Supplementary data for article:

Mészáros, J. P.; Geisler, H.; Poljarević, J. M.; Roller, A.; Legina, M. S.; Hejl, M.; Jakupec, M. A.; Keppler, B. K.; Kandioller, W.; Enyedy, É. A. Naphthoquinones of Natural Origin: Aqueous Chemistry and Coordination to Half-Sandwich Organometallic Cations. *Journal of Organometallic Chemistry* **2020**, *907*. https://doi.org/10.1016/j.jorganchem.2019.121070

SUPPORTING INFORMATION:

Naphthoquinones of natural origin: aqueous chemistry and coordination to half-sandwich organometallic cations

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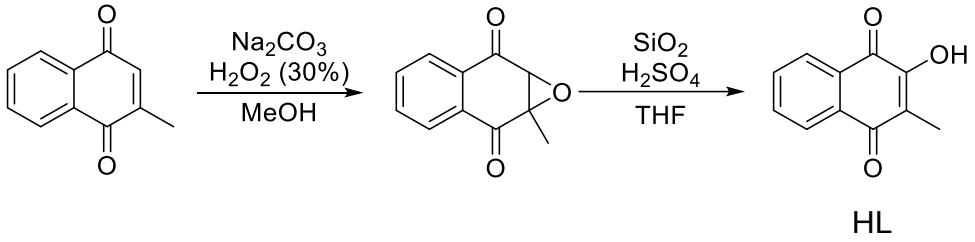

Scheme S1. Synthetic pathway to phthiocol (Hphth).

Table S1. Experiment parameters and CCDC codes

Sample	Machine	Source	Temp.	Detector Distance	Time/ Frame	#Frames	Frame width	CCDC
	Bruker		[K]	[mm]	[s]		[°]	
[Ru(η^6-*p*-cymene)(phth)Cl] (**1**)	D8	Mo	100	30	50	332	0.700	1961119
[Ru(η^6-*p*-cymene)(phth)Br] (**2**)	D8	Mo	100	30	12	919	0.700	1961118
[Ru(η^6-*p*-cymene)(phth)I] (**3**)	D8	Mo	130	30	4	2883	0.700	1961117
[Os(η^6-*p*-cymene)(phth)Cl] (**5**)	D8	Mo	100	30	20	2145	0.500	1961120
[Rh(η^5-C_5Me_5)(phth)Cl] (**6**)	D8	Mo	100	30	7	4803	0.500	1961121

Table S2. Sample and crystal data; parameters of data collection and structure refinement for [Ru(η^6-*p*-cymene)(phth)Cl] (**1**)

Chemical formula	$C_{21}H_{21}ClO_3Ru$	**Crystal system**	monoclinic	
Formula weight [g/mol]	457.9	**Space group**	*P2₁/c*	
Temperature [K]	100	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å³]**	1814.80(11)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	11.7550(4)	90
Crystal size / [mm³]	0.255 × 0.098 × 0.016		8.2073(3)	105.3088(17)
Crystal habit	clear brown plate		19.5028(7)	90
Density (calculated) / [g/cm³]	1.676	**Absorption coefficient / [mm⁻¹]**	1.029	
Abs. correction Tmin	0.6692	**Abs. correction Tmax**	0.7452	
Abs. correction type	multiscan	**F(000) [e⁻]**	928	
Index ranges	$-14 \le h \le 14$, $-9 \le k \le 9$, $-23 \le l \le 18$	**θ range for data collection [°]**	5.416 to 50.706	
Reflections number	12270	**Data / restraints / parameters**	3268/0/239	
Refinement method	Least squares	**Final R indices**	all data	$R_1 = 0.0426$, $wR_2 = 0.0635$
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		$I>2\sigma(I)$	$R_1 = 0.0288$, $wR_2 = 0.0599$
Goodness-of-fit on F^2	1.008	**Weighting scheme**	w=1/[σ2(Fo2)+(0.0207P)2 +2.9362P]	
Largest diff. peak and hole [e Å⁻³]	0.76/-0.44		where $P=(F_o^2+2F_c^2)/3$	

Table S3. Sample and crystal data; parameters of data collection and structure refinement for [Ru(η^6-*p*-cymene)(phth)Br] (**2**)

Chemical formula	$C_{21}H_{21}BrO_3Ru$	**Crystal system**	triclinic	
Formula weight [g/mol]	502.36	**Space group**	$P\bar{1}$	
Temperature [K]	100	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å^3]**	1882.14(9)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	8.1014(2)	93.9012(11)
Crystal size / [mm^3]	0.145 × 0.085 × 0.079		10.3088(3)	94.8743(10)
Crystal habit	clear red block		23.4681(6)	104.5458(9)
Density (calculated) / [g/cm^3]	1.773	**Absorption coefficient / [mm^{-1}]**	2.974	
Abs. correction Tmin	0.6858	**Abs. correction Tmax**	0.746	
Abs. correction type	multiscan	**F(000) [e$^-$]**	1000	
Index ranges	$-11 \le h \le 9$, $-14 \le k \le 14$, $-32 \le l \le 33$	**θ range for data collection [°]**	5.138 to 60.154	
Reflections number	54596	**Data / restraints / parameters**	11023/0/477	
Refinement method	Least squares	**Final R indices**	all data	$R_1 = 0.0535$, $wR_2 = 0.0702$
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		I>2σ(I)	$R_1 = 0.0350$, $wR_2 = 0.0661$
Goodness-of-fit on F^2	1.052	**Weighting scheme**	w=1/[σ2(Fo2)+(0.0155P)2 +4.3226P]	
Largest diff. peak and hole [e Å^{-3}]	2.17/-1.06		where $P=(F_o^2+2F_c^2)/3$	

Table S4. Sample and crystal data; parameters of data collection and structure refinement for [Ru(η^6-*p*-cymene)(phth)I] (**3**)

Chemical formula	$C_{21}H_{21}IO_3Ru$	**Crystal system**	triclinic	
Formula weight [g/mol]	549.35	**Space group**	$P\bar{1}$	
Temperature [K]	130	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å^3]**	1970.9(2)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	8.3517(5)	95.322(2)
Crystal size / [mm^3]	0.3 × 0.11 × 0.1		10.3559(6)	93.646(2)
Crystal habit	clear red block		23.7603(13)	104.719(2)
Density (calculated) / [g/cm^3]	1.851	**Absorption coefficient / [mm^{-1}]**	2.379	
Abs. correction T_{min}	0.5118	**Abs. correction Tmax**	0.7471	
Abs. correction type	multiscan	**F(000) [e$^-$]**	1072	
Index ranges	$-11 \le h \le 11$, $-14 \le k \le 14$, $-33 \le l \le 33$	**θ range for data collection [°]**	3.458 to 60.068	
Reflections number	88929	**Data / restraints / parameters**	11510/0/477	
Refinement method	Least squares	**Final R indices**	all data	$R_1 = 0.0434$, $wR_2 = 0.0819$
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		$I>2\sigma(I)$	$R_1 = 0.0380$, $wR_2 = 0.0799$
Goodness-of-fit on F^2	1.196	**Weighting scheme**	w=1/[σ2(Fo2)+(6.5880P)2]	
Largest diff. peak and hole [e Å^{-3}]	2.10/-1.36		where $P=(F_o^2+2F_c^2)/3$	

Table S5. Sample and crystal data; parameters of data collection and structure refinement for [Os(η^6-*p*-cymene)(phth)Cl] (**5**)

Chemical formula	$C_{21}H_{21}ClO_3Os$	**Crystal system**	monoclinic	
Formula weight [g/mol]	547.03	**Space group**	*P2₁/c*	
Temperature [K]	100	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å³]**	1819.20(12)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	11.7467(5)	90
Crystal size / [mm³]	0.168 × 0.03 × 0.027		8.1972(3)	105.6377(15)
Crystal habit	clear blue needle		19.6191(7)	90
Density (calculated) / [g/cm³]	1.997	**Absorption coefficient / [mm⁻¹]**	7.175	
Abs. correction Tmin	0.5757	**Abs. correction Tmax**	0.746	
Abs. correction type	multiscan	**F(000) [e⁻]**	1056	
Index ranges	$-14 \le h \le 14$, $-9 \le k \le 9$, $-23 \le l \le 23$	**θ range for data collection [°]**	4.816 to 50.698	
Reflections number	56514	**Data / restraints / parameters**	3310/0/239	
Refinement method	Least squares	**Final R indices**	all data	$R_1 = 0.0273$, $wR_2 = 0.0673$
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		$I>2\sigma(I)$	$R_1 = 0.0252$, $wR_2 = 0.0655$
Goodness-of-fit on F²	1.06	**Weighting scheme**	w=1/[σ2(Fo2)+(0.0393P)2 +7.3956P]	
Largest diff. peak and hole [e Å⁻³]	2.96/-1.50		where $P=(F_o^2+2F_c^2)/3$	

Table S6. Sample and crystal data; parameters of data collection and structure refinement for [Rh(η^5-C_5Me_5)(phth)Cl] (**6**)

Chemical formula	$C_{23}H_{26}Cl_5O_3Rh$	**Crystal system**	triclinic	
Formula weight [g/mol]	630.6	**Space group**	$P\bar{1}$	
Temperature [K]	100	**Z**	4	
Measurement method	\f and \w scans	**Volume [Å^3]**	2564.8(5)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	11.9980(12)	69.718(5)
Crystal size / [mm^3]	0.2 × 0.14 × 0.1		14.4950(16)	71.194(5)
Crystal habit	dark red block		17.1948(19)	70.035(5)
Density (calculated) / [g/cm^3]	1.633	**Absorption coefficient / [mm^{-1}]**	1.21	
Abs. correction Tmin	0.6814	**Abs. correction Tmax**	0.746	
Abs. correction type	multiscan	**F(000) [e$^-$]**	1272	
Index ranges	$-14 \le h \le 14$, $-17 \le k \le 17$, $-20 \le l \le 20$	**θ range for data collection [°]**	2.596 to 50.368	
Reflections number	108284	**Data / restraints / parameters**	9211/0/589	
Refinement method	Least squares	**Final R indices**	all data	R_1 = 0.0772, wR_2 = 0.1611
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$		I>2σ(I)	R_1 = 0.0582, wR_2 = 0.1390
Goodness-of-fit on F^2	1.068	**Weighting scheme**	w=1/[σ2(Fo2)+(0.0563P)2 +25.7055P]	
Largest diff. peak and hole [e Å^{-3}]	1.99/-1.38		where $P=(F_o^2+2F_c^2)/3$	

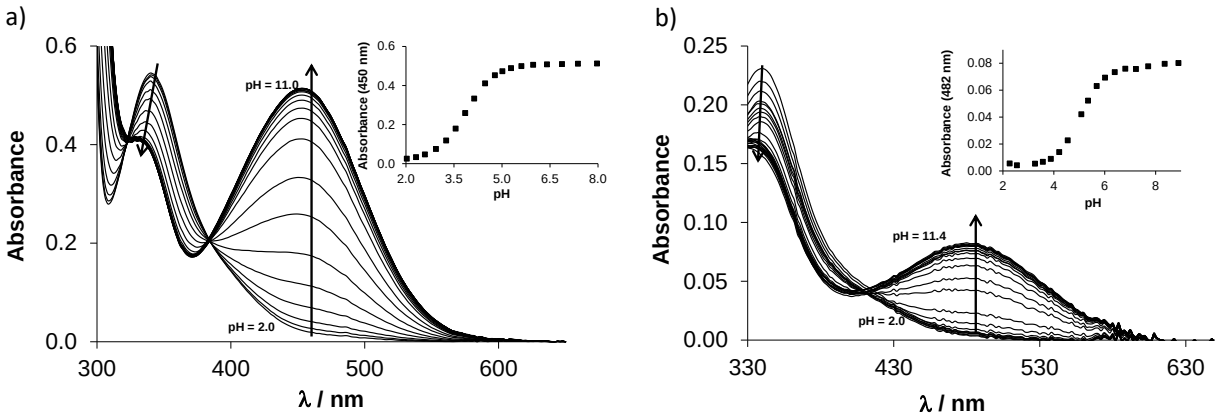

Fig. S1. pH-dependent (pH = 2.0-11.5) UV-Vis spectra of a) lawsone and b) phthiocol. The inserted Figs. show the changes of absorbance at a chosen wavelength. {*c*(lawsone) = 200 μM; *c*(phthiocol) = 100 μM; *I* = 0.2 M (KCl); *T* = 25.0 °C, *l* = 2 cm}

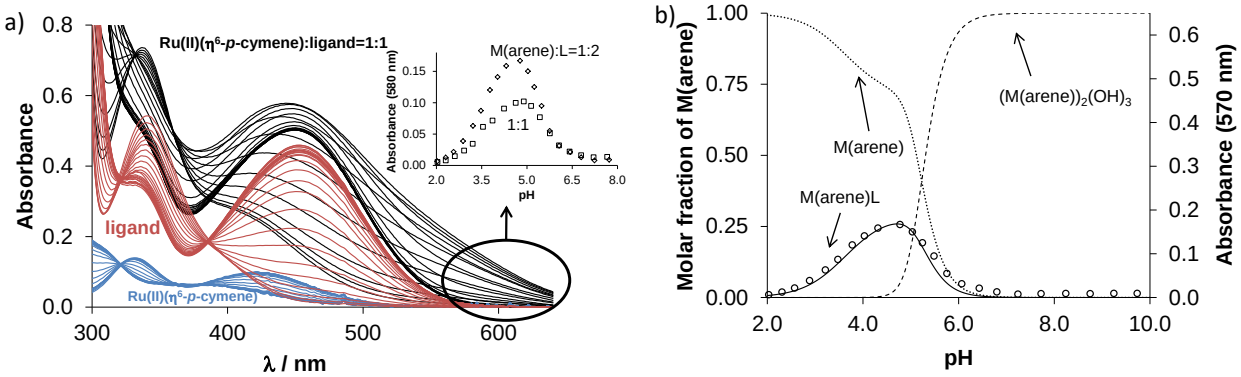

Fig. S2. a) UV-Vis absorption spectra of lawsone, $[Ru(\eta^6\text{-}p\text{-cymene})(H_2O)_3]^{2+}$ and the $[Ru(\eta^6\text{-}p\text{-cymene})(H_2O)_3]^{2+}$ – lawsone 1:1 system at pH = 2.0-11.5. b) Concentration distribution curves calculated with the determined constant from Table 3. Absorbance at 570 nm (○) shows the formation of [ML] complex. {*c*(lawsone) = *c*($[Ru(\eta^6\text{-}p\text{-cymene})(H_2O)_3]^{2+}$) = 200 μM; *I* = 0.2 M (KCl); *T* = 25.0 °C; *l* = 2 cm}

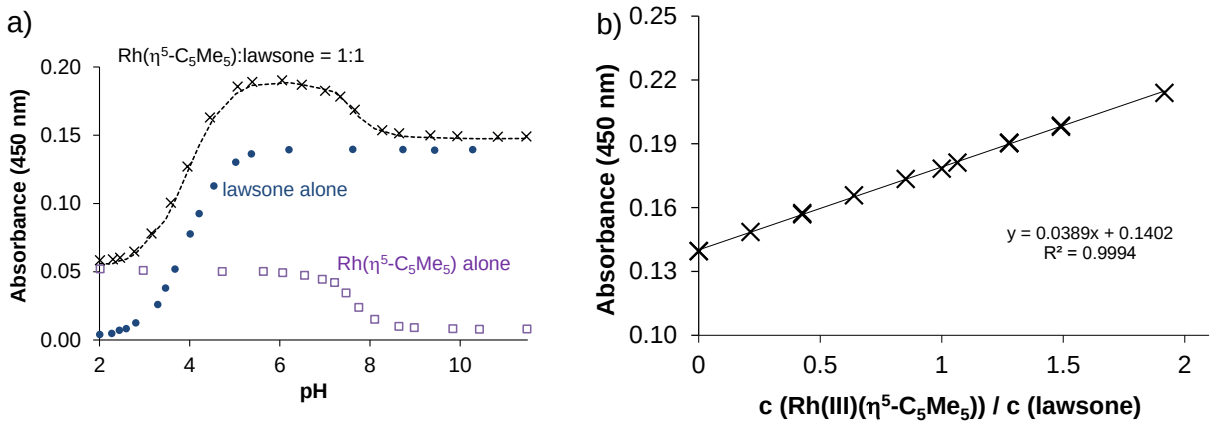

Fig. S3. a) Absorbance values at 450 nm for lawsone, $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ and the $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$ – lawsone 1:1 system at pH = 2.0-11.5. Dashed curve shows the addition of the separate ligand and metal ion titration. {*c*(lawsone) = *c*($[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$) = 50 μM; *I* = 0.2 M (KCl); *T* = 25.0 °C; *l* = 2 cm} b) Absorbance values at 450 nm at various $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$-to-lawsone ratios. Linearity of the curve proves the lack of complex formation. {*c*(lawsone) = 50 μM; *c*($[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$) = 0-100 μM; pH = 7.40 (20 mM phosphate buffer); *I* = 0.2 M (KCl); *T* = 25.0 °C; *l* = 1 cm}

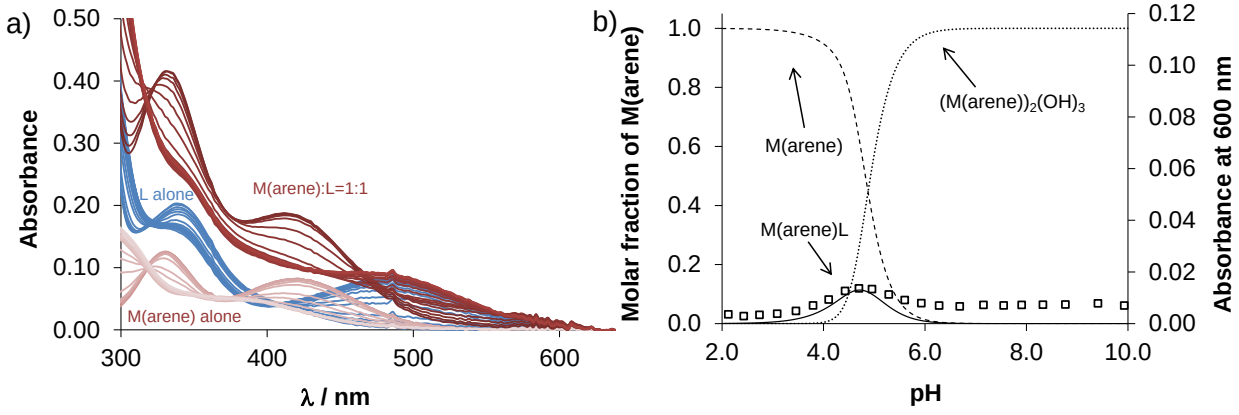

Fig. S4. a) UV-Vis absorption spectra of phthiocol, $[Ru(\eta^6\text{-toluene})(H_2O)_3]^{2+}$ and the $[Ru(\eta^6\text{-toluene})(H_2O)_3]^{2+}$ – phthiocol 1:1 system at pH = 2.0-11.5. b) Concentration distribution curves calculated with the determined constant from Table 3. Absorbance at 600 nm (□) shows the formation of [ML] complex. {*c*(phthiocol) = *c*($[Ru(\eta^6\text{-toluene})(H_2O)_3]^{2+}$) = 100 μM; *I* = 0.2 M (KCl); *T* = 25.0 °C; *l* = 2 cm}

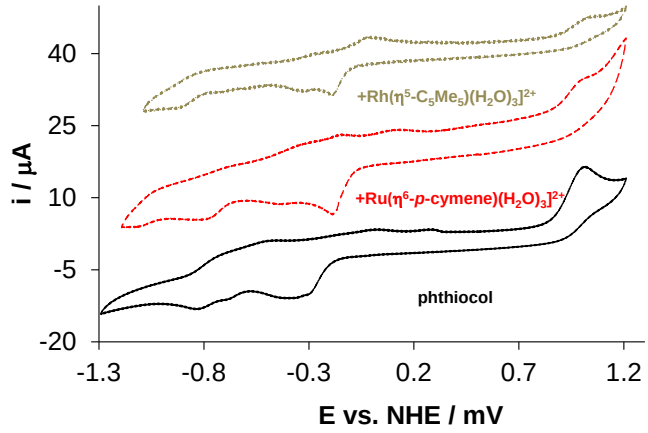

Fig. S5. Cyclic voltammograms of phthiocol in the absence and in the presence of organometallic cations: phthiocol without any metal (—), with $[Ru(\eta^6\text{-}p\text{-cymene})(H_2O)_3]^{2+}$ (- - -) and with $[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$] (-·-·-). Voltammograms are shifted on y-axis for clarity. {c(**phth**) = c(M) =1 mM; solvent: DMF:water = 9:1; pH of water part = 7.40 (phosphate buffer); T = 25.0 °C; I = 0.2 M [n-Bu_4N][BF_4]; scan rate = 50 mV/s}.

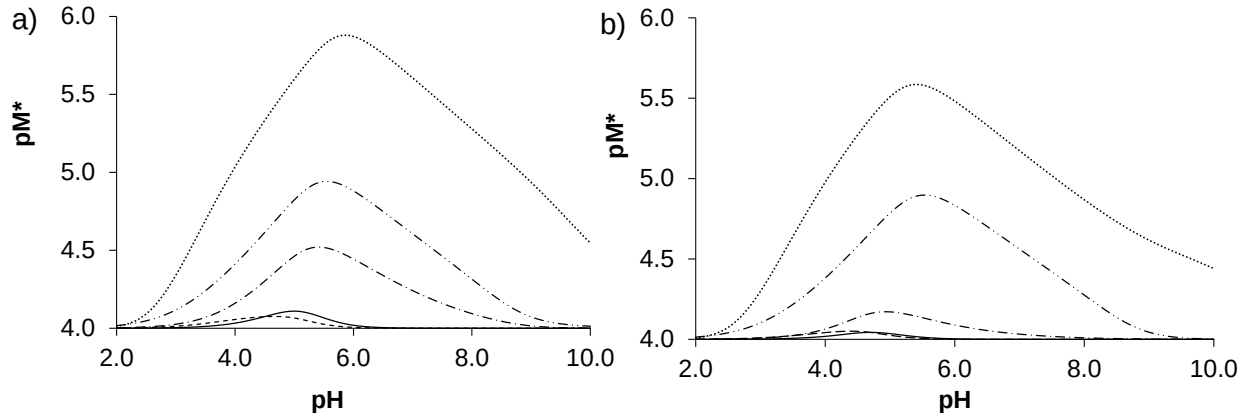

Fig. S6. Calculated pM*-curves obtained for the a) $[Ru(\eta^6\text{-toluene})(H_2O)_3]^{2+}$ – (O,O) bidentate ligand b) $[Ru(\eta^6\text{-}p\text{-cymene})(H_2O)_3]^{2+}$ – (O,O) bidentate ligand systems plotted against the pH. L = lawsone (- - -); phthiocol (—); acetylacetone (-·-·-) [SI-1]; maltol (-··-··-) [SI-1,SI-2]; deferiprone (·····) [SI-2]. {c(L) = c($[Rh(\eta^5\text{-}C_5Me_5)(H_2O)_3]^{2+}$) = 100 µM; T = 25.0 °C; I = 0.2 M (KCl)}

[1]H NMR spectra

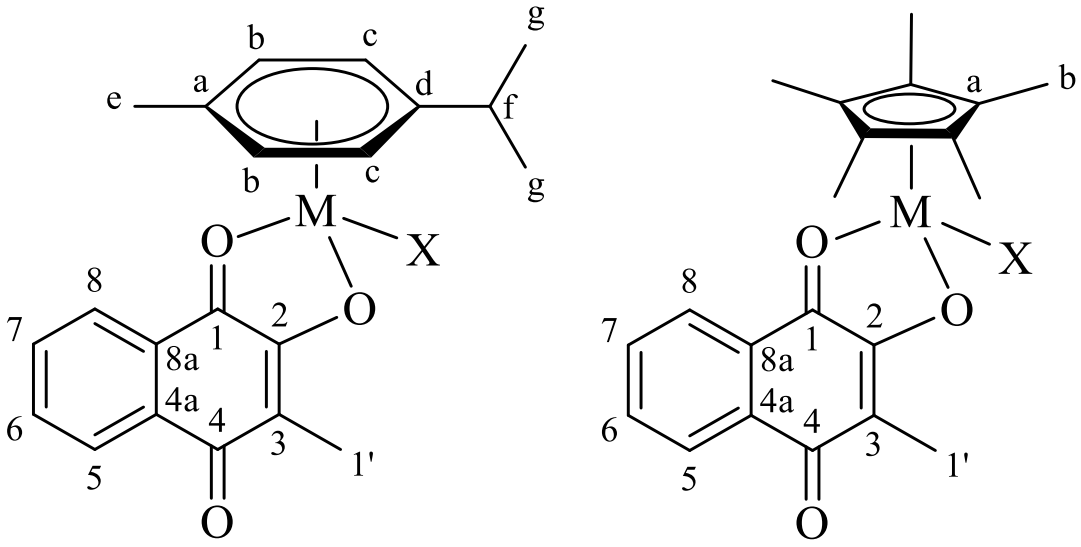

Chart S1. General numbering scheme of complexes.

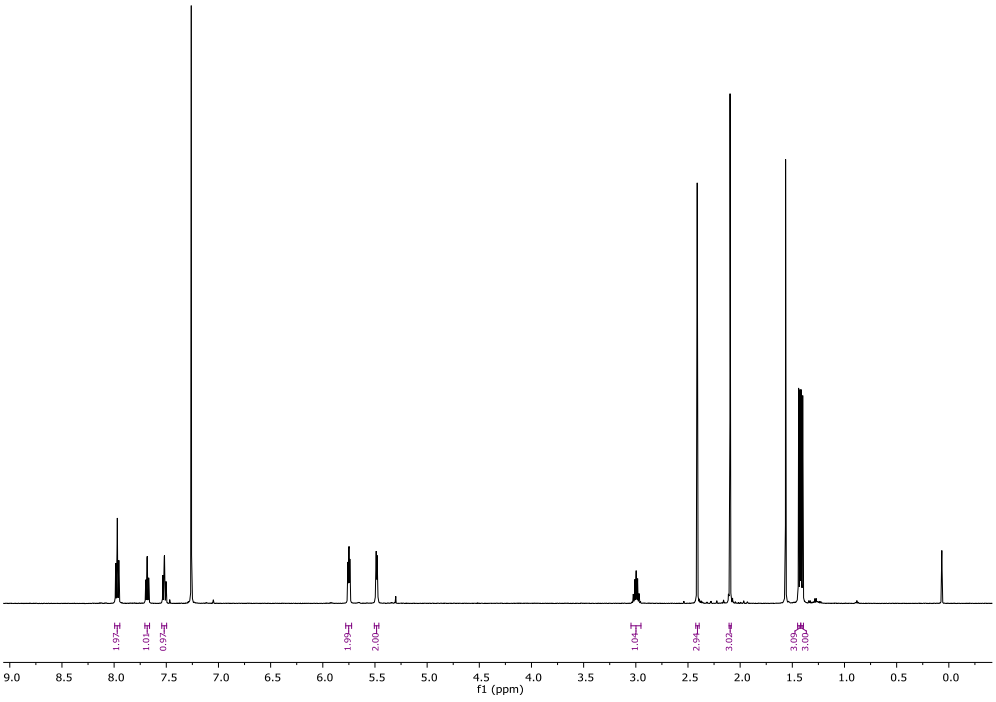

Fig. S7. [1]H NMR spectrum of [**Ru(η[6]-*p*-cymene)(phth)Cl]** (**1**) complex

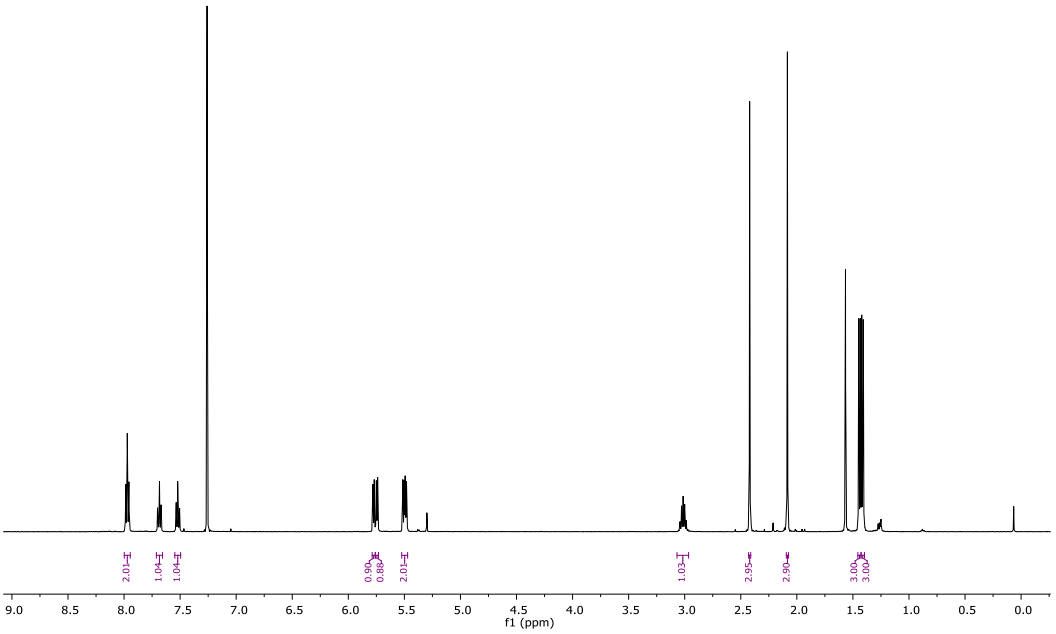

Fig. S8. ^{1}H NMR spectrum of [**Ru(η^{6}-*p*-cymene)(phth)Br]** (**2**) complex.

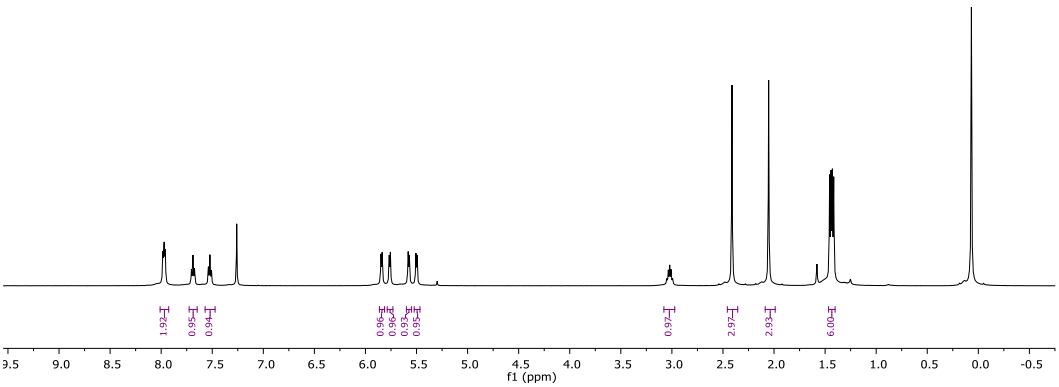

Fig. S9. ^{1}H NMR spectrum of [**Ru(η^{6}-*p*-cymene)(phth)I]** (**3**) complex.

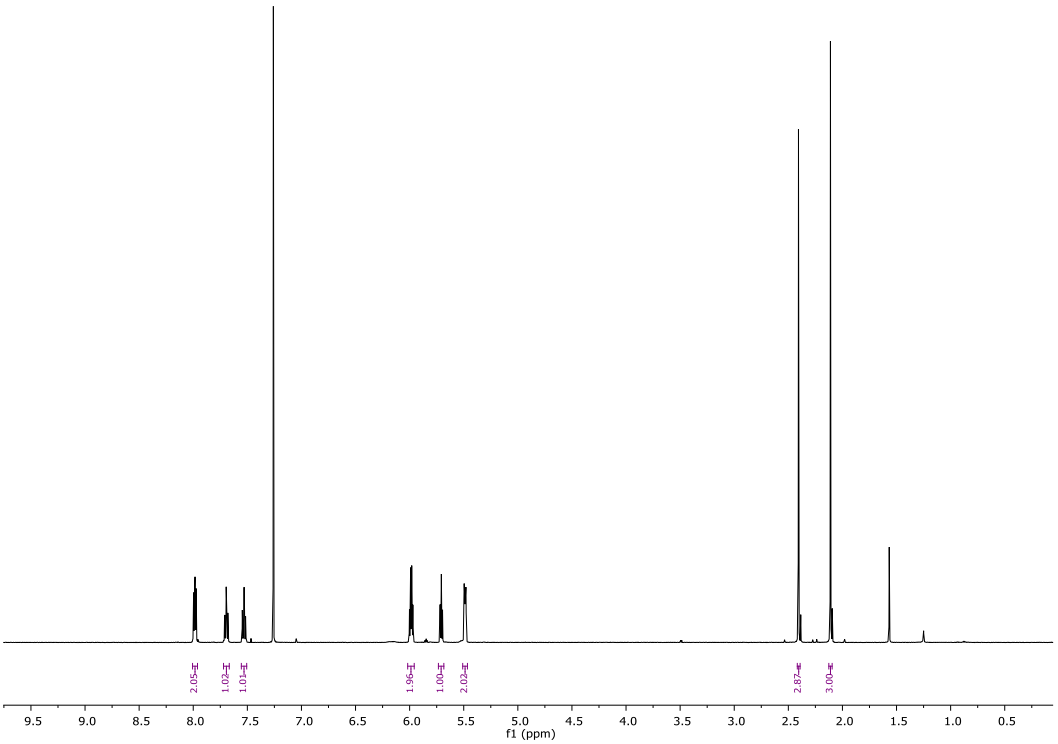

Fig. S10. ^{1}H NMR spectrum **[Ru(η^{6}-toluene)(phth)Cl]** (**4**) complex.

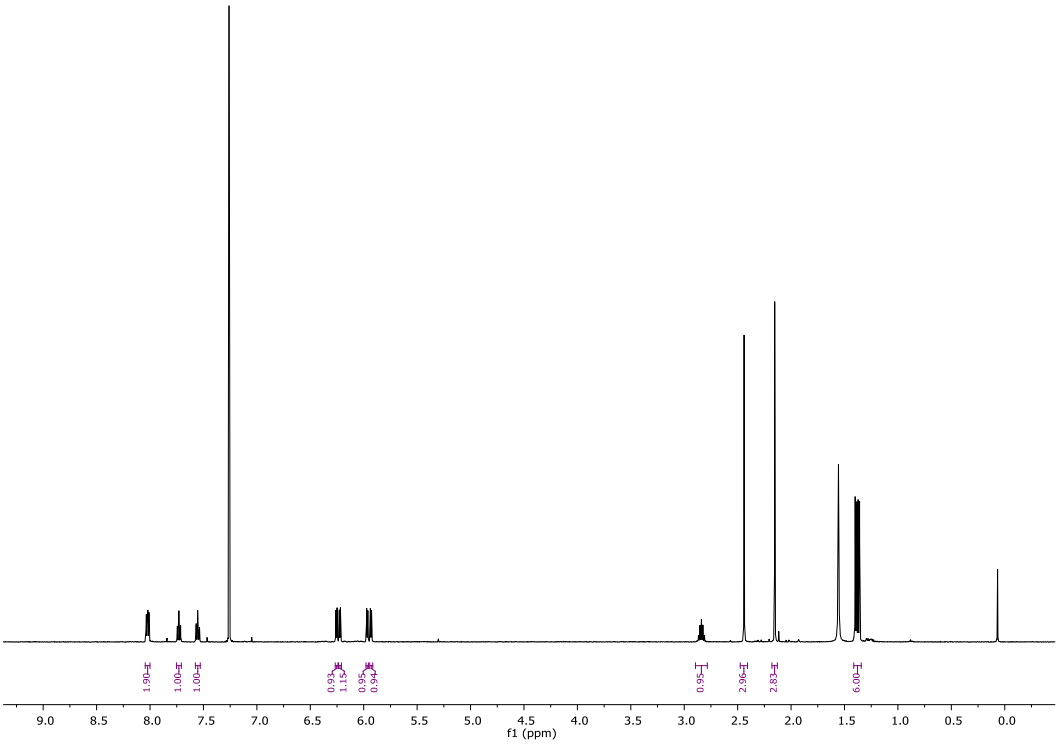

Fig. S11. ^{1}H NMR spectrum of [**Os(η^{6}-*p*-cymene)(phth)Cl]** (**5**) complex.

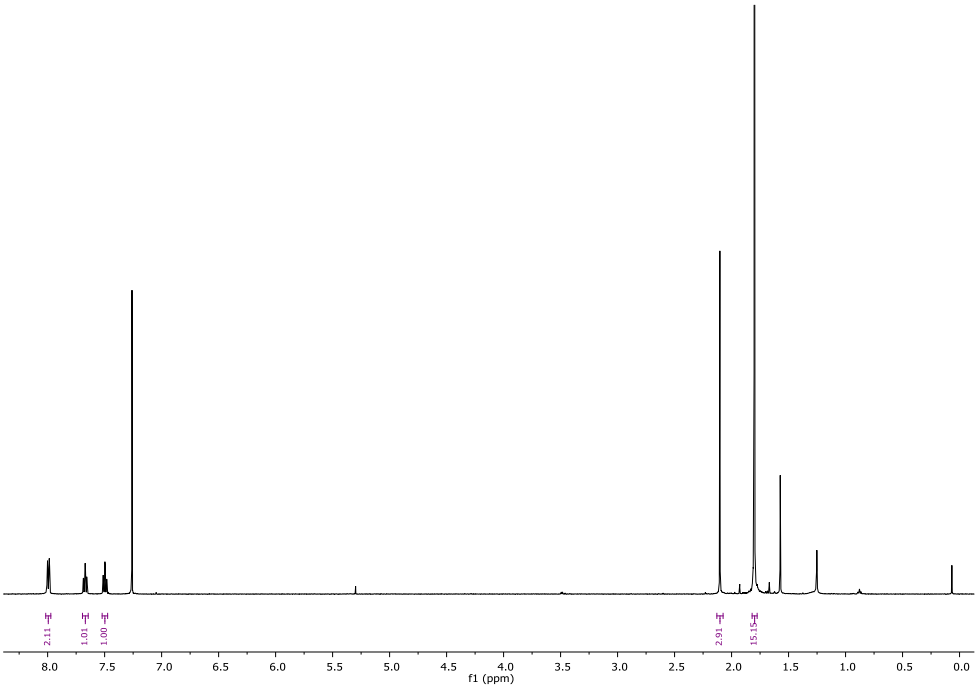

Fig. S12. ^{1}H NMR spectrum of [**Rh(η^{5}-C$_{5}$Me$_{5}$)(phth)Cl]** (**6**) complex.

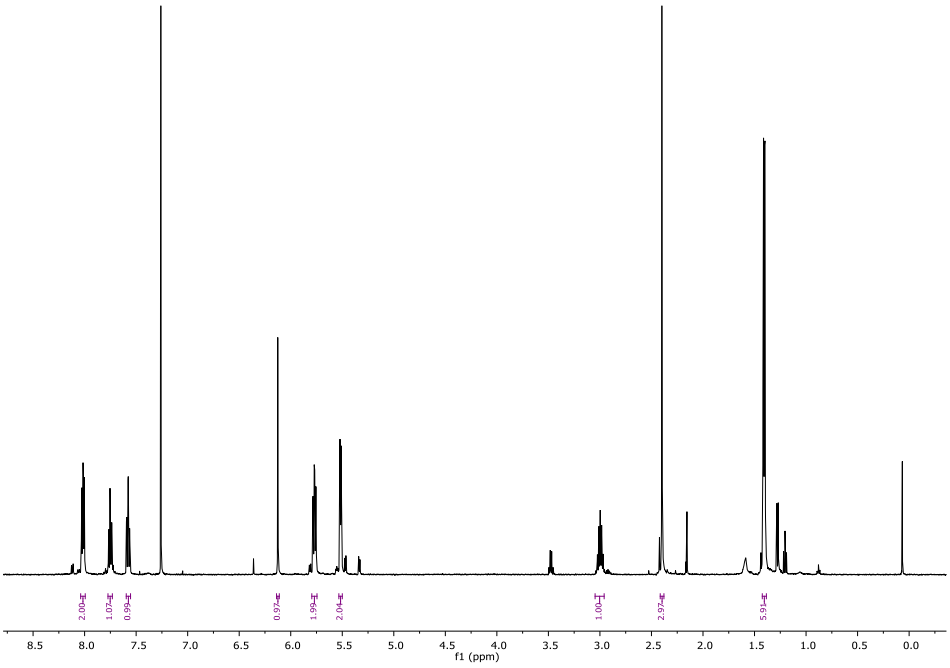

Fig. S13. ^{1}H NMR spectrum of [**Ru(η^{6}-*p*-cymene)(lawsone)Cl]** (**7**)complex.

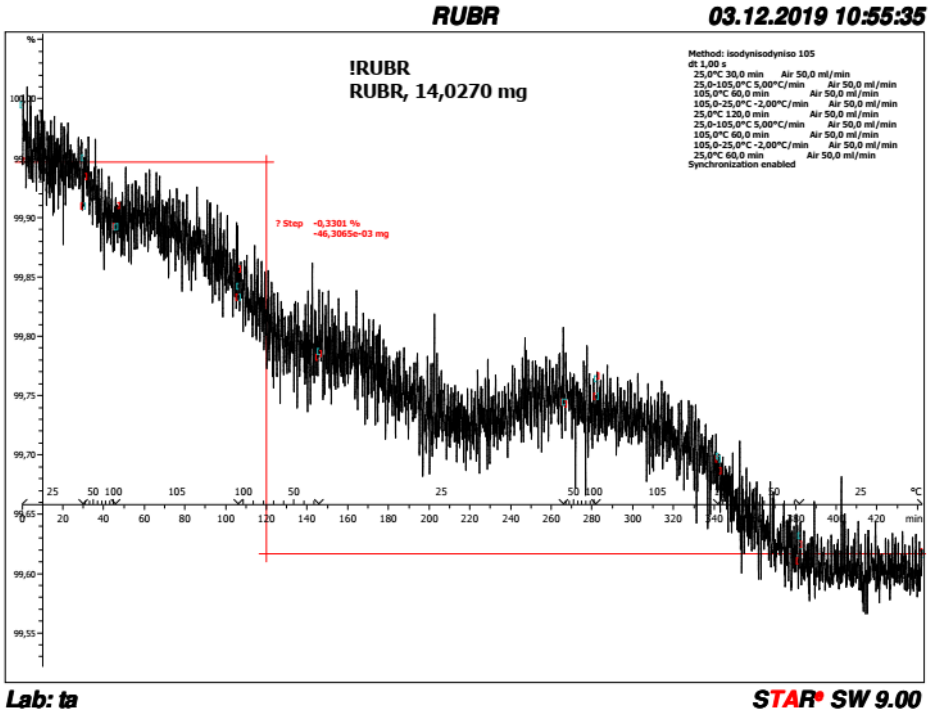

Fig. S14. TGA curve recorded for complex [**Ru(η^6-*p*-cymene)(phth)Br]** (**2**).

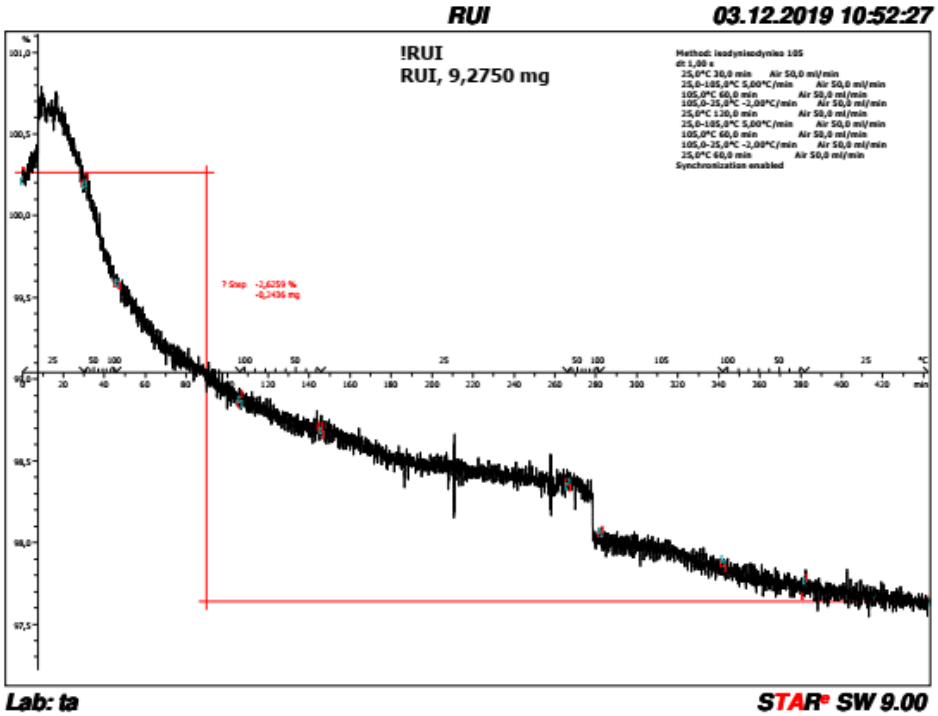

Fig. S15. TGA curve recorded for complex [**Ru(η^6-*p*-cymene)(phth)I]** (**3**).

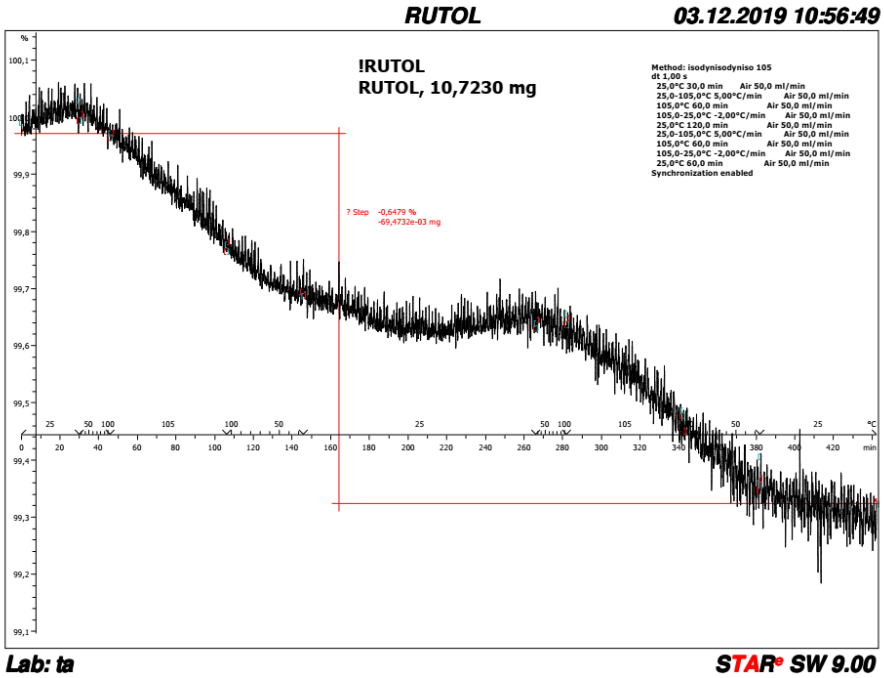

Fig. S16. TGA curve recorded for complex **[Ru(η^6-toluene)(phth)Cl]** (**4**).

References:

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