Supporting Information

For

Bis(4-carboxylpyrazol-1-yl)acetic acid: A scorpionate ligand for complexes with improved water solubility

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1. Single Crystal X-ray Diffraction Experiments

Table S1. Methods and solvents used in the preparation of single crystals of ligand **2** and complexes **4** - **6**.

Compound	Technique	Solution in	Solvent for solvent diffusion	Temperature
2	liquid-liquid diffusion	tetrahydrofurane	*n*-pentane	ambient
4	liquid-liquid diffusion	acetonitrile	chloroform	ambient
5	liquid-liquid diffusion	acetone	dichloromethane	ambient
6a-**1**	liquid-liquid diffusion	methanol	diethylether	ambient
6a-**2**	slow evaporation	water	-	4°C

Table S2. Crystal data and refinement details of compounds **2** and **4**-**6**.

	2	**4**	**5**	**6a-1**	**6a-2**
CCDC number	2130703	2130704	2130706	2130707	2130708
empirical formula	$C_{10}H_8N_4O_6 \times C_4H_8O$	$C_{13}H_7MnN_4O_9$	$C_{13}H_7N_4O_9Re \times 0.5\ H_2O$	$C_{12}H_7ClN_4O_8Ru \times CH_4O$	$C_{12}H_7ClN_4O_8Ru \times H_2O$
formula mass [g mol^{-1}]	352.31	418.17	558.43	503.78	489.75
crystal color/habit	colourless/ block	light yellow/ block	colourless/ block	metallic yellow/ block	yellow/ plate
crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group, Z	*I*2/*a*, 8	$P2_1/n$, 4	*P*−1, 8	*C*2/*c*, 8	$P2_1/c$, 4
a [Å]	15.8518(3)	14.9306(5)	14.3811(5)	33.2013(8)	12.5010(2)
b [Å]	15.4697(4)	5.6066(2)	15.1010(5)	11.7943(3)	14.0811(2)
c [Å]	13.9712(2)	20.6630(8)	17.2257(6)	10.7307(2)	9.18410(10)
α [°]	90	90	107.251(3)	90	90
β [°]	100.252(2)	107.404(4)	94.748(3)	96.218(2)	93.0360(10)
γ [°]	90	90	110.515(3)	90	90
V [Å^3]	3371.35(12)	1650.51(11)	3272.3(2)	4177.27(17)	1614.39(4)
Θ[°]	4.025 to 72.726	3.238 to 72.278	2.747 to 72.529	3.980 to 72.544	3.541 to 72.586
h	−19 to 19	−18 to 18	−17 to 17	−40 to 37	−15 to 8
k	−19 to 18	−6 to 6	−13 to 18	−14 to 10	−17 to 16
l	−17 to 11	−17 to 25	−21 to 16	−13 to 10	−11 to 11
F(000)	1472	840	2120	2000	968
μ (Cu-K_α) [mm^{-1}]	0.970	7.077	15.146	7.726	9.973
crystal size [mm]	0.451 × 0.131 × 0.099	0.107 × 0.078 × 0.031	0.075 × 0.062 × 0.026	0.366 × 0.083 × 0.081	0.248 × 0.115 × 0.076
D_c [g cm^{-3}], *T* [K]	1.388, 99.99(10)	1.683, 99.9(3)	2.267, 99.9(4)	1.602, 99.9(5)	2.015, 99.9(4)
reflections collected	9810	7946	21454	8112	5952
independent reflections	3302	3171	12476	4030	3100
obs. Reflections, $I > 2\sigma I$	2949	2540	10901	3810	2970
Parameters, restraints	348, 296	246, 0	1008, 0	262, 19	260, 21
weight parameter *a*	0.0652	0.0382	0.0291	0.0611	0.0458
weight parameter *b*	4.7913	0.4141	1.6826	19.7346	1.4266
R_1 (observed)	0.0508	0.0415	0.0305	0.0423	0.0290
R_1 (overall)	0.0552	0.0589	0.0381	0.0438	0.0300
wR_2 (observed)	0.1306	0.0907	0.0698	0.1113	0.0759
wR_2 (overall)	0.1345	0.0991	0.0733	0.1128	0.0768
diff. peak/hole [e/Å]	0.713/ −0.379	0.392/−0.346	1.894/ −1.299	1.207/ −0.778	0.970/ −1.058
goodness-of-fit on F^2	1.061	1.040	1.036	1.041	1.058

Table S3. Selected bond lengths and angles of molecular structure of H_3bcpza (**2**).

Selected bond lengths [Å]	**H_3bcpza (2))**
C2–O1	1.275(3)
C2–O2	1.232(3))
N11–N12	1.362(2)
N11–C12	1.324(2)
C12–C13	1.406(2)
O11–C16	1.322(2)
O12–C16	1.216(2)
Selected angles [°]	
N12–C1–C2	111.63(14)
N11–N12–C1	118.85(13)

Table S4. Selected bond lengths and angles of molecular structure of [Mn(H_2bcpza)$(CO)_3$] (**4**).

Selected bond lengths [Å]	**[Mn(H_2bcpza)$(CO)_3$] (4)**
Mn–O1	2.061(2)
Mn–N11	2.041(3)
Mn–N21	2.051(2)
Mn–C3	1.818(3)
Mn–C4	1.809(3)
Mn–C5	1.809(3)
Selected angles [°]	
O1–Mn–N11	85.61(9)
O1–Mn–N21	84.72(9)
N11–Mn–N21	84.54(10)

Table S5. Selected bond lengths and angles of molecular structure of [Re(H_2bcpza)$(CO)_3$] (**5**). The four independent molecules in the asymmetric unit are marked with superscripts **a**-**d**.

Selected bond lengths [Å]	**[Re(H_2bcpza)$(CO)_3$] (5)**
Re–O1	2.189(3)[a], 2.154(3)[b], 2.168(3)[c], 2.172(4)[d]
Re–N11	2.181(4)[a], 2.187(4)[b], 2.182(4)[c], 2.194(5)[d]
Re–N21	2.183(5)[a], 2.163(4)[b], 2.186(4)[c], 2.158(4)[d]
Re–C3	1.937(6)[a], 1.927(6)[b], 1.924(6)[c], 1.937(6)[d]
Re–C4	1.903(6)[a], 1.909(6)[b], 1.902(6)[c], 1.905(6)[d]
Re–C5	1.915(6)[a], 1.916(6)[b], 1.929(5)[c], 1.945(6)[d]
Selected angles [°]	
O1–Re–N11	81.80(14)[a], 82.83(14)[b], 80.80(14)[c], 78.80(15)[d]
O1–Re–N21	80.17(15)[a], 80.30(15)[b], 80.82(14)[c], 83.44(15)[d]
N11–Re–N21	80.61(16)[a], 82.68(15)[b], 82.04(15)[c], 82.08(16)[d]

Table S6. Selected distances and angles of molecular structure of [Ru(H_2bcpza)Cl$(CO)_2$] (**6a-1** + **6a-2**).

Selected bond lengths [Å]	**[Ru(H_2bcpza)Cl$(CO)_2$] (6a-1)**	**[Ru(H_2bcpza)Cl$(CO)_2$] (6a-2)**
Ru–O1	2.108(3)	2.1123(19)
Ru–N11	2.118(3)	2.118(2)
Ru–N21	2.099(3)	2.131(2)
Ru–C3	1.956(5)	1.934(3)
Ru–C4	1.919(4)	1.910(3)
Ru–Cl	2.3690(11)	2.3596(8)
Selected angles [°]		
O1–Ru–N11	85.28(11)	85.24(8)
N21–Ru–O1	85.50(11)	85.47(7)
N21–Ru–N11	83.78(12)	83.76(9)

2. ^{1}H NMR and ^{13}C NMR spectra

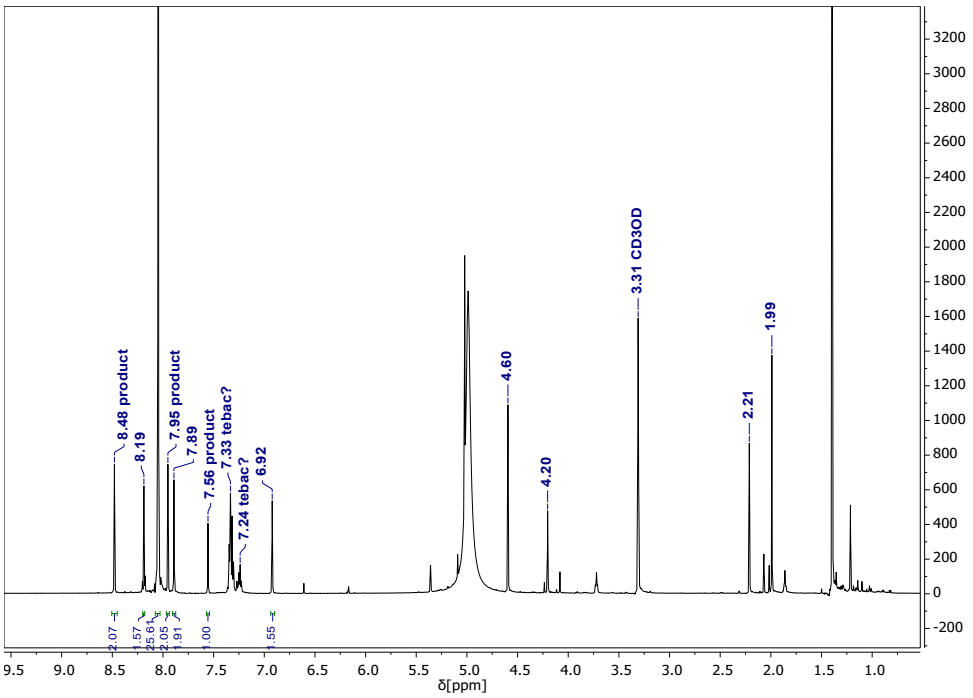


Figure S1. ^{1}H NMR spectrum (methanol-d_4) of the extracted organic phase regarding the attempted synthesis of H_3bcpza (**2**) by using pyrazole-4-carboxylic acid as precursor.

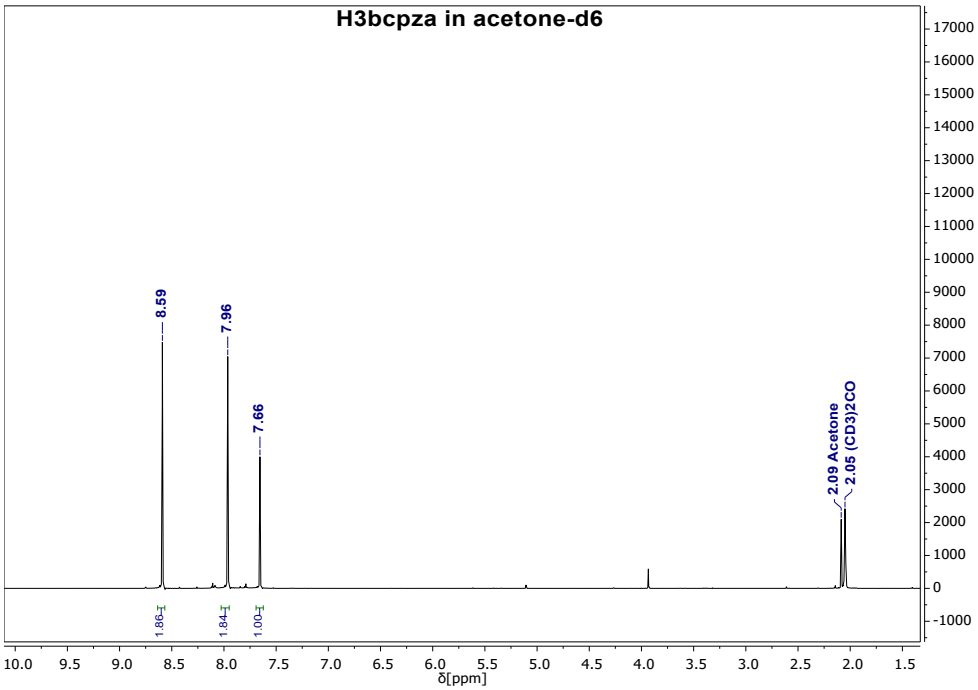


Figure S2. ^{1}H NMR spectrum of H_3bcpza (**2**) in acetone-d_6.

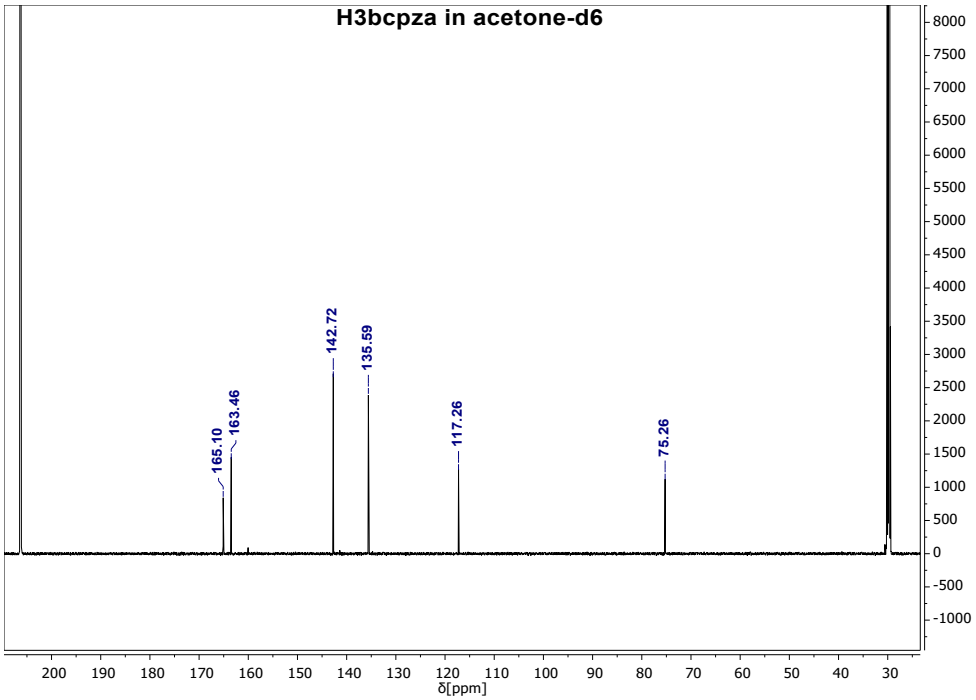


Figure S3. ^{13}C NMR spectrum of H_3bcpza (**2**) in acetone-d_6.

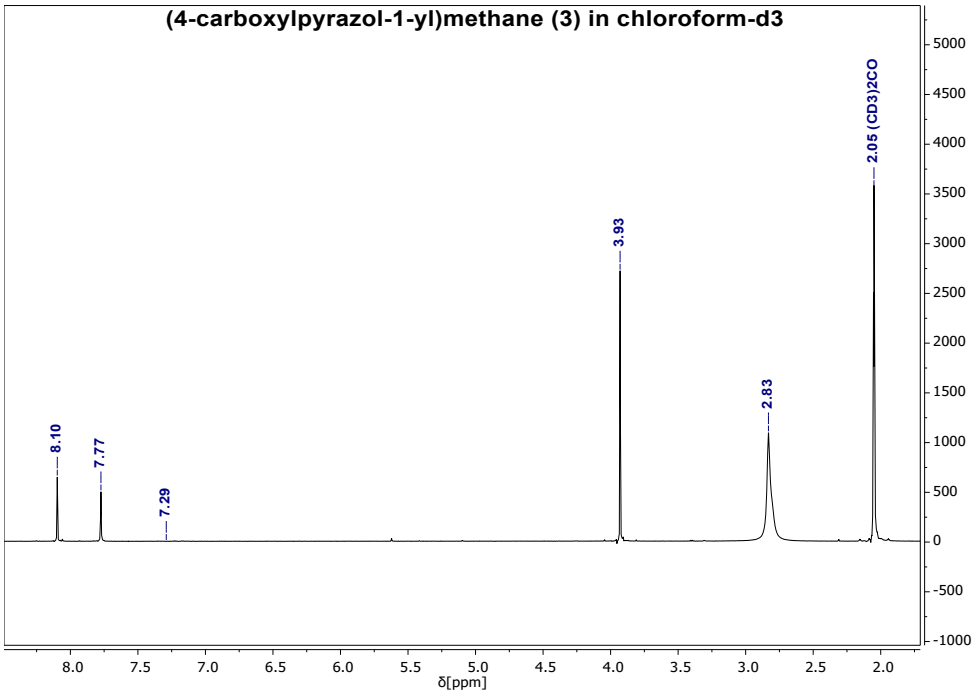


Figure S4. ^{1}H NMR spectrum of (4-carboxylpyrazol-1-yl)methane (**3**) in chloroform-d_3.

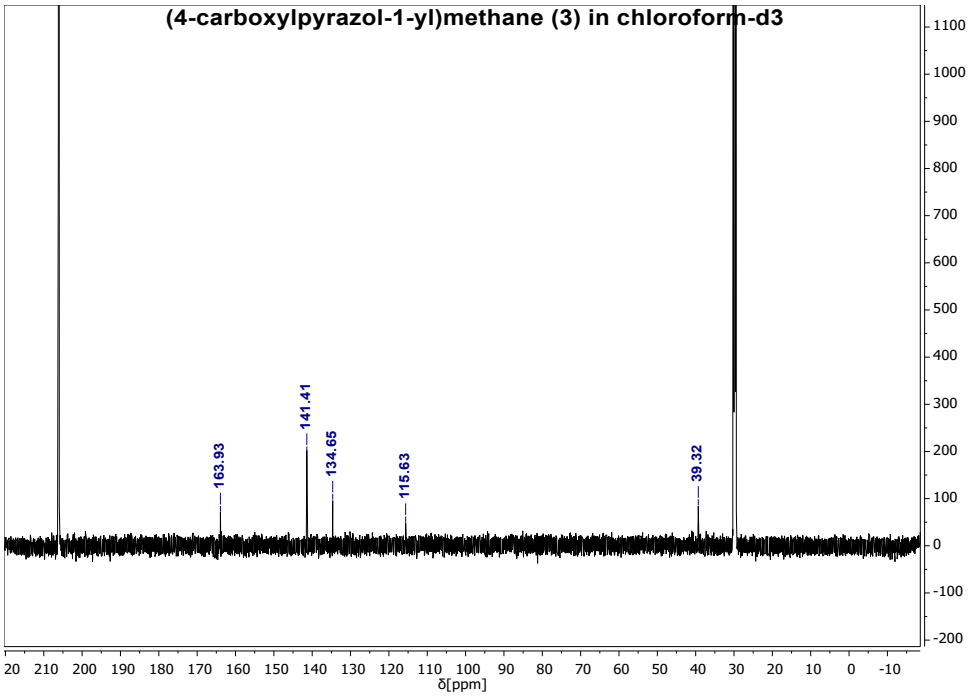


Figure S5. ^{13}C NMR spectrum of (4-carboxylpyrazol-1-yl)methane (**3**) in chloroform-d_3.

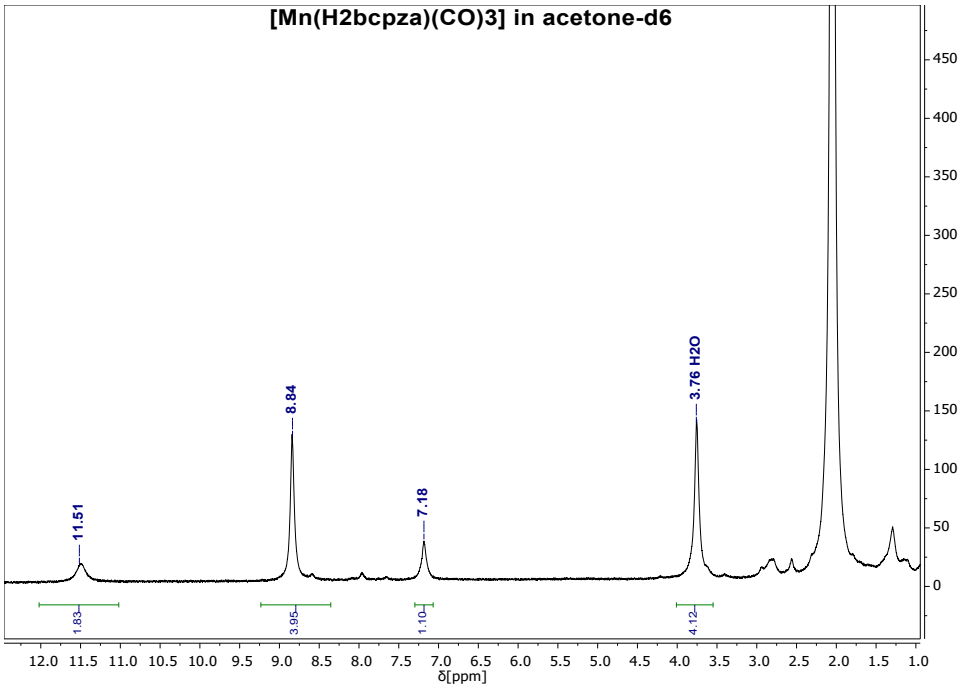


Figure S6. ^{1}H NMR spectrum of [Mn(H_2bcpza)($CO)_3$] (**4**) in acetone-d_6.

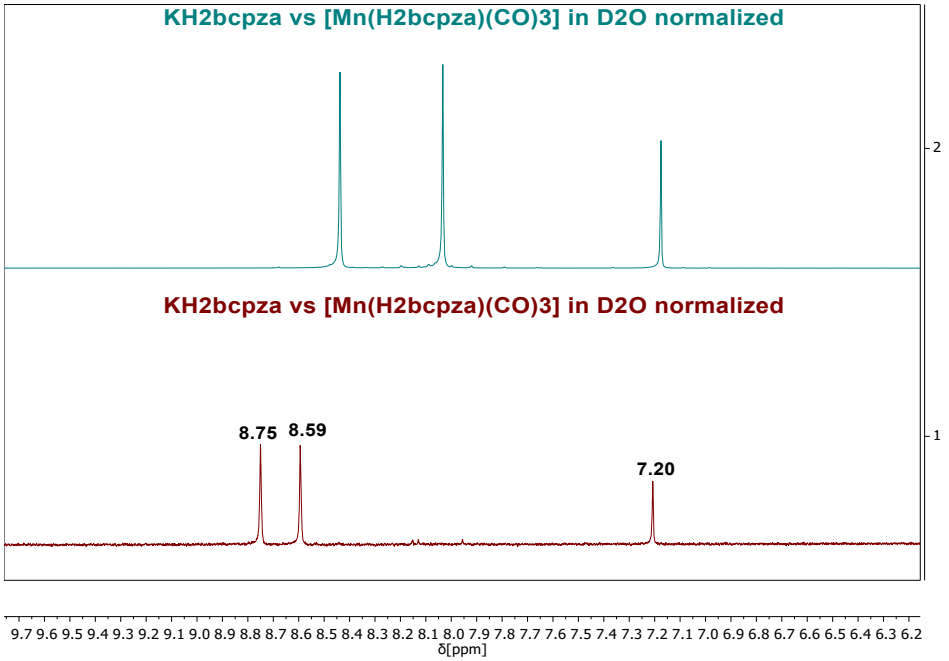


Figure S7. ^{1}H NMR of KH_2bcpza in D_2O (top) and [Mn(H_2bcpza)($CO)_3$] (**4**) in D_2O (bottom, normalized).

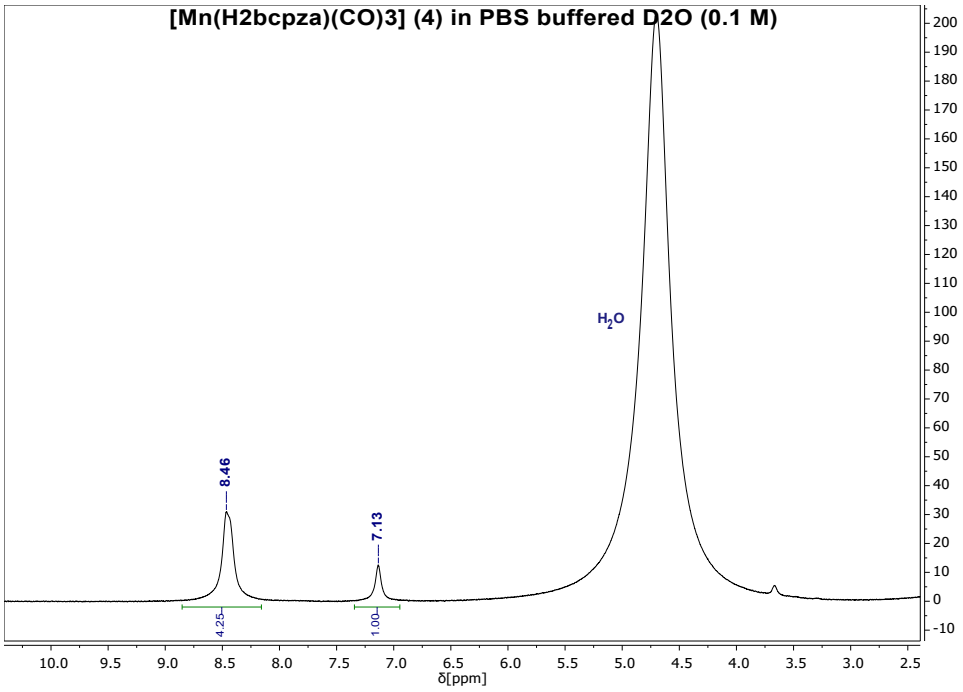


Figure S8. 1H NMR spectrum of [Mn(H_2bcpza)($CO)_3$] (**4**) in PBS buffered D_2O (0.1 M).

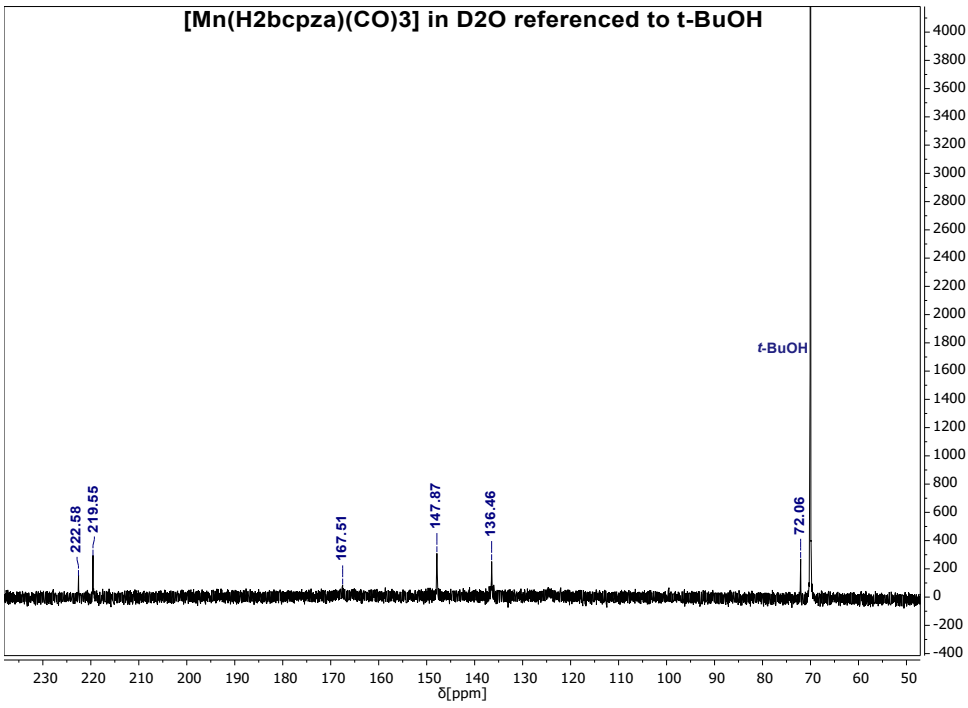


Figure S9. ^{13}C NMR spectrum of [Mn(H_2bcpza)($CO)_3$] (**4**) in PBS buffered (0.1 M) D_2O referenced to *t*-BuOH. The second carboxyl group as well as the quartenary carbon atom C^4_{pz} could not be resolved.

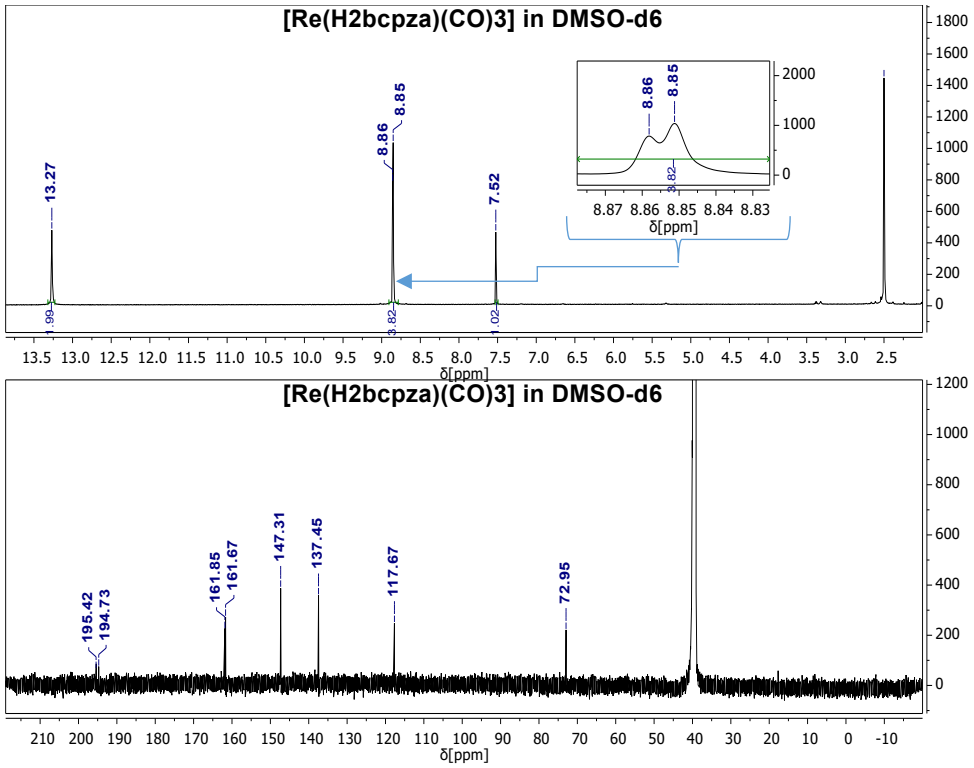


Figure S10. ^{1}H & ^{13}C NMR spectrum of [Re(H_2bcpza)($CO)_3$] (**5**) in dmso-d_6.

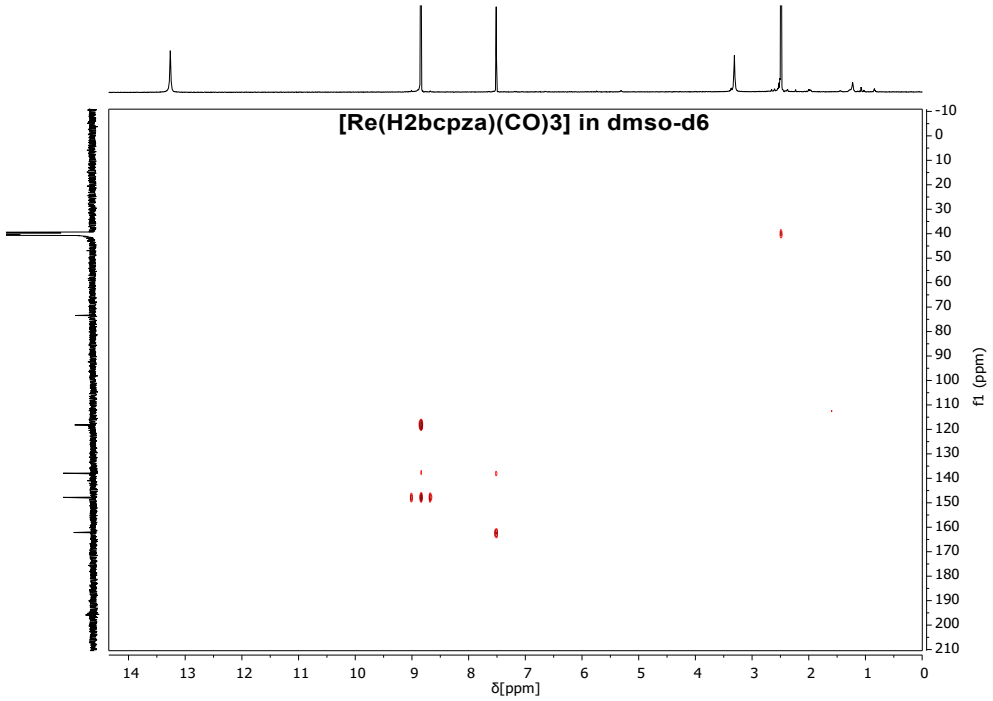


Figure S11. 2D HMBC spectrum of [Re(H_2bcpza)($CO)_3$] (**5**) in dmso-d_6.

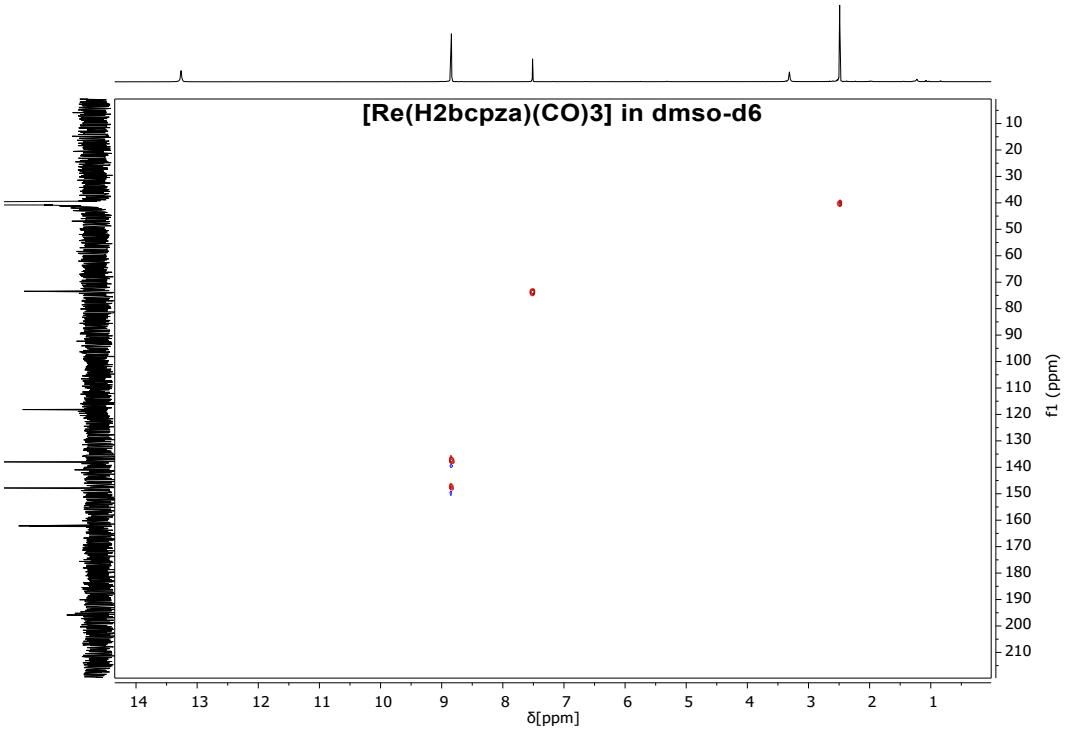


Figure S12. 2D HSQC spectrum of [Re(H_2bcpza)($CO)_3$] (**5**) in dmso-d_6.

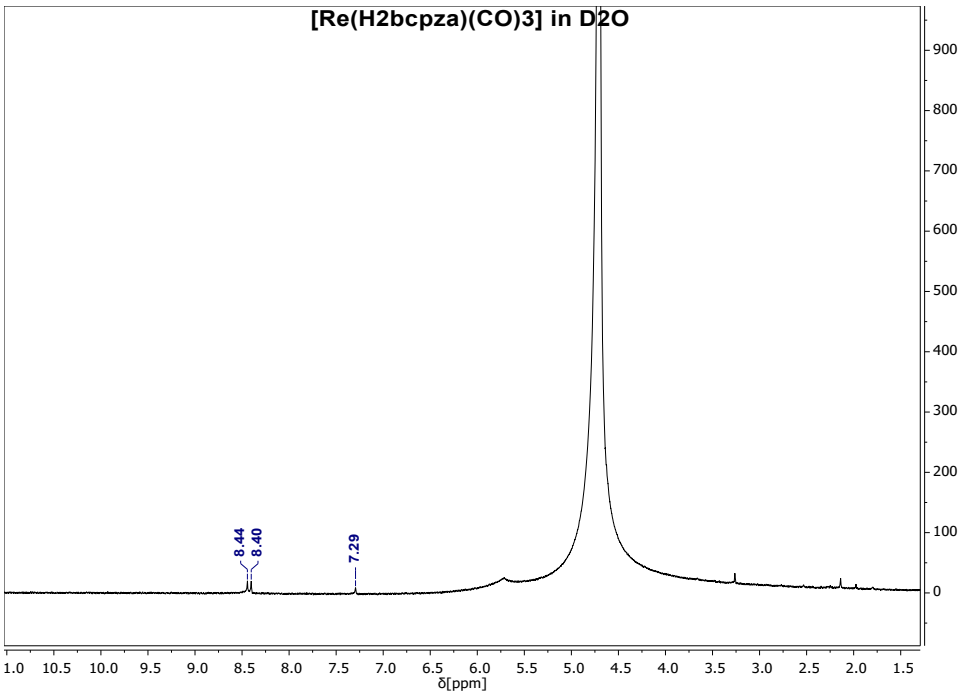


Figure S13. ^{1}H NMR spectrum of [Re(H_2bcpza)($CO)_3$] (5) in D_2O.

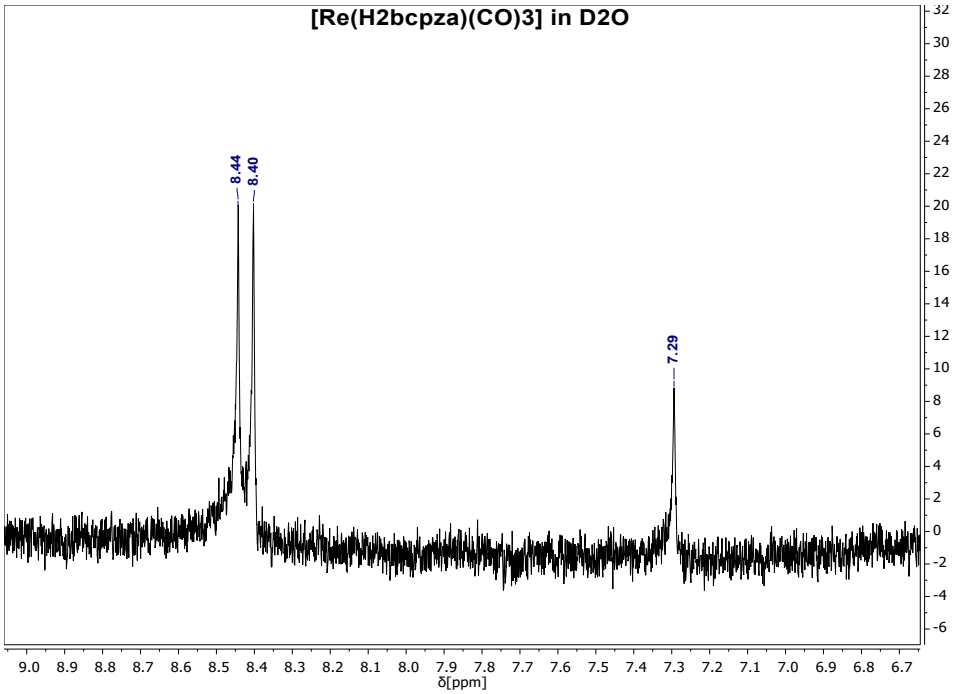


Figure S14. ^{1}H NMR spectrum of [Re(H_2bcpza)($CO)_3$] (**5**) in D_2O.

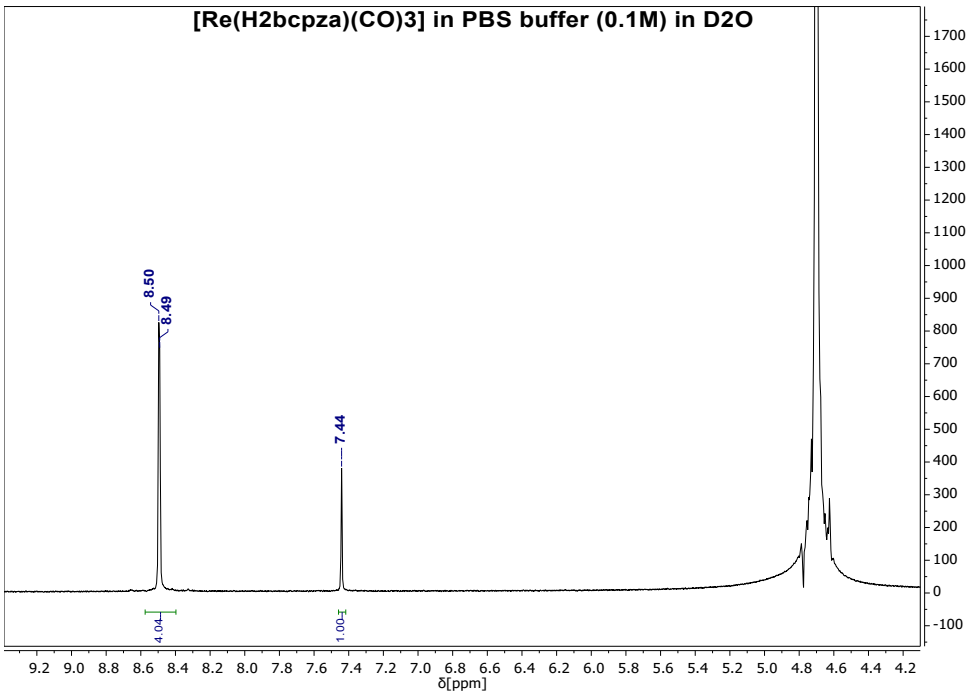


Figure S15. ^{13}C NMR spectrum of [Re(H_2bcpza)($CO)_3$] (**5**) in PBS buffered (0.1M) D_2O.

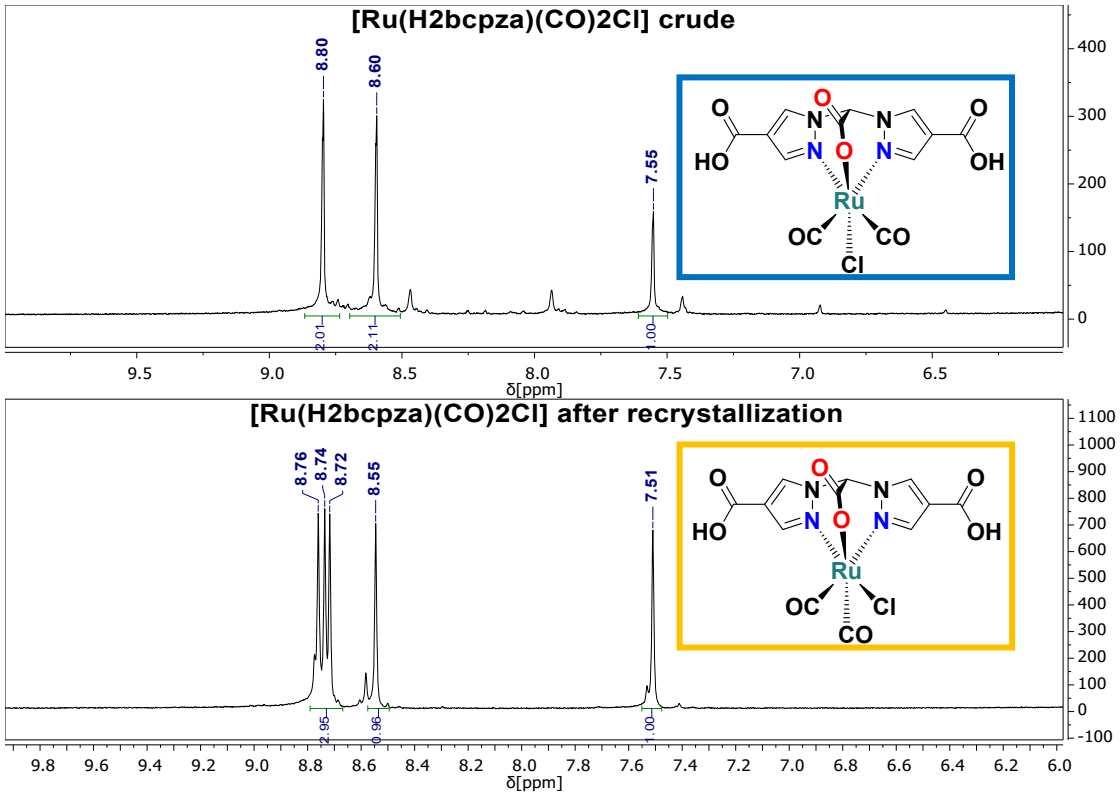


Figure S16. Top: ^{1}H NMR spectrum of the crude product [Ru(H_2bcpza)Cl(CO)$_2$] obtained by removing the solvent of the reaction mixture. The spectrum was recorded in methanol-d_4 and mainly displays the symmetric isomer [Ru(H_2bcpza)Cl(CO)$_2$] (**6a**). Bottom: ^{1}H NMR spectrum of the asymmetric [Ru(H_2bcpza)Cl(CO)$_2$] (**6b**) obtained after purification of **6a** and subsequent recrystallization from methanol. The spectrum was recorded in methanol-d_4.

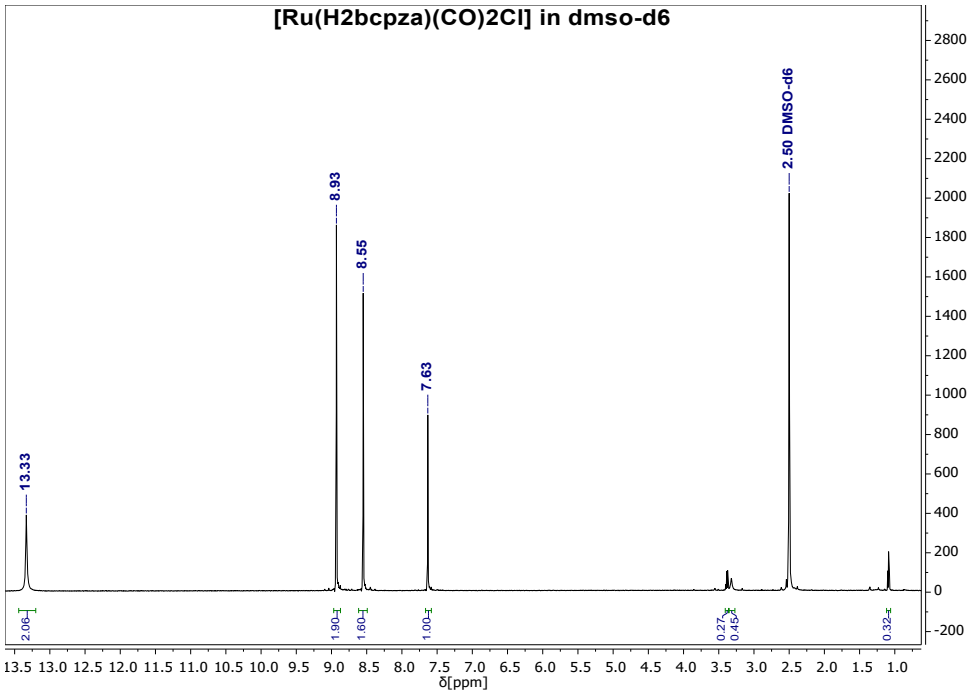


Figure S17. ^{1}H NMR spectrum of [Ru(H_2bcpza)Cl($CO)_2$] (**6a**) in dmso-d_6.

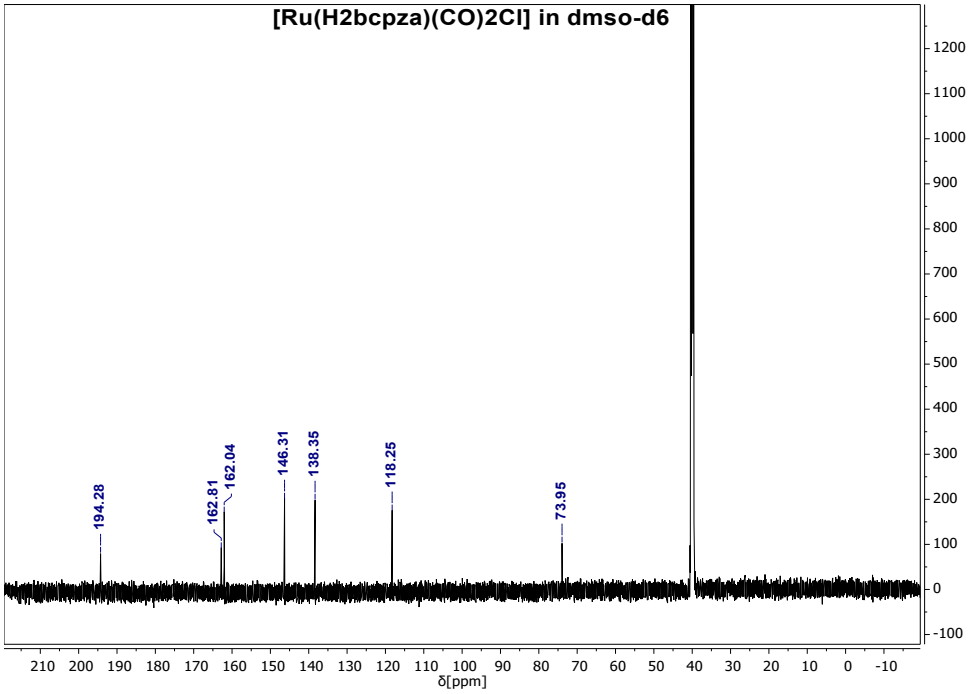


Figure S18. ^{13}C NMR spectrum of [Ru(H_2bcpza)Cl($CO)_2$] (**6a**) in dmso-d_6.

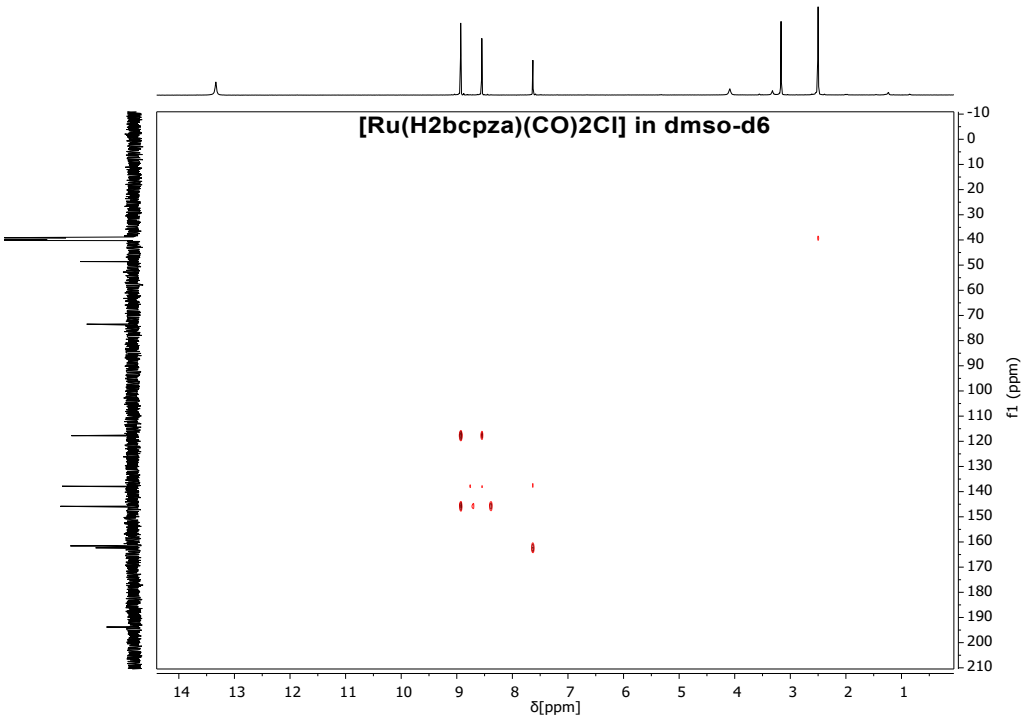


Figure S19. 2D HMBC spectrum of [Ru(H_2bcpza)Cl(CO)$_2$] (**6a**) in dmso-d_6.

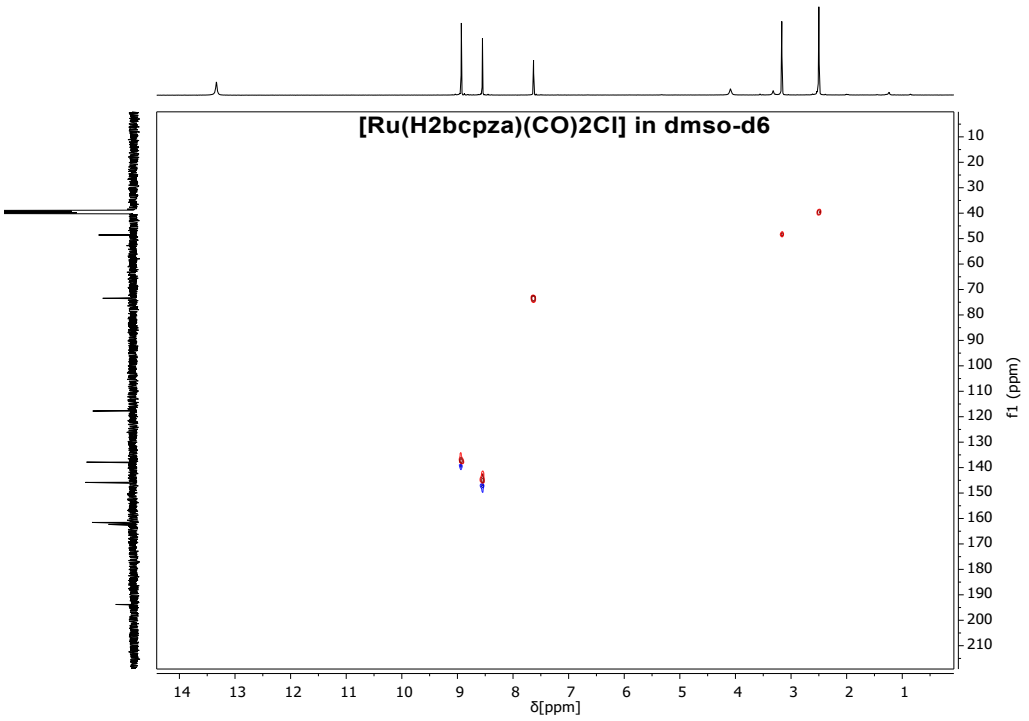


Figure S20. 2D HSQC spectrum of [Ru(H_2bcpza)Cl(CO)$_2$] (**6a**) in dmso-d_6.

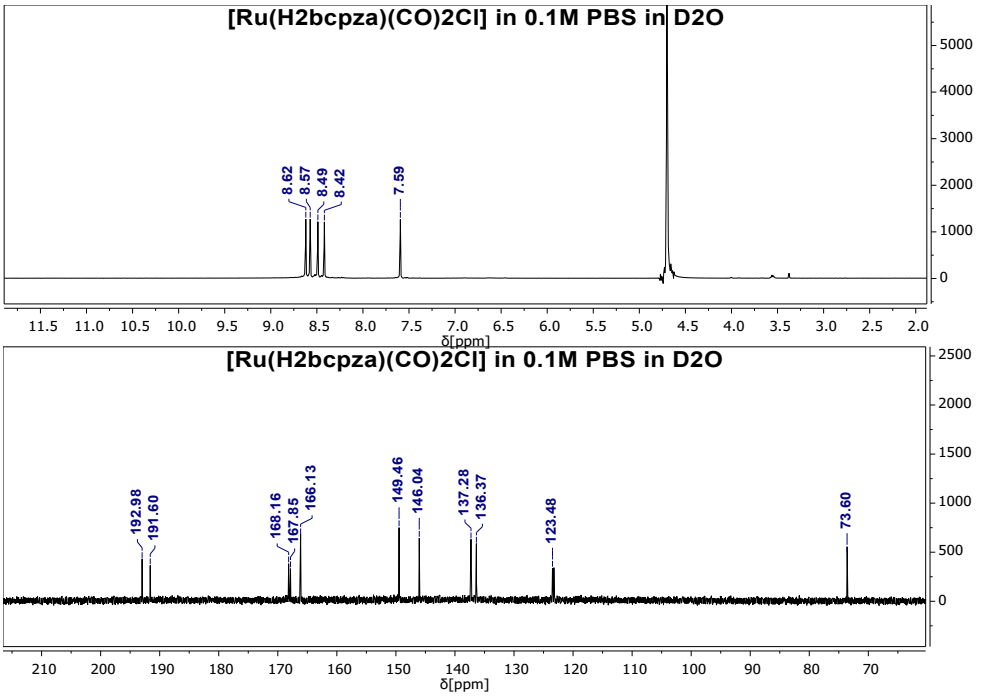


Figure S21. ^{1}H & ^{13}C NMR spectrum of [Ru(H_2bcpza)Cl($CO)_2$] (**6b**) in PBS buffer (0.1 M) in D_2O.

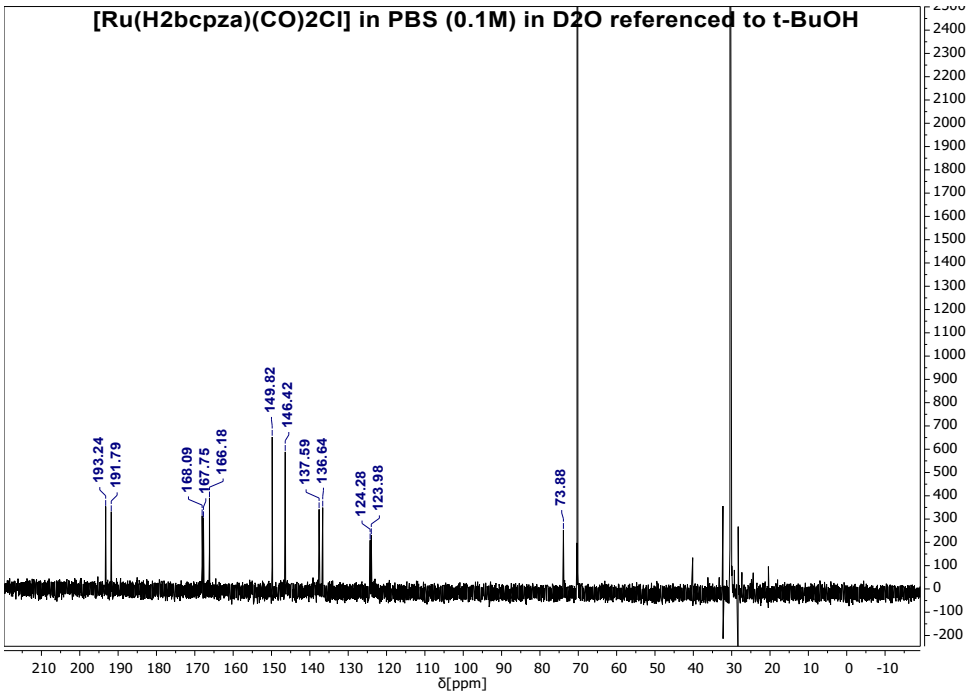


Figure S22. ^{13}C NMR spectrum of [Ru(H_2bcpza)Cl($CO)_2$] (**6b**) in PBS buffer (0.1 M) in D_2O referenced to *t*-BuOH.

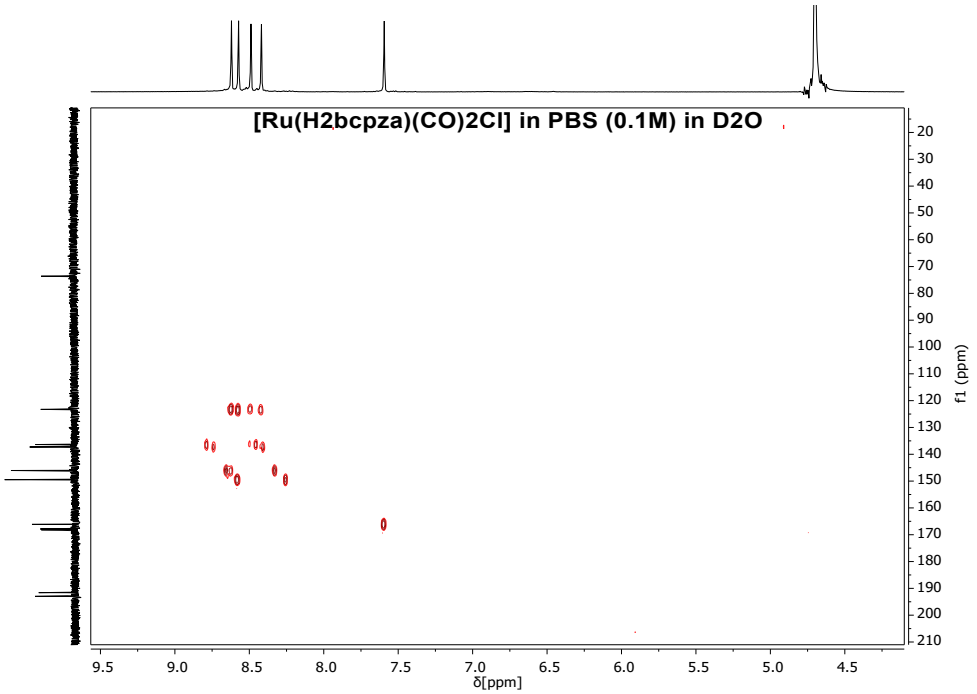


Figure S23. 2D HMBC spectrum of [Ru(H_2bcpza)Cl$(CO)_2$] (**6b**) in PBS buffer (0.1 M) in D_2O.

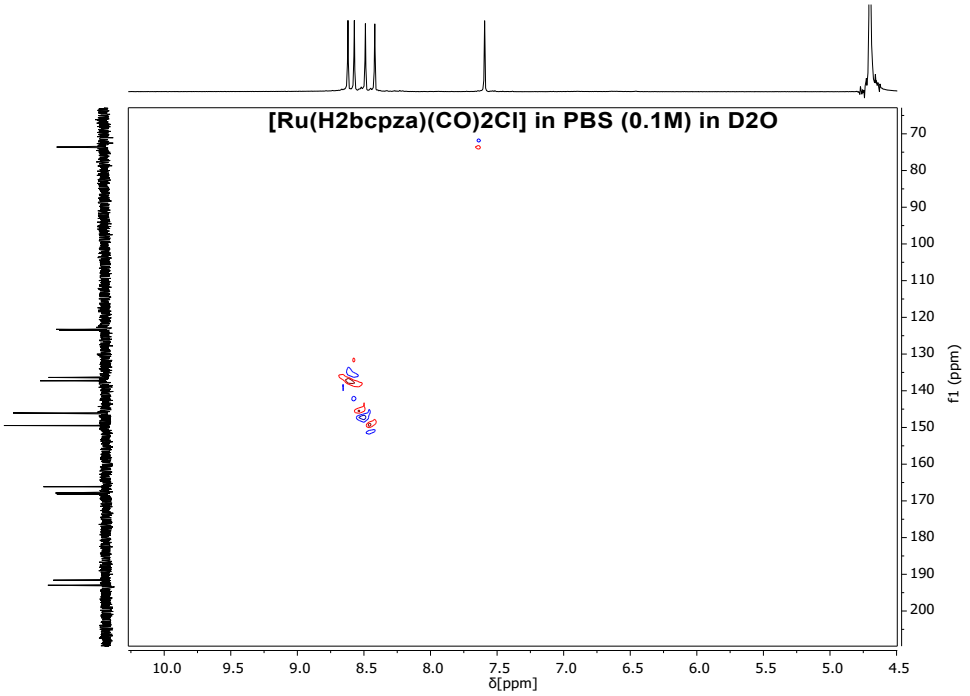


Figure S24. 2D HSQC spectrum of [Ru(H_2bcpza)Cl$(CO)_2$] (**6b**) in PBS buffer (0.1 M) in D_2O.

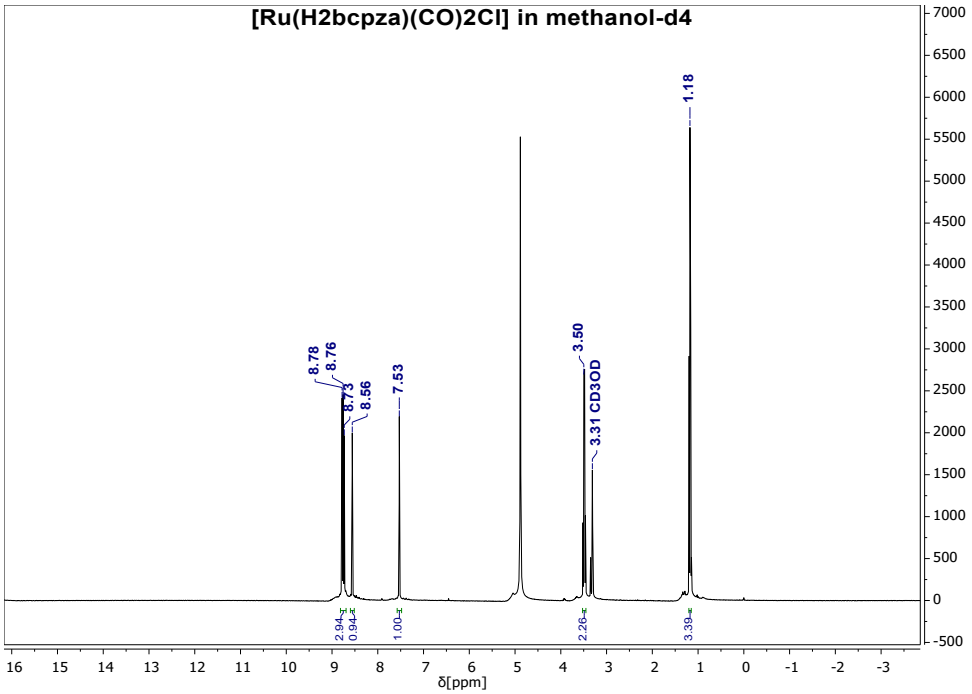


Figure S25. ^{1}H NMR spectrum of [Ru(H_2bcpza)Cl($CO)_2$] (**6b**) in methanol-d_4.

3. UV-vis spectra

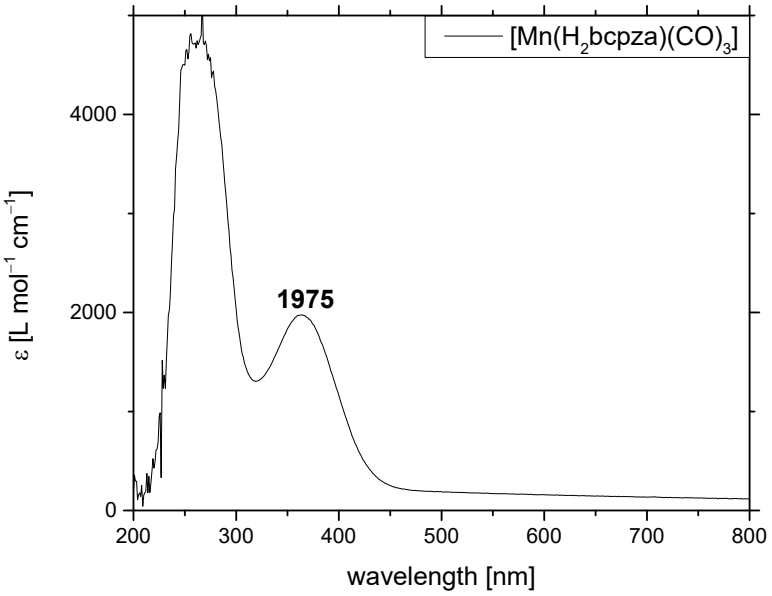


Figure S26. UV-vis spectrum of [Mn(H_2bcpza)(CO)$_3$] (**4**) (0.536 mM) in PBS buffer (0.1 M) with ε_{363} = 1975 L mol^{-1} cm^{-1}.

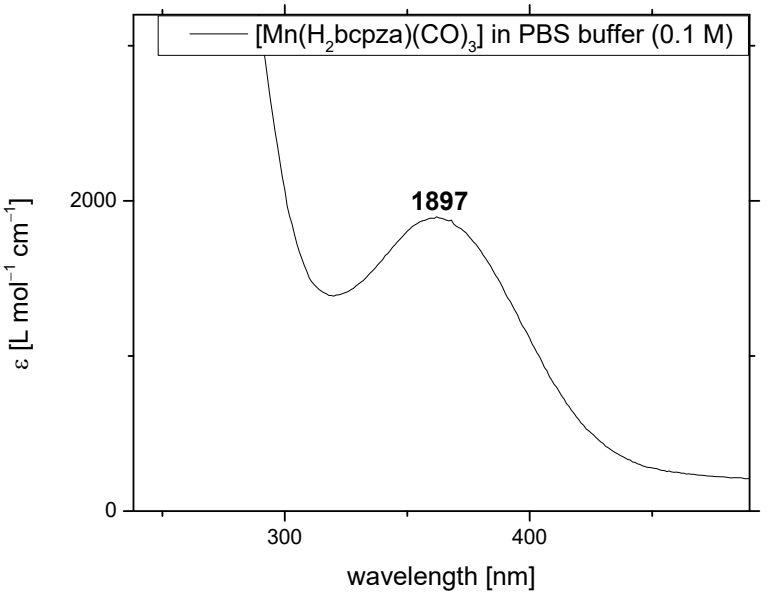


Figure S27. UV-vis spectrum of [Mn(H_2bcpza)(CO)$_3$] (**4**) (0.383 mM) in PBS buffer (0.1 M) with ε_{363} = 1897 L mol^{-1} cm^{-1}.

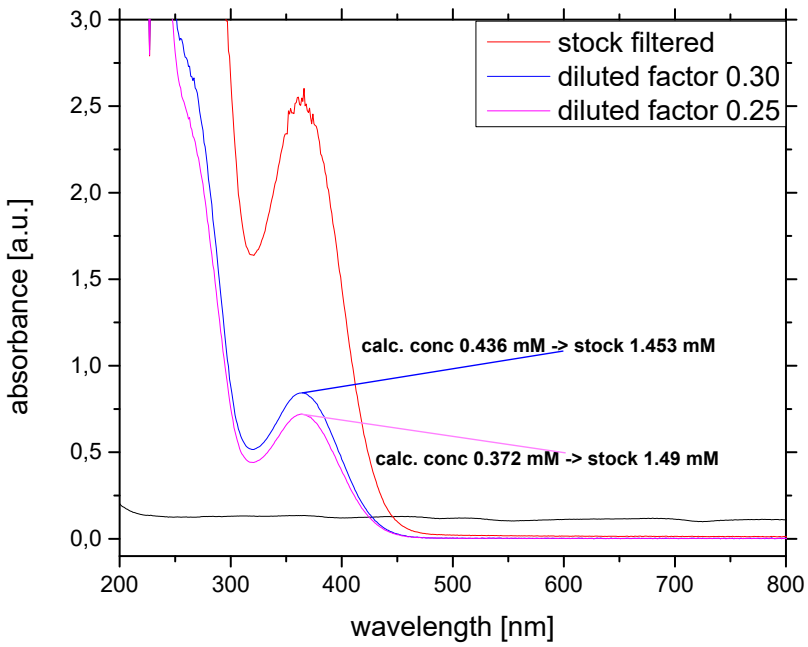


Figure S28. UV-vis spectrum of [Mn(H_2bcpza)$(CO)_3$] (**4**) in H_2O with different dilutions of stock solution.

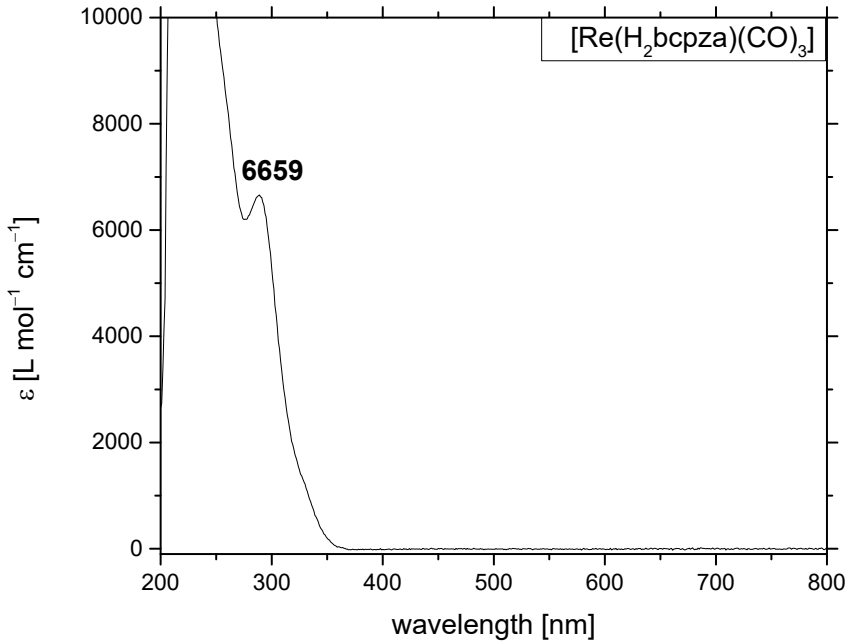


Figure S29. UV-vis spectrum of [Re(H_2bcpza)$(CO)_3$] (**5**) (0.0837 mM) in methanol.

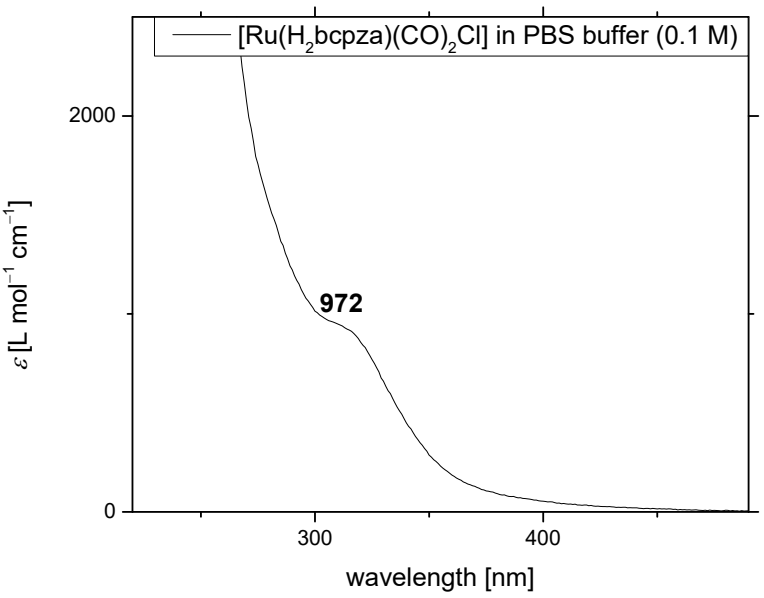


Figure S30. UV-vis spectrum of [Ru(H_2bcpza)Cl($CO)_2$] (**6b**) (PBS 0.1 M). λ_{max} (ε [L mol^{-1} cm^{-1}]) = 310 (972) nm.

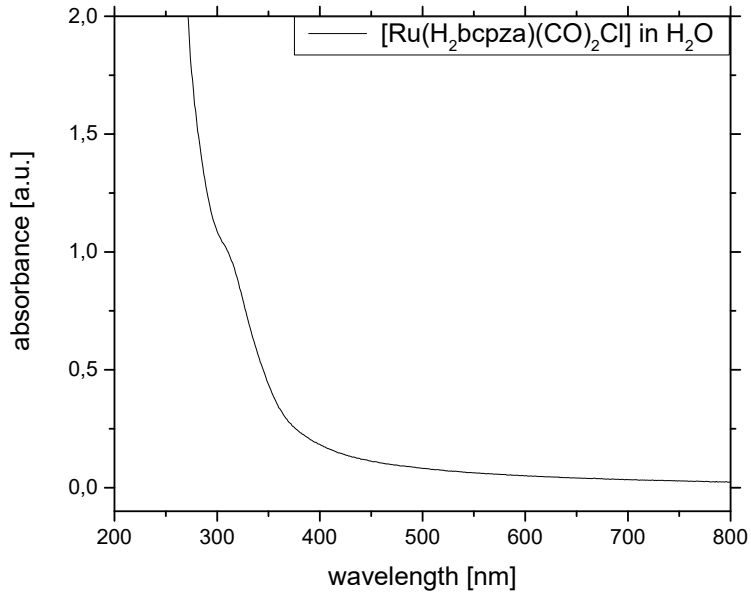


Figure S31. UV-vis spectrum of a saturated solution of [Ru(H_2bcpza)Cl($CO)_2$] (**6b**) in H_2O. Concentration according to Beer-Lambert law was calculated to 1.03 mmol.

4. IR spectra

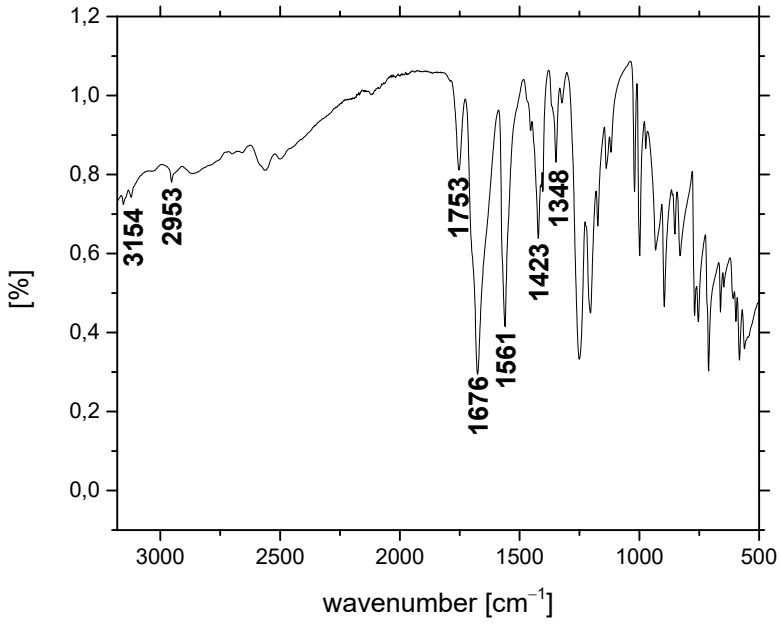


Figure S32. IR(ATR) spectrum of H_3bcpza (**2**).

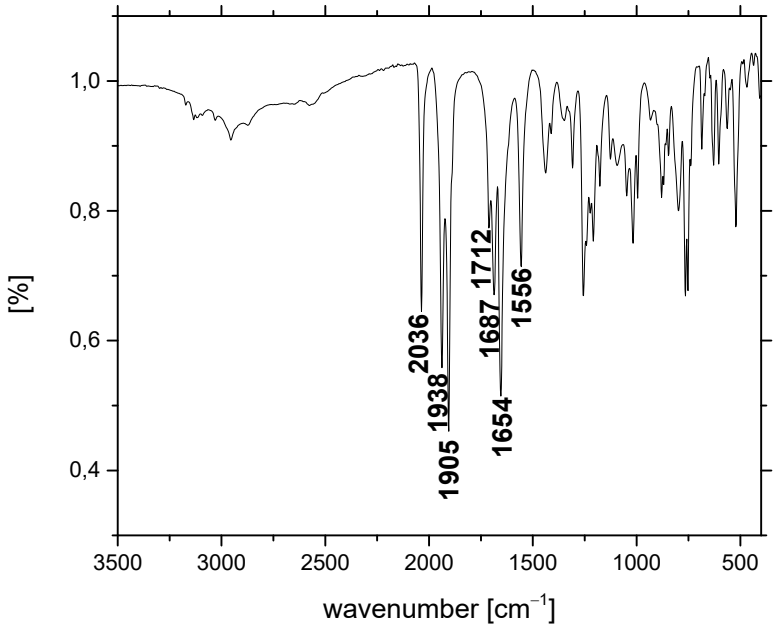


Figure S33. IR (ATR) spectrum of [Mn(H_2bcpza)$(CO)_3$] (**4**).

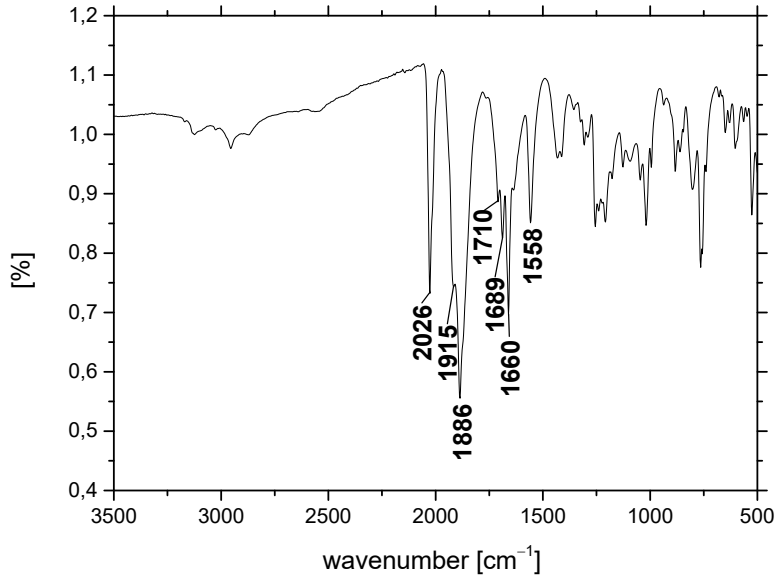


Figure S34. IR (ATR) spectrum of [Re(H_2bcpza)(CO)$_3$] (**5**).

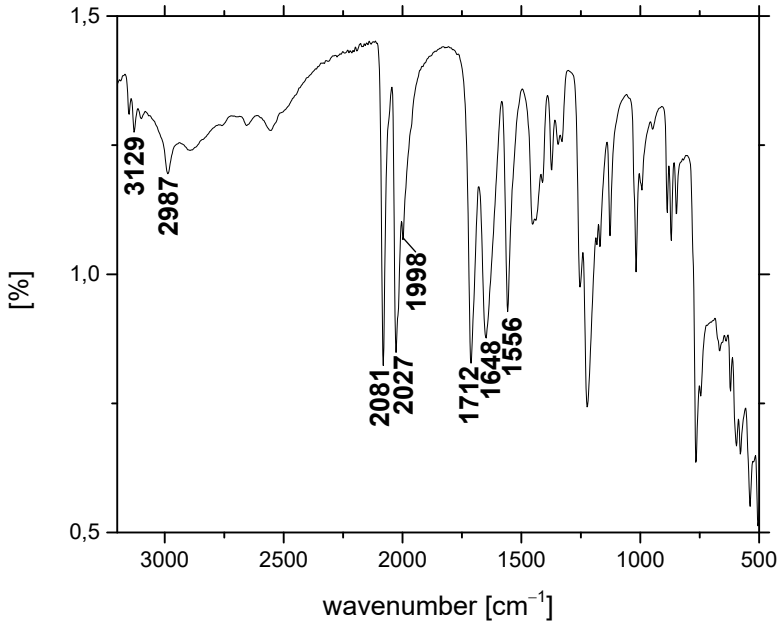


Figure S35. IR spectrum of crystals grown from crude aqueous phase of **6a/6b** after washing process.

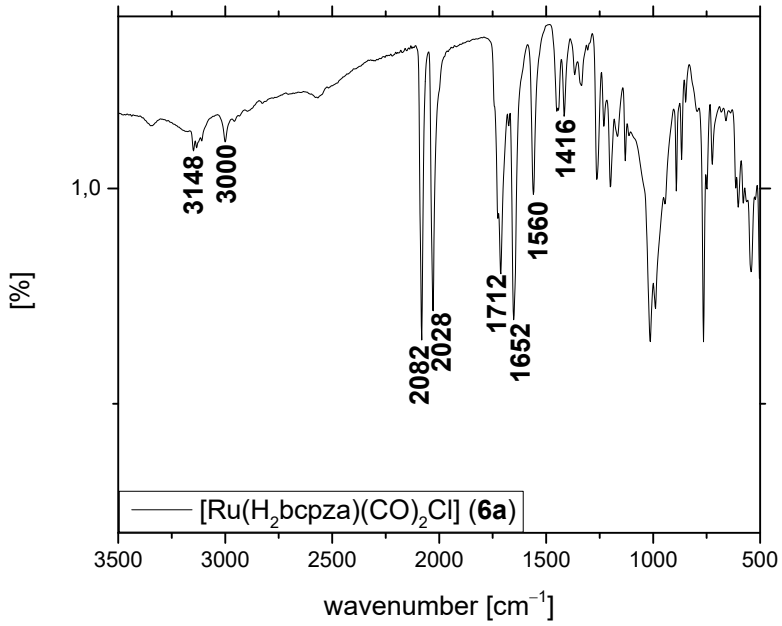


Figure S36. IR(ATR) spectrum of [Ru(H_2bcpza)Cl($CO)_2$] (**6a**).

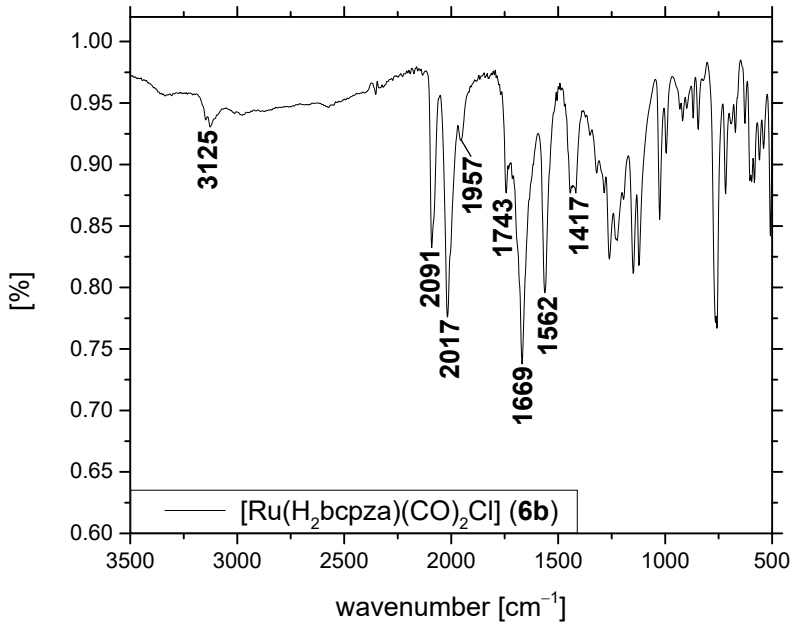


Figure S37. IR(ATR) spectrum of [Ru(H_2bcpza)Cl($CO)_2$] (**6b**).

5. MS data

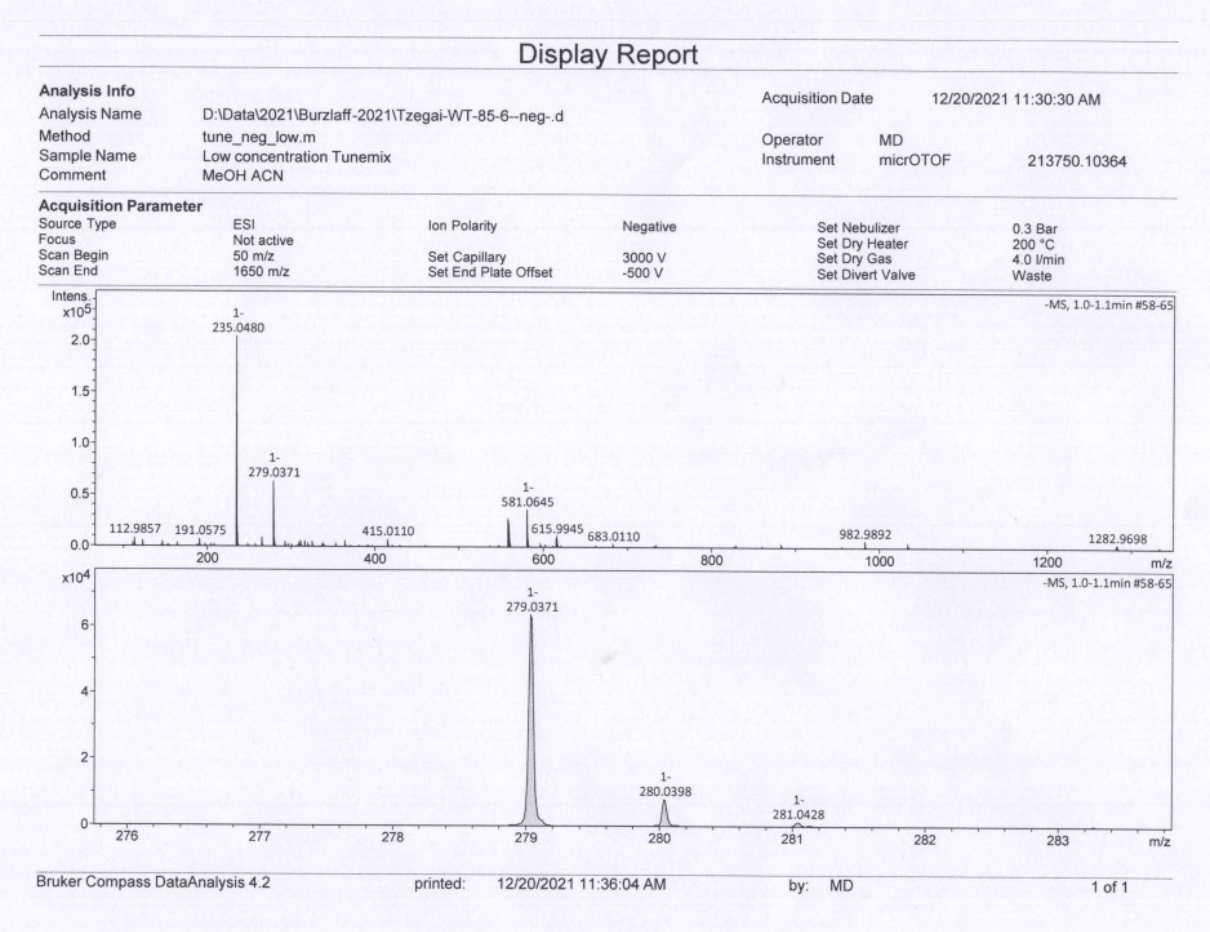


Figure S38. ESI-MS (negative ion mode) of H_3bcpza (**2**) in methanol+acetonitrile.

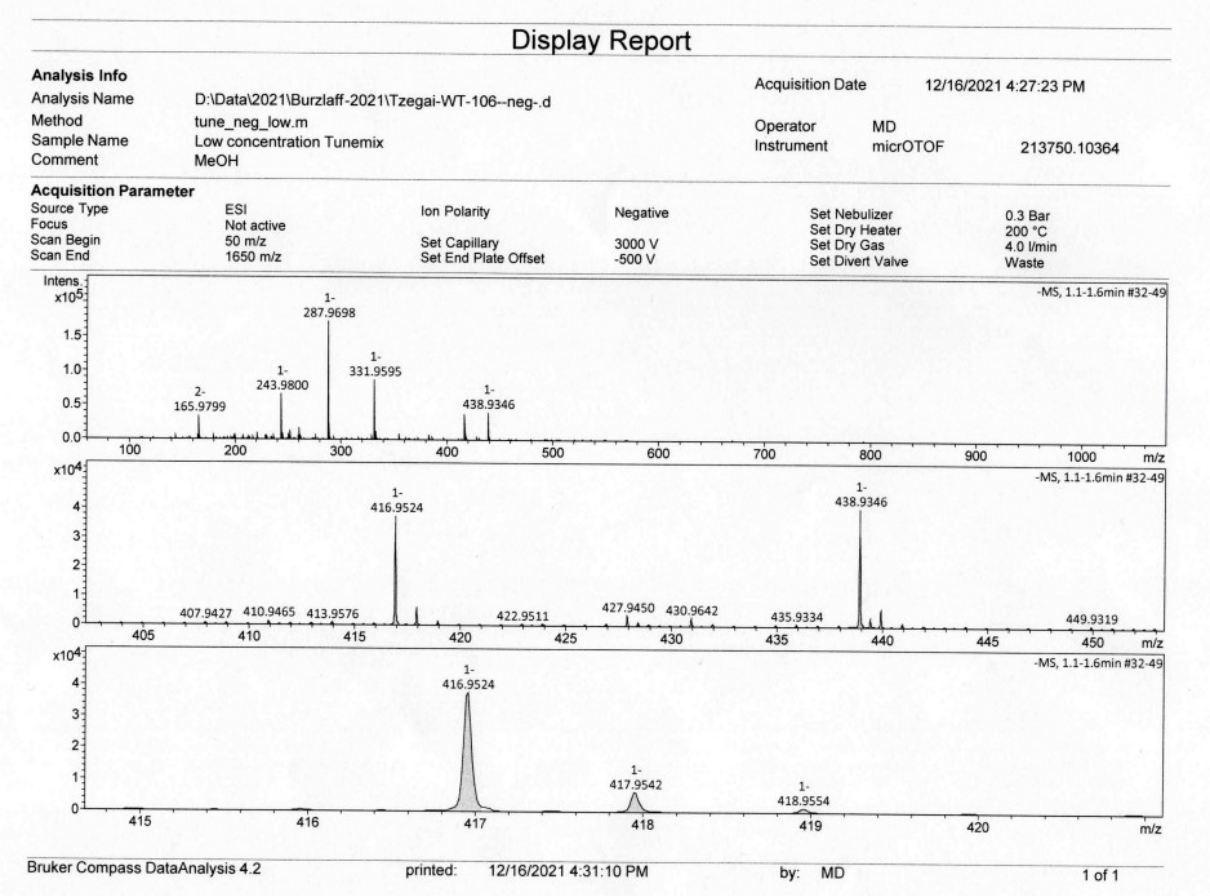


Figure S39 ESI-MS (negative ion mode) spectrum of [Mn(H_2bcpza)($CO)_3$] (**4**) in methanol.

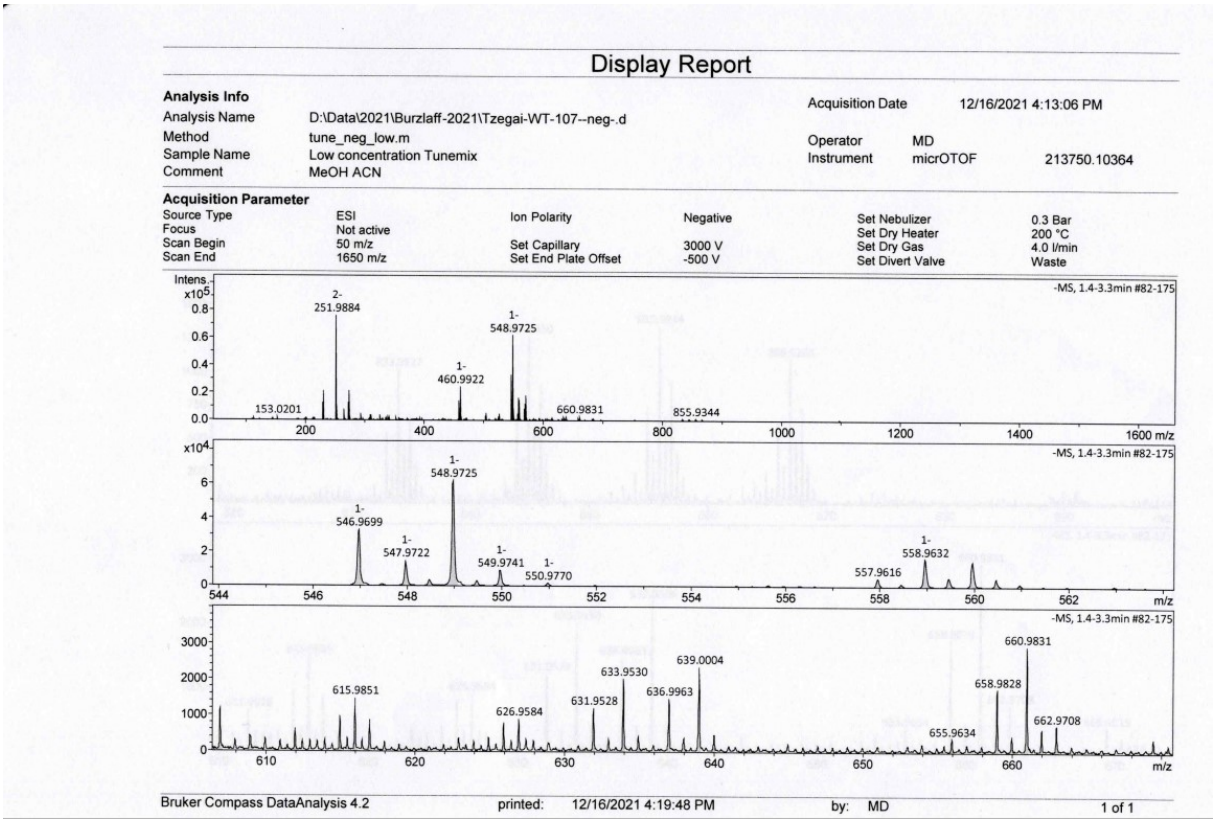


Figure S40. ESI-MS (negative ion mode) of $[Re(H_2bcpza)(CO)_3]$ (**5**) recorded in methanol/acetonitrile.

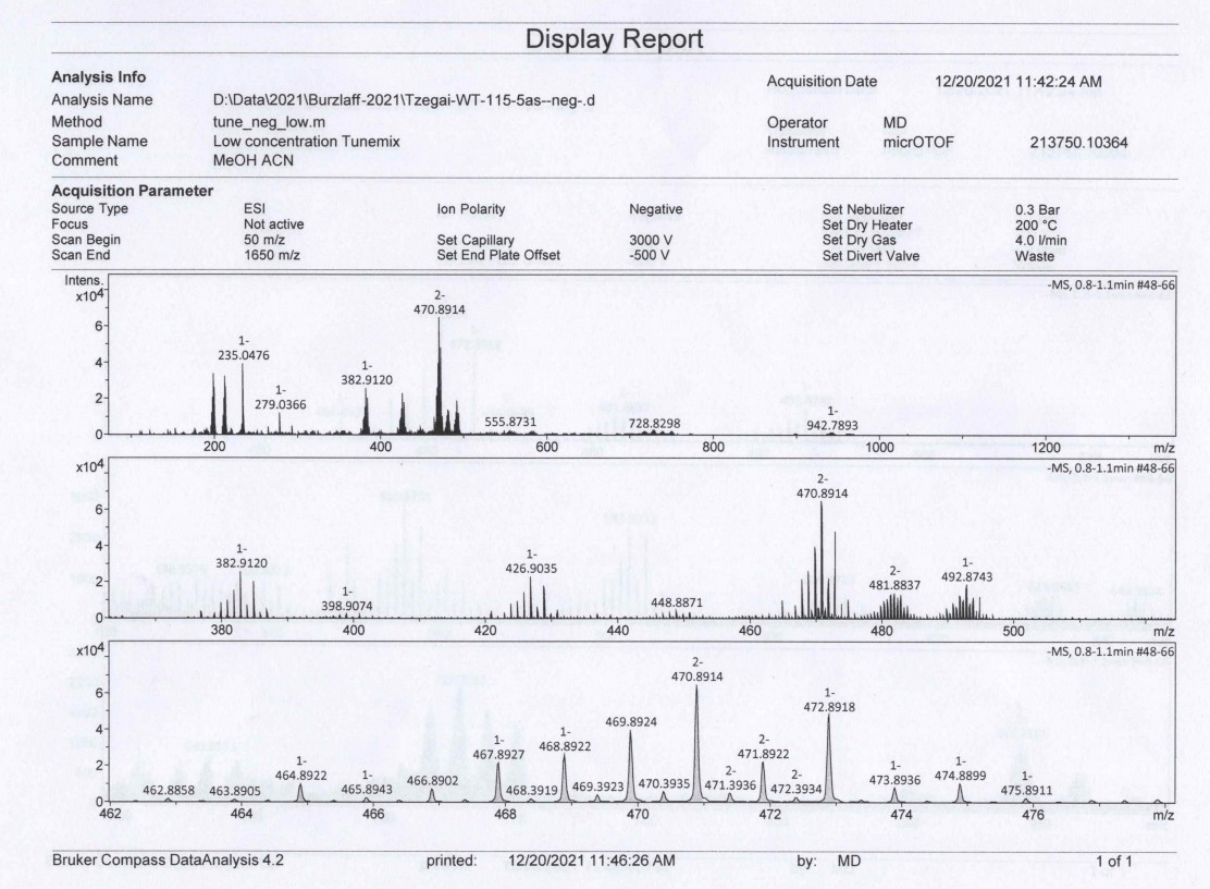
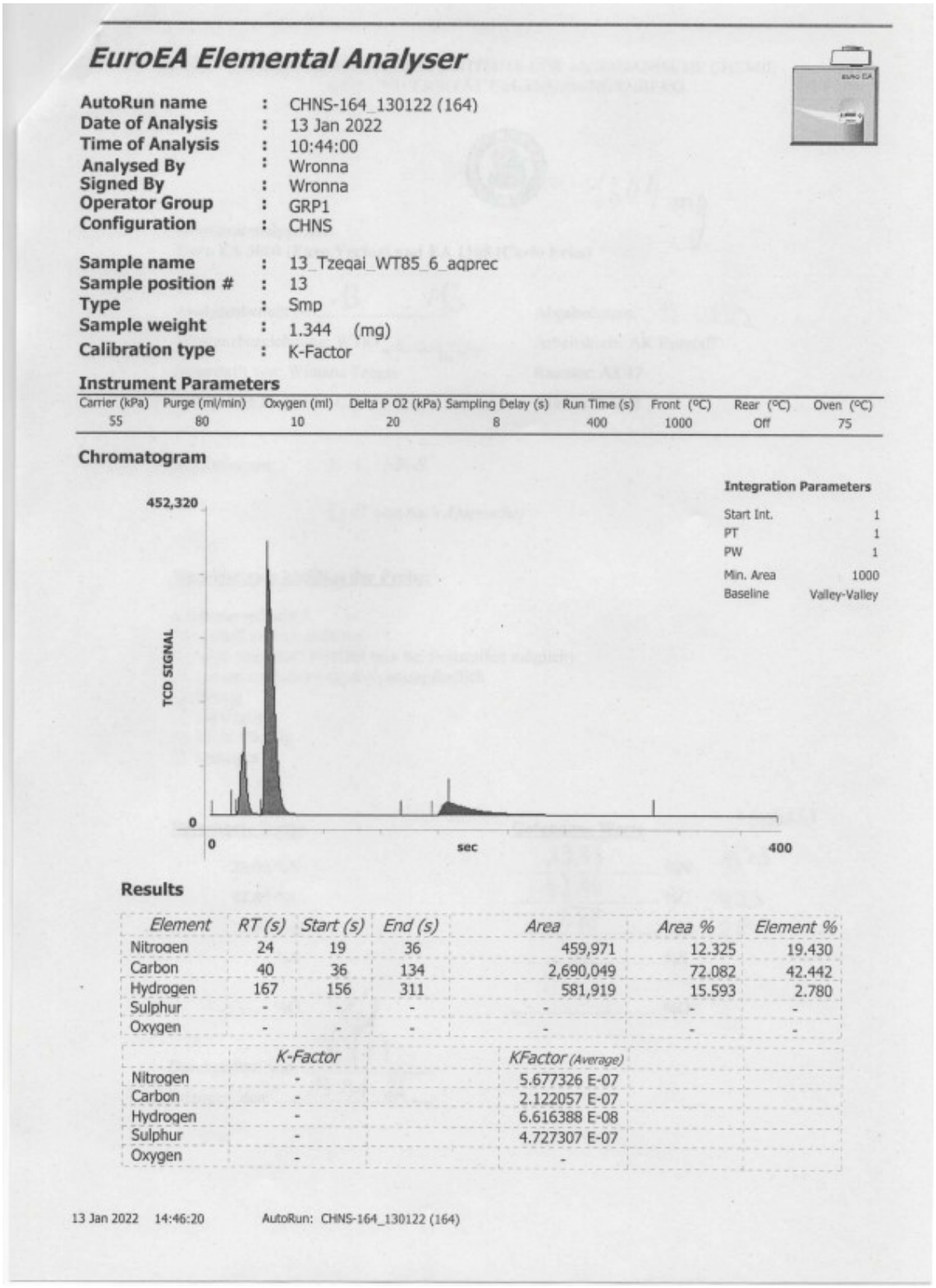


Figure S41. ESI-MS (negative ion mode) of $[Ru(H_2bcpza)Cl(CO)_2]$ (**6b**) recorded in methanol+acetonitrile.

6. Elemental analyses



EuroEA Elemental Analyser

AutoRun name	:	CHNS-164_130122 (164)
Date of Analysis	:	13 Jan 2022
Time of Analysis	:	10:44:00
Analysed By	:	Wronna
Signed By	:	Wronna
Operator Group	:	GRP1
Configuration	:	CHNS
Sample name	:	13_Tzeqai_WT85_6_aqprec
Sample position #	:	13
Type	:	Smp
Sample weight	:	1.344 (mg)
Calibration type	:	K-Factor

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (°C)	Rear (°C)	Oven (°C)
55	80	10	20	8	400	1000	Off	75

Chromatogram

Integration Parameters

Start Int.	1
PT	1
PW	1
Min. Area	1000
Baseline	Valley-Valley

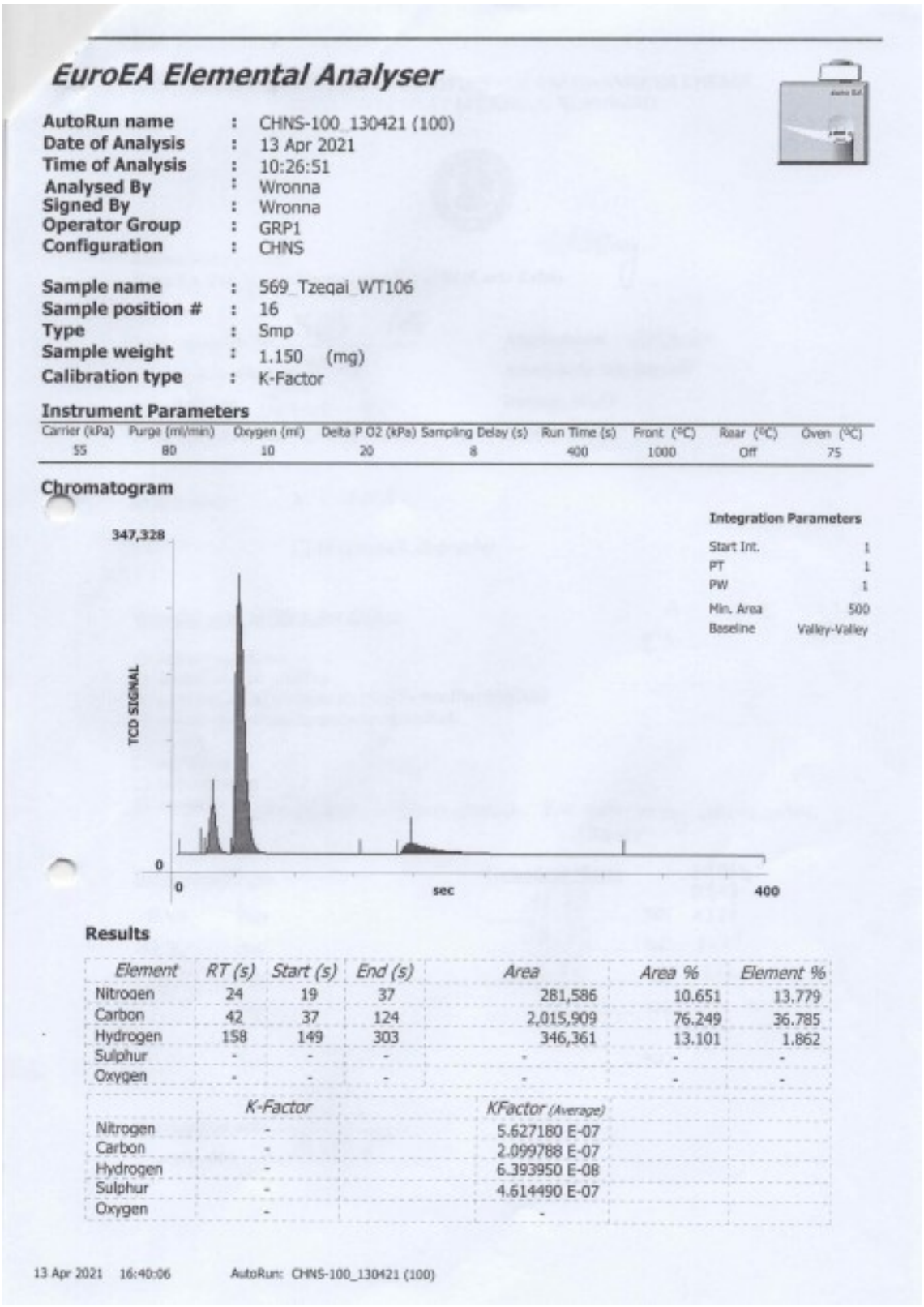
Results

Element	*RT (s)*	*Start (s)*	*End (s)*	*Area*	*Area %*	*Element %*
Nitrogen	24	19	36	459,971	12.325	19.430
Carbon	40	36	134	2,690,049	72.082	42.442
Hydrogen	167	156	311	581,919	15.593	2.780
Sulphur	-	-	-	-	-	-
Oxygen	-	-	-	-	-	-

	K-Factor	*KFactor (Average)*
Nitrogen	-	5.677326 E-07
Carbon	-	2.122057 E-07
Hydrogen	-	6.616388 E-08
Sulphur	-	4.727307 E-07
Oxygen	-	-

13 Jan 2022 14:46:20 AutoRun: CHNS-164_130122 (164)

Figure S42. Elemental analysis of H_3bcpza (**2**).



EuroEA Elemental Analyser

AutoRun name : CHNS-100_130421 (100)
Date of Analysis : 13 Apr 2021
Time of Analysis : 10:26:51
Analysed By : Wronna
Signed By : Wronna
Operator Group : GRP1
Configuration : CHNS

Sample name : 569_Tzeqal_WT106
Sample position # : 16
Type : Smp
Sample weight : 1.150 (mg)
Calibration type : K-Factor

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (°C)	Rear (°C)	Oven (°C)
55	80	10	20	8	400	1000	Off	75

Chromatogram

Integration Parameters

Start Int.	1
PT	1
PW	1
Min. Area	500
Baseline	Valley-Valley

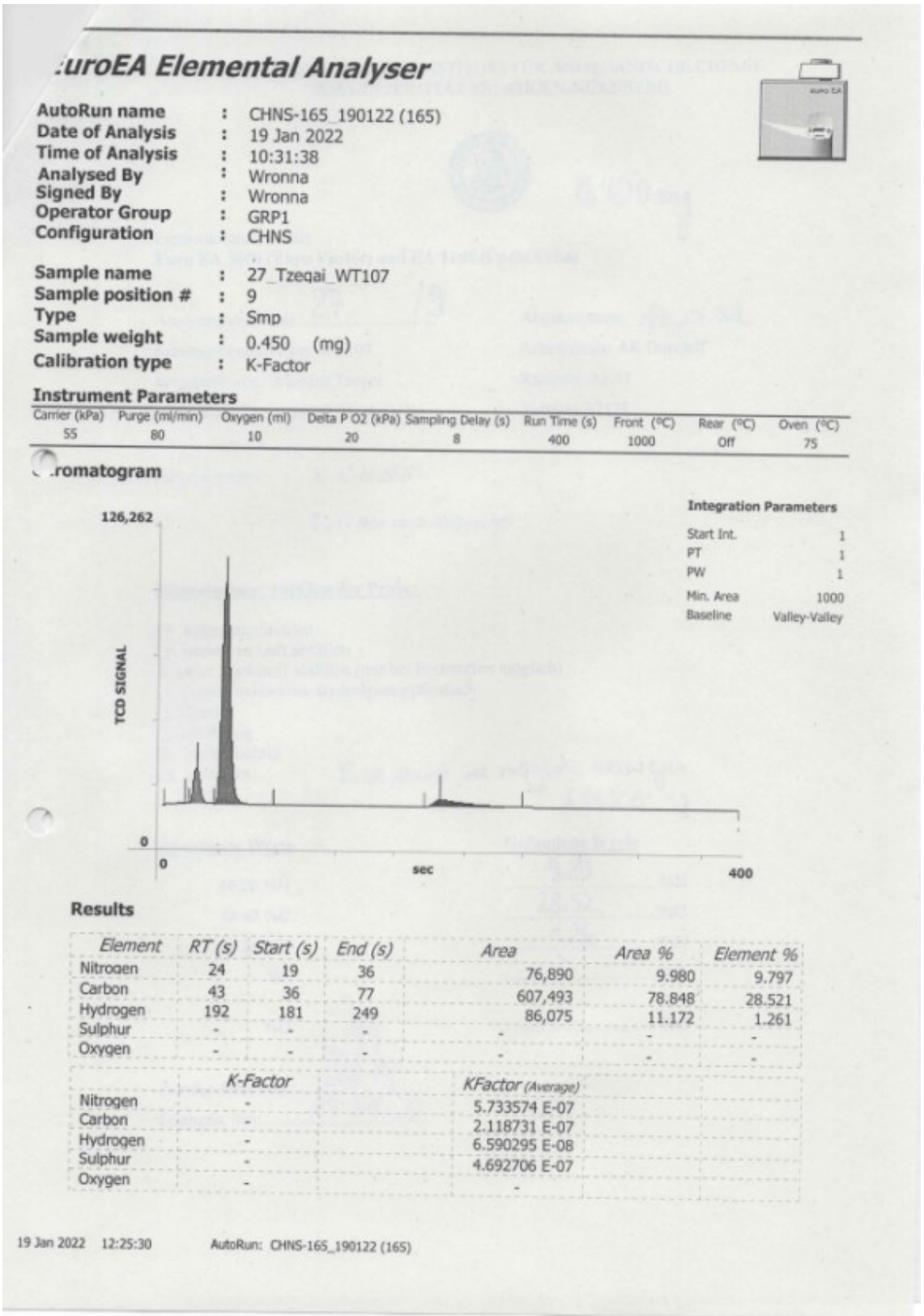
Results

Element	RT (s)	Start (s)	End (s)	Area	Area %	Element %
Nitrogen	24	19	37	281,586	10.651	13.779
Carbon	42	37	124	2,015,909	76.249	36.785
Hydrogen	158	149	303	346,361	13.101	1.862
Sulphur	-	-	-	-	-	-
Oxygen	-	-	-	-	-	-

	K-Factor	KFactor (Average)
Nitrogen	-	5.627180 E-07
Carbon	-	2.099788 E-07
Hydrogen	-	6.393950 E-08
Sulphur	-	4.614490 E-07
Oxygen	-	-

13 Apr 2021 16:40:06 AutoRun: CHNS-100_130421 (100)

Figure S43. Elemental analysis of [Mn(H_2bcpza)($CO)_3$] (**4**).



:uroEA Elemental Analyser

AutoRun name	:	CHNS-165_190122 (165)
Date of Analysis	:	19 Jan 2022
Time of Analysis	:	10:31:38
Analysed By	:	Wronna
Signed By	:	Wronna
Operator Group	:	GRP1
Configuration	:	CHNS
Sample name	:	27_Tzeqai_WT107
Sample position #	:	9
Type	:	Smp
Sample weight	:	0.450 (mg)
Calibration type	:	K-Factor

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (°C)	Rear (°C)	Oven (°C)
55	80	10	20	8	400	1000	Off	75

.romatogram

Integration Parameters

Start Int.	1
PT	1
PW	1
Min. Area	1000
Baseline	Valley-Valley

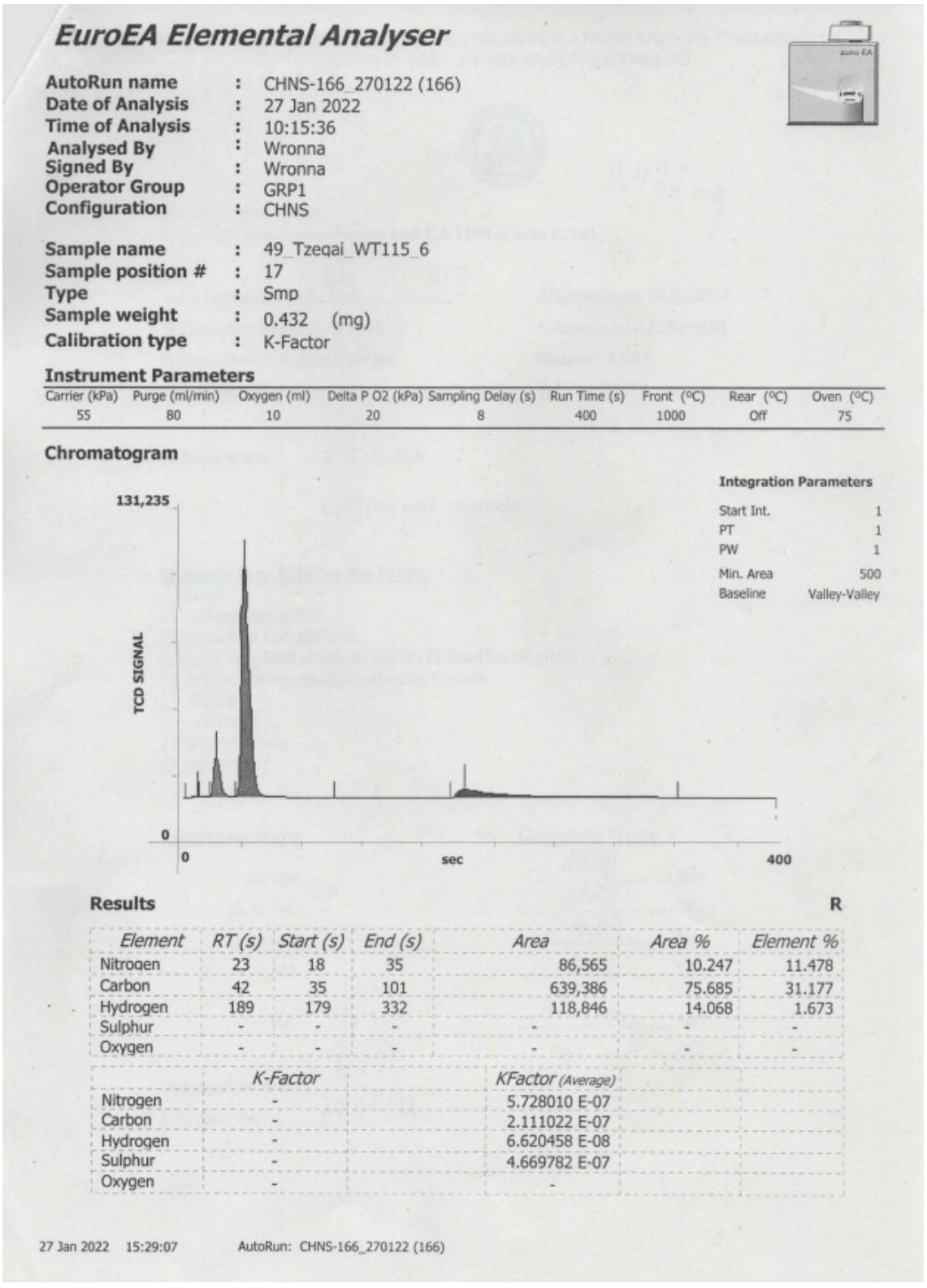
Results

Element	RT (s)	Start (s)	End (s)	Area	Area %	Element %
Nitrogen	24	19	36	76,890	9.980	9.797
Carbon	43	36	77	607,493	78.848	28.521
Hydrogen	192	181	249	86,075	11.172	1.261
Sulphur	-	-	-	-	-	-
Oxygen	-	-	-	-	-	-

	K-Factor	KFactor (Average)
Nitrogen	-	5.733574 E-07
Carbon	-	2.118731 E-07
Hydrogen	-	6.590295 E-08
Sulphur	-	4.692706 E-07
Oxygen	-	-

19 Jan 2022 12:25:30 AutoRun: CHNS-165_190122 (165)

Figure S44. Elemental analysis of [Re(H_2bcpza)($CO)_3$] (**5**).



EuroEA Elemental Analyser

AutoRun name	:	CHNS-166_270122 (166)
Date of Analysis	:	27 Jan 2022
Time of Analysis	:	10:15:36
Analysed By	:	Wronna
Signed By	:	Wronna
Operator Group	:	GRP1
Configuration	:	CHNS
Sample name	:	49_Tzeqai_WT115_6
Sample position #	:	17
Type	:	Smp
Sample weight	:	0.432 (mg)
Calibration type	:	K-Factor

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (°C)	Rear (°C)	Oven (°C)
55	80	10	20	8	400	1000	Off	75

Chromatogram

Integration Parameters

Start Int.	1
PT	1
PW	1
Min. Area	500
Baseline	Valley-Valley

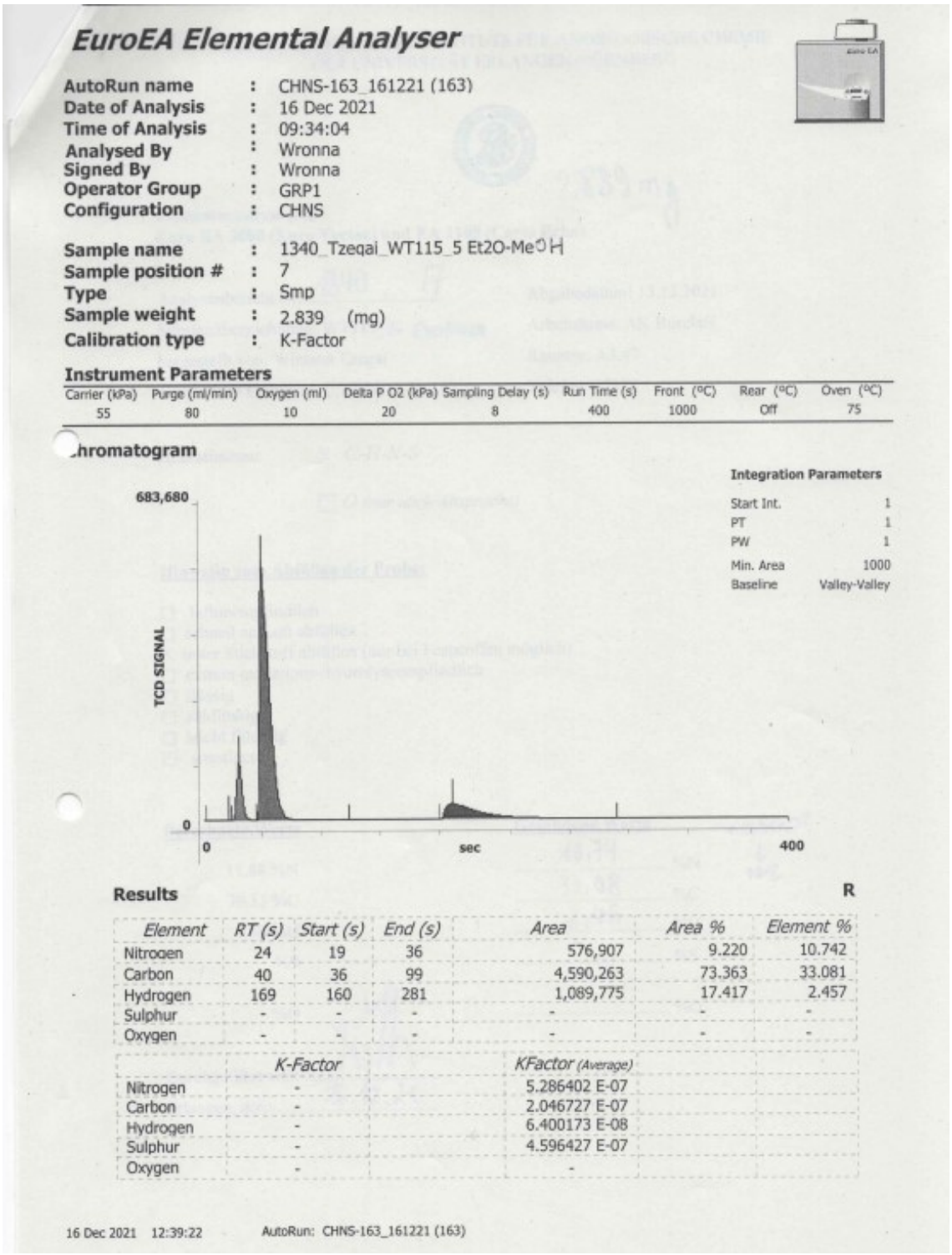
Results R

Element	*RT (s)*	*Start (s)*	*End (s)*	*Area*	*Area %*	*Element %*
Nitrogen	23	18	35	86,565	10.247	11.478
Carbon	42	35	101	639,386	75.685	31.177
Hydrogen	189	179	332	118,846	14.068	1.673
Sulphur	-	-	-	-	-	-
Oxygen	-	-	-	-	-	-

	K-Factor	*KFactor (Average)*
Nitrogen	-	5.728010 E-07
Carbon	-	2.111022 E-07
Hydrogen	-	6.620458 E-08
Sulphur	-	4.669782 E-07
Oxygen	-	-

27 Jan 2022 15:29:07 AutoRun: CHNS-166_270122 (166)

Figure S45. Elemental analysis of [Ru(H_2bcpza)Cl($CO)_2$] (**6a**).



EuroEA Elemental Analyser

AutoRun name	:	CHNS-163_161221 (163)
Date of Analysis	:	16 Dec 2021
Time of Analysis	:	09:34:04
Analysed By	:	Wronna
Signed By	:	Wronna
Operator Group	:	GRP1
Configuration	:	CHNS
Sample name	:	1340_Tzeqai_WT115_5 Et2O-MeOH
Sample position #	:	7
Type	:	Smp
Sample weight	:	2.839 (mg)
Calibration type	:	K-Factor

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (°C)	Rear (°C)	Oven (°C)
55	80	10	20	8	400	1000	Off	75

Chromatogram

Integration Parameters

Start Int.	1
PT	1
PW	1
Min. Area	1000
Baseline	Valley-Valley

Results

Element	*RT (s)*	*Start (s)*	*End (s)*	*Area*	*Area %*	*Element %*
Nitrogen	24	19	36	576,907	9.220	10.742
Carbon	40	36	99	4,590,263	73.363	33.081
Hydrogen	169	160	281	1,089,775	17.417	2.457
Sulphur	-	-	-	-	-	-
Oxygen	-	-	-	-	-	-

	K-Factor	*KFactor (Average)*
Nitrogen	-	5.286402 E-07
Carbon	-	2.046727 E-07
Hydrogen	-	6.400173 E-08
Sulphur	-	4.596427 E-07
Oxygen	-	-

16 Dec 2021 12:39:22 AutoRun: CHNS-163_161221 (163)

Figure S46. Elemental analysis of [Ru(H_2bcpza)Cl($CO)_2$] (**6b**).