Supporting Information

Synthesis, characterization and bioimaging of fluorescent polyoxometalates

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Table of Contents

^{31}P NMR spectrum of {$P_2W_{17}O_{61}$Fluo}

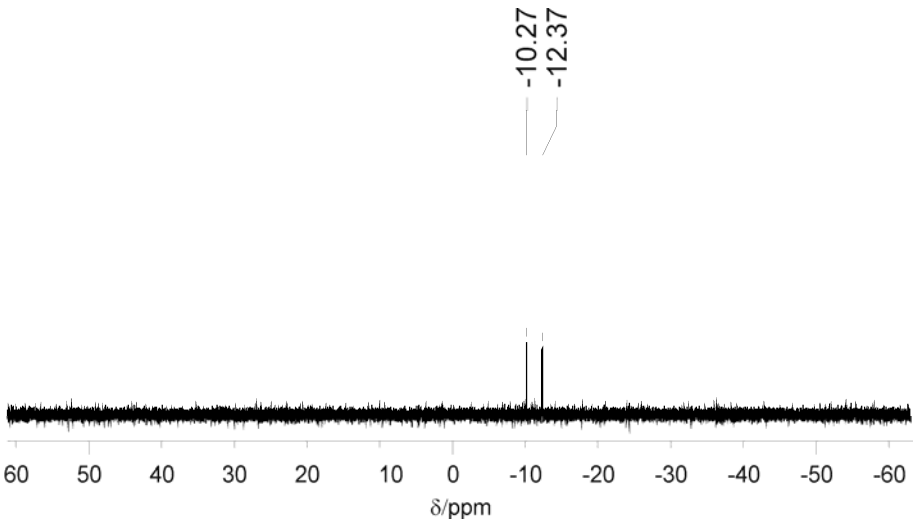

Figure S1. ^{31}P NMR spectrum of {$P_2W_{17}O_{61}$Fluo}.

^{1}H NMR spectrum of {$P_2W_{17}O_{61}$Fluo}

The ^{1}H spectrum of fluorinated POM {$P_2W_{17}O_{61}$Fluo} is similar to the one of its non-fluorinated precursor. The protons of tetrabutyl ammonium ions give rise to signals at 0.99, 1.42, 1.65 and 3.16 ppm. The two multiplets at 1.28 and 2.75 ppm can be assigned to the organic linker. In comparison to the spectra of the non-fluorinated Wells-Dawson POM only the signal at 1.28 is shifted slightly. This, however, can be attributed to the formation of the amide binding adjacent to the methyl group. The signals of the nine aromatic fluorescein protons can be found between 6.5 and 7.2 ppm which is further evidence for the successful linkage of the fluorescein to the POM. The broad signal at 7.4 ppm corresponds to the H-atom of the amide bond.

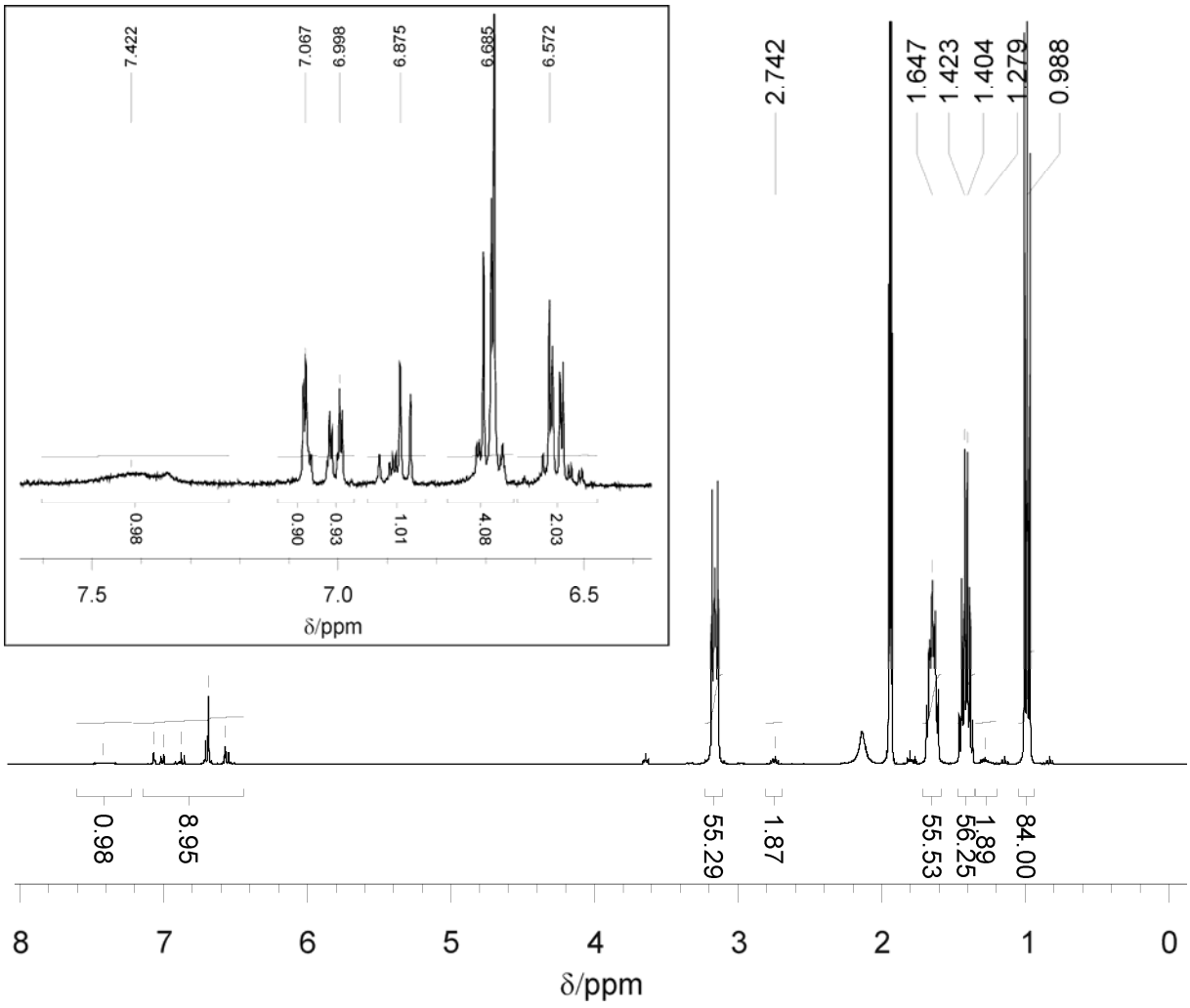

Figure S2. ^{1}H NMR spectrum of {$P_2W_{17}O_{61}$Fluo}.

^{13}C NMR spectrum of {$P_2W_{17}O_{61}$Fluo}

In the ^{13}C NMR spectrum the signals of the C-atoms of the organic linker can be found 2.0 (Sn*C*H_2) and 32.1 ppm (*C*H_2CON). A signal arising from the quaternary C of fluorescein can be seen at 68.3 ppm. The visible signals between 103 and 131 ppm can be assigned to the aromatic carbon atoms of the fluorescein residue. The aromatic C atoms connected to the OH and NH groups in the fluorescein residue give rise to the signals at 150.9 and 153.4 ppm. At 159.7 ppm and 170.7 ppm the signal of the C atom of the carboxylic group and the signal of the C atom in the amide group can be observed. The remaining signals derive from the solvent (1.3 and 118.3 ppm) and from the tetrabutyl ammonium groups (14.0 (N($CH_2CH_2CH_2$*C*H_3)$_4$), 20.4 (N(CH_2CH_2*C*H_2CH_3)$_4$), 24.5 (N(CH_2*C*$H_2CH_2CH_3$)$_4$) and 59.4 (N(*C*$H_2CH_2CH_2CH_3$)$_4$ ppm).

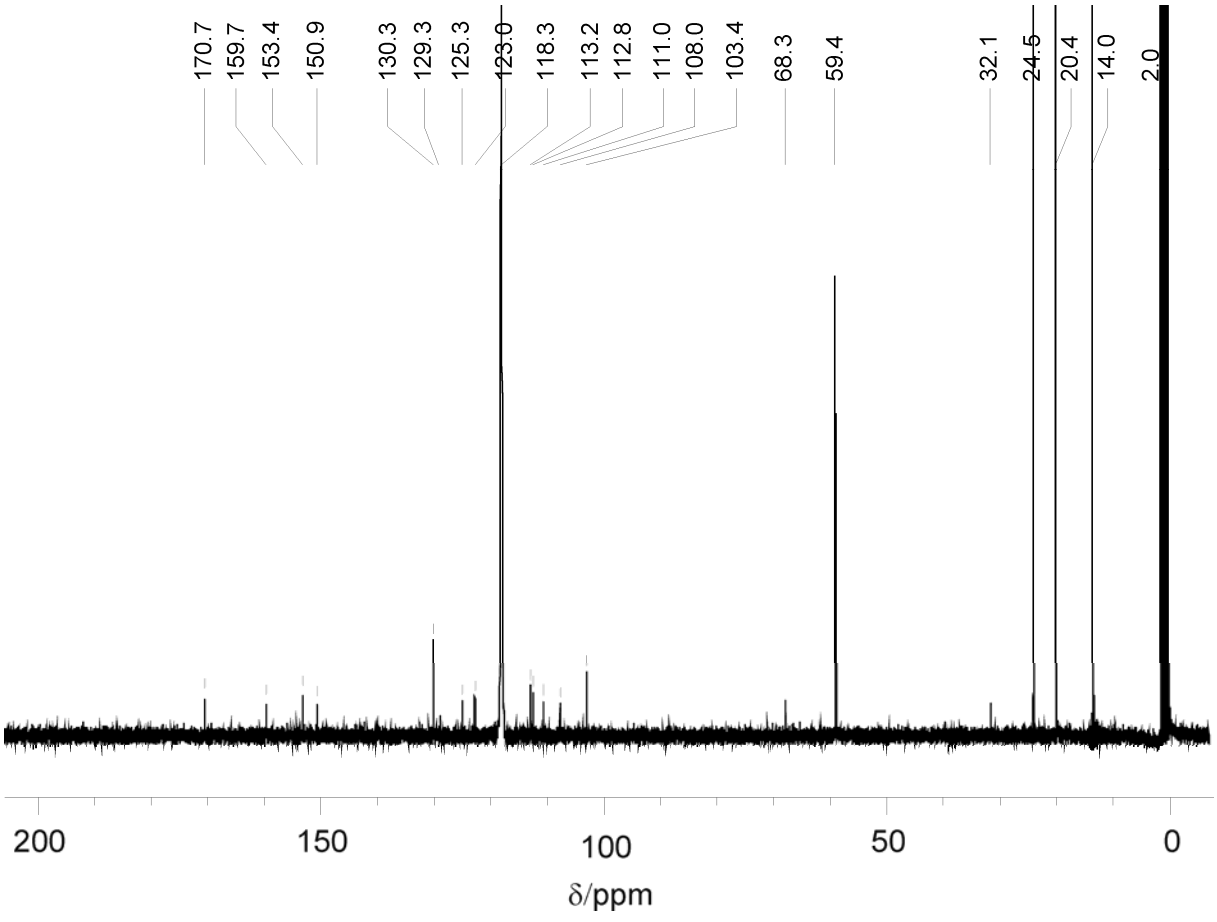

Figure S3. ^{1}H NMR spectrum of {$P_2W_{17}O_{61}$Fluo}.

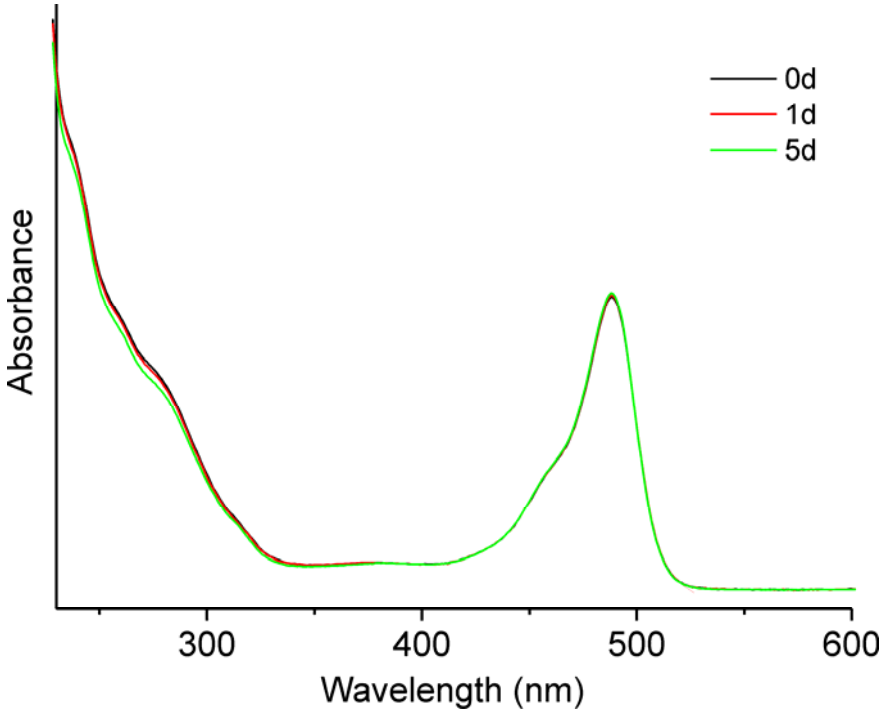

Figure S4. UV/vis spectra of $\{P_2W_{17}O_{61}Fluo\}$ in PBS after 0, 1 and 5 days.

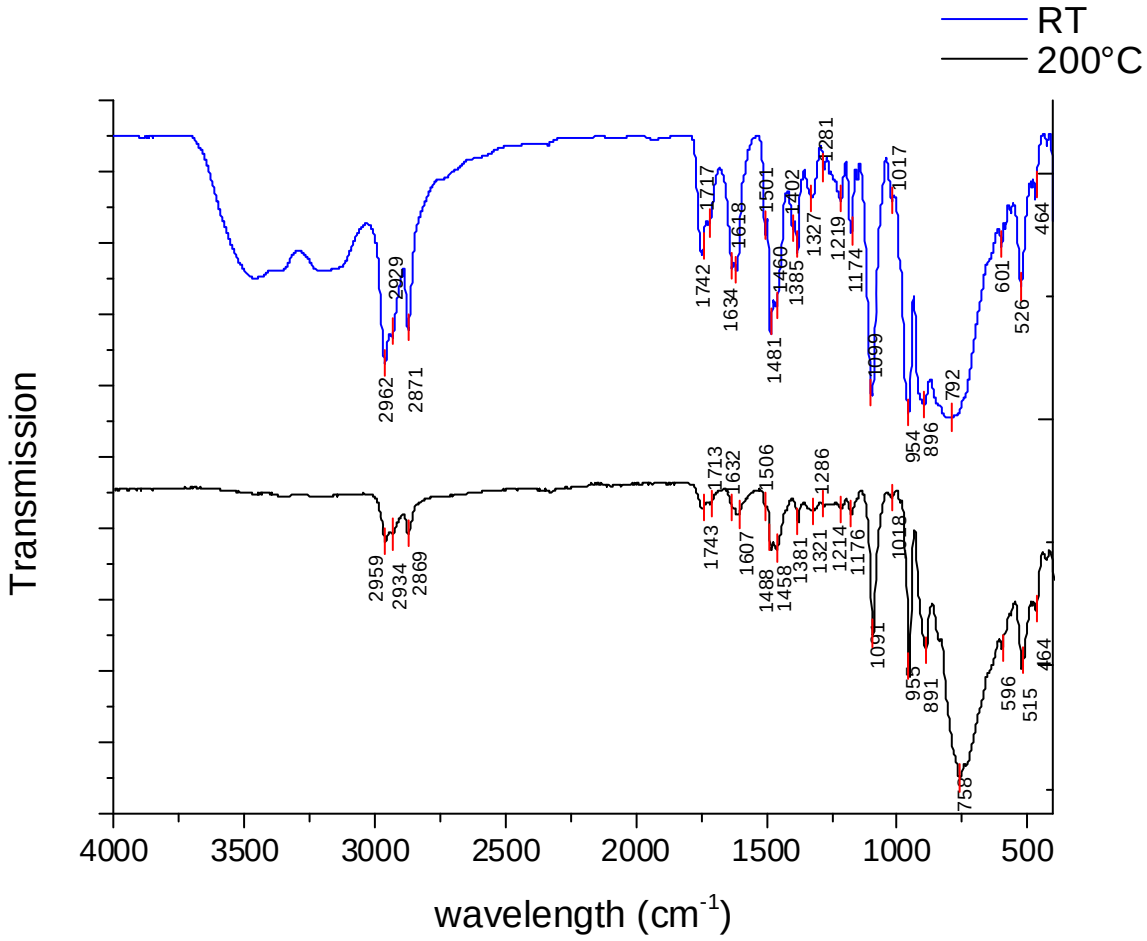

Figure S5. FT-IR spectra of $\{P_2W_{17}O_{61}Fluo\}$ before (top) and after (bottom) thermal treatment at 200 °C.

Section-view and the 3D maximum intensity projection of HeLa cells

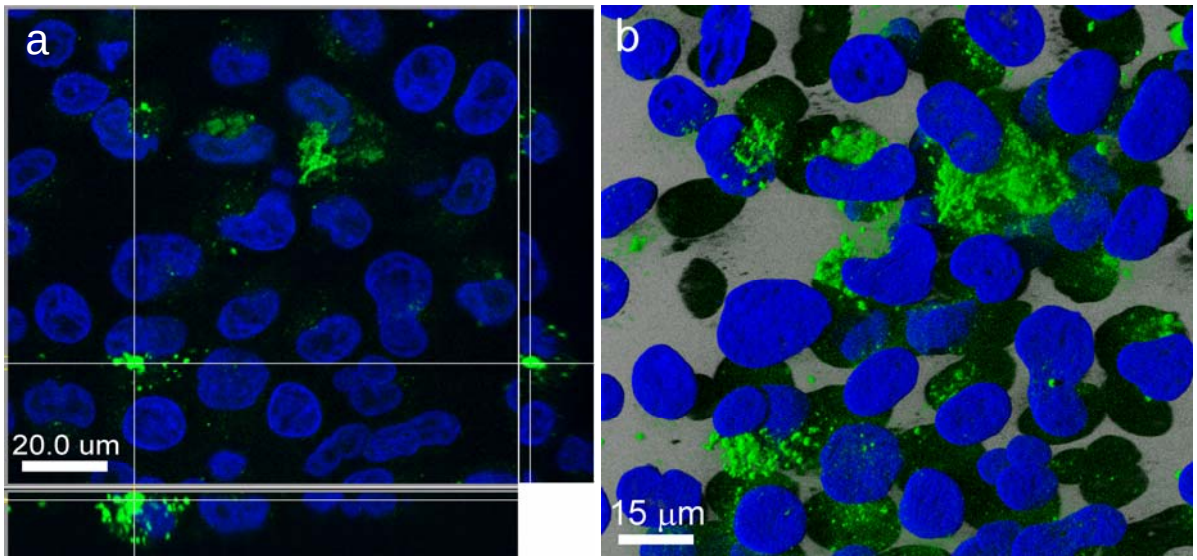

Figure S6. Section-view (a) and the 3D maximum intensity projection (b) of HeLa cells incubated with 50 µg/mL $\{P_2W_{17}O_{61}Fluo\}$ (green) for 24 h (nuclei = blue).

Confocal picture of control cells

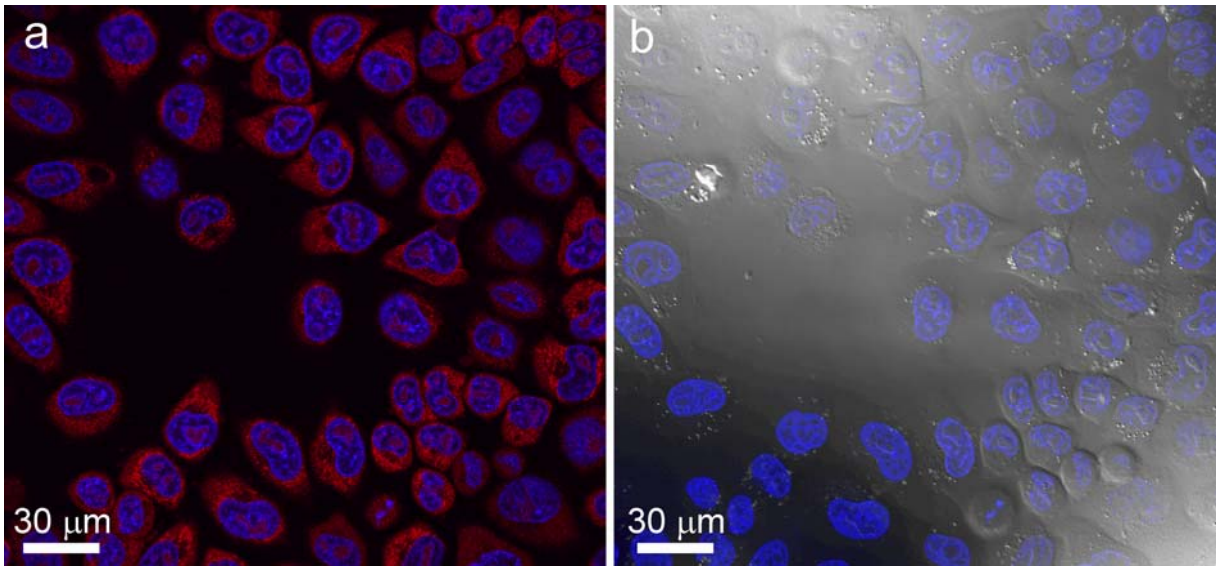

Figure S7. (a) Confocal picture of HeLa cells without POM incubation which served as controls; (b) confocal picture merged with the DIC image (mitochondria = red, nuclei = blue).

Confocal pictures of HeLa cells after 1 h and 5 h of POM incubation

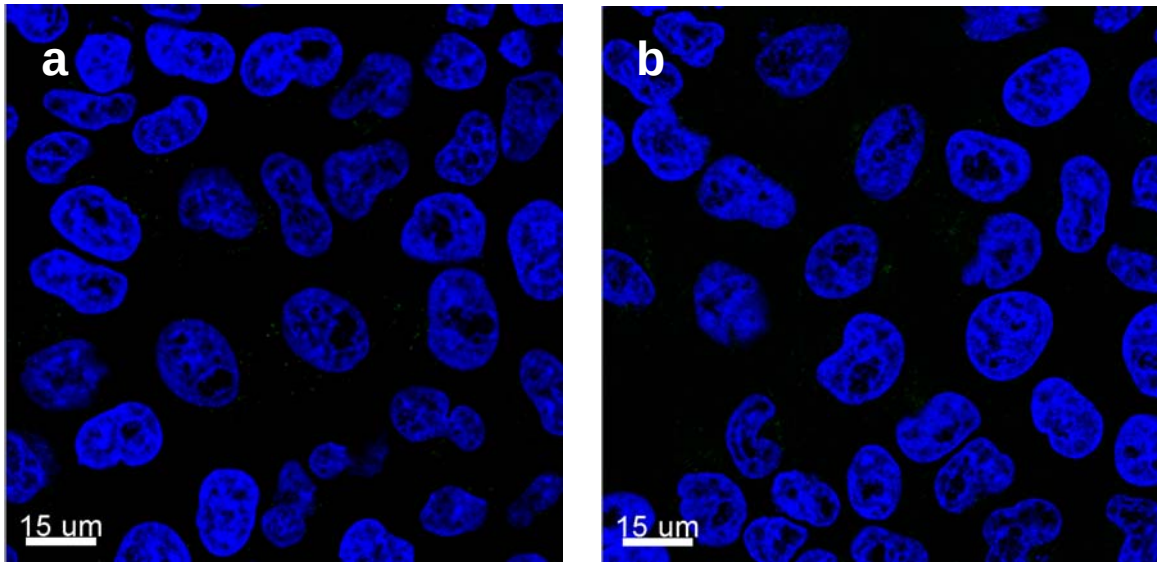

Figure S8. Confocal pictures of HeLa cells after (a) 1 h and (b) 5 h of POM (green) incubation (nuclei = blue).

Table S1. Characteristic FT-IR bands of $TBA_6K[\alpha_2\text{-}P_2W_{17}O_{61}\{Sn(CH_2)_2COOH\}]$ (cm^{-1}).

Peak	Intensity	Assignment
2963	s	ν(-OH)
2874	s	ν(-CH_2)
1711	w	ν(C=O)
1485	m	alkane
1091	s	ν(P-O)
1018	w	ν(P-O)
954	s	ν(W-O)
904	s	ν(W-O)
786	s	ν(W-O)