

Supporting Information

First Cycloruthenation of 2-Alkenylpyridines: Synthesis, Characterization and Properties

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Table S1. Crystal data and structure refinement for **2**·2CH₃OH.

Empirical formula	C ₃₃ H ₂₆ F ₆ N ₅ PRu·2CH ₃ OH	
Formula weight	802.71	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	$a = 7.5639(4)$ Å	$\alpha = 99.165(3)^\circ$
	$b = 12.0236(5)$ Å	$\beta = 93.603(3)^\circ$
	$c = 19.0129(9)$ Å	$\gamma = 91.597(3)^\circ$
Volume	1702.43(14) Å ³	
Z	2	
Density (calculated)	1.566 Mg/m ³	
Absorption coefficient	0.581 mm ⁻¹	
F(000)	816.0	
2 θ range for data collection	3.434 to 49.992	
Index ranges	$-8 \leq h \leq 8$, $-14 \leq k \leq 14$, $-22 \leq l \leq 22$	
Reflections collected	29410	
Independent reflections	29410 [$R_{\text{int}} = -$, $R_{\text{sigma}} = 0.0866$]	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	29410/0/416	
Goodness-of-fit on F ²	1.090	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0671$, $wR_2 = 0.1864$	
R indices (all data)	$R_1 = 0.0889$, $wR_2 = 0.2026$	
Largest diff. peak and hole	0.857/-0.770 eÅ ⁻³	

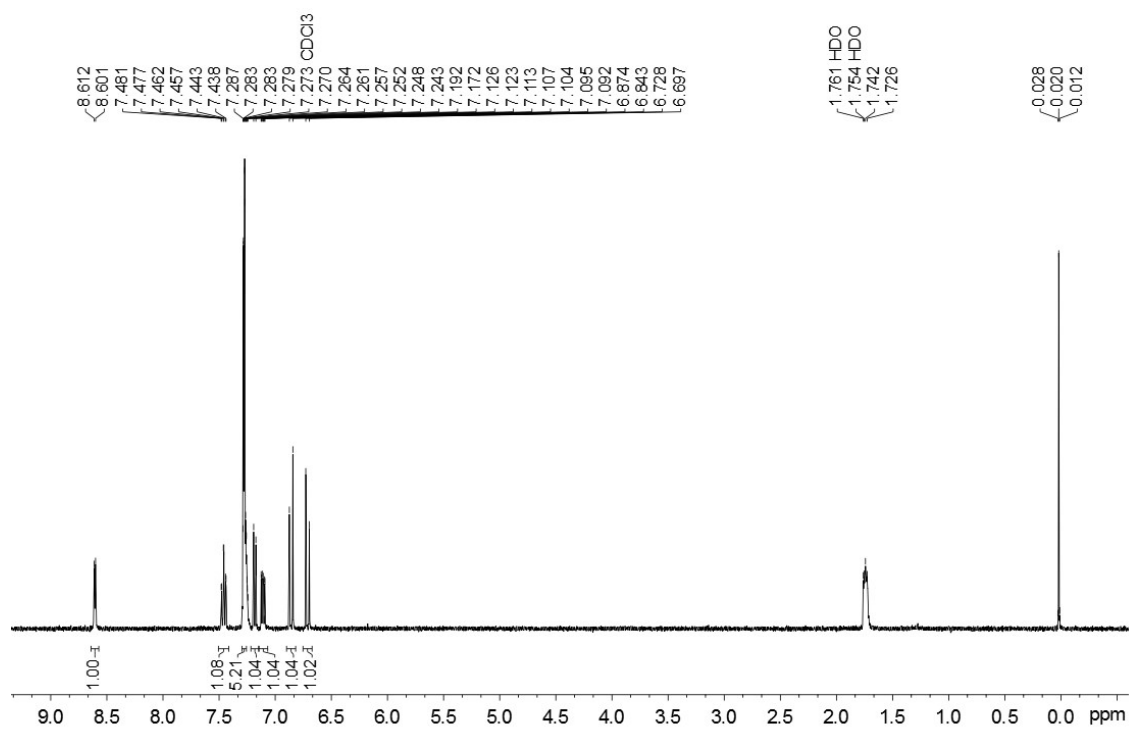


Fig. S1 ¹H NMR spectrum of (E)-2-styrylpyridine in CDCl₃.

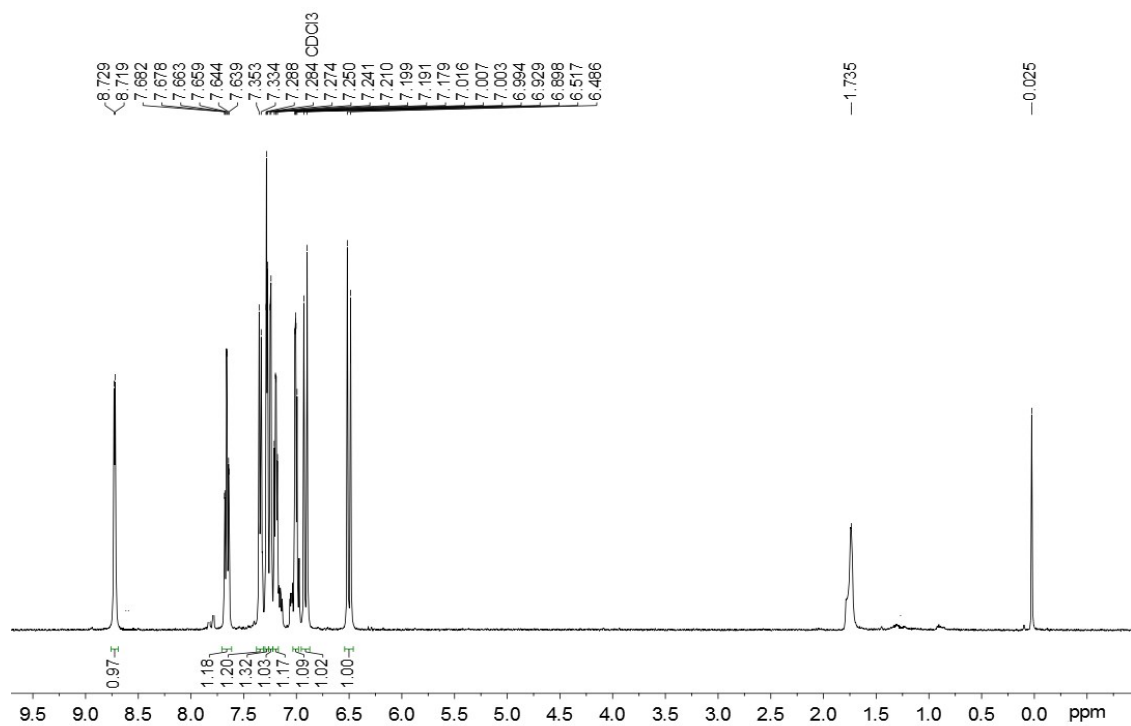


Fig. S2 ¹H NMR spectrum of (E)-2-(2-(thiophen-2-yl)vinyl)pyridine in CDCl₃.

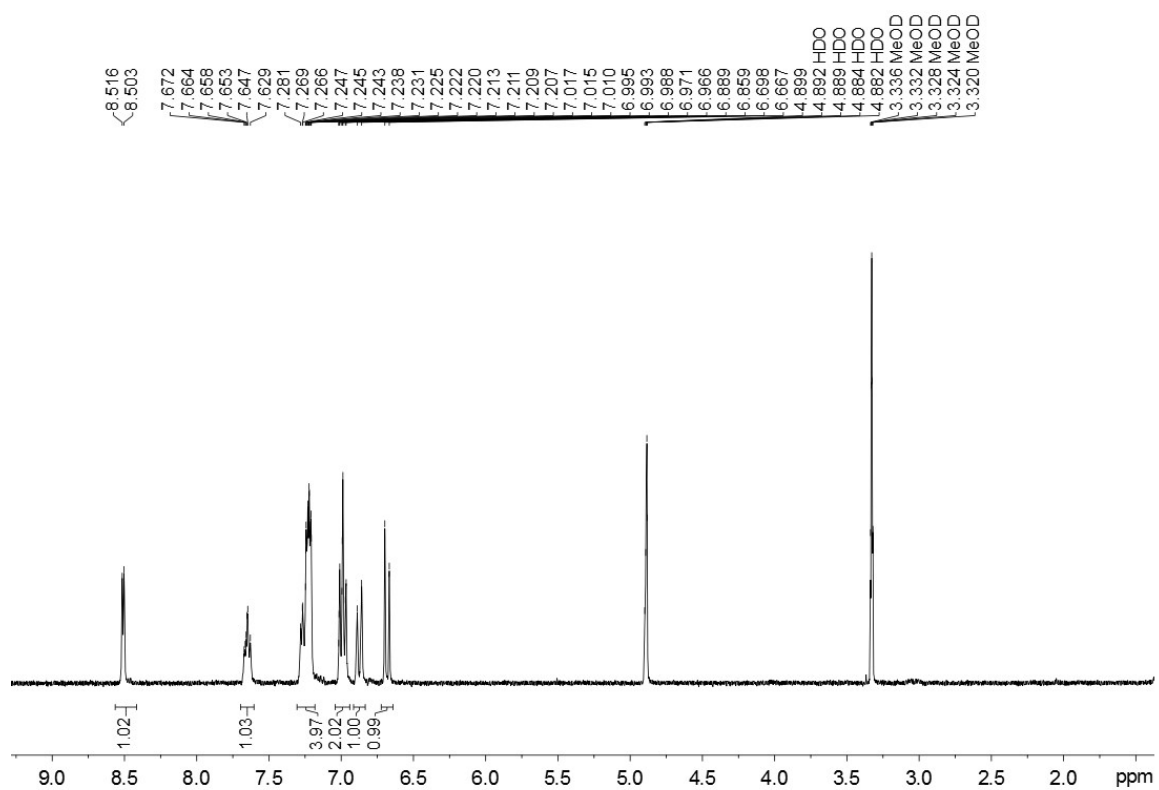


Fig. S3 ¹H NMR spectrum of (E)-2-(4-fluorostyryl)pyridine in CD₃OD.

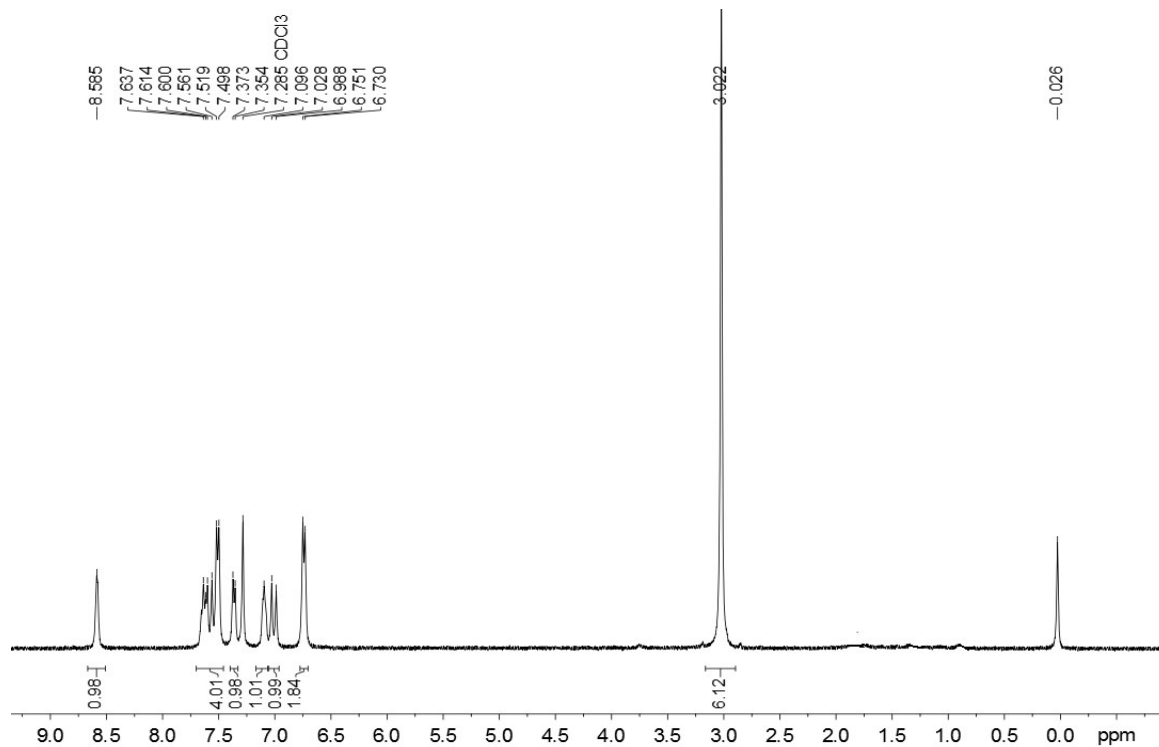


Fig. S4 ¹H NMR spectrum of (E)-N,N-dimethyl-4-(2-(pyridin-2-yl)vinyl)aniline in CDCl₃.

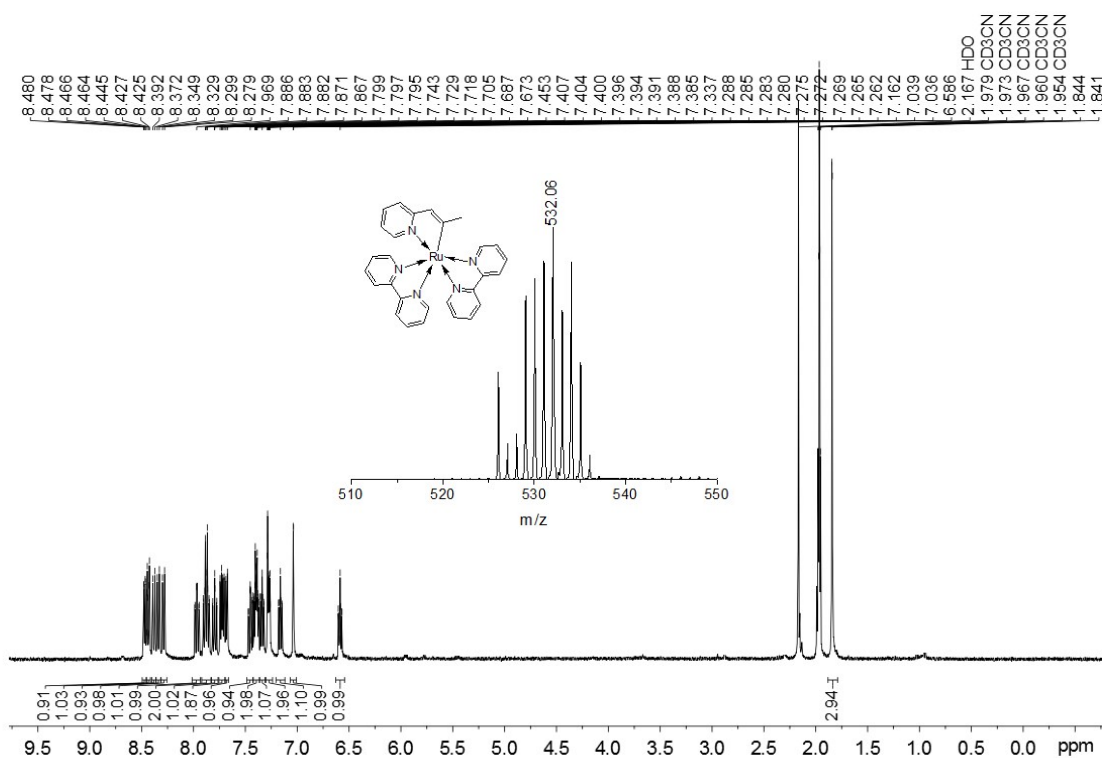


Fig. S5 ¹H NMR spectrum of complex **1** in CD₃CN. Inset: The MS spectrum of complex **1**.

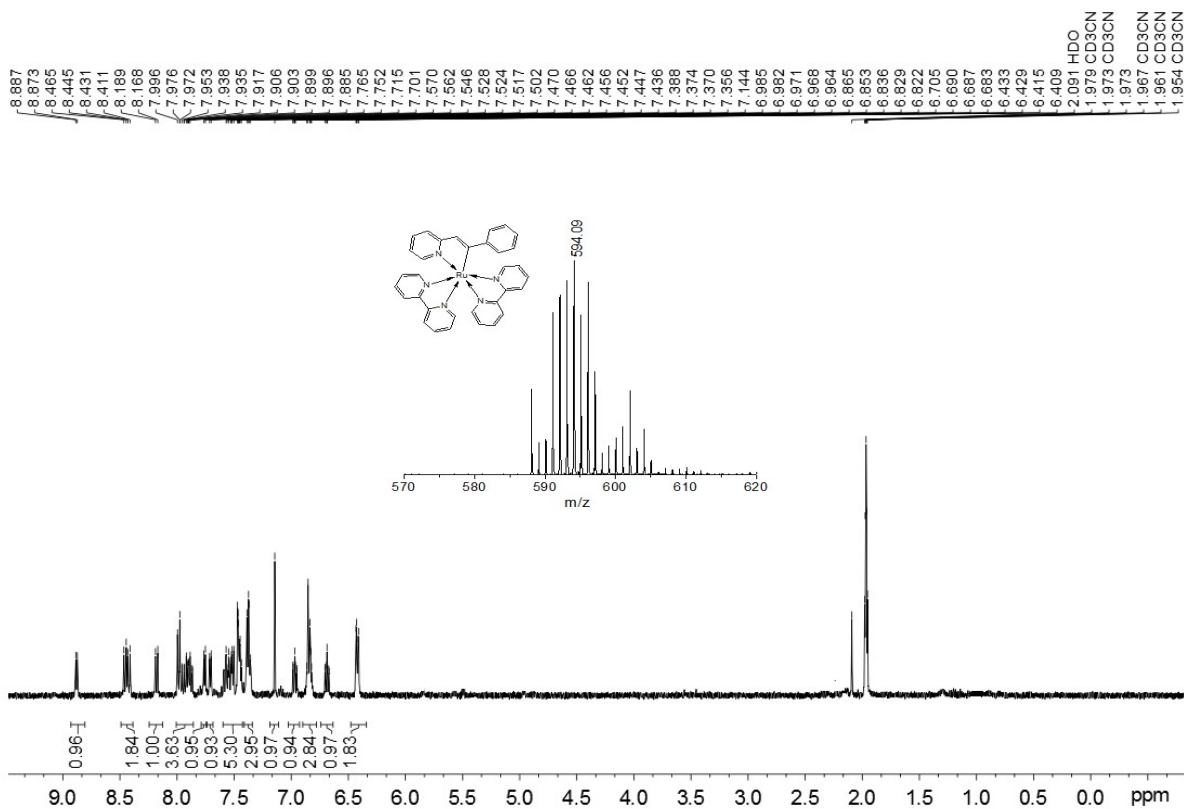


Fig. S6 ¹H NMR spectrum of complex **2** in CD₃CN. Inset: The MS spectrum of complex **2**.

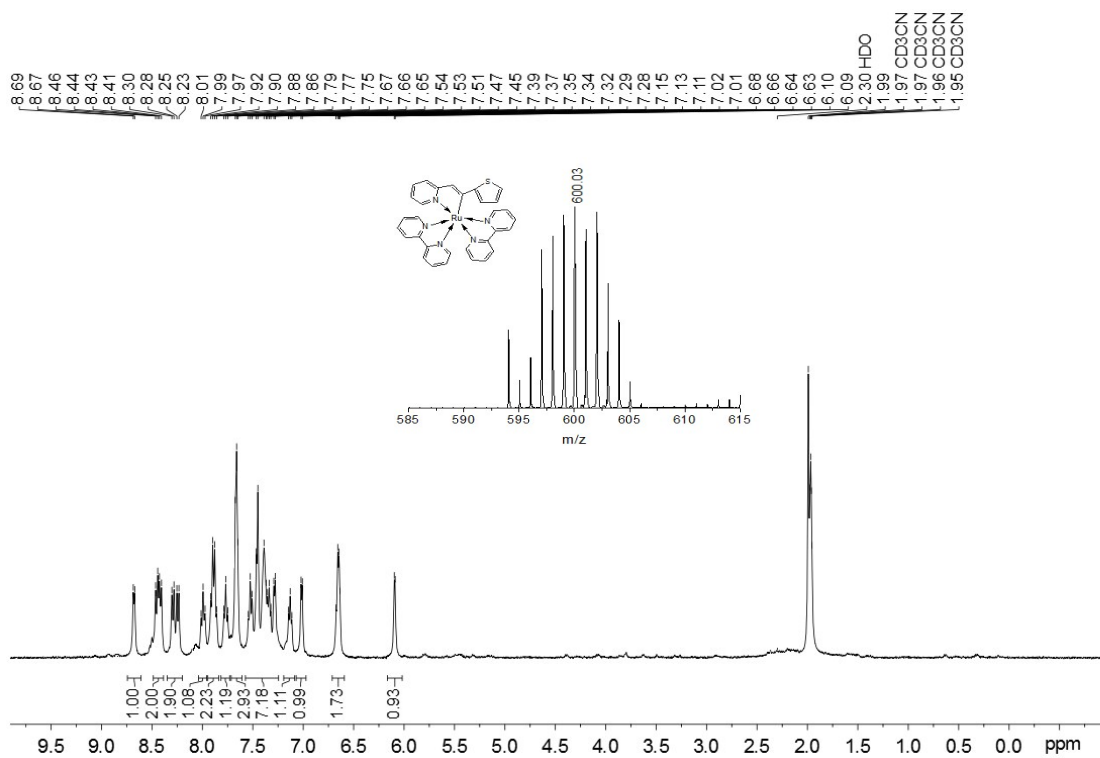


Fig. S7 ¹HNMR spectrum of complex **3** in CD₃CN. Inset: The MS spectrum of complex **3**.

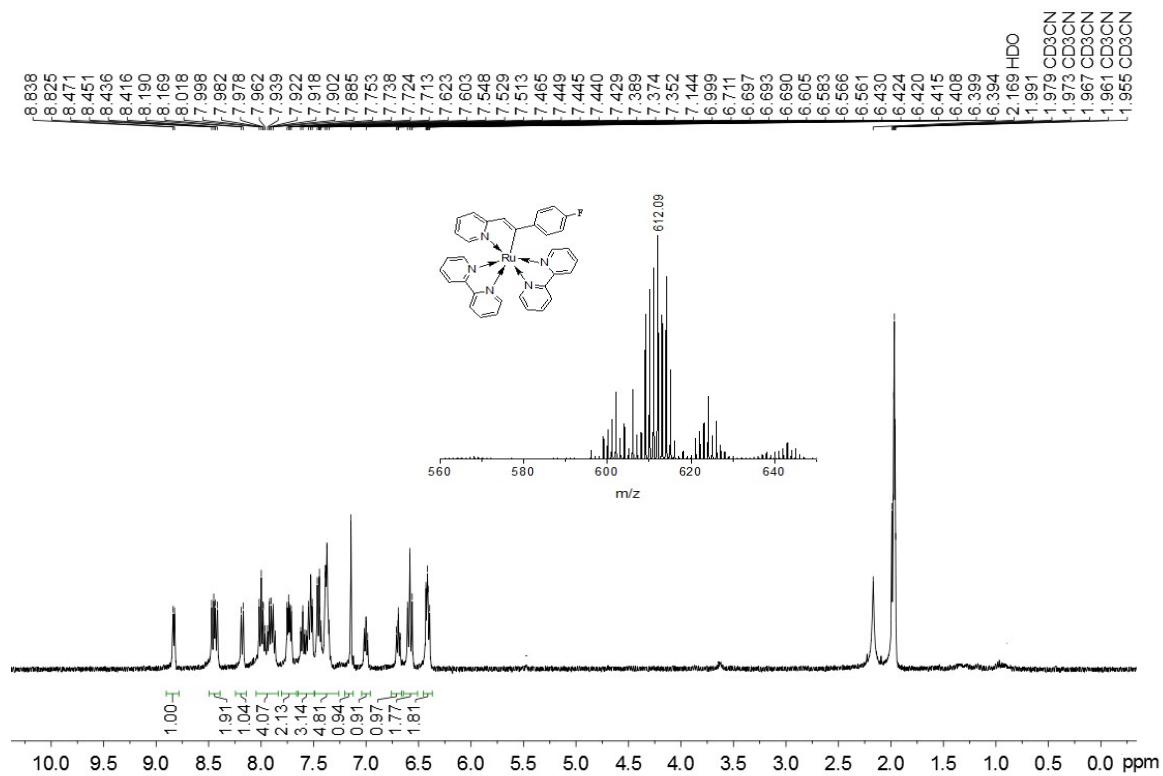


Fig. S8 ¹HNMR spectrum of complex **4** in CD₃CN. Inset: The MS spectrum of complex **4**.

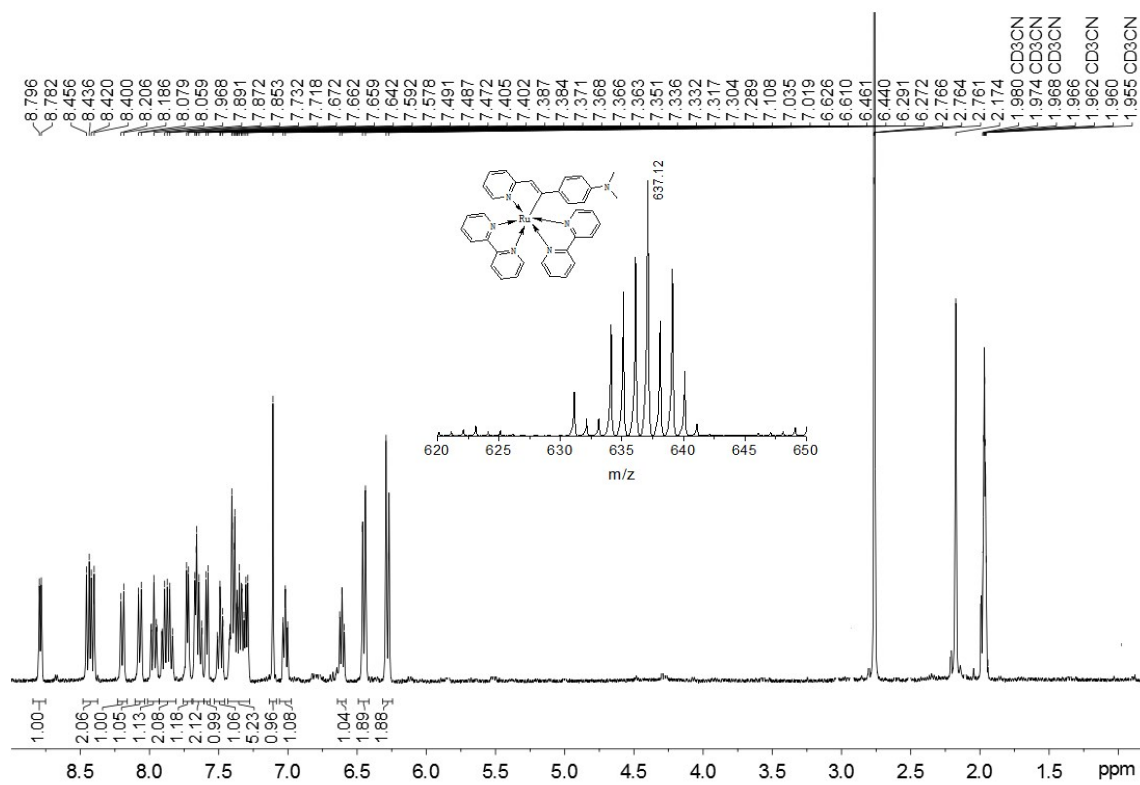


Fig. S9 ¹H NMR spectrum of complex 5 in CD₃CN. Inset: The MS spectrum of complex 5.

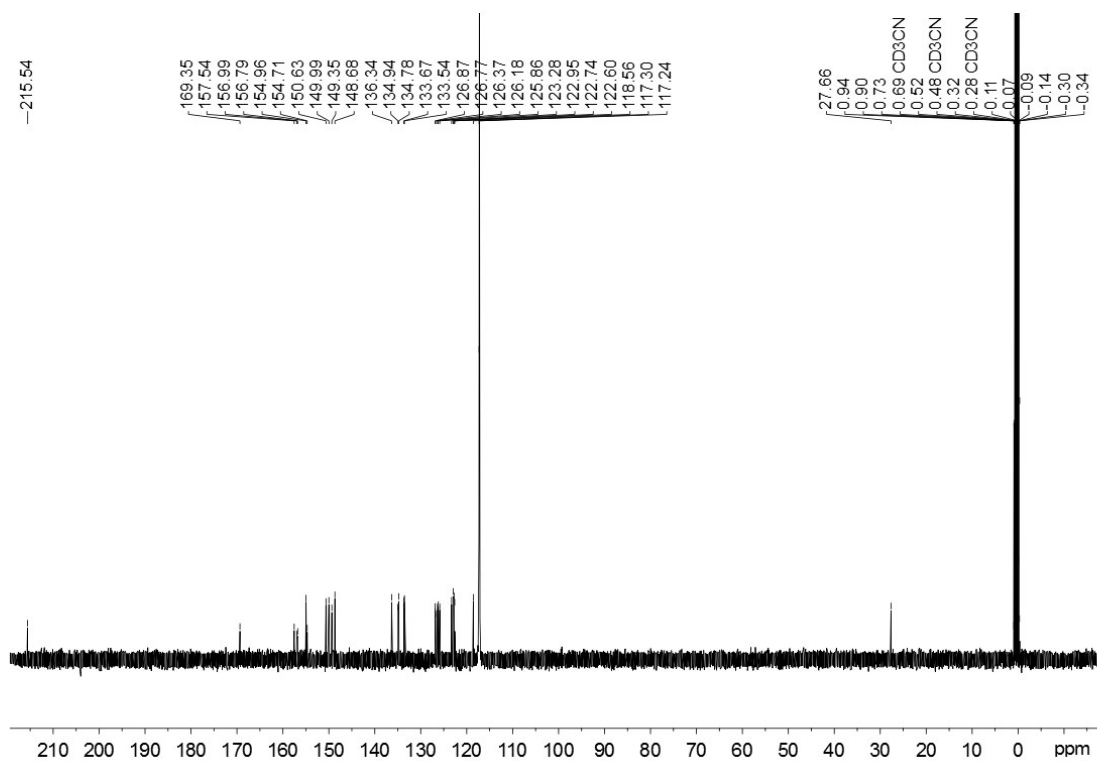


Fig. S10 ¹³C NMR spectrum of complex 1 in CD₃CN.

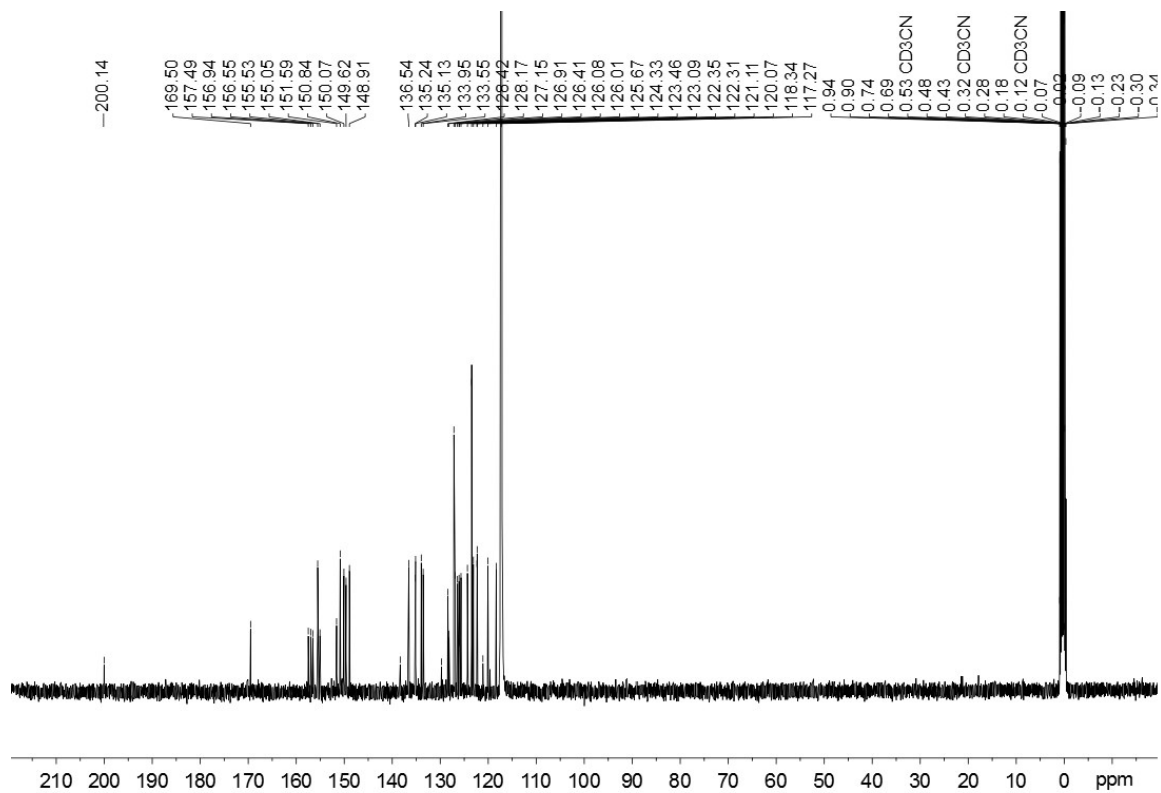


Fig. S11 ^{13}C NMR spectrum of complex **2** in CD_3CN .

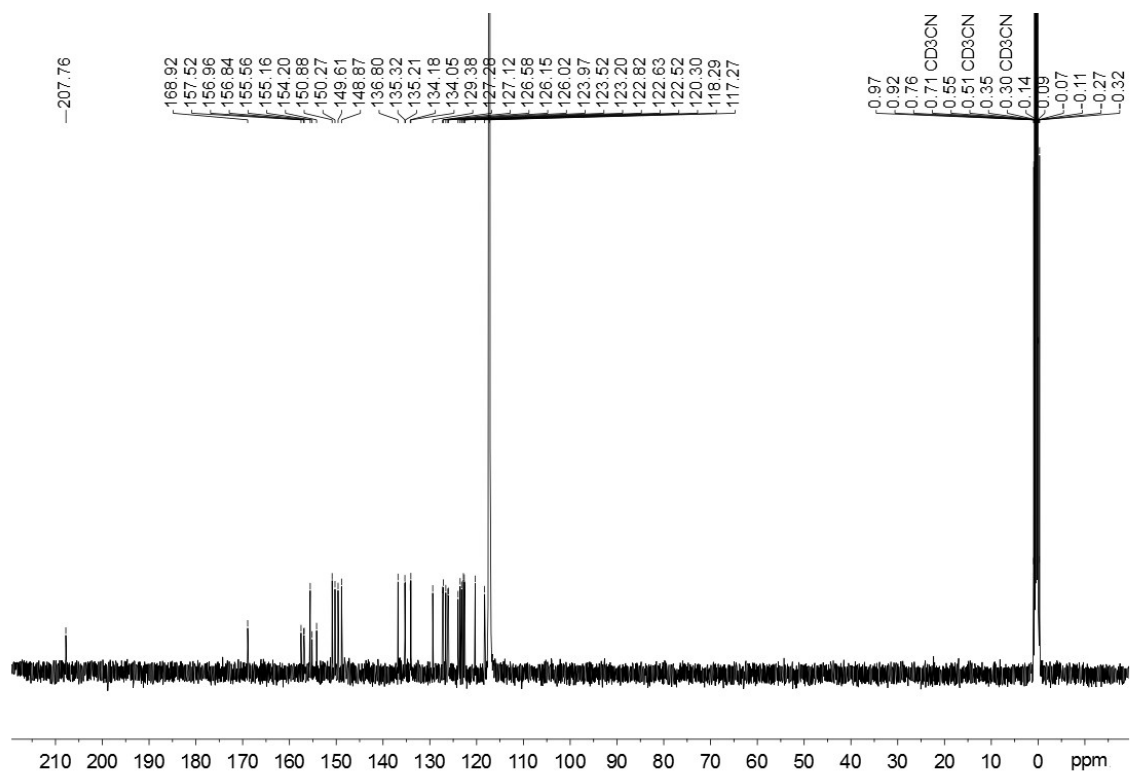


Fig. S12 ^{13}C NMR spectrum of complex **3** in CD_3CN .

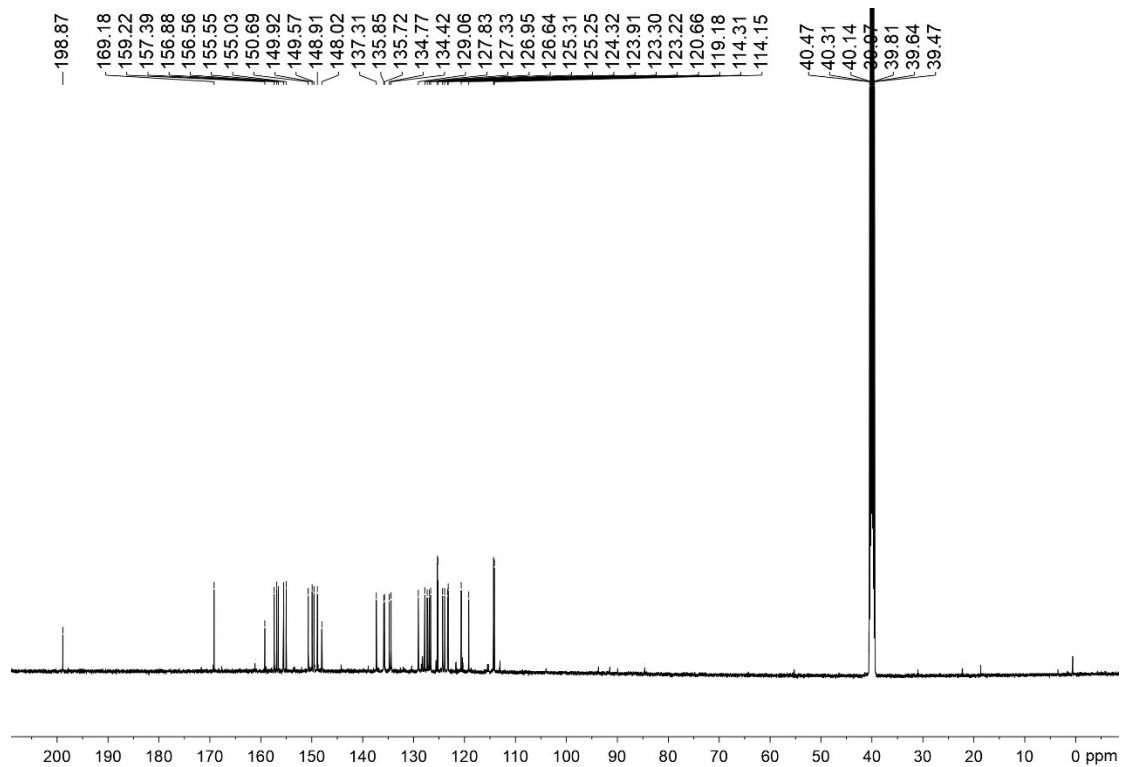


Fig. S13 ^{13}C NMR spectrum of complex **4** in d_6 -DMSO.

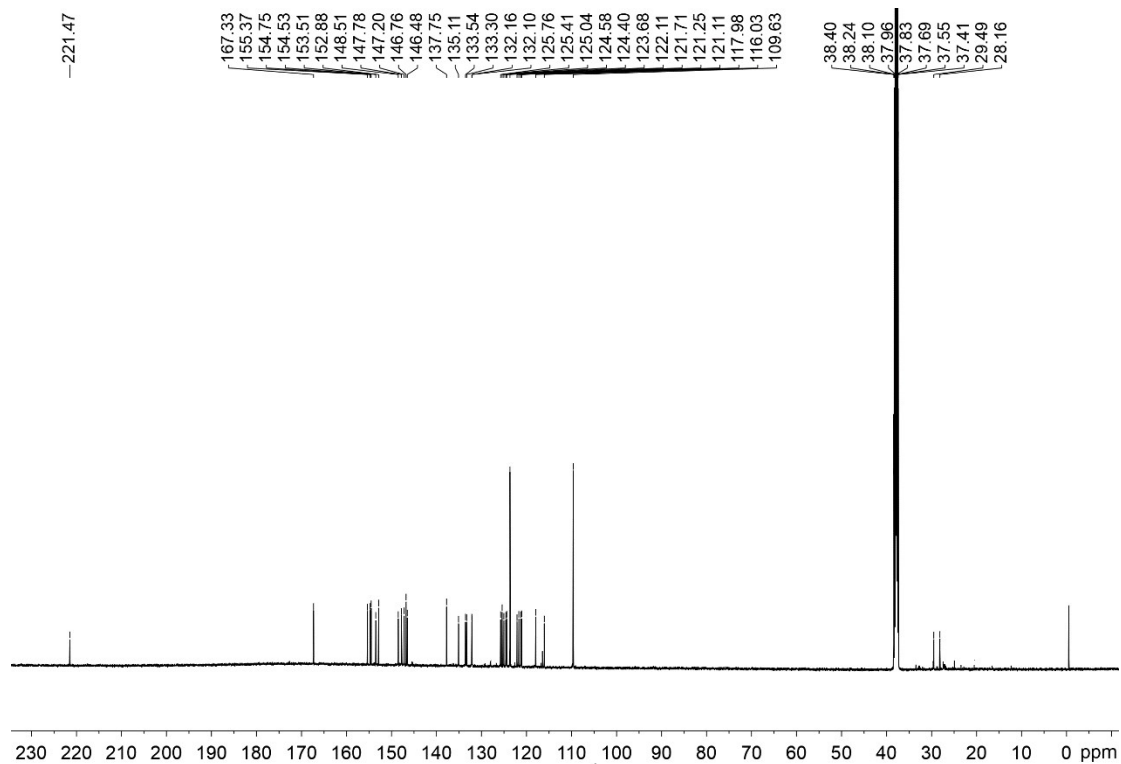


Fig. S14 ^{13}C NMR spectrum of complex **5** in d_6 -DMSO.

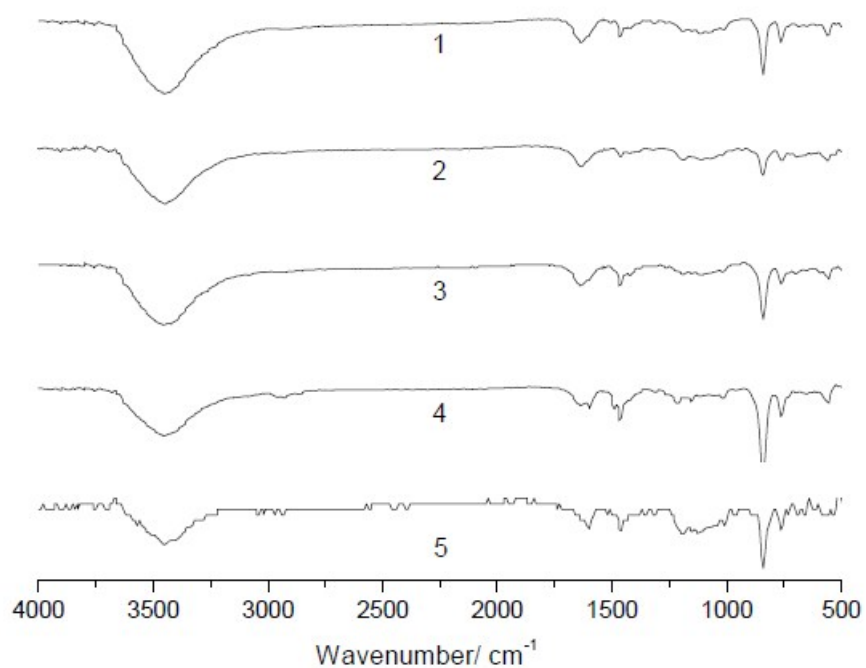


Fig. S15 FT-IR spectra of complexes **1–5** in KBr pellets.

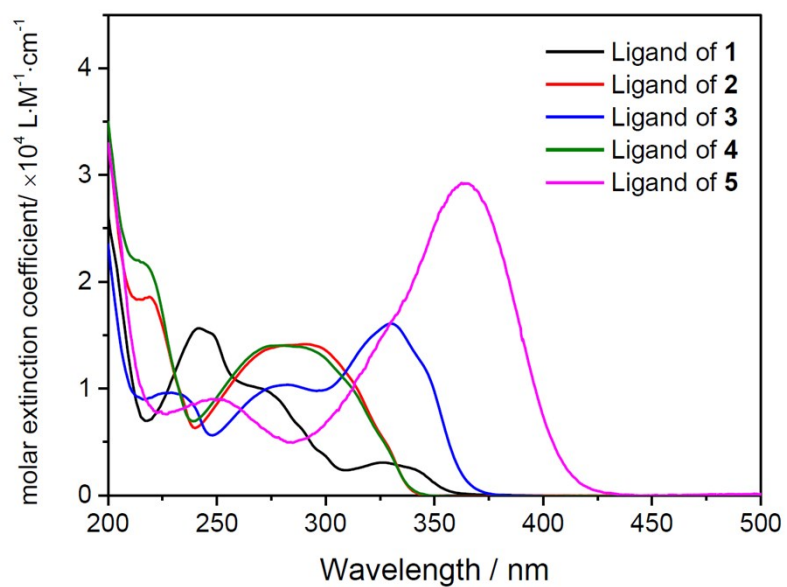


Fig. S16 Absorption spectra of 2-alkenylpyridine ligands (20 μM) of complexes **1–5** in CH_3CN .

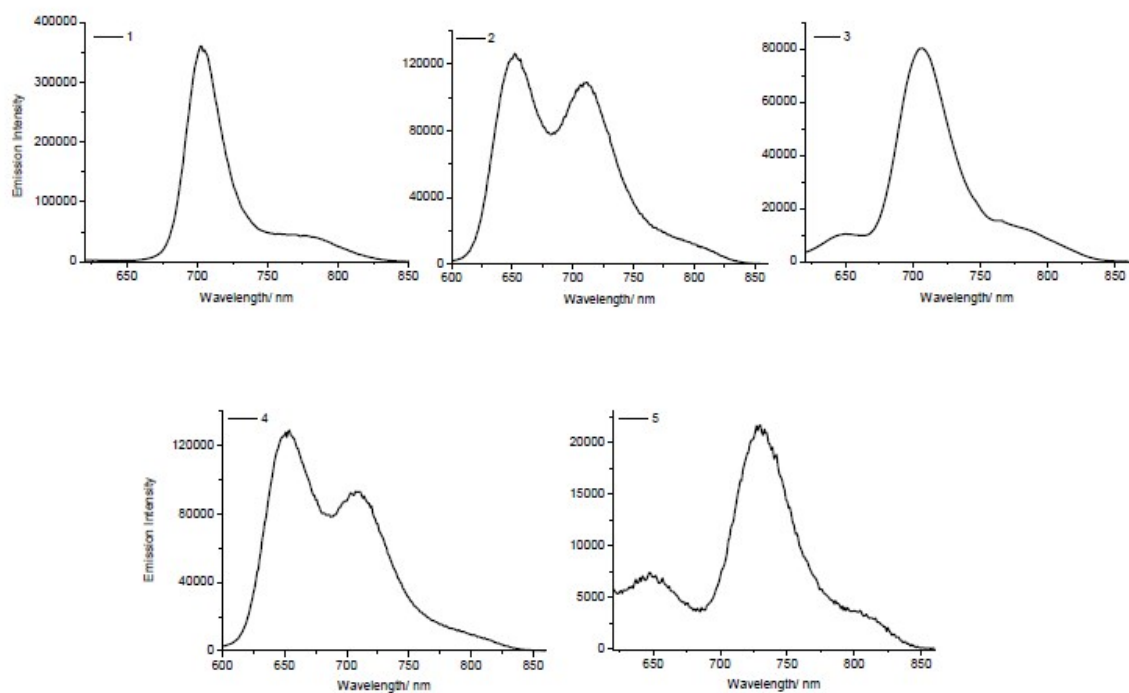


Fig. S17 Emission spectra of complexes **1–5** in 2-methyltetrahydrofuran glasses at 77 K ($\lambda_{\text{ex}} = 500$ nm).

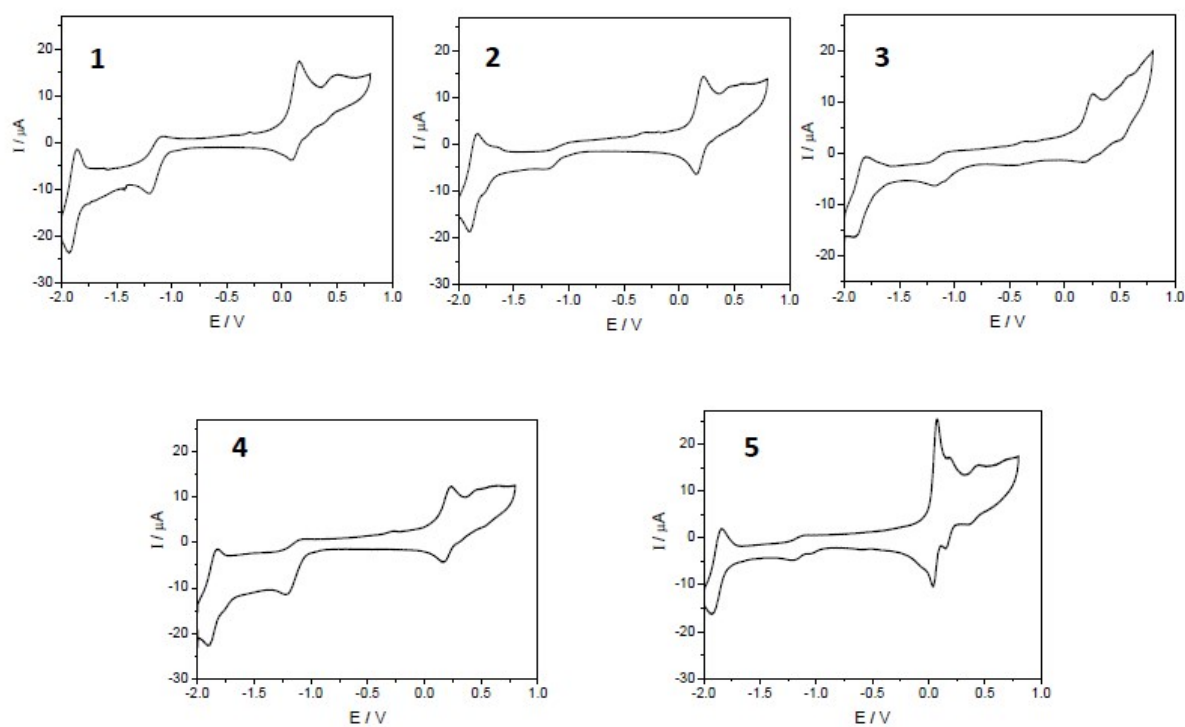


Fig. S18 Cyclic voltammetric responses for complexes **1–5** (1×10^{-4} M) dissolved in acetonitrile containing 0.1 M $[n\text{-Bu}_4\text{N}]\text{PF}_6$.

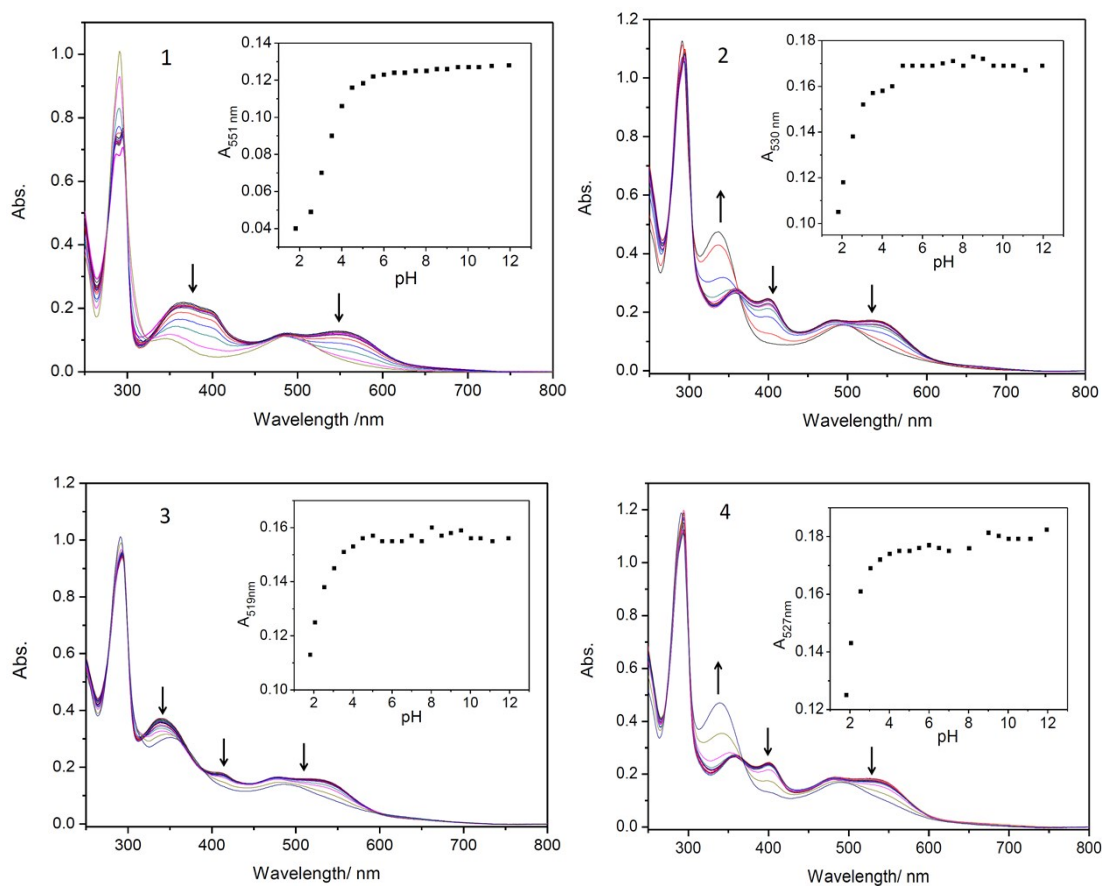


Fig. S19 Absorption spectral changes of complexes 1–4 (20 μM) after being incubated for 4 h in ethanol/Britton–Robinson buffer solutions (v/v=1:2, pH 11.95–1.82), respectively. Arrows show spectral changes upon decreasing pH. Inset: Changes of absorption intensity at different pHs.

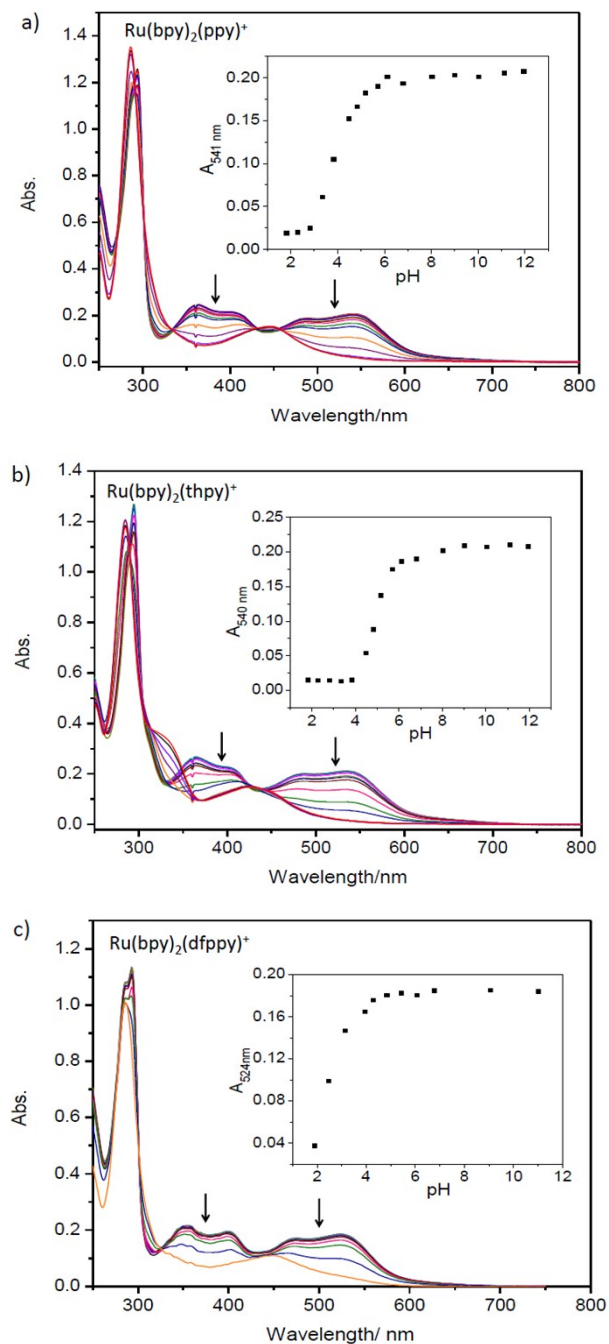


Fig. S20 Absorption spectral changes of complexes (20 μM) after being incubated for 4 h in CH₃CN/ethanol/Britton-Robinson buffer solutions (v/v/v = 2:8:90), respectively. Arrows show spectral changes upon decreasing pH. Inset: Changes of absorption intensity at different pHs. (a) pH=11.95–1.82; (b) pH = 11.95–1.82 (c) pH=11.02–1.91.

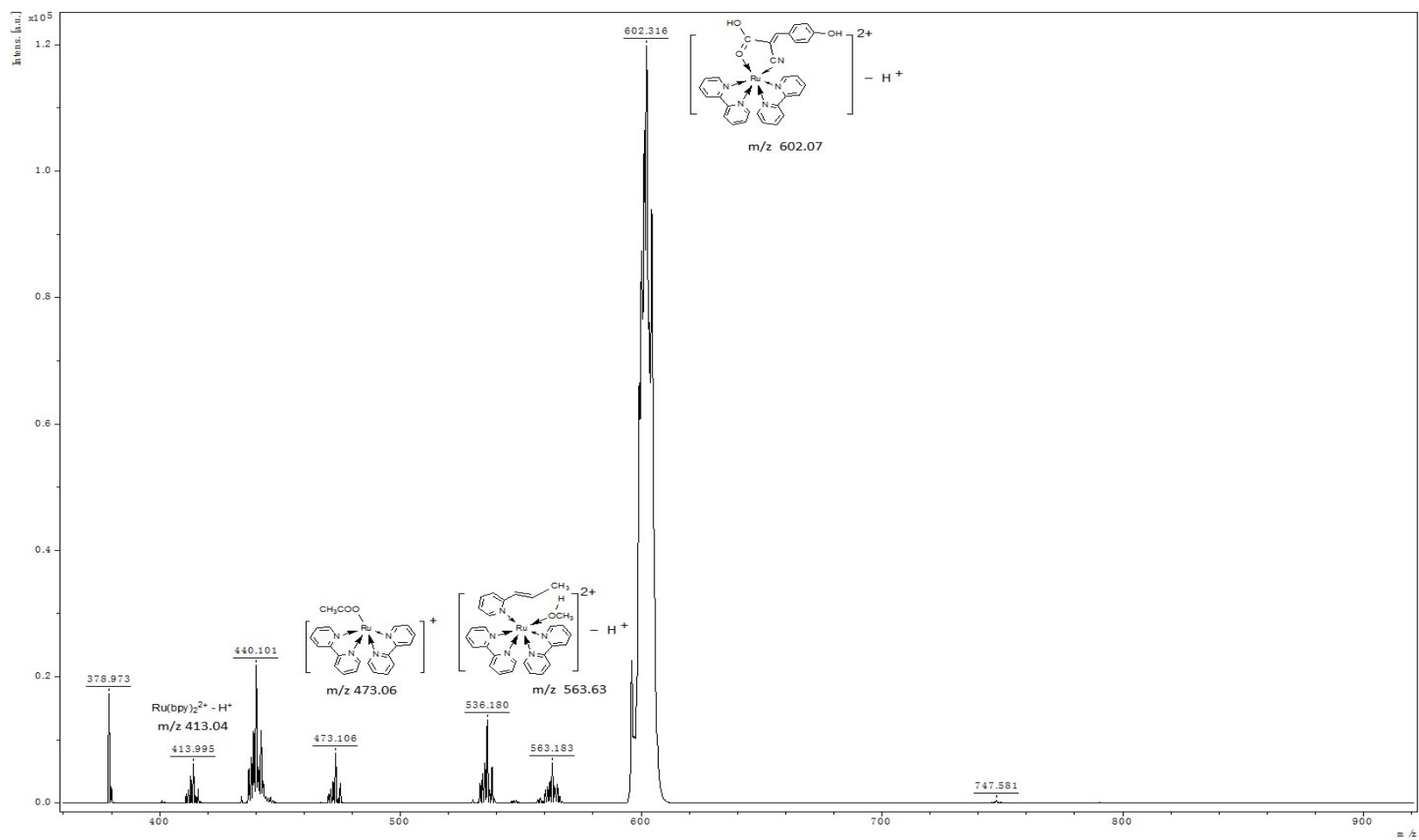


Fig. S21 MS spectrum of complex **1** incubated in $\text{CH}_3\text{OH}/\text{HAc}/\text{H}_2\text{O}$ ($v/v/v=1:1:1$) for 4 h.

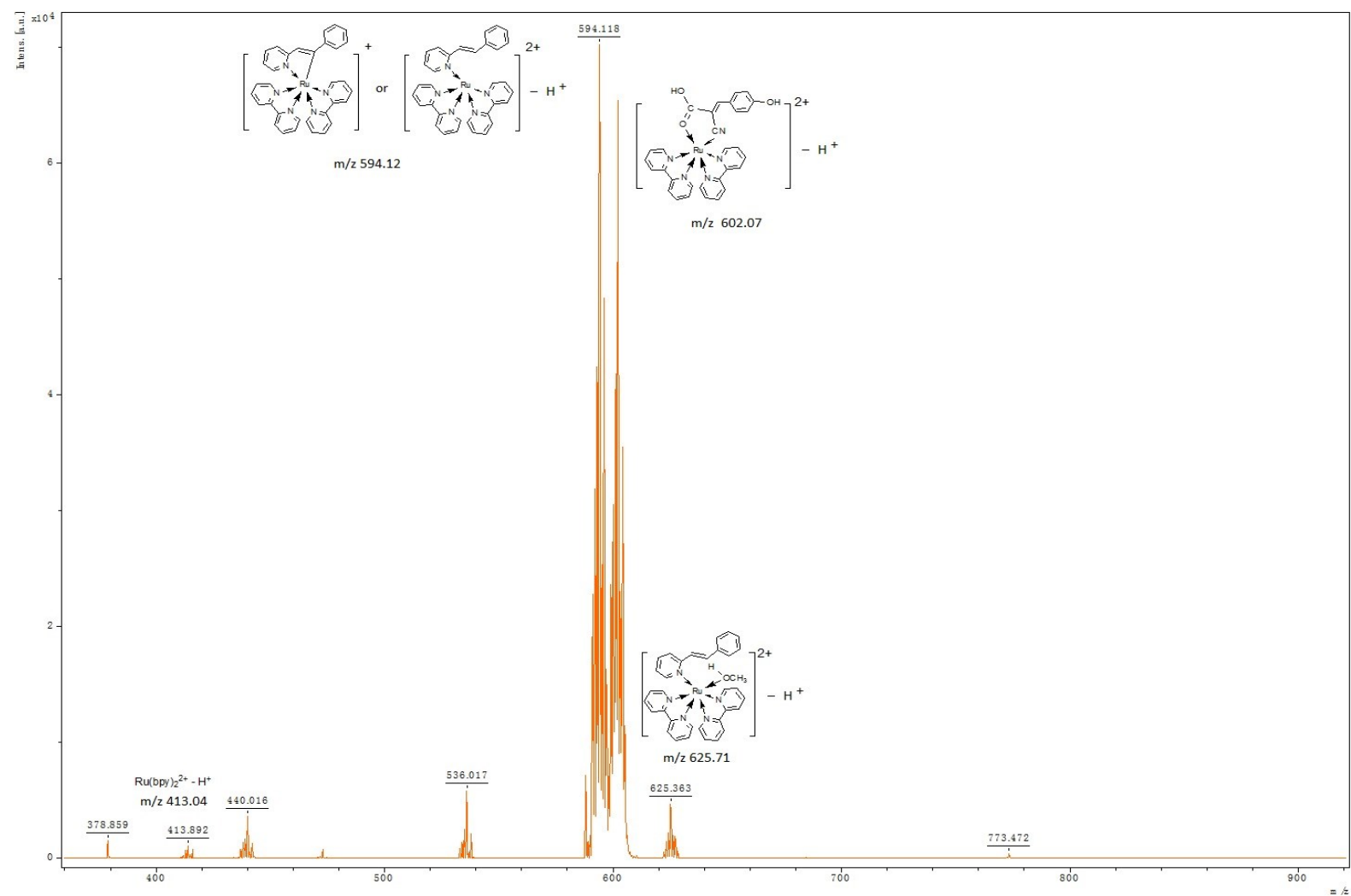


Fig. S22 MS spectrum of complex **2** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 4 h.

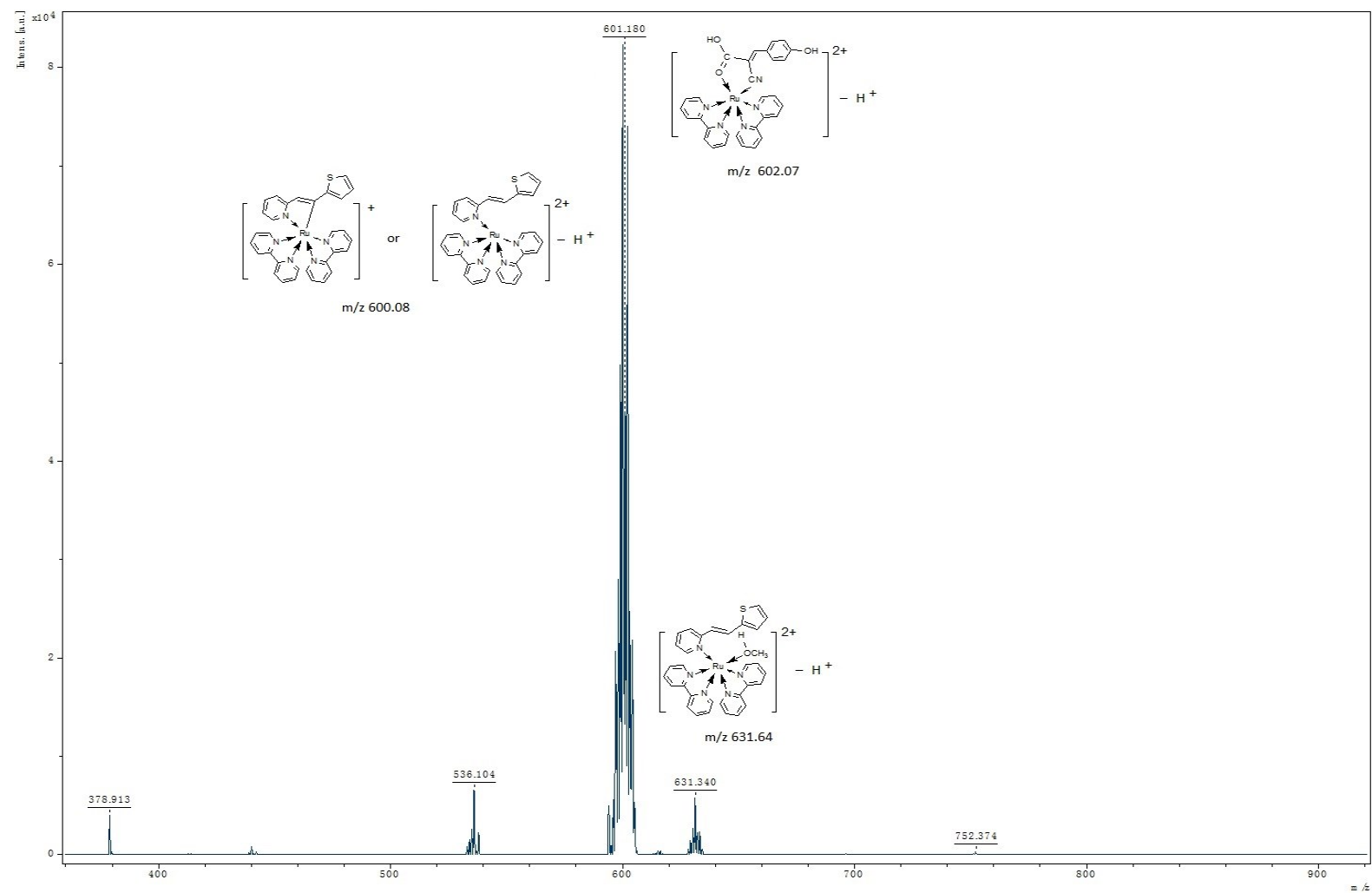


Fig. S23 MS spectrum of complex **3** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 4 h.

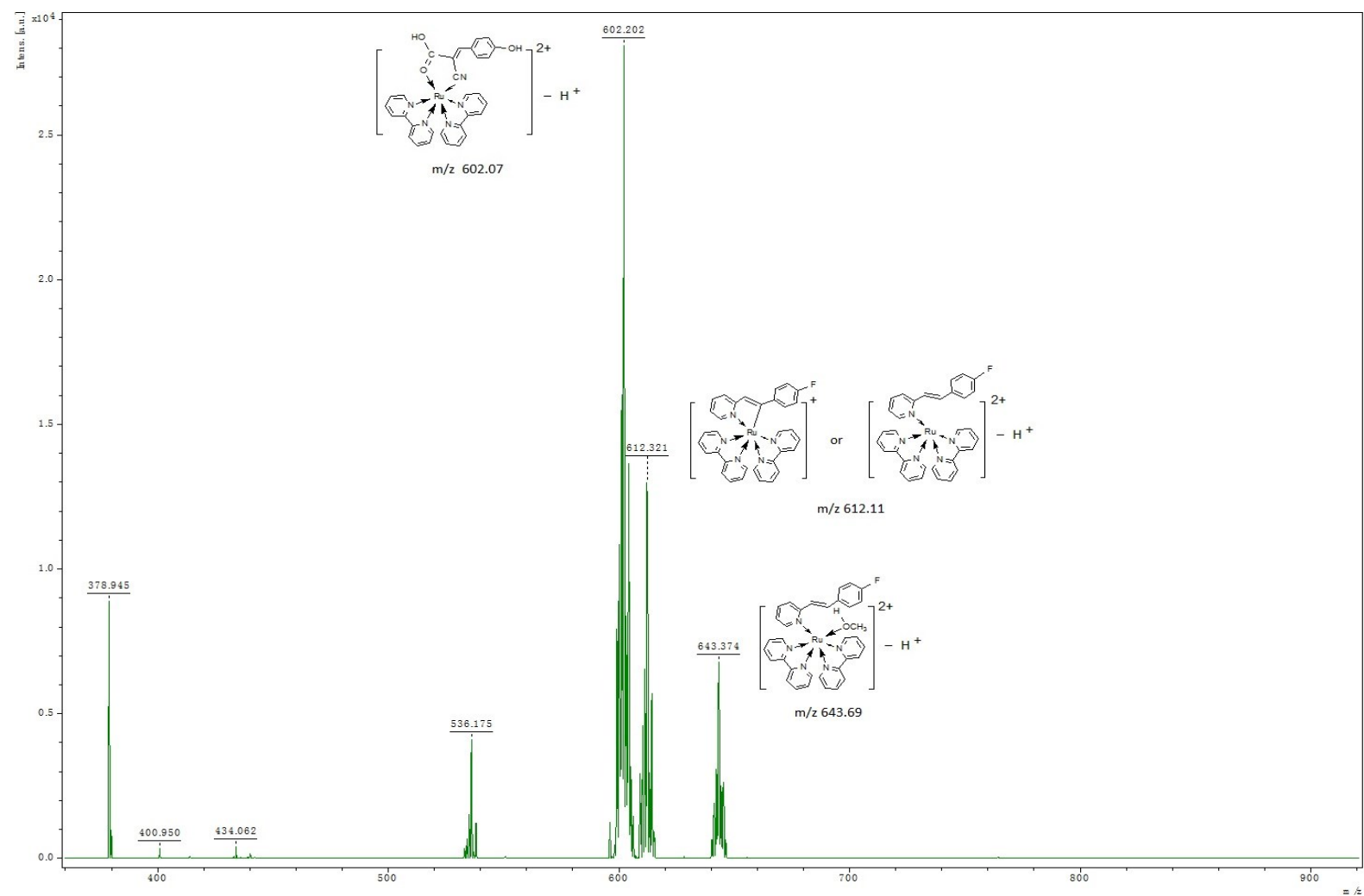


Fig. S24 MS spectrum of complex **4** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 4 h.

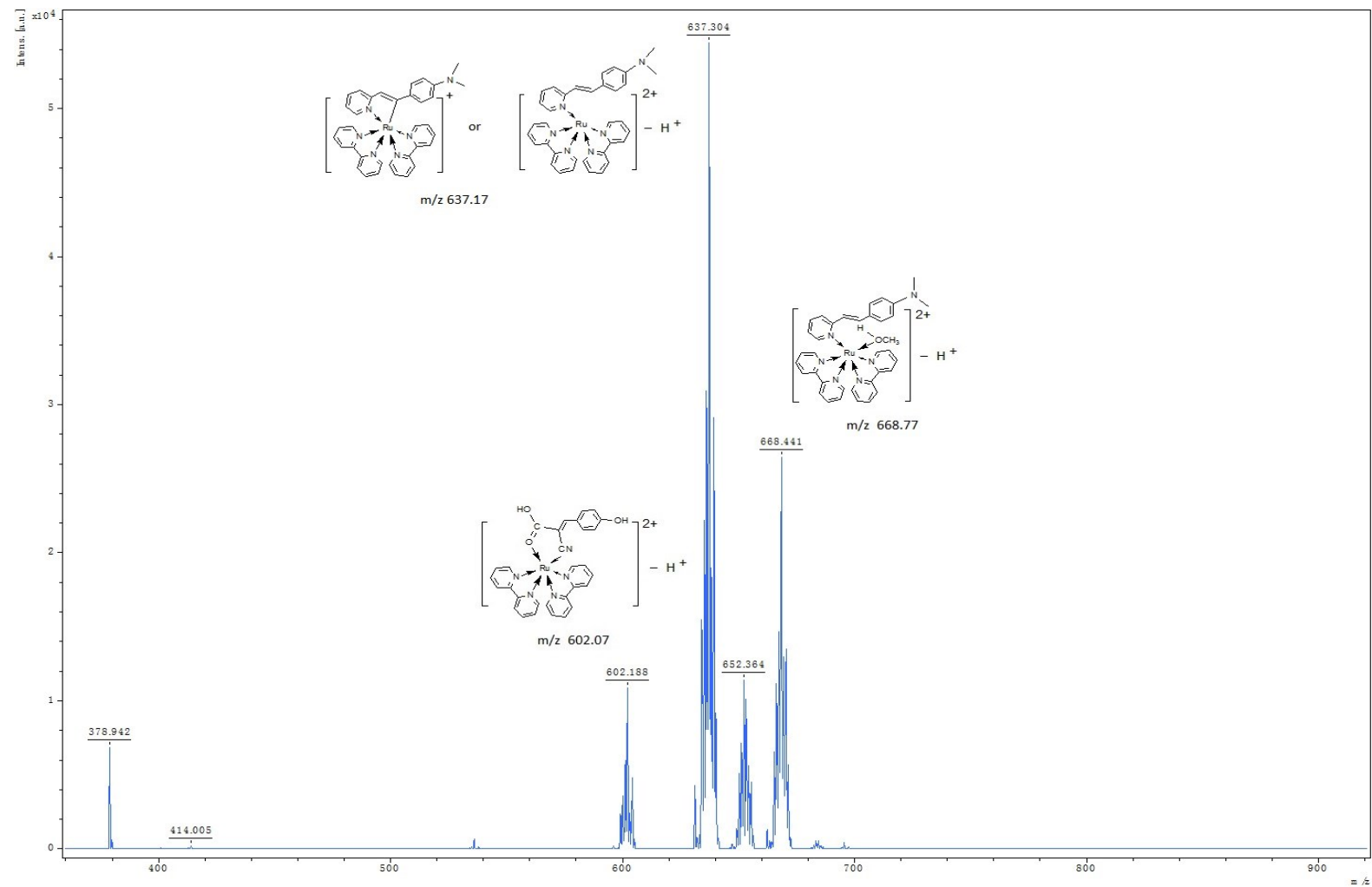


Fig. S25 MS spectrum of complex **5** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 4 h.

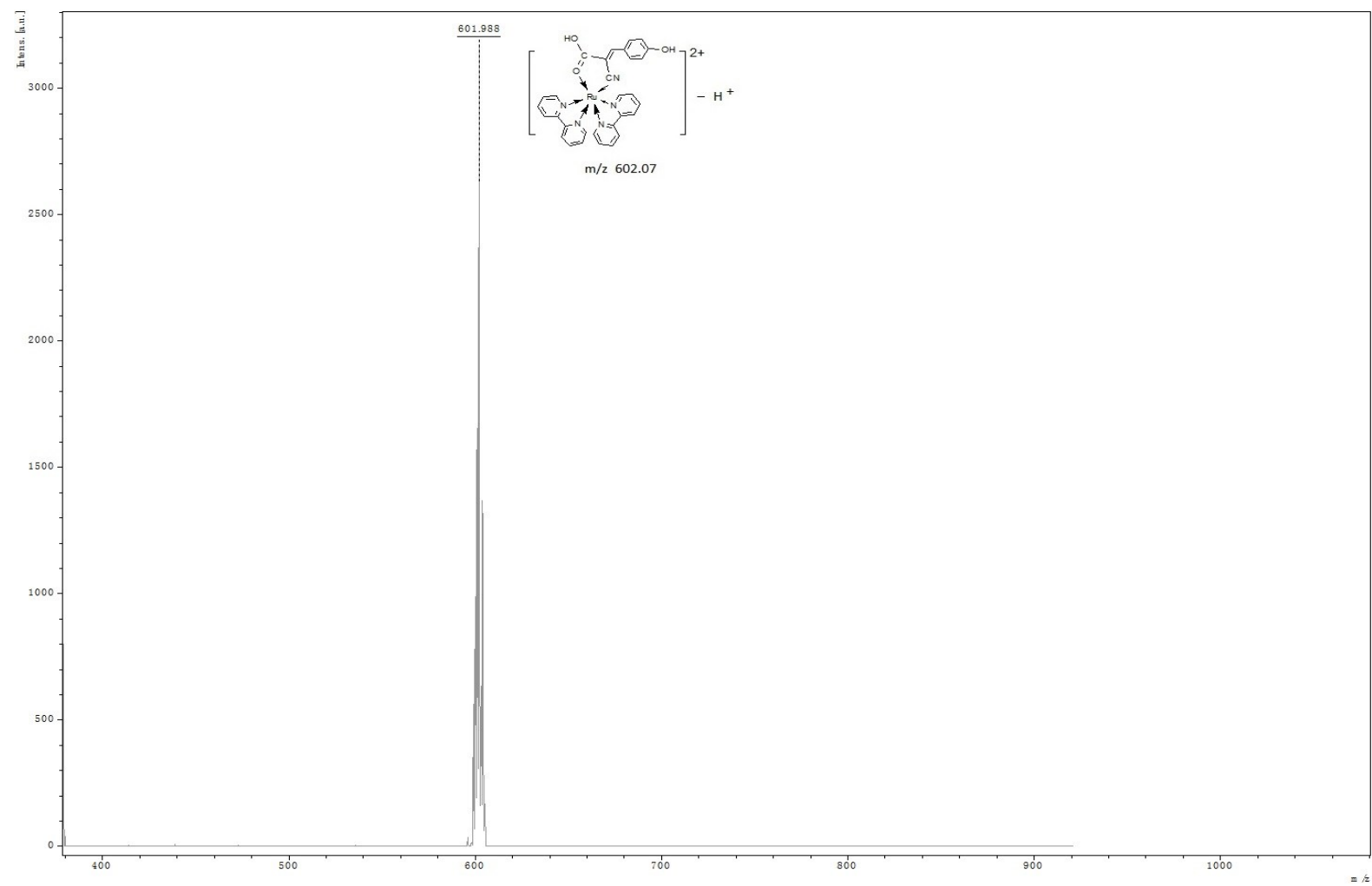


Fig. S26 MS spectrum of complex **1** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 20 h

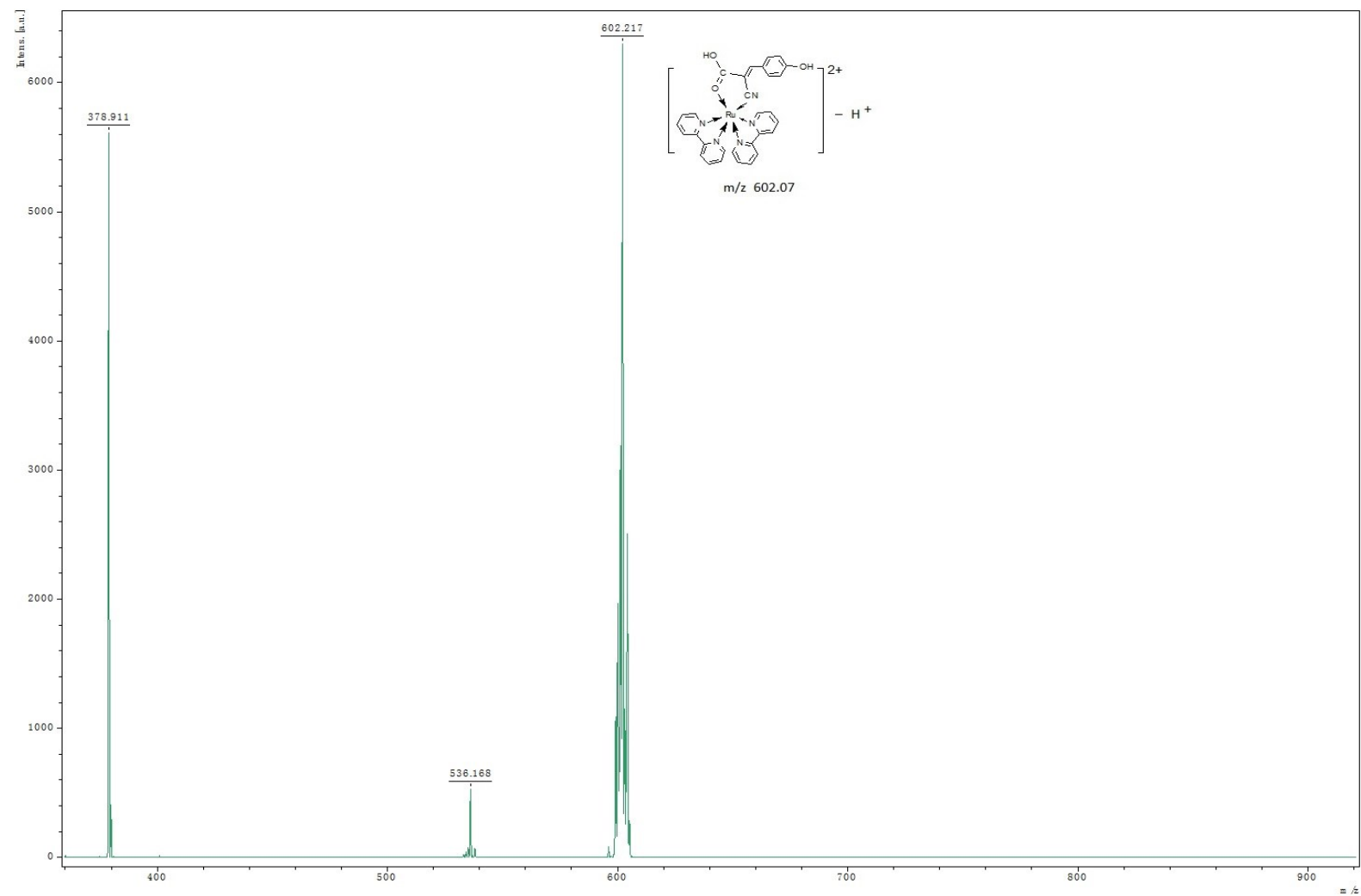


Fig. S27 MS spectrum of complex **2** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 20 h.

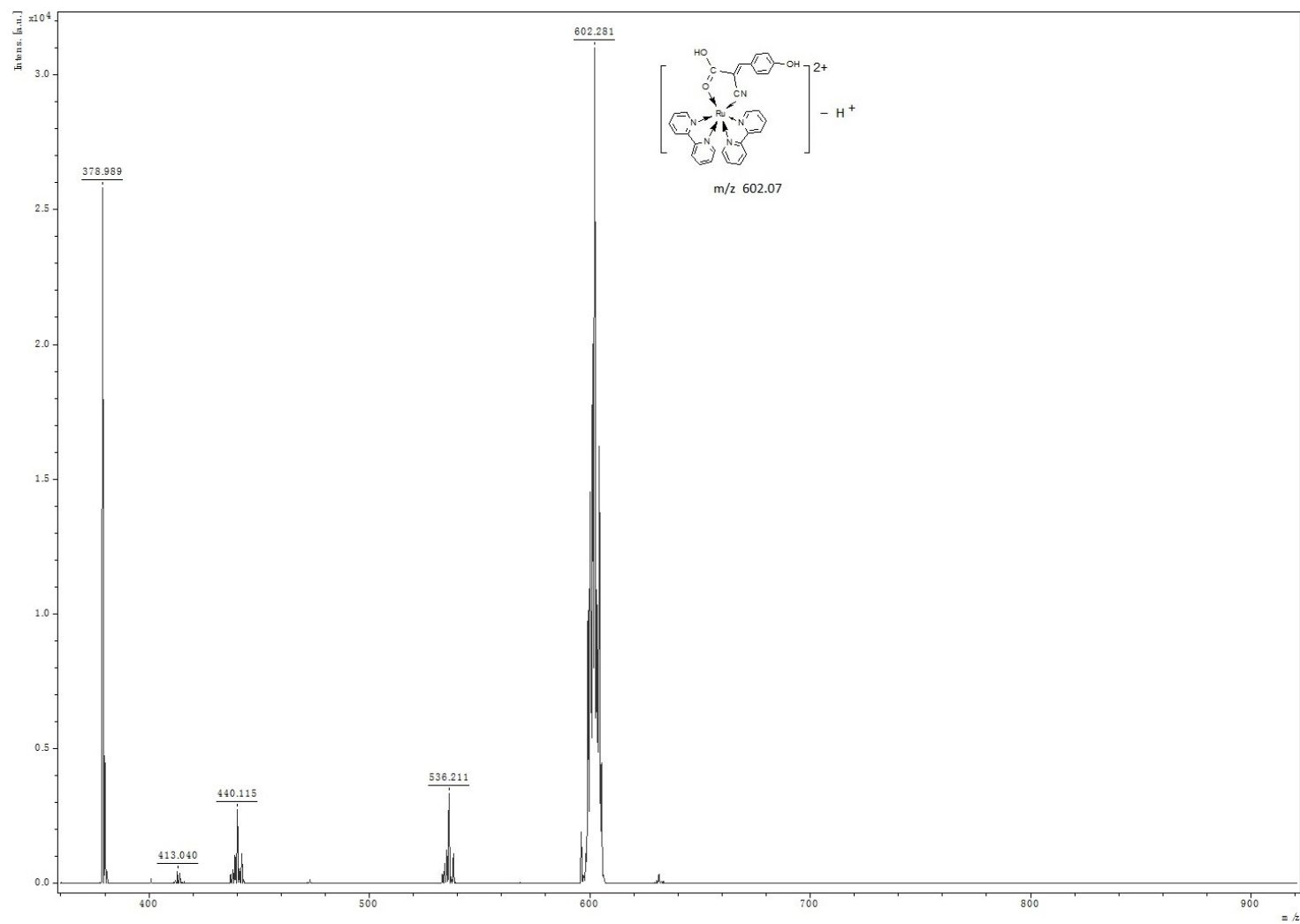


Fig. S28 MS spectrum of complex **3** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 20 h.

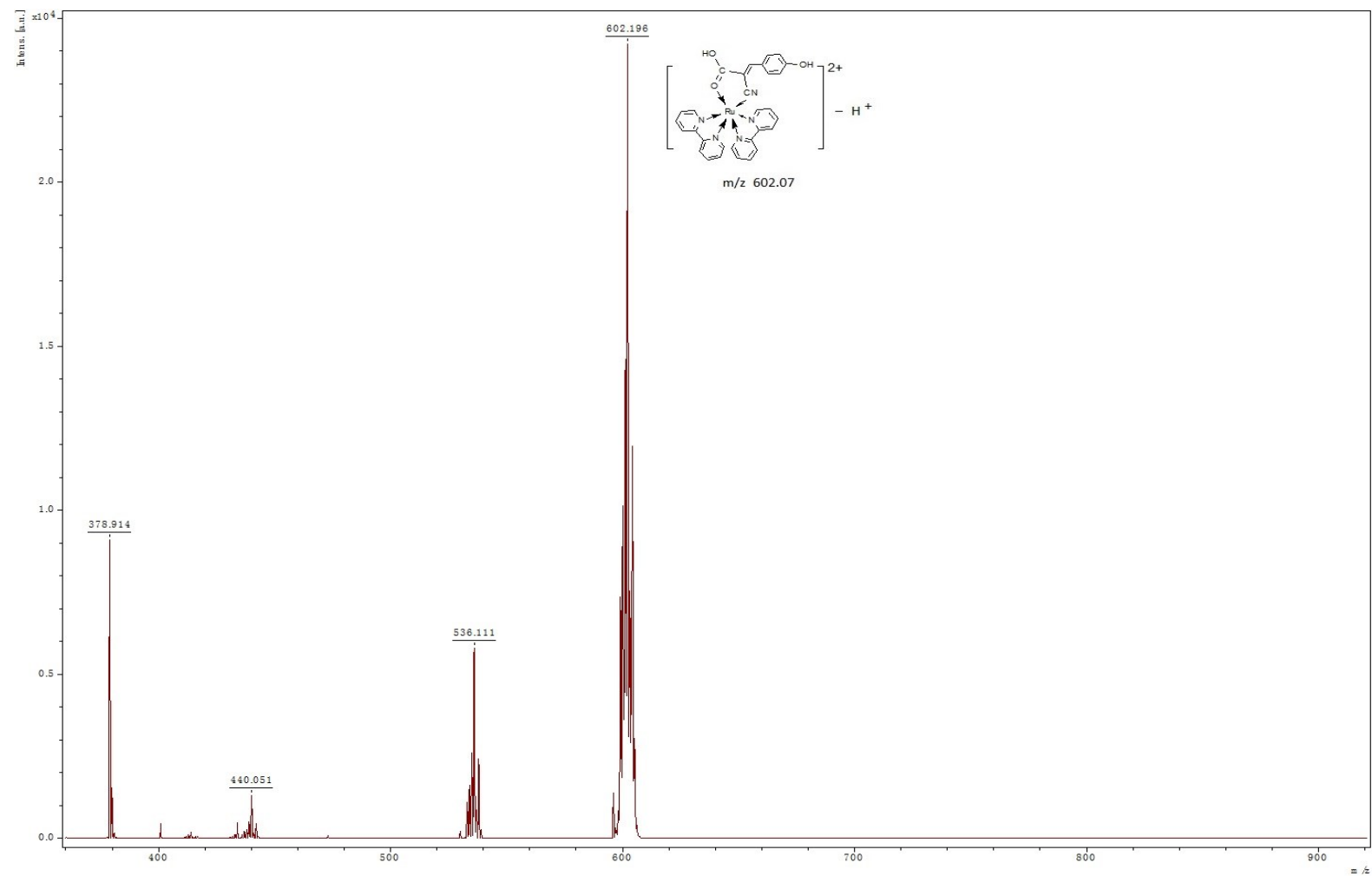


Fig. S29 MS spectrum of complex **4** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 20 h.

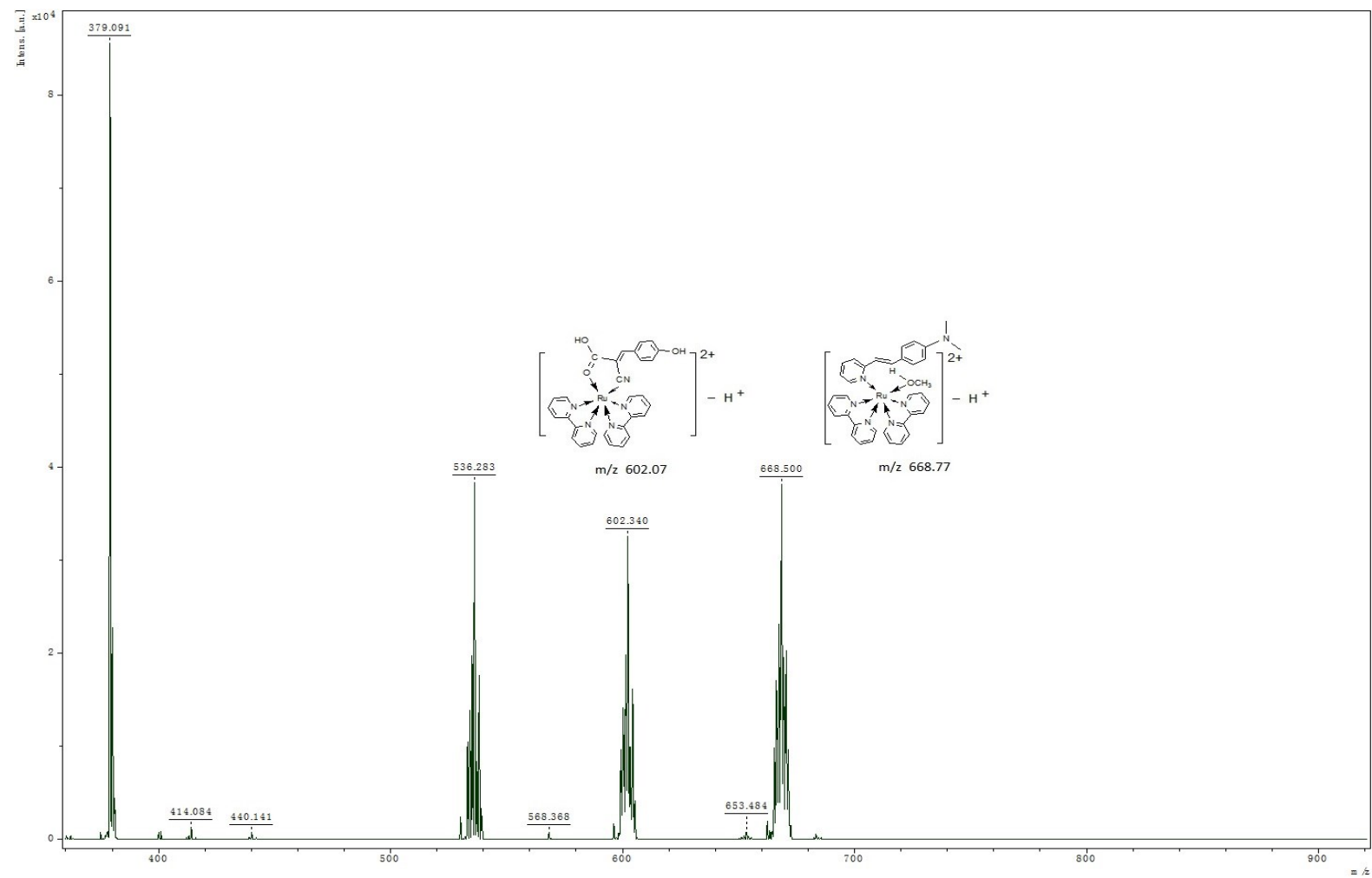


Fig. S30 MS spectrum of complex **5** incubated in CH₃OH/HAc/H₂O (v/v/v=1:1:1) for 20 h.

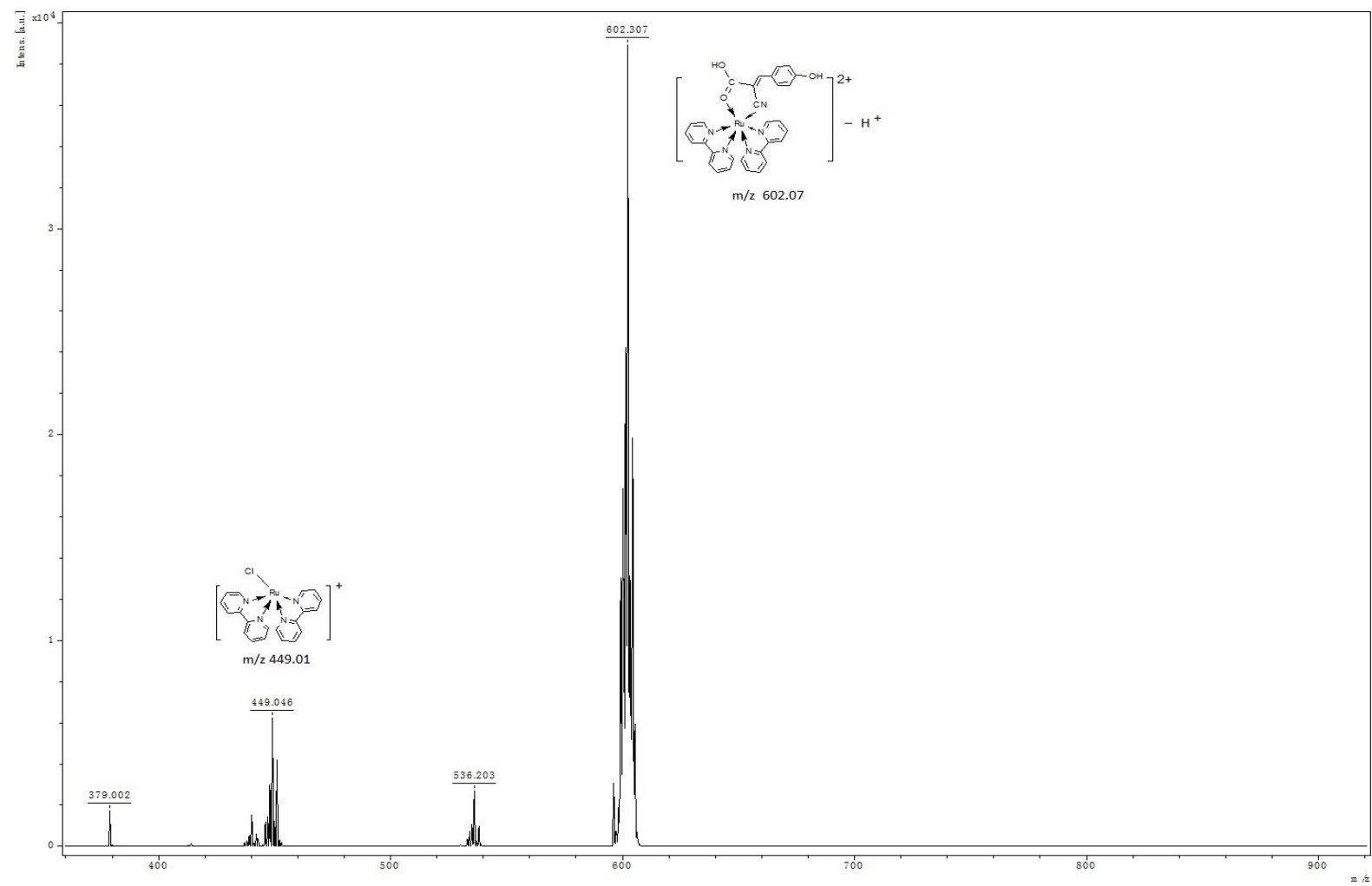


Fig. S31 MS spectrum of complex **1** incubated in CH₃OH/HCl/H₂O (v/v =1:1:1) for 20 h.

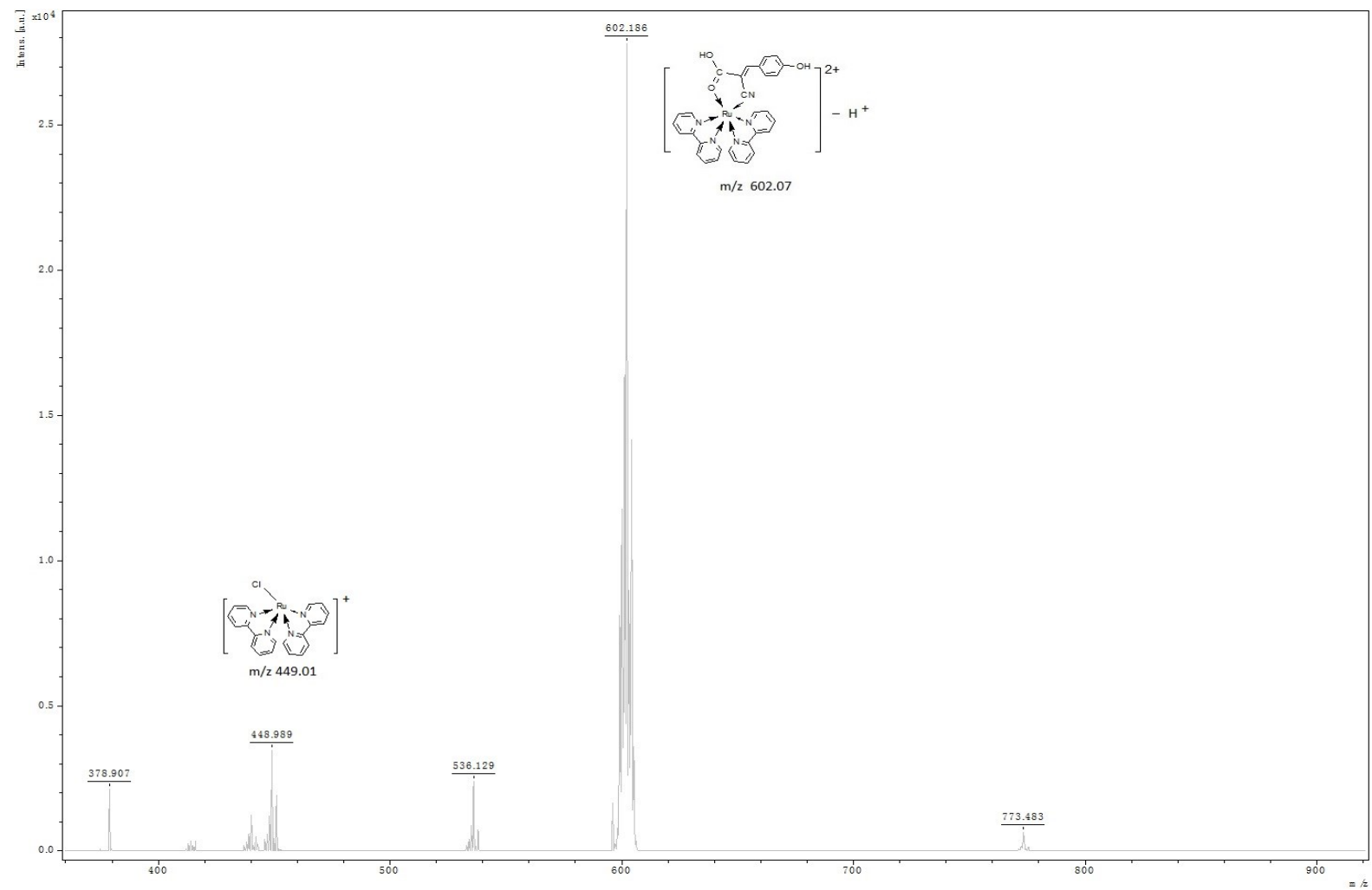


Fig. S32 MS spectrum of complex **2** incubated in $\text{CH}_3\text{OH}/\text{HCl}/\text{H}_2\text{O}$ (v/v = 1:1:1) for 20 h

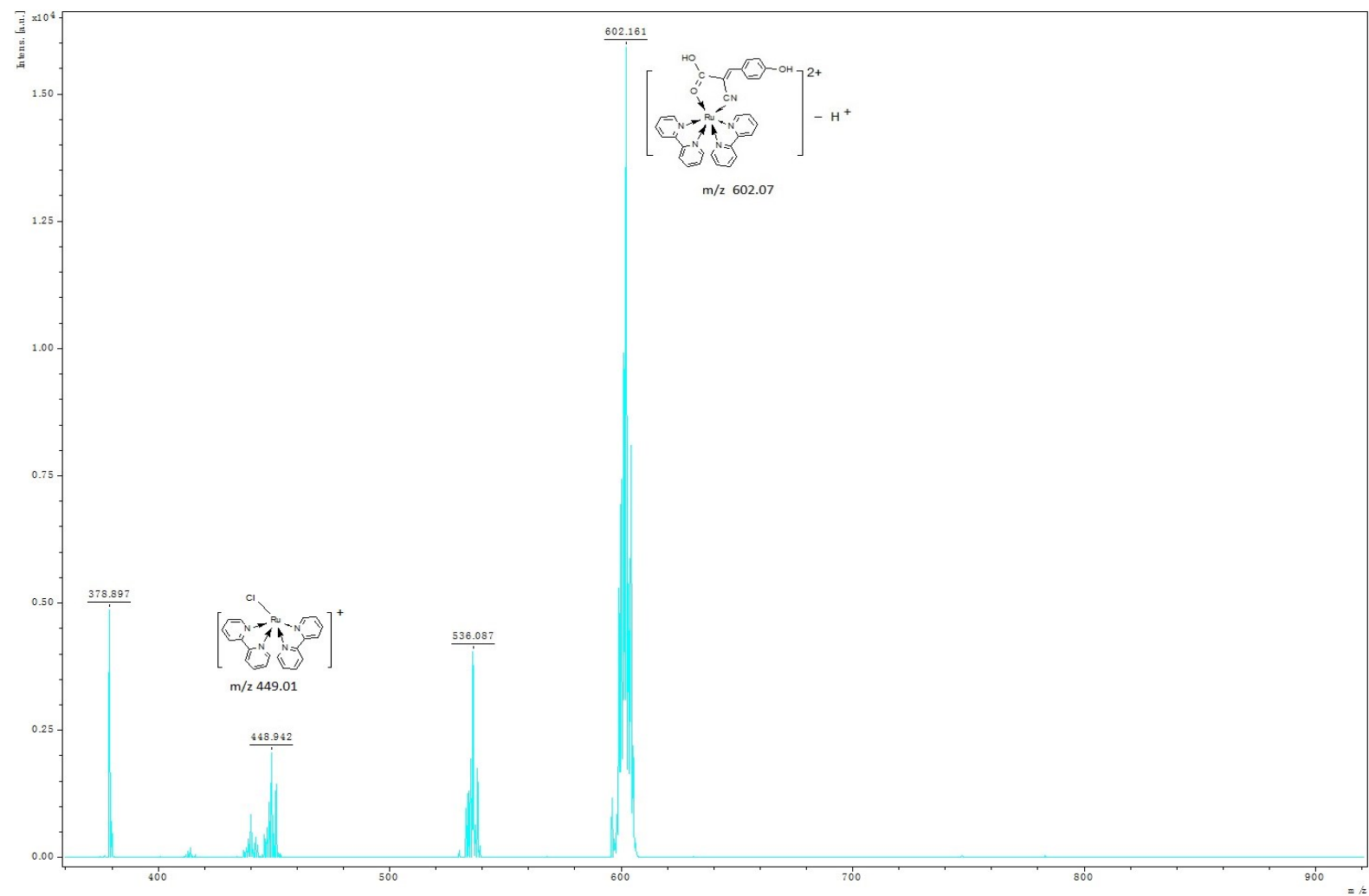


Fig. S33 MS spectrum of complex **3** incubated in CH₃OH/HCl/H₂O (v/v =1:1:1) for 20 h

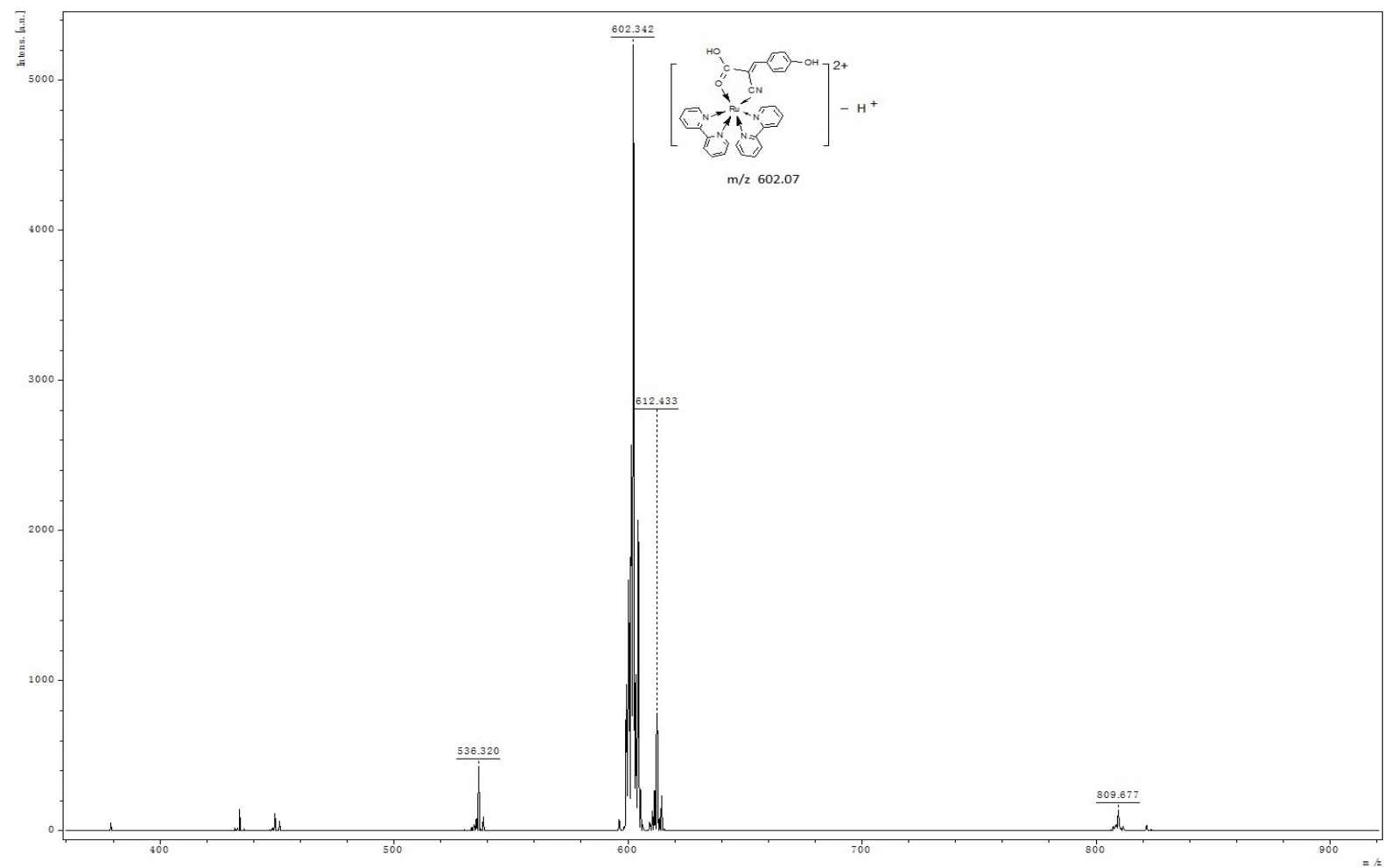


Fig. S34 MS spectrum of complex **4** incubated in CH₃OH/HCl/H₂O (v/v =1:1:1) for 20 h

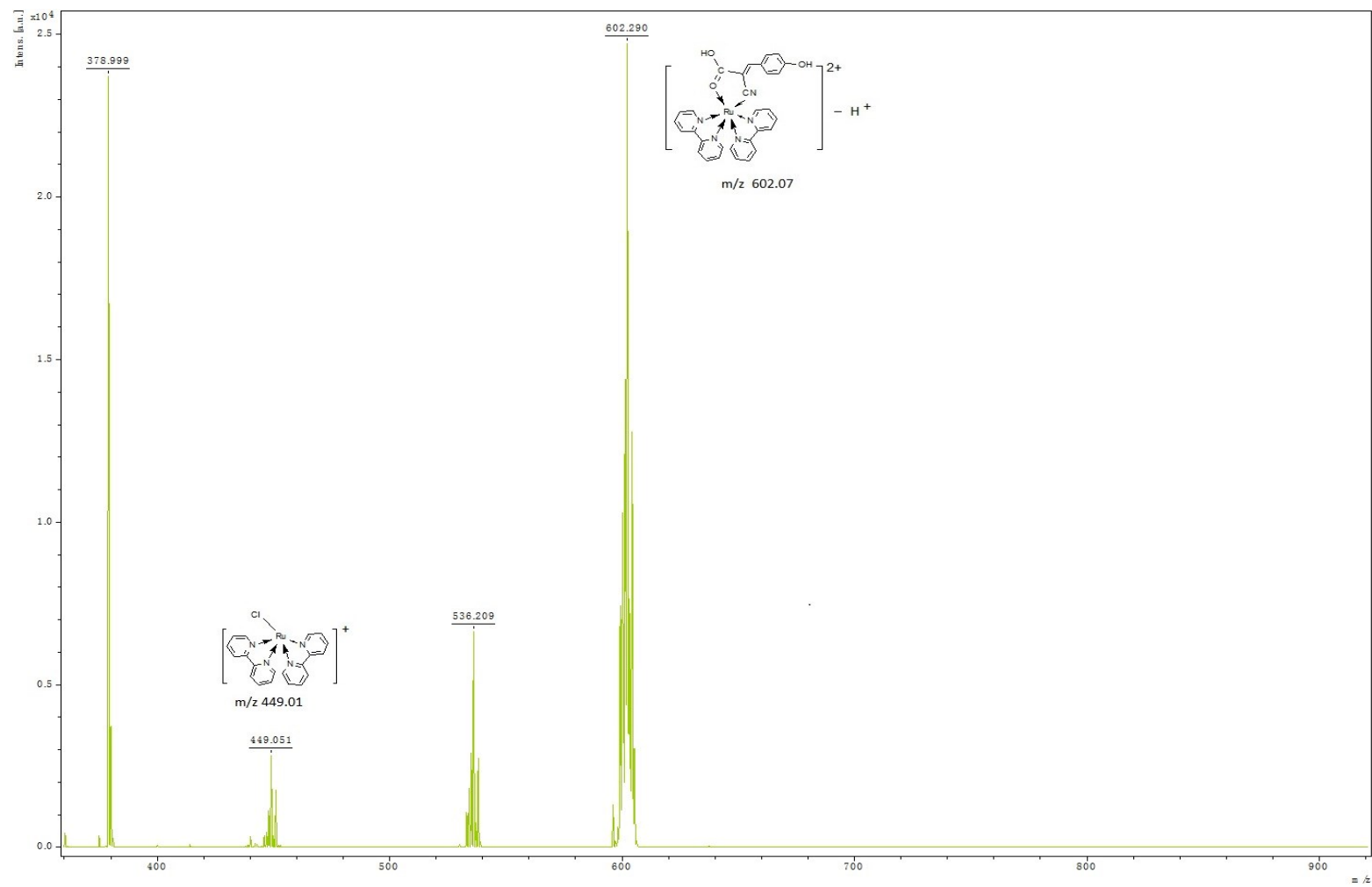


Fig. S35 MS spectrum of complex **5** incubated in CH₃OH/HCl/H₂O (v/v =1:1:1) for 20 h

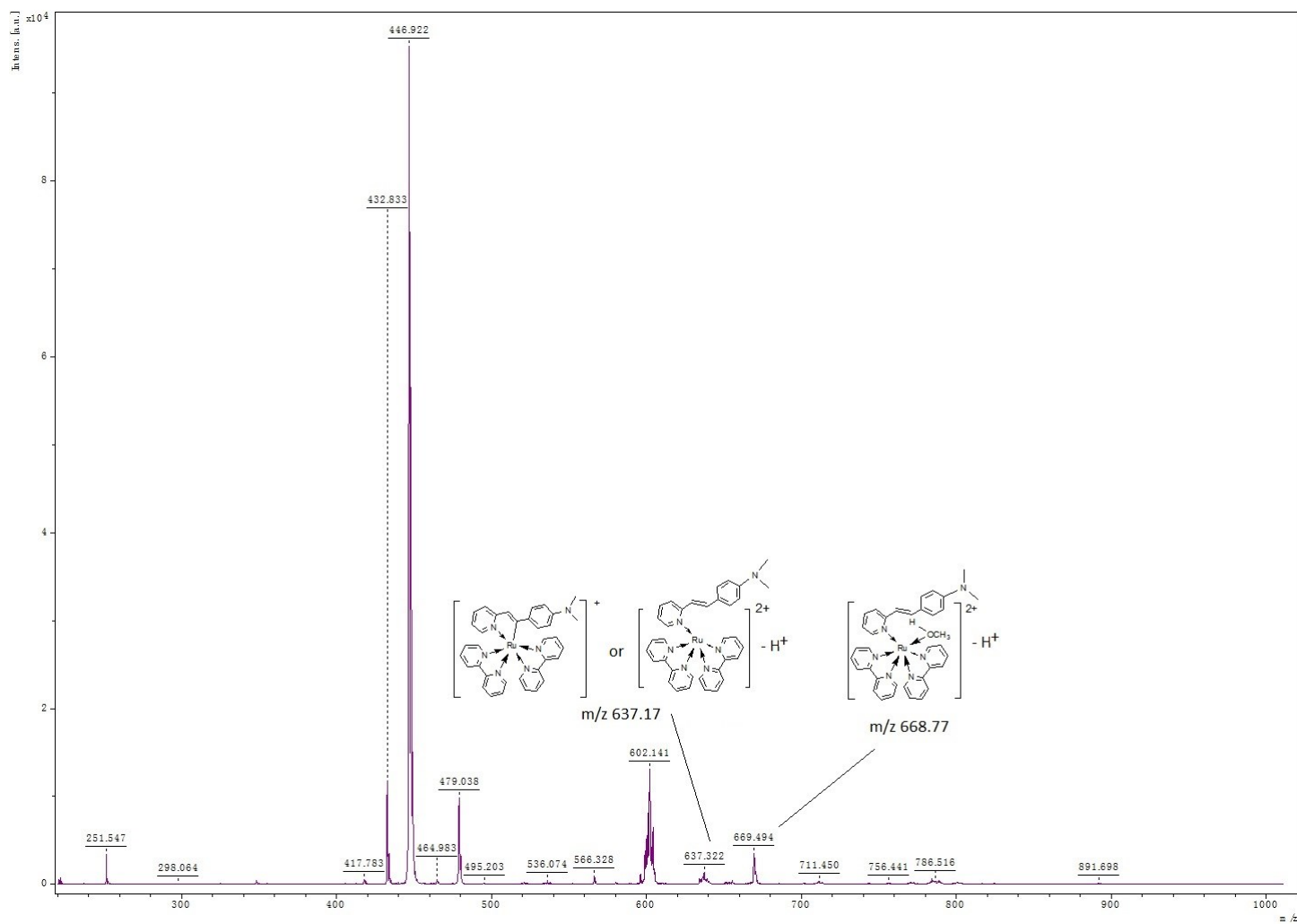


Fig. S36 MS spectrum of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ with ligand of complex **5** in CH_3OH treated with AgBF_4 and then NaOH .