Electronic Supplementary Material (ESI) for Dalton Transactions

Reactions of an Organoruthenium Anticancer Complex with 2-Mercaptobenzanilide - a Model for the Active-site Cysteine of Protein Tyrosine Phosphatase 1B

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Supporting Information

Figure S1-S11

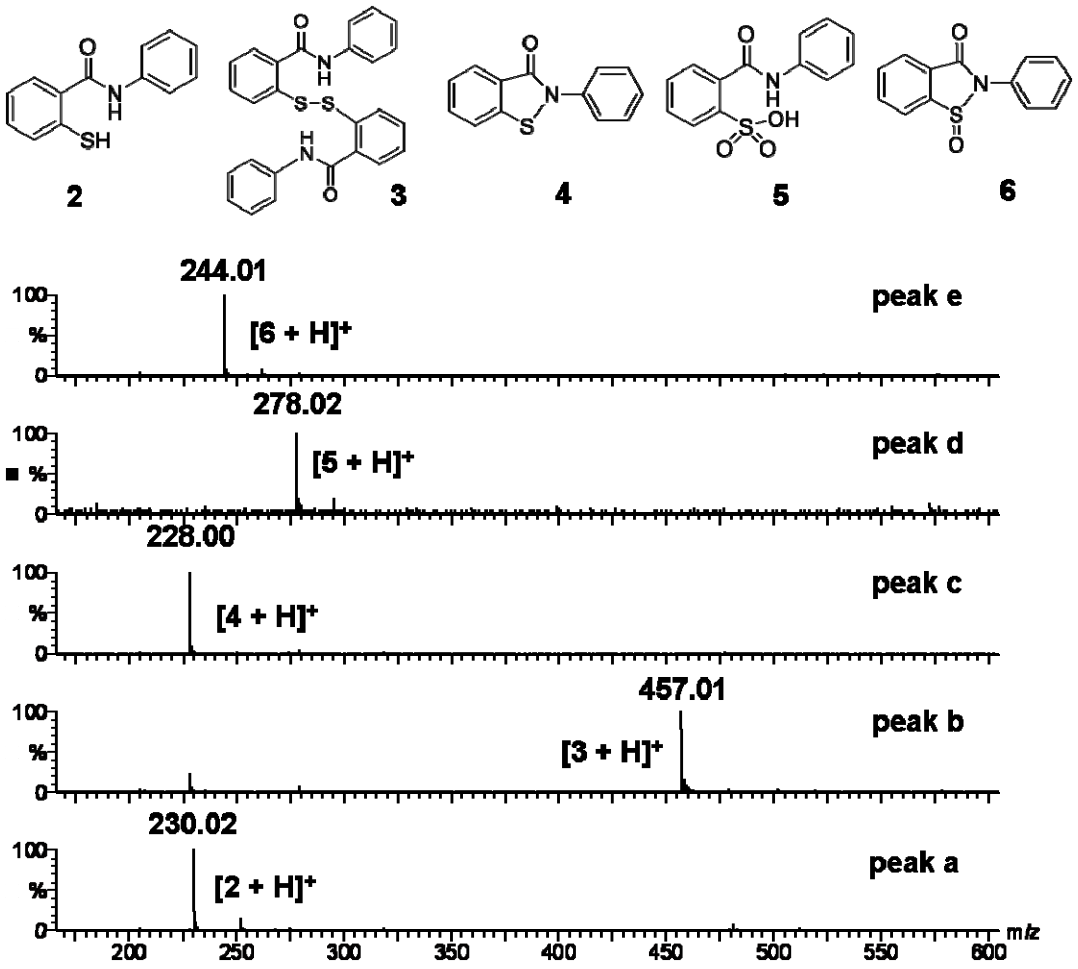

Figure S1. Mass spectra for HPLC fractions a, b, c, d and e in Figure 2a from the reaction mixture of compound **2** with H_2O_2 (1 mM :1.4 mM) in 50 mM phosphate buffer at 298 K for 24 h.

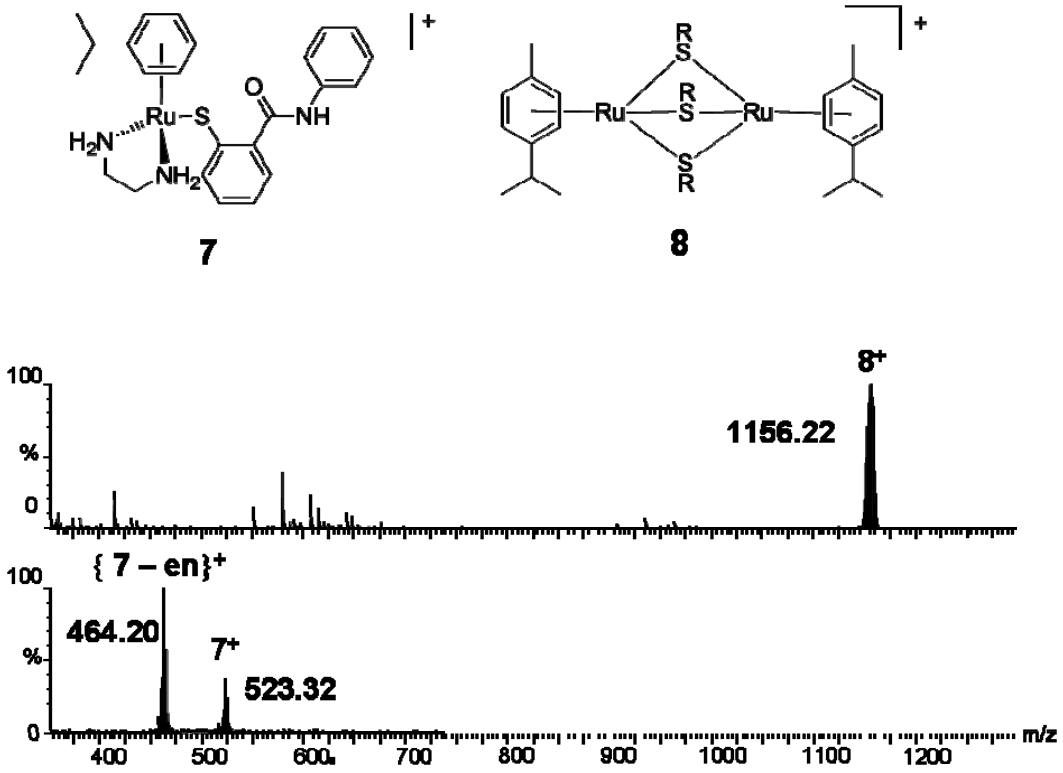

Figure S2. Mass spectra for m ono- and di-ruthenium thiolato com plexes **7** and **8** formed by the reaction of ruthenium complex **1** with thiolate **2**.

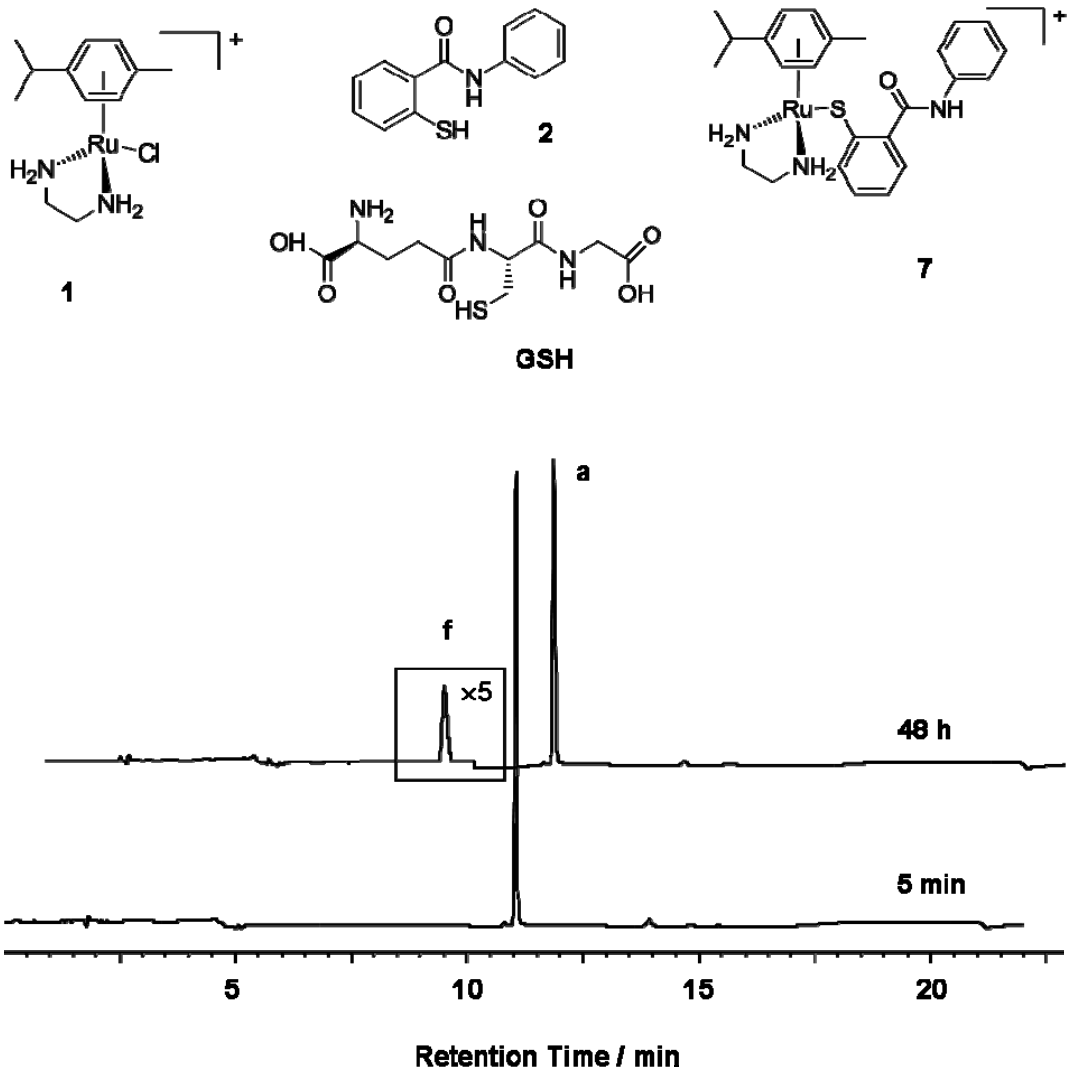

Figure S3. HPLC chrom atograms with UV detection at 2 60 nm for reaction of **1** (1 mM) with 1 m ol equiv com pound **2** in the presence of 10 m ol equiv GSH i n phosphate buffer (pH 7.4) at 298 K. Peak assignments: a, **2**; f, complex **7**.

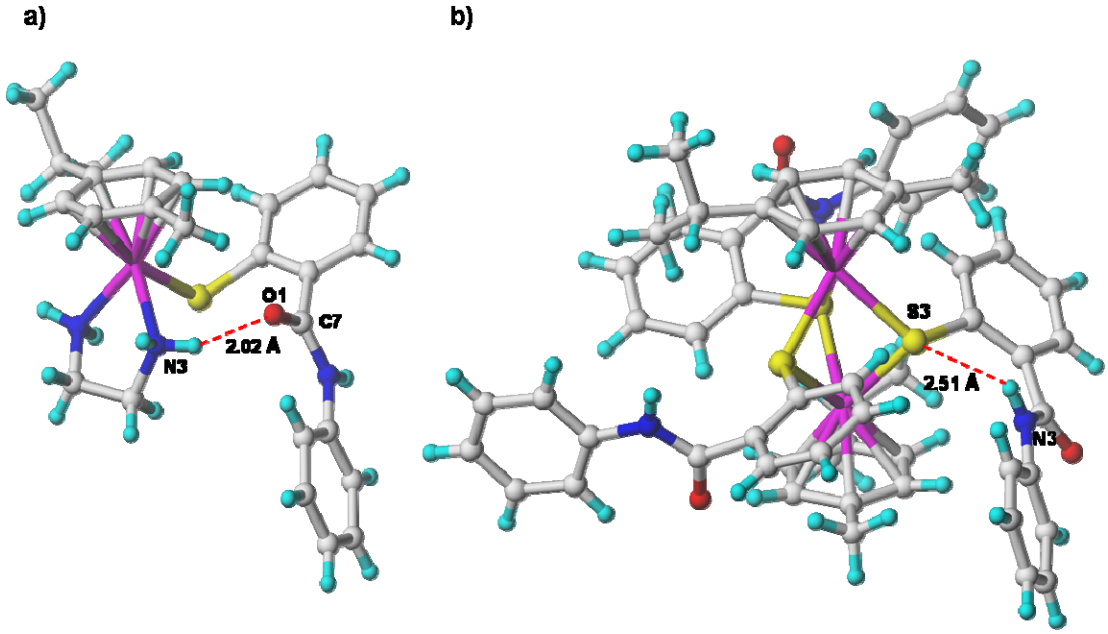

Figure S4. X-ray structures for cations of a) [(η^6-cym)Ru(en)(RS)]PF_6 (**7**) and b) [($(\eta^6$-cym)Ru)$_2$(RS)$_3$]PF_6 (**8**) are indicative of the form ation of H-bonds between the NH of en ligand and the carbonyl oxygen in **7** (a) and between the am ide N3-H and the adjacent sulfur atom S3 in **8** (b). R = $(C_6H_5)CONH(C_6H_5)$.

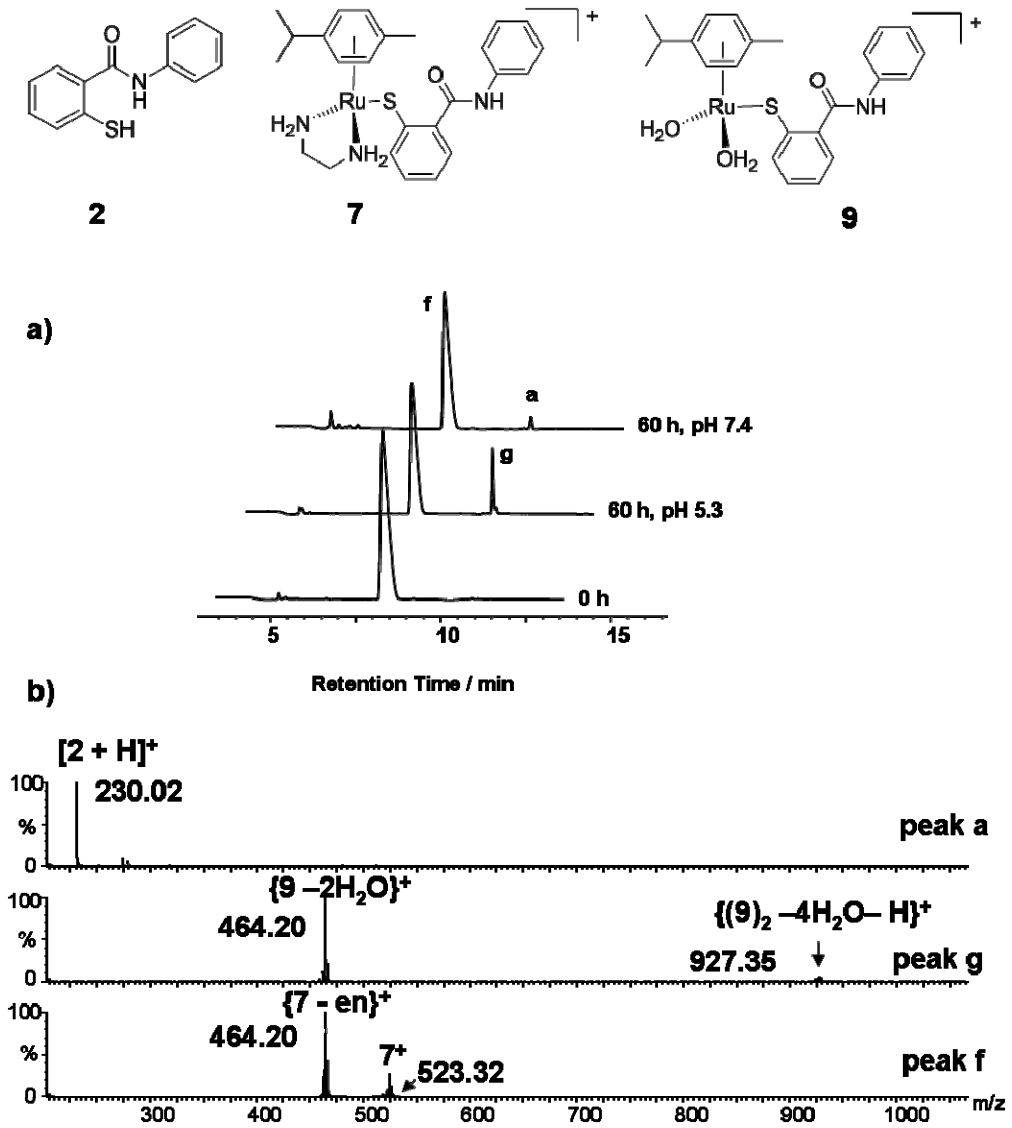

Figure S5. a) HPLC chrom atograms with UV detection at 260 nm for the hydrolysis of **7** (1 mM) at 298 K. On the basis of HPLC peak areas, ca. 93.5% and 85.3% of complex **7** rem ains intact after 60 h at pH 7.4 and pH 5.3, respectively . b) Mass spectra for HPLC fract ions shown in (a). Assignm ents: f , com plex **7**; a, **2**; g, hydrolysis adduct **9**.

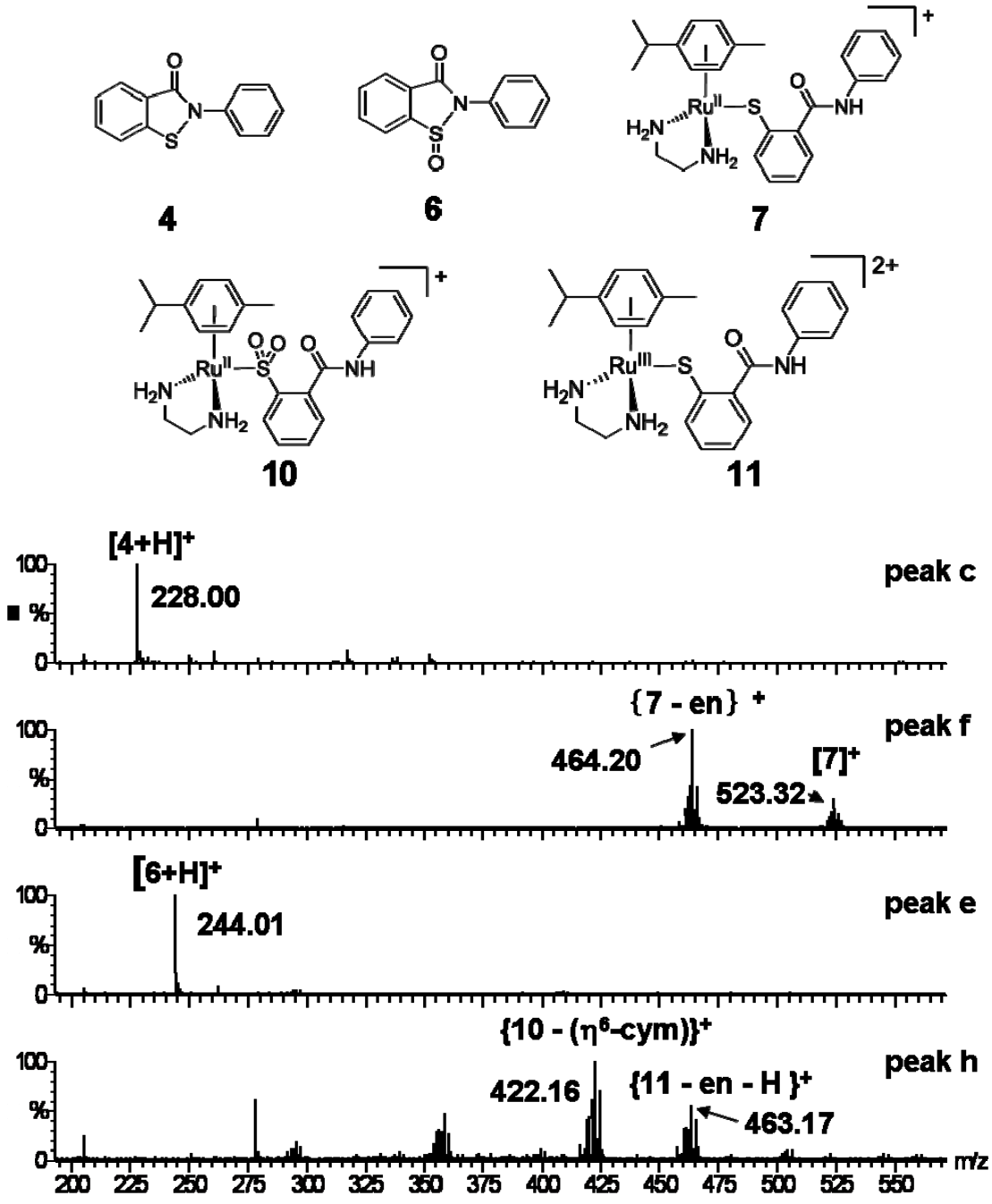

Figure S6. Mass spectra for fractio ns corresponding to HP LC peaks f, g, e and c in Figure 4a for the reaction m ixture of com plex **7** with H_2O_2 (1 m M :1.4 m M) in 50 mM phosphate buffer (pH 7.4) at 298 K for 72 h.

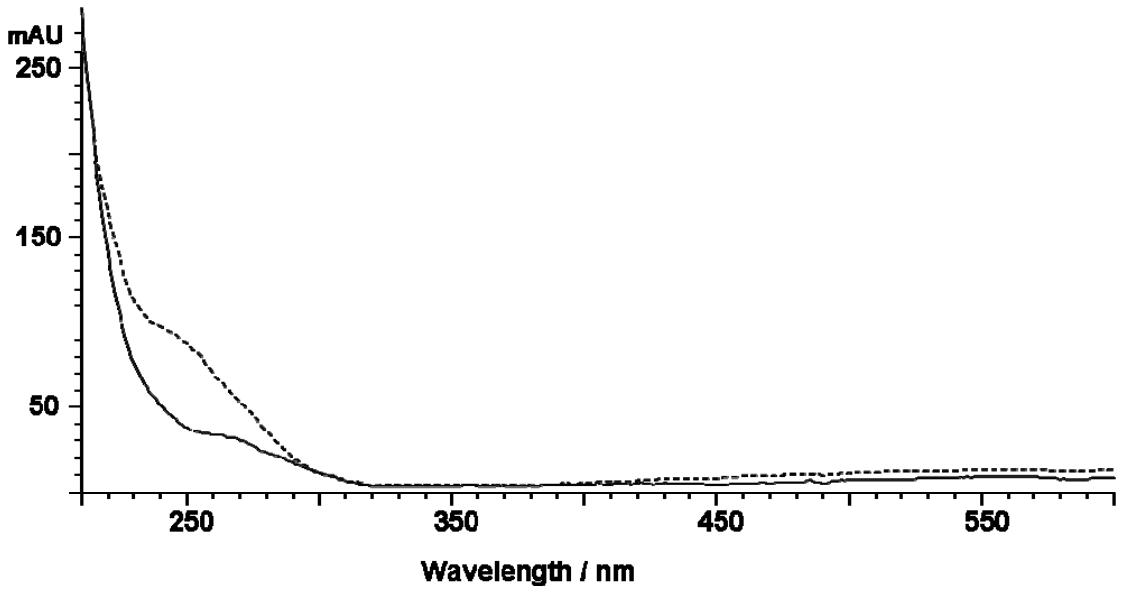

Figure S7. UV-VS spectra of HPLC fractions eluting at 5.00 and 5.05 min (Figure 4a), indicating that th is fraction con tains a m ixture of the sulfin ato Ru^{II} complex **10** and the thiolato Ru^{III} complex **11**.

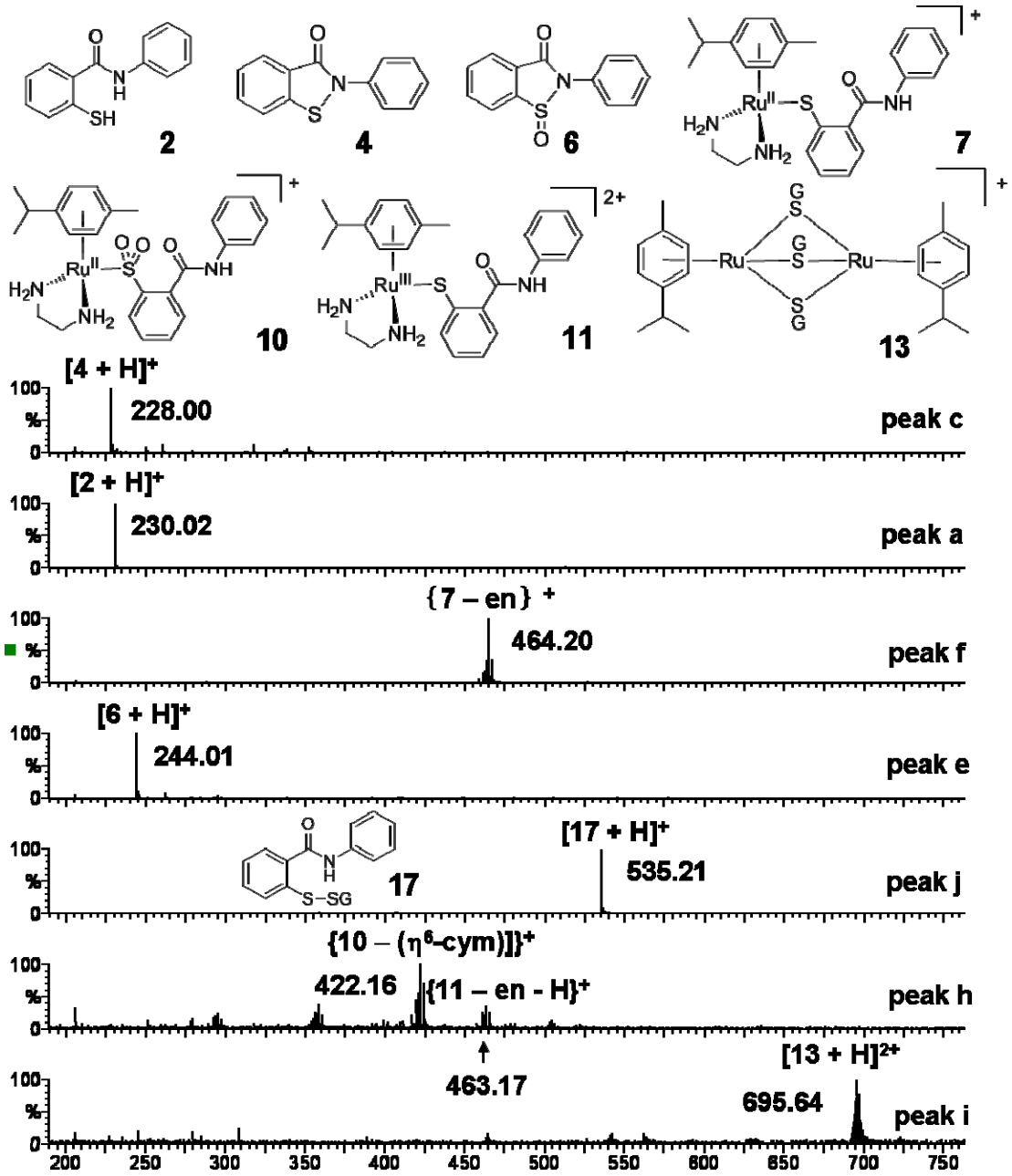

Figure S8. Mass spectra for fractions corresponding to HPLC peaks j, g, n, e, f, a and c in Figure 4b from the reaction of complex **7** (1 mM) with 10 mol equiv GSH in phosphate buffer (pH 7.4) after complex **7** reacted with H_2O_2 (1.4 mM) at 298 K for 24 h.

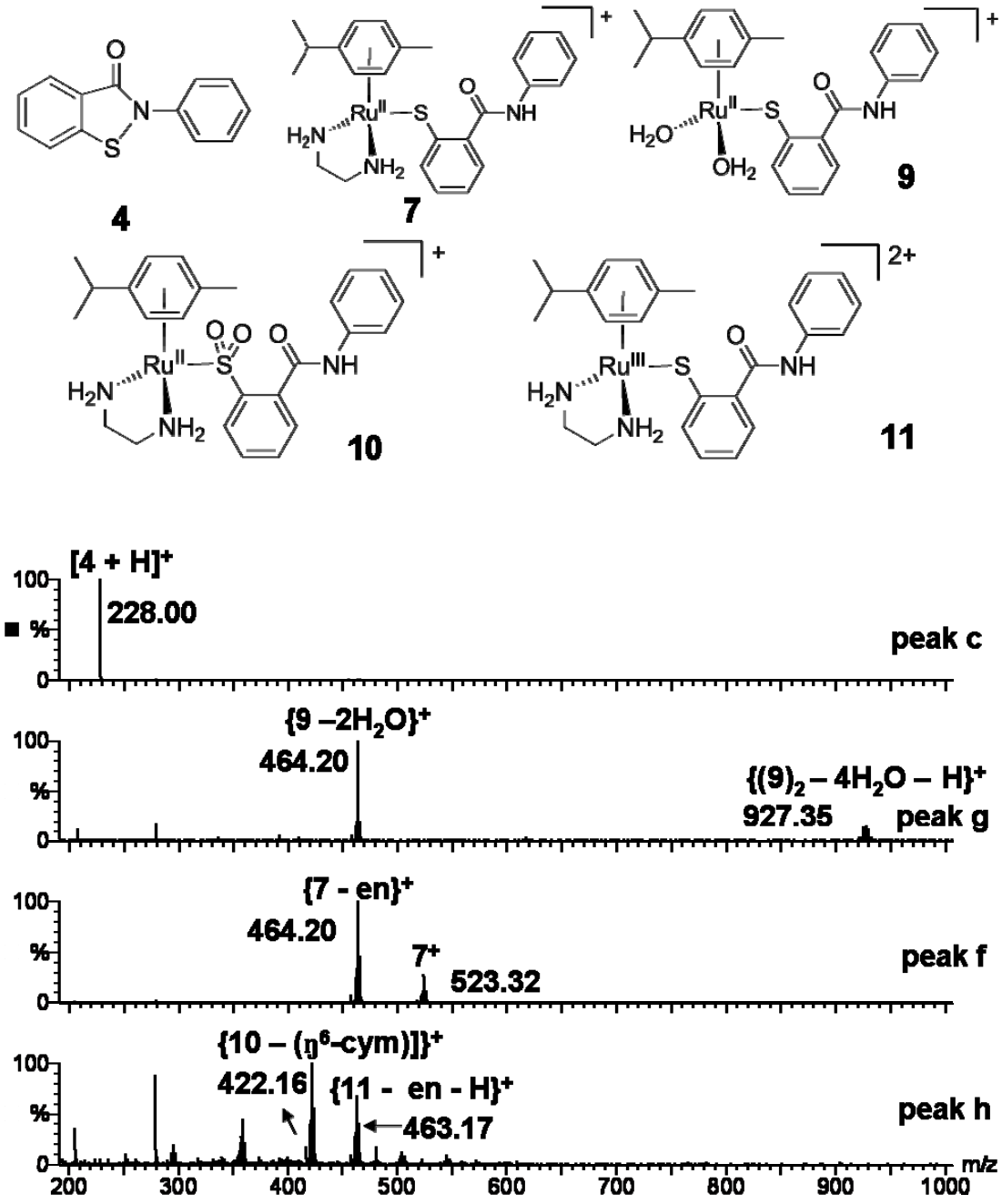

Figure S9. Mass spectra of fractions corresp onding to HPLC peaks h, f, g and c in Figure 5 for the reacti on mixture of complex **7** with H_2O_2 in 50 mM phosphate buffer (pH 5.3) at 298 K for 72 h.

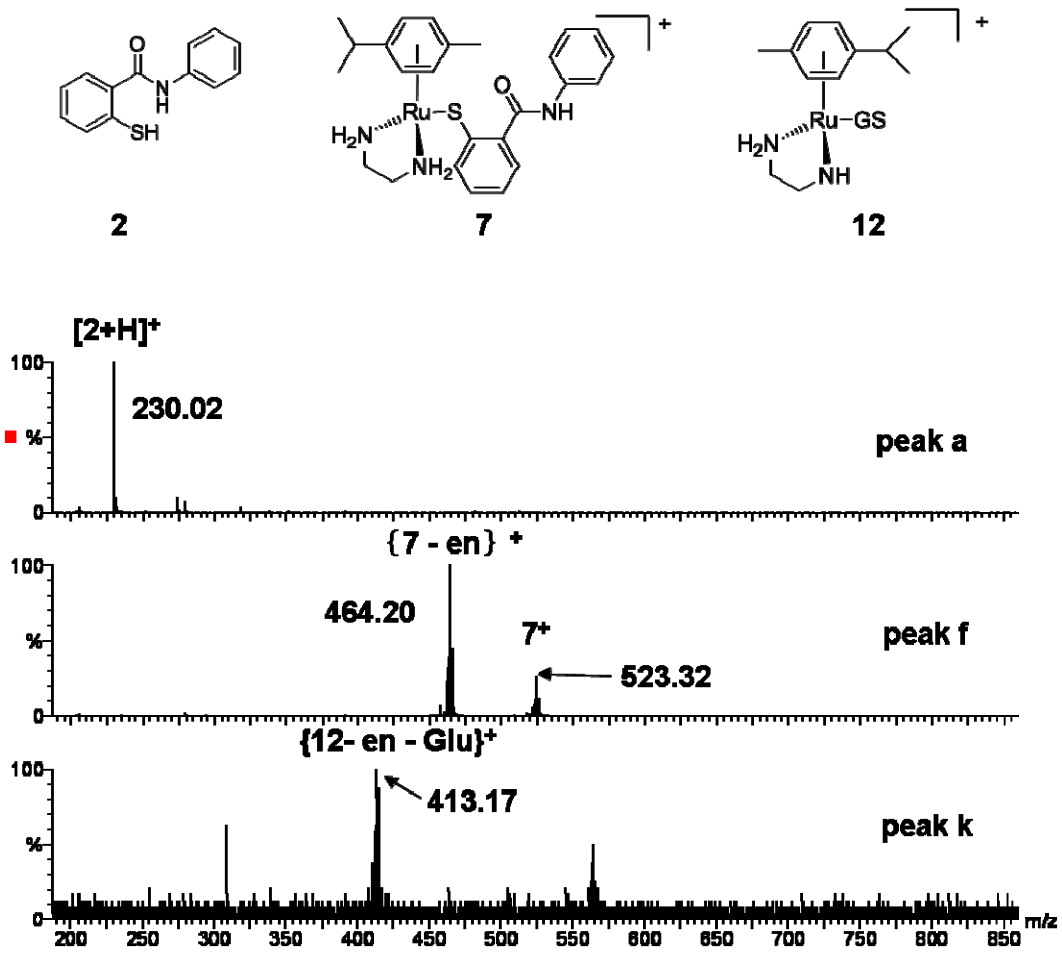

Figure S10. Mass spectra of fractions corre sponding to HPLC peaks a, f and h in Figure 6a for the reaction mixture of complex **7** with GSH (1 mM :10 mM) in 50 mM phosphate buffer (pH 7.4) at 298 K for 72 h.

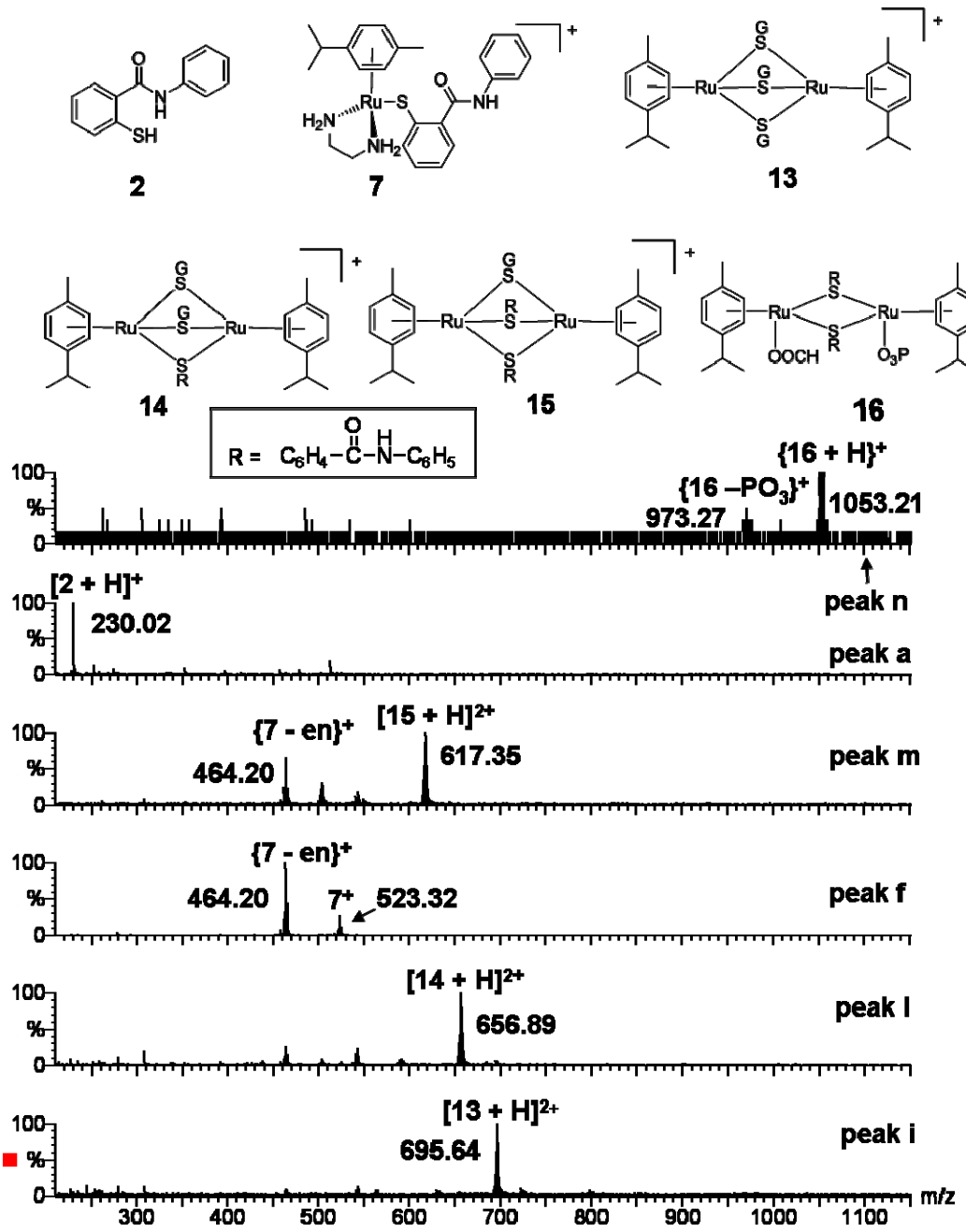

Figure S11. Mass spectra of fractions correspond ing to HPLC peaks i, l, f, m , a and n in Figure 6b for the reaction m ixture of com plex **7** with GSH in 50 mM phosphate buffer (pH 5.3) at 298 K for 72 h.