Organometallic derivatives of Rh- and Ir-substituted polyoxotungstates with Keggin structure: reactivity screening by electrospray ionization mass-spectrometry

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Experimental details

In all cases, tetrabutylammonium (TBA) salts were obtained as final products by adding an excess of TBABr to the reaction solutions with consequent collecting, washing precipitates with H_2O and drying *in vacuo*. Stock solutions of $[PW_{11}O_{39}RhCl]^{5-}$ and $[PW_{11}O_{39}Ir(H_2O)]^{4-}$ were obtained according to published procedures (see ref. 7 and 9 inthe article).

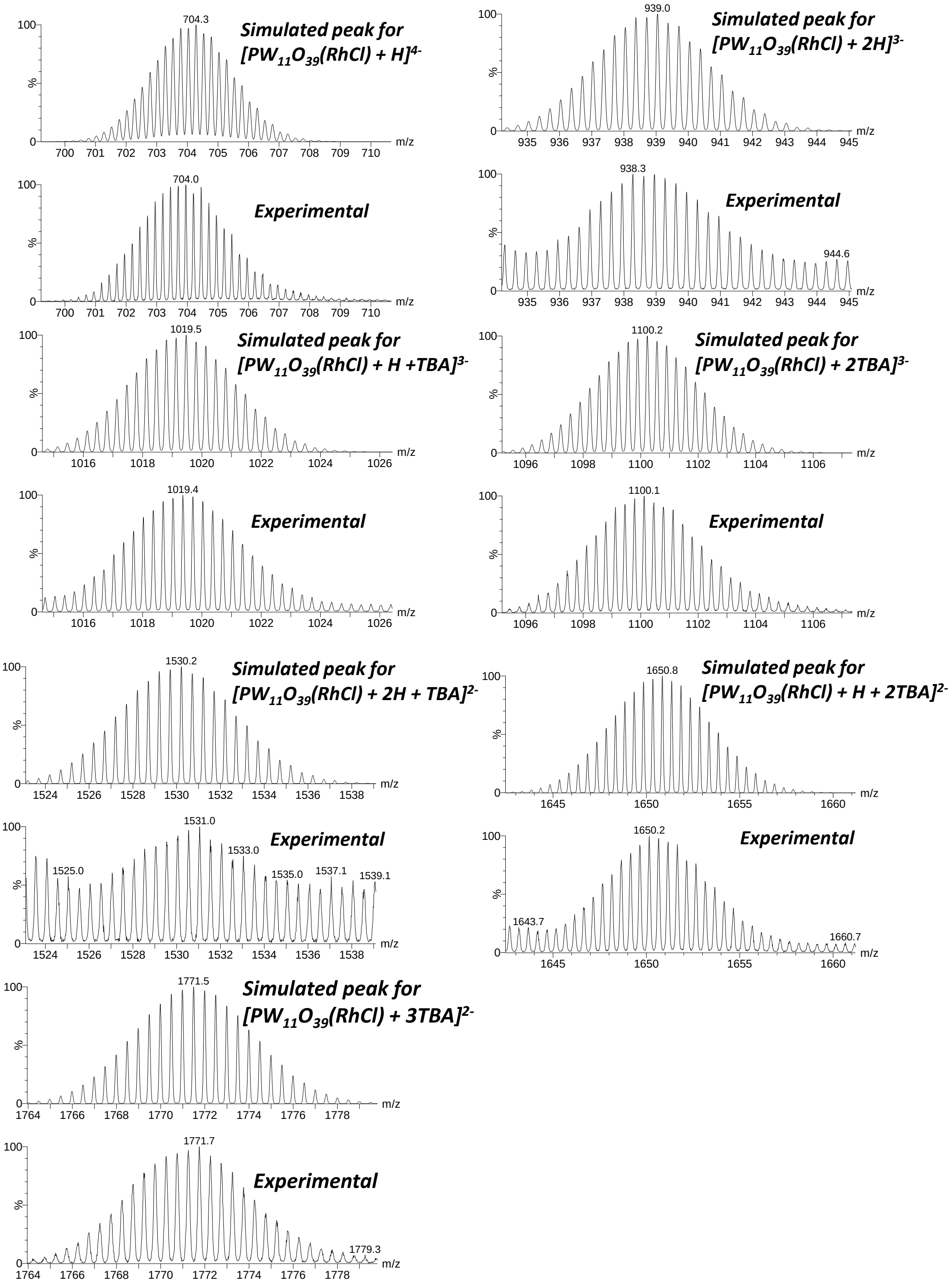
Reactions of $[PW_{11}O_{39}RhCl]^{5-}$ with phenylacetate and malonate. In both cases, either solution of pre-synthesized $[PW_{11}O_{39}RhCl]^{5-}$ (ref. 7 of the article) or stoichiometric amounts of $K_7[PW_{11}O_{39}]$ and $RhCl_3{\cdot}3H_2O$ were used. The concentration of POM was 17 mM. After adding an excess (up to 15-fold molar ratio) of the organic acid, pH was adjusted by solution of KOH; then solutions were placed in Teflon-lined Parr digestion bomb and heated (17h at 120°C for phenylacetic acid and 12h at 100°C for malonic acid). Then the Bu_4N salts **1** and **2** were precipitated. Analysis: for $(Bu_4N)_5[PW_{11}O_{39}Rh(CH(COOH)_2)]$ (**1**) calc. C, 24.3; H, 4.5; N, 1.7 %. Found: C, 24.1; H, 4.4; N, 1.7 %. $(Bu_4N)_5[PW_{11}O_{39}Rh(CH(Ph)COOH)]$ (**2**) calc. C, 25.6; H, 4.6; N, 1.7%. Found: C, 25.4; H, 4.8; N, 1.6 %.

Reactions of $[PW_{11}O_{39}RhCl]^{5-}$ and $[PW_{11}O_{39}Ir(H_2O)]^{4-}$ with Me_3SnCl. To the solutions containing corresponding polyoxoanions, a stoichiometric amount of Me_3SnCl were added. Solutions were placed in Teflon-lined Parr digestion bomb and heated (10h at 100°C for Rh complex and 14h at 100°C for Ir complex). Then the Bu_4N salts were precipitated. ESI-MS show the presence of **6** and **7** together with unreacted POM.

Reactions with boronic acids. A stoichiometric amounts of phenyl- and ferrocenylboronic acid were added to solutions of pre-synthesized $[PW_{11}O_{39}RhCl]^{5-}$ with stirring. In the case of phenylboronic acid, the solution was kept at 40-50 °C for 2-5 h. In the case of ferrocenylboronic acid, the color of solution started to change for brownish green almost immediately; reaction was considered to complete after 2h. Then the Bu_4N salts were precipitated. The ESI-MS and optimization of the synthesis with $PhB(OH)_2$ are discussed in the text.

Electrospray ionization mass spectrometry

A Q-TOF premier mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, UK) was used. The temperature of the source block was set to 100 ºC and the desolvation temperature to 120 ºC. A capillary voltage of 3.3 kV was used in the negative scanmode and the cone voltage was set to 5 V to control the extent of fragmentation of the identifiedspecies. TOF mass spectra were acquired in the W-mode operating at a resolution of ca. 15000(FWHM). Mass calibration wasperformed using a solution of sodium iodide in isopropanol:water (50:50) from m/z 50 to 3000.Solid samples as tetrabutylammonium salts (see experimental details) were dissolved in acetonitrile to an estimated concentration of 5 x 10^{-5} M (based on the initial amount of $[PW_{11}O_{39}RhCl]^{5-}$or $[PW_{11}O_{39}Ir(H_2O)]^{4-}$) and were infused via syringe pump directly connected to the ESI source at a flow rateof 10 μL/min. The observed isotopic pattern of each compound perfectly matched the theoreticalisotope pattern calculated from their elemental composition using the MassLynx 4.1 program.



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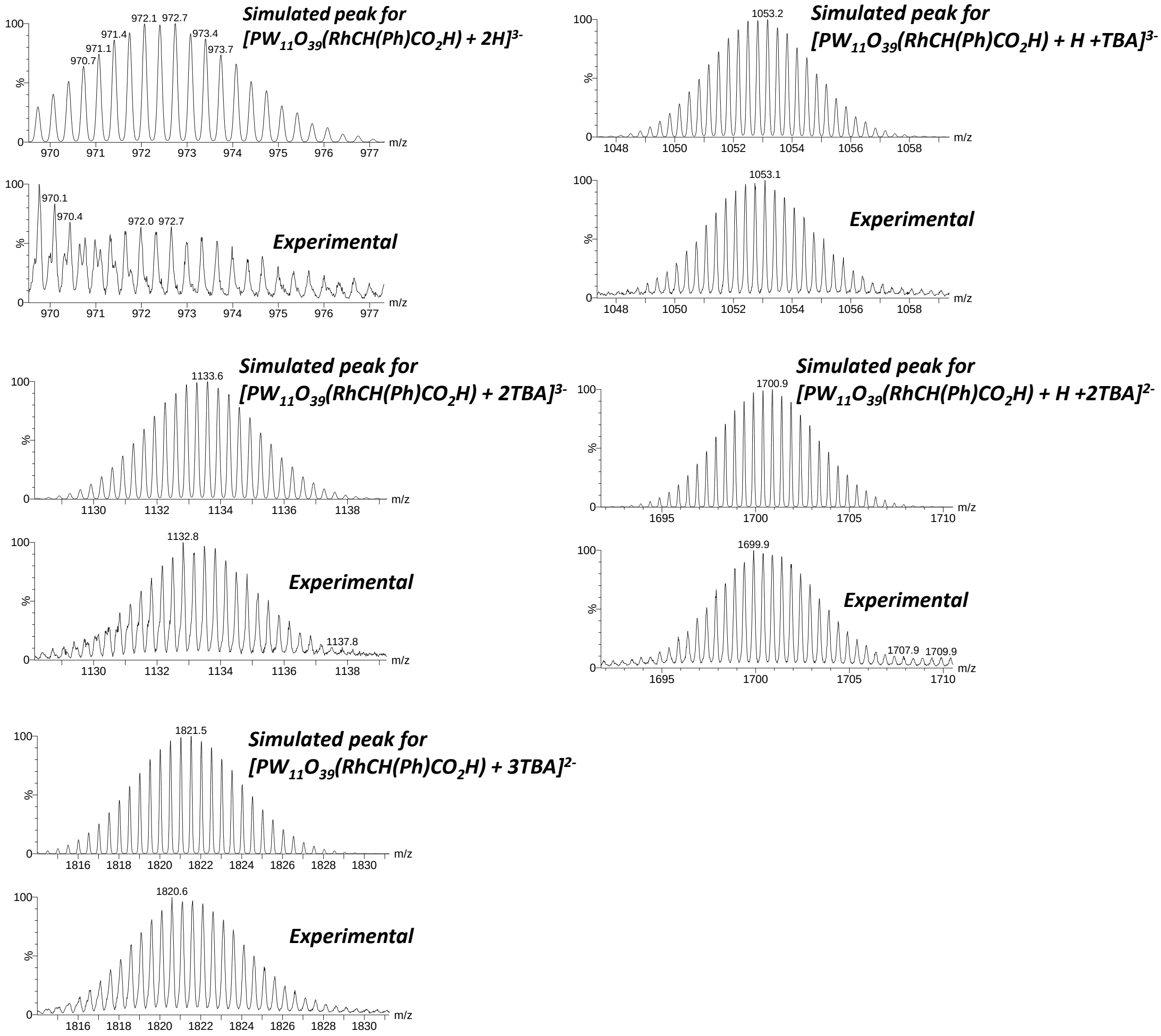

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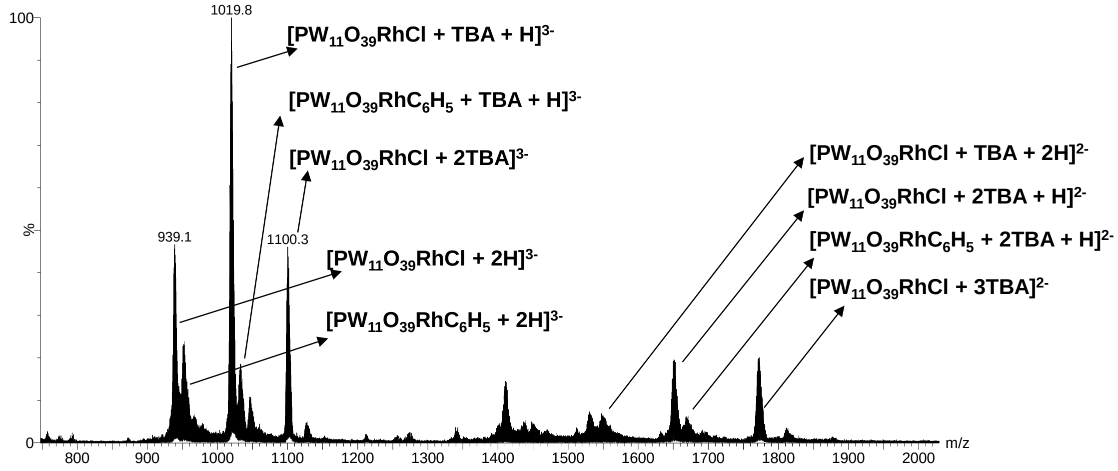

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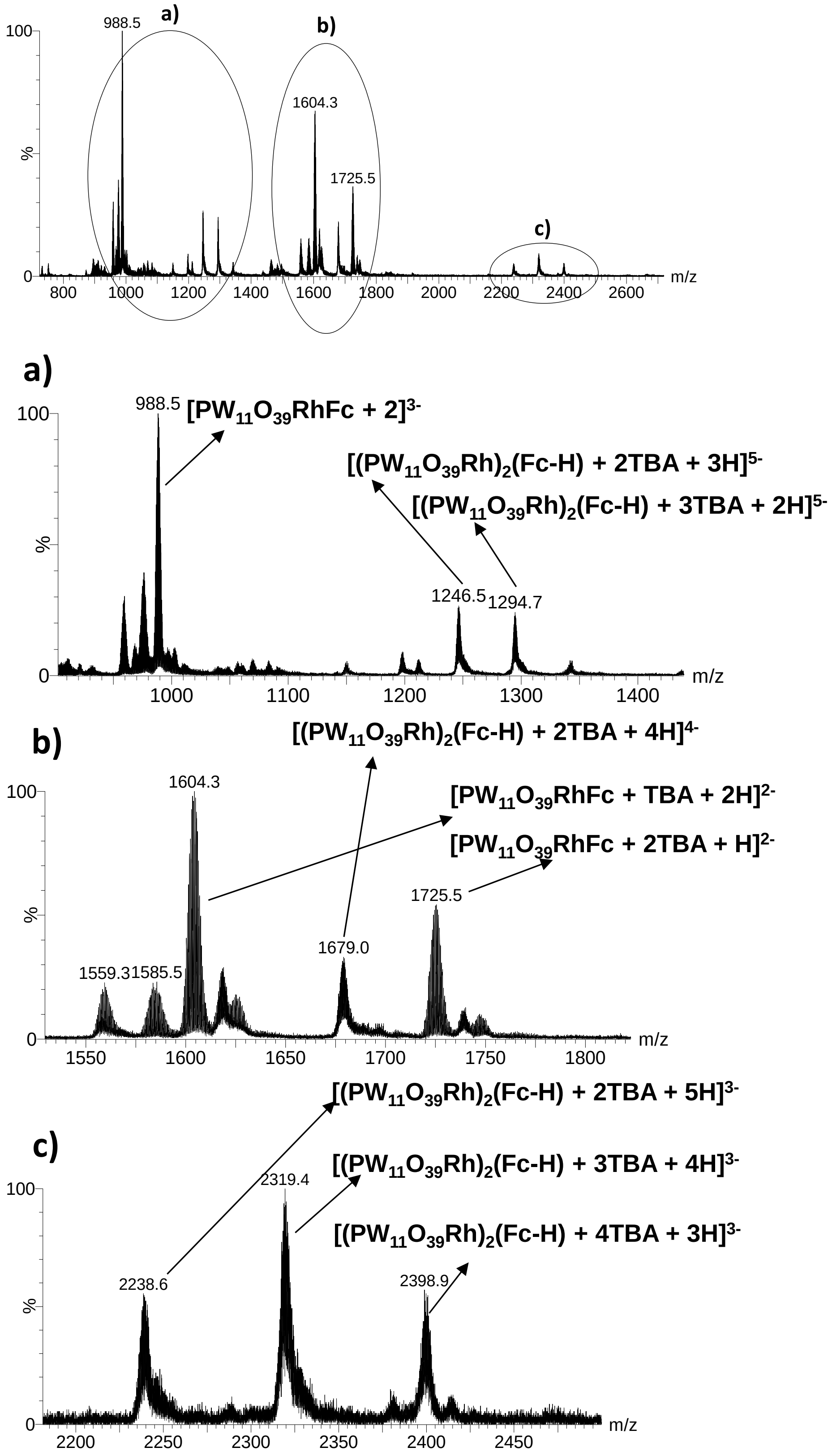

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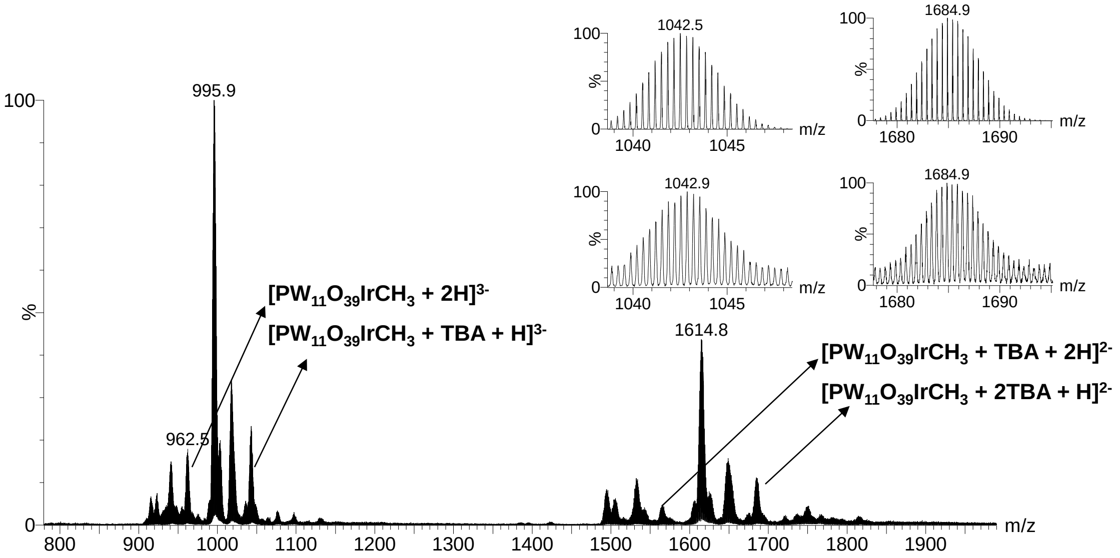

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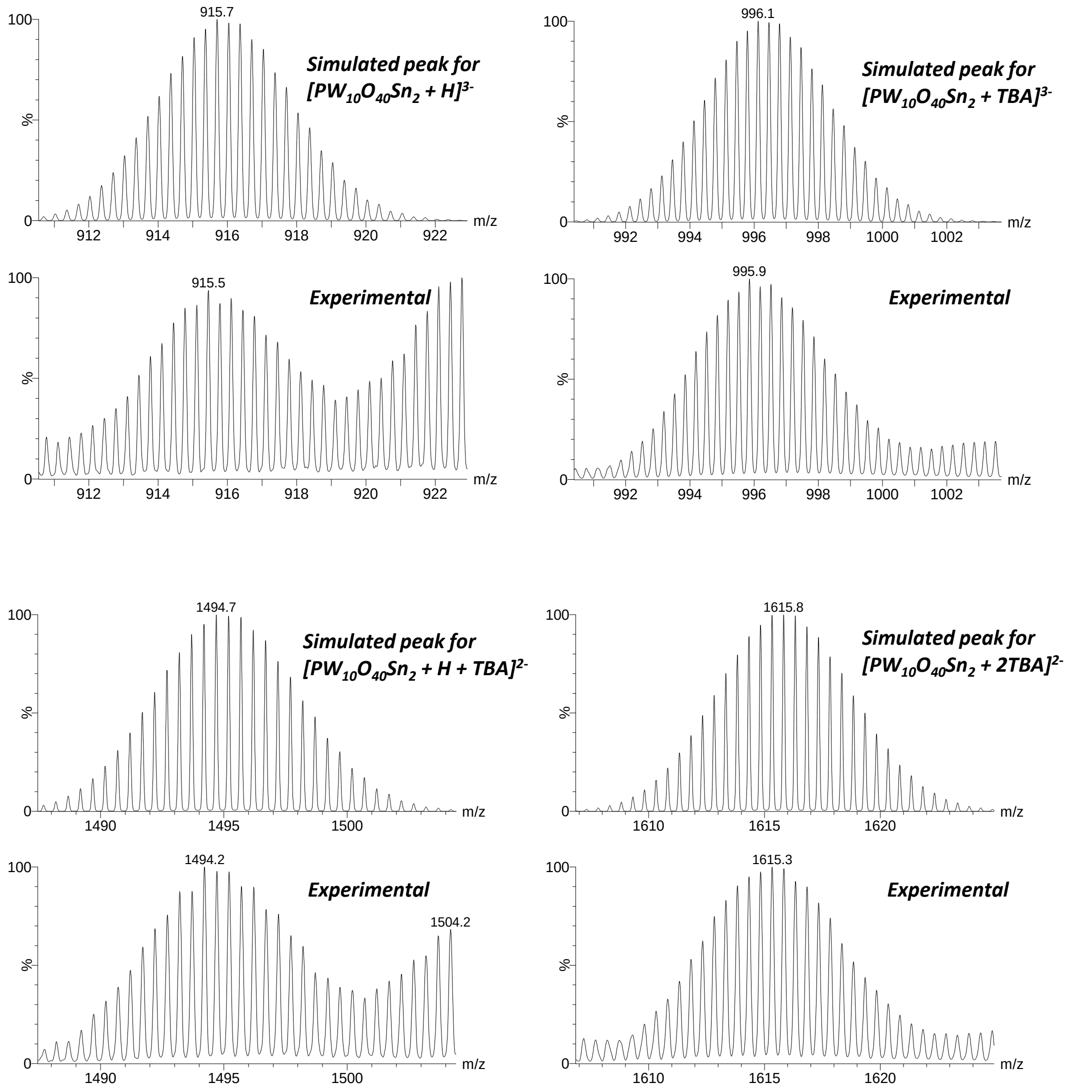

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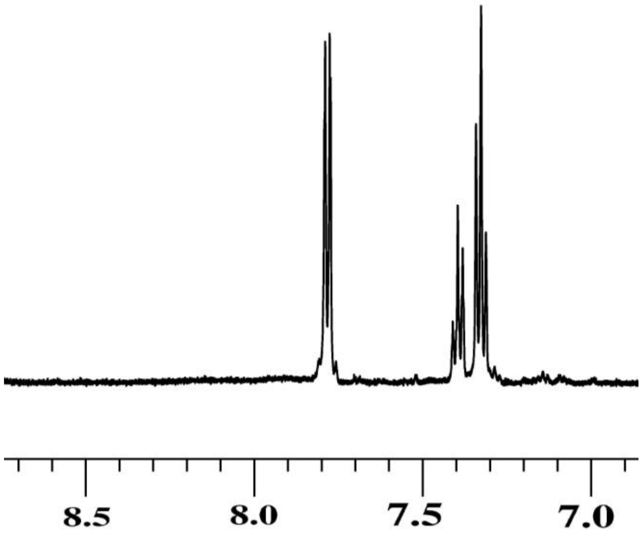

Figure S7. ^1H NMR spectra of the reaction mixture between $[PW_{11}O_{39}RhCl]^{5-}$ and $PhB(OH)_2$ (area corresponding to aryl group)

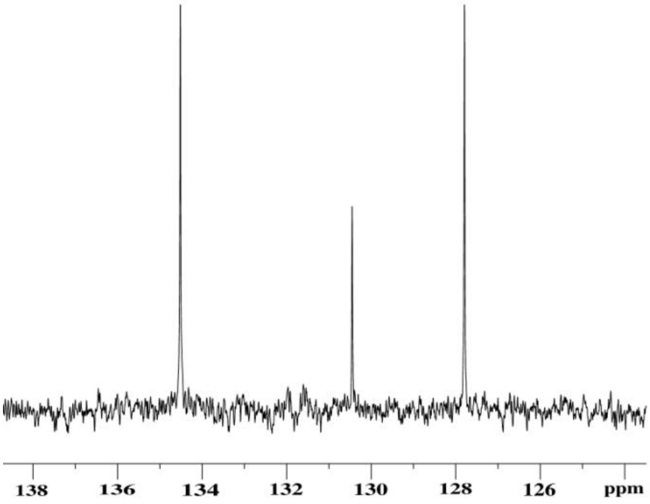

Figure S8. ^{13}C NMR spectra of the reaction mixture between $[PW_{11}O_{39}RhCl]^{5-}$ and $PhB(OH)_2$ (area corresponding to aryl group)