Table of Contents

NMR SPECTRA

S1

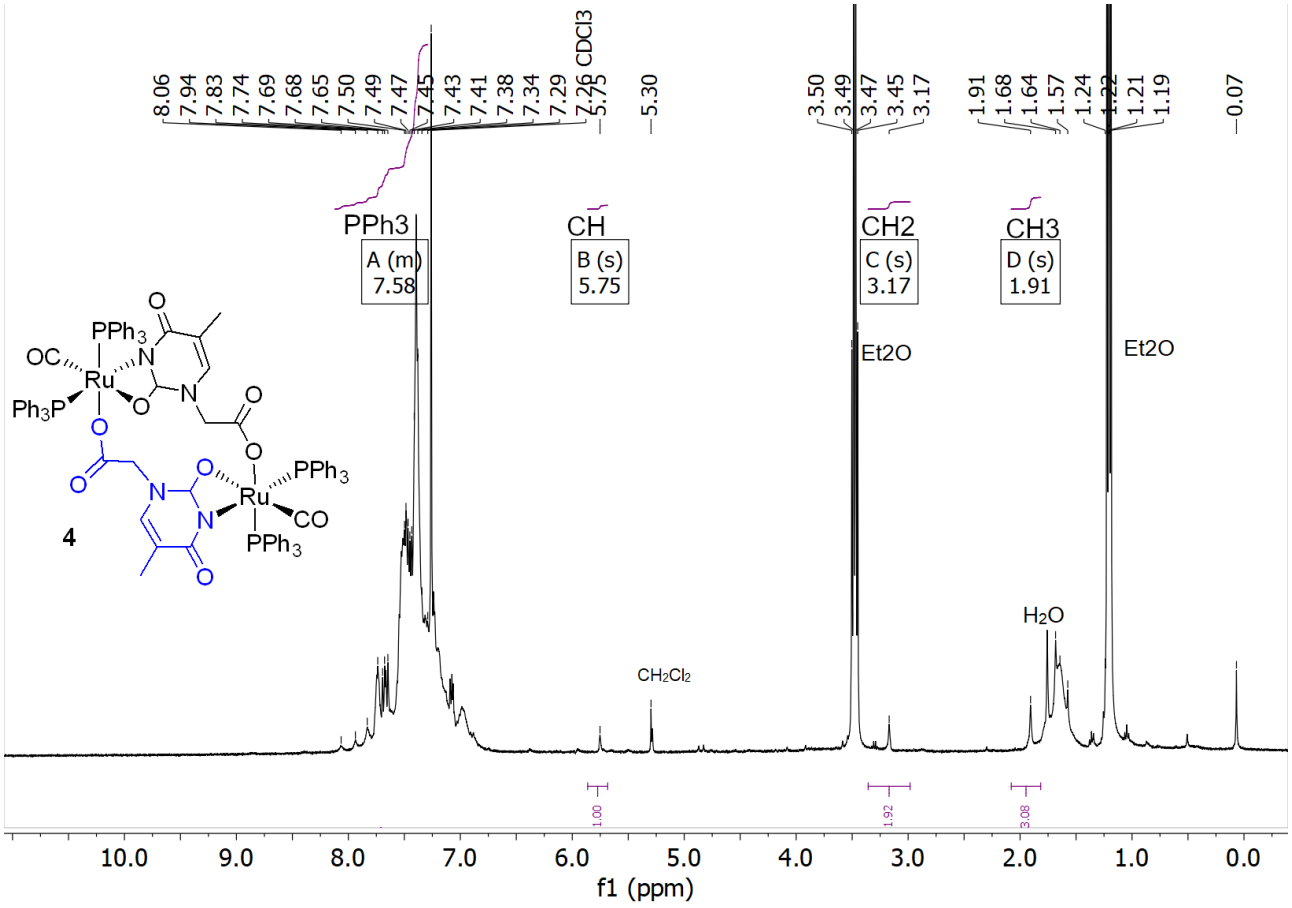


Figure S1: *^1H NMR spectrum of* ***4*** in $CDCl_3$ (300 Mhz)

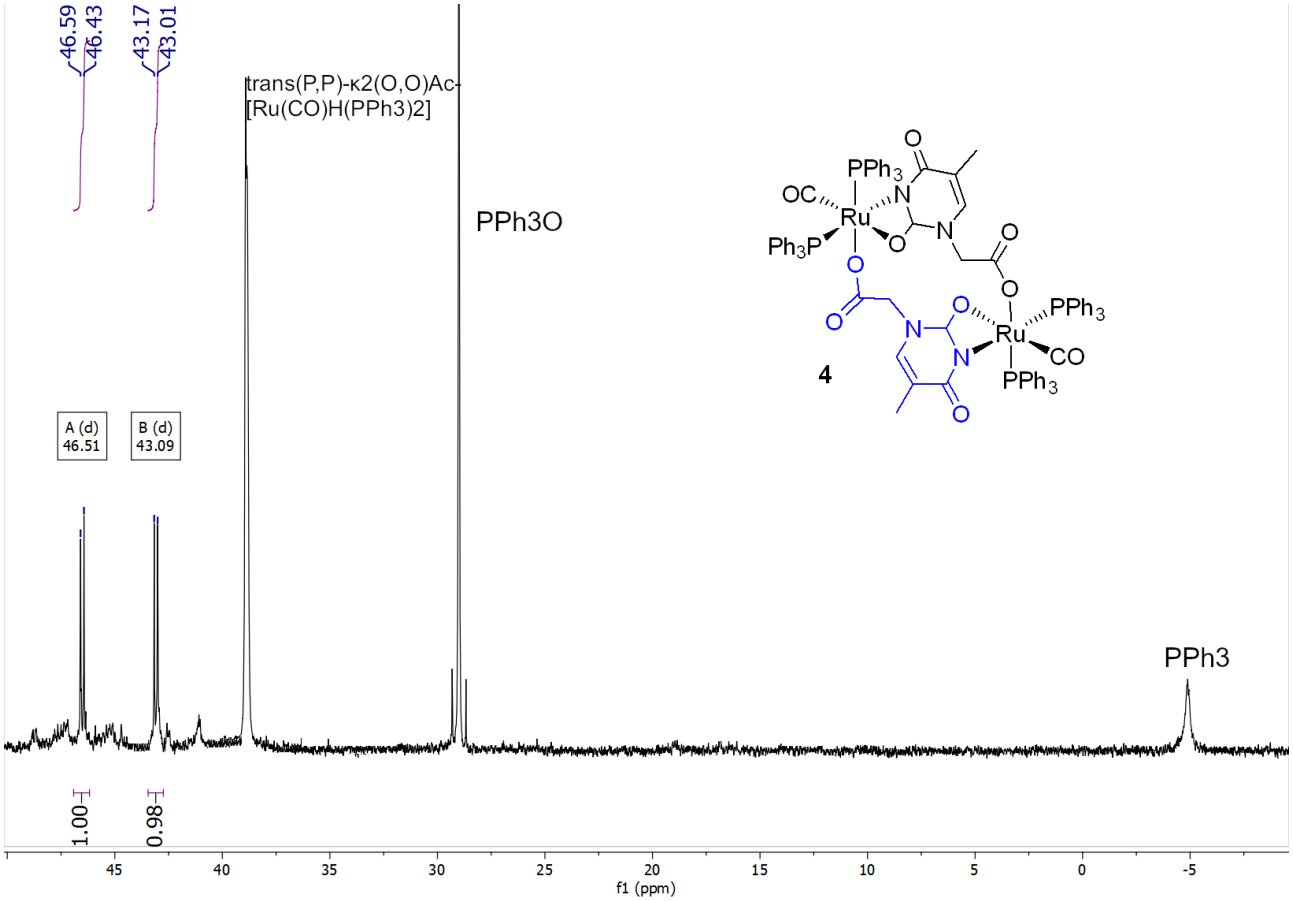


Figure S2: *^{31}P NMR spectrum of **4** in $CDCl_3$ (162 Mhz)*

S3

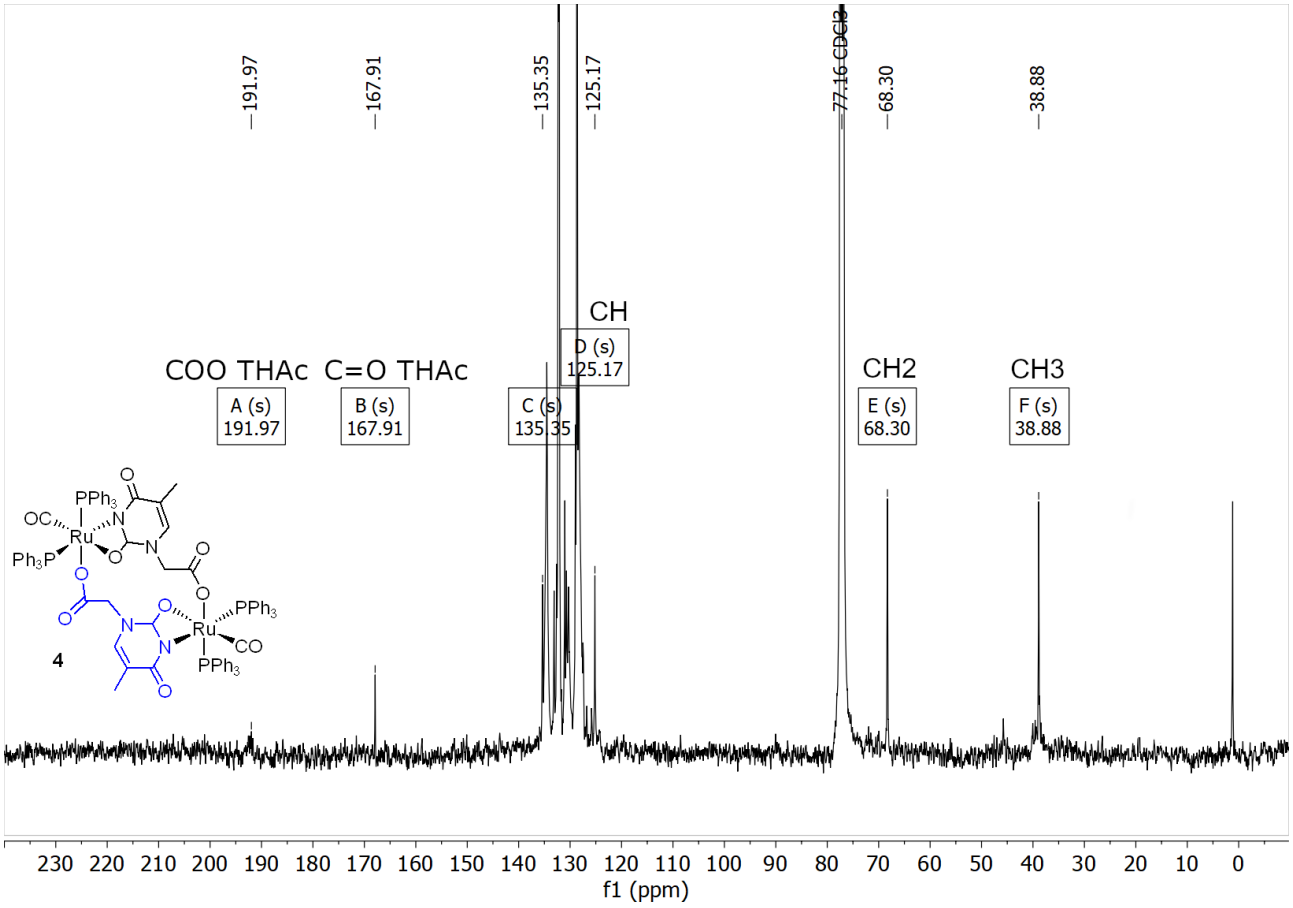


Figure S3: *^{13}C NMR spectrum of **4** in $CDCl_3$ (101 Mhz)*

IR SPECTRA

S4

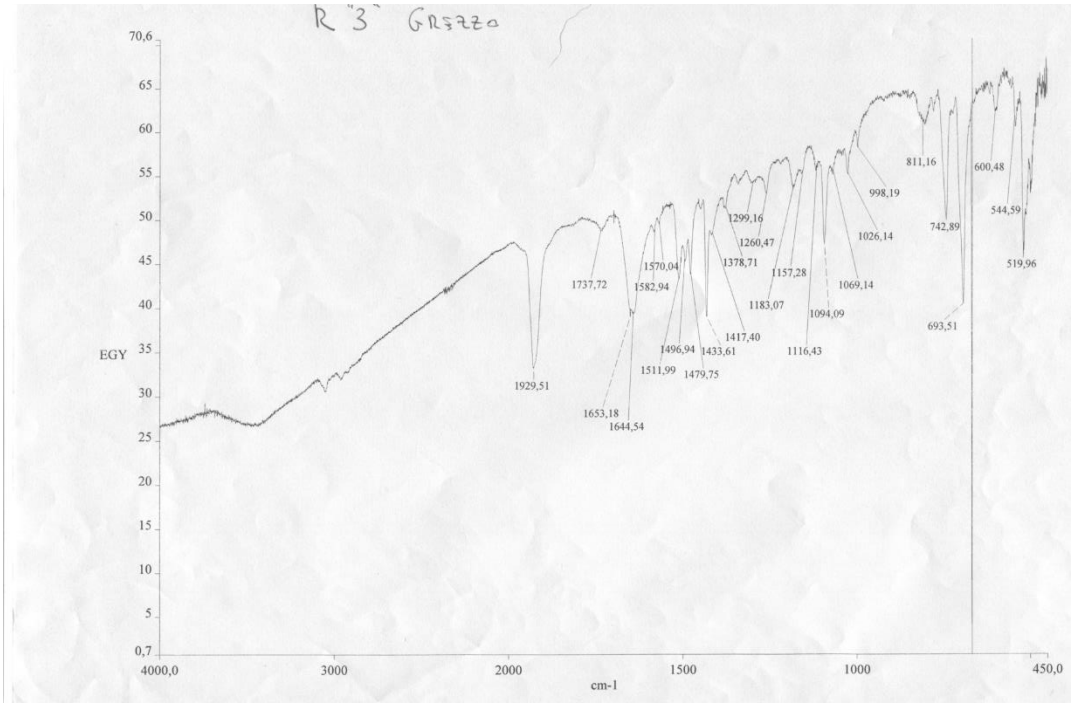


Figure **S4:** IR spectrum of k 1 (O)-**2a** enolic form. The band at 1511 cm-1 is attributable to the incipient transformation to the enol moiety of the precursor of **4.**

S5

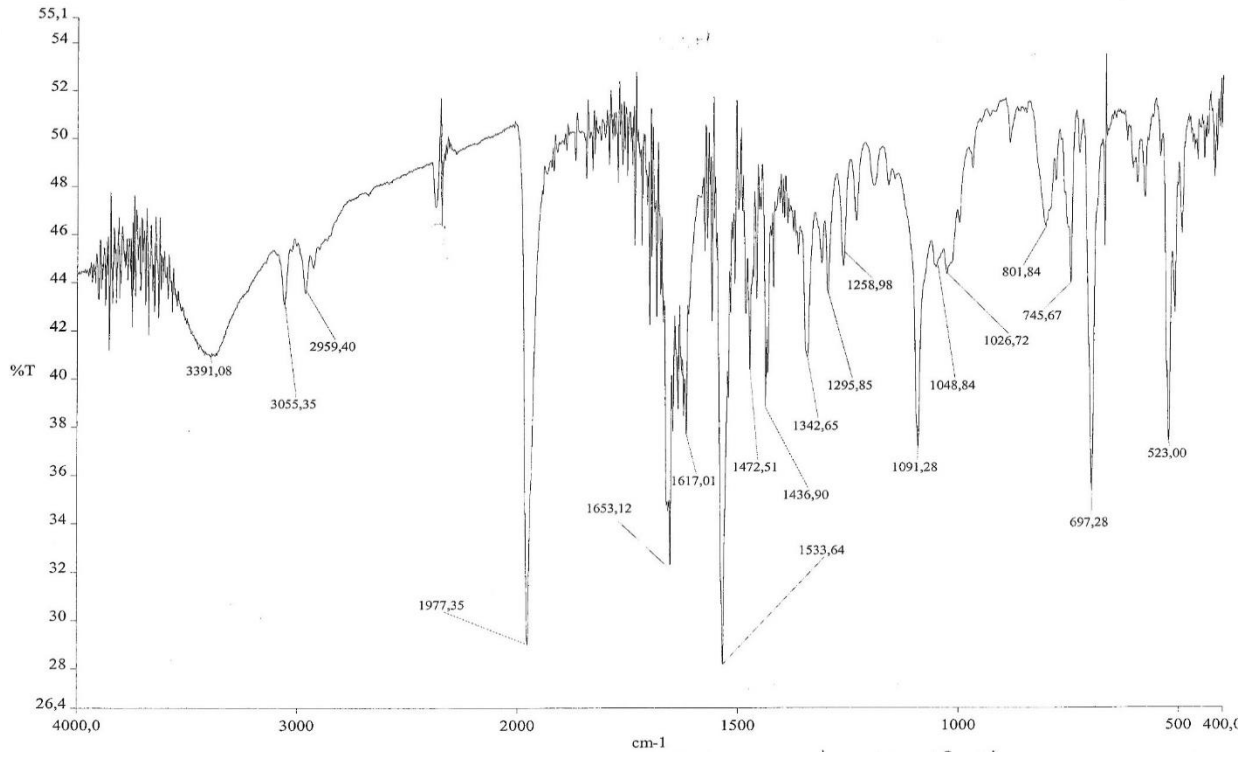


Figure S5*:* IR spectrum of microcrystalline powder **4** of a different preparation: the band atν = 1533.64 is characteristic for the lactim tautomeric form.

S6

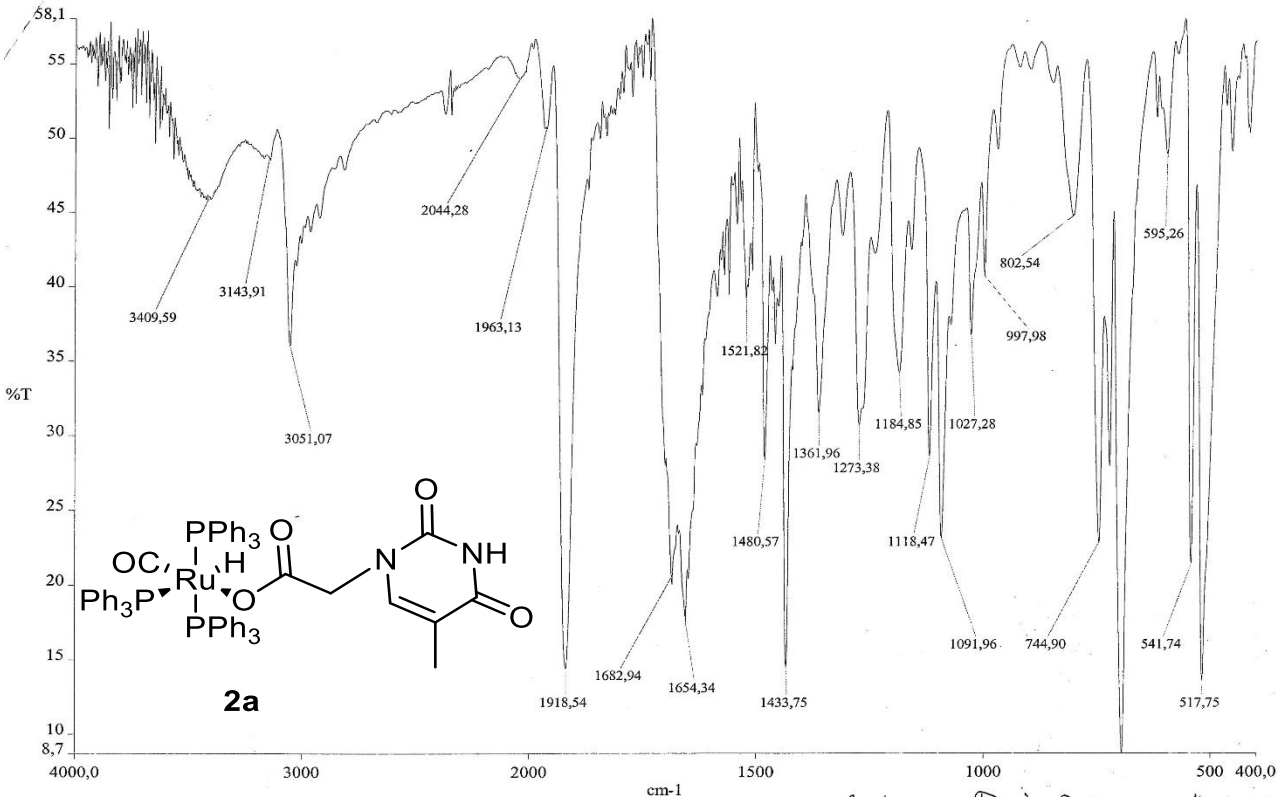


Figure S6: IR spectrum of KETO **2a**, after extraction in DCM/Et2 1:1

MASS SPECTRA

S7

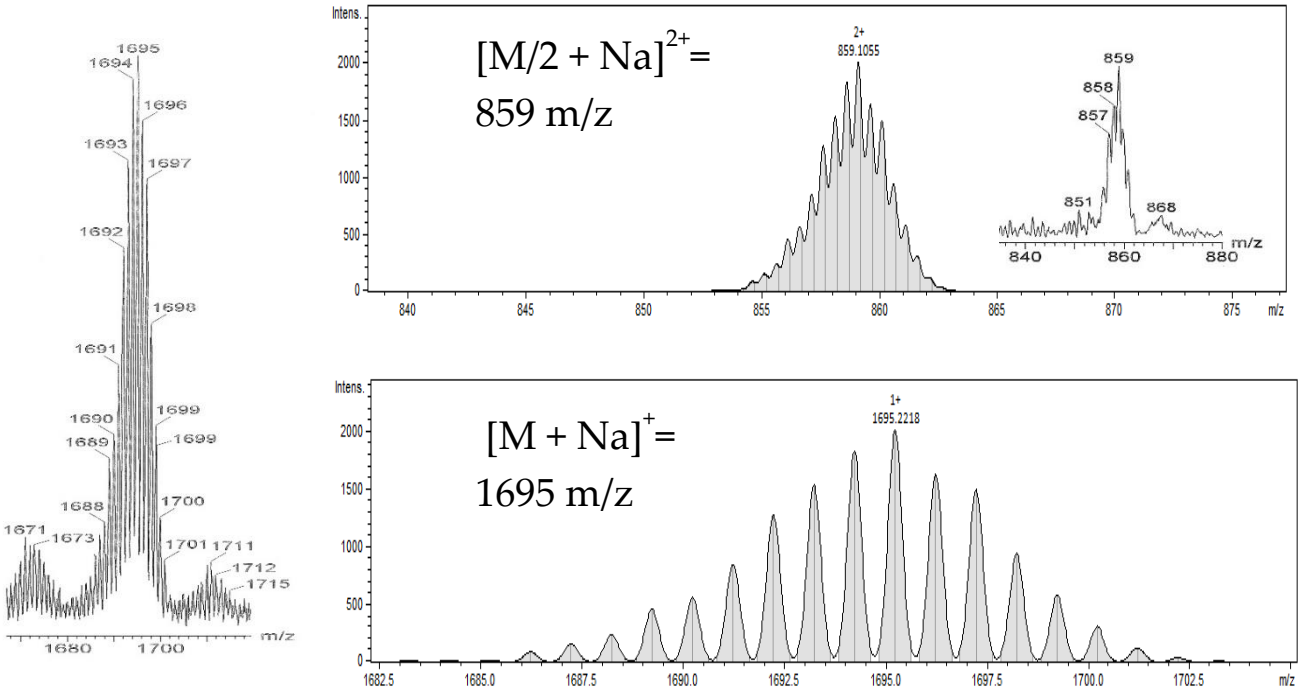
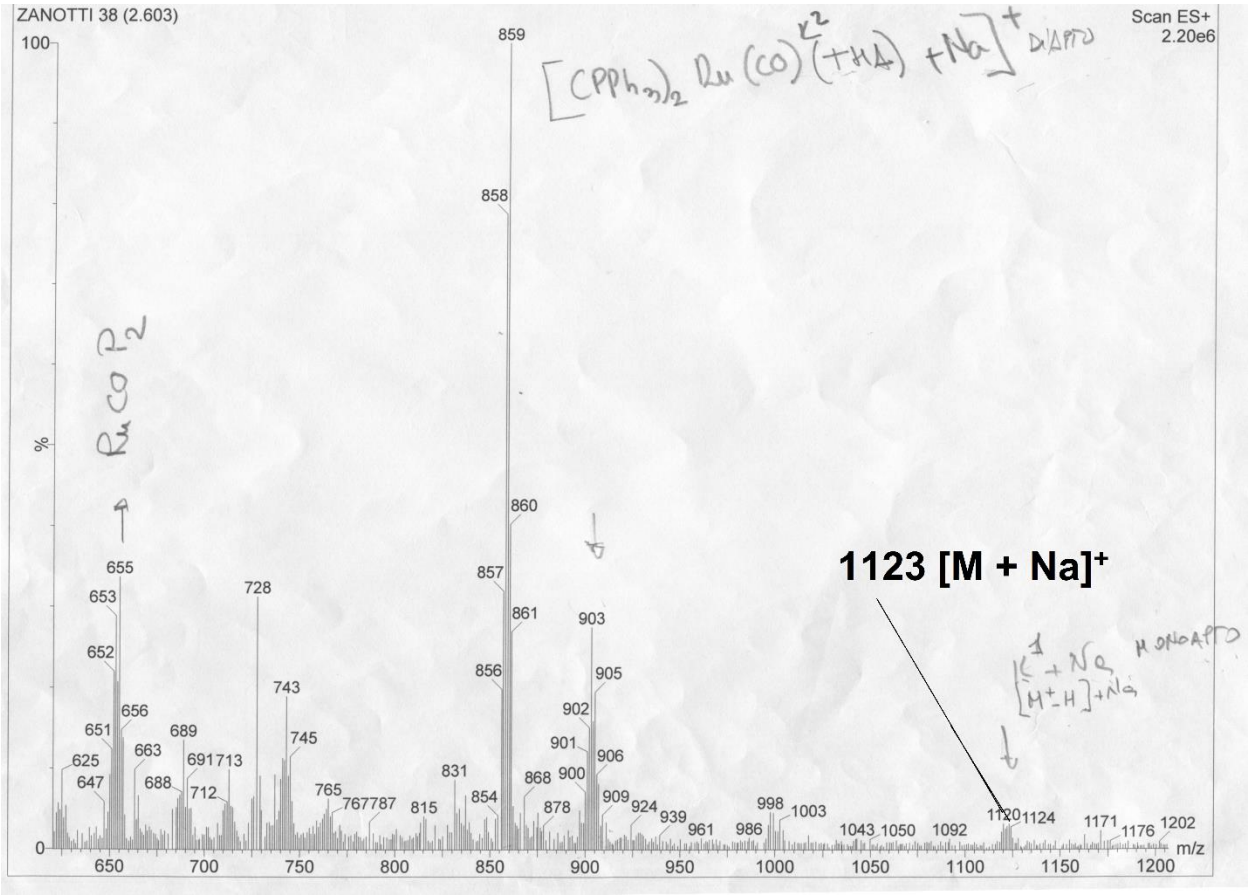


Figure S7: Mass spectrum of **4** compared to simulations.

A



B

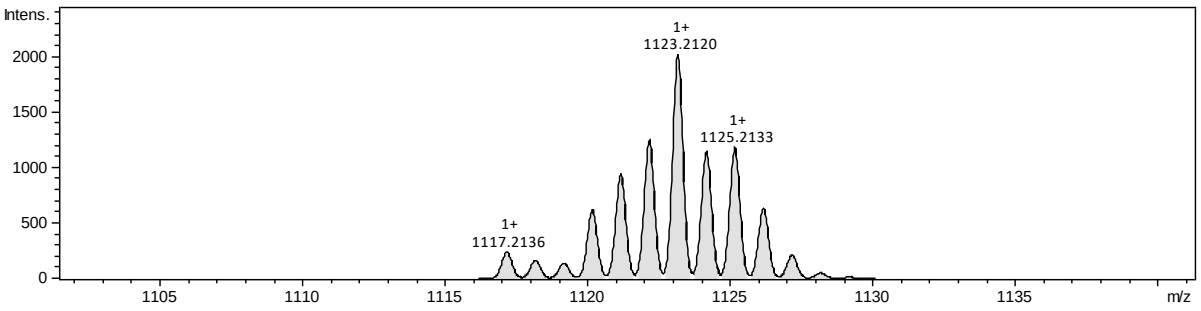
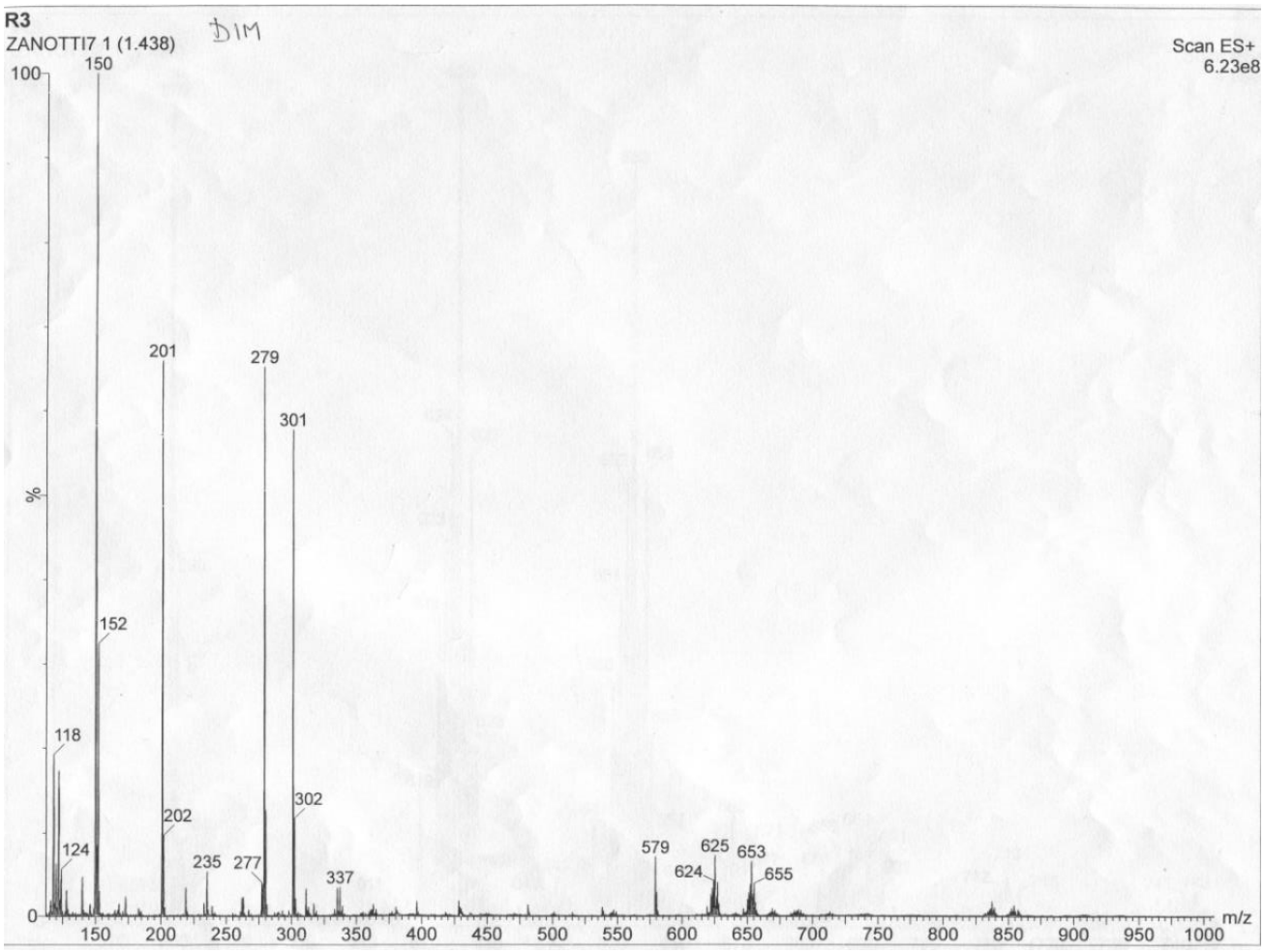


Figure *S8: (**A**) Mass spectrum of k¹(O)-**2a**. (**B**)* simulation of [M + Na]⁺

A


R3
ZANOTTI7 1 (1.438)
DIM
Scan ES+
6.23e8
100
%
0
150
201
279
301
152
118
202
302
124
235
277
337
579
625
624
653
655
m/z
150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

B

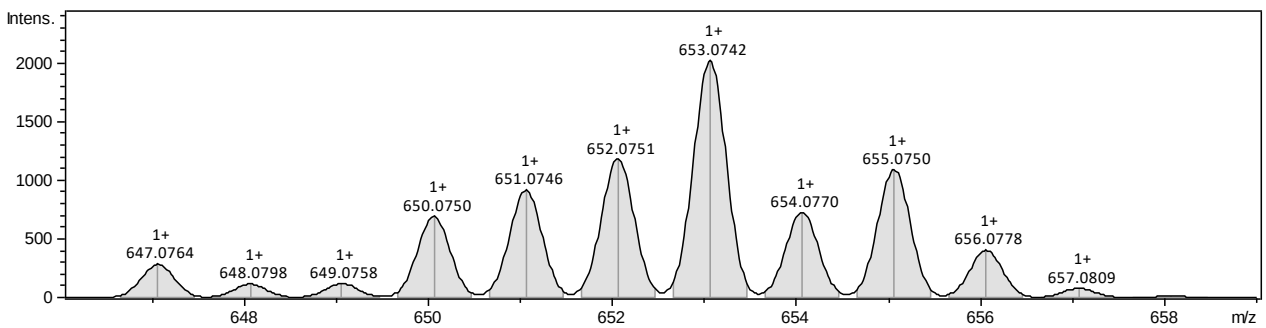
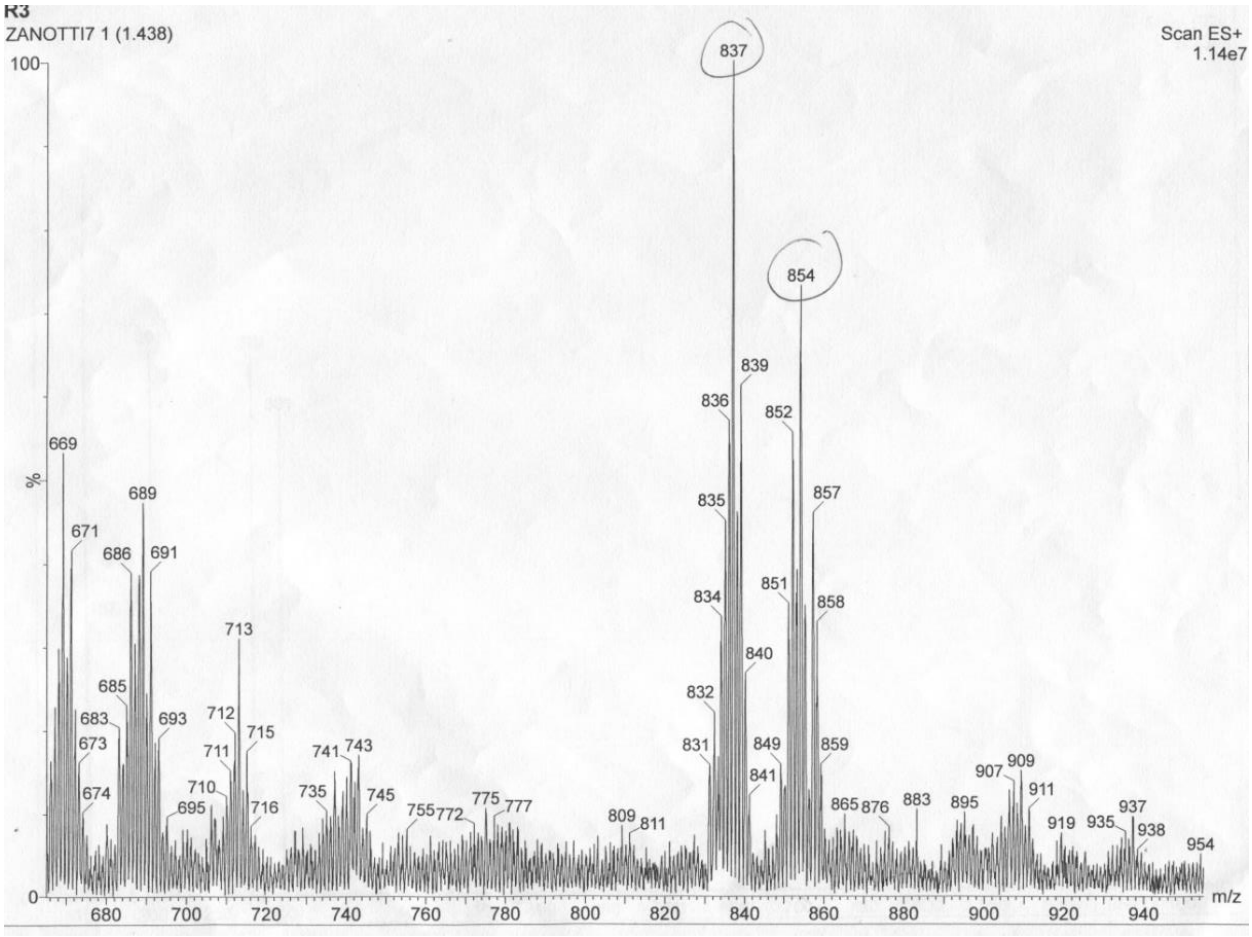

Intens.
2000
1500
1000
500
0
1+ 647.0764
1+ 648.0798
1+ 649.0758
1+ 650.0750
1+ 651.0746
1+ 652.0751
1+ 653.0742
1+ 654.0770
1+ 655.0750
1+ 656.0778
1+ 657.0809
648
650
652
654
656
658
m/z

Figure S9: ***(A)*** *Mass spectrum of k²(O,O)-**3*** (positive mode). ***(B)*** simulation of [M – THAc]+

S10

A



B

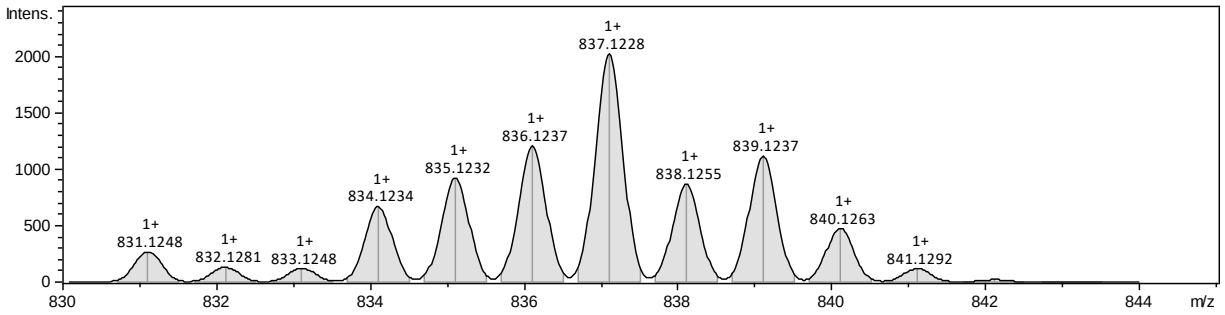


Figure S10: *(**A**) Mass spectrum of k²(O,O)-**3*** (positive mode, m/z: 680 – 940). (**B**) Simulation of $[M - H]^+$

COMPUTATIONAL

S11

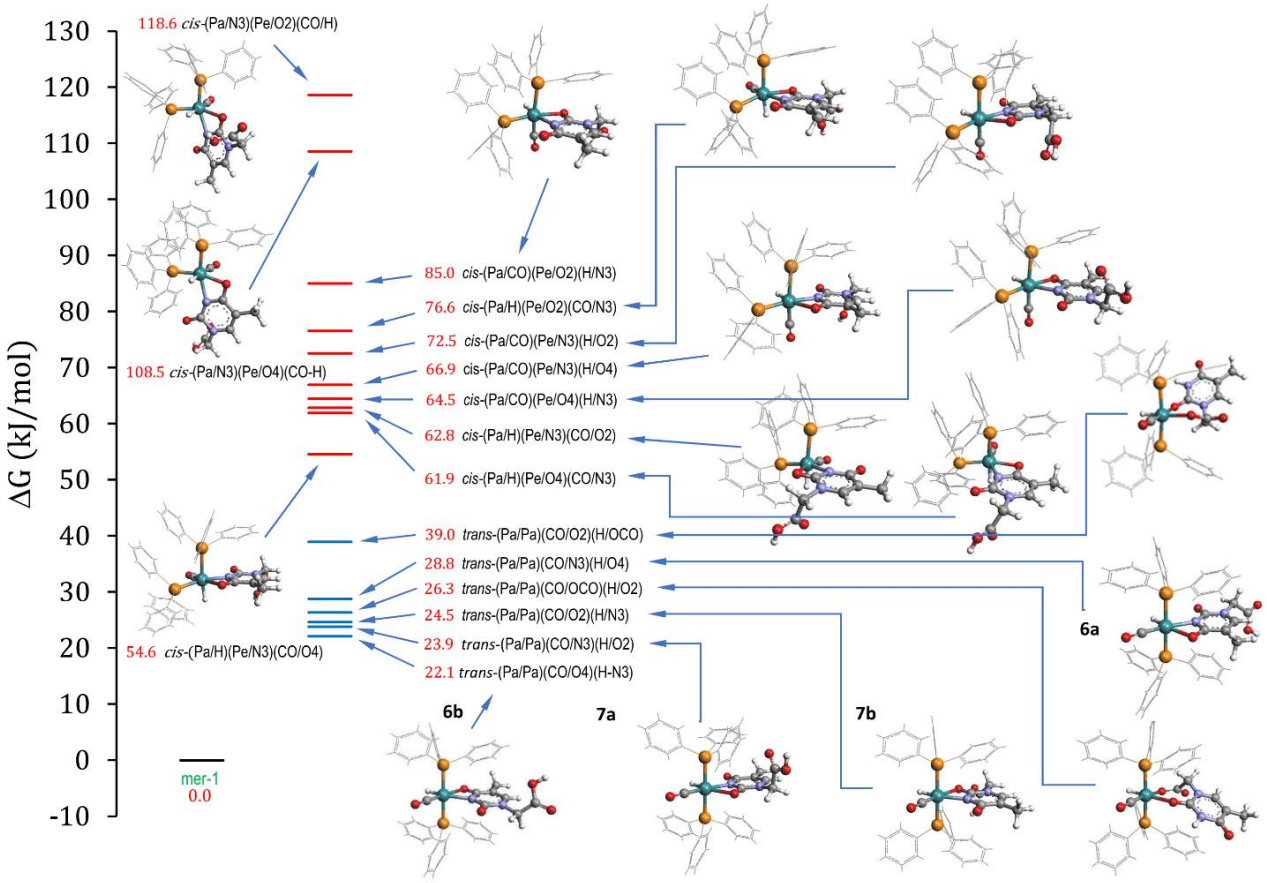


Figure S11: DFT calculations of all four membered- k2(N,O)- heteroleptic and k2(O,O)- heptacycles. All energies are calculated relative to the energy of mer-1 + thymine-acetic acid reactants. All species are named using the following scheme: the three couples of ligands at opposite vertex of the octahedron are enclosed in parentheses, with the additional specification of relative phosphine position. Legend: Pa=axial phosphine, Pe=equatorial phosphine, CO=carbonyl, H=hydride, OCO=thymine carboxylate, O2=thymine oxygen in 2 position, N3=thymine nitrogen in 3 position, O4=thymine oxygen in 4 position

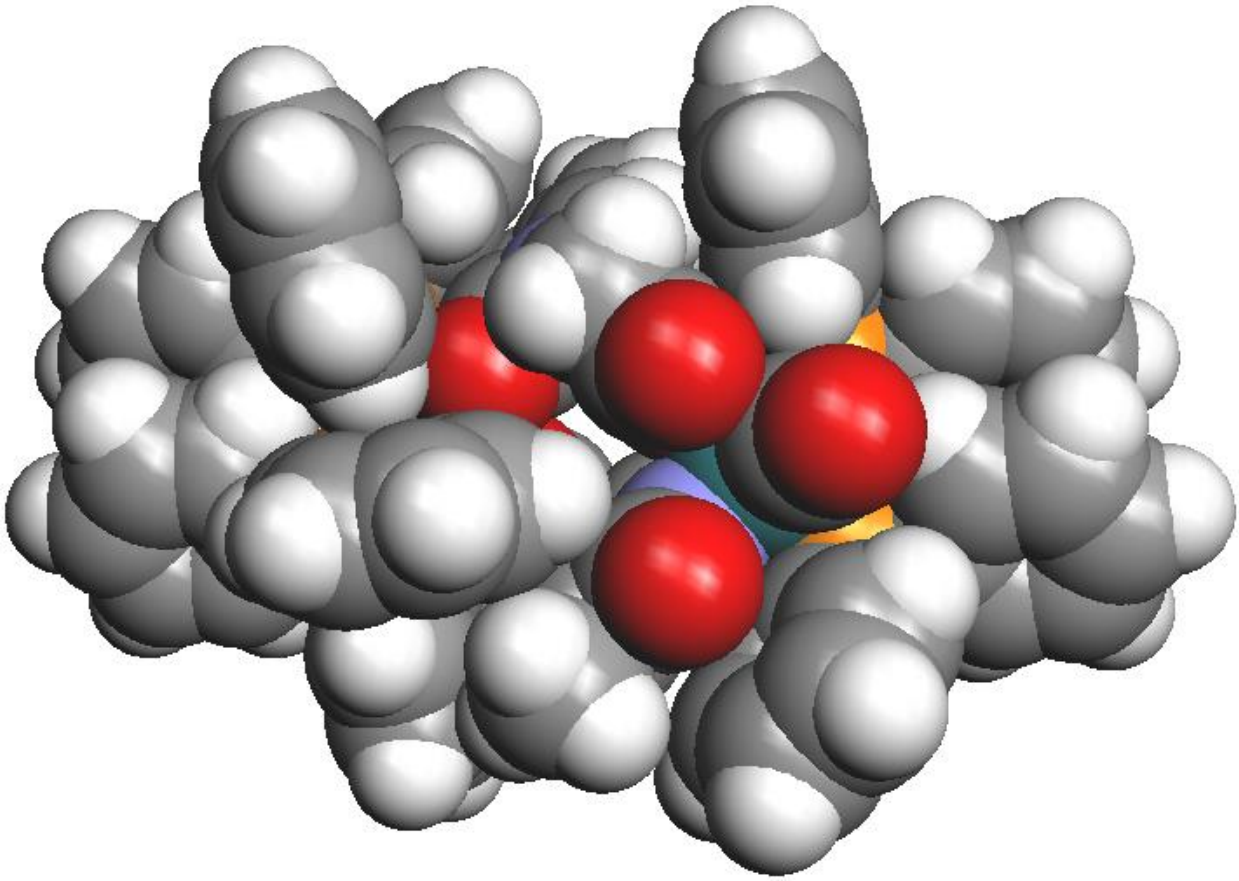


Figure S12: Space filling of **4**

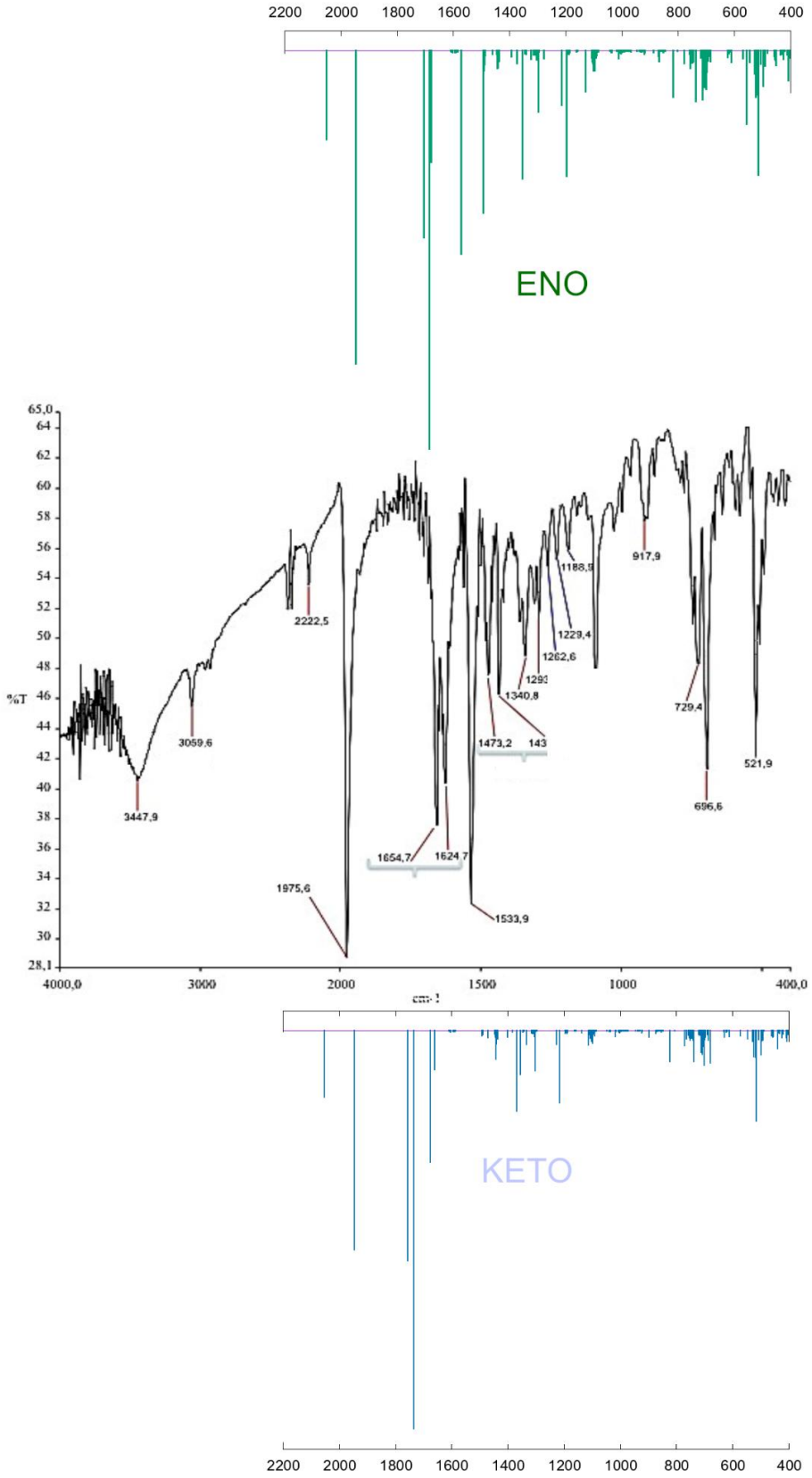


Figure S13: Comparison between the experimental IR spectrum of DFT-simulated IR spectra of keto and Enol form relative to the dimer **4**.

CRYSTAL STRUCTURE

Table S1

Table S1. Crystal data and experimental details for **4**

Compound	**4**
Formula	$C_{88}H_{72}N_4O_{10}P_4Ru_2.2CHCl_3.2H_2O$
Fw	1942.25
T, K	296(2)
λ, Å	0.71073
Crystal symmetry	Monoclinic
Space group	$P2_1/c$
a, Å	10.220(2)
b, Å	29.771(7)
c, Å	14.713(3)
α	90
β	90.005(2)
γ	90
Cell volume, $Å^3$	4476.7(17)
Z	2
D_c, Mg m^{-3}	1.441
μ(Mo–K_α), mm^{-1}	0.649
F(000)	1976
Crystal size/ mm	0.15 x 0.05 x 0.05
θ limits, °	1.368 to 25.000
Reflections collected	36382
Unique obs. Reflections [$F_o > 4\sigma(F_o)$]	7816 [R(int) = 0.1264]
Goodness-of-fit-on F^2	0.983
R_1 (F)[a], wR_2 (F^2) [$I > 2\sigma(I)$][b]	0.0738, 0.1418
Largest diff. peak and hole, e. $Å^{-3}$	0.773 and -0.616

[a)] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

S14

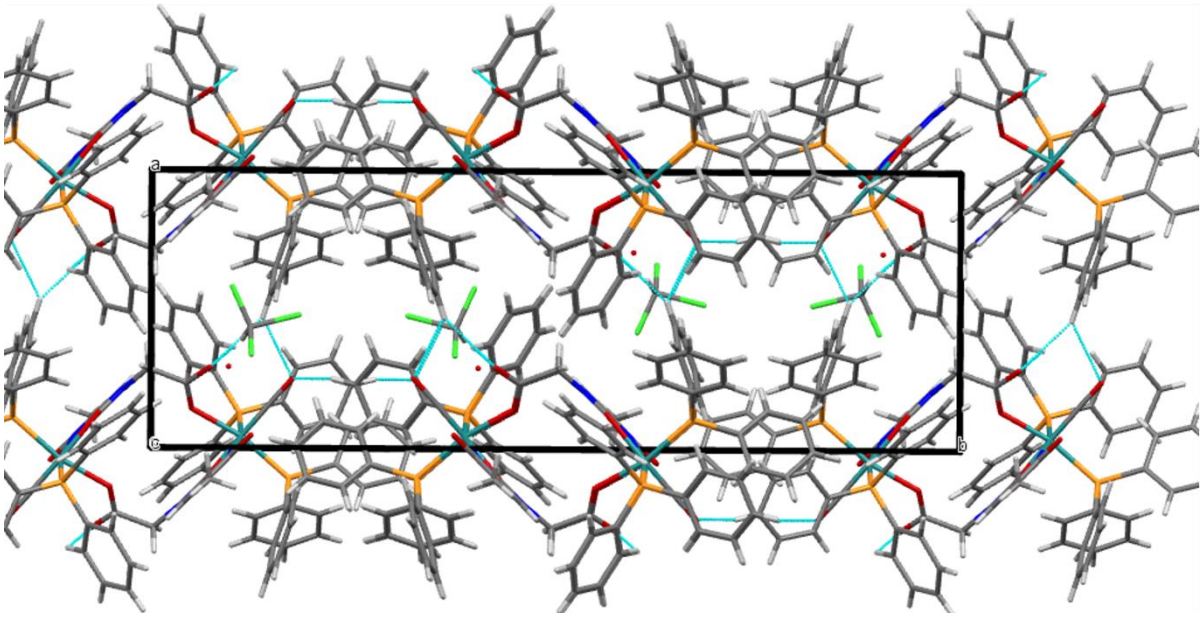


Figure S14: View down the c axis of the crystal packing of **4.** Light blue dotted lines represent H bonding interactions.

PXRD

S15

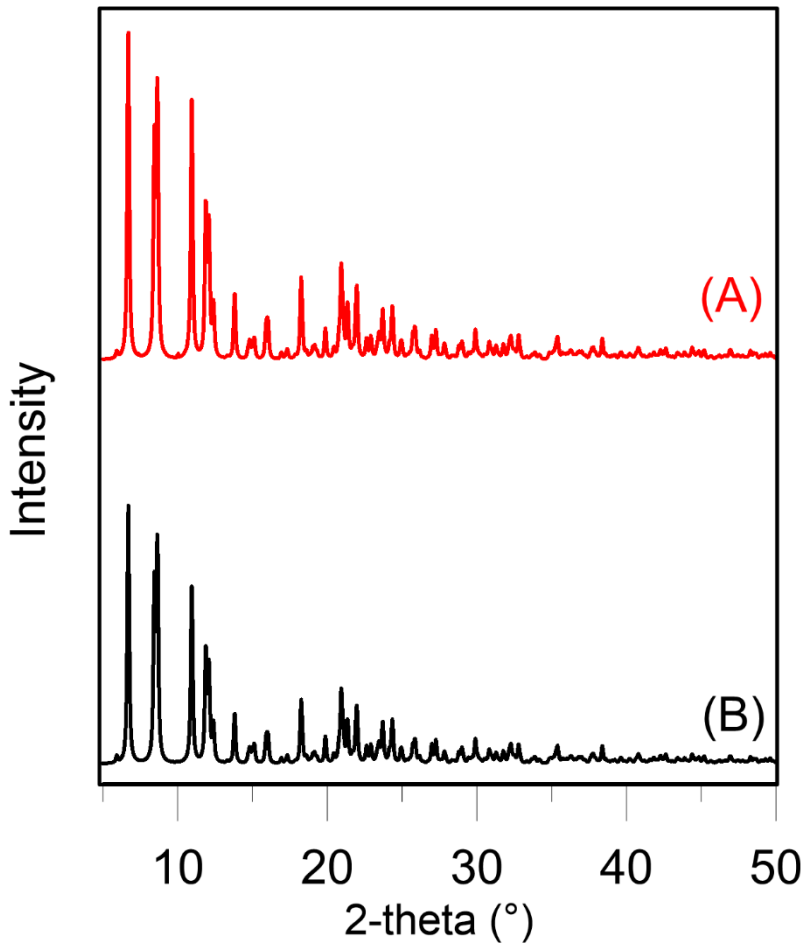


Figure S15: Comparison between the experimental (**A**) and simulated (**B**) PXRD spectra of **4**, which supports the phase purity of compound **4**.