Electronic Supplementary Material (ESI) for Dalton Transactions.

Figures and Tables.

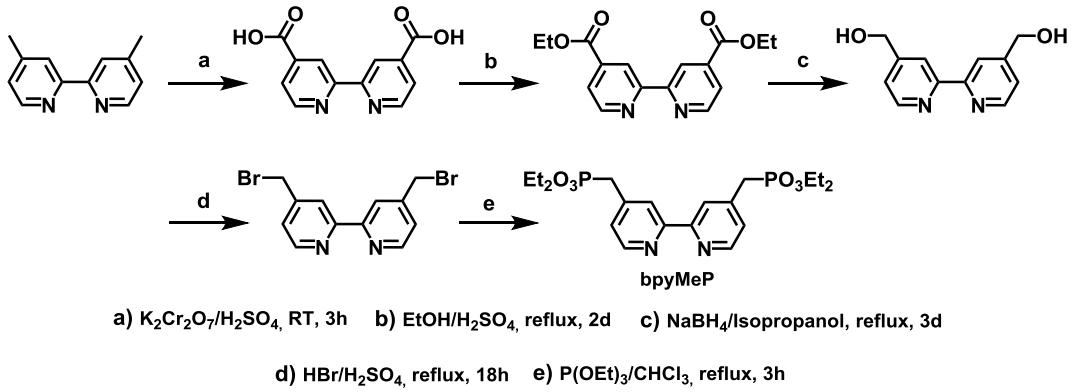

Figure S1. Synthetic scheme for the preparation of bpyMeP

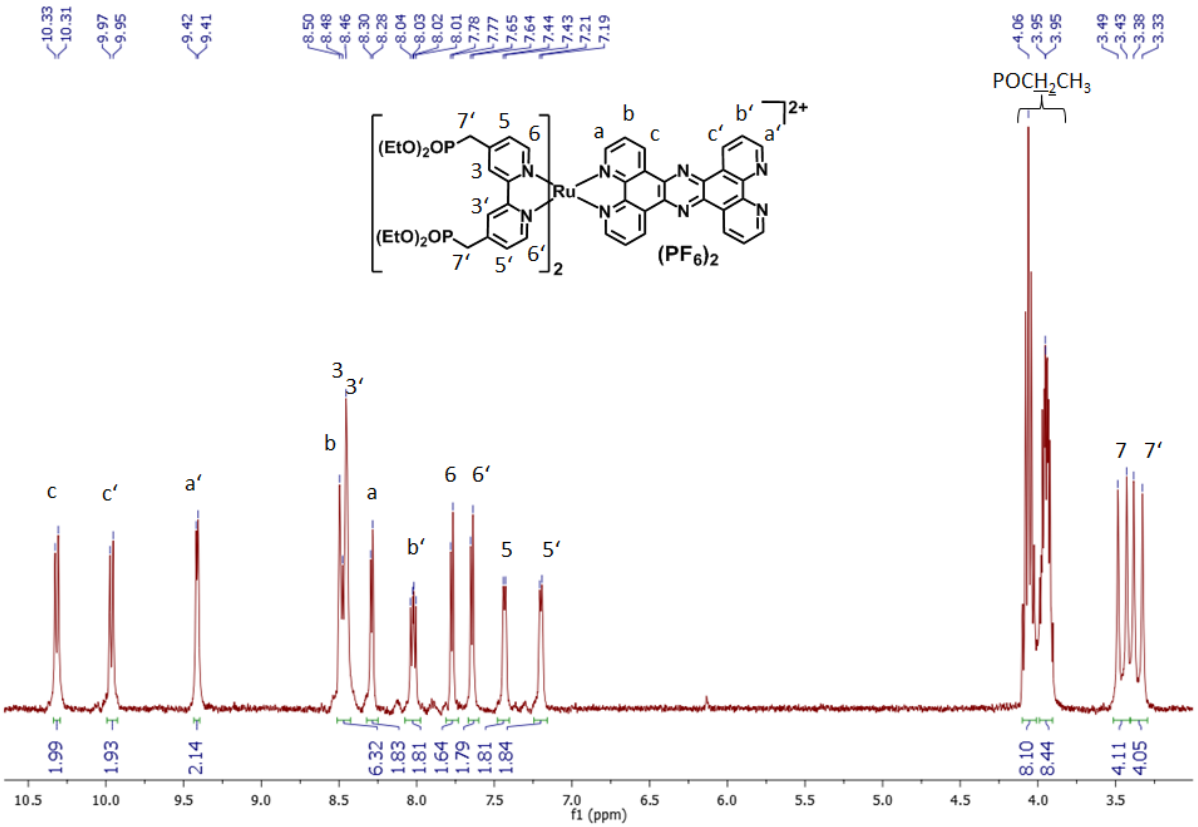

Figure S2. ^{1}H-NMR-spectrum of **(3)**. By comparing the results for **(3)** with known Ru-tpphz-complexes the proton signals were assigned as depicted.

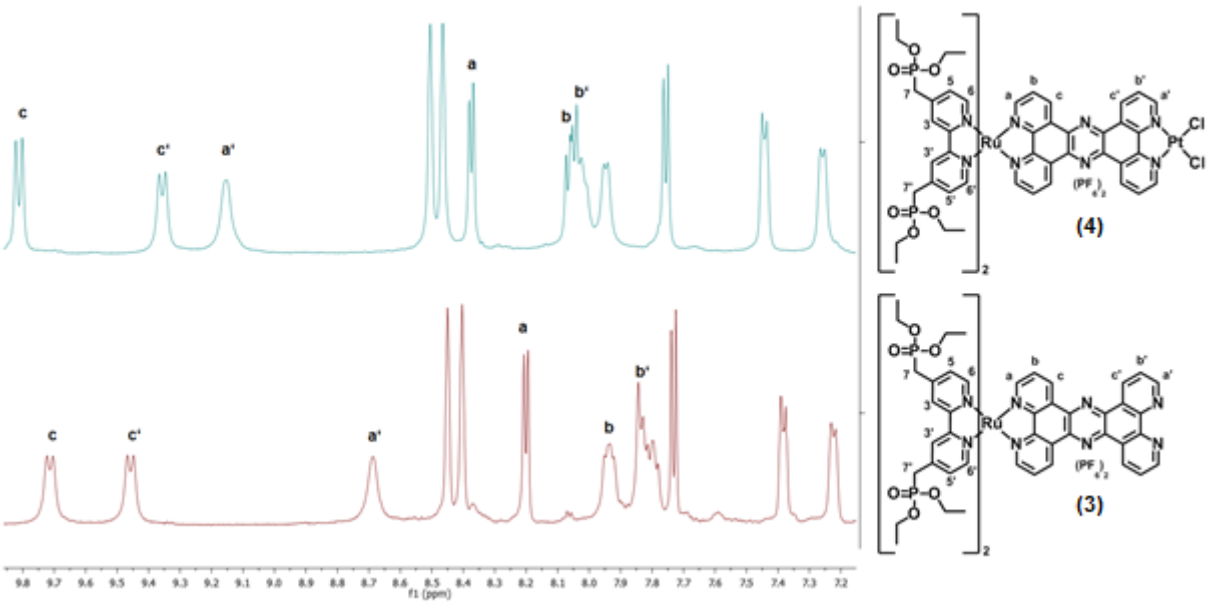

Figure S3. Comparison of ^{1}H-NMR spectra of **(3)** and **(4)**.

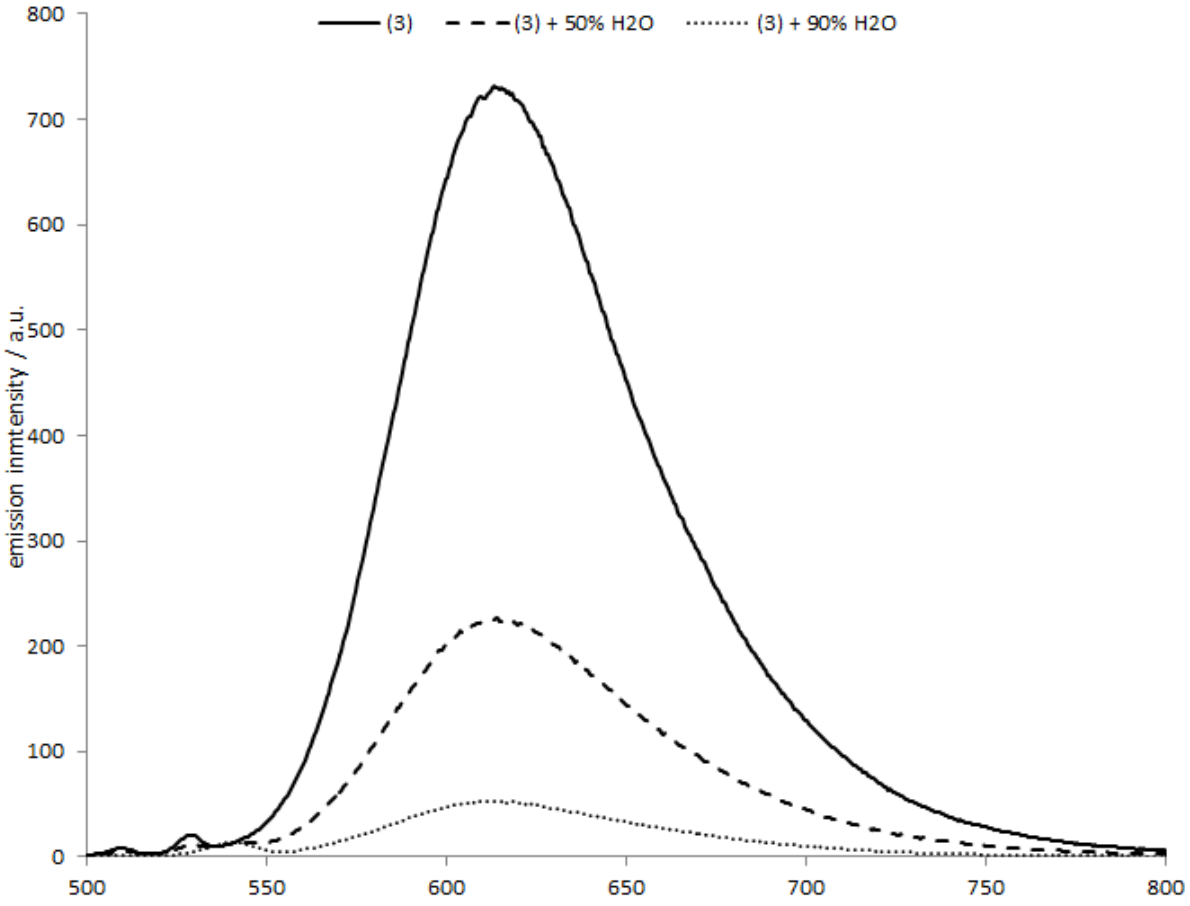

Figure S4. Emission quenching upon the addition of water to an acetonitrile solution of **(3)**.*
*=excitation at identical optical density at 459 nm.

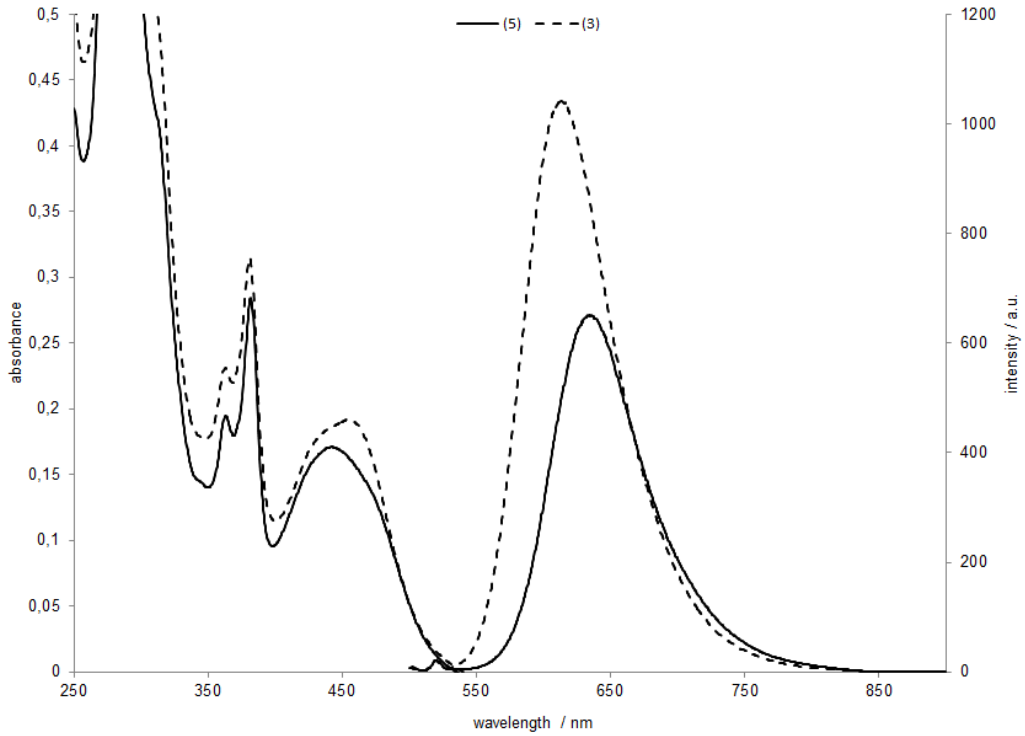

Figure S5. UV/vis and emission spectra of (3) and (5).*
*=excitation at a concentration of 5 x 10^{-6} M at 450 nm.

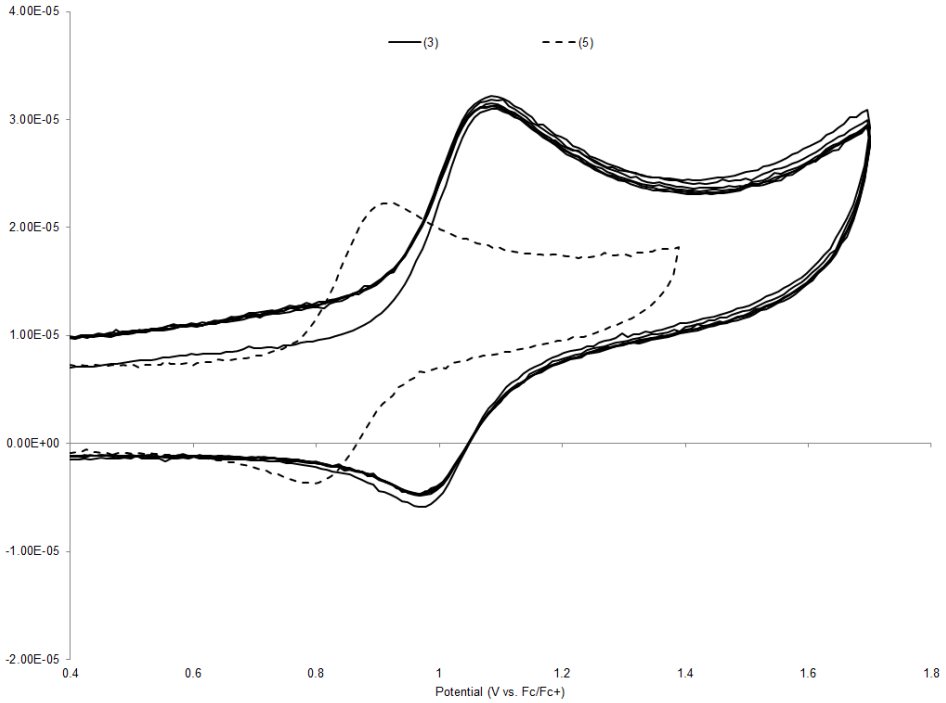

Figure S6. Cyclovoltamogram of (3) and (5) (oxidation part).

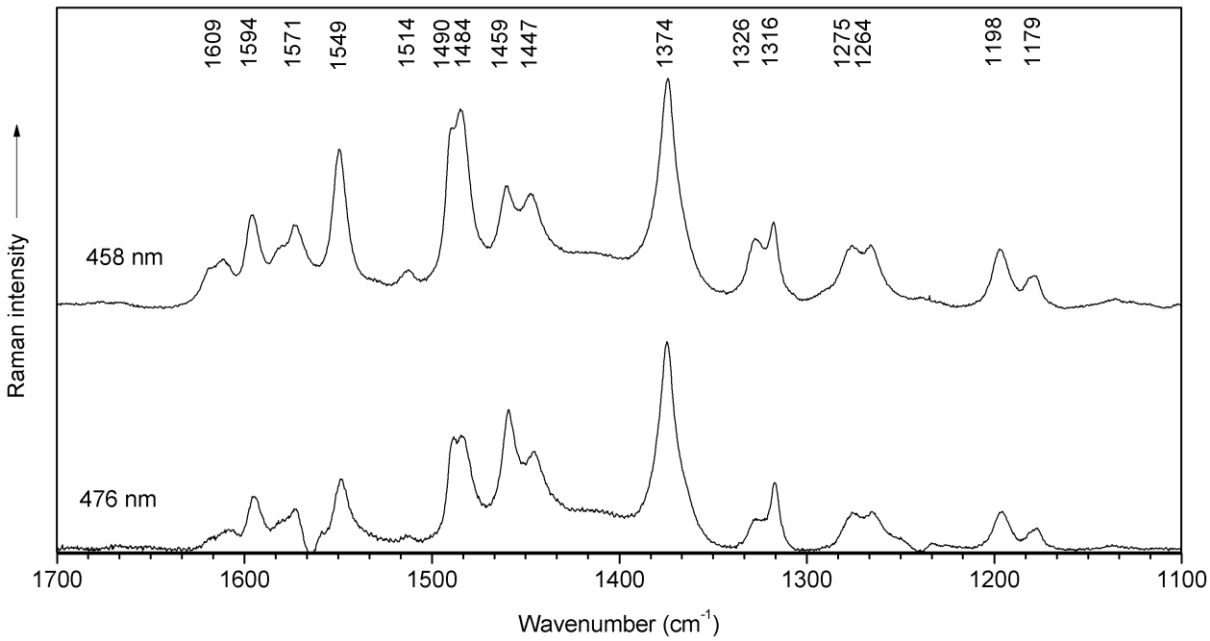

Figure S7. Resonance-Raman spectra (λ_{exc} = 458 nm and 476 nm) of the Ru-complex **(4)**

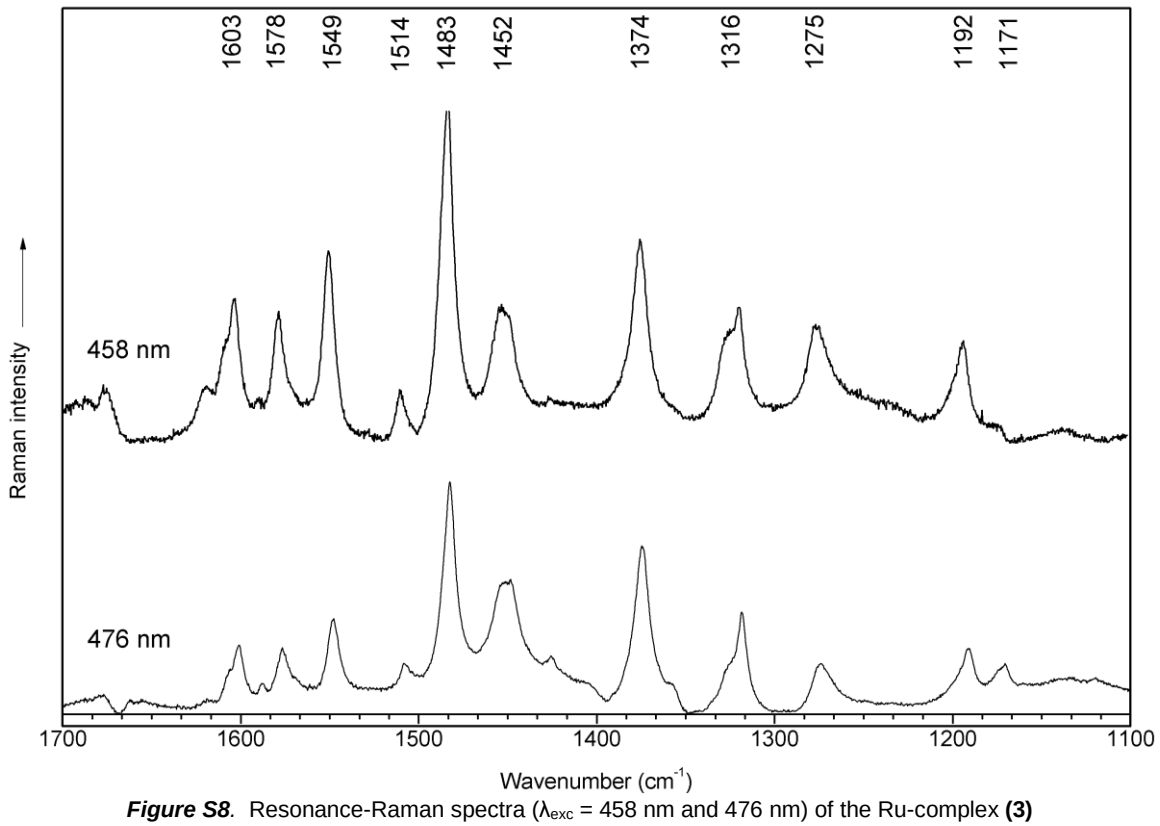

Figure S8. Resonance-Raman spectra (λ_{exc} = 458 nm and 476 nm) of the Ru-complex **(3)**

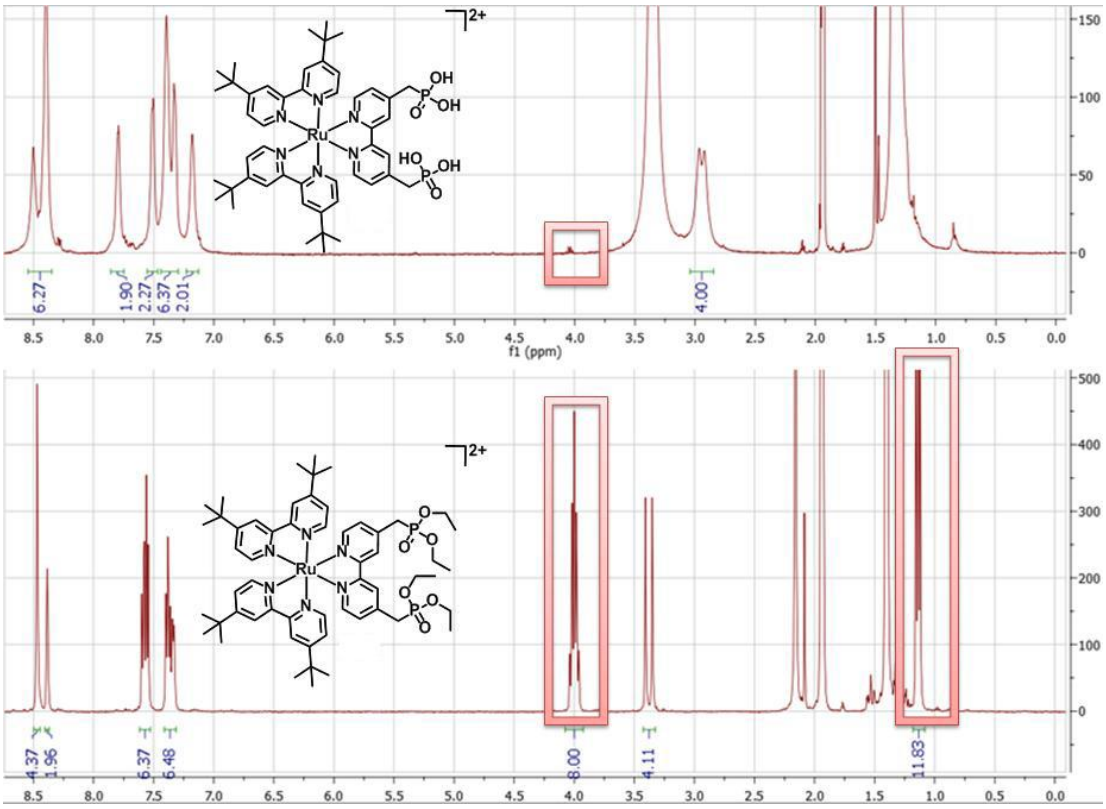

Figure S10. ^{1}H-NMR-spectra of [Ru^{II}(tbbpy)$_2$bpyMeP] **(M)** in [D3]MeCN (bottom) and [Ru^{II}(tbbpy)2(bpy(CH$_2$PO$_3$H$_2$)$_2$)] **(M$_{hydrolyzed}$)** in D$_2$O (top). The protons of the ethyl groups (highlighted by red rectangles) disappear upon deprotection.

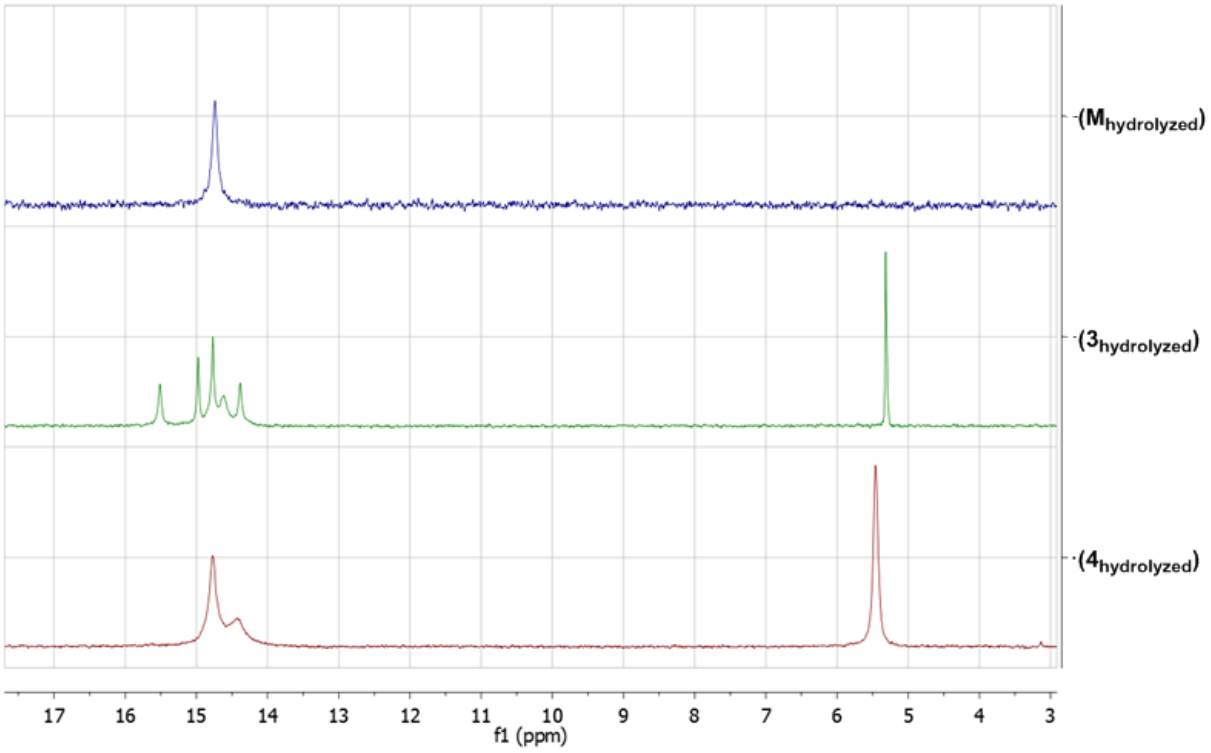

Figure S11. ^{31}P-NMR spectra of **(M$_{hydrolyzed}$)** in D2O and **(3$_{hydrolyzed}$)** and **(4$_{hydrolyzed}$)** in D2O + 4% NaOD

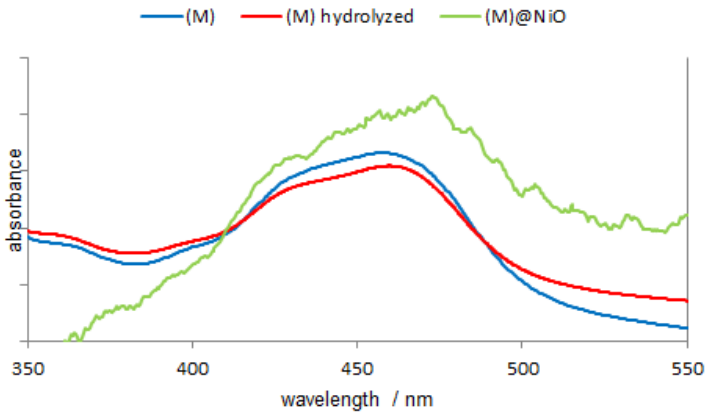

Figure S12.: Absorption spectra of **(M)** in acetonitrile, **($M_{hydrolyzed}$)** in water and **(M)@NiO****
**= NiO and FTO glass background substracted

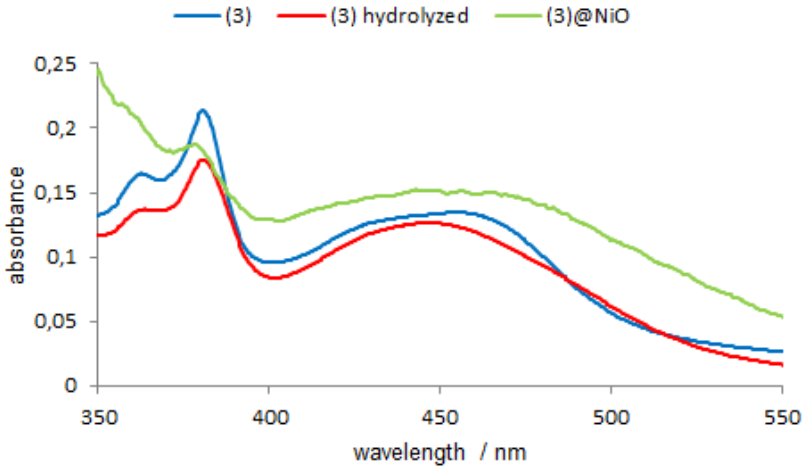

Figure S13.: Absorption spectra of **(3)** in acetonitrile, **($3_{hydrolyzed}$)** in water + 4% NaOH and **(3)@NiO****
**= NiO and FTO glass background substracted

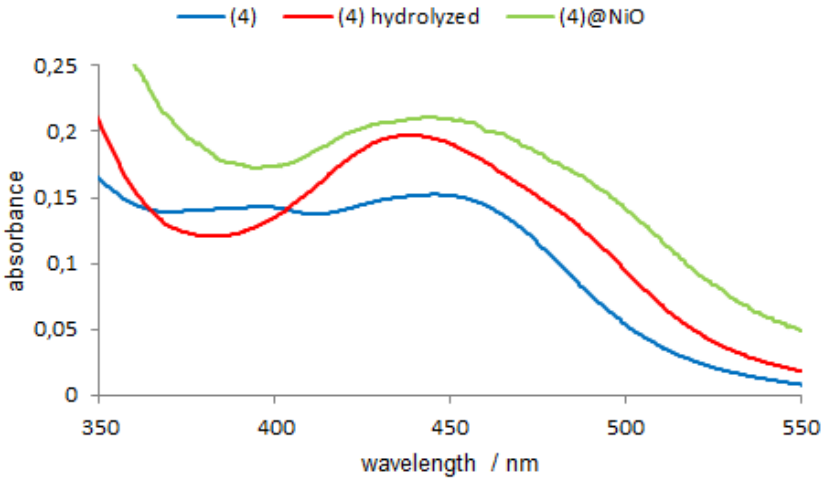

Figure S14.: Absorption spectra of **(4)** in acetonitrile, **($4_{hydrolyzed}$)** in water + 4% NaOH and **(4)@NiO****
**= NiO and FTO glass background substracted

Table S1. Crystal data and structure refinement for 4,4'-bis(diethyl(methylene)phosphonate)-2,2'-bipyridine.

Empirical formula	C20 H30 N2 O6 P2	
Formula weight	456.40	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.3747(3) Å	□= 97.051(4)°.
	b = 8.5221(4) Å	□= 97.098(4)°.
	c = 9.7222(6) Å	□ = 107.244(4)°.
Volume	570.84(5) $Å^3$	
Z	1	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	2.058 mm^{-1}	
F(000)	242	
Crystal size	0.213 x 0.158 x 0.088 mm^3	
Theta range for data collection	7.801 to 73.042°.	
Index ranges	-8<=h<=9, -10<=k<=10, -12<=l<=11	
Reflections collected	5287	
Independent reflections	2215 [R(int) = 0.0139]	
Completeness to theta = 67.684°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2215 / 0 / 138	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1033	
R indices (all data)	R1 = 0.0393, wR2 = 0.1044	
Largest diff. peak and hole	0.769 and -0.466 e.$Å^{-3}$	

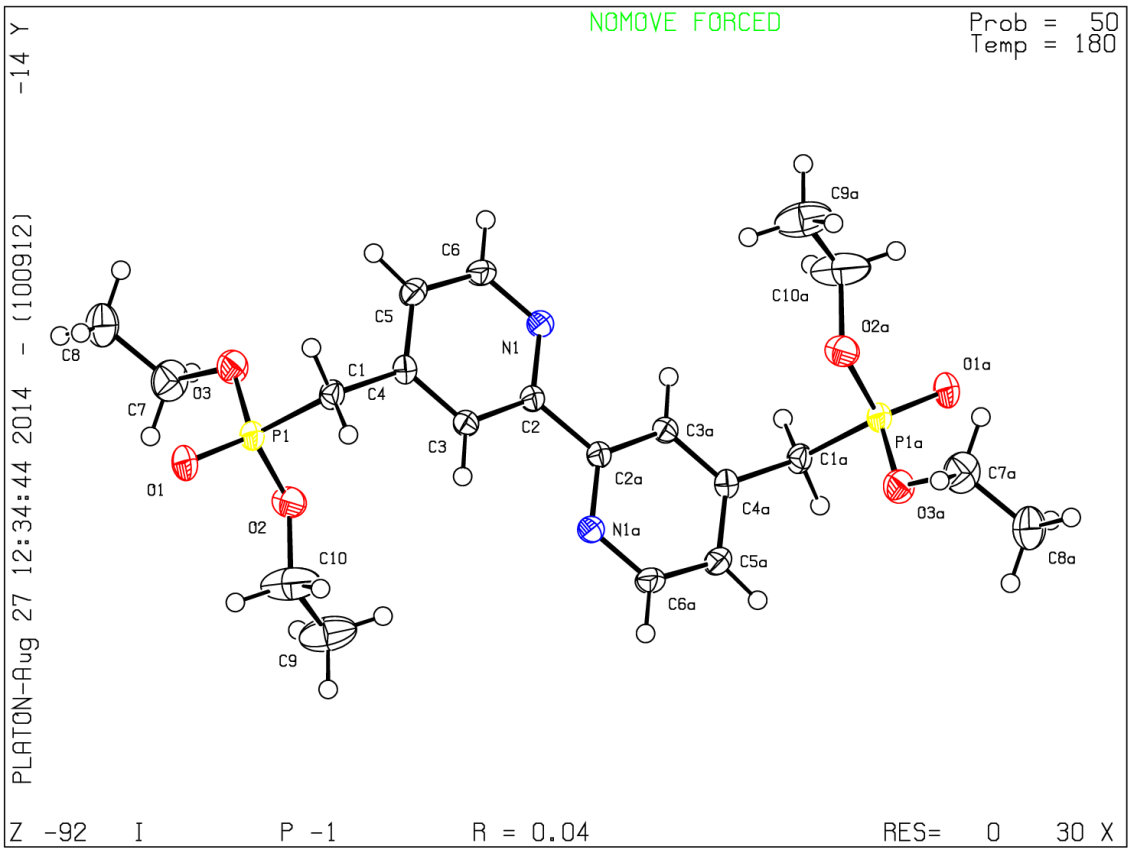

Figure S15. ORTEP depiction of 4,4'-bis(diethyl(methylene)phosphonate)-2,2'-bipyridine (bpyMeP) in the solid state (ellipsoids drawn at 50% probability).

Table S2. Crystal data and structure refinement for $[Ru^{II}(tbbpy)_2(bpyMeP)](PF_6)_2$ **(M)**

Empirical formula	C62 H93 F12 N6 O7.50 P4 Ru	
Formula weight	1495.37	
Temperature	180(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 46.4406(8) Å	□= 90°.
	b = 12.6539(2) Å	□= 121.496(3)°.
	c = 30.2705(6) Å	□ = 90°.
Volume	15167.9(6) Å3	
Z	8	
Density (calculated)	1.277 Mg/m3	
Absorption coefficient	3.144 mm-1	
F(000)	6064	
Crystal size	0.1211 x 0.0645 x 0.0487 mm3	

Theta range for data collection	7.517 to 73.818°.
Index ranges	-57<=h<=40, -15<=k<=15, -35<=l<=36
Reflections collected	44485
Independent reflections	14953 [R(int) = 0.0384]
Completeness to theta = 67.679°	99.5 %
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	14953 / 70 / 864
Goodness-of-fit on F2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1549
R indices (all data)	R1 = 0.0705, wR2 = 0.1662
Largest diff. peak and hole	1.145 and -0.652 e·Å-3

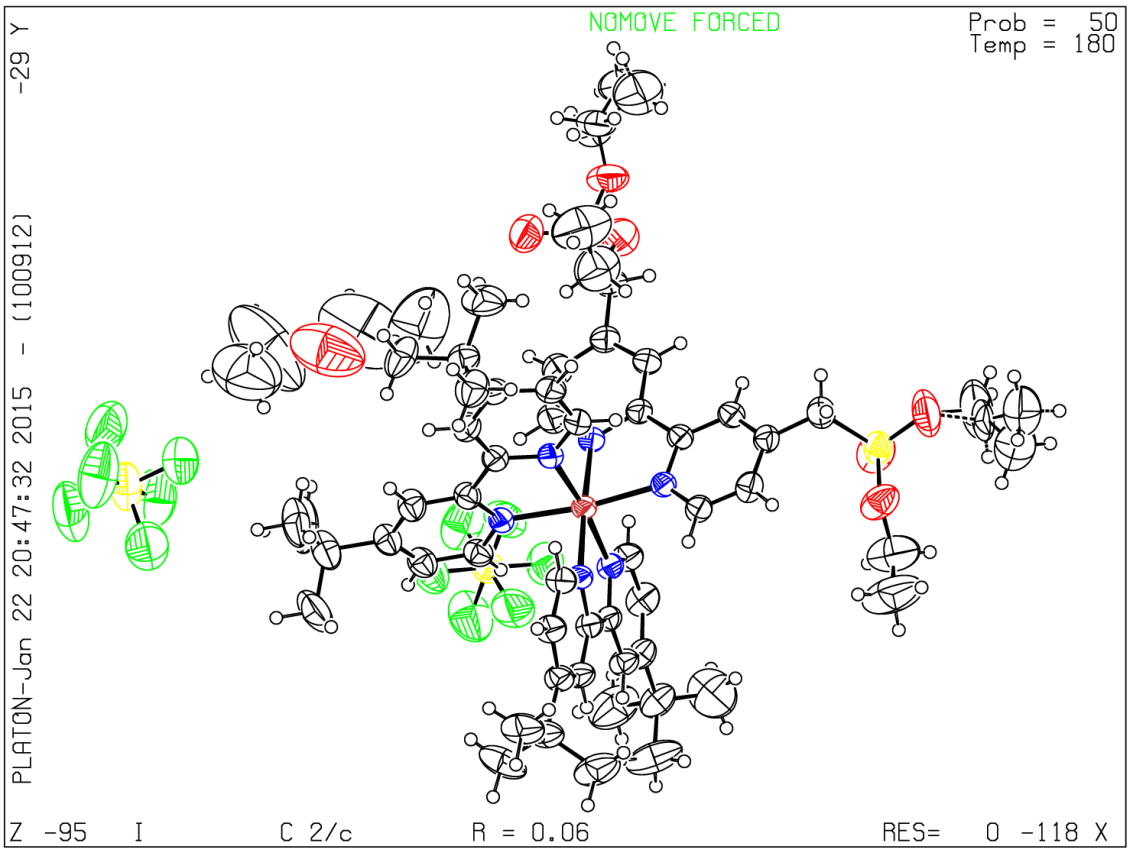

Figure S16. ORTEP depiction of [RuII(tbbpy)2(bpyMeP)](PF6)2 **(M)** in the solid state (ellipsoids drawn at 50% probability).