## Supporting Information

# Biotinylated Polymer-Ruthenium Conjugates: In Vitro and In Vivo Studies in a Triple-Negative Breast Cancer Model

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**FT-IR spectra**

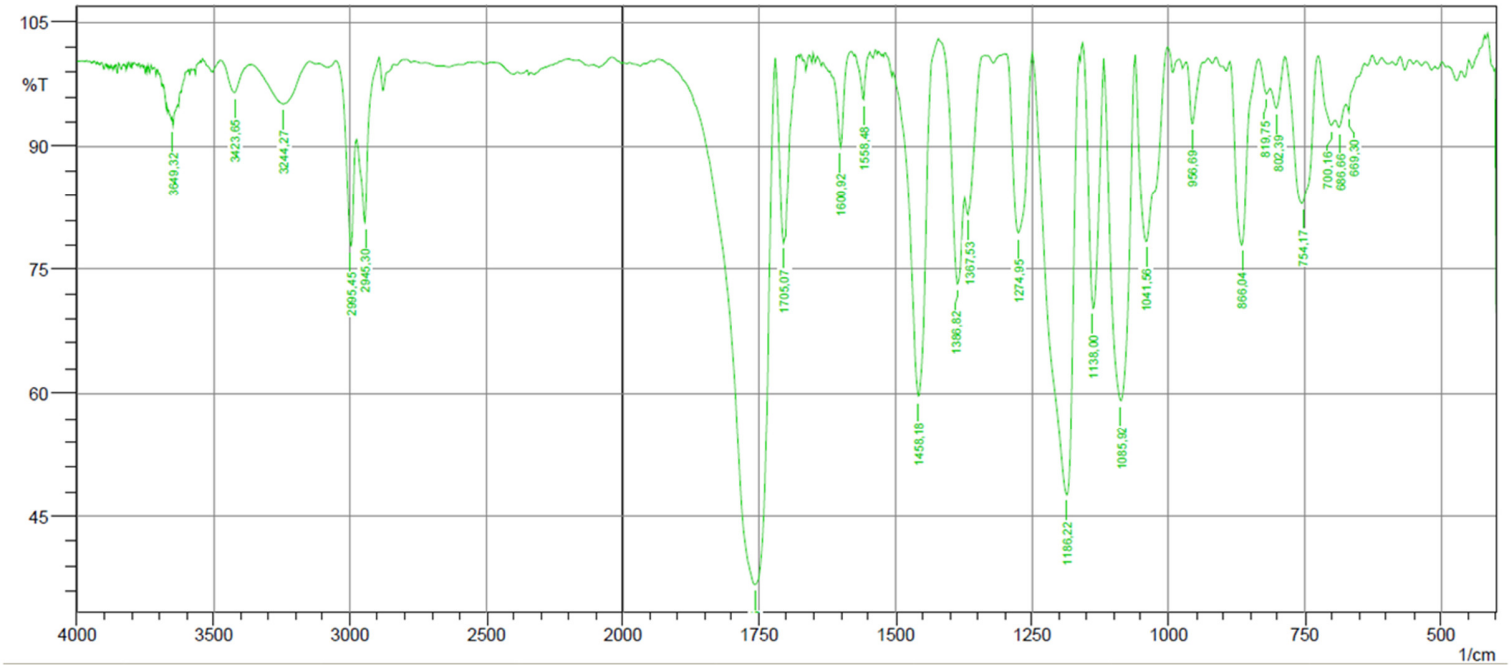


**Figure S1.** FT-IR spectrum of Ligand L1.

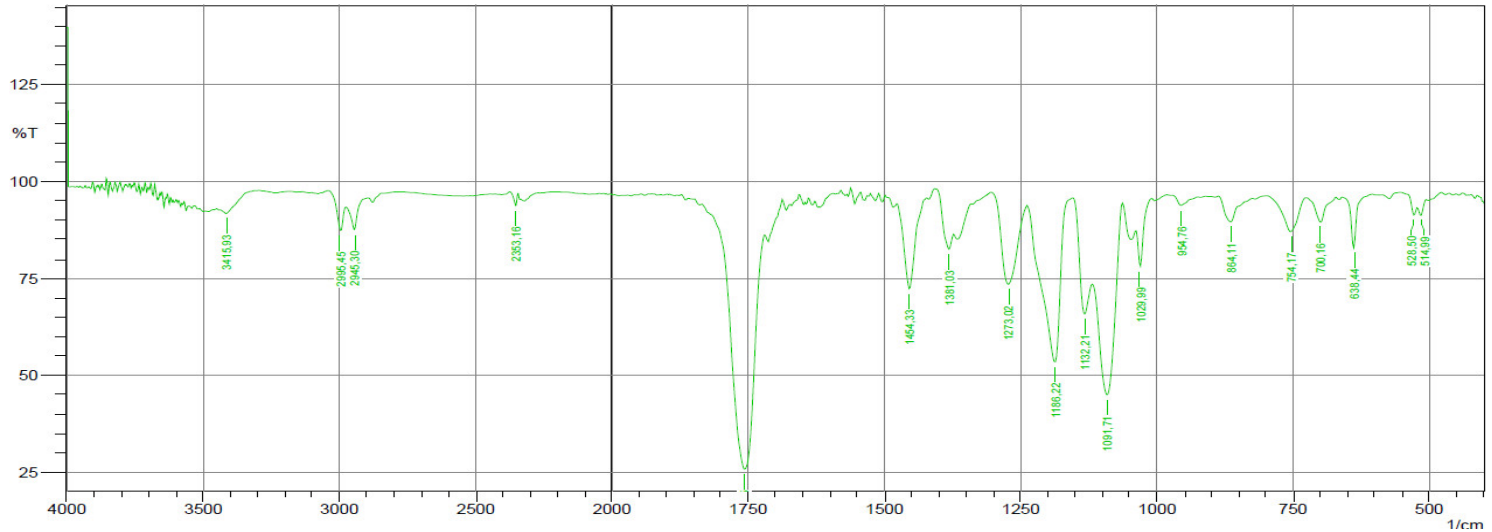


**Figure S2.** FT-IR spectrum of Complex **1**.

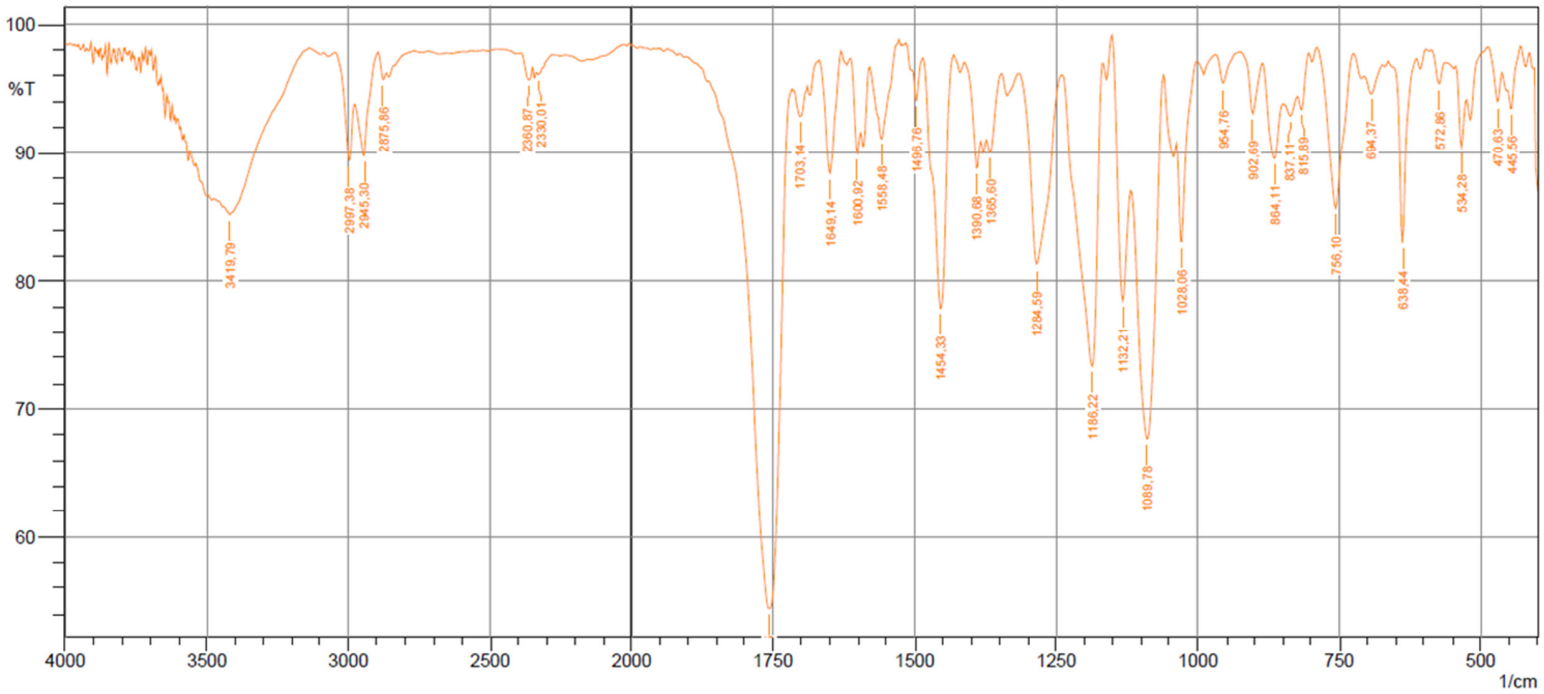


**Figure S3.** FT-IR spectrum of complex **2**.

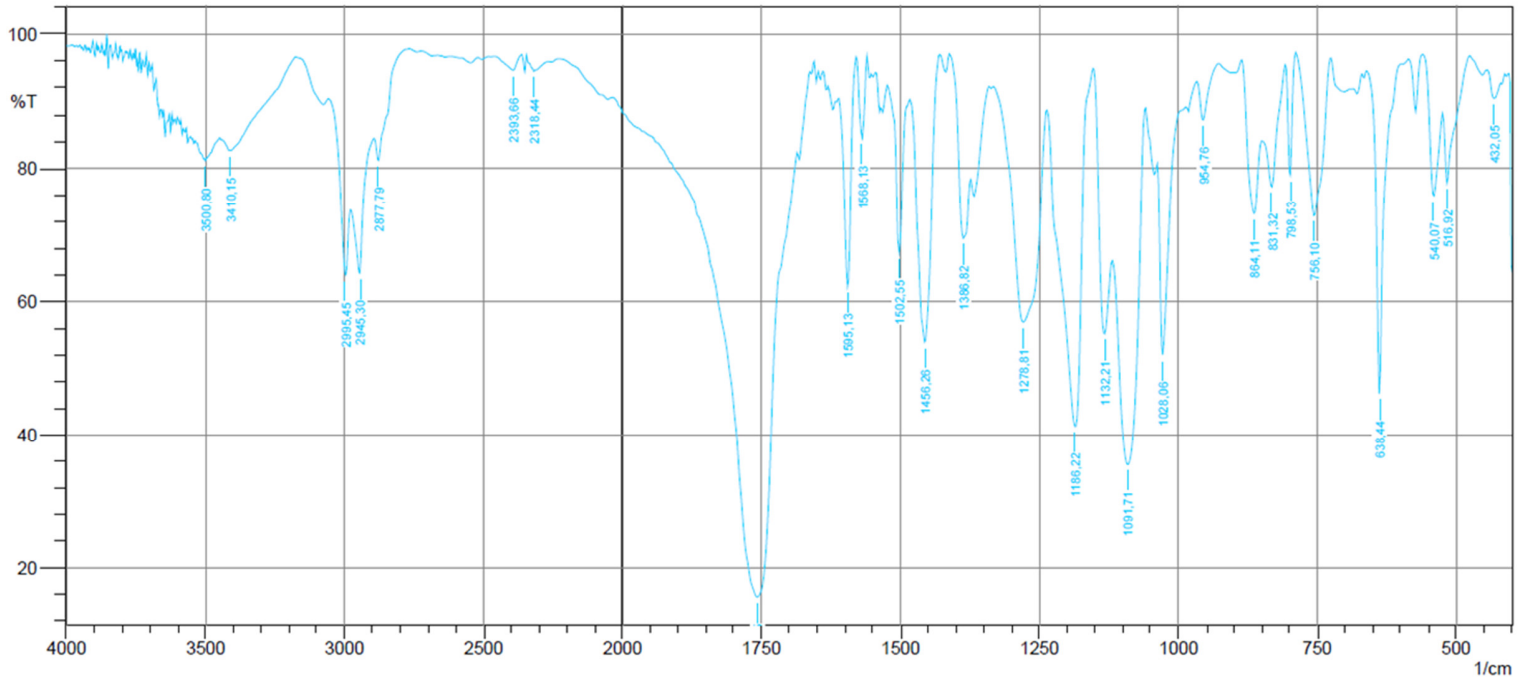


**Figure S4.** FT-IR spectrum of complex **3**.

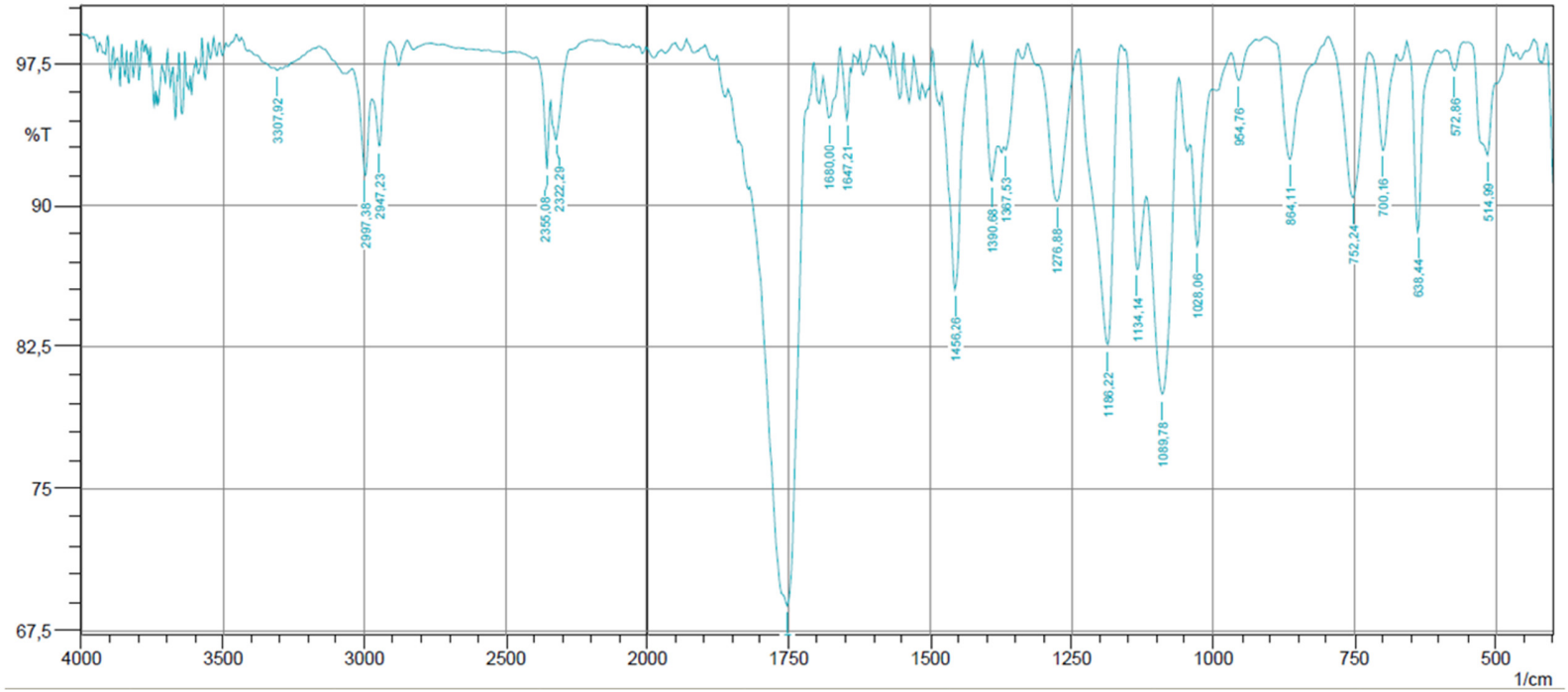


**Figure S5.** FT-IR spectrum of complex **4**.

**NMR spectra**

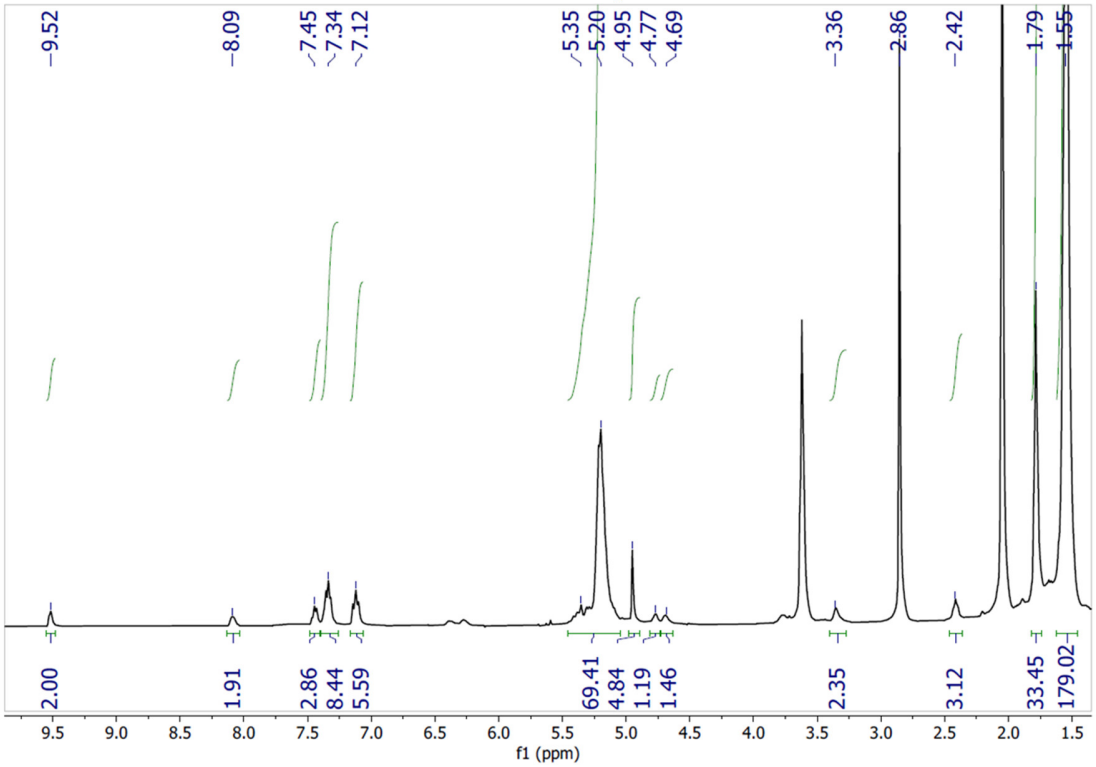


**Figure S6.** $^{1}$H-NMR spectrum of complex **1** in acetone-$d_6$ at 298 K.

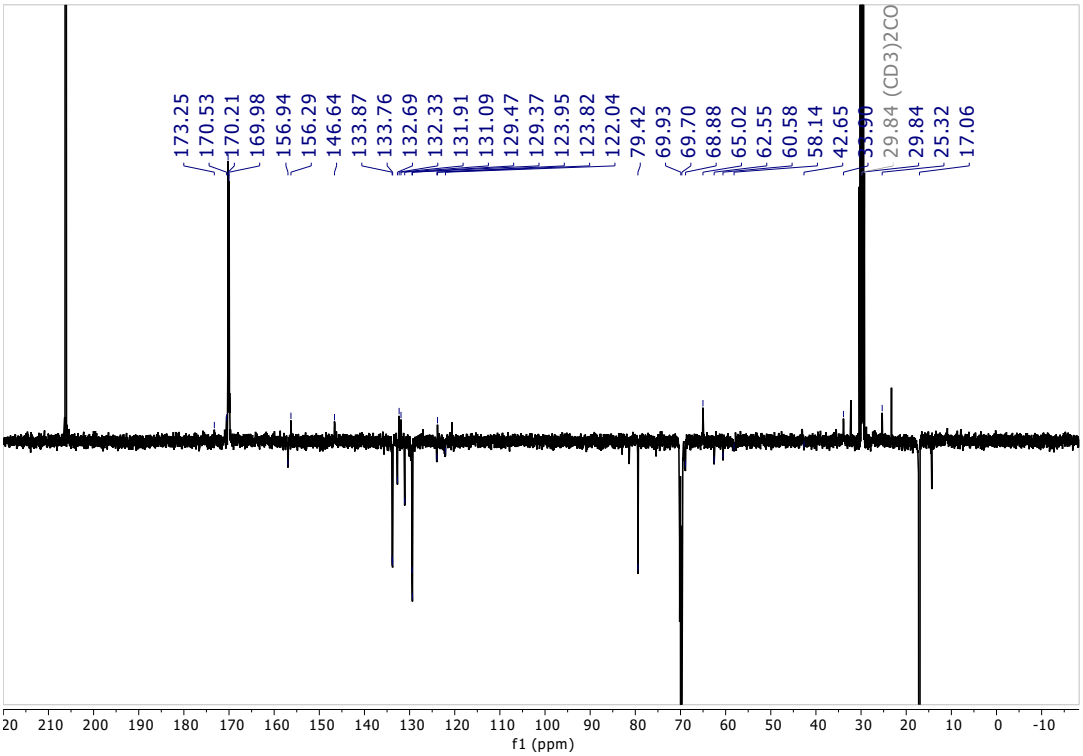


**Figure S7.** APT $^{13}$C{$^{1}$H}-NMR spectrum of complex **1** in acetone-$d_6$ at 298 K.

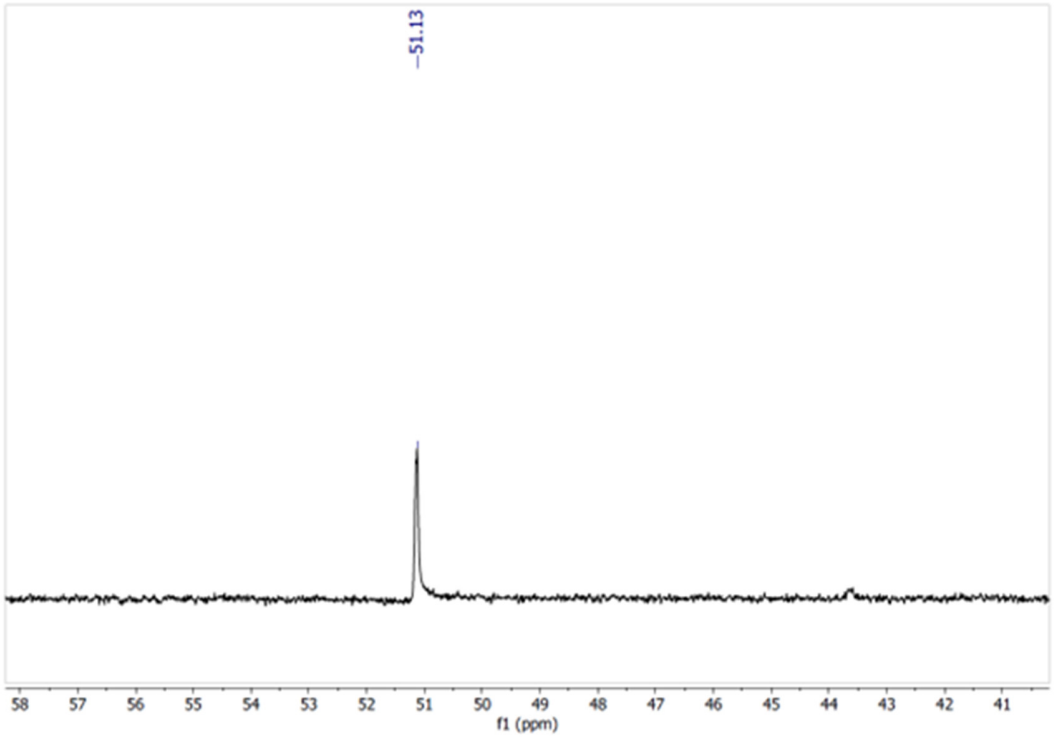


**Figure S8.** $^{31}P\{^{1}H\}$-NMR spectrum of complex **1** in acetone-$d_6$ at 298 K.

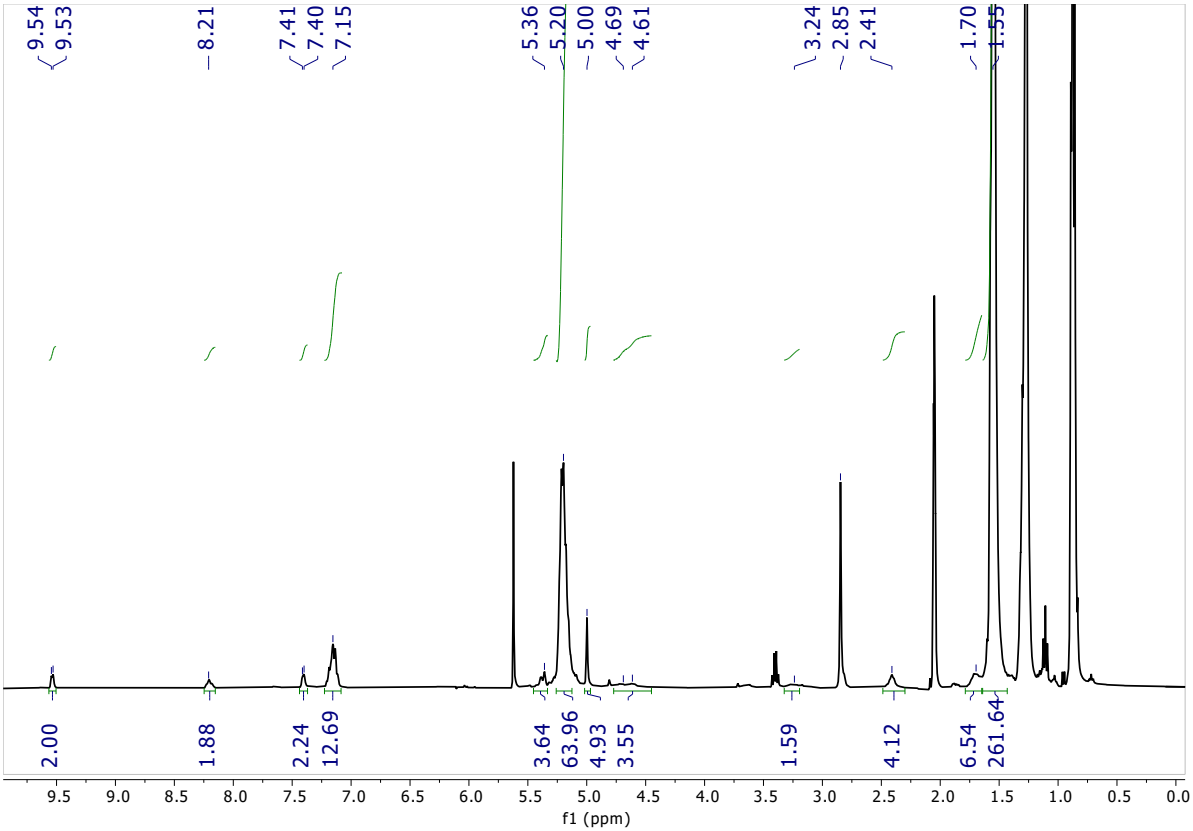


**Figure S9.** $^{1}H$-NMR spectrum of complex **2** in acetone-$d_6$ at 298 K.

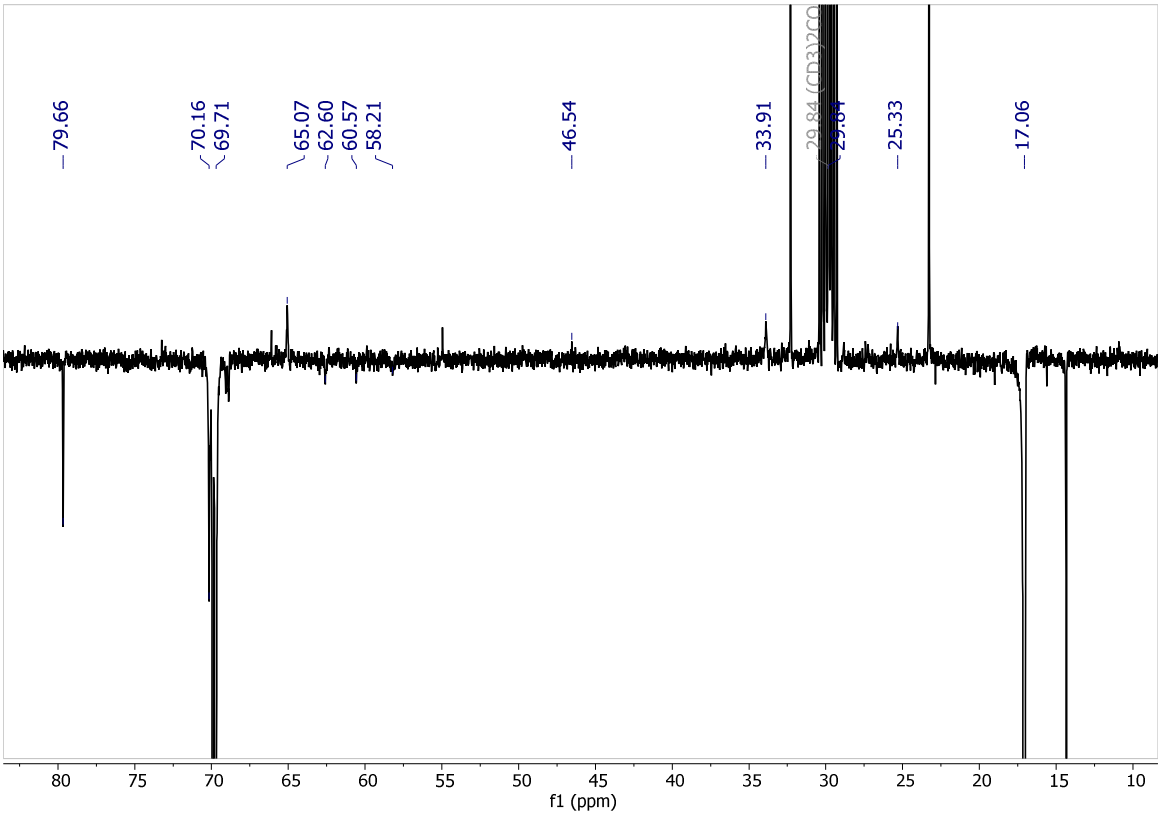


**Figure S10.** APT $^{13}C\{^{1}H\}$-NMR spectrum of complex **2** in acetone-$d_6$ at 298 K.

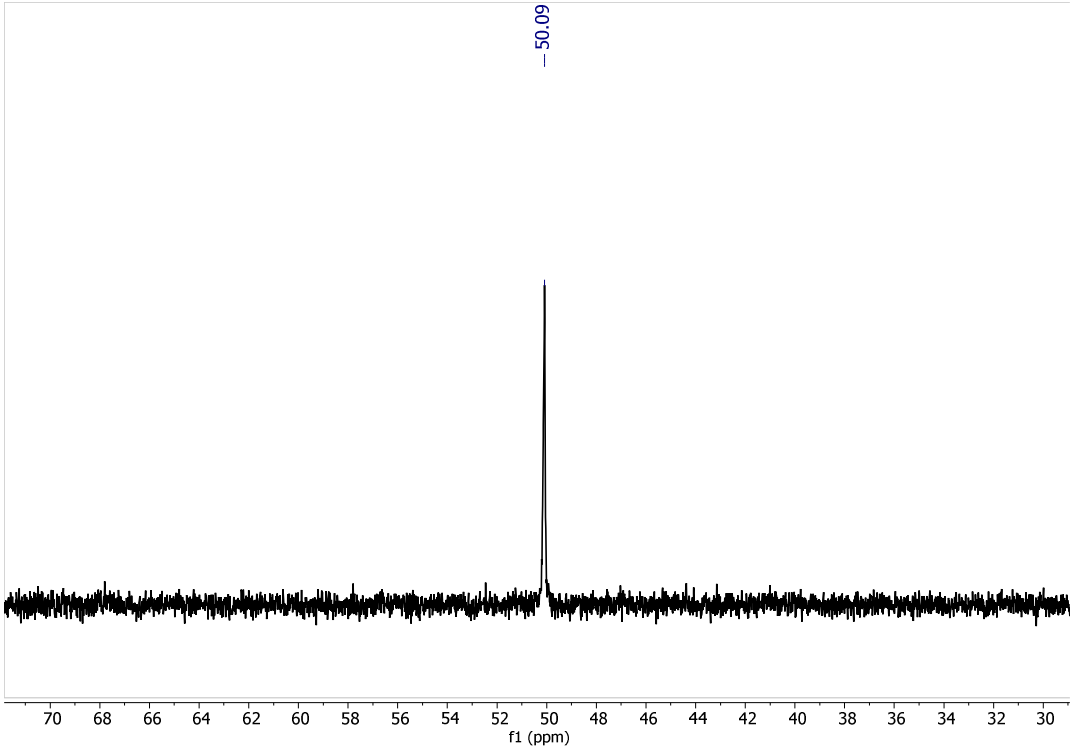


**Figure S11.** $^{31}P\{^{1}H\}$-NMR spectrum of complex **2** in acetone-$d_6$ at 298 K.

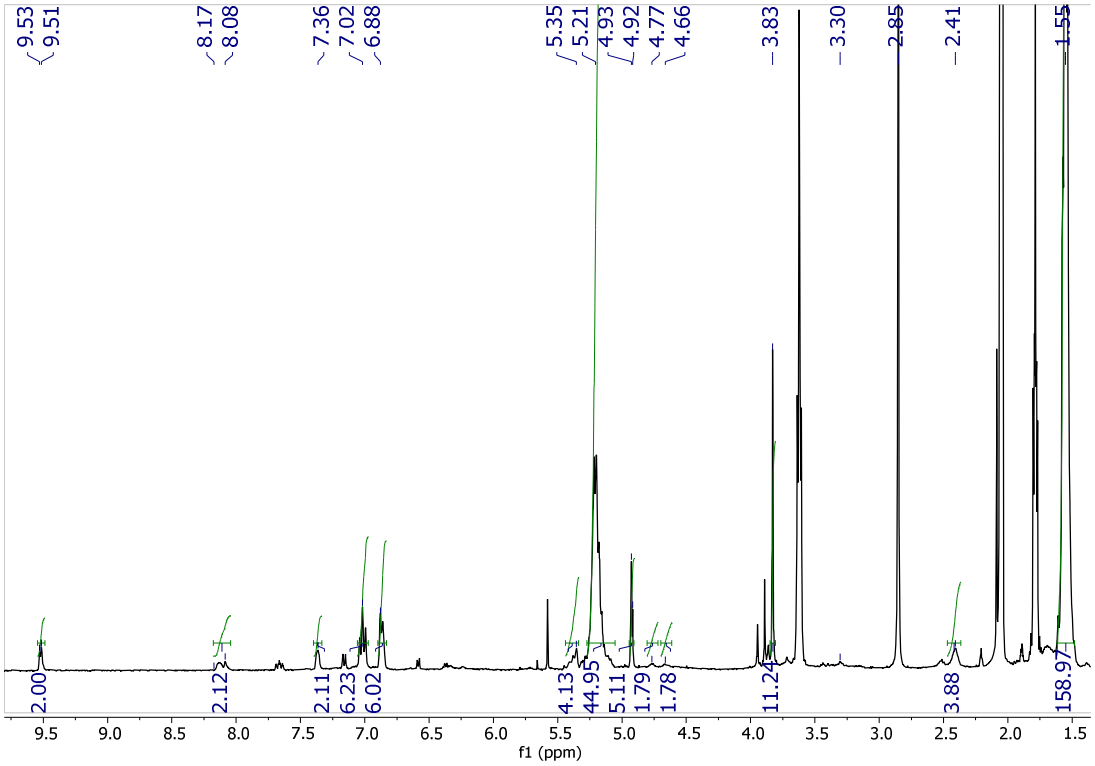


**Figure S12.** $^{1}$H-NMR spectrum of complex **3** in acetone-$d_6$ at 298 K.

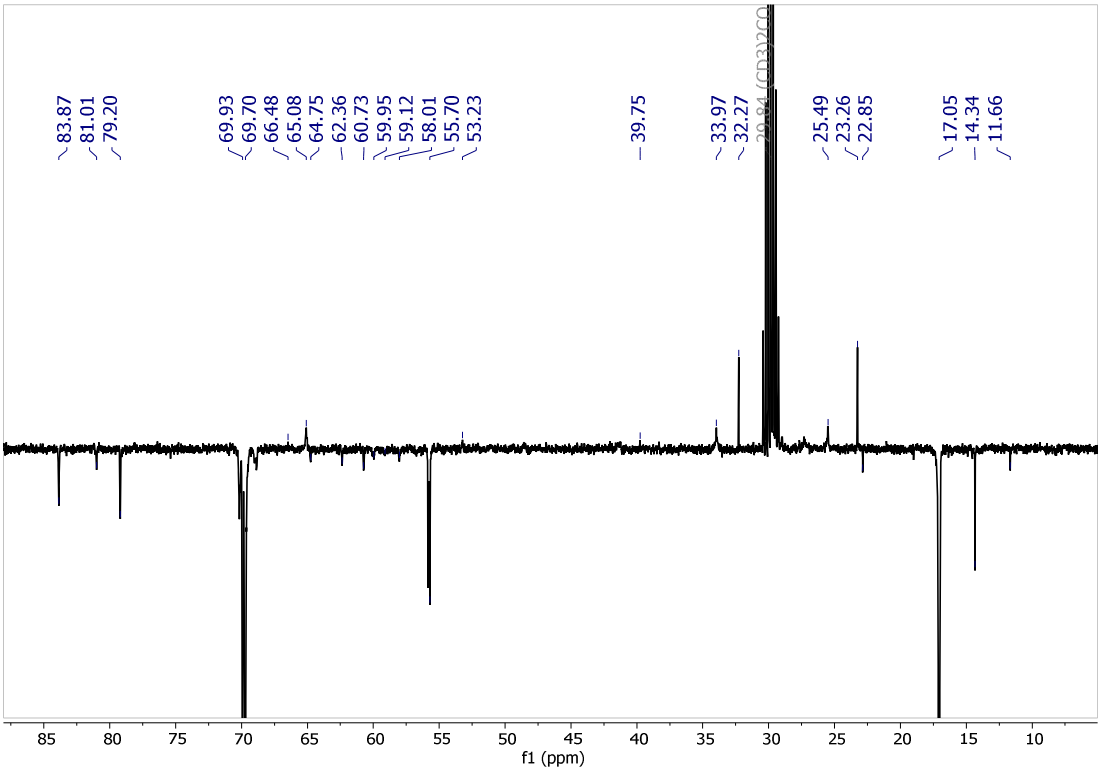


**Figure S13.** APT $^{13}$C{$^{1}$H}-NMR spectrum of complex **3** in acetone-$d_6$ at 298 K.

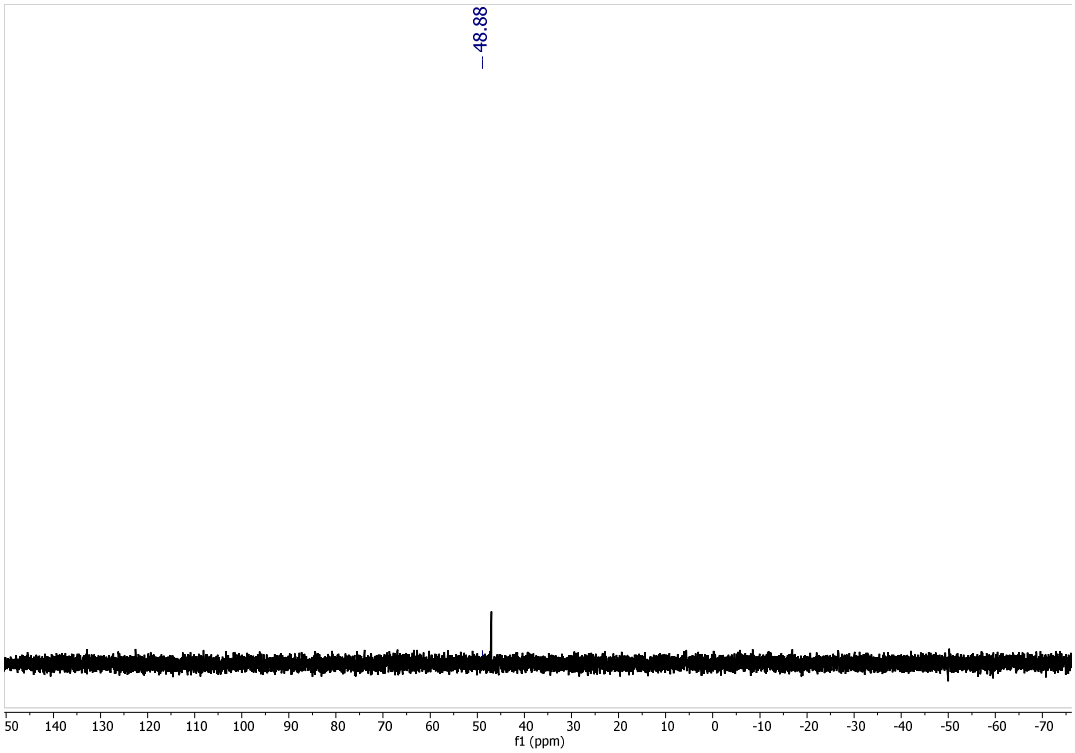


**Figure S14.** $^{31}P\{^{1}H\}$-NMR spectrum of complex **3** in acetone-$d_6$ at 298 K.

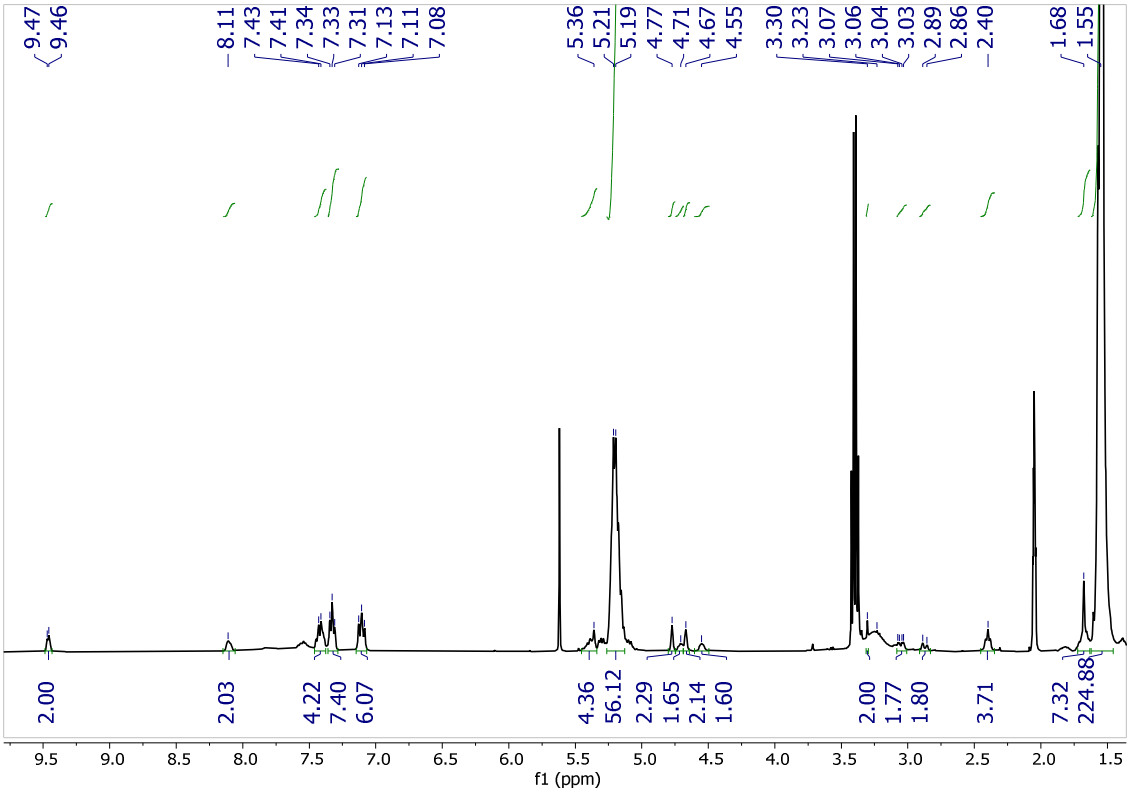


**Figure S15.** $^{1}H$-NMR spectrum of complex **4** in acetone-$d_6$ at 298 K.

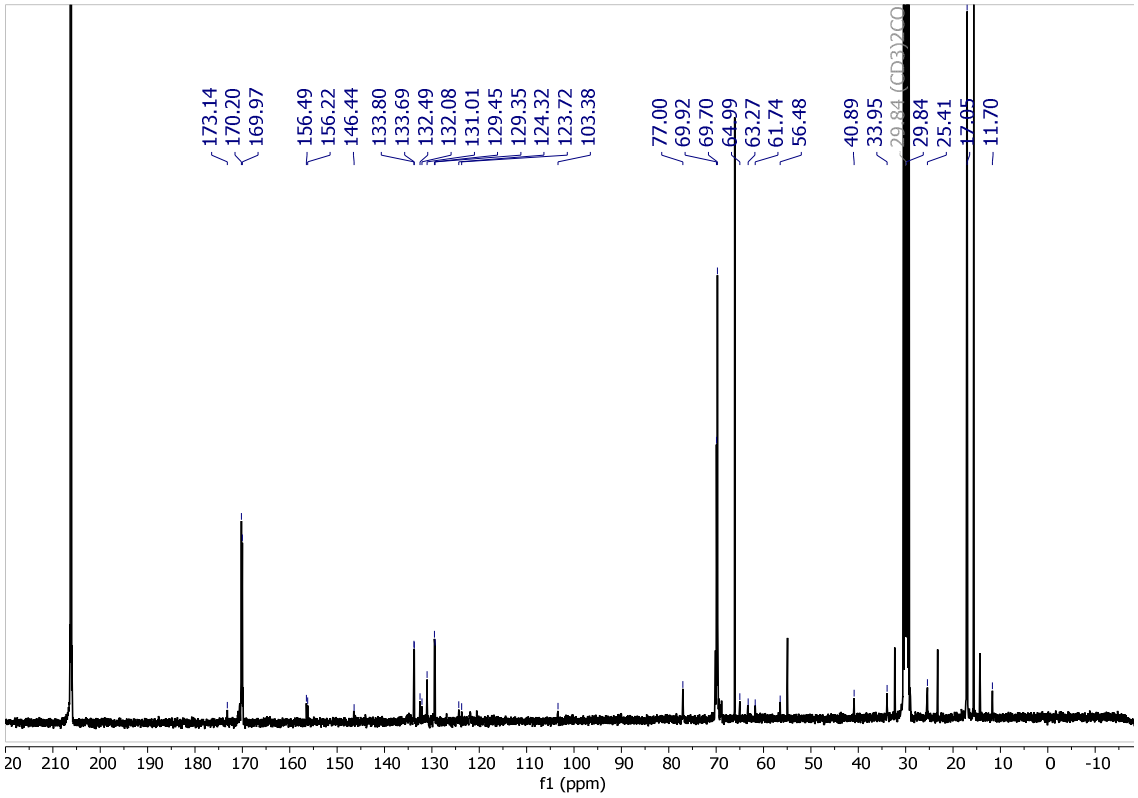


**Figure S16.** $^{13}C\{^{1}H\}$-NMR spectrum of complex **4** in acetone-$d_6$ at 298 K.

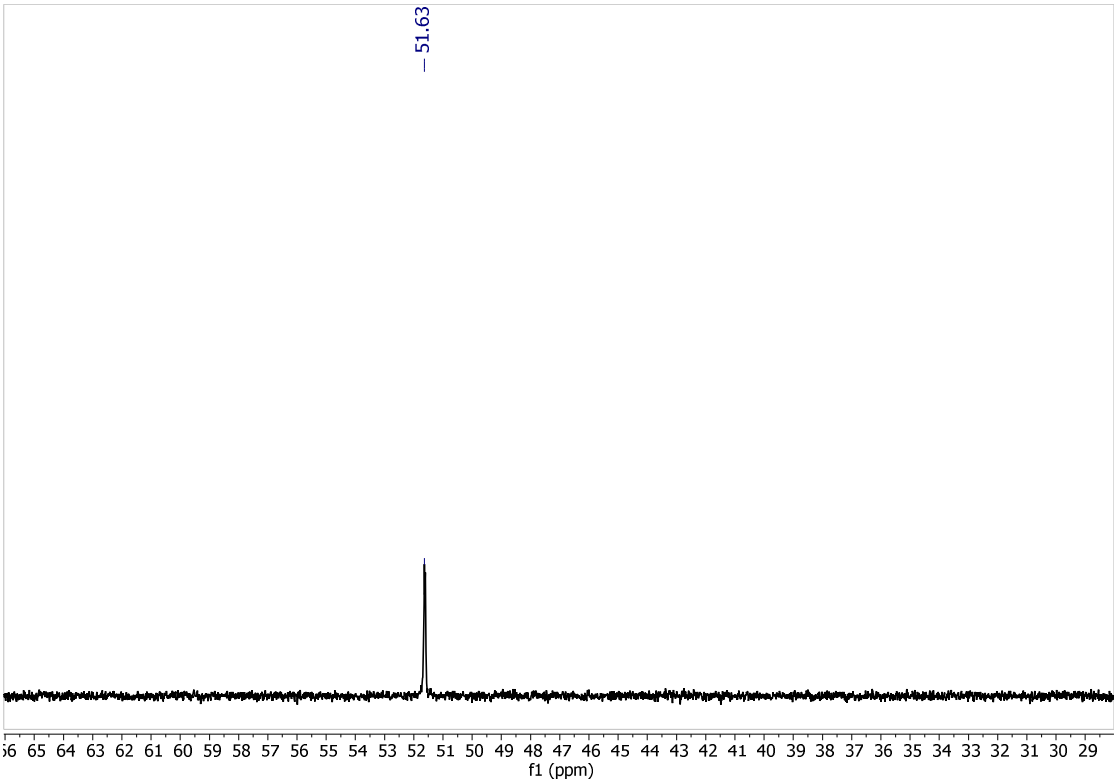


**Figure S17.** $^{31}P\{^{1}H\}$-NMR spectrum of complex **4** in acetone-$d_6$ at 298 K.

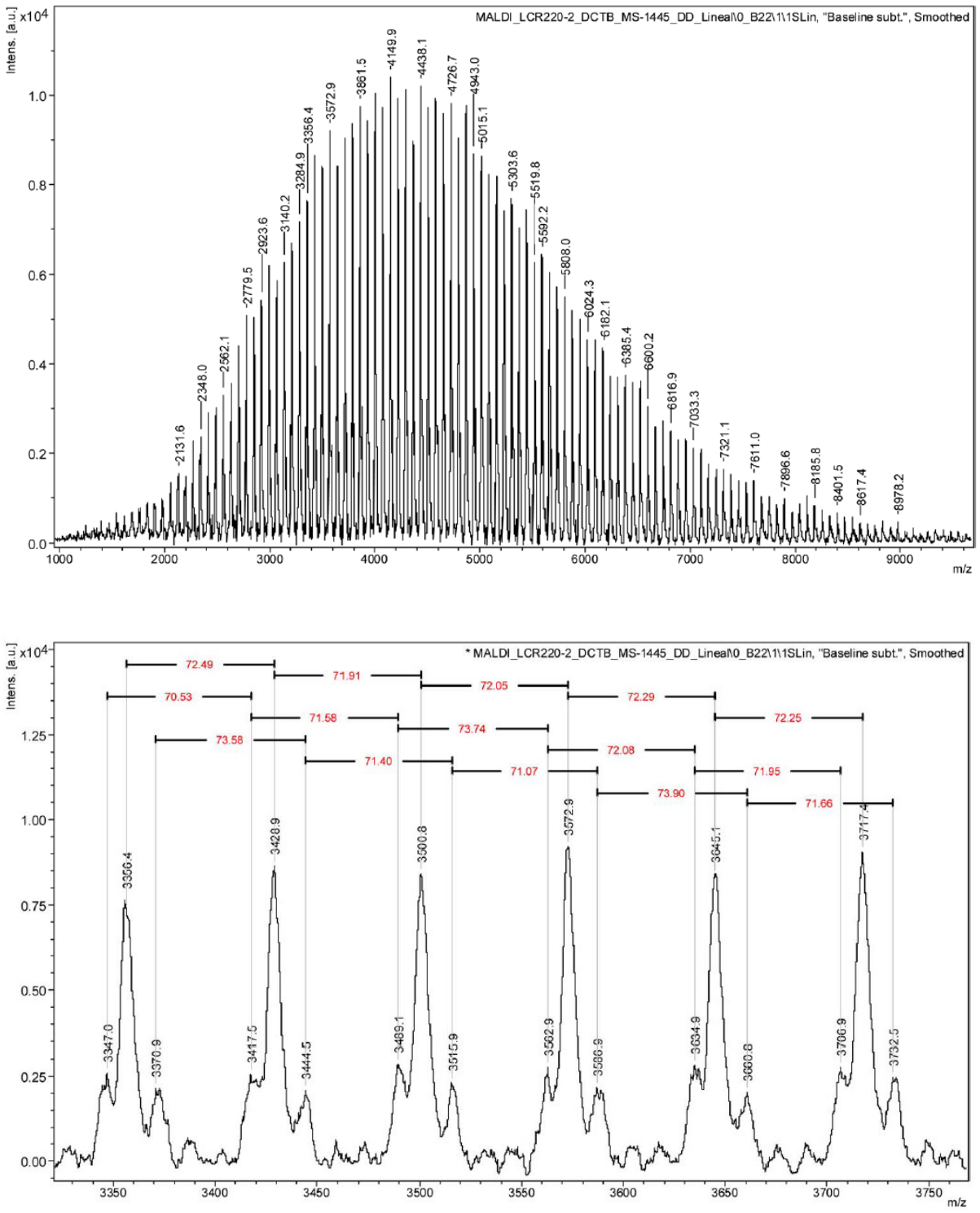


**Figure S18.** MALDI-TOF MS analysis of Compound **1.**

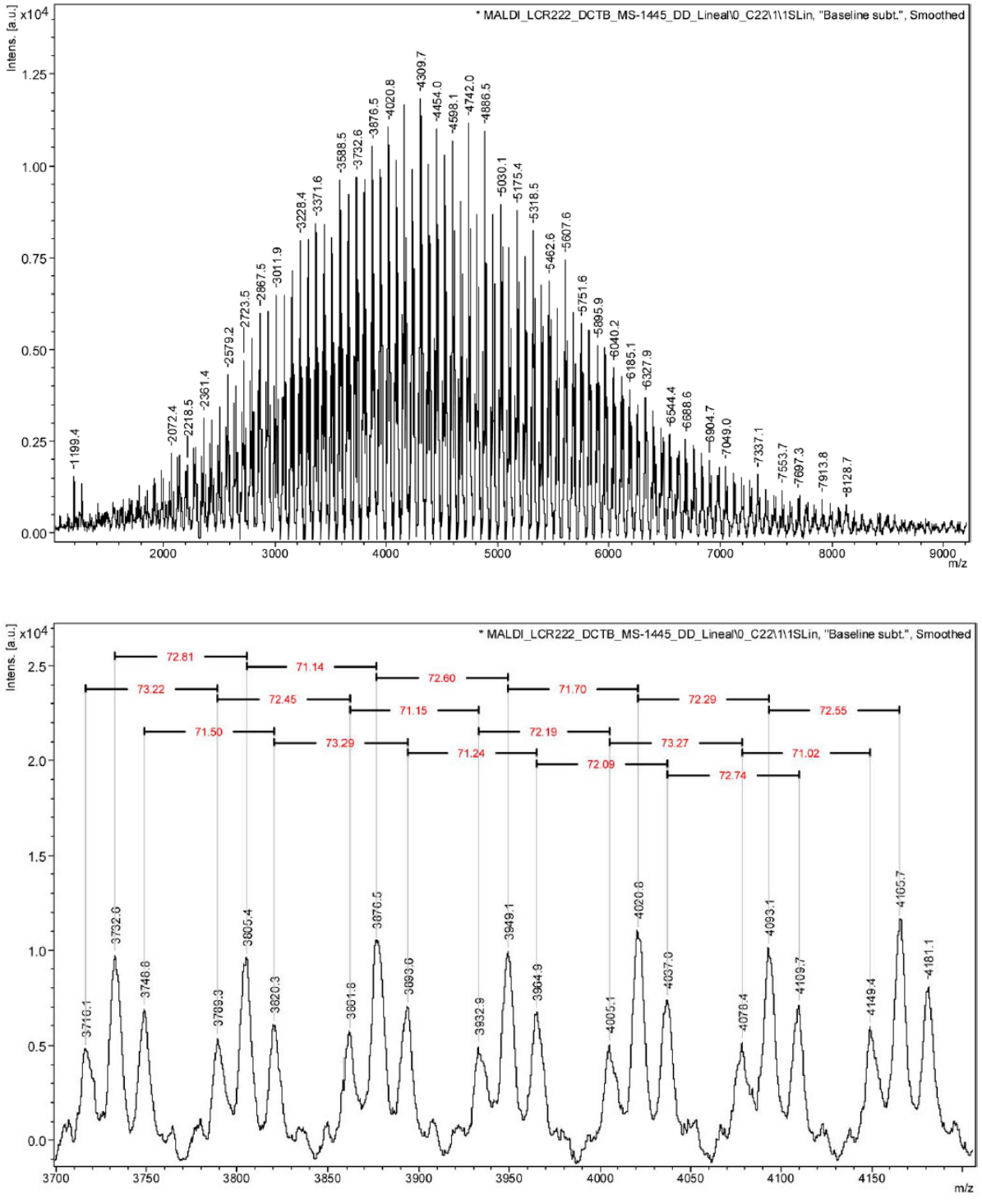


**Figure S19.** MALDI-TOF MS analysis of Compound **2.**

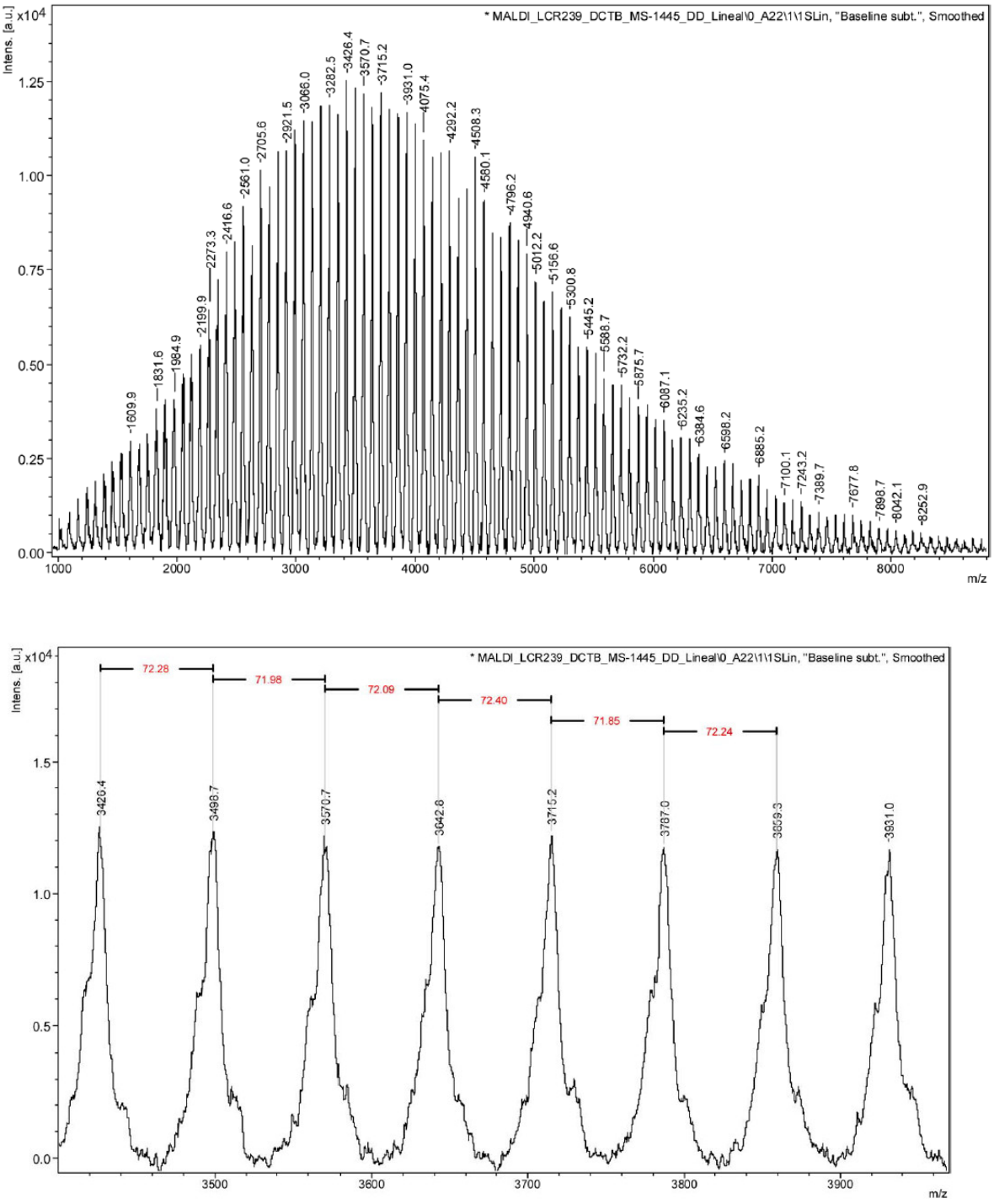


**Figure S20.** MALDI-TOF MS analysis of Compound **3.**

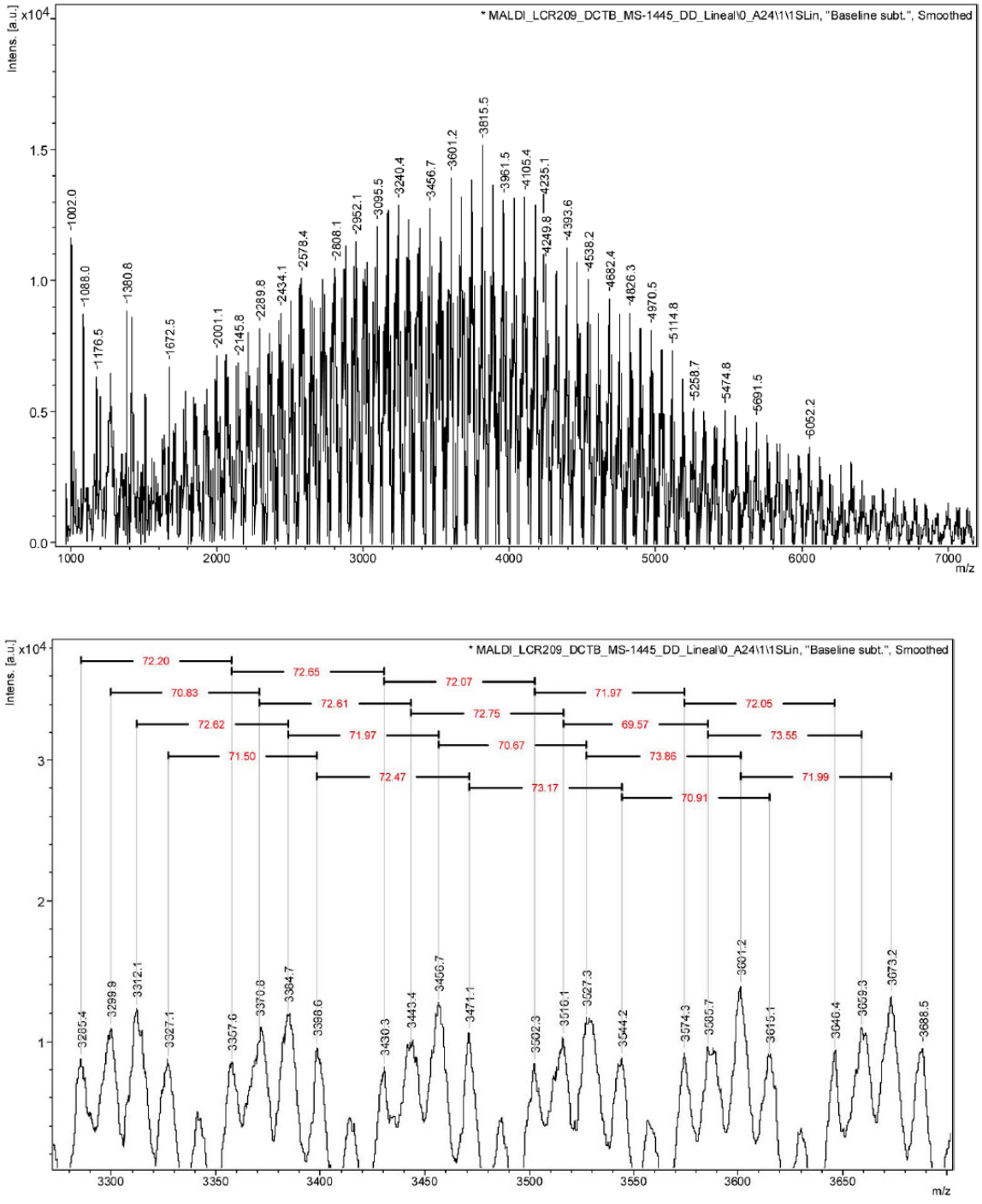


**Figure S21.** MALDI-TOF MS analysis of Compound **4.**

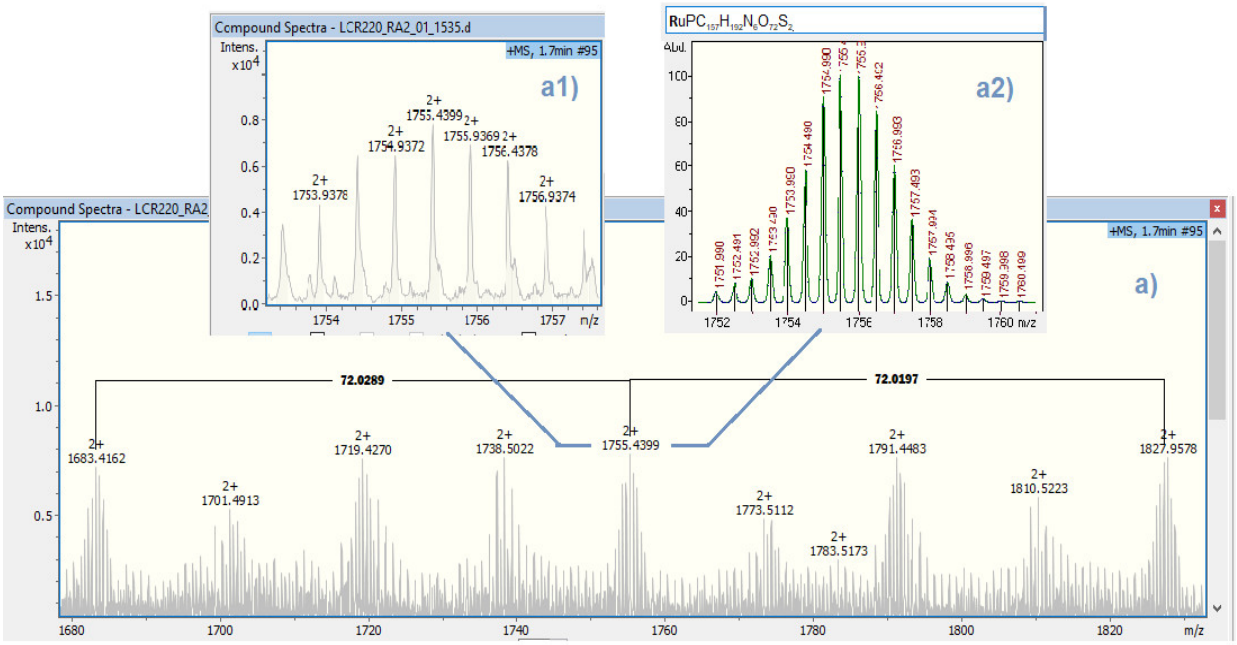


**Figure S22.** Partial HR mass spectrum obtained in the ESI positive mode of a methanolic solution of complex **1. a**) series of double charge ions attributed to $[Ru(\eta^5\text{-}Cp)(P(C_6H_5)_3)(2,2'\text{-bipy-}4,4'\text{-}(PLA)_{n=16;17;18}\text{-biotin})]^{2+}$ structures spaced by 72.02 u; **a1**) the group of peaks at *m*/*z* 1755.44 assigned to $[Ru(\eta^5\text{-}Cp)(P(C_6H_5)_3)(2,2'\text{-bipy-}4,4'\text{-}(PLA)_{n=16;17;18}\text{-biotin})]^{2+}$ exhibited a measured isotopic pattern as the calculated for the sum $[RuPC_{157}H_{192}N_6O_{72}S_2]^{2+}$ shown in **a2**).

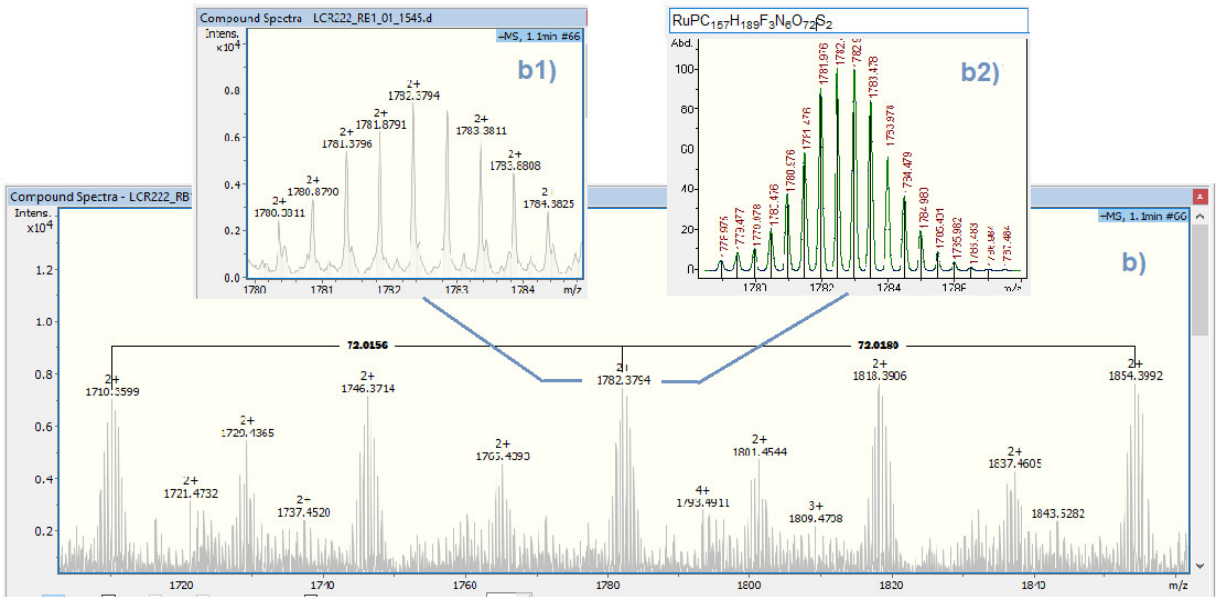


**Figure S23.** Partial HR mass spectrum obtained in the ESI positive mode of a methanolic solution of complex **2. b**) series of double charge ions attributed to $[Ru(\eta^5\text{-}Cp)(P(C_6H_4F)_3)(2,2'\text{-bipy-}4,4'\text{-}(PLA)_{n=16;17;18}\text{-biotin})]^{2+}$ structures spaced by 72.02 u; **b1**) the group of peaks at *m*/*z* 1782.47 assigned to $[Ru(\eta^5\text{-}Cp)(P(C_6H_4F)_3)(2,2'\text{-bipy-}4,4'\text{-}(PLA)_{n=16;17;18}\text{-biotin})]^{2+}$ exhibited a measured isotopic pattern as the calculated for the sum $[RuPC_{157}H_{189}F_3N_6O_{72}S_2]^{2+}$ shown in **b2**).

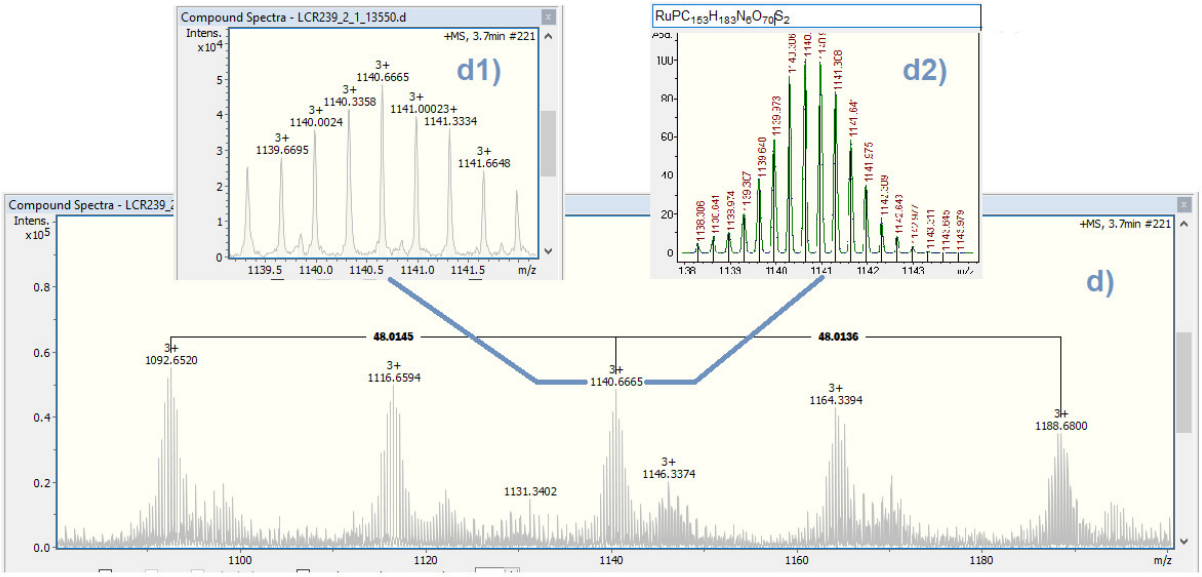


**Figure S24.** Partial HR mass spectrum obtained in the ESI positive mode of a methanolic solution of complex **3. d**) series of triple charge ions attributed to $[Ru(\eta^5\text{-}Cp)(P(C_6H_4OCH_3)_3(2,2'\text{-bipy-}4,4'\text{-}(PLA)_{n=15;16;17})\text{-biotin})]^{3+}$ structures spaced by 48.01 u; **d1**) the group of peaks at *m*/*z* 1188.35 assigned to $[Ru(\eta^5\text{-}Cp)[P(C_6H_4)_3(CHO)_2](2,2'\text{-bipy-}4,4'\text{-}(PLA)_{n=16}\text{-biotin})]^{3+}$ exhibited a measured isotopic pattern as the calculated for the sum $[RuPC_{153}H_{183}N_6O_{70}S_2]^{3+}$ shown in **d2**).

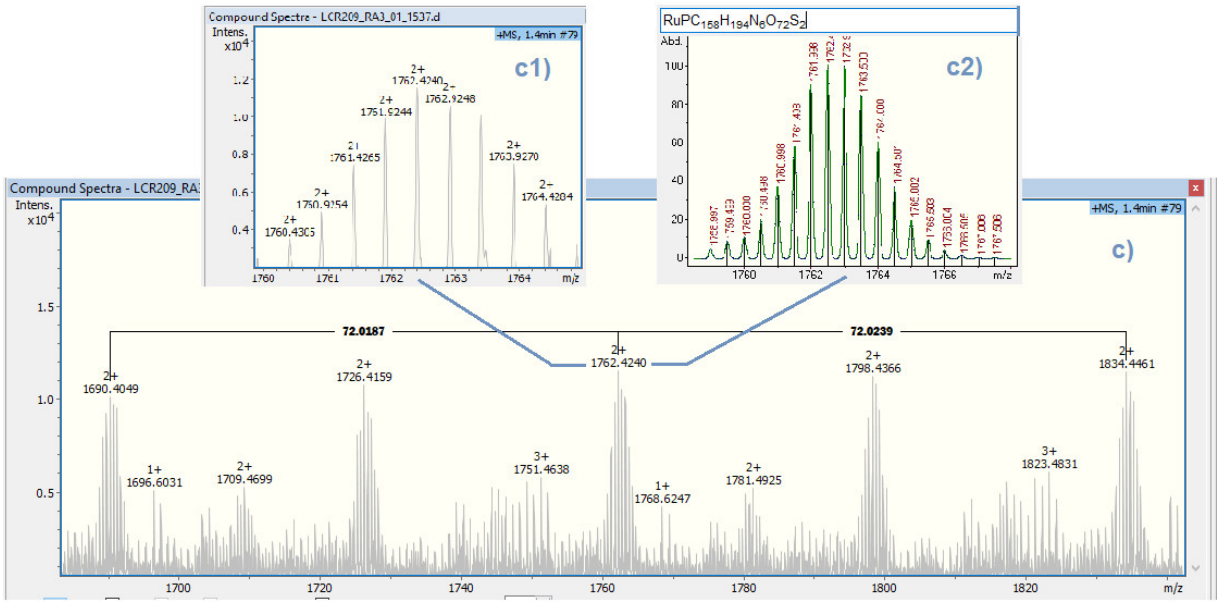


**Figure S25.** Partial HR mass spectrum obtained in the ESI positive mode of a methanolic solution of complex **4. c**) series of double charge ions attributed to $[Ru(\eta^5\text{-}CpCH_3)(P(C_6H_5)_3)(2,2'\text{-bipy-}4,4'\text{-}(PLA)_{n=16;17;18})\text{-biotin})]^{2+}$ structures spaced by 72.02 u; **c1**) the group of peaks at *m*/*z* 1762.42 assigned to $[Ru(\eta^5\text{-}CpCH_3)(P(C_6H_5)_3)(2,2'\text{-bipy-}4,4'\text{-}(PLA)_{n=16;17;18})\text{-biotin})]^{2+}$ exhibited a measured isotopic pattern as the calculated for the sum $[RuPC_{158}H_{194}N_6O_{72}S_2]^{2+}$ shown in **c2**).

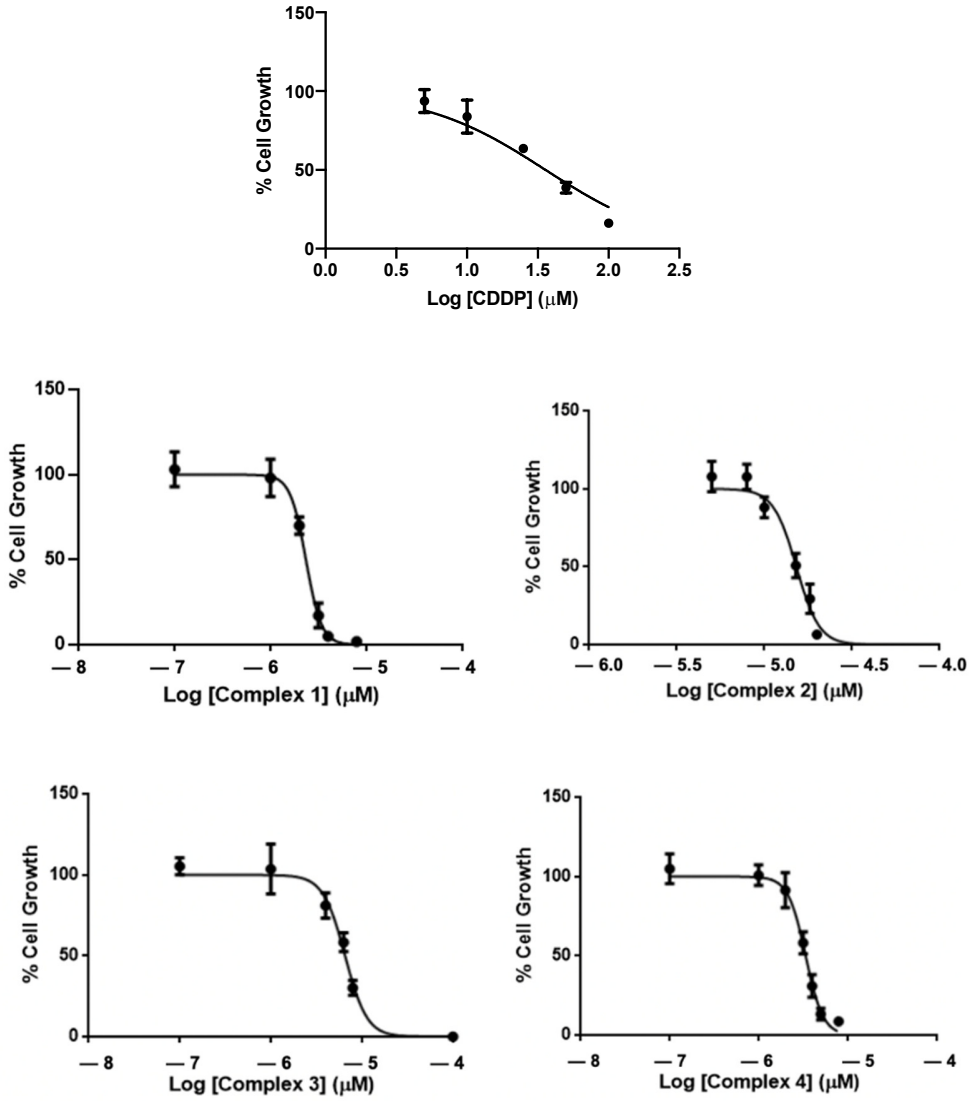


**Figure S26.** Dose-response curve of cell viability in MDA-MB-231 cell line for determination of $IC_{50}$ by MTT (complexes **1**-**4**) or Sulforhodamine B (Cisplatin) after 48 h incubation.

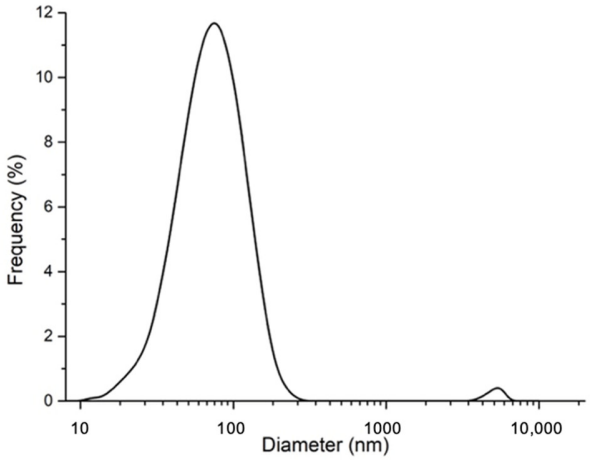


**Figure S27.** Hydrodynamic diameter distribution (obtained by DLS) of complex **1**.

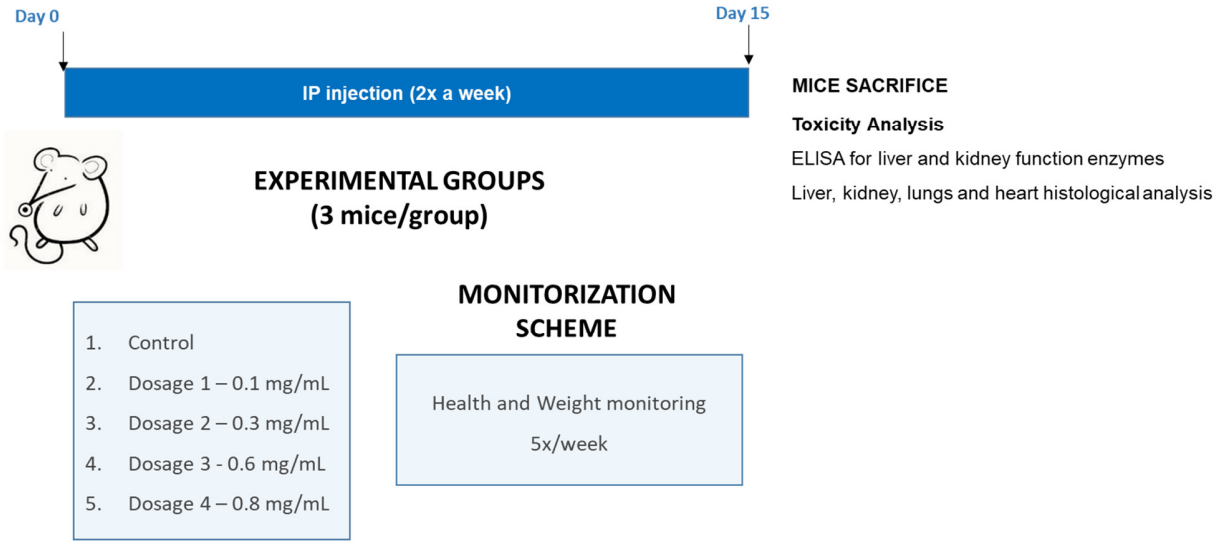


**Figure S28**. Experimental design of toxicology assay performed.

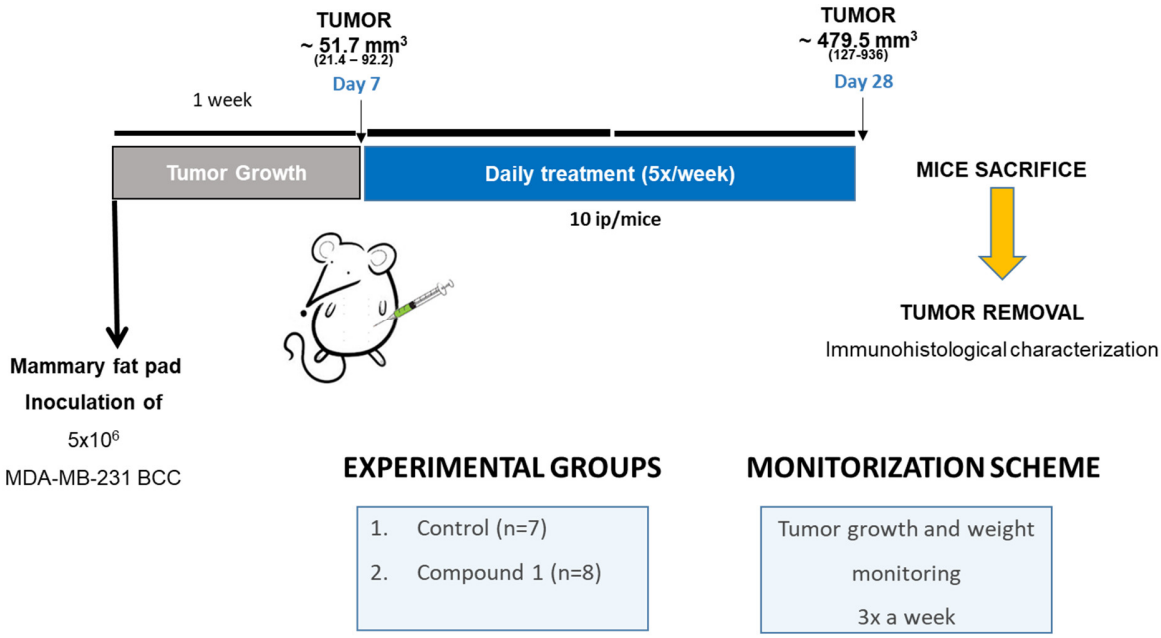


**Figure S29.** Experimental design of tumor growth assay.