Supplementary Material for

Novel Tetradentate N_2O_2 water–soluble Schiff Base and its Al(III) complex: synthesis, structural characterization, and correlations between structure and stability against hydrolysis

Hajer Bouznif[1,2,*], Licínia L. G. Justino[2,*], Maria I. L. Soares[2], Telma Costa[2], M. Luísa Ramos[2], Timur Nikitin[2], Teresa M. V. D. Pinho e Melo[2], Nabil Zouari[1] , and Rui Fausto[2,3]

[1] *Laboratory Physico–Chemistry of the Solid State. Department of Chemistry. Faculty of Sciences of Sfax. B. P. 1171. Sfax 3000. University of Sfax. Tunisia*
[2] *CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga 3004-535 Coimbra, Portugal*
[3] *Faculty of Sciences and Letters. Department of Physics. Istanbul Kultur University. Ataköy Campus. Bakirköy 34156. Istanbul. Turkey*

Corresponding authors e-mails:

bouznifhajer13@gmail.com (Hajer Bouznif),

liciniaj@ci.uc.pt (Licínia L. G. Justino)

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Synthesis of the Schiff base SS and of 5-S-3-OMe

*Synthesis of N,N'-bis(5-sulfonatosalicylidene)-1,2-ethylenediamine disodium salt (Schiff base **SS**).* Sodium salicylaldehyde-5-sulfonate (**5-S**) was prepared according to a procedure described in the literature (Scheme I) [39]. A mixture of salicylaldehyde (3.66 g, 30.0 mmol) and aniline (3.56 mL, 39.0 mmol) in ethanol (25 mL) was heated at reflux for 2 h. After cooling to room temperature, the solvent was evaporated to give *N*-phenyl-salicylaldimine as a pale-yellow solid. Yield: 4.32 g (21.9 mmol, 73%). Then, *N*-phenyl-salicylaldimine (3.24 g, 16.5 mmol) was added to concentrated sulfuric acid (9 mL, 98 wt %), and the mixture was stirred at 100 ºC for 2 h. After cooling, the solution was slowly added to ice water with vigorous stirring and a yellowish solid precipitated. The mixture was reheated until all the solid was dissolved and then allowed to cool. *N*-Phenyl-salicylaldimine-5-sulfonic acid was obtained as a yellow precipitate, which was filtered, washed with ice water and ethanol, and dried under vacuum. Yield: 2.80 g (10.0 mmol, 61%). *N*-phenyl-salicylaldimine-5-sulfonic acid (2.30 g) was dissolved in boiling water (45 mL) and anhydrous sodium carbonate (0.75 g) was slowly added in small portions. After CO_2 evolution had ceased, aniline was removed by passing a continuous stream of air through the boiling solution for several hours, with water added as necessary to maintain the volume. After cooling, glacial acetic acid was slowly added up to pH 5 followed by addition of ethanol (50 mL). The mixture was cooled to 0 ºC to give sodium salicylaldehyde 5-sulfonate (**5-S**) as a yellow precipitate, which was filtered, washed with ethanol, and dried under vacuum. Yield: 1.61 g (7.2 mmol, 86%). ^{1}H NMR (D_2O, 400 MHz, Figure SI): δ (ppm) 10.05 (s, 1H), 8.20 (d, *J* = 2.4 Hz, 1H), 8.00 (dd, *J* = 2.4 and 8.8 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 1H). This data in accordance with that previously described for this compound [75]. To a suspension of compound **5-S** (112 mg, 0.5 mmol) in methanol (4 mL), a solution of 1,2-ethylenediamine (23 mg, 0.3 mmol) in ethanol (0.5 mL) was added dropwise, and the reaction mixture was stirred at 80 °C for 5 h. After cooling to room temperature, the precipitate was filtered and washed with methanol and diethyl ether to give **SS** as a yellow powder. Yield: 142 mg (0.3 mmol, 60%). ^{1}H NMR (DMSO-d_6, 400 MHz, Figure S11 (a)): δ (ppm) 13.61 (bs, 2H), 8.67 (s, 2H), 7.69 (s, 2H), 7.54 (d, *J* = 7.1 Hz, 2H), 6.80 (d, *J* = 7.1 Hz, 2H), 3.92 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz, Figure S11 (b)): δ (ppm) 167.4, 161.5, 139.6, 130.4, 129.4, 117.5, 116.3, 58.9. This data is consistent with that previously described for this compound [47,76].

*Synthesis of sodium 3-methoxy-salicylaldehyde-5-sulfonate (**5-S-3-OMe**).* Sodium 3-methoxy-salicylaldehyde-5-sulfonate (**5-S-3-OMe**) was prepared by a procedure similar to that used for **5-S** (Scheme I) [39]. A mixture of 3-methoxysalicaldehyde (4.56 g, 30.0 mmol) and aniline (3.6 mL, 39.0 mmol) in ethanol (25 mL) was heated at reflux for 2 h. After cooling to room temperature, the solvent was evaporated to give *N*-phenyl-3-methoxysalicylaldimine as an orange solid. Yield: 6.32 g (27.8 mmol, 93%). Then, *N*-phenyl-3-methoxysalicylaldimine (5.99 g, 26.4 mmol) was added to concentrated sulfuric acid (35 mL, 98 wt %), and the mixture was stirred at 100 ºC for 2 h. After cooling, the solution was slowly added to ice water with vigorous stirring and a yellowish solid precipitated. The mixture was reheated until all the solid was dissolved and then allowed to cool. *N*-Phenyl-3-methoxysalicylaldimine-5-sulfonic acid was obtained as a yellow precipitate, which was filtered, washed with ice water and ethanol, and dried under vacuum. Yield: 5.98 g (19.7 mmol, 75%). *N*-Phenyl-3-methoxysalicylaldimine-5-sulfonic acid (3.50 g) was dissolved in boiling water (62 mL) and anhydrous sodium carbonate (1.04 g) was slowly added in small portions. After CO_2 evolution had ceased, aniline was removed by passing a continuous stream of air through the boiling solution for several hours, with water added as necessary to maintain the volume. After cooling, glacial acetic acid was slowly added up to pH 5. The mixture was cooled to 0°C to give sodium 3-methoxy-salicylaldehyde-5-sulfonate (**5-S-3-OMe**) as an earthy yellow precipitate, which was filtered, washed with ethanol, and dried under vacuum. Yield: 2.69 g (10.6 mmol, 93%). ^{1}H NMR (D_2O, 400 MHz, Figure S12 (a)): δ (ppm) 10.06 (s, 1H), 7.71 (d, J = 2.2 Hz, 1H), 7.45 (d, J = 2.1 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (D_2O, 100 MHz, Figure S12 (b)) 196.4, 152.4, 148.2, 134.4, 121.3, 120.4, 114.4, 56.4. This data in accordance with that previously described for this compound [75].

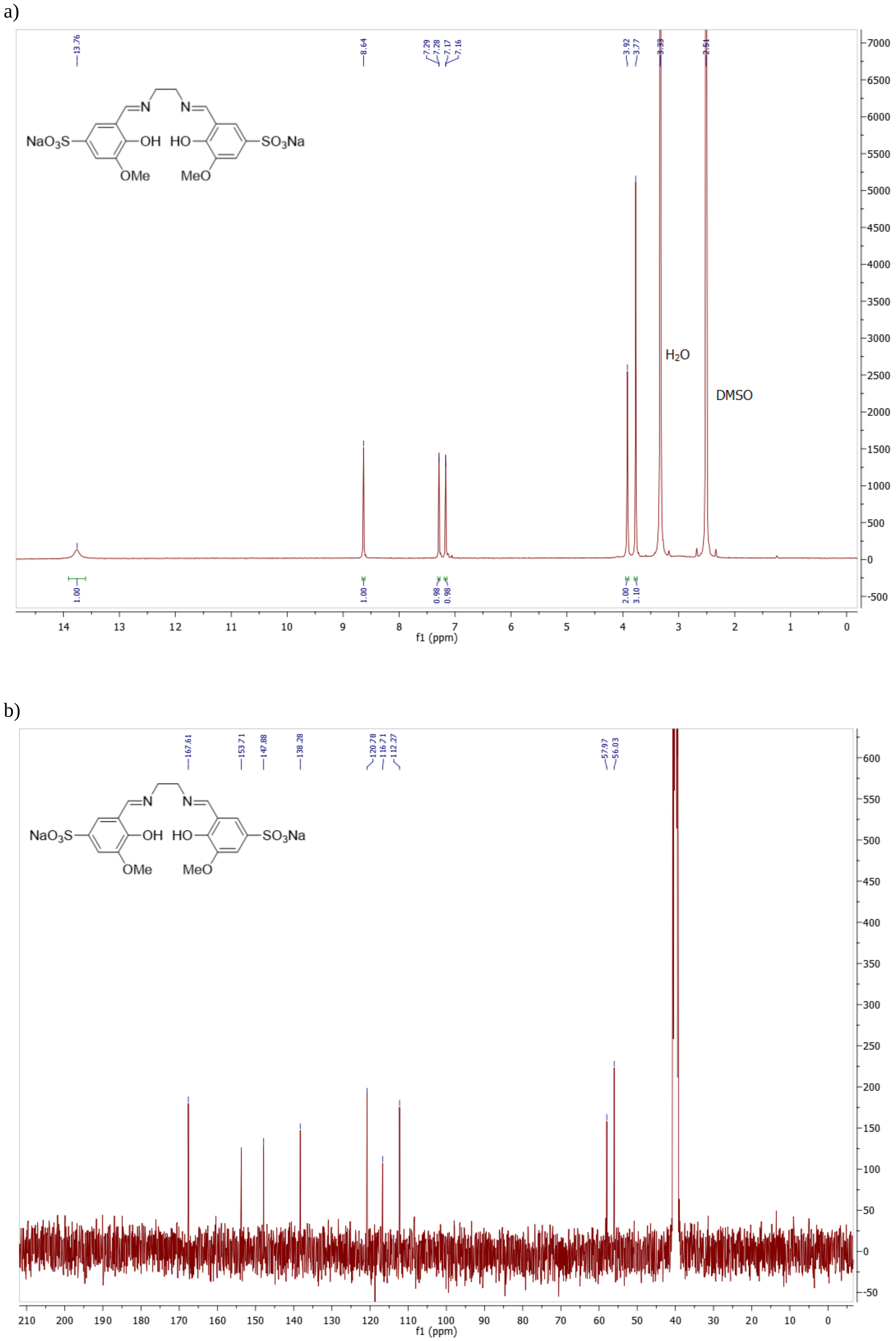


Figure S1. a) ^{1}H NMR spectrum of compound **MSS** (400 MHz, DMSO- d_6); b) ^{13}C NMR spectrum of compound **MSS** (100 MHz, DMSO- d_6).

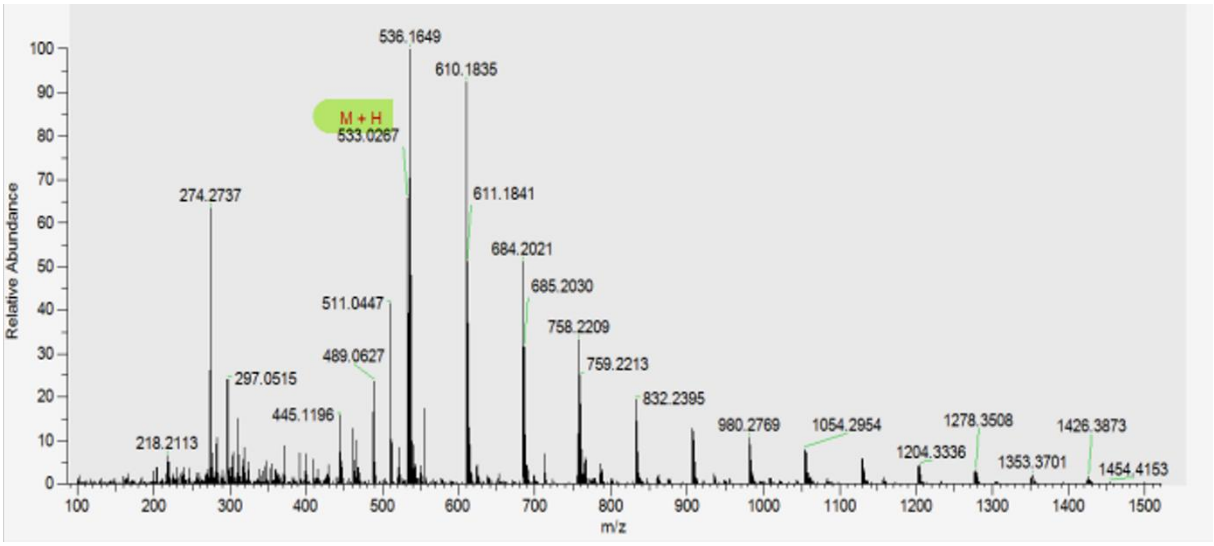


Figure S2. High-resolution full scan mass spectrum obtained in the ESI positive mode for **MSS**, (Δ = - 0.81 ppm). Calc. for $C_{18}H_{19}N_2Na_2O_{10}S_2$ $[M+H]^+$ 533.0271.

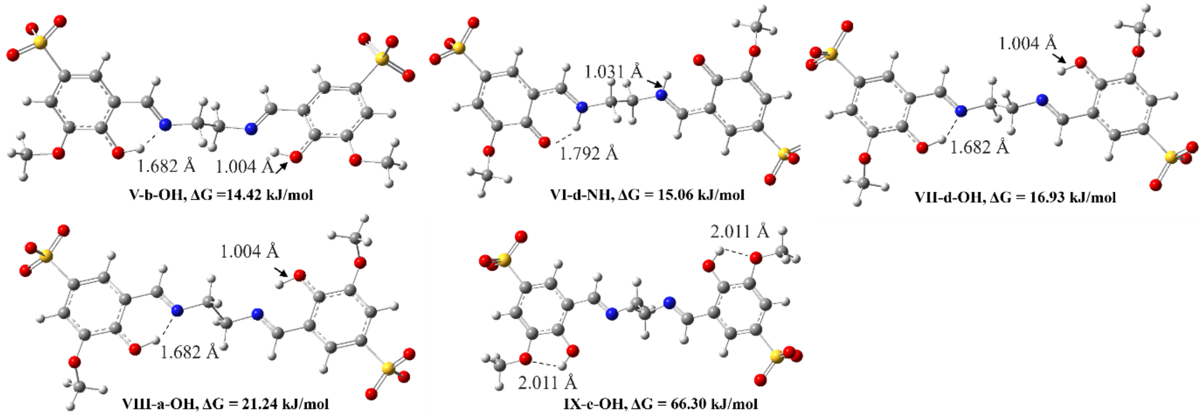


Figure S3. DFT(B3LYP)/6–311++G(d,p) optimized geometries of additional conformers and tautomers of *N.N*'-bis(3-methoxyl-5-sulfonatosalicylidene)-1.2- ethylenediamine (**MSS**) considering the bulk effects of the water solvent (the numbering of the conformers/tautomers from **V** to **IX** follows the order of their decreasing relative stability and population in water. The letters from **a, b, d** and **e** are related to the conformational arrangement of the conformer).

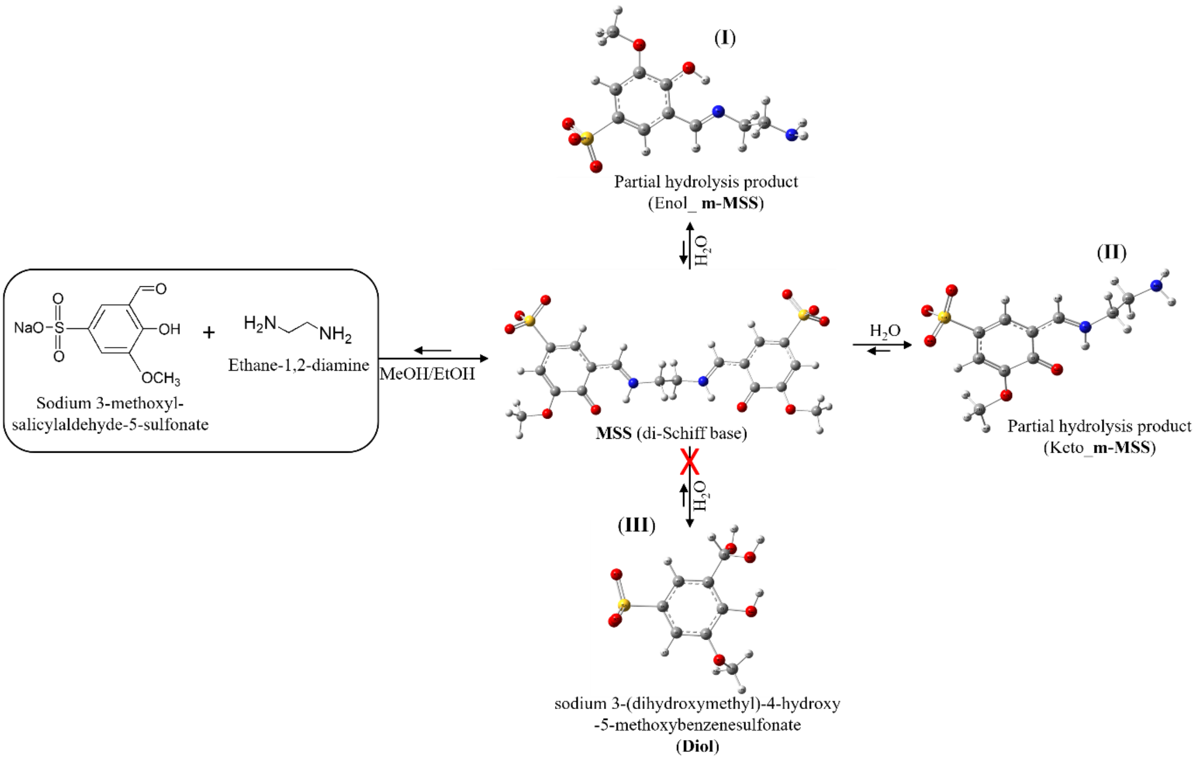


Figure S4. Proposed products of the hydrolysis of **MSS** with a sequential equilibrium (DFT(B3LYP)/6–311++G(d,p) optimized geometries of **Enol_m-MSS** (I), **Keto_m-MSS** (II) and **Diol** (III) considering the bulk solvent effects of water).

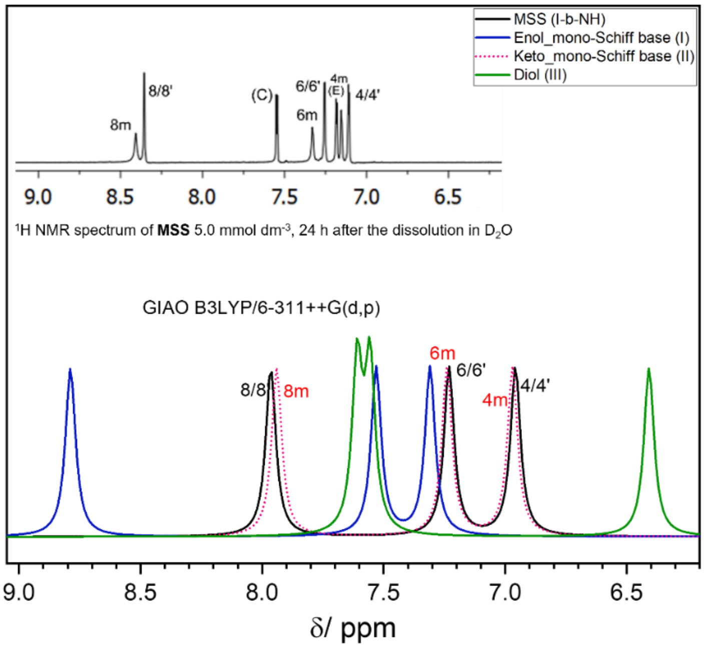
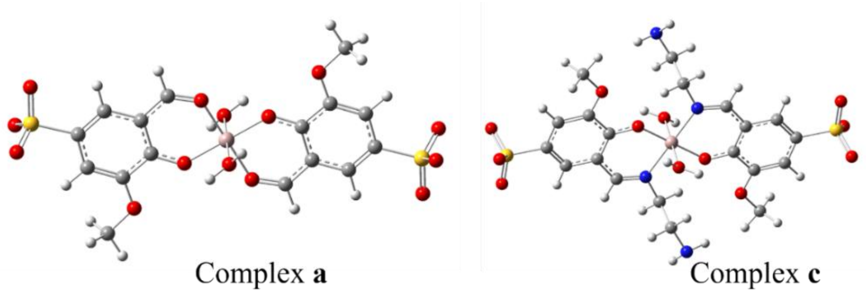


Figure S5. Simulated NMR spectra of **MSS** (I-b-NH), **Enol_m-MSS** (I), **Keto_m-MSS** (II) and Diol (III) (B3LYP/GIAO (6-311++G(d,p)) considering the bulk effects of the water solvent, in comparison with the experimental spectrum of **MSS** showing signals from the decomposition products mono-Schiff base, m-MSS, (identified with the letter m) and aldehyde (identified with capital letters).



Complex **a** Complex **c**

Figure S6. Optimized geometries of complexes **a** and **c**.

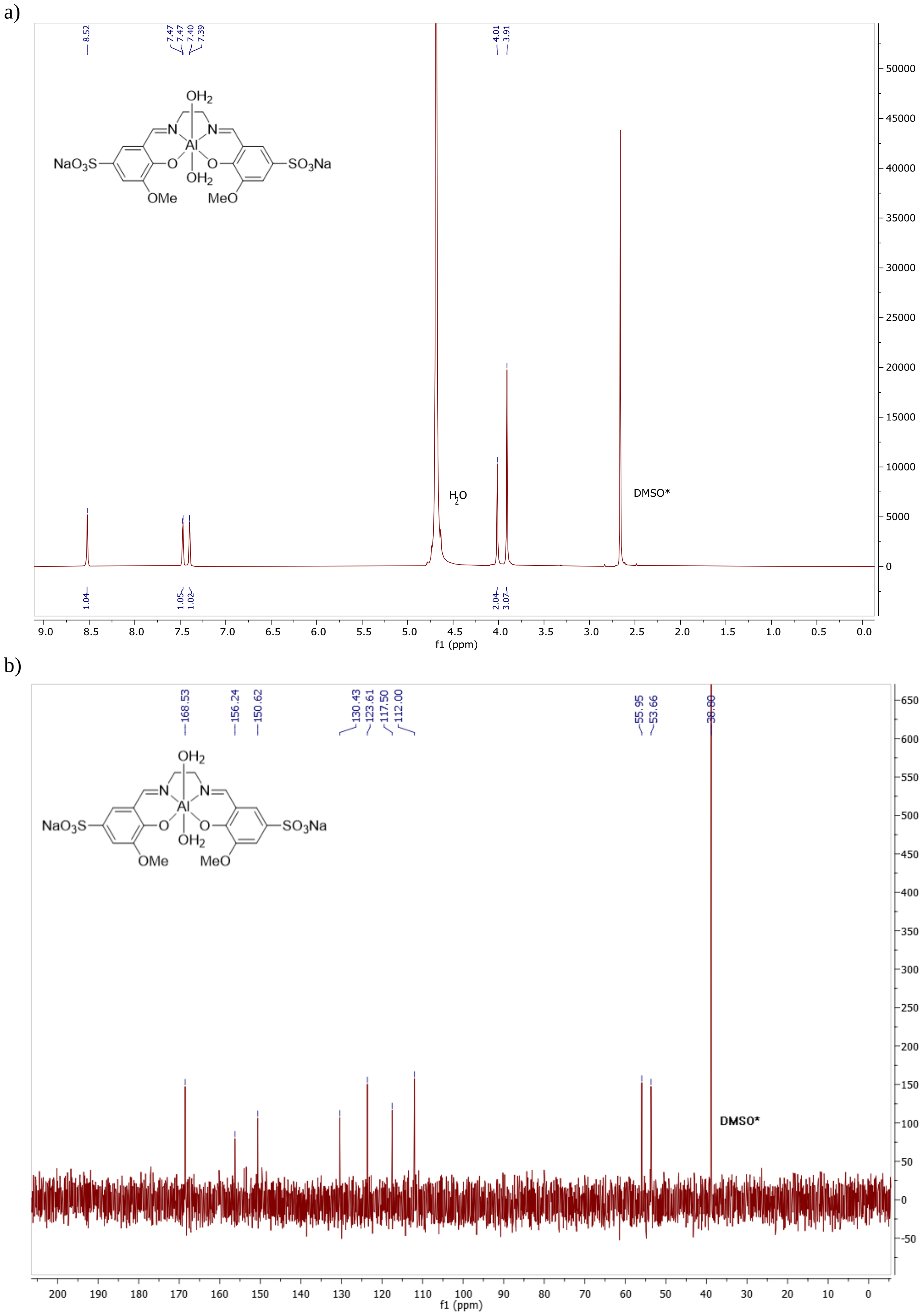


Figure S7. a) ^{1}H NMR spectrum of compound **Al(III) / MSS** complex (400 MHz, D_2O); b) ^{13}C NMR spectrum of compound **Al(III) / MSS** complex (100 MHz, D_2O) *DMSO from synthesis.

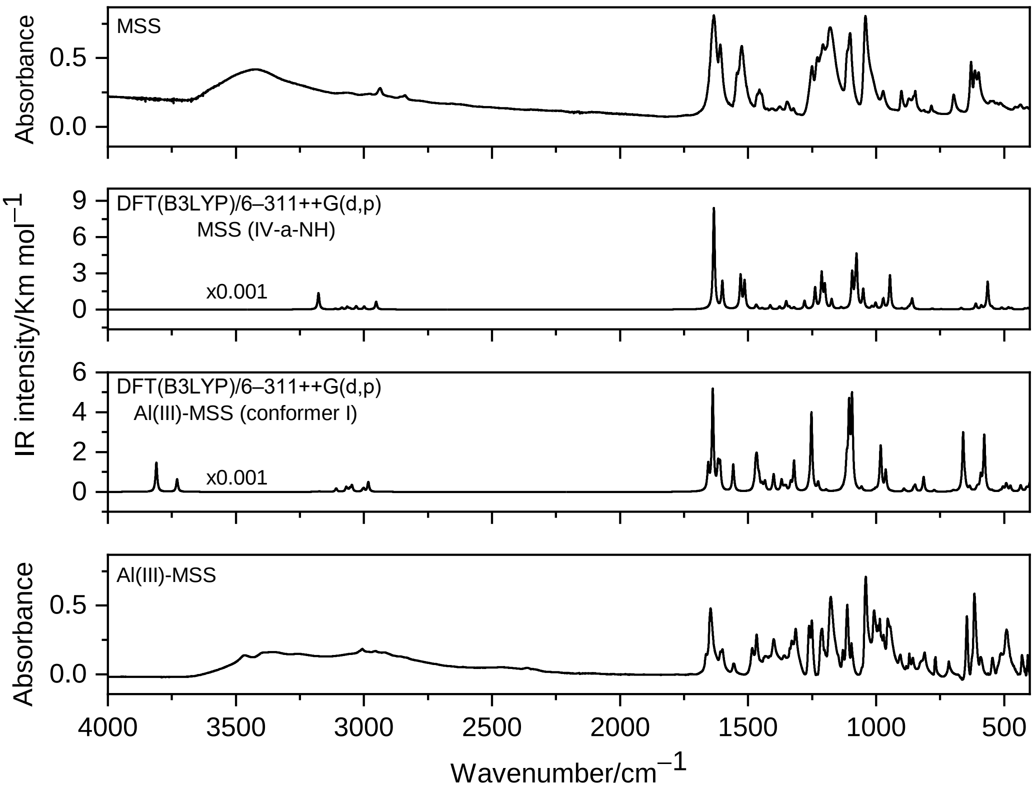


Figure S8. ATR–FTIR spectra (4000 – 400 cm^{-1}) of solid **Al(III) / MSS** (bottom), and solid **MSS** (top), compared with the DFT(B3LYP)/6–311++G(d,p) calculated spectra of **MSS** (middle top) and **Al(III) / MSS** (middle bottom). Note the multiplication factor 0.001 for the theoretical spectra.

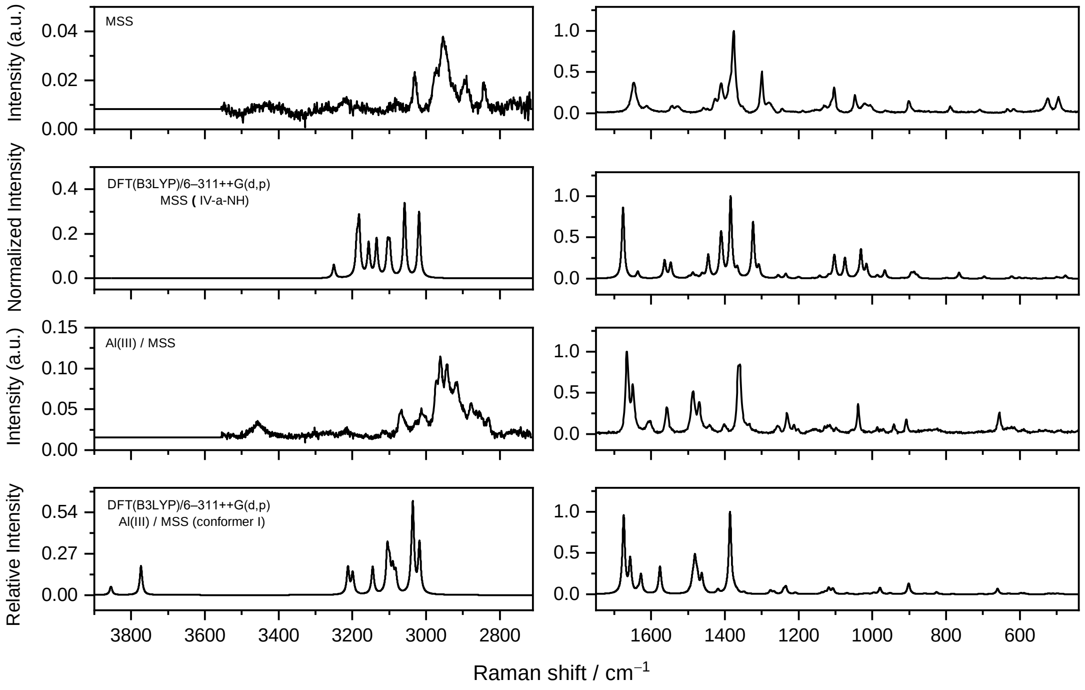


Figure S9. Raman spectra (4000 – 400 cm^{-1}) of solid **MSS** (top) and solid **Al(III) / MSS** (middle bottom), compared with the DFT(B3LYP)/6–311++G(d,p) calculated spectra of **MSS** (middle top) and **Al(III) / MSS** (bottom). The baseline due to photoluminescence has been subtracted from the experimental spectra.

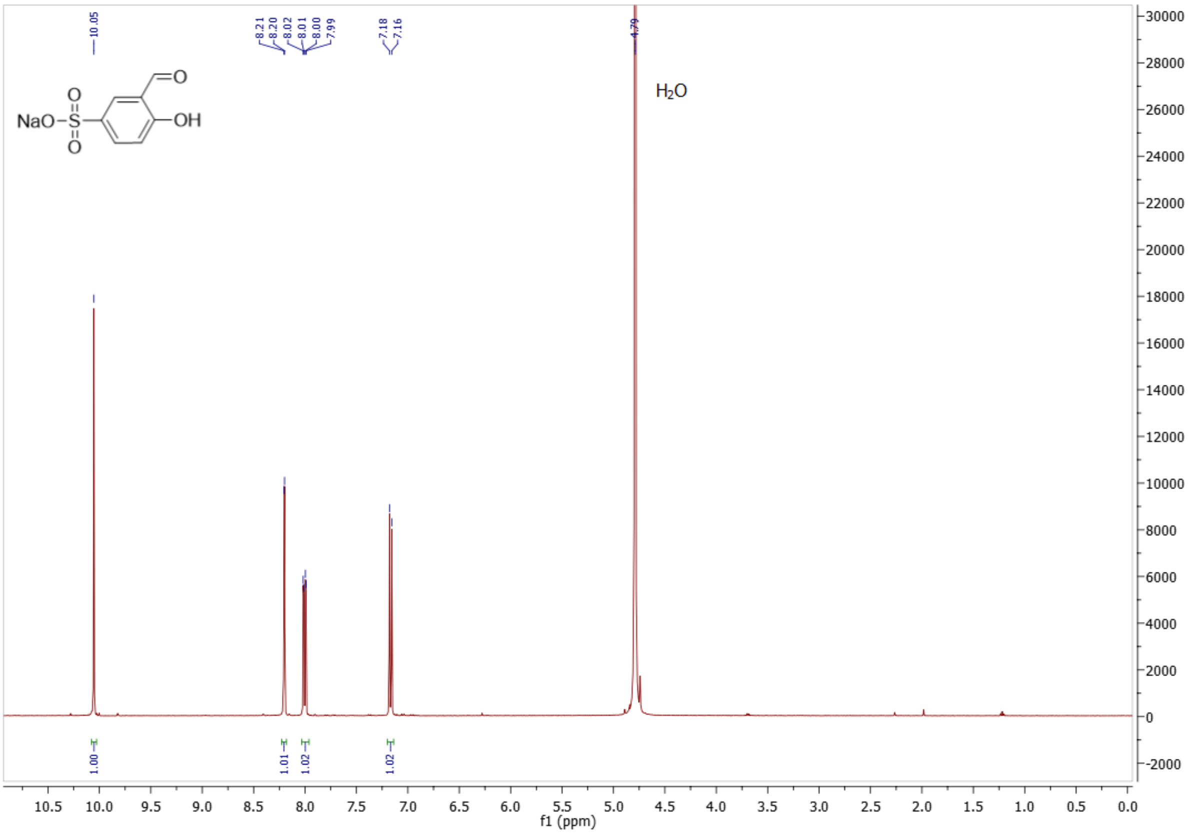


Figure S10. ^1H NMR spectrum of compound **5-S** (400 MHz, D_2O).

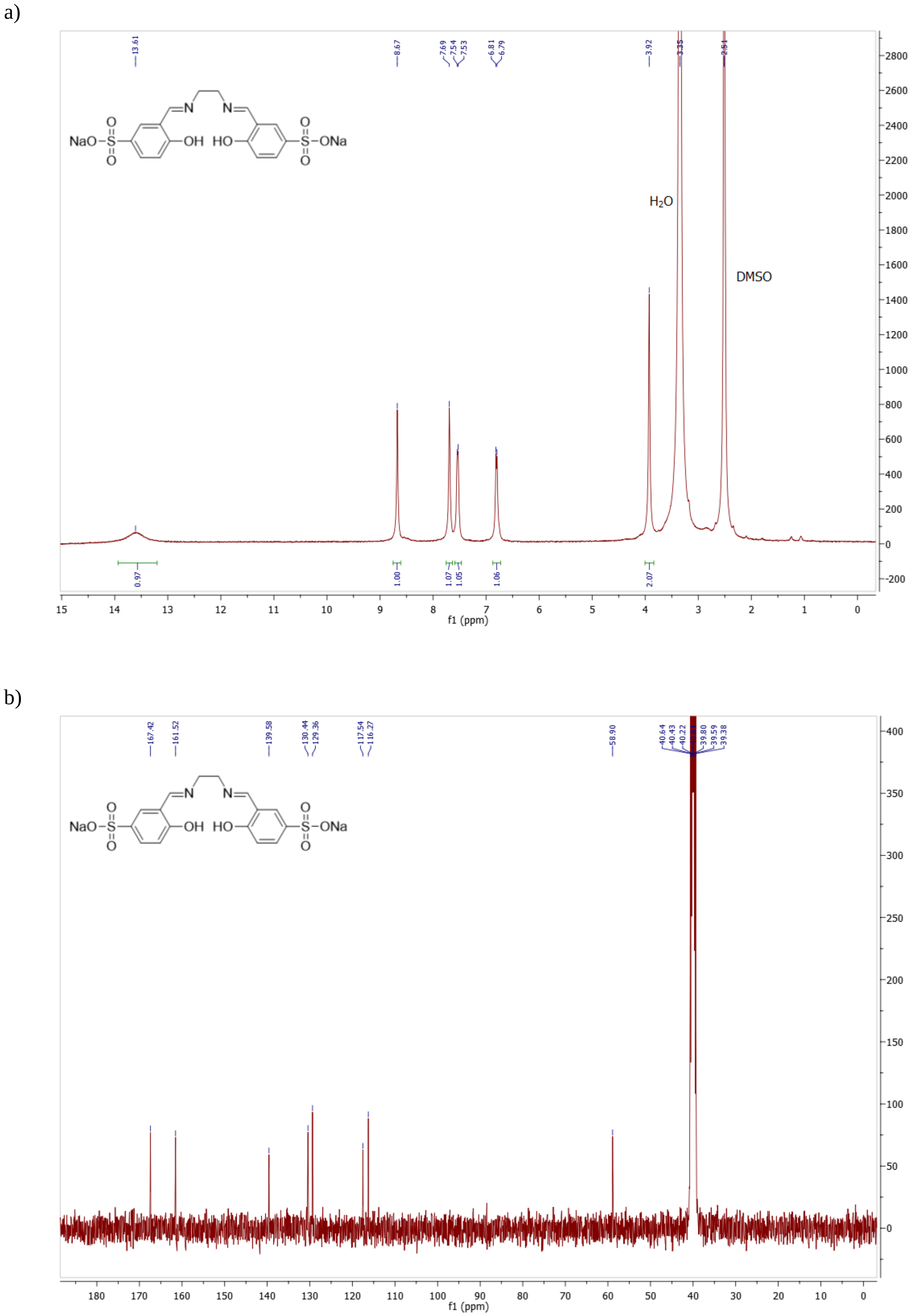


Figure S11. a) ^{1}H NMR spectrum of compound **SS** (400 MHz, DMSO-d_6); b) ^{13}C NMR spectrum of compound **SS** (100 MHz, DMSO-d_6).

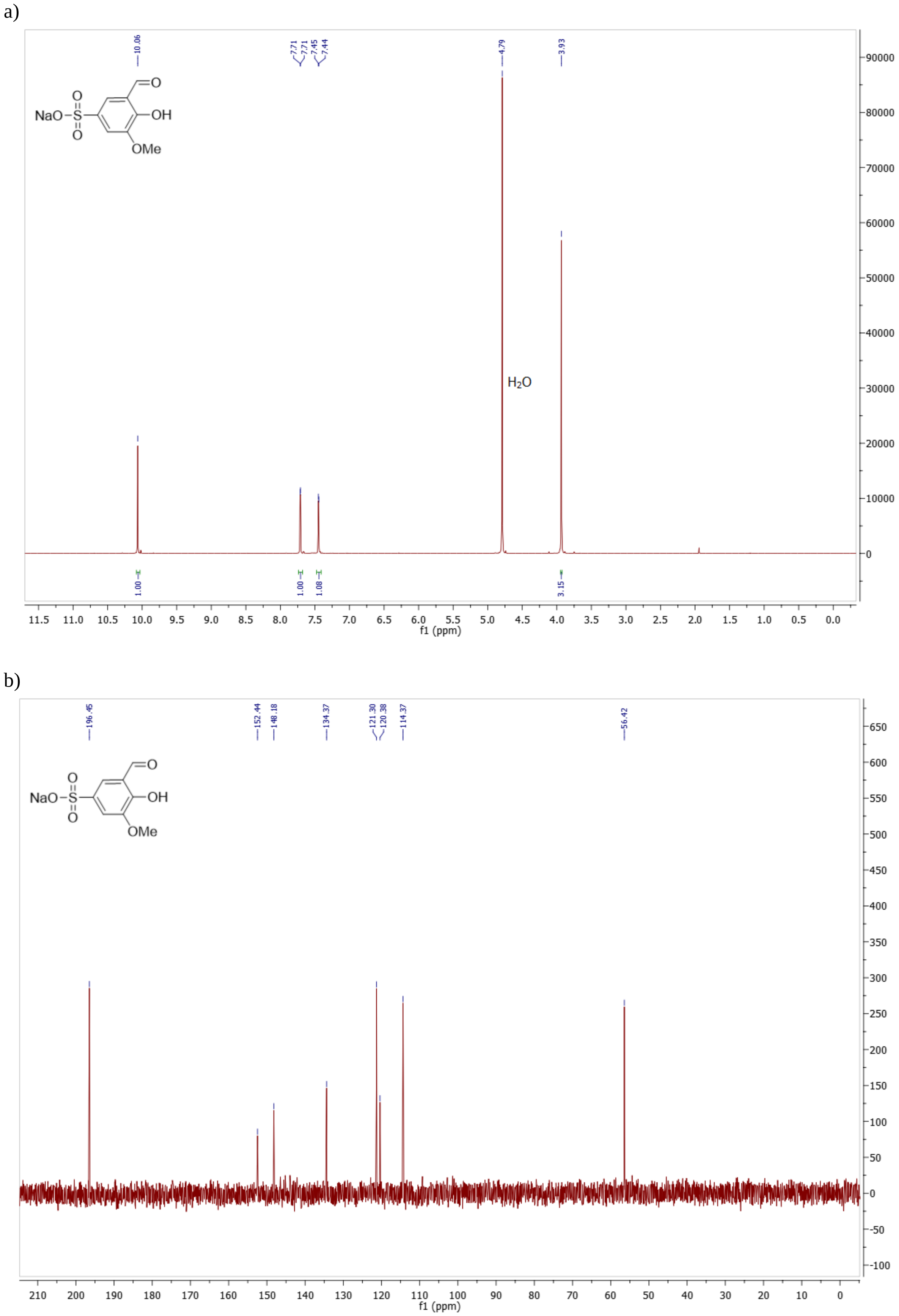


Figure S12. a) ^{1}H NMR spectrum of compound **5-S-3-OMe** (400 MHz, D_2O); b) ^{13}C NMR spectrum of compound **5-S-3-OMe** (100 MHz, D_2O).

Table S1. Reaction times, yields, melting points and physical properties of the ligand, **MSS,** and its Al(III) complex.

Molecular Formula	Abbreviated name	Conventional		Microwave		M.P. °C	Color	$[M+H]^+$ found (calc.) %
		Time	Yield	Time	Yield			
$C_{18}H_{18}N_2Na_2O_{10}S_2$	MSS	120 min	66 %	45 min	87 %	> 300	Yellow	533.0267 (533.0271)
$AlC_{18}H_{20}N_2Na_2O_{12}S_2$	Al(III) / MSS	50 min	52 %	-	-	> 300	pale-yellow	(594.45)

Table S2. Relative electronic energies (ΔE_{el}) (kJ mol^{-1}), zero-point-corrected electronic energies (ΔE_{Total}), Gibbs energies at 298.15 K (ΔG_{298K}), and equilibrium populations (%) estimated from the relative Gibbs energies (P_{298}) calculated for the lowest energy conformers and tautomers of **MSS** (DFT(B3LYP)/6–311++G(d,p)) considering the bulk effects of the DMSO solvent.

Structure	**I-b-NH**	**II-c-NH**	**III-c-OH**	**IV-a-NH**	**V-b-OH**	**VI-d-NH**	**VII-d-OH**	**VIII-a-OH**
Symmetry	C_2	C_i	C_i	C_i	C_2	C_i	C_i	C_i
ΔE_{el} (kJ/mol)	0.03	0.00	9.73	18.73	9.00	18.71	27.58	27.50
$\Delta(E_{total})$ (kJ/mol)	0.00	0.29	5.69	15.77	5.58	15.95	20.73	20.8
ΔG_{298k}	0.00	1.12	7.43	12.60	12.40	13.58	17.58	19.03
P_{298} (%)	58.62	37.37	2.93	0.36	0.40	0.25	0.05	0.03

Table S3. Relative electronic energies (ΔE_{el}) (kJ mol^{-1}), zero-point-corrected electronic energies (ΔE_{Total}), Gibbs energies at 298.15 K (ΔG_{298K}), and equilibrium populations (%) estimated from the relative Gibbs energies (P_{298}) calculated for the lowest energy conformers and tautomers of **MSS** (DFT(B3LYP)/6–311++G(d,p)) in gas phase (isolated molecule in vacuum).

Structure	**I-b-NH**	**II-c-NH**	**III-c-OH**	**IV-a-NH**	**V-b-OH**	**VI-d-NH**	**VII-d-OH**	**VIII-a-OH**
Symmetry	C_2	C_i	C_i	C_i	C_2	C_i	C_i	C_i
ΔE_{el} (kJ/mol)	36.04	33.88	0.00	36.36	1.55	36.48	5.18	4.92
$\Delta(E_{total})$ (kJ/mol)	35.29	33.47	0.00	33.90	1.44	33.98	3.09	2.67
ΔG_{298k}	38.97	35.7	2.06	35.11	3.09	35.28	3.35	0.00
P_{298} (%)	0.00	0.00	21.98	0.00	14.52	0.00	13.05	50.45

Table S4. Mulliken charges on the imine carbon atoms and equilibrium populations (%) (P_{298}) of the lowest energy conformers and tautomers of **SS** and **MSS** (DFT(B3LYP)/6–311++G(d,p)), considering the bulk solvent effects of water.

Conformer	**MSS (in water)**		**SS (in water)**	
	Mulliken charge Imine carbon	**P_{298K} (%)**	**Mulliken charge Imine carbon**	**P_{298K} (%)**
I-b-NH	**0.205**	**67.24**	0.229	7.79
II-c-NH	-0.238	30.64	*[a]*	-
III-c-OH	-0.239	1.42	*[b]*	-
IV-a-NH	0.058	0.30	0.269	1.34
V-b-OH	-0.318	0.20	-0.164	7.66
VI-d-NH	0.050	0.15	**-0.034**	**50.58**
VII-d-OH	-0.044	0.05	*[b]*	-
VIII-a-OH	-0.027	0.00	**-0.067**	**32.63**

[a] Same structure as for VI-d-NH

[b] Same structure as for VIII-a-OH

Table S5. Calculated (B3LYP/GIAO) ^{1}H NMR chemical shifts for **MSS**, **m-MSS** (phenol-imine (I) and keto-enamine (II) forms), diol and complexes **a**, **b** and **c**, in comparison with the respective experimental chemical shifts[a] (D_2O solutions, 298 K).

MSS[b]	H-8/8’	H-6/6’	H-4/4’	H-9/9’	H-7/7’
pH* 4.0	8.50	7.41	7.23	4.03	3.92
pH* 7.0	8.37	7.30	7.12	4.02	3.80
B3LYP/GIAO)[d]	7.90	7.25	7.00	3.89	3.71
m-MSS[b]	H-8m	H-6m	H-4m	H-9m/H-9’m	H-7m
pH* 4.0	8.47	7.38	7.20	3.43	3.81
pH* 7.0	8.45	7.37	7.19	3.40 (broad)	3.76
(**I**) B3LYP/GIAO	7.94	7.24	6.97	3.31	3.89
(**II**) B3LYP/GIAO	8.78	7.53	7.3	3.43	4.01
Diol	H-8	H-6	H-4	H-7	
(**III**) B3LYP/GIAO	6.4	7.61	7.55	3.97	
Complex a[c]	(A)	(C)	(E)	(H)	
pH* 4.0	9.34	7.66	7.47	3.89	
B3LYP/GIAO	9.35	7.67	7.53	3.85	
Complex b [c]	H-8/8’	H-6/6’	H-4/4’	H-9/9’	H-7/7’
pH* 7.0	8.52	7.47	7.25	3.96	3.78
B3LYP/GIAO	8.61	7.55	7.37	4.07	4.02
Complex c [c]	H-8m	H-6m	H-4m	H-9m/H-9’m	H-7m
pH* 7.0	8.09	7.39	7.27	3.61 / 3.39	3.82
B3LYP/GIAO	8.49	7.51	7.39	3.33 / 3.00	4.00

[a] δ values, in ppm, relative to Me4Si, using tert-butyl alcohol (δ_H = 1.2) as an internal reference.

[b] 5 mmol dm^{-3} **MSS** solution. [c] 5: 5 mmol dm^{-3} Al(III) /**MSS** solution; [d] calculated values.