Supporting Information

Synthesis, Crystal Structure and Photoluminescence Studies of a Ruthenocenyl-decorated Sn/S Cluster

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1. Supplementary figures of the crystal structure of 1

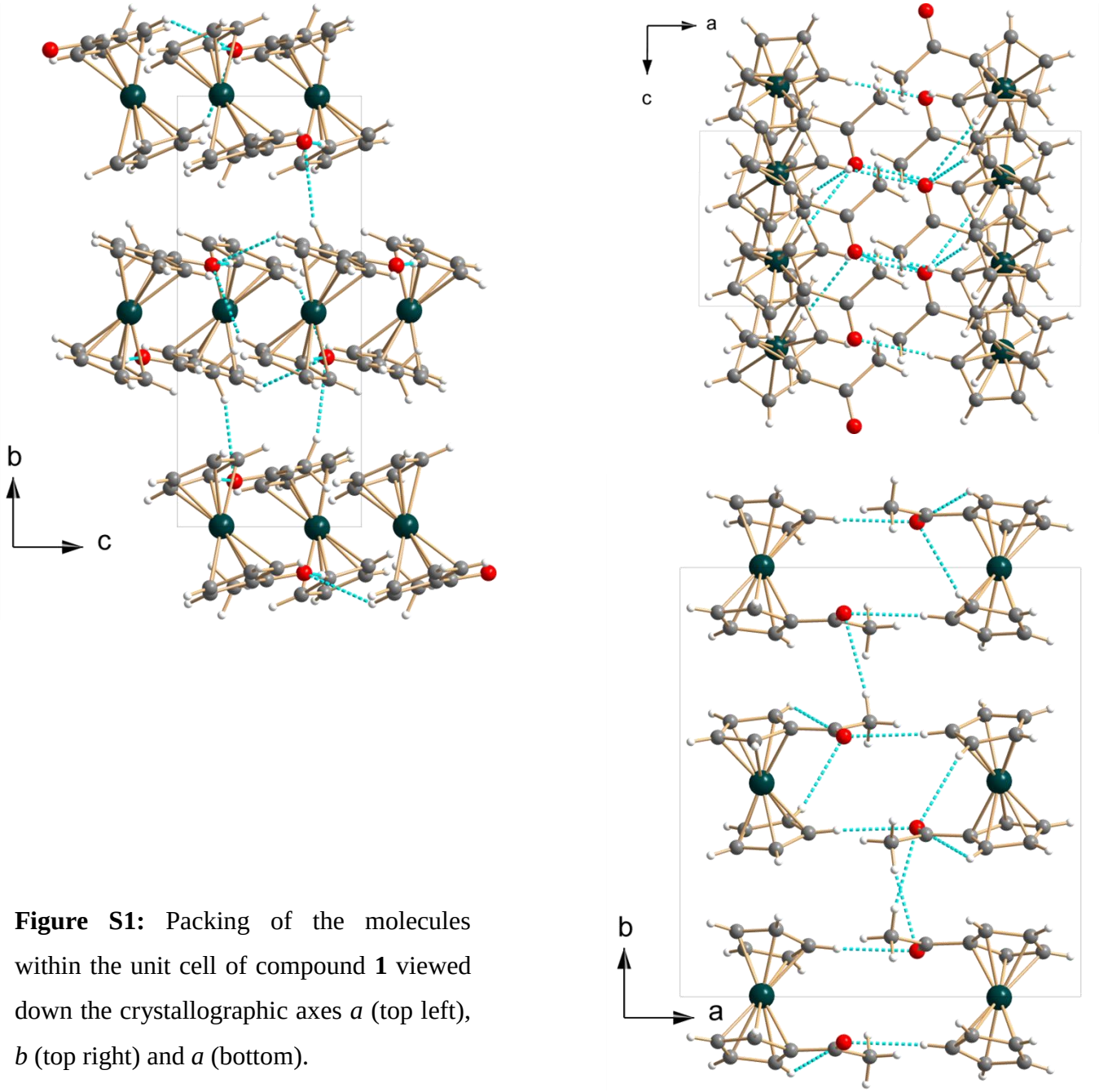

Figure S1: Packing of the molecules within the unit cell of compound **1** viewed down the crystallographic axes *a* (top left), *b* (top right) and *a* (bottom).

2. Further analyses of compound 1

^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 5.09 (t, 2H, *J* = 1.8 Hz), 4.78 (t, 2H, *J* = 1.8 Hz), 4.59 (s, 5H), 2.29 (s, 3H) ppm.

ESI (+) mass spectrum of compound **1** in CH_2Cl_2, $C_{12}H_{12}O_1Ru_1Na_1$: calculated m/z 296.9827, measured m/z 276.9821. The spectra are shown in Figures S2 and S3.

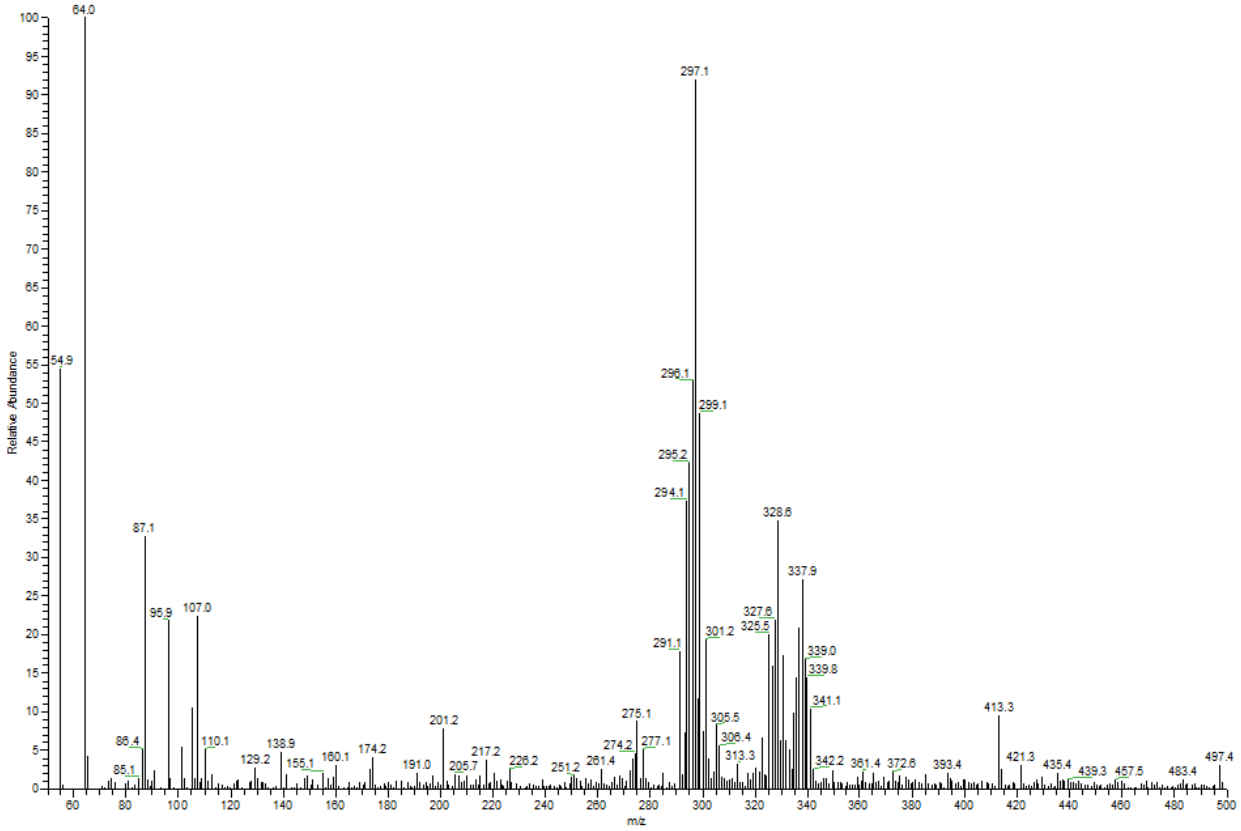

Figure S2: Full ESI (+) mass spectrum of compound **1**.

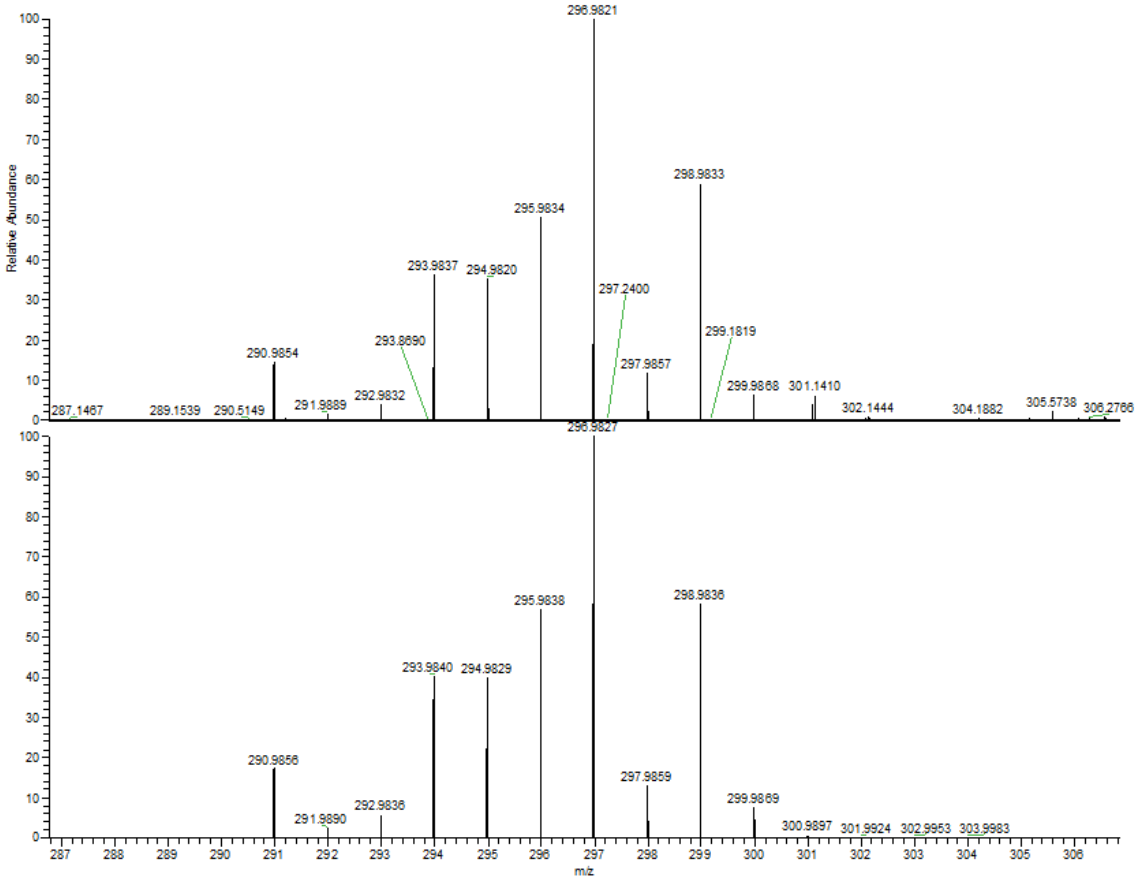

Figure S3: Detail of the ESI (+) mass spectrum of compound **1**, measured as $C_{12}H_{12}O_1Ru_1Na_1^+$ (top: measured, bottom: calculated).

3. Further analyses of $[(Ru^{Ac}N{=}NCMeCH_2CMe_2)_2Sn_3S_4(\mu\text{-}S)]_2$ (compound 2)

NMR spectroscopy

^{1}H NMR (Figure S4, CD_2Cl_2, 400 MHz): δ = 5.05 (m, 2H), 4.68 (m, 1H), 4.65 (s, 1H), 4.64 (s, 3H), 4.50 (m, 1H), 2.68 (s, 1H), 2.12 (s, 6H), 1.95 (s, 3H), 1.81 (s, 3H), 1.36 (m, 6H) ppm. ^{13}C NMR (Figure S5, CD_2Cl_2, 100 MHz): δ = 163, 162, 129.4, 128.6, 72, 70, 51, 39, 31, 27, 20, 18 ppm. ^{119}Sn NMR (Figure S6, CD_2Cl_2, 150 MHz): δ = –96, –114 ppm.

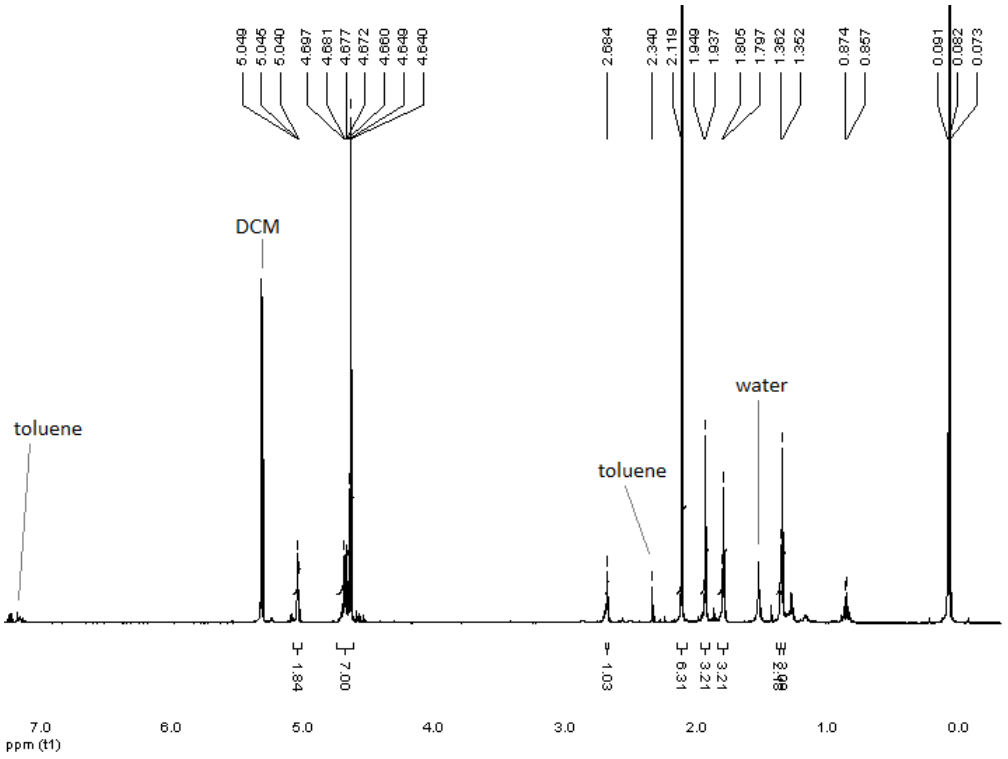

Figure S4: Relevant section of the ^{1}H NMR spectrum of **2**.

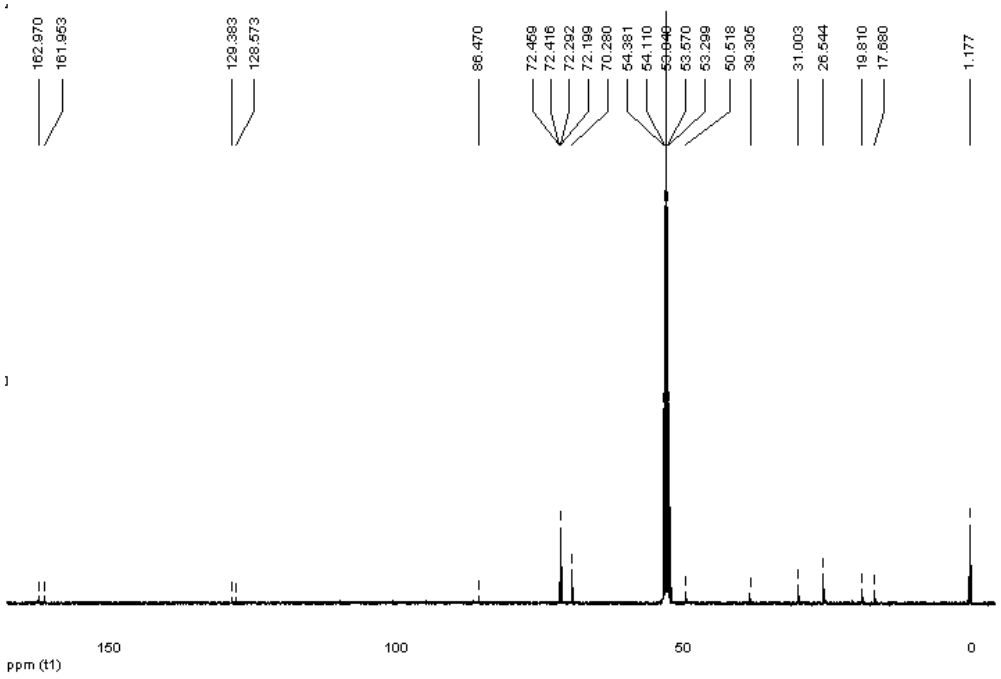

Figure S5: Relevant section of the ^{13}C NMR spectrum of **2**.

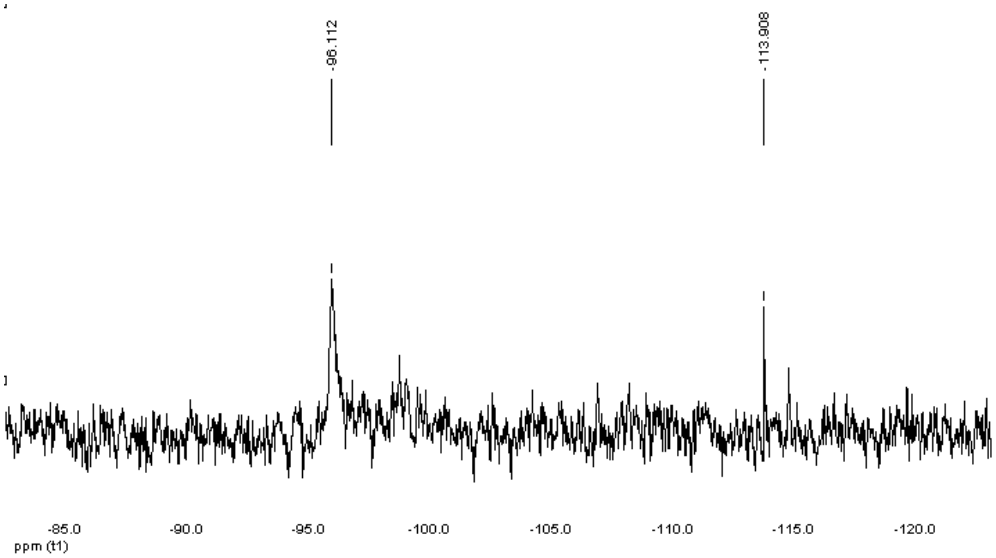

Figure S6: Relevant section of the ^{119}Sn NMR spectrum of **2** (c.f. values found for the ferrocenyl-decorated analog: –95.32; –108.34 ppm).[1]

All signals correspond with expected values. The large variety of proton signals hints towards high flexibility of the organic groups in solution, causing manifold secondary interactions and biases between the organic moieties. The peak intensities in the ^{119}Sn NMR spectrum reflect approximately the expected 2:1 ratio due to the presence of two chemically different Sn atoms, similar to the situation observed in the ferrocenyl-decorated analogue; however, due to the poor signal quality, the spectrum can be only regarded as a hint toward the identity of the solved compound(s).[1]

Electrospray ionization (ESI) mass spectrometry

ESI (+) mass spectrum of compound **2**, measured as $[C_{54}H_{70}N_6Ru_3S_4Sn_3]^+$: caluclated m/z 1590.8772, measured m/z 1590.8723. The overview ESI (+) mass spectrum is given in Figure S7, mass peaks along with simulations and structure diagrams are shown in Figures S9 and S10.

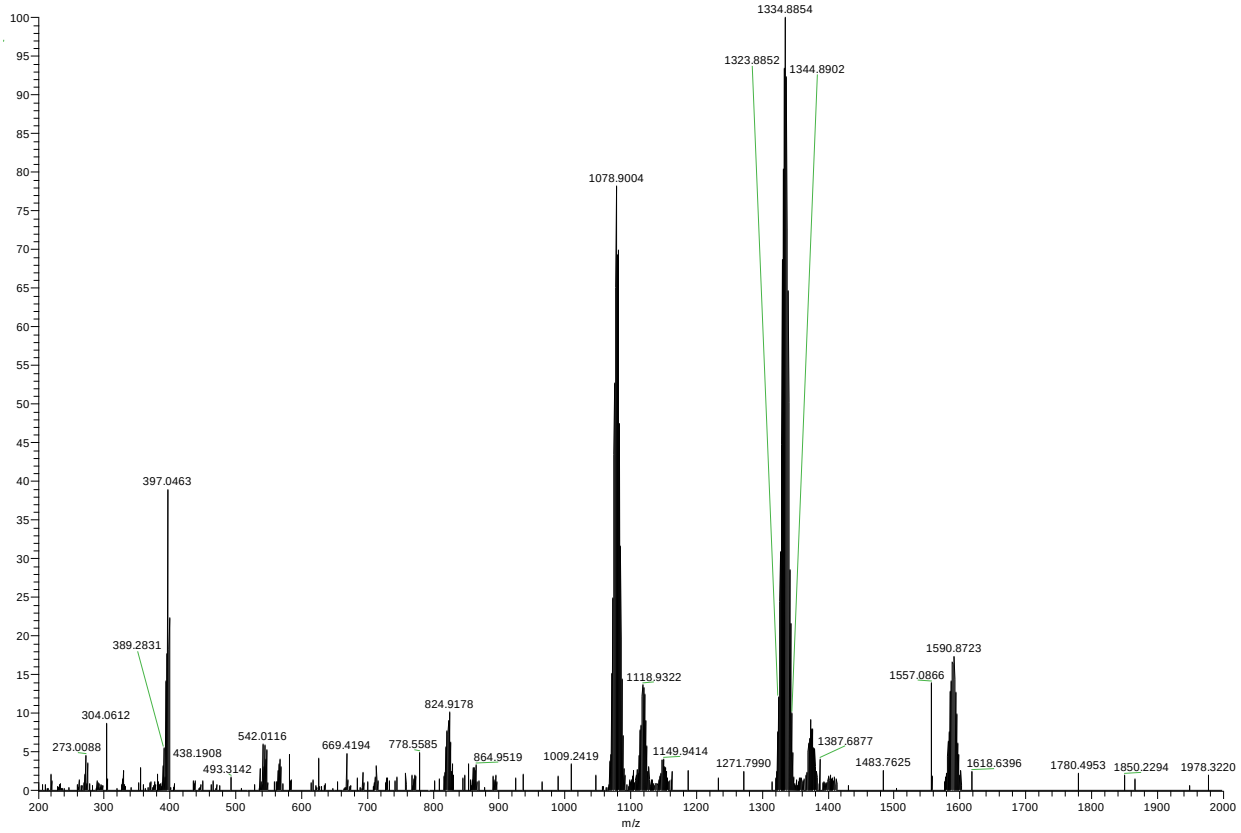

Figure S7: Full ESI(+) mass spectrum of compound **2**.

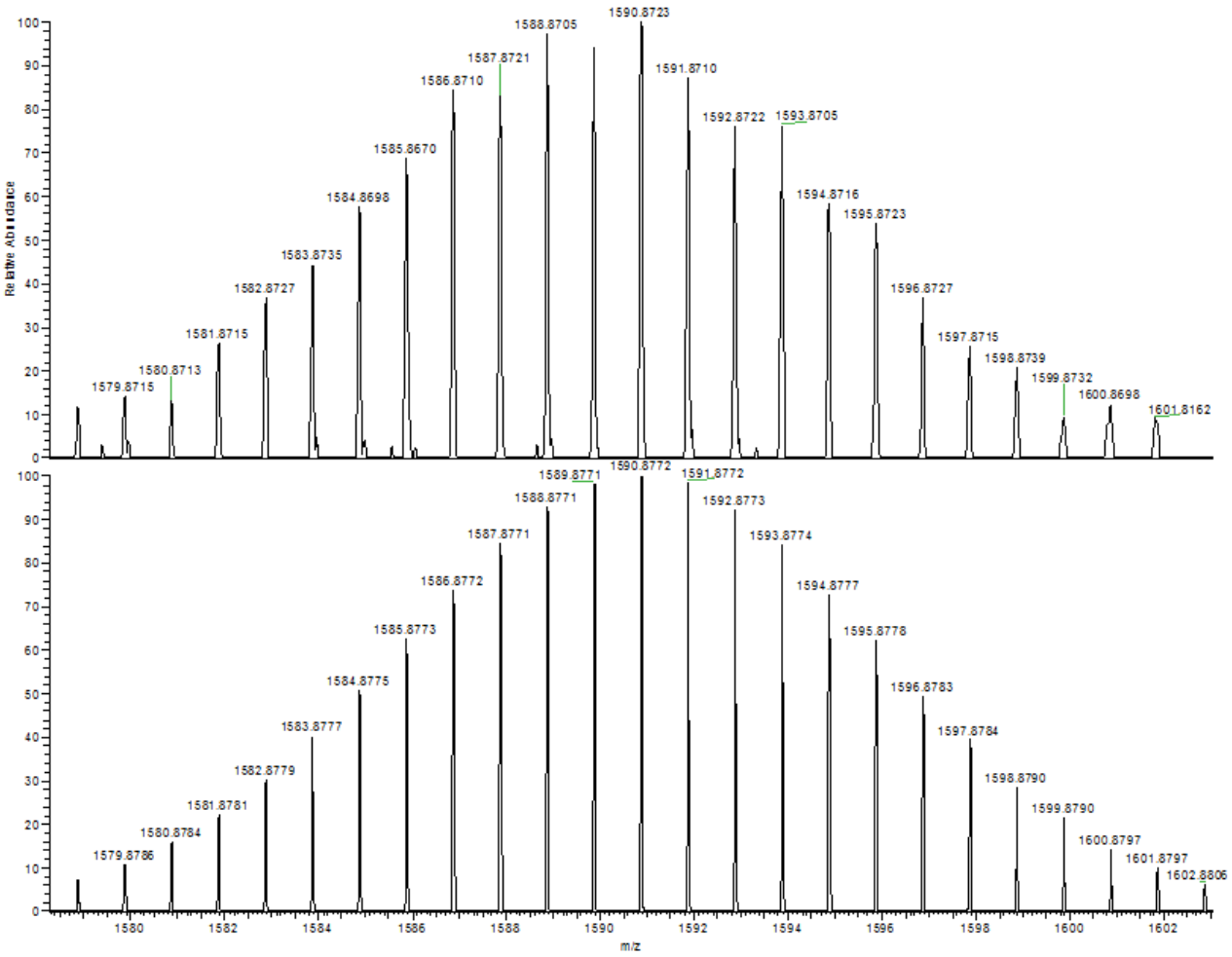

Figure S8: Detail of the ESI (+) mass spectrum of compound **2**, measured as $[C_{54}H_{70}N_6Ru_3S_4Sn_3]^+$ (top: measured, bottom: calculated).

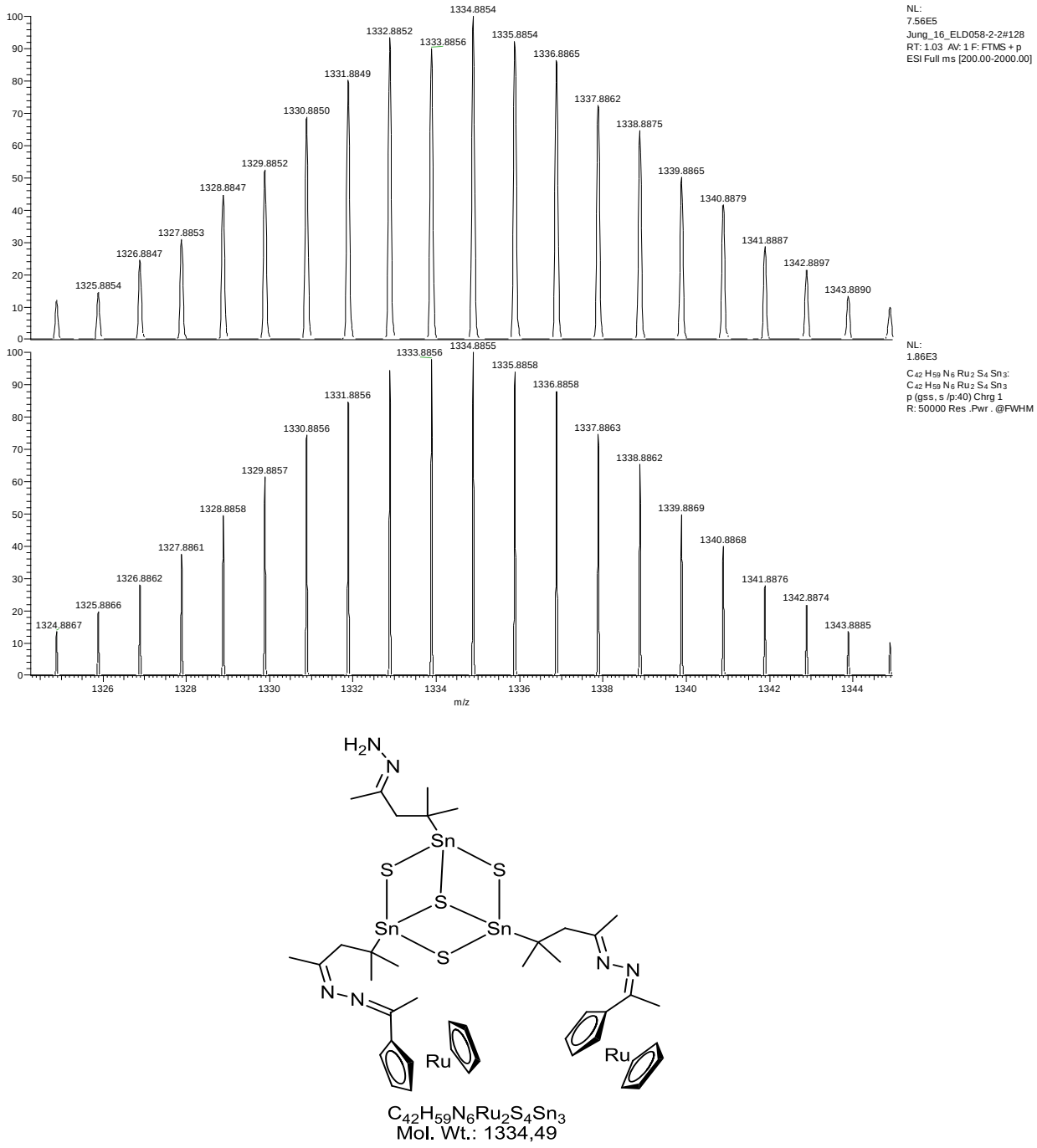

Figure S9: Detail of the ESI (+) mass spectrum of a fragment of compound **2**, measured as $[C_{42}H_{59}N_6Ru_2S_4Sn_3]^+$ (top: measured, center: calculated, bottom: drawing of the proposed heterocubane-type structure).

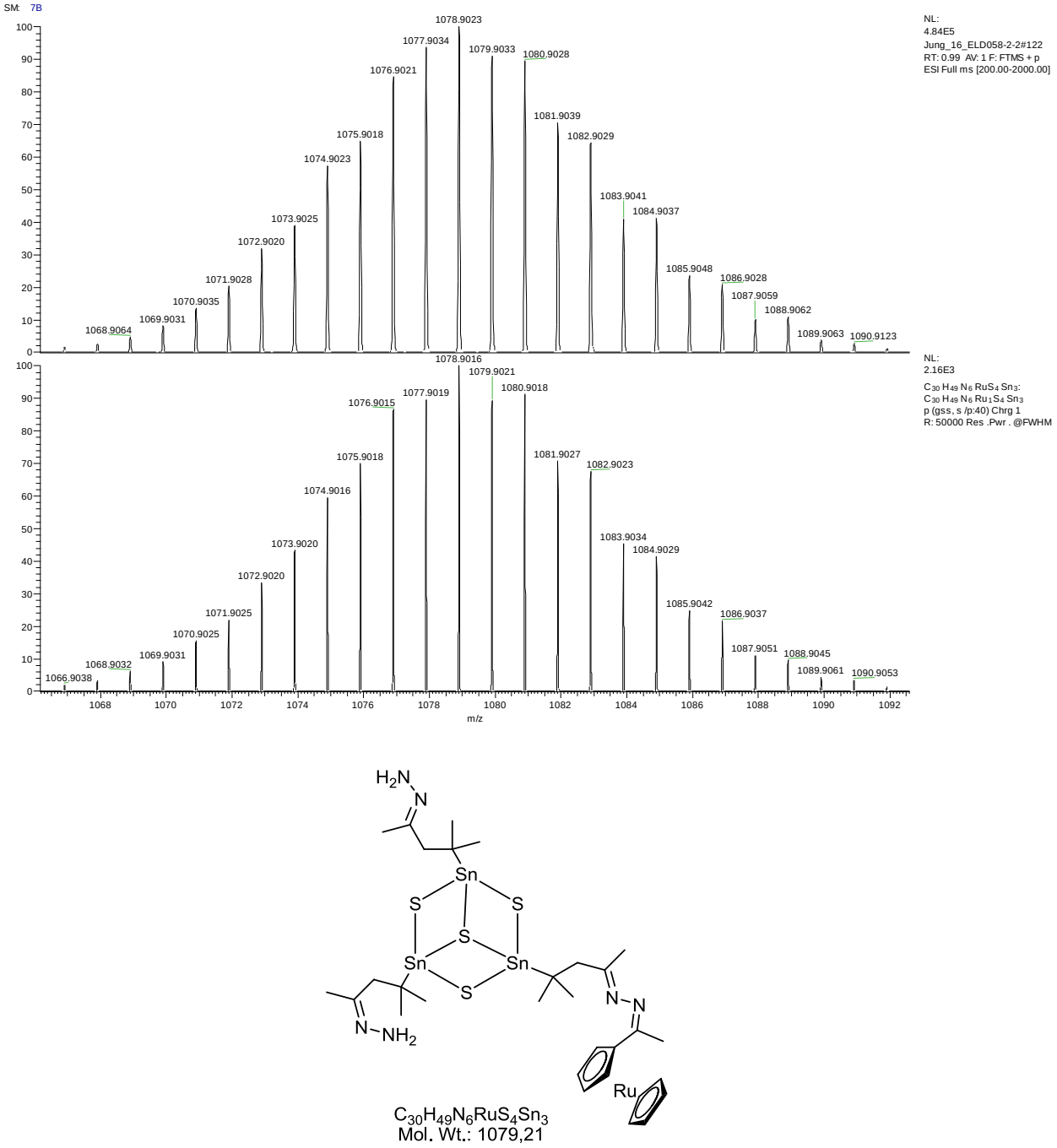

Figure S10: Detail of the ESI (+) mass spectrum of a fragment of compound **2**, measured as $[C_{30}H_{49}N_6RuS_4Sn_3]^+$ (top: measured, center: calculated, bottom: drawing of the proposed heterocubane-type structure).

Energy-dispersive X-ray (EDX) spectroscopy

EDX analyses on single-crystals of **2** (Figure S9) were performed using the EDX device Voyager 4.0 of Noran Instruments coupled with the electron microscope CamScan CS 4DV. Data acquisition was performed with an acceleration voltage of 20 kV and 100 s accumulation time. Results are listed in Table S1. In two cases, the percentages of Sn and S are slightly increased with respect to the Ru content, which can be put down to a slight impurity by SnS_2 powder along with traces of elemental tin that tends to form during the transfer of the sample into the instrument.

Table S1: Results of the EDX spectroscopic analyses of compound **2** (three different crystals).

Element	k-ratio	ZAF	Atom %	Atomic ratio observed (calc)	Element wt %	wt % Err. (1-sigma)
Sn-L	0.3699	1.369	31.08	1.55 (1.50)	50.65	+/- 0.73
S-K	0.1909	1.127	48.86	2.44 (2.50)	21.51	+/- 0.22
Ru-L	0.2125	1.310	20.06	1.00 (1.00)	27.84	+/- 0.64
Total			100		100	
Sn-L	0.3920	1.351	32.82	1.73 (1.50)	52.95	+/- 0.68
S-K	0.1857	1.131	48.21	2.54 (2.50)	21.01	+/- 0.21
Ru-L	0.1994	1.306	18.96	1.00 (1.00)	26.04	+/- 0.59
Total			100		100	
Sn-L	0.4085	1.337	34.17	1.87 (1.50)	54.61	+/- 0.74
S-K	0.1811	1.135	47.59	2.61 (2.50)	20.55	+/- 0.22
Ru-L	0.1907	1.303	18.25	1.00 (1.00)	24.84	+/- 0.62
Total			100		100	

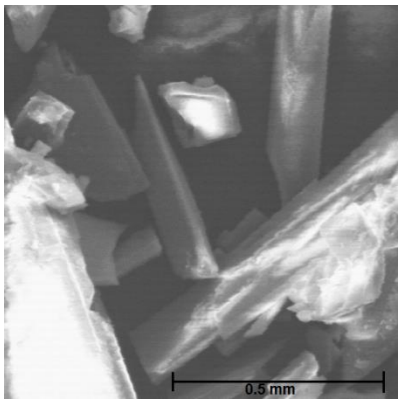

Figure S11: Photograph of single-crystals of **2** taken with an electron microscope CamScan CS 4DV.

4. Cyclic voltammetry of 2 in the presence of ferrocene

The cyclic voltamogram of a CH_2Cl_2 solution of **2** (5 mM) in the presence of $[NBu_4][PF_6]$ (50 mM) with ferrocene as internal reference is shown in Figure S9. It indicates rapid decomposition of **2** in the presence of the related iron complex.

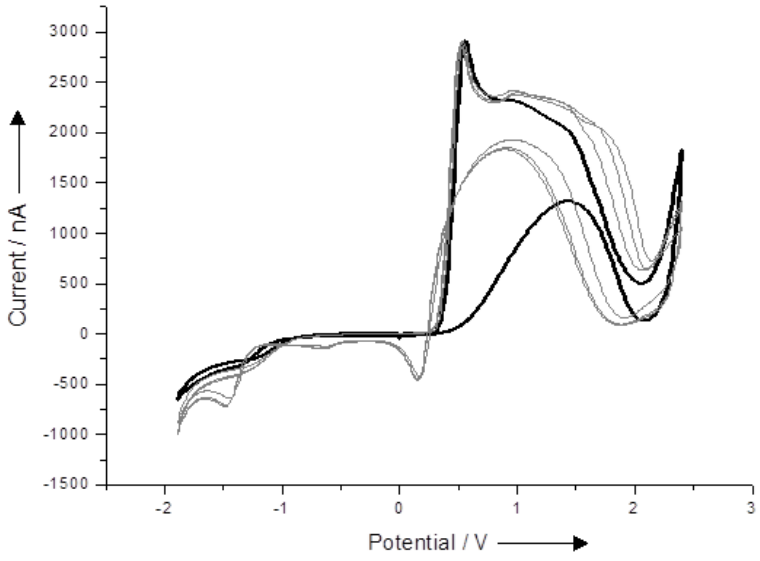

Figure S12: Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution of **2** (5 mM) in the presence of $[NBu_4][PF_6]$ (50 mM) with ferrocene as internal reference with the first cycle shown in black. Scan range and rate: –1.89 to 2.4 V, 0.05 V s–1.

5. Reference for the Supporting Information

[1] You, Z.; Dehnen, S.; *Inorg. Chem.* **2013**, *52*, 12332–12334.