le k \le 28$, $-8 \le l \le 9$
Reflections collected	27511	60517	20832	10290
Indep. ref. (R_{int}, R_{sigma})	1913 (0.0268, 0.0140)	1941 (0.0357, 0.0095)	2135 (0.0658, 0.0511)	1222 (0.0497, 0.0483)
Data/restraints/parameters	1913/0/112	1941/0/110	2135/0/120	1222/1/87
Goodness-of-fit on F^2	1.193	1.229	1.145	1.083
Final R [I>=2σ (I)] (R1, wR_2)	0.0361, 0.0851	0.0411, 0.0938	0.0449, 0.0974	0.0444, 0.1009
Final R [all data] (R1, wR_2)	0.0381, 0.0861	0.0442, 0.0959	0.0559, 0.1019	0.0465, 0.1021
Largest diff. peak/hole / e $Å^{-3}$	0.51/-0.21	0.35/-0.24	0.41/-0.26	1.11/-0.34

Table S16. Crystal data and structure refinement for crystals (**V**)-(**VIII**)

Identification code	[Cu(imidazole-TSCH$_{-1}$)Cl]×NaCl×H$_2$O (**V**)	[Cu(imidazole-Me-TSC)Cl$_2$]×0.5H$_2$O (**VI**)	[Cu(imidazole-Me$_2$-TSCH$_{-1}$)Cl]×1.5H$_2$O (**VII**)	[Fe(imidazole-Me$_2$-TSCH$_{-1}$)2]×Cl×MeOH (**VIII**)
Empirical formula	$C_{10}H_{14}Cl_4Cu_2N_{10}Na_2OS_2$	$C_{12}H_{20}Cl_4Cu_2N_{10}OS_2$	$C_{14}H_{25}Cl_2Cu_2N_{10}O_3S_2$	$C_{15}H_{24}ClFeN_{10}OS_2$
Formula weight	669.303	653.393	643.549	515.854
Temperature/K	113(2)	103(2)	120(2)	103(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2$_1$/*c*	*I*2/*a*	*P*2$_1$/*c*
a/Å	15.3254(12)	15.4545(15)	17.136(4)	20.1353(7)
b/Å	4.0308(4)	7.6025(7)	6.8880(14)	14.3233(4)
c/Å	34.173(3)	20.508(2)	20.579(5)	15.9141(5)
β/°	102.906(7)	108.077(8)	98.284(9)	92.489(7)
Volume/Å^3	2057.6(3)	2290.7(4)	2403.7(10)	4585.4(3)
Z	4	4	4	8
ρ_{calc}g/cm^3	2.161	1.895	1.778	1.494
μ/mm^{-1}	2.862	2.535	2.205	0.985
F(000)	1335.1	1318.8	1313.7	2143.2
Crystal size/mm^3	0.25 × 0.1 × 0.1	0.5 × 0.2 × 0.2	0.5 × 0.25 × 0.1	0.5 × 0.5 × 0.2
Radiation (λ)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71075)
2Θ range for data collection/°	10.48 to 50.68	6.04 to 50.7	6.24 to 54.96	6.04 to 54.96
Index ranges	-19 ≤ h ≤ 19, -5 ≤ k ≤ 5, -44 ≤ l ≤ 44	-18 ≤ h ≤ 18, -9 ≤ k ≤ 9, -24 ≤ l ≤ 24	-22 ≤ h ≤ 22, -8 ≤ k ≤ 8, -26 ≤ l ≤ 26	-28 ≤ h ≤ 28, -20 ≤ k ≤ 20, -22 ≤ l ≤ 22
Reflections collected	14893	53400	26300	229198
Indep. ref. (R_{int}, R_{sigma})	1878 (0.1506, 0.0912)	4187 (0.2117, 0.1044)	2742 (0.0549, 0.0288)	10506 (0.0858, 0.0379)

Data/restraints/parameters	1878/0/152	4187/0/282	2742/0/152	10506/0/553
Goodness-of-fit on F^2	1.120	1.081	1.085	1.077
Final R [I>=2σ (I)] (R1, wR_2)	0.0648, 0.0971	0.1478, 0.3375	0.0336, 0.0670	0.0543, 0.1151
Final R [all data] (R1, wR_2)	0.1009, 0.1065	0.1895, 0.3683	0.0417, 0.0697	0.0685, 0.1212
Largest diff. peak/hole / e $Å^{-3}$	1.44/-1.39	4.23/-1.51	0.68/-0.50	1.74/-0.73