Supplementary Material

Characterization of tioconazole mesylate. Single crystal X-ray diffraction, Hirshfeld surface analysis, stability and DFT-assisted infrared spectral assignment

Aldana B. Moroni,[a,b,§] María Florencia Silveira[a] and Natalia L. Calvo[a,b,*]

[a]Instituto de Química Rosario "Dr. Edmundo A. Rúveda" (IQUIR, CONICET-UNR), Suipacha 531, Rosario S2002LRK, Argentina; [b]Área de Análisis de Medicamentos, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, Rosario S2002LRK, Argentina; [§]Present address: Instituto de Investigaciones en Ingeniería Ambiental, Química y Biotecnología Aplicada (INGEBIO), Av. Pellegrini 3314, Rosario S2002QEO, Argentina

Email: calvo@iquir-conicet.gov.ar

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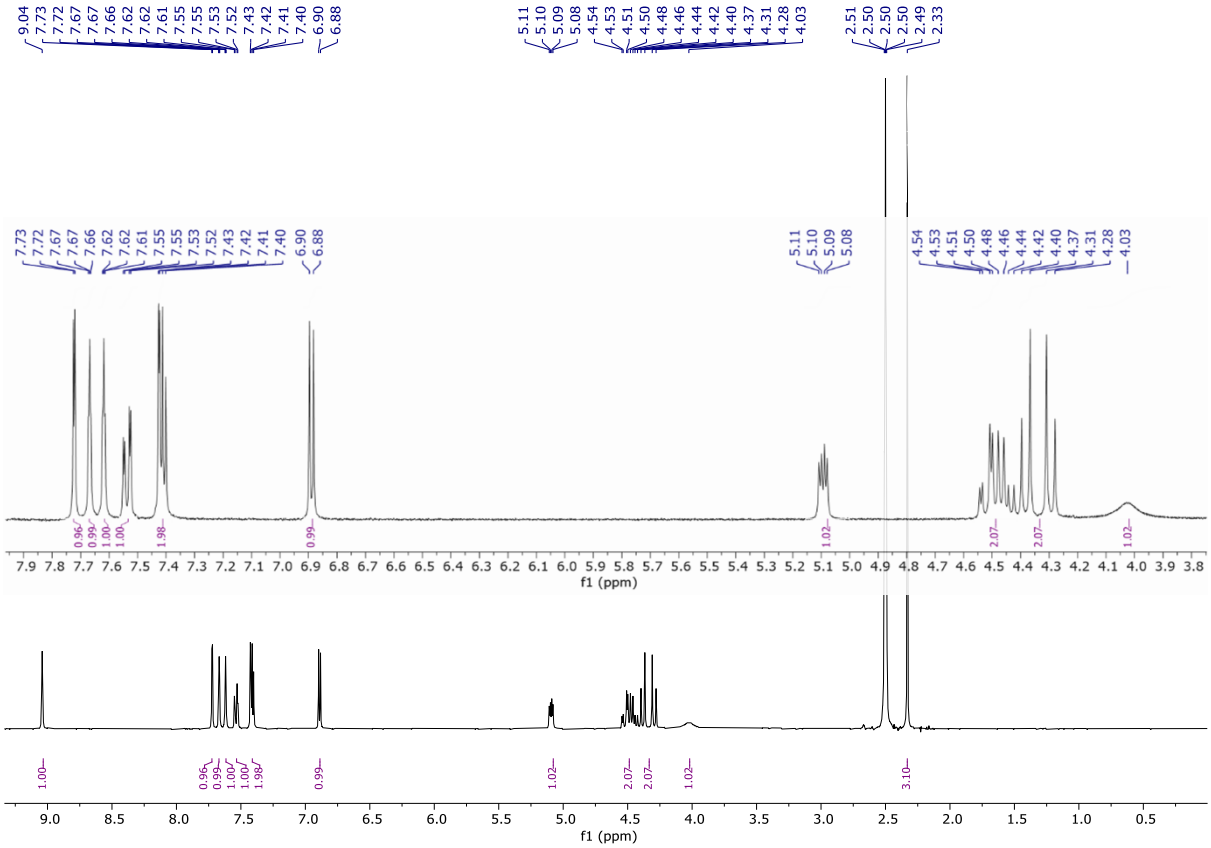

Figure S1. 400 MHz ^{1}H NMR spectrum of TCZ-Ms in DMSO-d_6 and expansion (3.7-8.0 ppm).

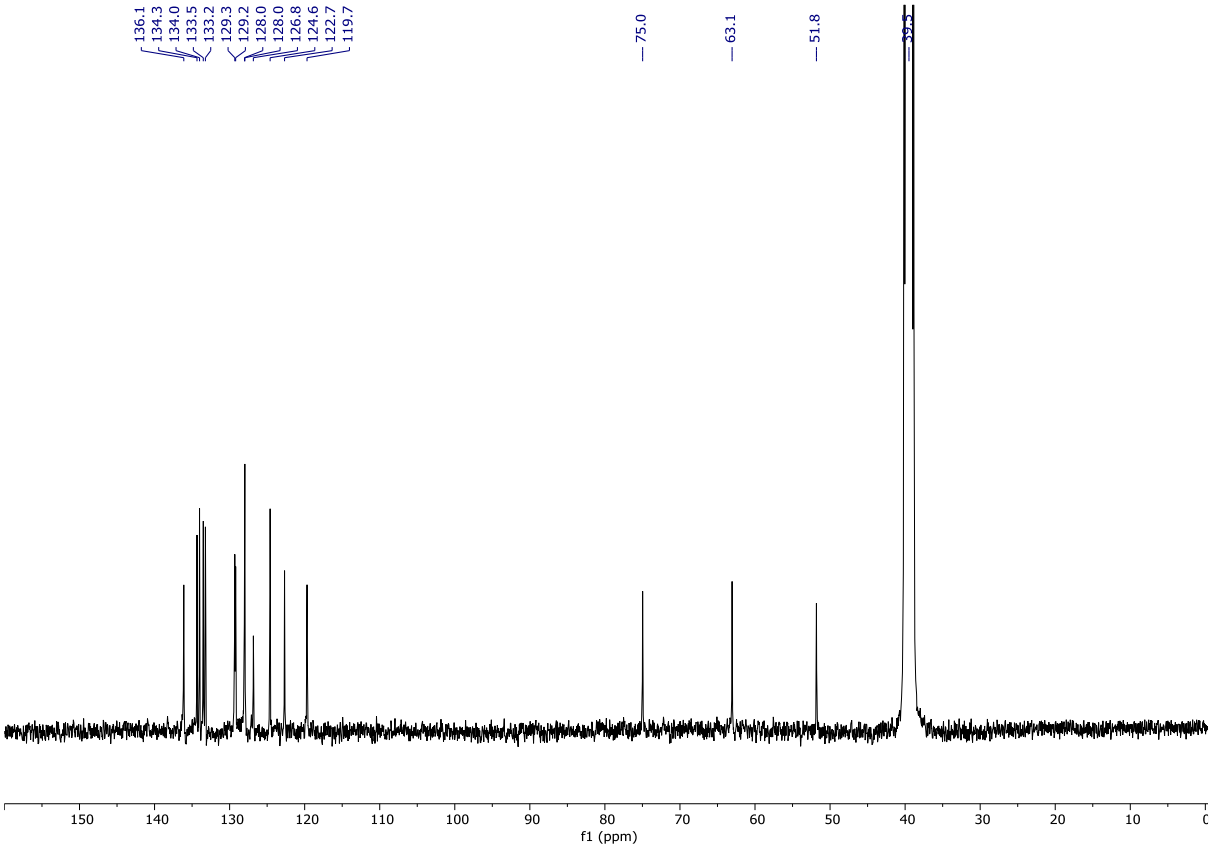

Figure S2. 100 MHz ^{13}C NMR spectrum of TCZ-Ms in DMSO-d_6.

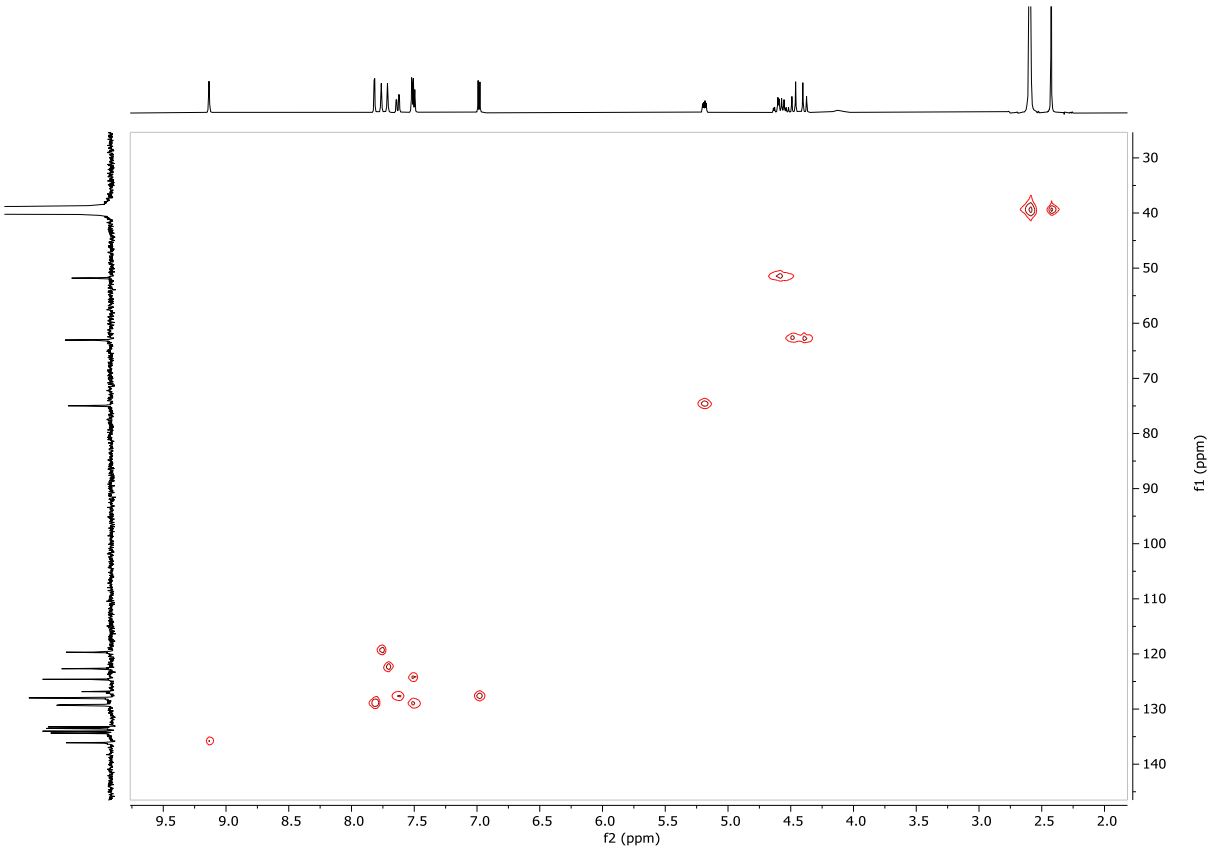

Figure S3. HSQC spectrum of TCZ-Ms in DMSO-d_6.

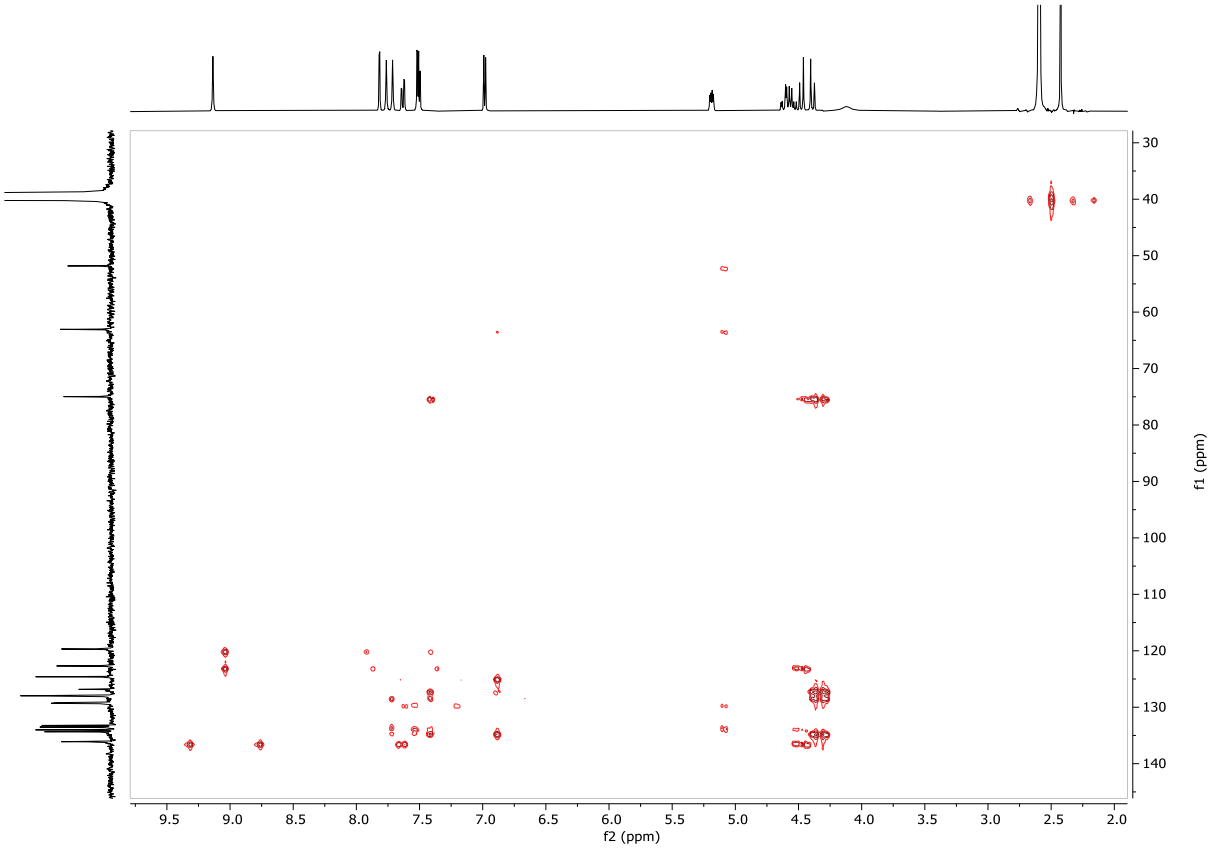

Figure S4. HMBC spectrum of TCZ-Ms in DMSO-d_6.

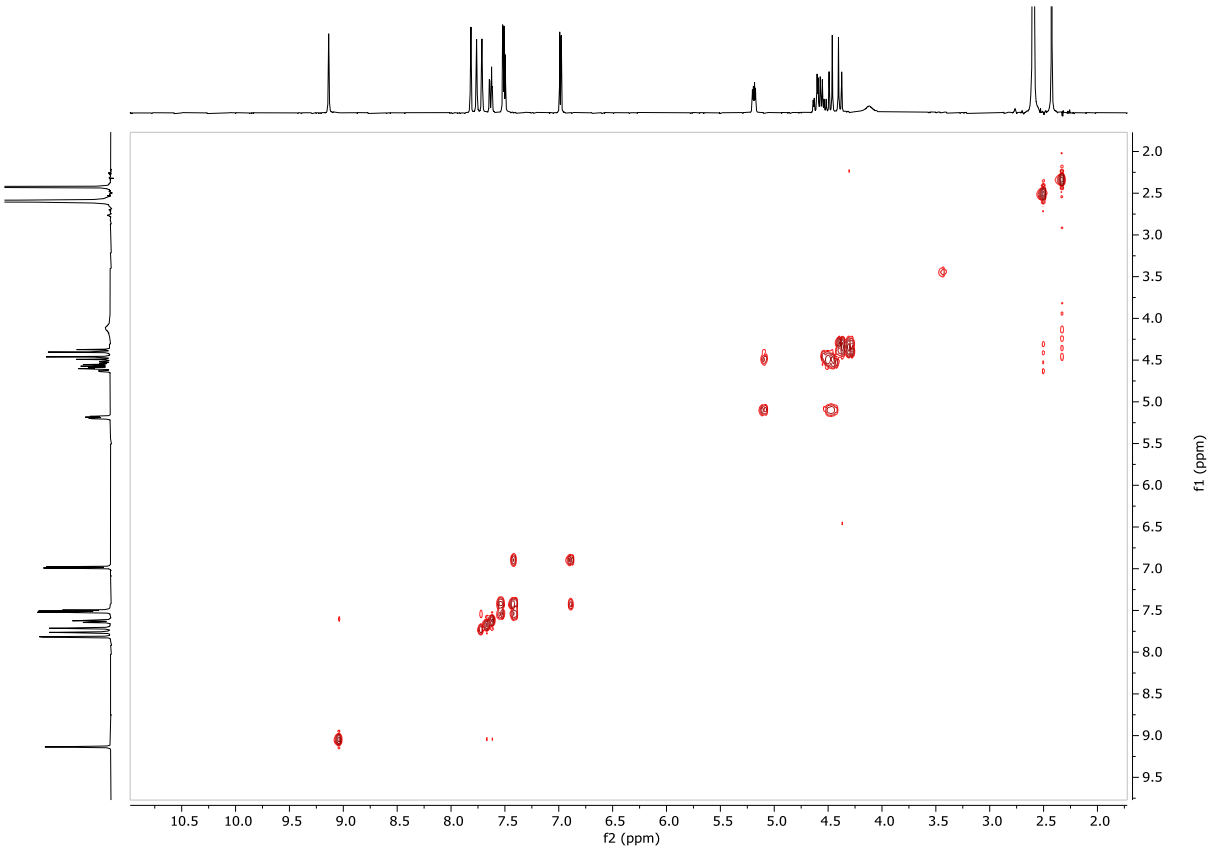

Figure S5. COSY spectrum of TCZ-Ms in DMSO-d_6.

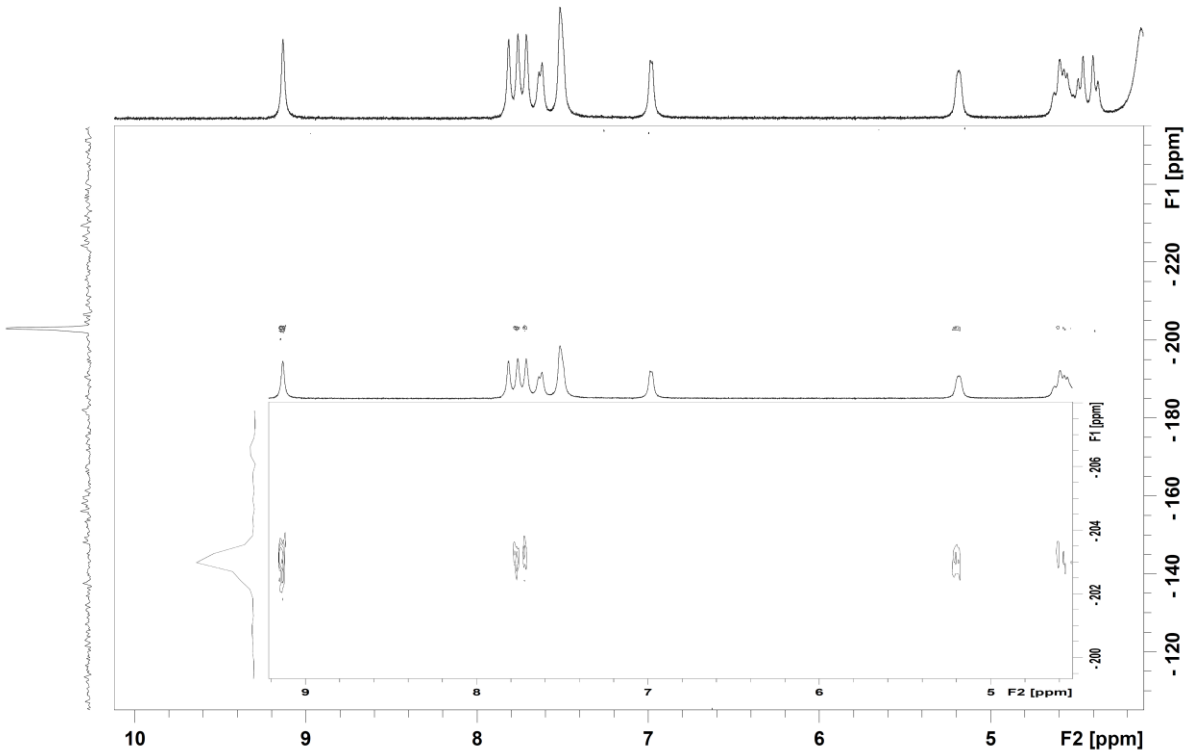

Figure S6. ^{15}N HMBC spectrum of TCZ-Ms in DMSO-d_6 and expanded view of y-axis.

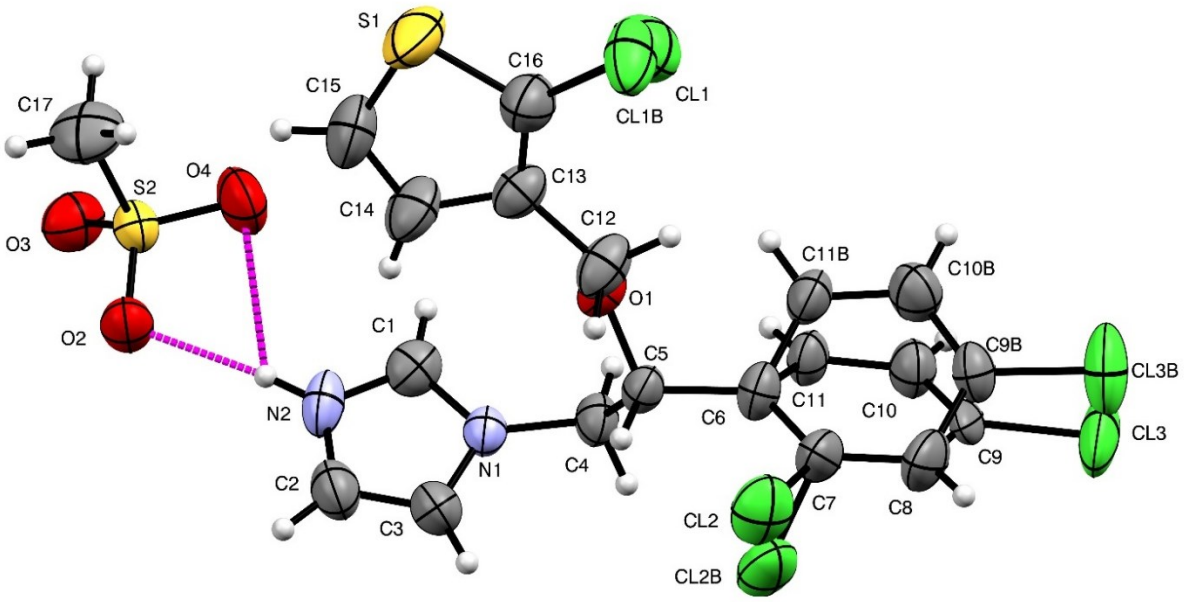

Figure S7. ORTEP representation and atom numbering of TCZ-Ms, with displacement ellipsoids drawn with a 50% probability level.

Tables S1-4. Crystallographic tables of TCZ-Ms. Bond lengths, angles, torsions and H-bonds.

Table S1. Hydrogen bonds of TCZ-Ms at 289 K [Å and °]

D—H···A	*d(D—H)*	*d(H···A)*	*d(D···A)*	*<(D—H···A)*
C10[a]-H10[a]···S1[i]	0.93	2.95	3.659(8)	133.7
$C10_B$[b]-$H10_B$[b]···S1[i]	0.93	2.97	3.549(8)	121.8
C4-$H4_A$···O3[ii]	0.97	2.47	3.423(5)	168.6
C4-$H4_B$···O3[iii]	0.97	2.48	3.319(5)	144.9
C15-H15···O2[v]	0.93	2.56	3.420(5)	153.0
C1-H1···O4[ii]	0.93	2.38	3.221(5)	149.9
C2-H2···O4[vi]	0.93	2.62	3.176(5)	118.6
N2-H2N···O2	0.86	1.95	2.804(4)	173.4
N2-H2N···O4	0.86	2.61	3.180(5)	125.3
C12-$H12_B$···Cl1[a/vi]	0.97	2.84	3.810(7)	174.3
C17-$H17_B$···O2[v]	0.96	2.63	3.375(5)	134.5
C11-H11···O3[ii]	0.93	2.55	3.463(8)	165.8

Symmetry transformations used to generate equivalent atoms: (i) x, -y+2, z+1/2; (ii) -x+3/2, -y+3/2, -z+1; (iii) -x+3/2, -y+1/2, -z+1; (iv) -x+1, -y, -z+1; (v) -x+3/2, y+1/2, -z+1/2; (vi) x, y-1, z.

[a] Partition 1.

[b] Partition 2.

Table S2. Bond distances of TCZ-Ms at 289 K [Å].

Atoms	*Distance*	*Atoms*	*Distance*
Cl2-C7	1.902(5)	C5-H5	0.9800
Cl3-C9	1.760(13)	C8-C7	1.387(5)
Cl1-C16	1.716(7)	C8-H8	0.9300
C10-C9	1.370(16)	C14-C15	1.340(5)
C10-C11	1.379(10)	C14-C13	1.454(5)
C10-H10	0.9300	C14-H14	0.9300
C11-C6	1.354(8)	C15-S1	1.678(5)
C11-H11	0.9300	C15-H15	0.9300
C9-C8	1.141(15)	O1-C12	1.421(4)
$Cl2_B$-C7	1.677(5)	N1-C1	1.335(4)
$Cl3_B$-$C9_B$	1.723(13)	C1-N2	1.317(5)
$Cl1_B$-C16	1.759(6)	C1-H1	0.9300
$C10_B$-$C9_B$	1.361(15)	C2-N2	1.348(5)
$C10_B$-$C11_B$	1.387(10)	C2-H2	0.9300
$C10_B$-$H10_B$	0.9300	N2-H2N	0.8600
$C11_B$-C6	1.496(9)	O2-S2	1.455(3)
$C11_B$-$H11_B$	0.9300	S1-C16	1.718(4)
$C9_B$-C8	1.530(13)	S2-O4	1.441(3)
C3-C2	1.335(5)	S2-C17	1.754(4)
C3-N1	1.372(5)	C6-C7	1.346(5)
C3-H3	0.9300	C12-C13	1.498(5)
O3-S2	1.435(2)	$C12-H12_A$	0.9700
C4-N1	1.467(4)	$C12-H12_B$	0.9700
C4-C5	1.514(4)	C13-C16	1.326(5)
$C4-H4_A$	0.9700	$C17-H17_A$	0.9600
$C4-H4_B$	0.9700	$C17-H17_B$	0.9600
C5-O1	1.423(4)	$C17-H17_C$	0.9600
C5-C6	1.515(4)		

Table S3. Bond angles of TCZ-Ms at 289 K [°].

Angle	*Value*	*Angle*	*Value*
C9-C10-C11	118.5(9)	C7-C8-H8	119.1
C9-C10-H10	120.8	C15-C14-C13	112.1(4)
C11-C10-H10	120.8	C15-C14-H14	123.9
C6-C11-C10	121.9(6)	C13-C14-H14	123.9
C6-C11-H11	119.1	C14-C15-S1	113.4(3)
C10-C11-H11	119.1	C14-C15-H15	123.3
C8-C9-C10	120.9(11)	S1-C15-H15	123.3
C8-C9-Cl3	121.9(10)	C12-O1-C5	114.3(3)
C10-C9-Cl3	117.1(10)	C1-N1-C3	108.1(3)
$C9_B$-$C10_B$-$C11_B$	119.8(9)	C1-N1-C4	126.5(3)
$C9_B$-$C10_B$-$H10_B$	120.1	C3-N1-C4	125.3(3)
$C11_B$-$C10_B$-$H10_B$	120.1	N2-C1-N1	107.4(3)
$C10_B$-$C11_B$-C6	120.3(7)	N2-C1-H1	126.3
$C10_B$-$C11_B$-$H11_B$	119.8	N1-C1-H1	126.3
C6-$C11_B$-$H11_B$	119.8	C3-C2-N2	107.0(4)
$C10_B$-$C9_B$-C8	120.4(9)	C3-C2-H2	126.5
$C10_B$-$C9_B$-$Cl3_B$	121.6(9)	N2-C2-H2	126.5
C8-$C9_B$-$Cl3_B$	117.6(8)	C1-N2-C2	110.1(3)
C2-C3-N1	107.3(4)	C1-N2-H2N	124.9
C2-C3-H3	126.3	C2-N2-H2N	124.9
N1-C3-H3	126.3	C15-S1-C16	90.5(2)
N1-C4-C5	110.4(3)	O3-S2-O4	113.80(17)
N1-C4-$H4_A$	109.6	O3-S2-O2	112.26(16)
C5-C4-$H4_A$	109.6	O4-S2-O2	110.81(17)
N1-C4-$H4_B$	109.6	O3-S2-C17	105.8(2)
C5-C4-$H4_B$	109.6	O4-S2-C17	106.6(2)
$H4_A$-C4-$H4_B$	108.1	O2-S2-C17	107.0(2)
O1-C5-C4	106.2(2)	C7-C6-C11	110.3(4)

Angle	*Value*	*Angle*	*Value*
O1-C5-C6	113.8(3)	C7-C6-C11*B*	116.5(4)
C4-C5-C6	109.9(3)	C7-C6-C5	124.2(3)
O1-C5-H5	108.9	C11-C6-C5	121.0(4)
C4-C5-H5	108.9	$C11_B$-C6-C5	116.6(4)
C6-C5-H5	108.9	C6-C7-C8	123.8(4)
C9-C8-C7	121.8(7)	C6-C7-$Cl2_B$	116.7(3)
C7-C8-$C9_B$	115.6(6)	C8-C7-$Cl2_B$	113.5(3)
C9-C8-H8	119.1	C6-C7-Cl2	115.7(3)
C8-C7-Cl2	117.5(3)	C13-C16-S1	113.9(3)
O1-C12-C13	108.6(3)	Cl1-C16-S1	122.9(3)
O1-C12-$H12_A$	110.0	C13-C16-$Cl1_B$	129.2(4)
C13-C12-$H12_A$	110.0	S1-C16-$Cl1_B$	115.6(3)
O1-C12-$H12_B$	110.0	S2-C17-$H17_A$	109.5
C13-C12-$H12_B$	110.0	S2-C17-$H17_B$	109.5
$H12_A$-C12-$H12_B$	108.4	$H17_A$-C17-$H17_B$	109.5
C16-C13-C14	110.0(3)	S2-C17-$H17_C$	109.5
C16-C13-C12	126.6(4)	$H17_A$-C17-$H17_C$	109.5
C14-C13-C12	123.3(4)	$H17_B$-C17-$H17_C$	109.5
C13-C16-Cl1	121.9(4)		

Table S4. Torsion angles [°] for TCZ-Ms.

Torsion angle	*Value*	*Torsion angle*	*Value*
C(9)-C(10)-C(11)-C(6)	5.7(14)	C(4)-C(5)-C(6)-C(7)	-115.3(4)
C(11)-C(10)-C(9)-C(8)	3.2(16)	O(1)-C(5)-C(6)-C(11)	-80.3(6)
C(11)-C(10)-C(9)-Cl(3)	178.5(7)	C(4)-C(5)-C(6)-C(11)	38.7(6)
C(9B)-C(10B)-C(11B)-C(6)	-2.4(14)	O(1)-C(5)-C(6)-C(11B)	-35.2(5)
C(11B)-C(10B)-C(9B)-C(8)	-8.2(15)	C(4)-C(5)-C(6)-C(11B)	83.7(5)
C(11B)-C(10B)-C(9B)-Cl(3B)	179.6(8)	C(11)-C(6)-C(7)-C(8)	20.3(7)
N(1)-C(4)-C(5)-O(1)	-63.8(3)	C(11B)-C(6)-C(7)-C(8)	-22.4(7)
N(1)-C(4)-C(5)-C(6)	172.7(3)	C(5)-C(6)-C(7)-C(8)	176.6(4)
C(10)-C(9)-C(8)-C(7)	0.4(14)	C(11B)-C(6)-C(7)-Cl(2B)	-173.4(5)
Cl(3)-C(9)-C(8)-C(7)	-174.7(5)	C(5)-C(6)-C(7)-Cl(2B)	25.6(6)
C(10B)-C(9B)-C(8)-C(7)	4.2(12)	C(11)-C(6)-C(7)-Cl(2)	-179.9(5)
Cl(3B)-C(9B)-C(8)-C(7)	176.7(6)	C(5)-C(6)-C(7)-Cl(2)	-23.5(5)
C(13)-C(14)-C(15)-S(1)	-1.3(5)	C(9)-C(8)-C(7)-C(6)	-13.6(10)
C(4)-C(5)-O(1)-C(12)	157.5(3)	C(9B)-C(8)-C(7)-C(6)	12.1(8)
C(6)-C(5)-O(1)-C(12)	-81.5(3)	C(9B)-C(8)-C(7)-Cl(2B)	163.9(6)
C(2)-C(3)-N(1)-C(1)	-0.4(4)	C(9)-C(8)-C(7)-Cl(2)	-173.2(7)
C(2)-C(3)-N(1)-C(4)	177.6(3)	C(5)-O(1)-C(12)-C(13)	-153.6(3)
C(5)-C(4)-N(1)-C(1)	108.2(4)	C(15)-C(14)-C(13)-C(16)	1.8(5)
C(5)-C(4)-N(1)-C(3)	-69.4(4)	C(15)-C(14)-C(13)-C(12)	179.1(4)
C(3)-N(1)-C(1)-N(2)	0.3(4)	O(1)-C(12)-C(13)-C(16)	-130.1(4)
C(4)-N(1)-C(1)-N(2)	-177.7(3)	O(1)-C(12)-C(13)-C(14)	53.1(5)
N(1)-C(3)-C(2)-N(2)	0.4(4)	C(14)-C(13)-C(16)-Cl(1)	-169.3(4)
N(1)-C(1)-N(2)-C(2)	0.0(4)	C(12)-C(13)-C(16)-Cl(1)	13.5(6)
C(3)-C(2)-N(2)-C(1)	-0.2(4)	C(14)-C(13)-C(16)-S(1)	-1.6(5)
C(14)-C(15)-S(1)-C(16)	0.3(4)	C(12)-C(13)-C(16)-S(1)	-178.8(3)
C(10)-C(11)-C(6)-C(7)	-16.1(10)	C(14)-C(13)-C(16)-Cl(1B)	164.7(4)
C(10)-C(11)-C(6)-C(5)	-173.3(7)	C(12)-C(13)-C(16)-Cl(1B)	-12.4(7)
C(10B)-C(11B)-C(6)-C(7)	17.5(10)	C(15)-S(1)-C(16)-C(13)	0.8(4)
C(10B)-C(11B)-C(6)-C(5)	180.0(7)	C(15)-S(1)-C(16)-Cl(1)	168.4(4)
O(1)-C(5)-C(6)-C(7)	125.8(4)	C(15)-S(1)-C(16)-Cl(1B)	-167.5(3)

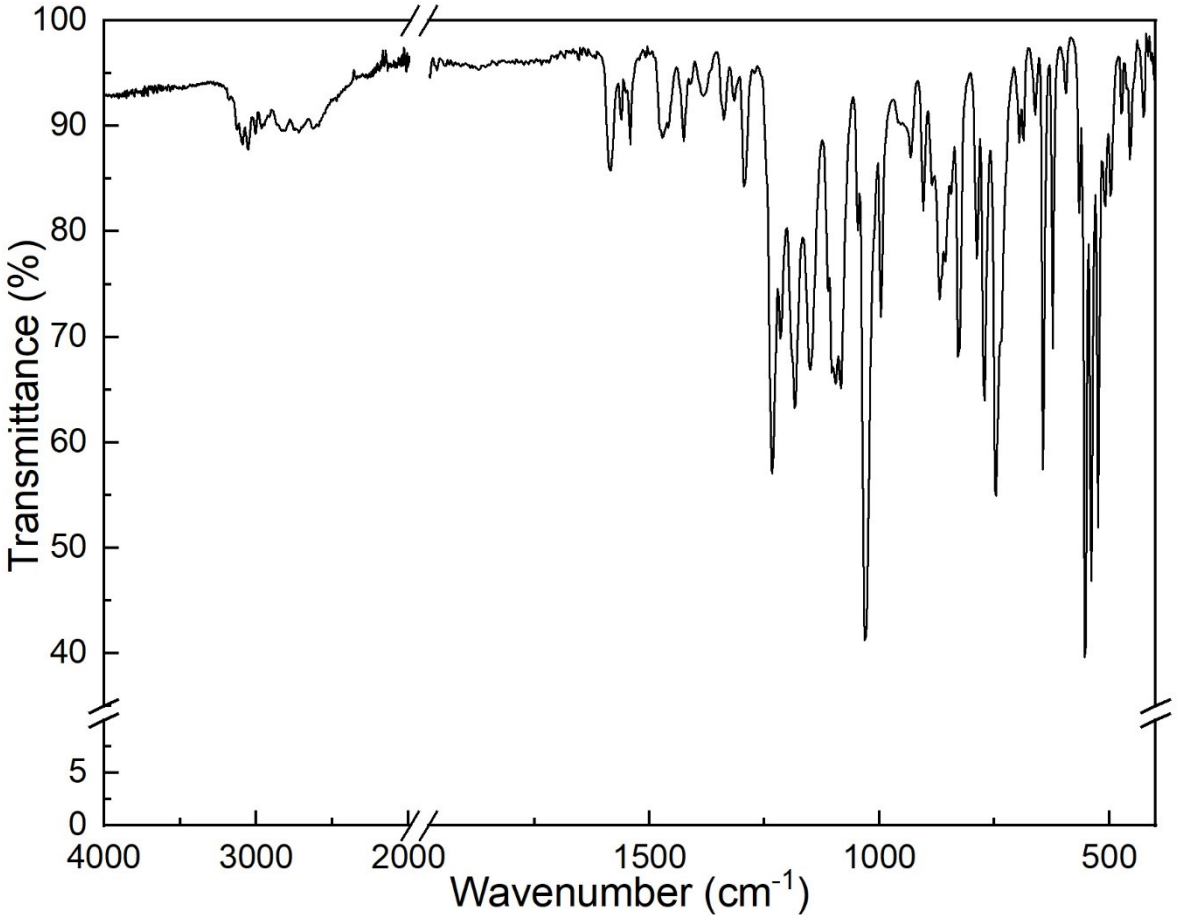

Figure S8. ATR/MIR spectrum of TCZ-Ms in the wavenumber range 400-4000 cm^{-1}.

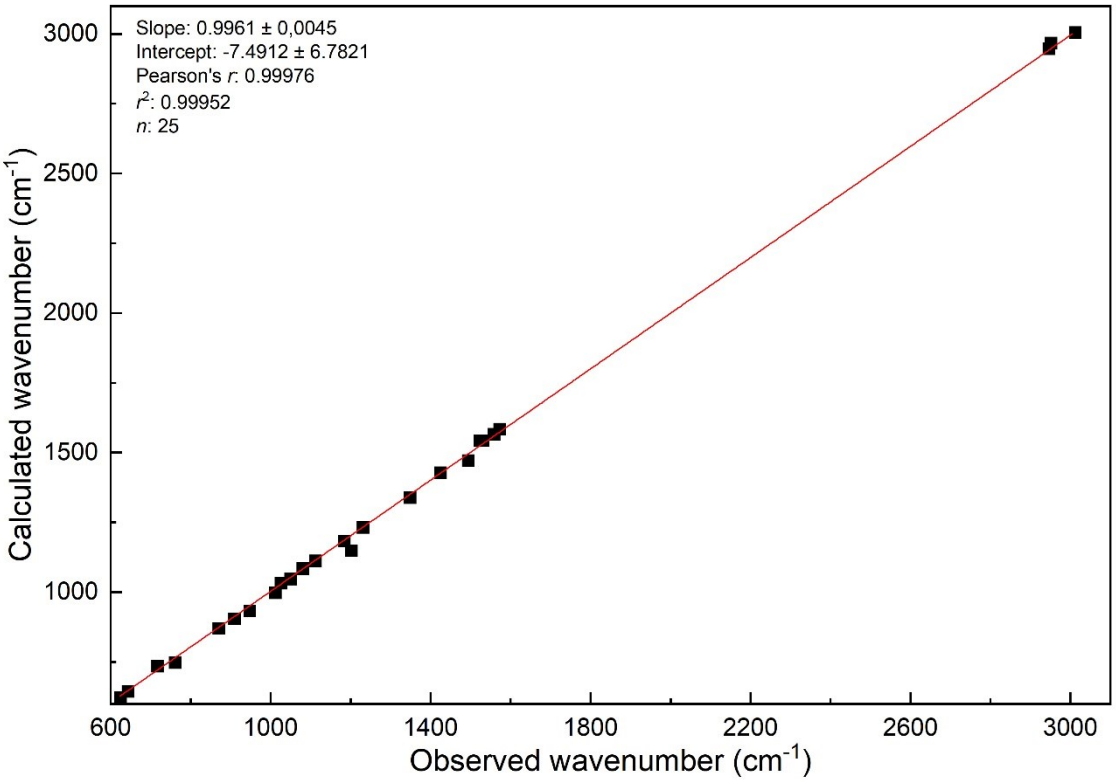

Figure S9. Correlation between observed and calculated vibrational frequencies of TCZ-Ms in the MIR region.

Table S5. Experimental ATR/MIR spectra of TCZ and TCZ-Ms along with the most relevant calculated bands for TCZ-Ms and their corresponding assignments.

Wavenumber (cm^{-1})			Assignment
TCZ	TCZ-Ms	TCZ-Ms (calcd.)[a]	
735, 692, 658, 629	747, 735, 644, 623	761, 717, 643, 625	γ_{C-H}, substitution pattern of aromatic rings
993, 907	997, 870	1012, 870	δ_{C-H}, aromatic ring
1098, 1067	1047	1050	ν_{C-O}, ether
-	932, 904	948, 910	$\nu_{S-O,}$ ν_{SO3-} (symmetric, asymmetric)
1118, 1030, 1022	1084	1081	ν_{C-N}, imidazole
-	1184, 1032	1184, 1026	$\nu_{S=O}$ (asymmetric, symmetric)
1562, 1433,	1543, 1338	1524, 1349	$\nu_{C=C}$, thiophene
1589, 1467, 1388, 1281, 1184, 1137	1565, 1543, 1427, 1231, 1149, 1112	1559, 1531, 1425, 1231, 1202, 1112	$\nu_{C=C}$, phenyl
1503	1472	1494	$\nu_{C=N}$, imidazole
-	1584	1573	ν_{N-H}, imidazole
2936, 2868 2885, 2949	3005, 2967, 2947	3012, 2952, 2946	ν_{C-H}, aliphatic (asymmetric, symmetric)
-	3178		ν_{N-H}, protonated imidazole

[a]The molecular geometries were optimized to their energy minima using Gaussian09W software.[1] All calculations were performed within the framework of density functional theory (DFT), employing the B3LYP functional in combination with the 6–311++G(d,p) basis set.[2] The absence of imaginary frequencies in the computed IR spectra confirmed that the optimized structures correspond to true minima on the potential energy surface. A frequency scaling factor of 0.9613 was applied.[3]

Table S6. Stability of TCZ-Ms. Main characteristics of the heating/cooling cycles.

Event	Cycle N°	1	2	4	8
Melting endotherm	T_{ons} (°C)	202.0	188.9	189.3	182.6
	T_{peak} (°C)	205.6	199.7	199.3	195.4
	T_{out} (°C)	210.0	205.5	204.4	201.8
	ΔH	-21.2	-16.4	-15.7	-12.4
	FWHM (°C)	3.6	5.8	4.9	7.3
Recrystallization exotherm	T_{ons} (°C)	119.3	113.7	116.0	109.9
	T_{peak} (°C)	113.7	108.4	109.1	102.1
	T_{out} (°C)	109.2	101.2	103.6	94.9
	ΔH	5.3	4.3	4.8	3.1
	FWHM (°C)	5.0	5.4	5.1	6.8

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