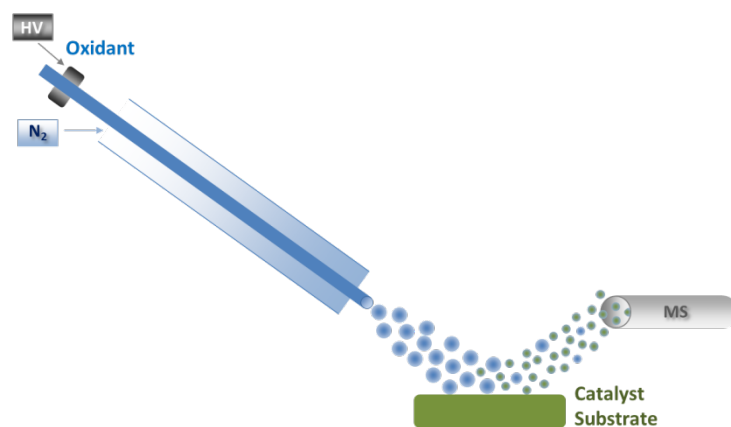


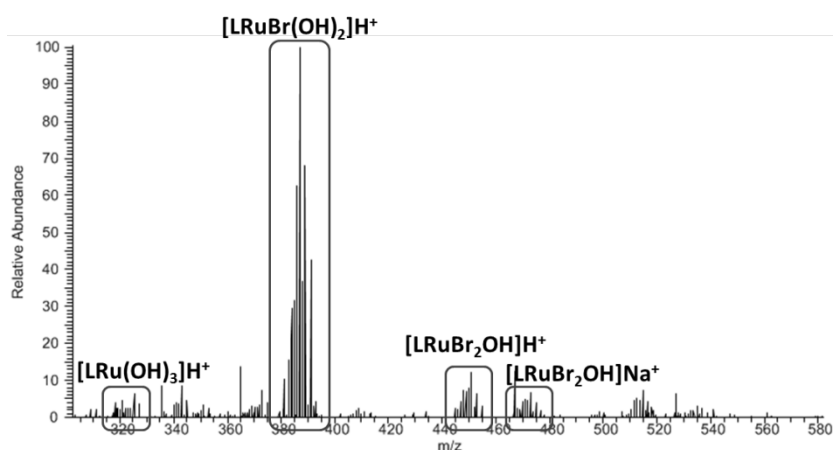
Speciation and decomposition pathways of ruthenium catalysts used for selective C-H hydroxylation

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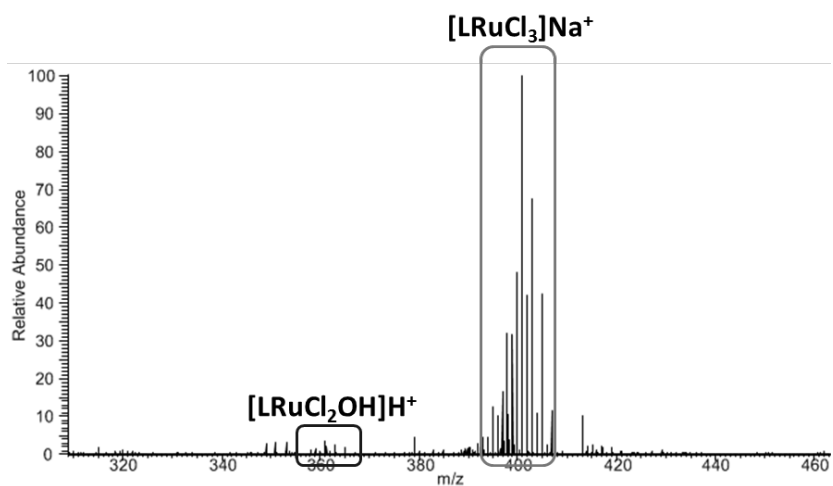
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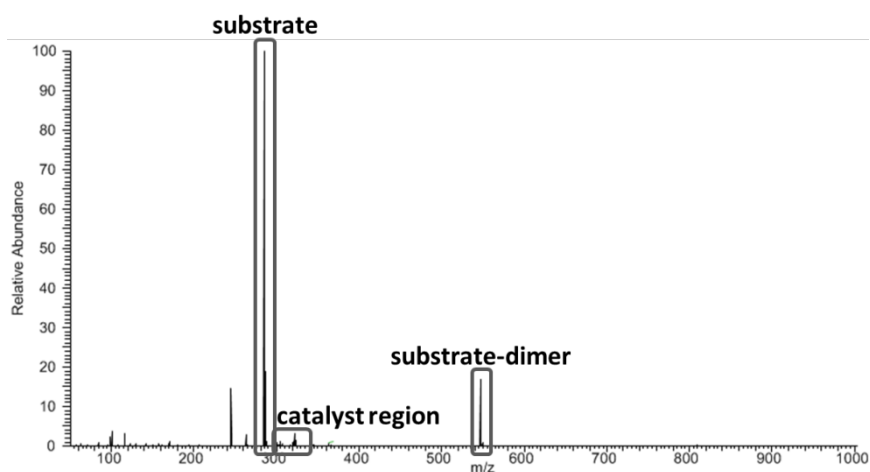
S1: DESI setup for reaction monitoring of ruthenium catalyzed hydroxylation. Homebuilt DESI-source: A fused silica tubing (100 μm i.d., 360 μm o.d.) was used to spray H₂O (or aqueous oxidant solution) at a flow rate of 15 $\mu\text{L}/\text{min}$ and 5 kV spray voltage. An outer metal capillary was connected to the nebulizing gas (140 psi N₂) using a Swagelok T-fitting. The inner capillary was adjusted to extend approx.. 1 mm from the outer capillary. The source was placed approx. 2 mm in front of the MS inlet capillary at an angle of appr. 55 degrees.



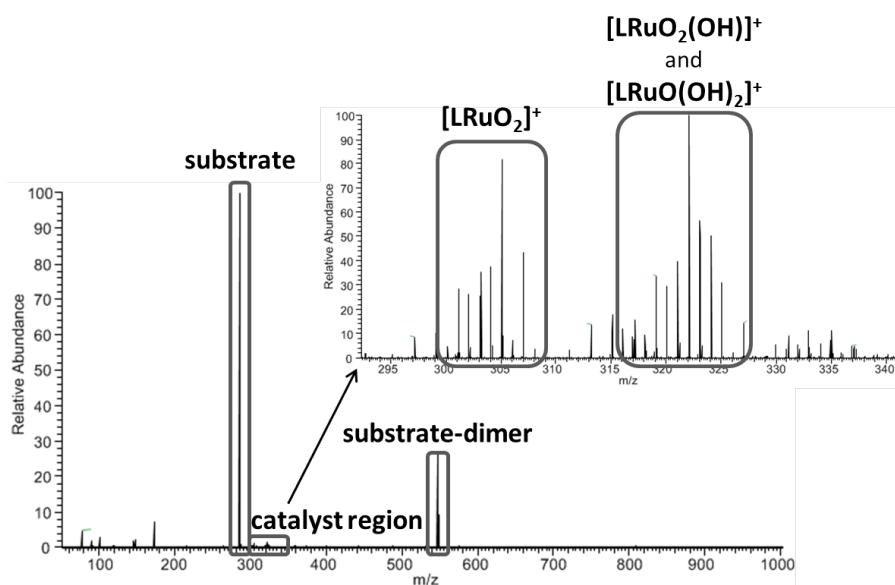
S2: DESI spectrum of 1mM (Me₃tacn)RuBr₃ spotted on paper and sprayed with H₂O.



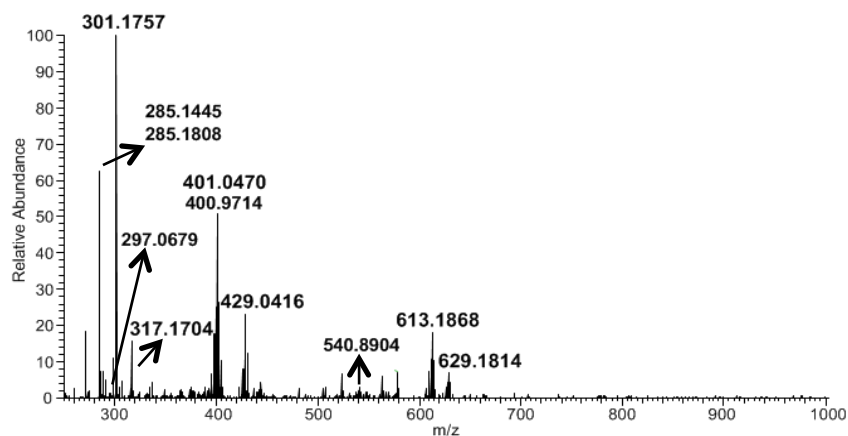
S3: DESI spectrum of 1 mM $(\text{Me}_3\text{tacn})\text{RuCl}_3$ spotted on paper and sprayed with H_2O .



S4: Full DESI spectrum of 1 mM $(\text{Me}_3\text{tacn})\text{RuCl}_3$ in H_2O , activated with AgClO_4 , treated with substrate, spotted on paper and sprayed with 0.1 mM NaIO_4 .



S5: 1 mmol activated $(\text{Me}_3\text{tacn})\text{RuBr}_3$ and substrate **2** sprayed with 0.1 mmol NaIO_4 .



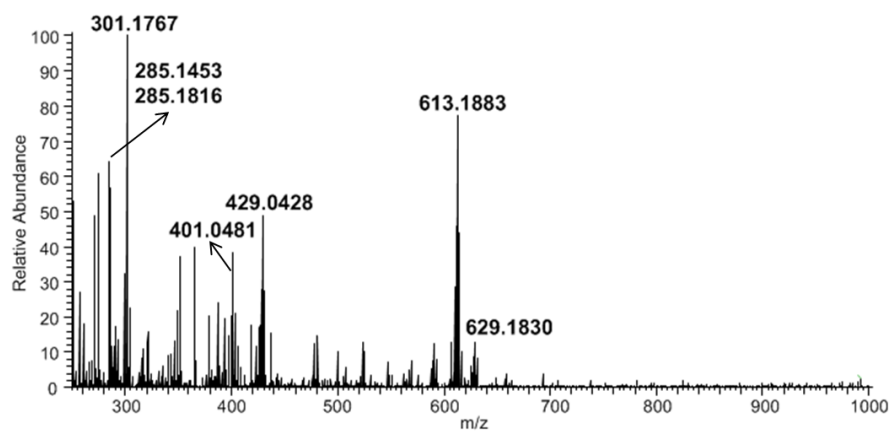
S6: DESI spectrum of the incubated reaction mixture containing $(\text{Me}_3\text{tacn})\text{RuCl}_3$, AgClO_4 and substrate **2**, sprayed with $5 \cdot 10^{-4}$ M NaIO_4 .

m/z	elemental composition	error in ppm	molecule
285.1458	$[\text{C}_{16}\text{H}_{22}\text{O}_3]\text{Na}^+$	-1.05	ketone product
285.1821	$[\text{C}_{17}\text{H}_{26}\text{O}_2]\text{Na}^+$	-1.40	Substrate 2
297.0692	$[\text{C}_{18}\text{H}_{42}\text{N}_6\text{O}_3\text{Ru}_2]^{++}$	-3.60	Decomposition product
301.1771	$[\text{C}_{17}\text{H}_{26}\text{O}_3]\text{Na}^+$	-1.00	Product 3
317.1718	$[\text{C}_{17}\text{H}_{26}\text{O}_4]\text{Na}^+$	-1.58	Bis-hydroxylated product
400.9732	$[\text{C}_9\text{H}_{21}\text{Cl}_3\text{N}_3\text{Ru}]\text{Na}^+$	-1.25	Starting material
401.0488	$[\text{C}_{11}\text{H}_{22}\text{N}_3\text{O}_5\text{Ru}]\text{Na}^+$	-1.75	Decomposition product
429.0433	$[\text{C}_{12}\text{H}_{22}\text{N}_3\text{O}_6\text{Ru}]\text{Na}^+$	-2.56	Decomposition product
540.8929	$[\text{C}_9\text{H}_{21}\text{Cl}_2\text{N}_3\text{O}_3\text{IRu}]\text{Na}^+$	-2.03	IO_3 -adduct to catalyst
613.1896	$[\text{C}_{23}\text{H}_{42}\text{N}_3\text{O}_8\text{Ru}]\text{Na}^+$	-1.96	Decomposition product
629.1843	$[\text{C}_{23}\text{H}_{42}\text{N}_3\text{O}_9\text{Ru}]\text{Na}^+$	-2.23	Decomposition product

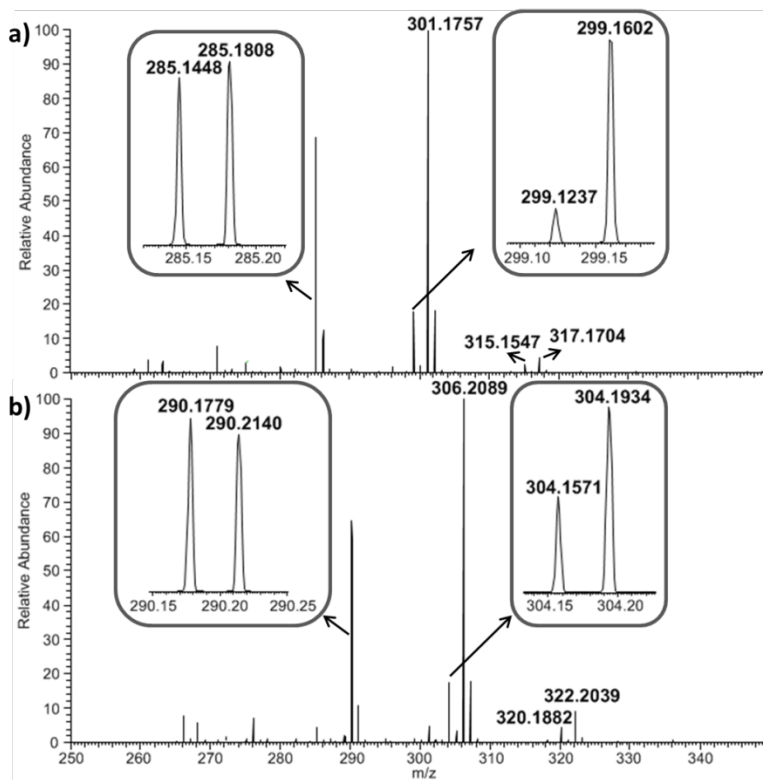
S7: Full list of identified signals in the aqueous layer of the incubated mixture of $(\text{Me}_3\text{tacn})\text{RuCl}_3$, NaIO_4 and substrate **2**. The monomeric ruthenium compounds are also decomposition products and are not catalytically active.

Compound	10 min	30 min	3 h	24 h
Organic layer				
285.1458	4	24	59	62
Substrate 2	162	68	54	57
Product 3	7	43	106	108
Aqueous layer				
297.0692	0	0	1.72	1.65
401.0448	0	0	25.39	47.09
540.8929	0	0	0.68	2.91
613.1896	0.12	0.56	2.15	17.06
629.1843	0	0.08	3.28	6.38

S8: Intensities of the most significant signals in the incubated mixture.



S9: Spectrum of incubated $(\text{Me}_3\text{tacn})\text{RuBr}_3$, AgClO_4 , NaIO_4 and substrate **2**.



S10: Ethereal layer of the incubated mixture of $(\text{Me}_3\text{tacn})\text{RuCl}_3$, AgClO_4 , NaIO_4 and a) substrate **2**, b) d_5 -labeled substrate **10**.