Electronic Supporting Information

Single-Crystal XRD Characterization, Physicochemical Properties and Catalytic Activity of Rhodium(III/IV) Coordination Compounds

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Legend

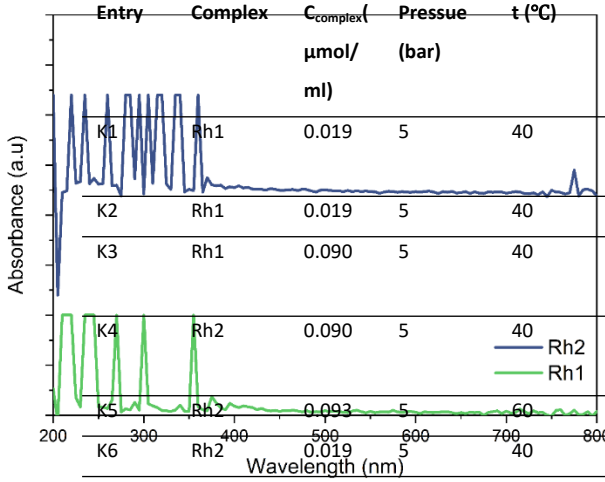

Figure S1. DRS spectra of Rh1 and Rh2.

Entry	Complex	$C_{complex}$ (µmol/ml)	Pressue (bar)	t (°C)	Rh/Ru (µmol)	Cocatalyst (mL)	Al/V	Comonomer (mL)
K1	Rh1	0.019	5	40	2	MMAO-12 (2.6)	3000	-
K2	Rh1	0.019	5	40	2	Et_2AlCl (3)	1500	-
K3	Rh1	0.090	5	40	10	MMAO-12 (8.6)	2000	-
K4	Rh2	0.090	5	40	10	MMAO-12 (8.6)	2000	-
K5	Rh2	0.093	5	60	10	Et_2AlCl (5)	500	-
K6	Rh2	0.019	5	40	2	$EtAlCl_2$ (3)	1500	-
K8	Ru1	0.094	5	40	10	Et_2AlCl (5)	500	-
K10	Rh1	0.019	5	40	2	$EtAlCl_2$ (3)	1500	-
K11	Rh1	0.180	5	40	20	Et_2AlCl (5)	250	-
K12	Rh1	0.367	5	40	40	Et_2AlCl (5)	125	-
K13	Rh1	0.377	5	40	40	Et_2AlCl (2)	50	-
K14	Rh1	0.357	5	40	40	Et_2AlCl (8)	200	-
K15	Rh1	0.354	5	40	40	Et_2AlCl (8)	200	O (1)
K16	Rh1	0.348	5	40	40	Et_2AlCl (8)	200	O (3)
K17	Rh1	0.600	0.5	40	3	Et_2AlCl (3)	1000	-
K18	Rh1	0.375	0.5	40	3	Et_2AlCl (3)	1000	H (3)
K19	Rh1	0.375	0.5	40	3	Et_2AlCl (3)	1000	MA (3)
K20	Rh2	0.375	0.5	40	3	Et_2AlCl (3)	1000	MA (3)
K21	Rh2	0.375	0.5	40	3	Et_2AlCl (3)	1000	H (3)
K22	Rh2	0.600	0.5	40	3	Et_2AlCl (3)	1000	-

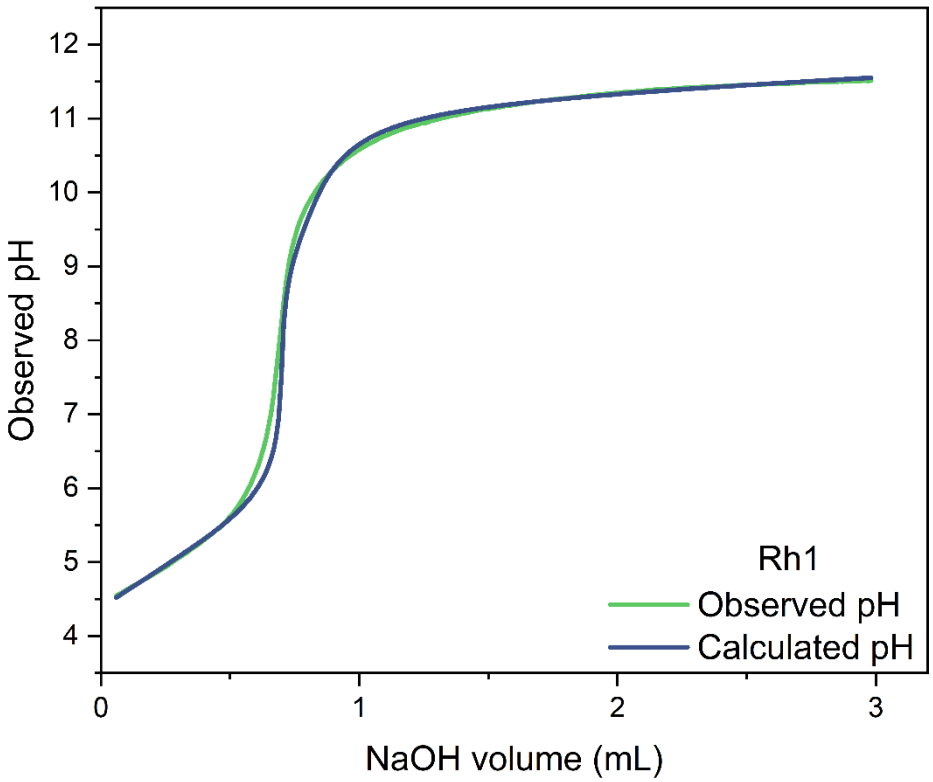

Figure S2. Potentiometric titration curve of Rh1 complex formation.

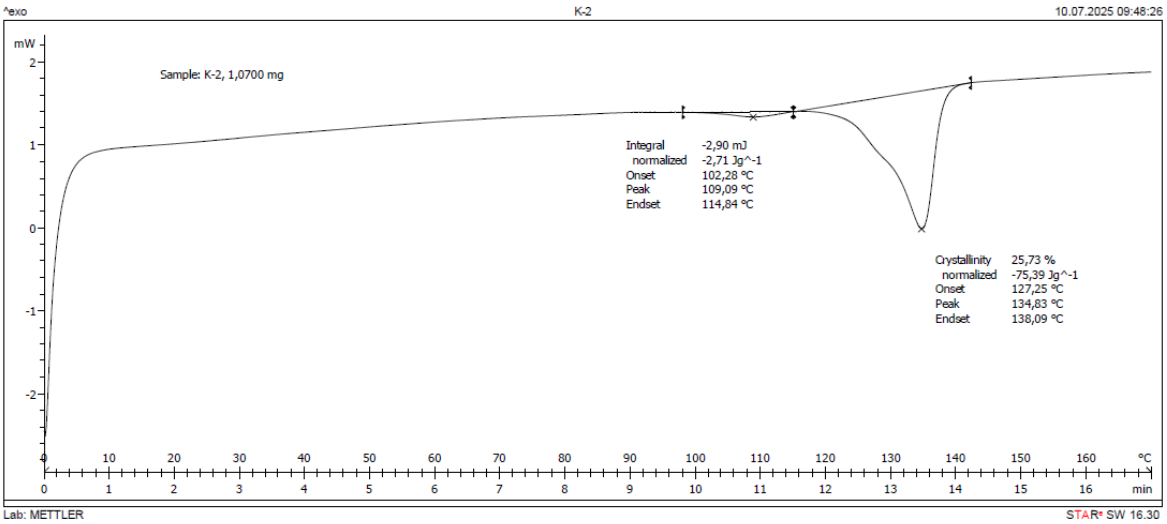

Figure S3. DSC curve of K2.

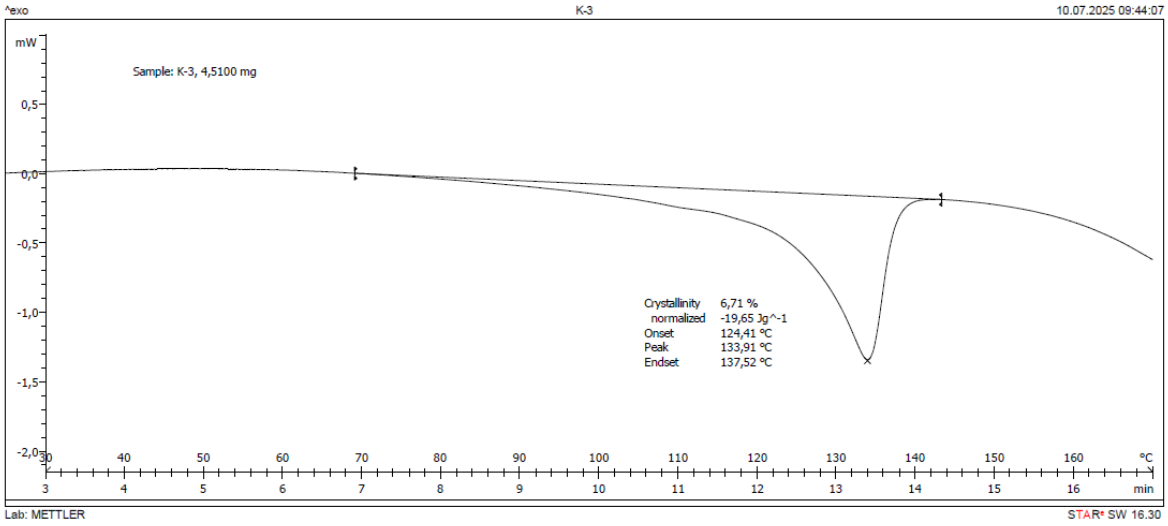

Figure S4. DSC curve of K3.

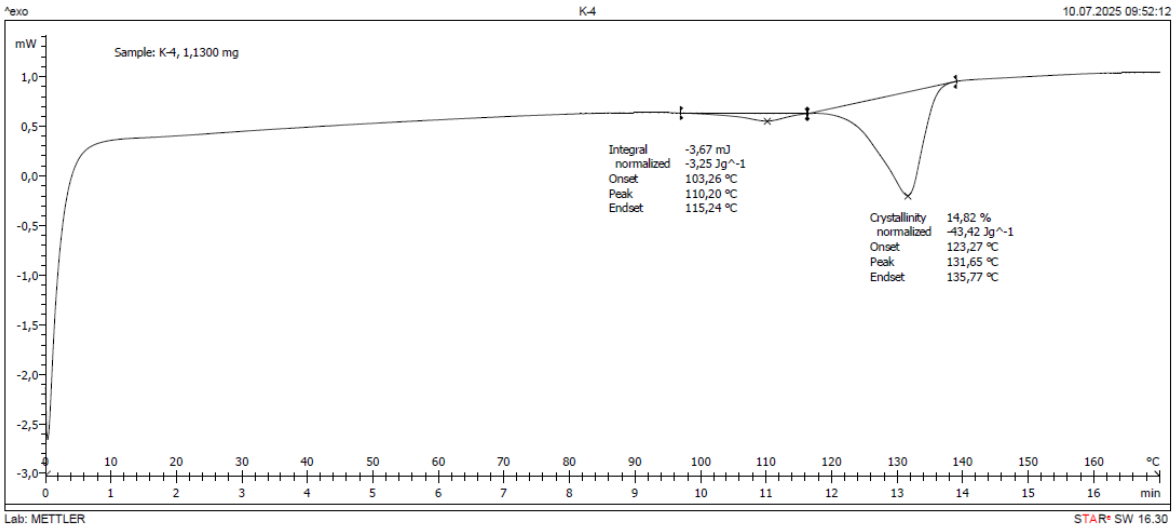

Figure S5. DSC curve of K4.

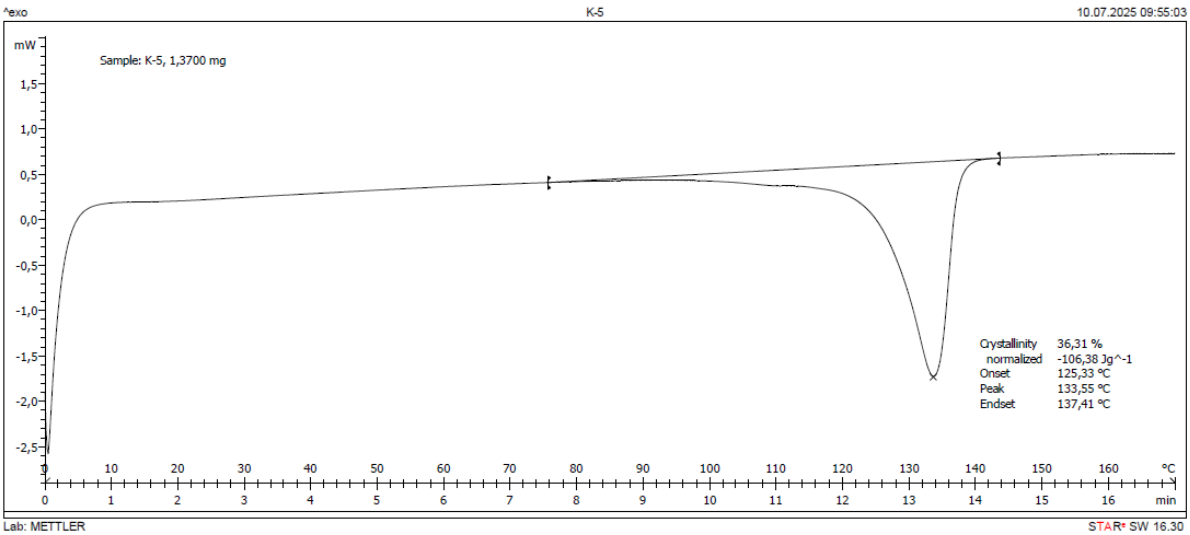

Figure S6. DSC curve of K5.

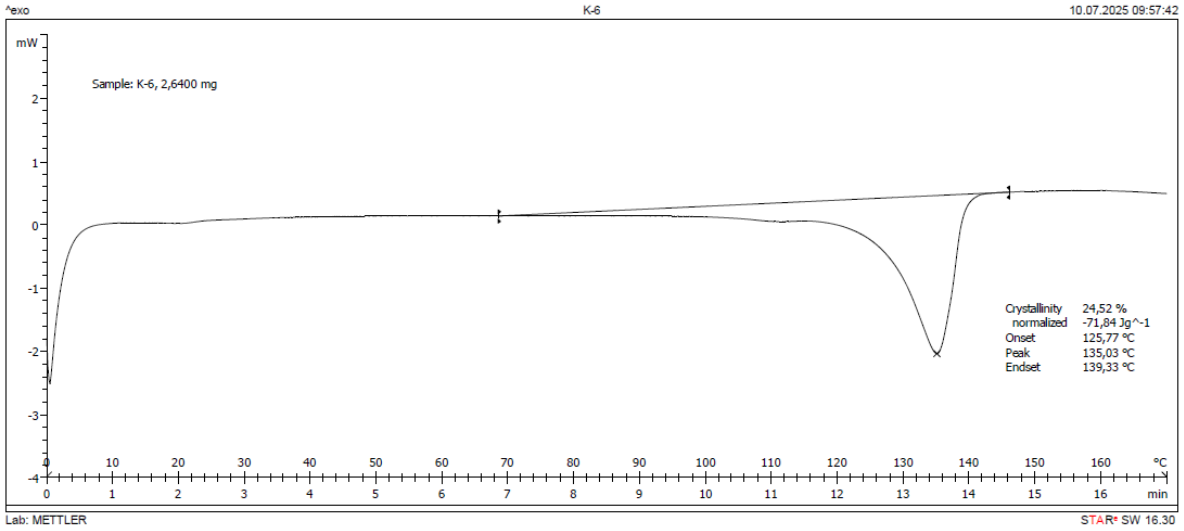

Figure S7. DSC curve of K6.

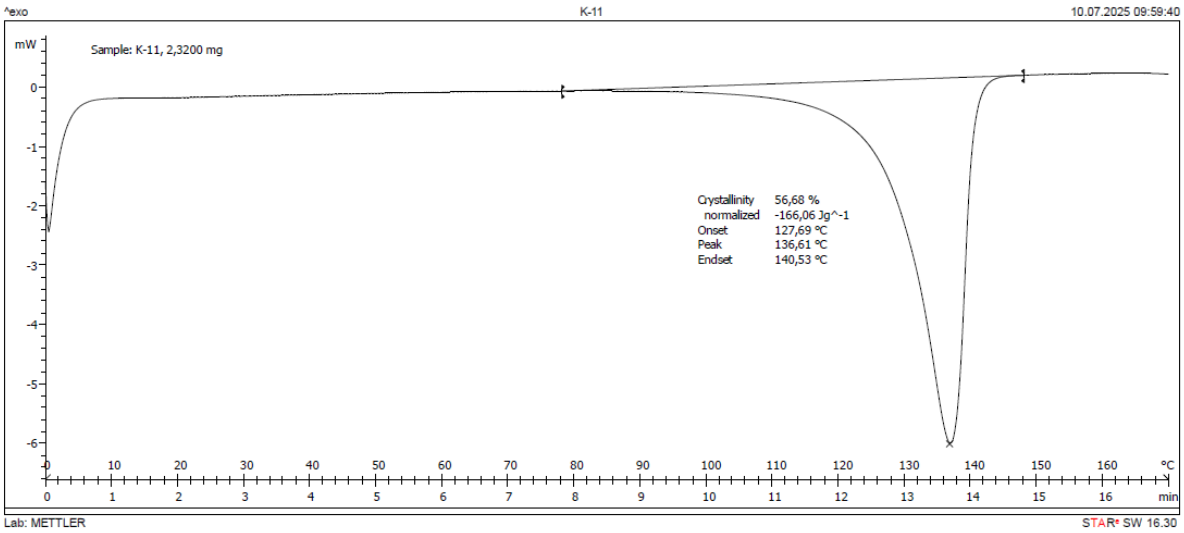

Figure S8. DSC curve of K11.

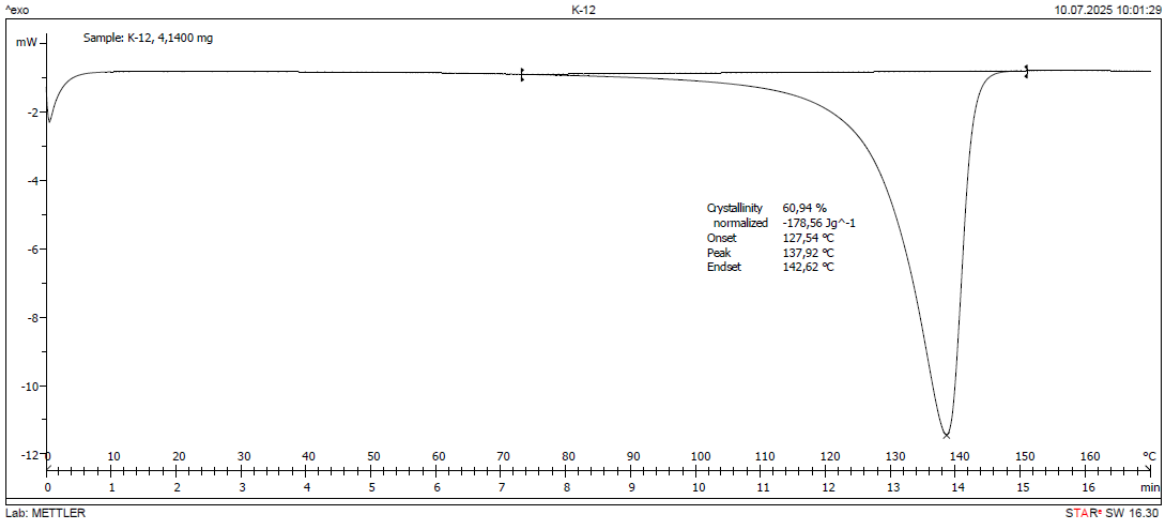

Figure S9. DSC curve of K12.

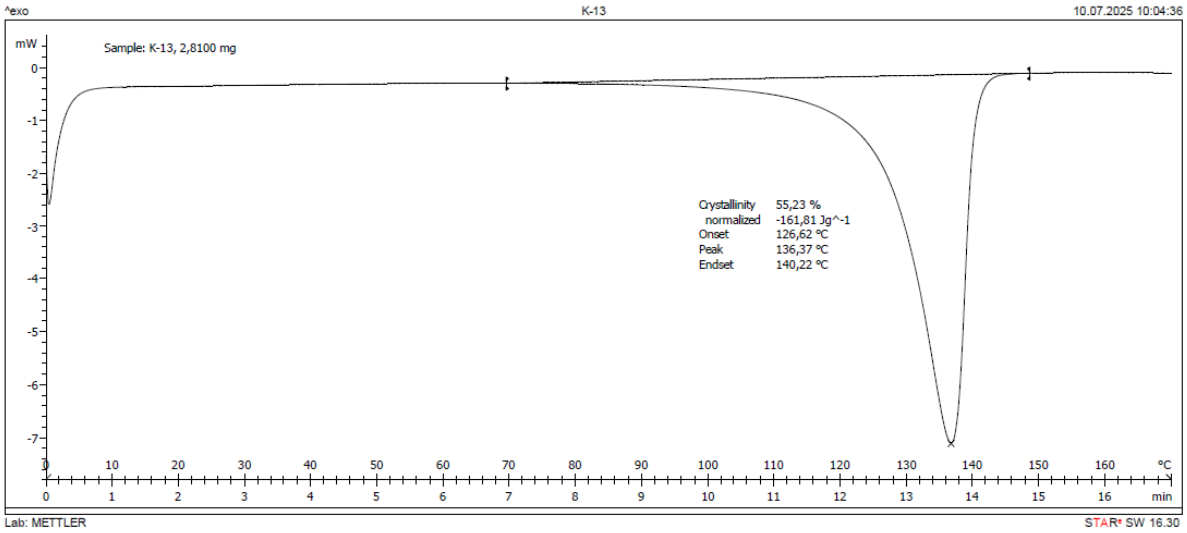

Figure S10. DSC curve of K13.

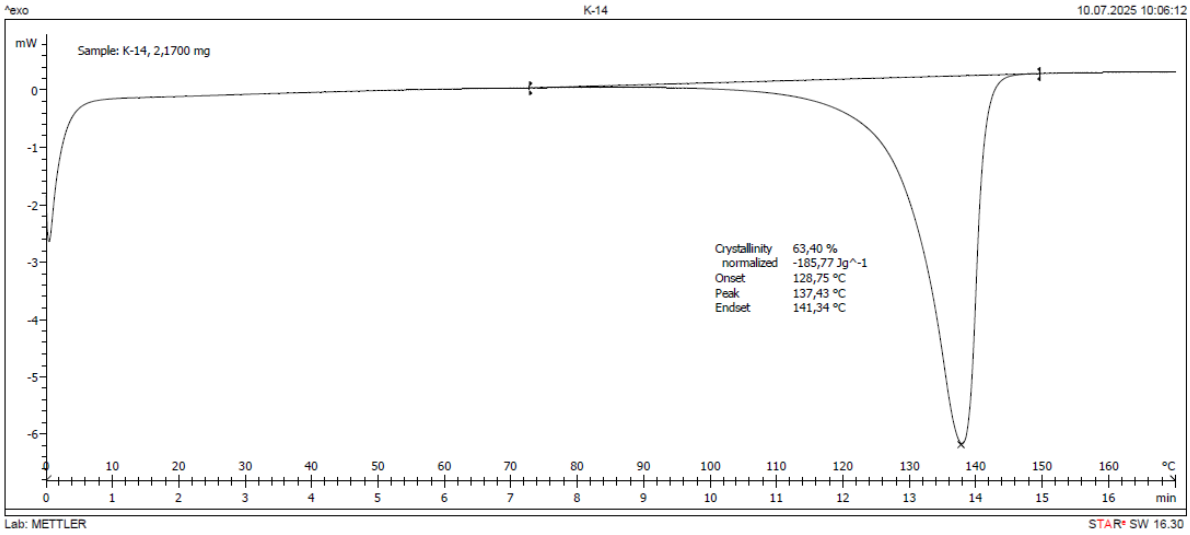

Figure S11. DSC curve of K14.

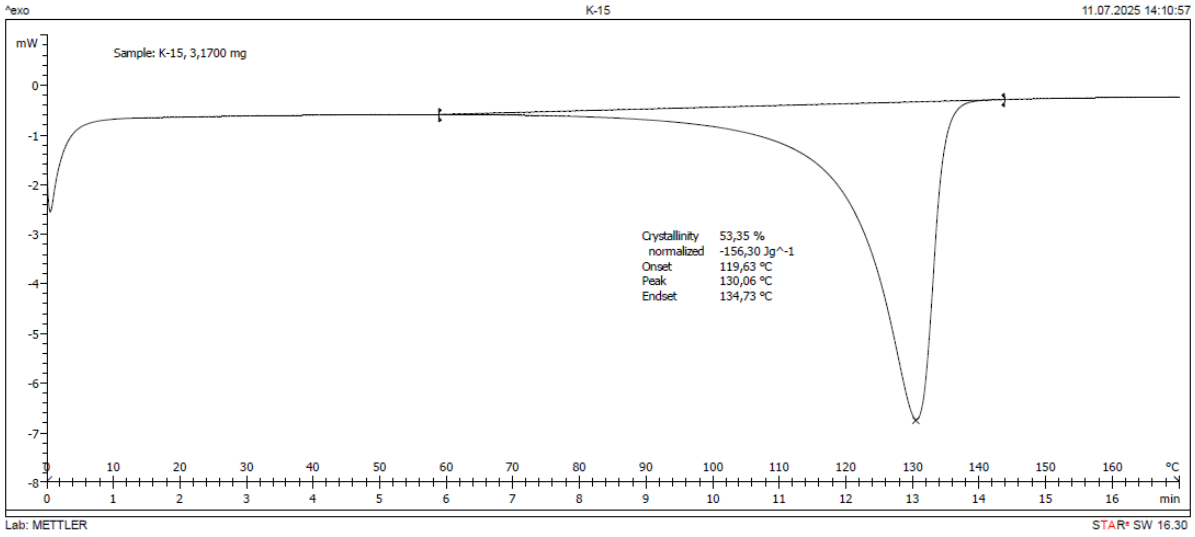

Figure S12. DSC curve of K15.

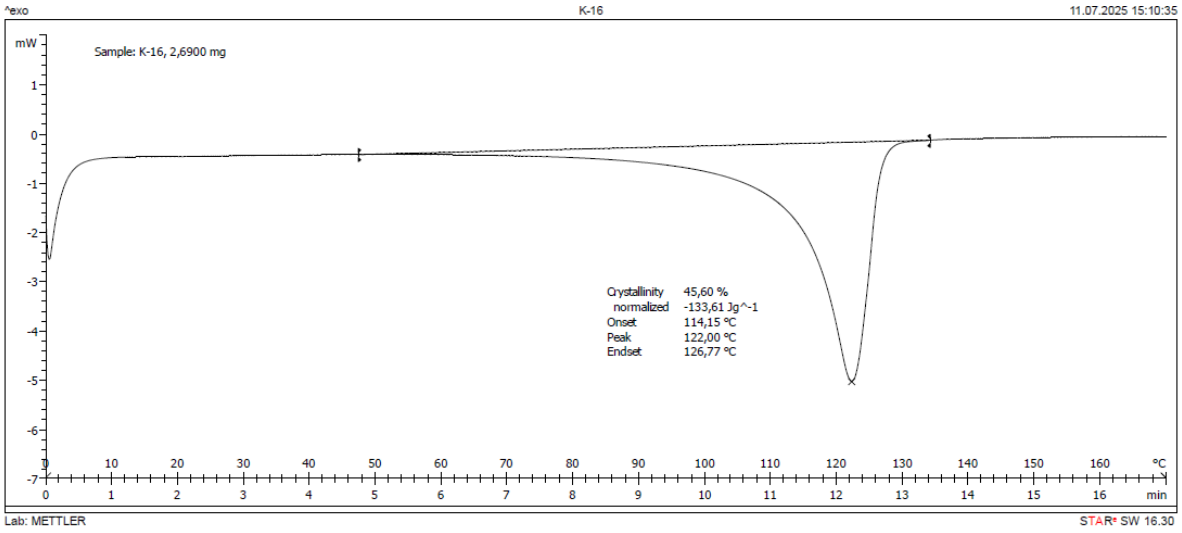

Figure S13. DSC curve of K16.

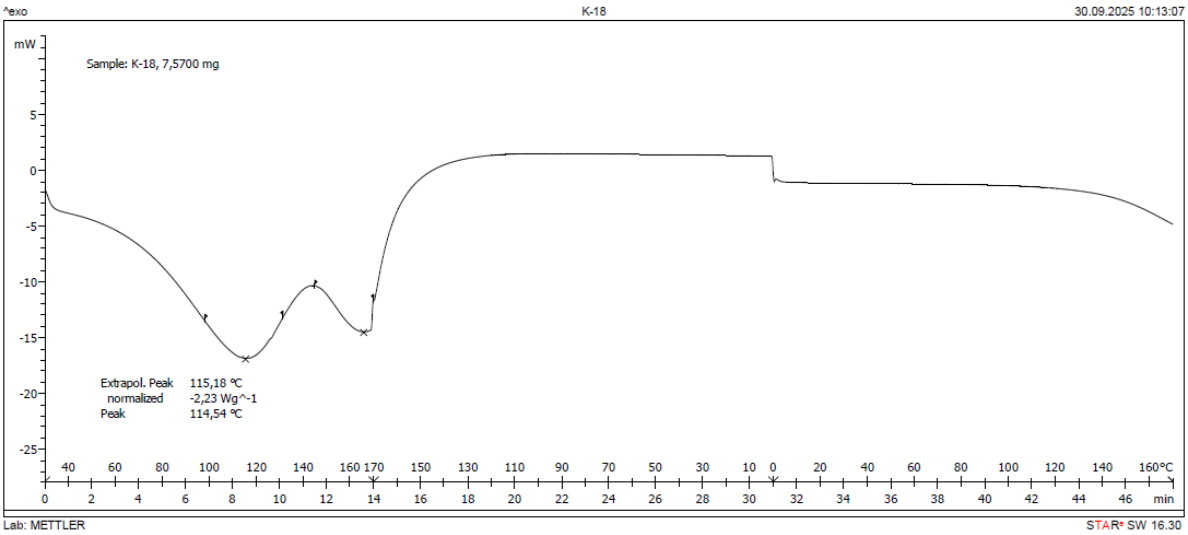

Figure S14. DSC curve of K18.

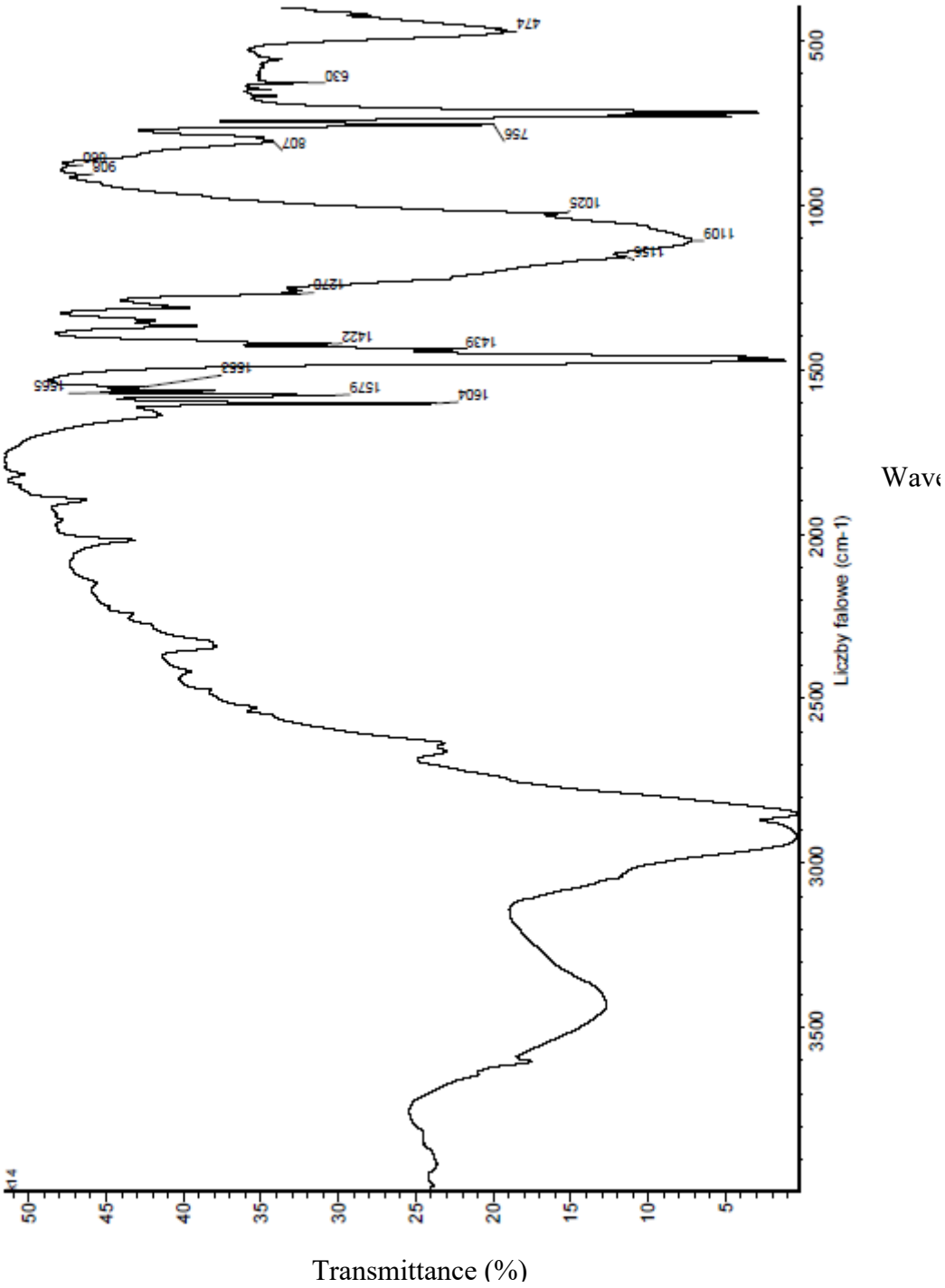

Figure S15. FT-IR spectra of K14.

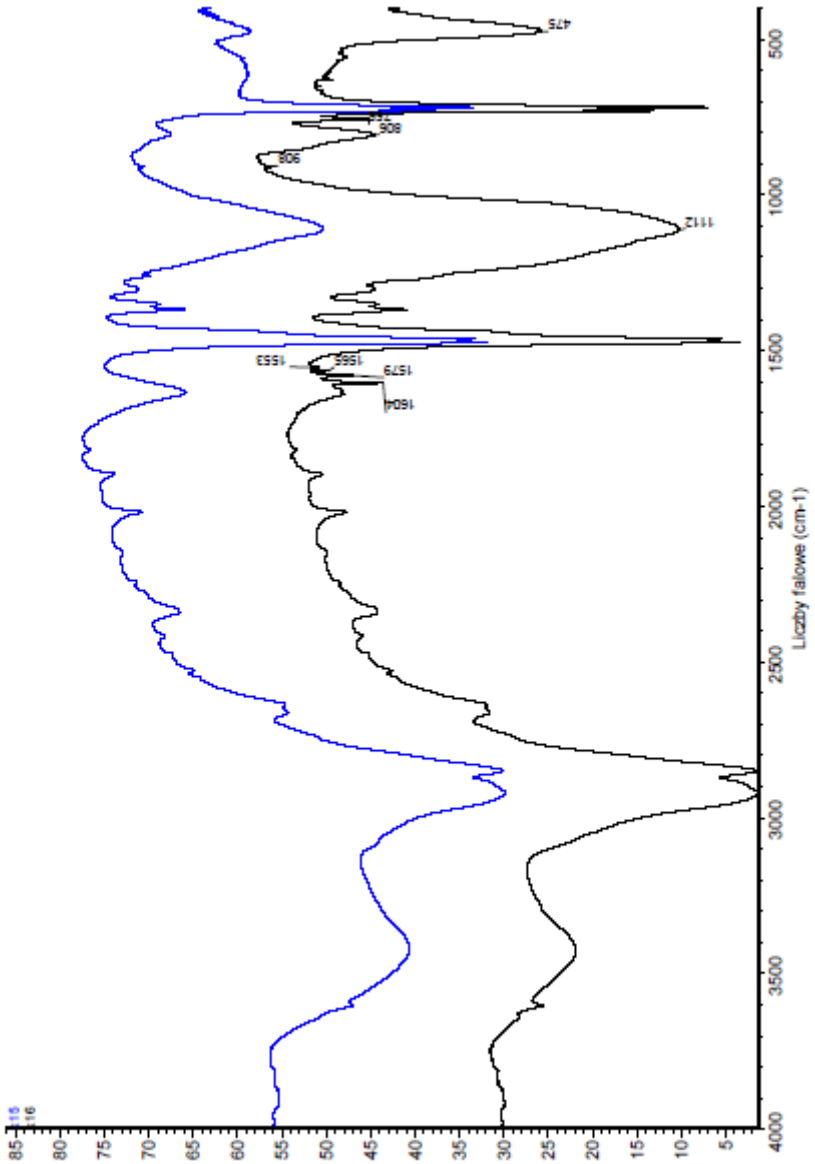

Figure S16. FT-IR spectra of K15 and K16.

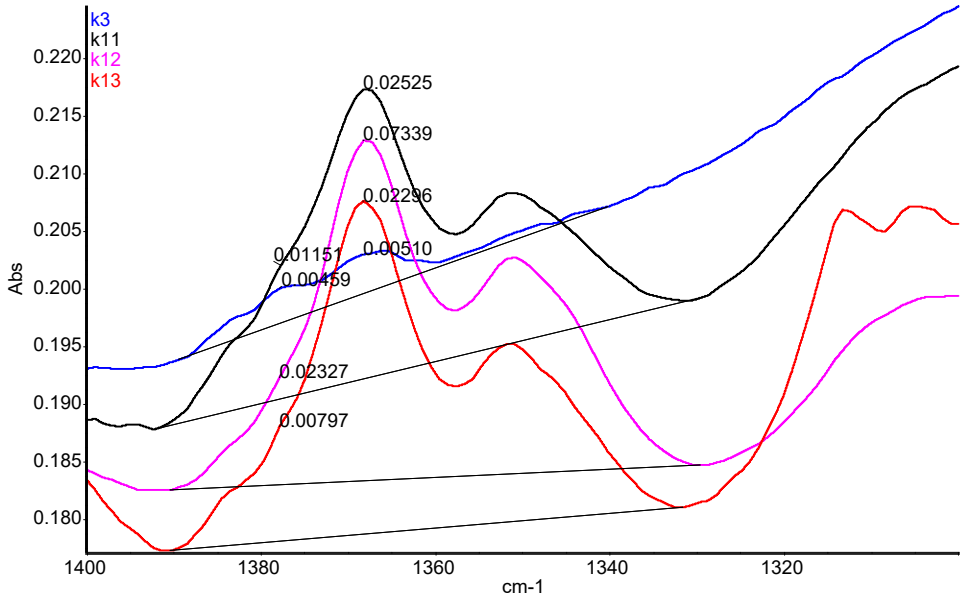

Figure S17. FT-IR spectra of K3, K11, K12 and K13.

Table S1. Selected X-ray data collection, processing and refinement parameters for the evaluated crystal structures of Rh1 and Rh2.

Data set	**Rh1** (1st data set)	**Rh1** (2nd data set)	**Rh2** (1st data set)	**Rh2** (2nd data set)
Formula	$C_{24}H_{22}N_3O_4RhS$		$C_{19}H_{11}N_3O_4RhS + H_2O$	
Formula mass, M / a.u.	551.42		498.29	
Crystal system	orthorhombic		monoclinic	
Space group	$Pbca$ (No. 61)		$P2_1/c$ (No. 14)	
Z	8		4	
F_{000}	2240		996	
Crystal colour & shape	colourless chipped-off plate	yellow small cut plate	clear light yellow plate	clear light yellow cut crystal
Crystal size / mm³	0.02×0.06×0.07	0.02×0.05×0.08	0.02×0.07×0.08	0.02×0.03×0.09
T / K	100	100	100	100
a / Å	10.288(2)	10.247(2)	13.670(3)	13.6552(5)
b / Å	15.184(3)	15.255(3)	9.858(2)	9.8730(3)
c / Å	27.605(6)	27.600(6)	13.826(3)	13.8328(6)
α / Å	90	90	90	90
β / Å	90	90	107.76(3)	107.743(4)
γ / Å	90	90	90	90
V / Å³	4312.1(15)	4314.5(15)	1774.4(7)	1776.20(12)
d_{calc} / g·cm⁻³	1.6988	1.6978	1.8653	1.8634
θ range	3.20–76.35°	3.20–76.35°	3.39–76.34°	3.40–73.92°
Absorption coefficient, μ / mm⁻¹ (radiation)	7.639 (Cu-K_α)	7.635 (Cu-K_α)	9.249 (Cu-K_α)	9.239 (Cu-K_α)
No. of reflections collected / unique (redundancy)	35477 / 4499 (7.9)	16076 / 4038 (4.0)	18885 / 3717 (5.1)	18814 / 3557 (5.3)
R_{int}	2.82%	3.57%	4.20%	4.13%
No. of reflections with $I > 3\sigma(I)$ (% of all data)	3715 (83%)	3121 (77%)	3213 (86%)	3066 (86%)
No. of parameters / restraints / constraints	280 / 2 / 106	280 / 2 / 106	268 / 2 / 46	268 / 2 / 46
$R[F]$ ($I > 3\sigma(I)$)	5.50%	6.13%	3.20%	3.10%
$wR[F^2]$ (all data)	13.00%	13.76%	9.37%	7.66%
$\varrho_{res}^{min/max}$ / e·Å⁻³	−3.01 / +4.05	−3.04 / +5.08	−0.82 / +1.40	−0.63 / +1.32
CCDC code	2498557	2498558	2498559	2498560

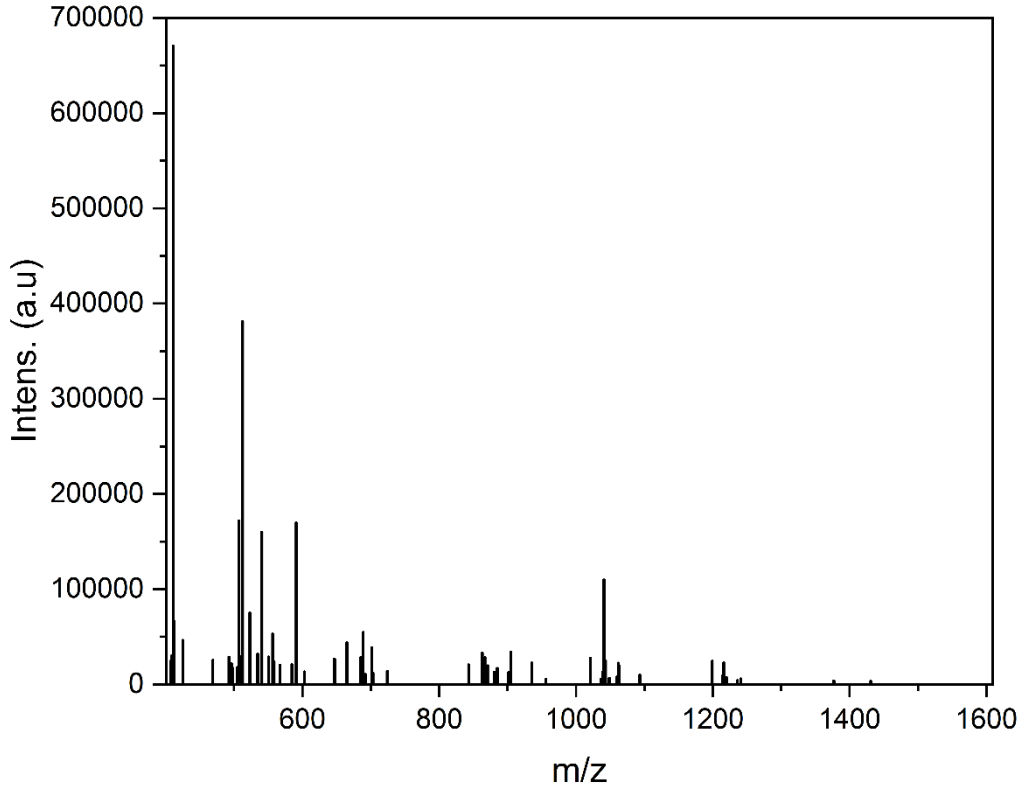

Figure S18. MALDI-TOF-MS spectrum of the K17 sample

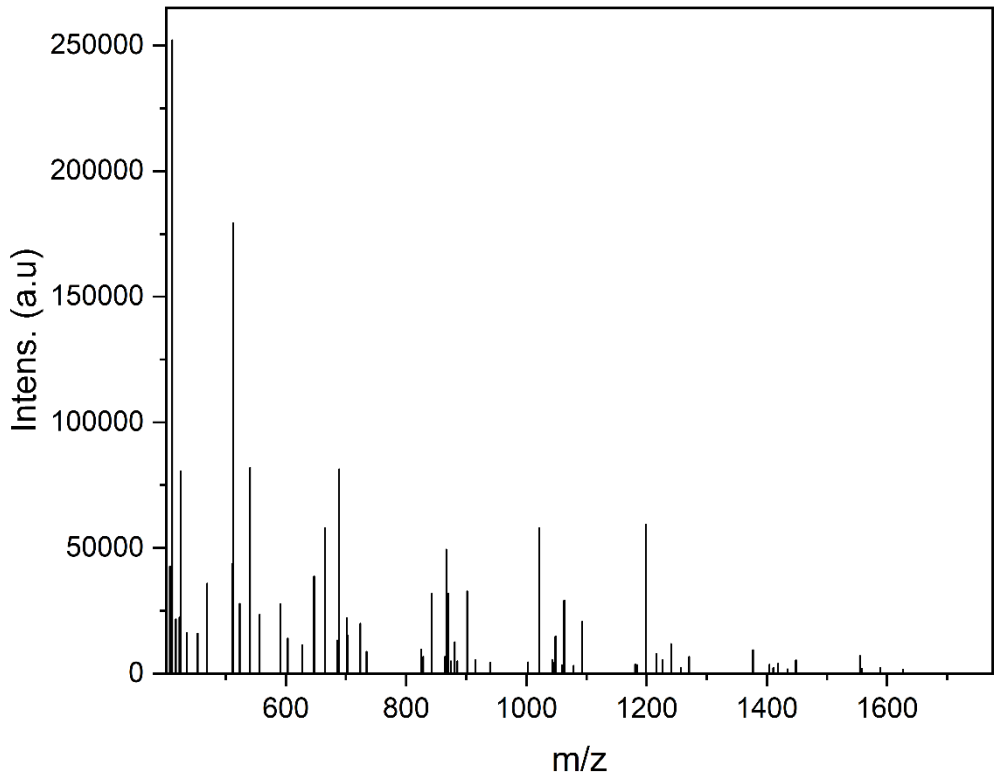

Figure S19. MALDI-TOF-MS spectrum of the K18 sample.

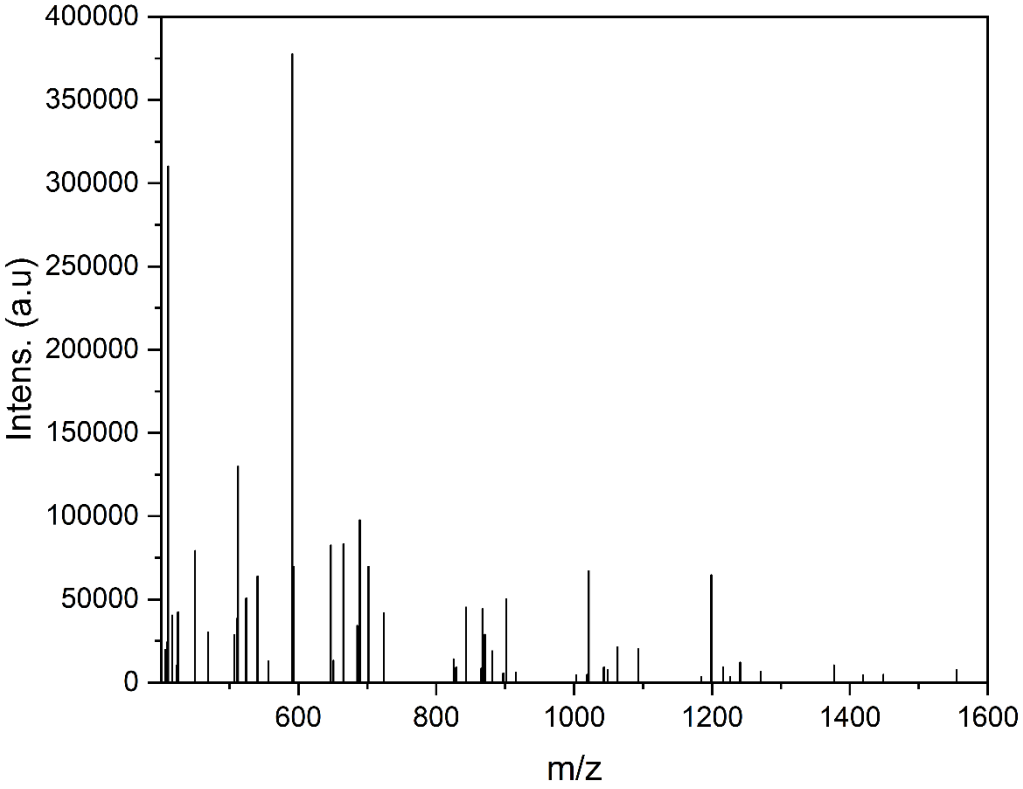

Figure S20. MALDI-TOF-MS spectrum of the K19 sample.

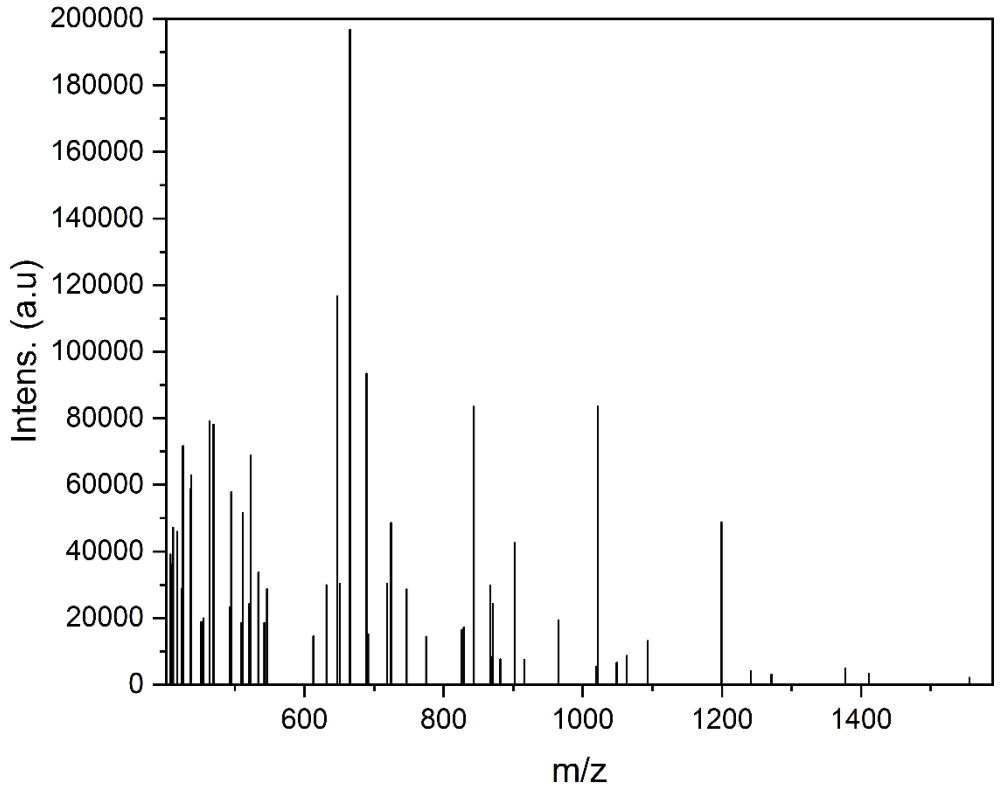

Figure S21. MALDI-TOF-MS spectrum of the K20 sample.

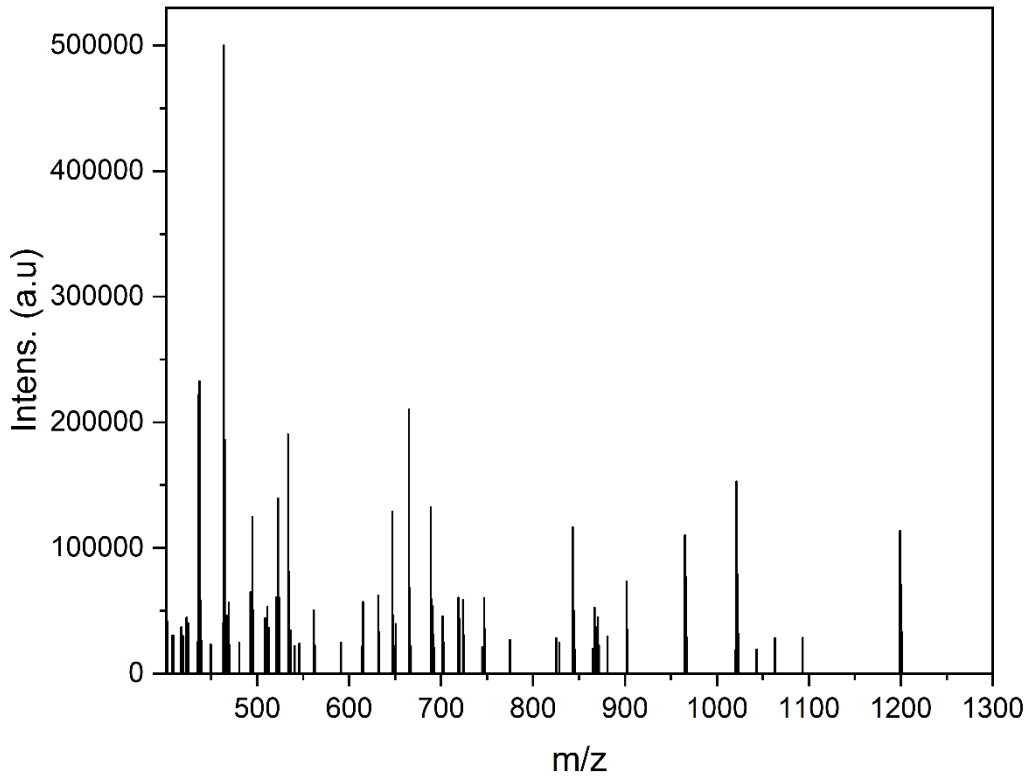

Figure S22. MALDI-TOF-MS spectrum of the K21 sample.

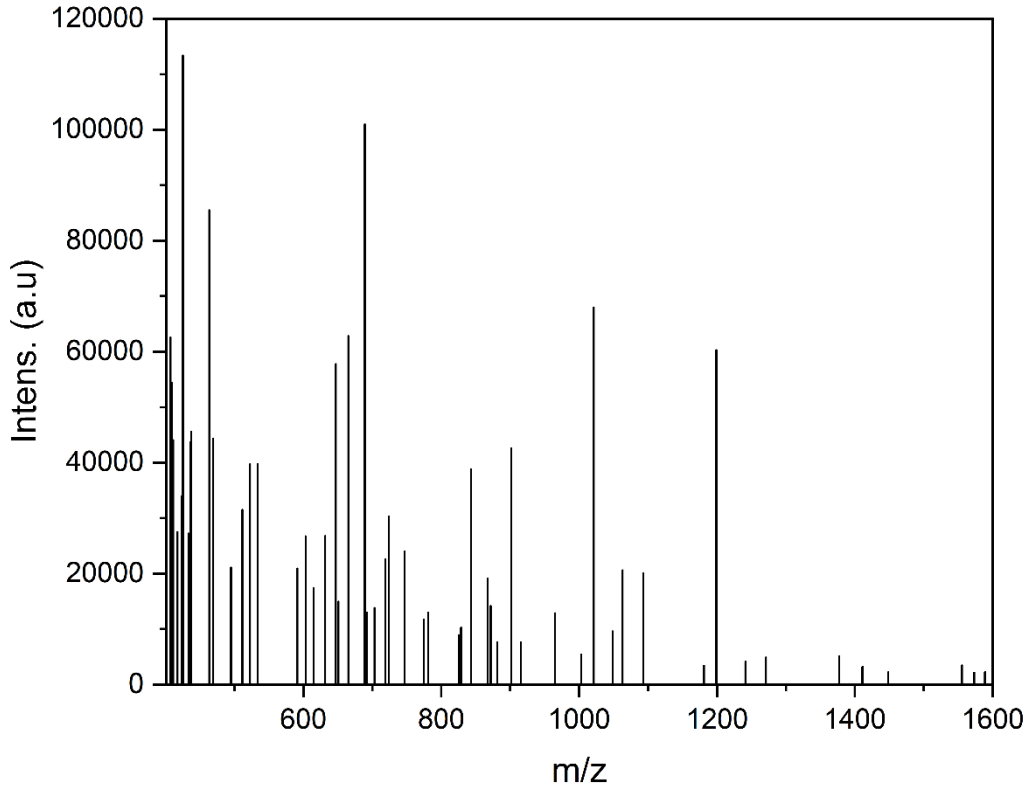

Figure S23. MALDI-TOF-MS spectrum of the K22 sample.