Supporting Information

for

Triphenyl Phosphonium (TPP)-Derived Protein Sulfenic Acid Trapping Agents: Synthesis, Reactivity and Effect on Mitochondrial Function

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General Considerations

All chemicals were purchased from commercial vendors and used as received. TLC was performed on Sorbent polyester-backed Silica G plates with UV254 indicator. Visualization was accomplished with UV light unless otherwise indicated. Solvents for extraction and purification were of technical grade and used as received. Liquid chromatography–mass spectrometry (LC-MS) solvents were HPLC grade. For small molecule experiments, ESI-MS was performed on an Agilent 100 Series LC/MSD ion trap. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 300 or 500 MHz NMR spectrometer. Chemical shifts are given in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). UV–vis spectroscopy was performed on a Cary 50 UV-vis spectrophotometer.

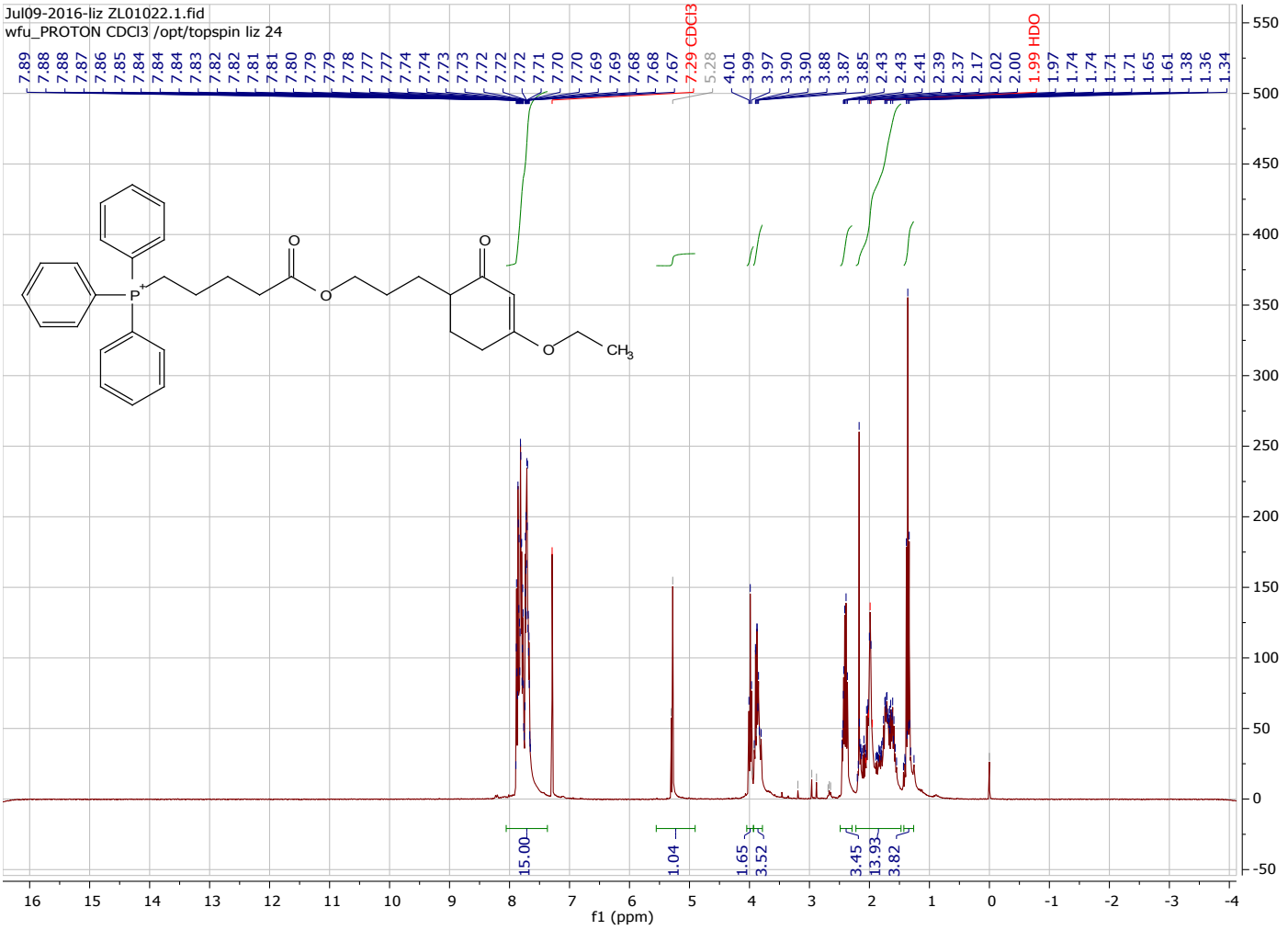

Figure S1. ^{1}H NMR Spectrum of **3**.

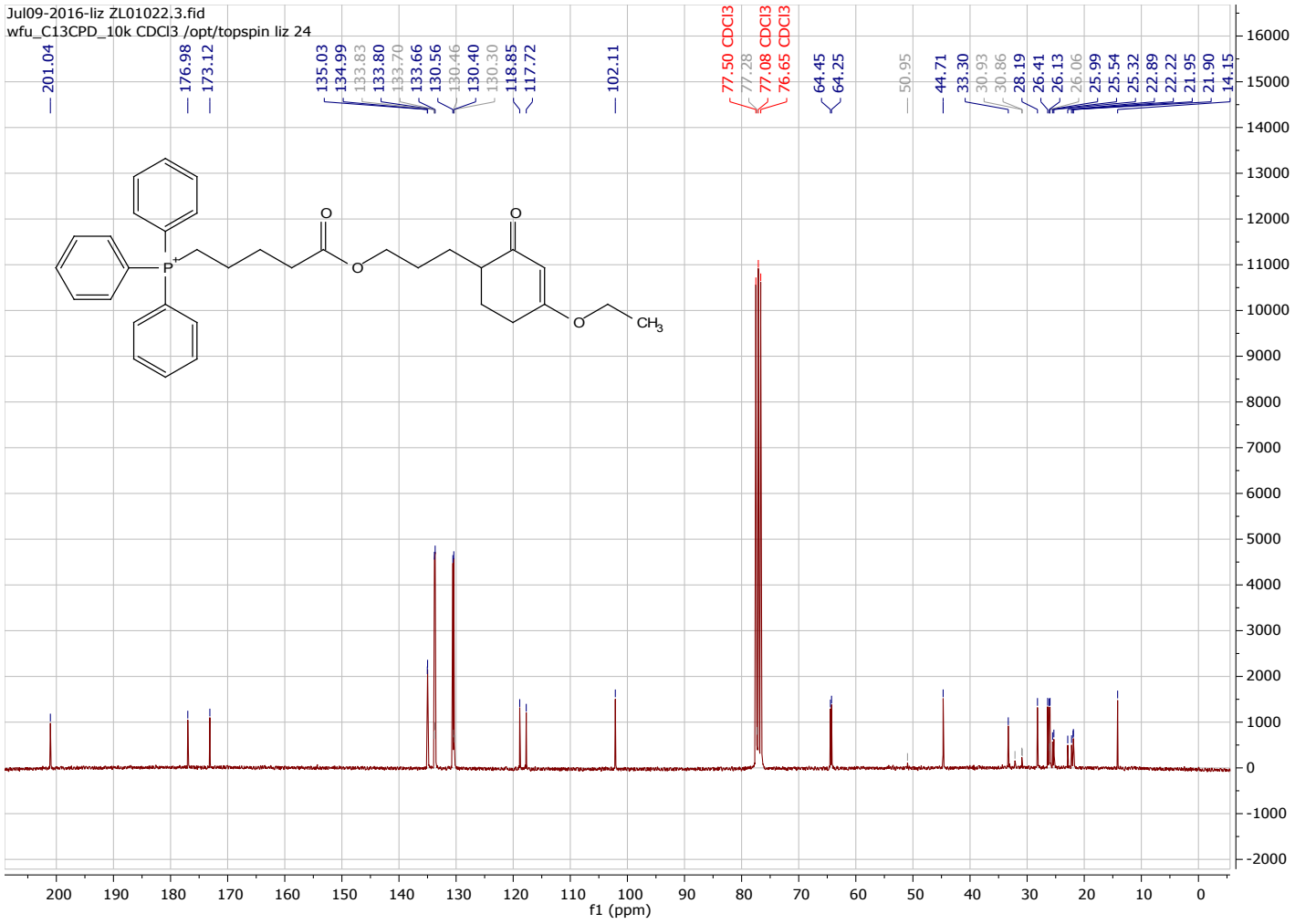

Figure S2. ^{13}C NMR Spectrum of **3**.

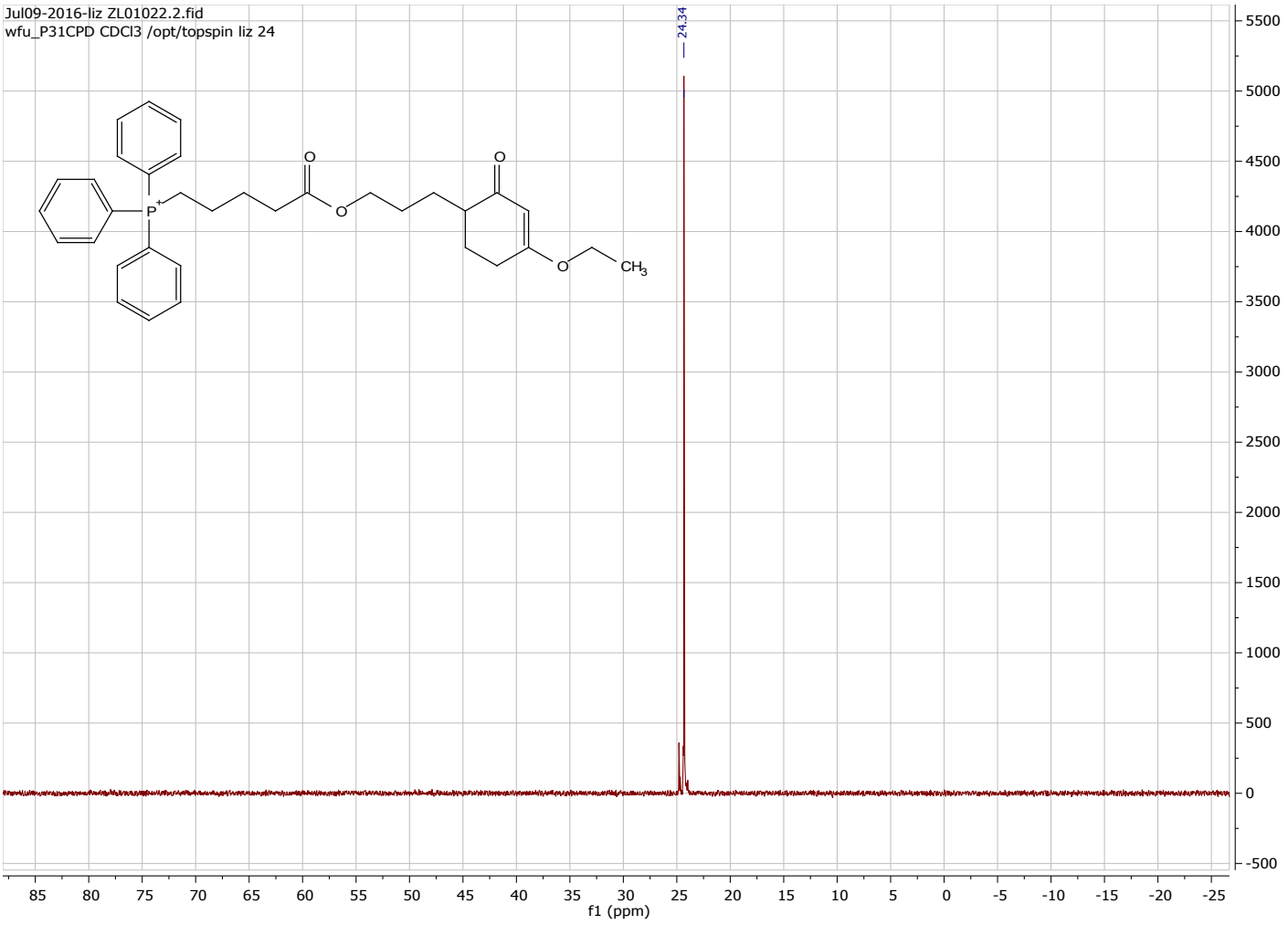

Figure S3. ^{31}P NMR Spectrum of **3**.

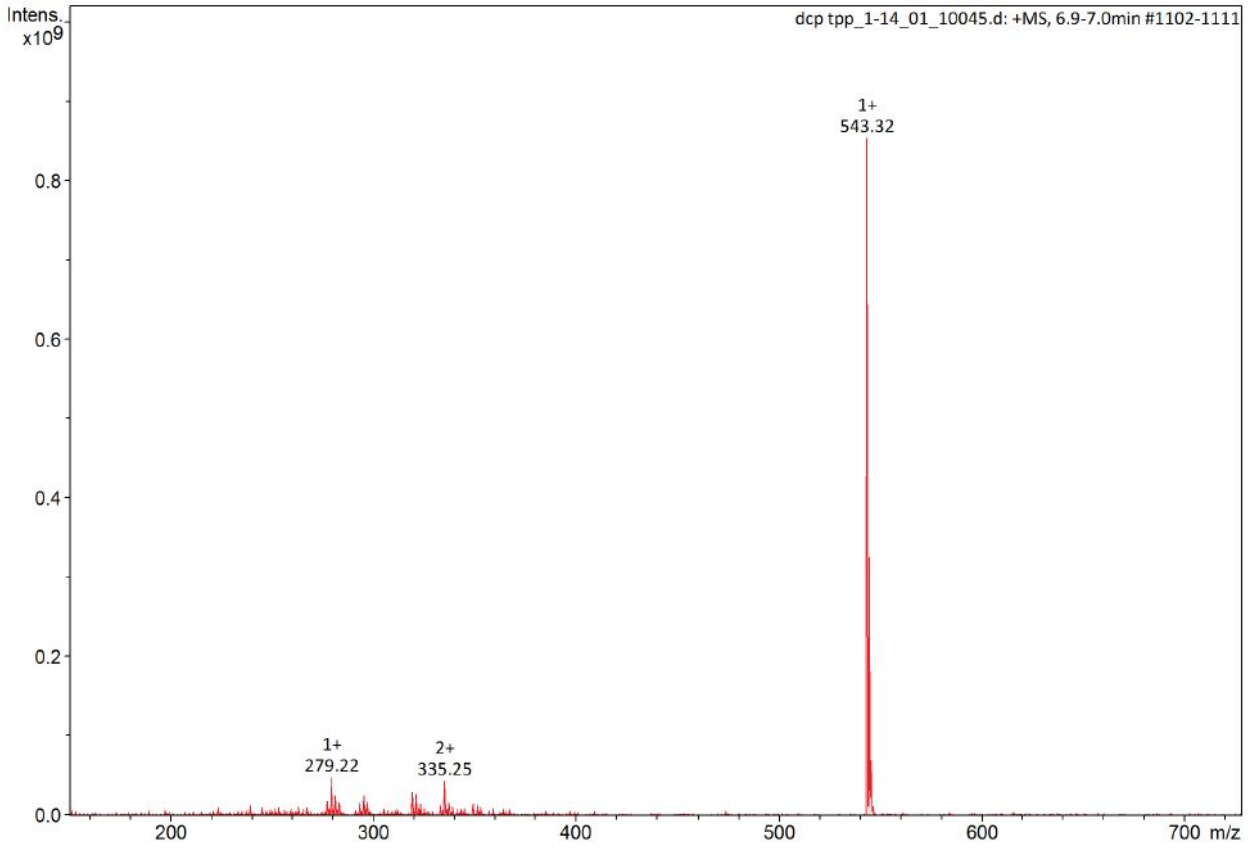

Figure S4. MS of **3**.

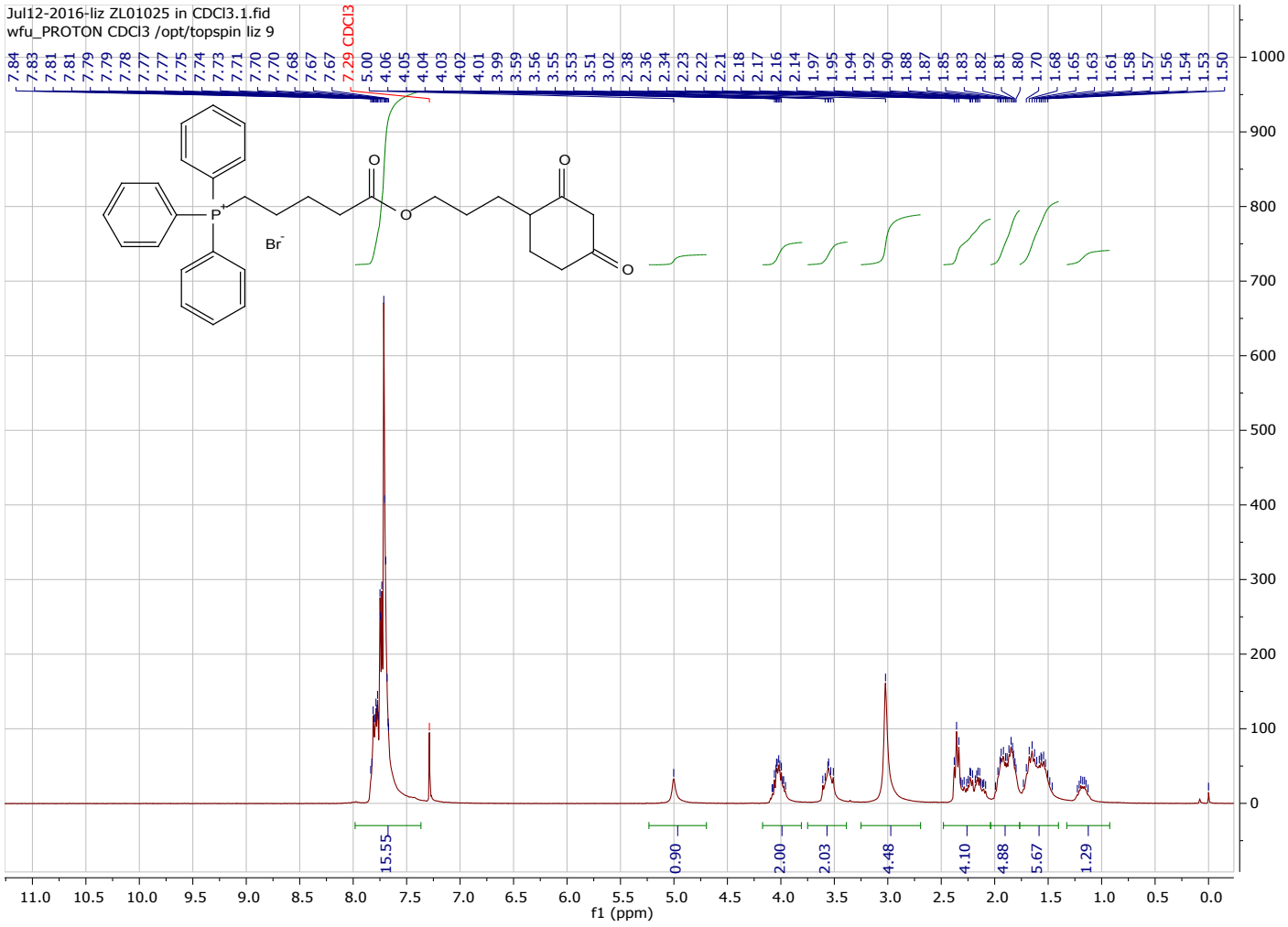

Figure S5. ^{1}H NMR Spectrum of **1**.

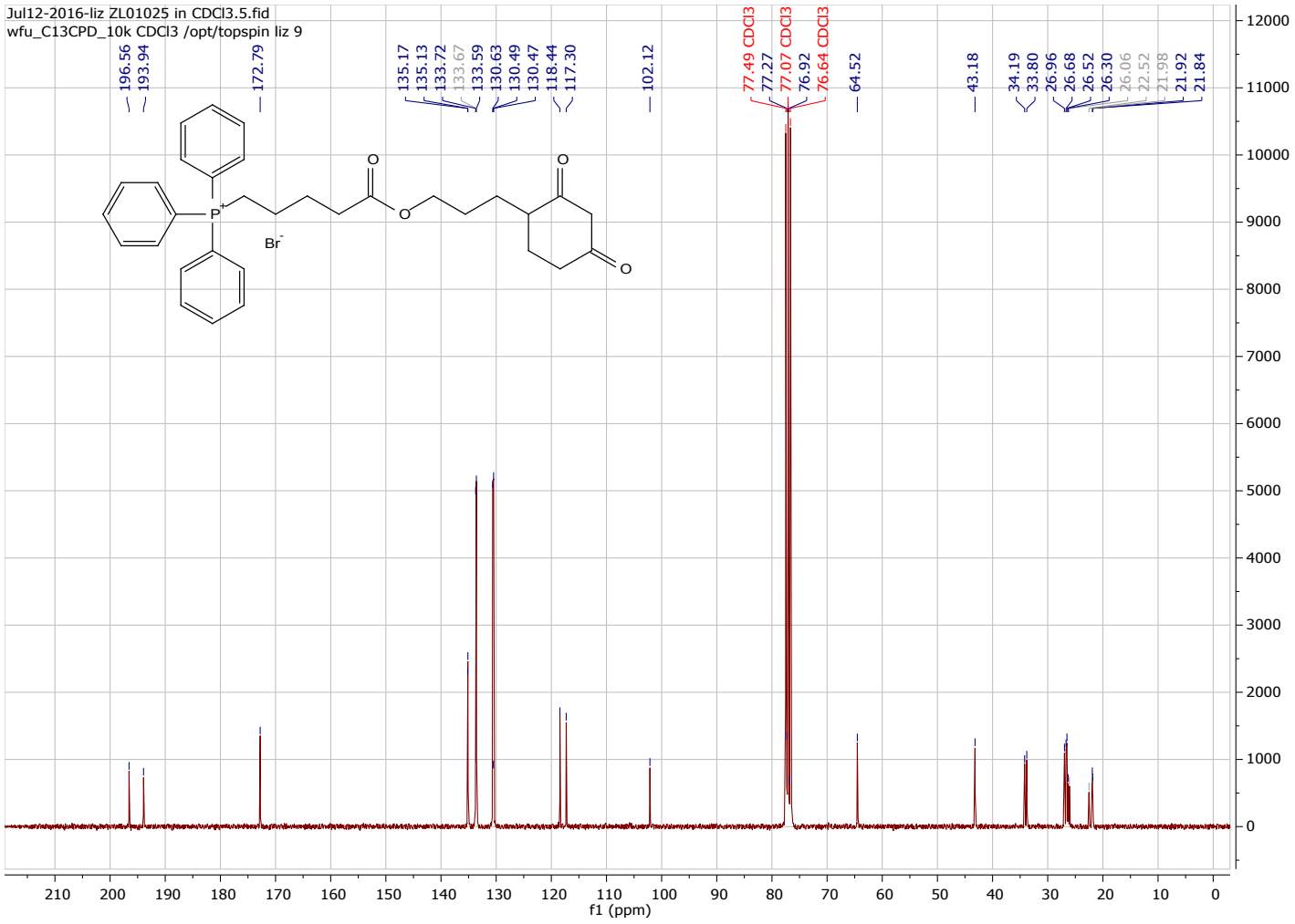

Figure S6. ^{13}C NMR Spectrum of **1**.

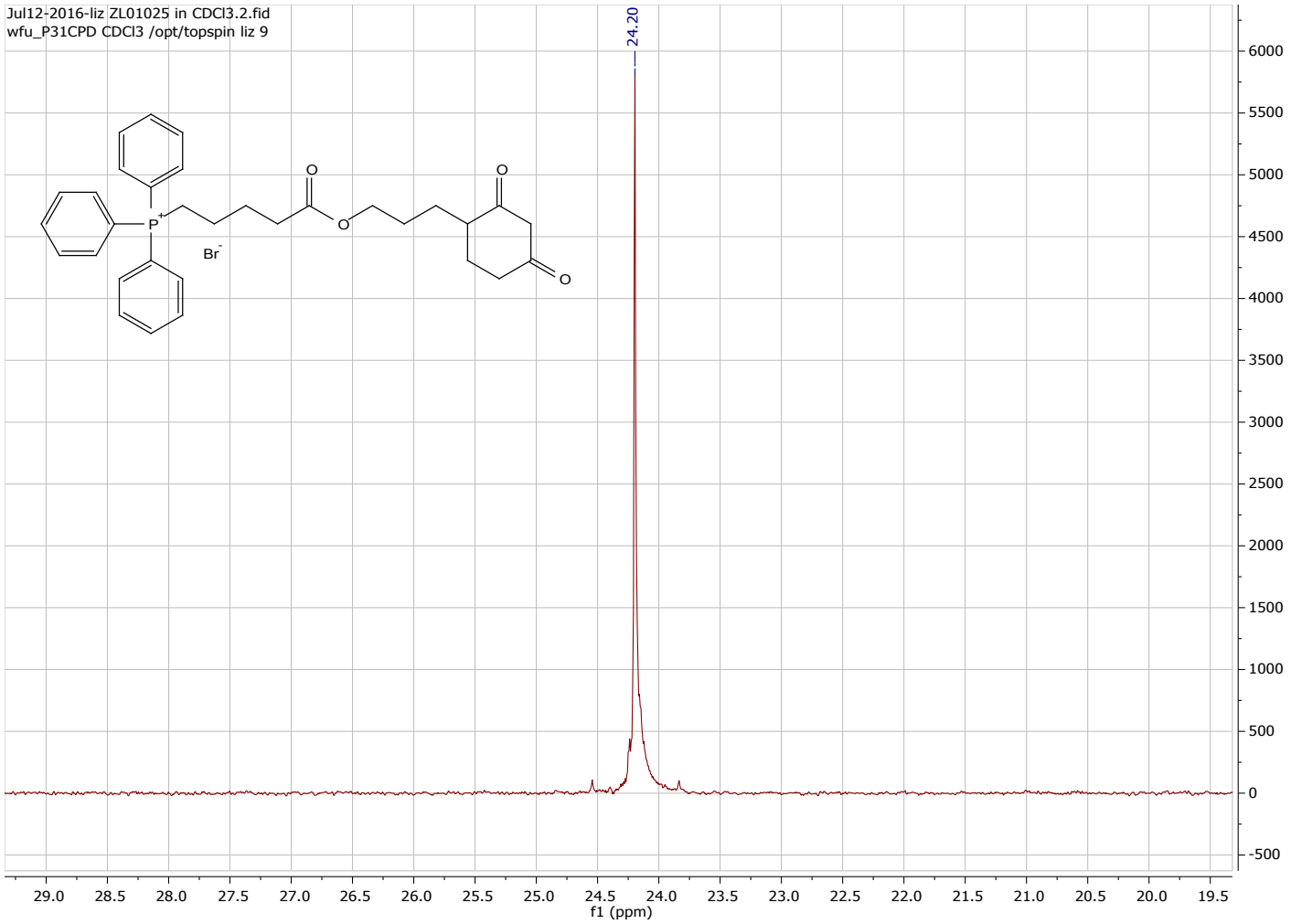

Figure S7. ^{31}P NMR Spectrum of **1**.

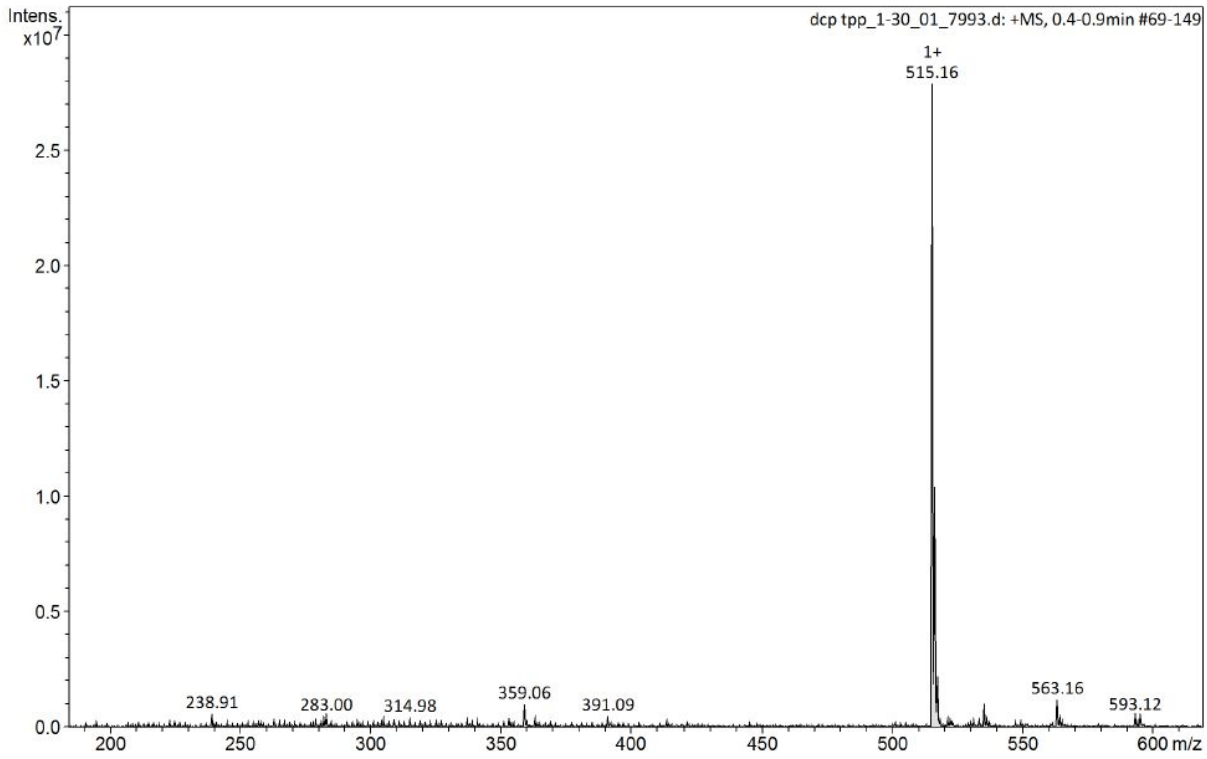

Figure S8. MS of **1**.

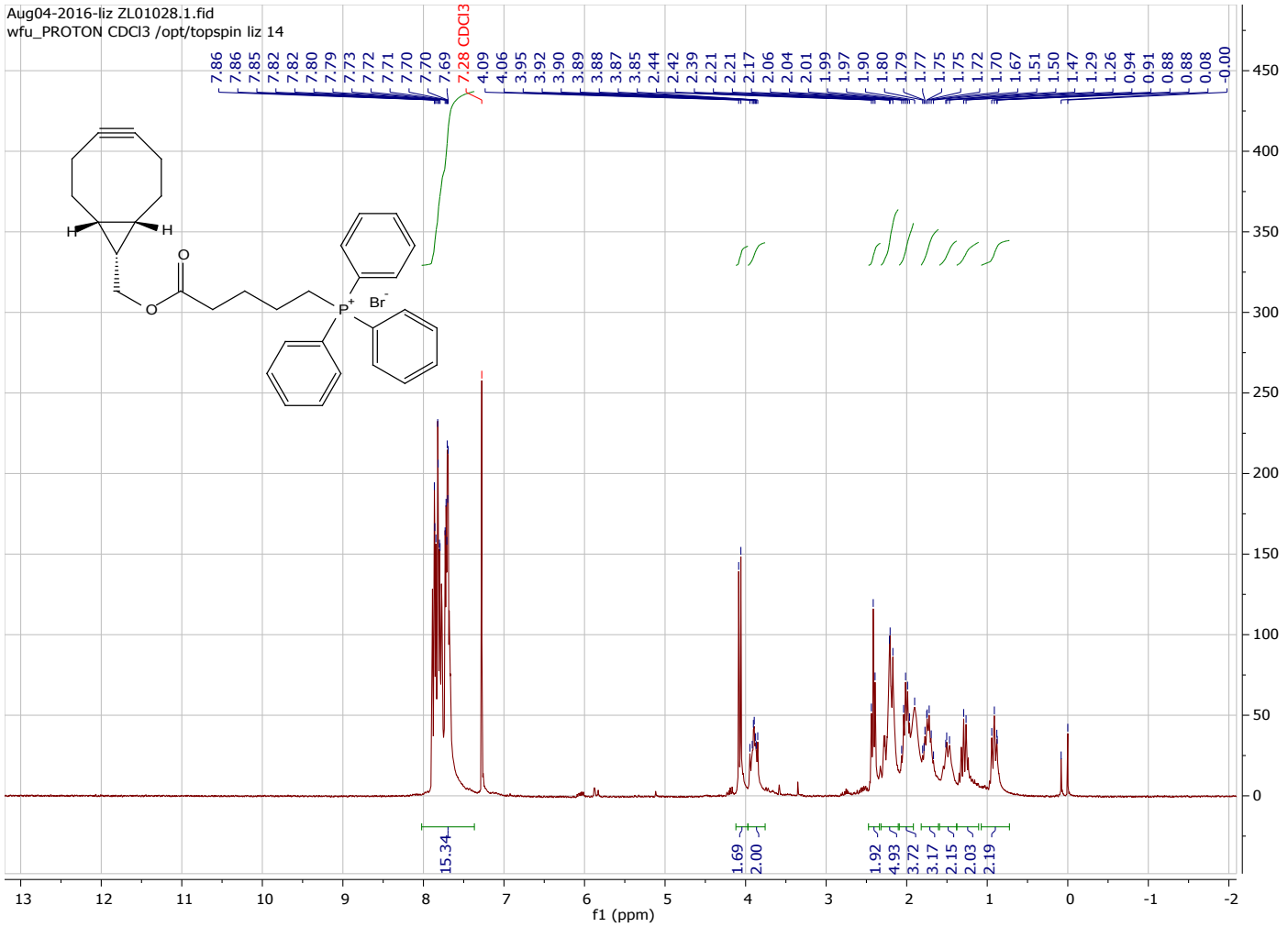

Figure S9. ^{1}H NMR Spectrum of **2**.

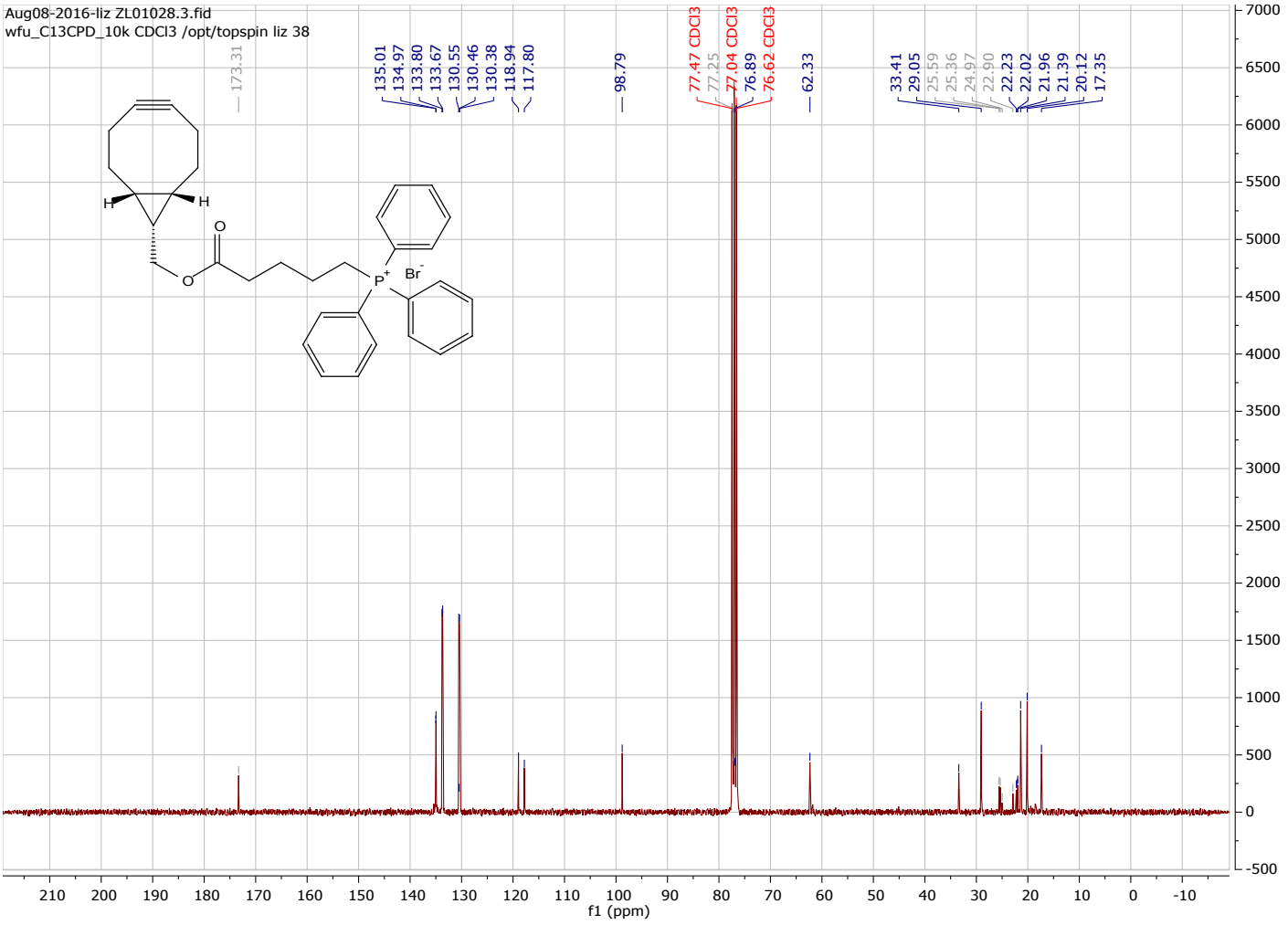

Figure S10. ^{13}C NMR Spectrum of **2**.

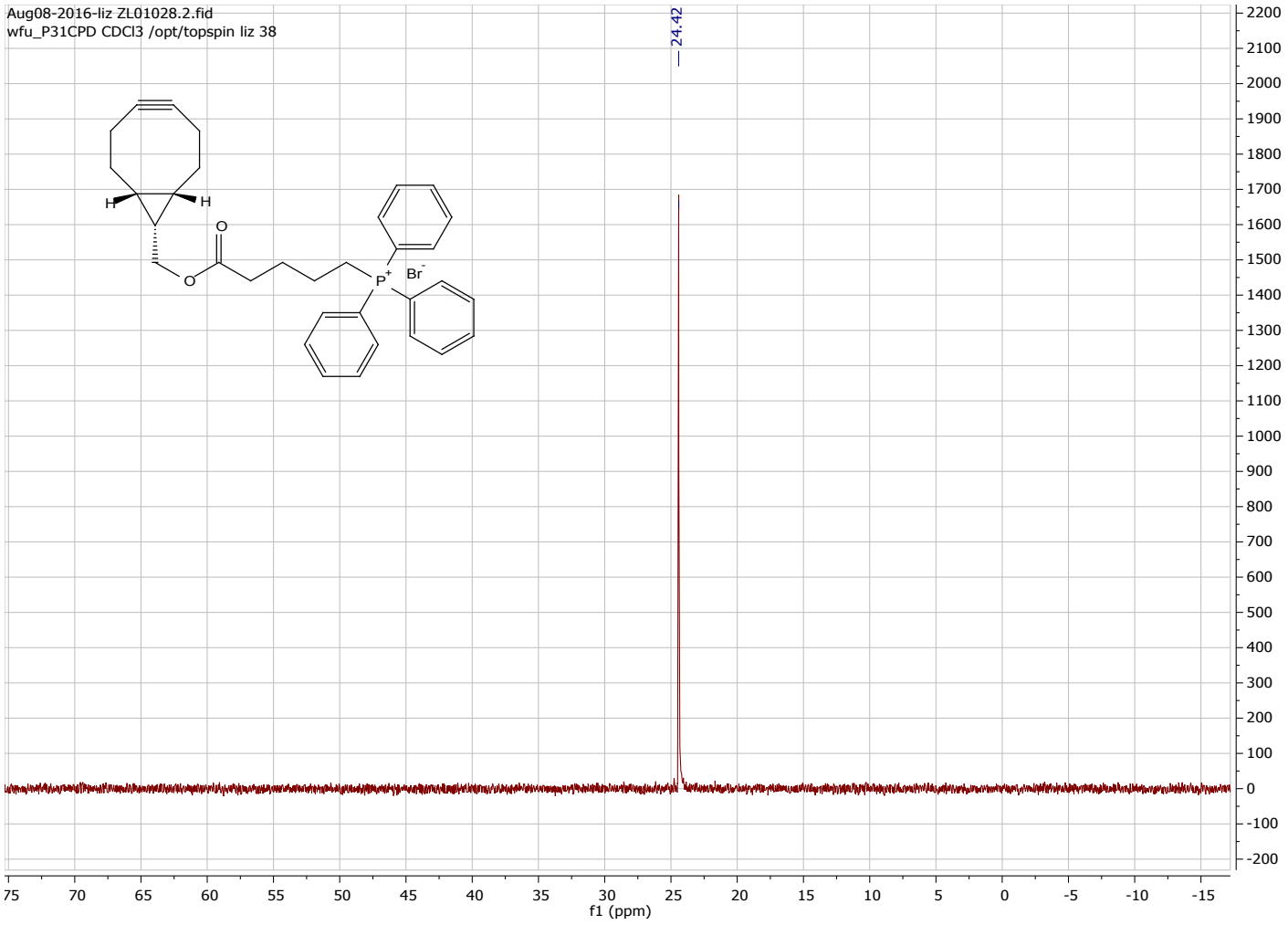

Figure S11. ^{31}P NMR Spectrum of **2**.

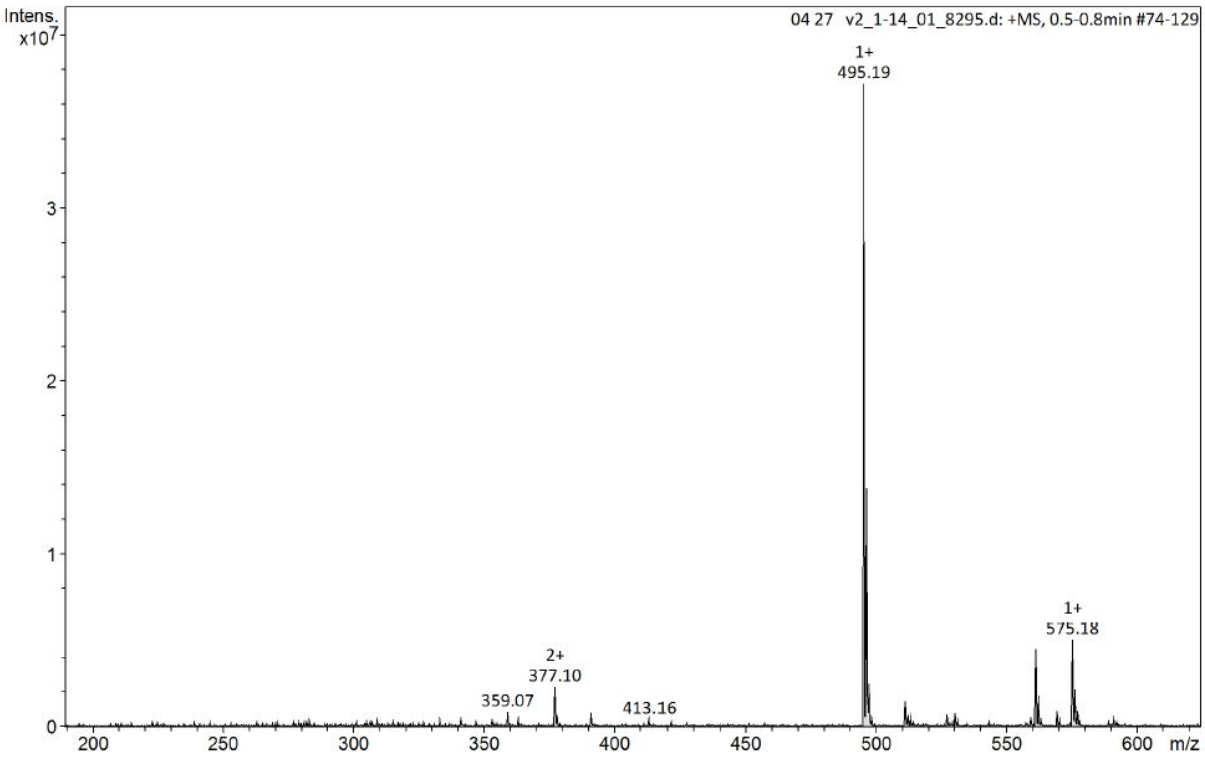

Figure S12. MS of **2**.

UV-Vis Kinetic Analysis; Fries Acid + BCN-TPP (2)

Stock solutions of Fries acid (1 mM) and BCN-TPP (**2**, 20 mM) in acetonitrile were prepared. In a 1 mL UV-Vis cuvette, the Fries acid stock solution (0.1 mL) was diluted with acetonitrile (0.8 mL) cuvette and lastly the stock solution of BCN-TPP (**2**, 0.1 mL) was added, followed by a quick shake of the cuvette. The cuvette was immediately loaded into a Varian Cary 50 Bio UV-Vis spectrophotometer and measurements began. This experiment was repeated at identical concentrations and twice at half the **2** concentrations (0.05 mL of **2** and 0.85 mL of MeCN). UV-vis data was recorded at 453 nm with 6 second intervals over 10 minutes and averaged at each time point. SigmaPlot was utilized to plot data using exponential decay with the equation: $f = y_0+a(e^{(-bx)})$. Data is shown in Figure S13.

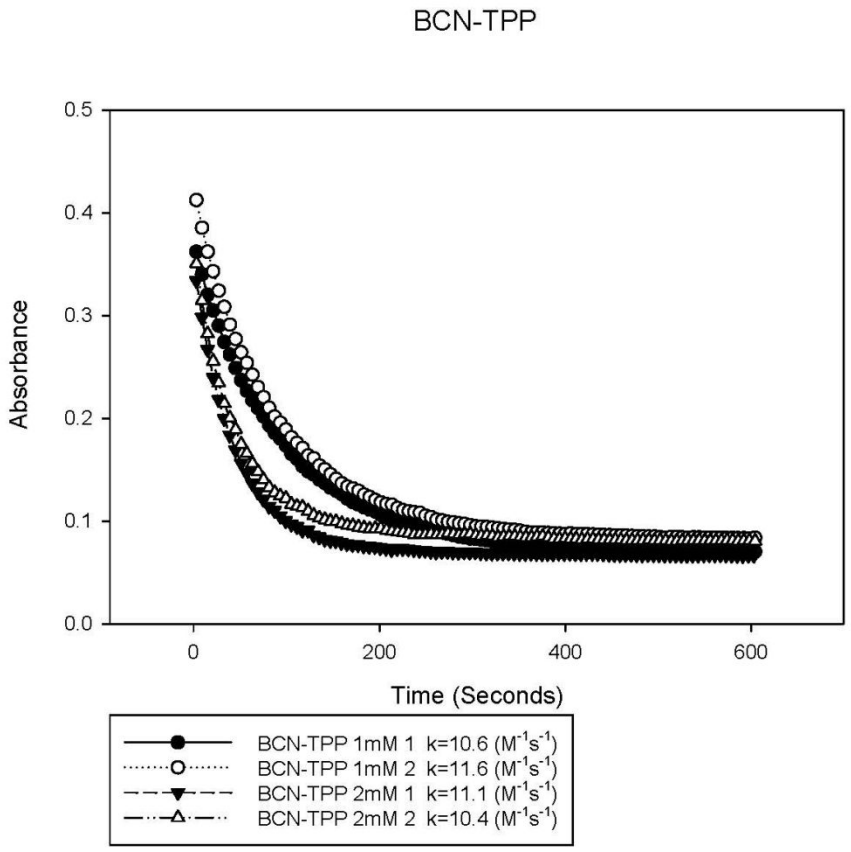

Figure S13. Kinetic monitoring of the reaction of Fries acid (0.1 mM) and TPP-BCN (**2**, 1 and 2 mM) in acetonitrile at room temperature at 453 nm.

Reactivity of BCN-OH with C165A AhpC-SSH

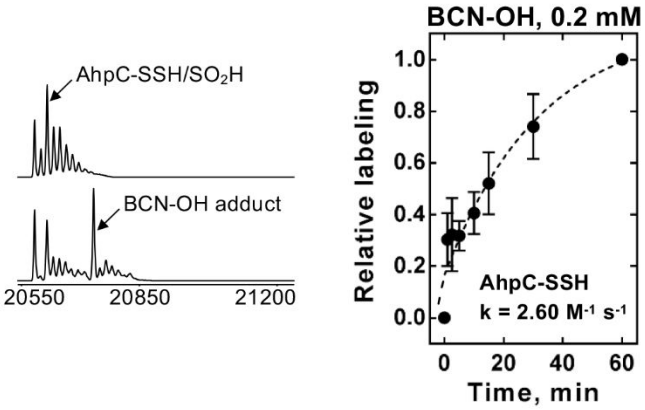

Figure S14. Reaction kinetics of BCN-OH with AhpC-SSH. Oxidized protein was reacted with BCN-OH and set timepoints samples were taken, desalted, and species abundance determined using ESI-TOF MS. To account for differences in batches of AhpC-SSH, the plateau of each reaction is normalized to a value of 1 and all data points are expressed as relatives of the plateau.