Supporting Information for

Visible-Light Photoredox Catalysis: Selective Reduction of Carbon Dioxide to Carbon Monoxide by a Nickel *N*-Heterocyclic Carbene-Isoquinoline Complex

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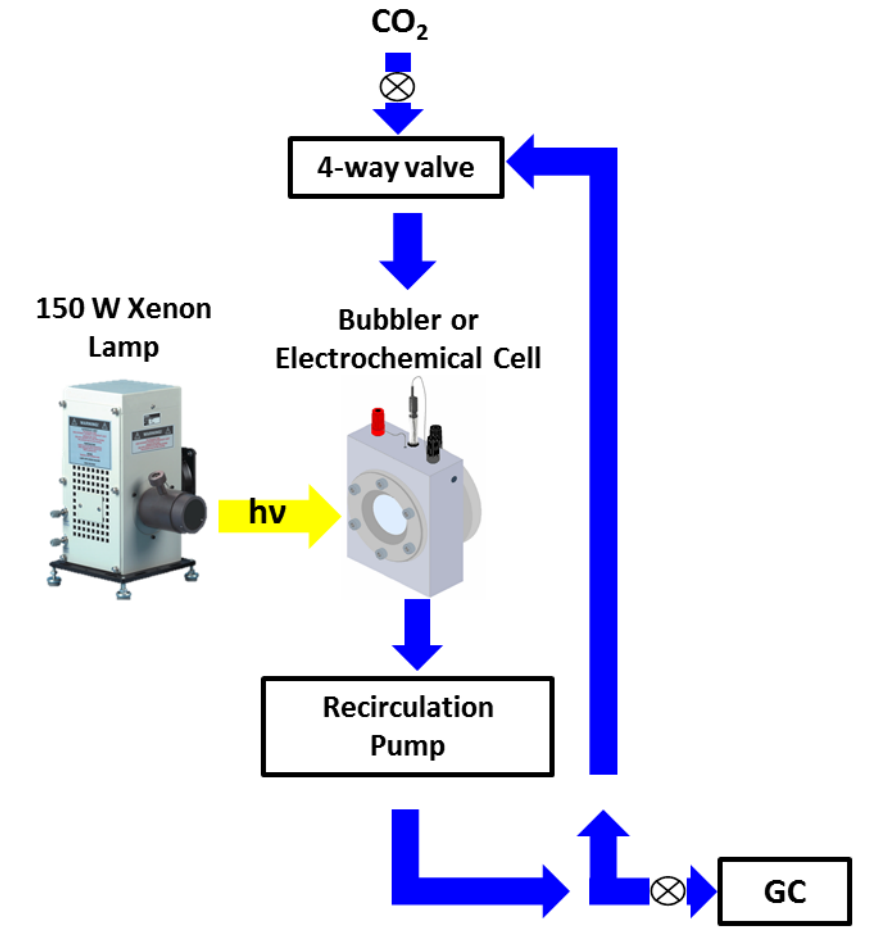

Figure S1. Schematic of experimental photolysis system connected a gas chromtograph.

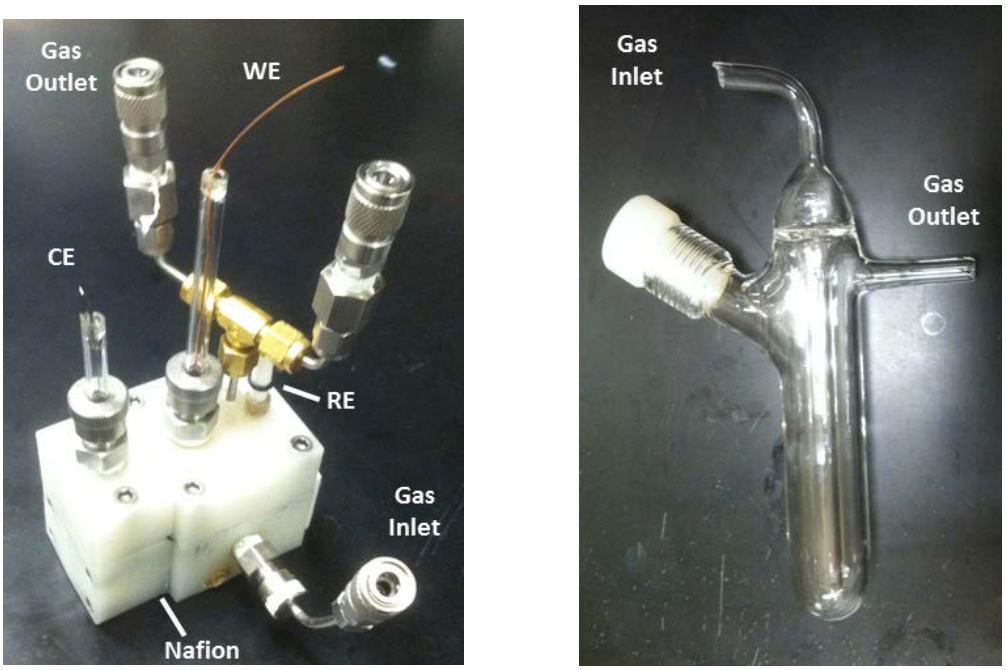

Figure S2. Photographs of electrochemical cell (left) and photolysis cell (right). WE = working electrode, CE = counter electrode, RE = reference electrode.

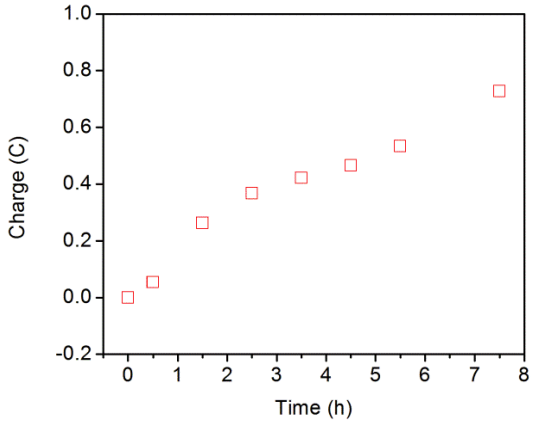

Figure S3. Plot of charge accumulated versus time for a controlled potential electrolysis in a 0.1 M M NBu_4PF_6 acetonitrile solution containing 2 μM **1c** at −1.8 V using a glassy carbon disk electrode under a CO_2 atmosphere.

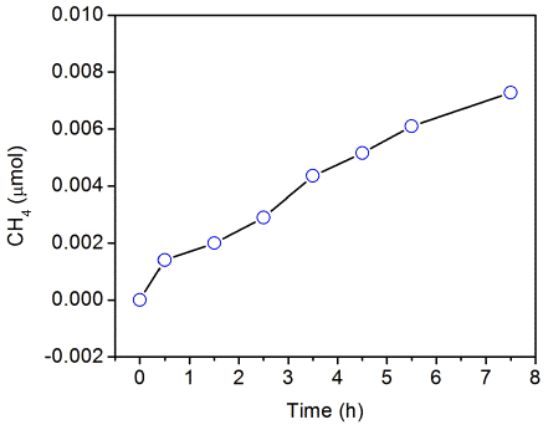

Figure S4. Methane production in a controlled potential electrolysis in a 0.1 M NBu_4PF_6 acetonitrile solution containing 2 μM **1c** at −1.8 V vs. SCE using a glassy carbon disk electrode under a CO_2 atmosphere.

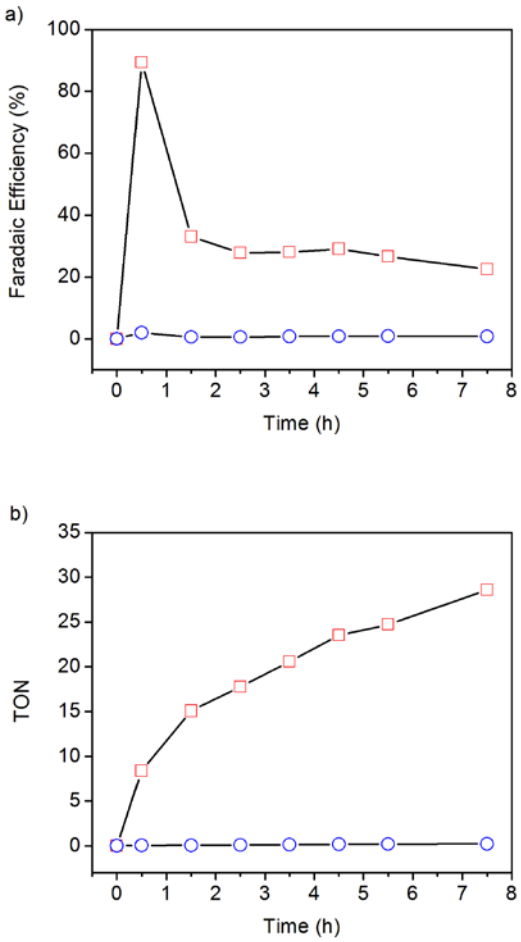

Figure S5. a) Faradaic efficiency versus time and b) gas product versus electrolysis time for CO (red squares) and CH_4 (blue circles) in a controlled potential electrolysis in a 0.1 M M NBu_4PF_6 acetonitrile solution containing 2 μM **1c** at −1.8 V using a glassy carbon rod electrode under a CO_2 atmosphere.

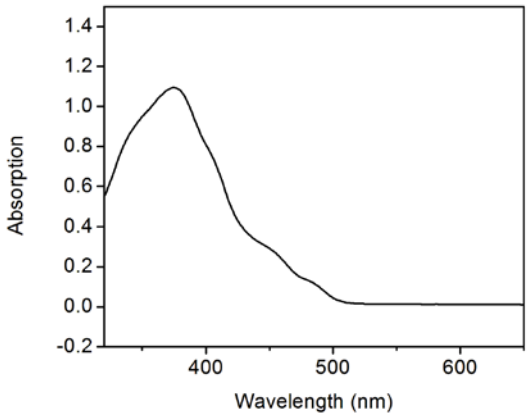

Figure S6. Absorption spectrum of $Ir(ppy)_3$.

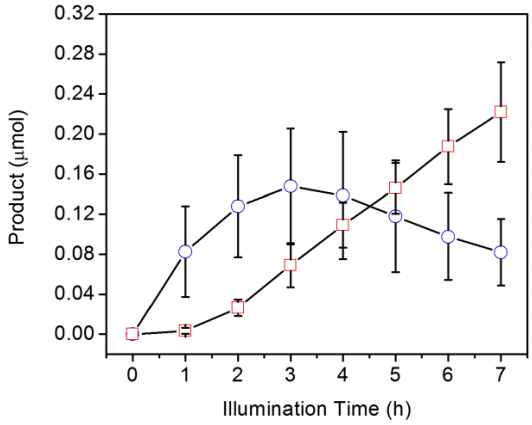

Figure S7. Photocatalytic reduction of CO_2 to minor products CH_4 (red squares) and C_2H_4 (blue circles) in a 0.07 M M TEA acetonitrile solution containing 0.2 μM **1c** and 0.2 mM $Ir(ppy)_3$, using a 130 $mW \cdot cm^{-2}$ Xe lamp fitted with an AM 1.5 filter.

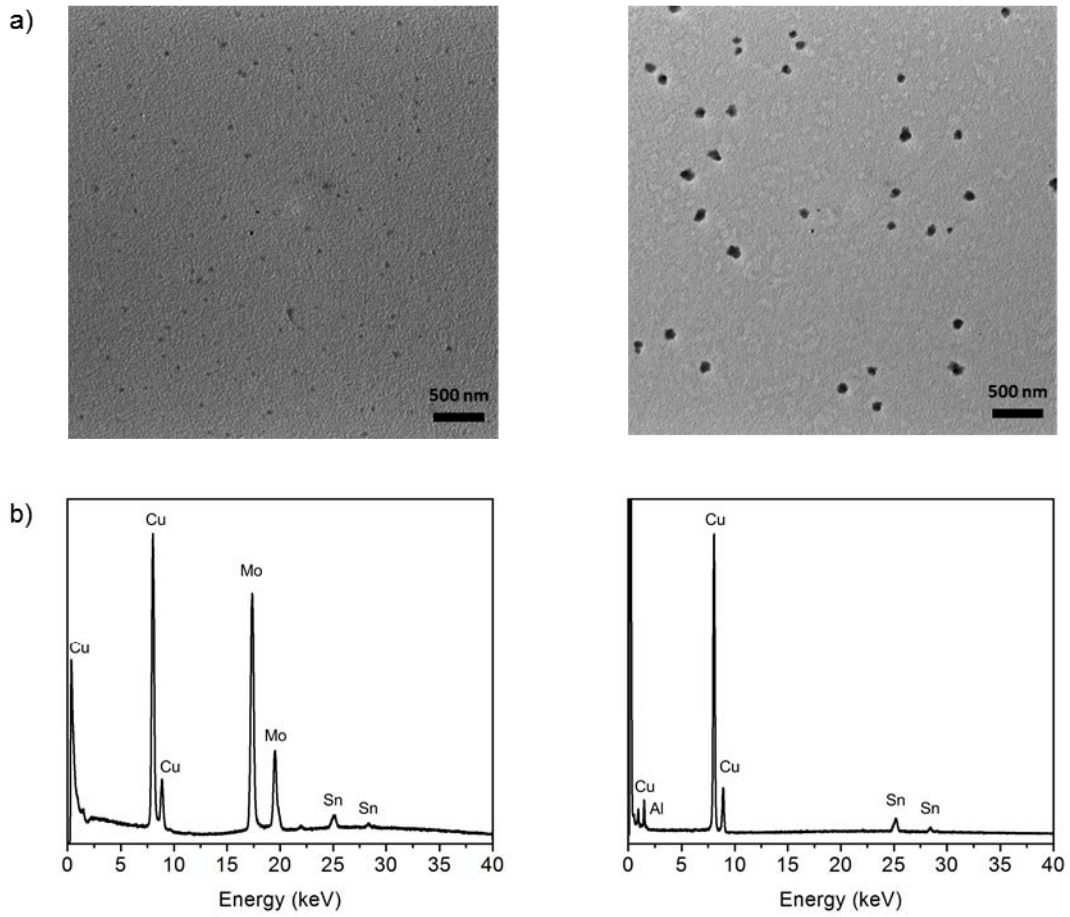

Figure S8. a) TEM images and b) EDS plots of 0.07 M M TEA acetonitrile solution containing 0.2 μM **1c** and 0.2 mM $Ir(ppy)_3$, before (left) and after photolysis (right), using a 130 $mW \cdot cm^{-2}$ Xe lamp fitted with an AM 1.5 filter. The copper, aluminum, and tin signals originate from the TEM grid holder and grid. A Pelco 300 Mesh molybdenum grid and copper grid (Ted Pella, Inc.) were used for the samples before and after photolysis, respectively.

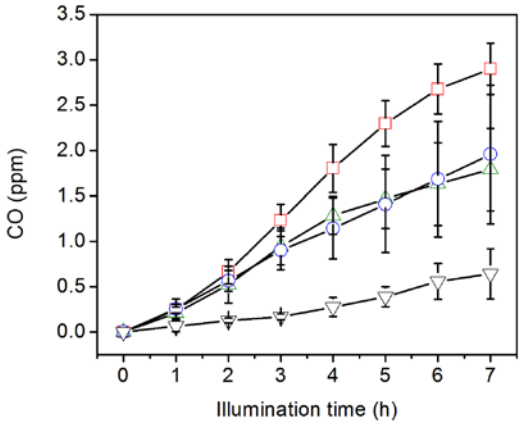

Figure S9. Photocatalytic reduction of CO_2 to CO in a 0.07 M M TEA acetonitrile solution containing 0.2 mM $Ir(ppy)_3$ and 200 nM (red squares), 20 nM (green triangles), 2 nM (blue circles), and 0 nM (black triangles) $Ir(ppy)_3$, using a 130 $mW \cdot cm^{-2}$ Xe lamp fitted with an AM 1.5 filter.

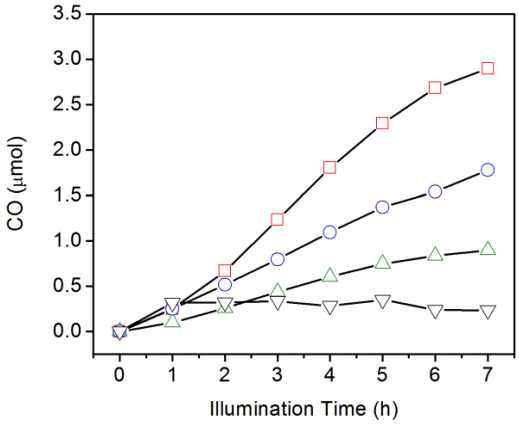

Figure S10. Photocatalytic reduction of CO_2 to CO in an acetonitrile solution containing 0.2 μM **1c** and 0.2 mM $Ir(ppy)_3$ in the presence of 0.07 M TEA (red squares), TEOA (blue circles), DMAE (green triangles), and IPA (black triangles), using a 130 $mW \cdot cm^{-2}$ Xe lamp fitted with an AM 1.5 filter.

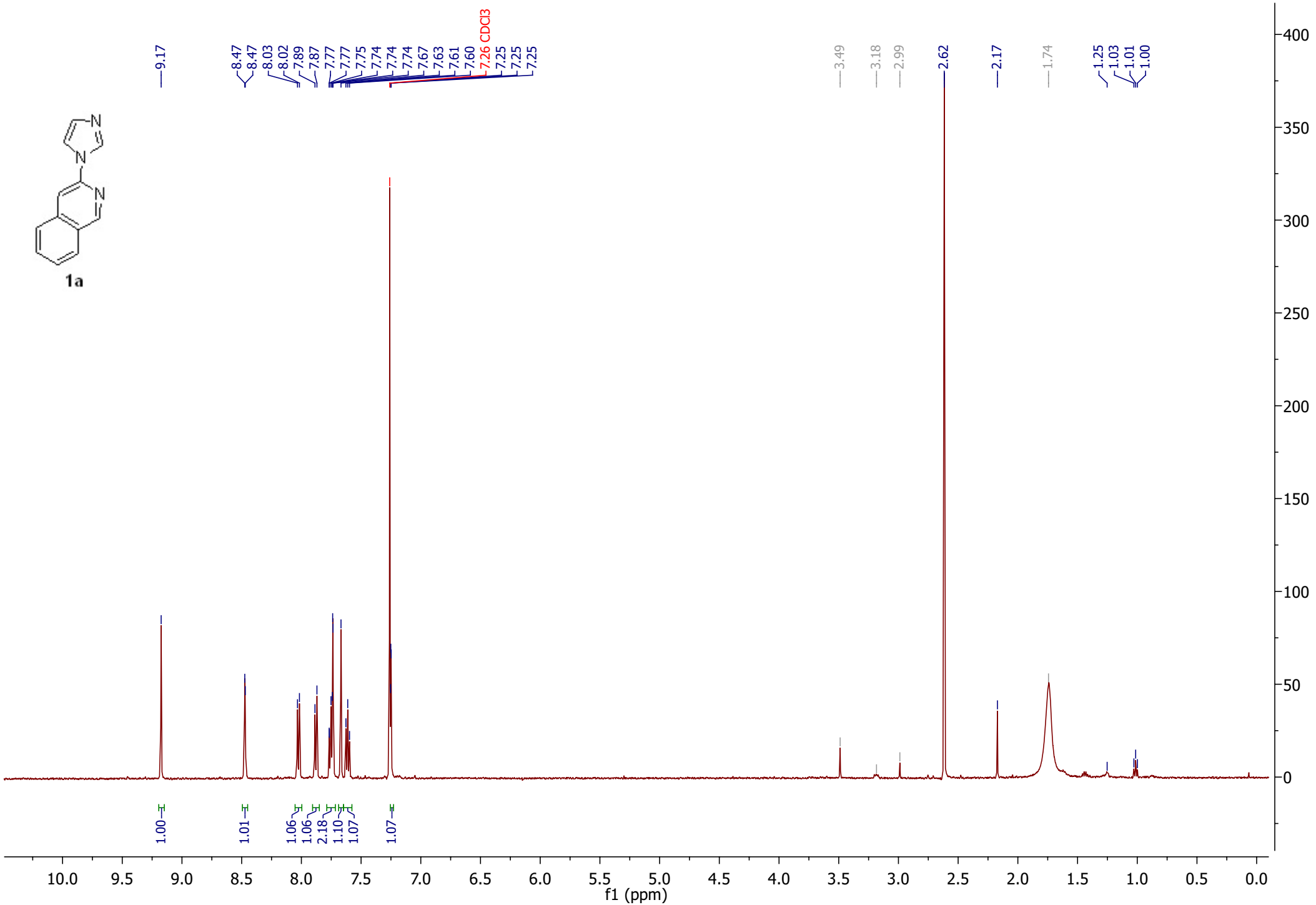

Figure S11. ^{1}H NMR Spectrum of **1a**.

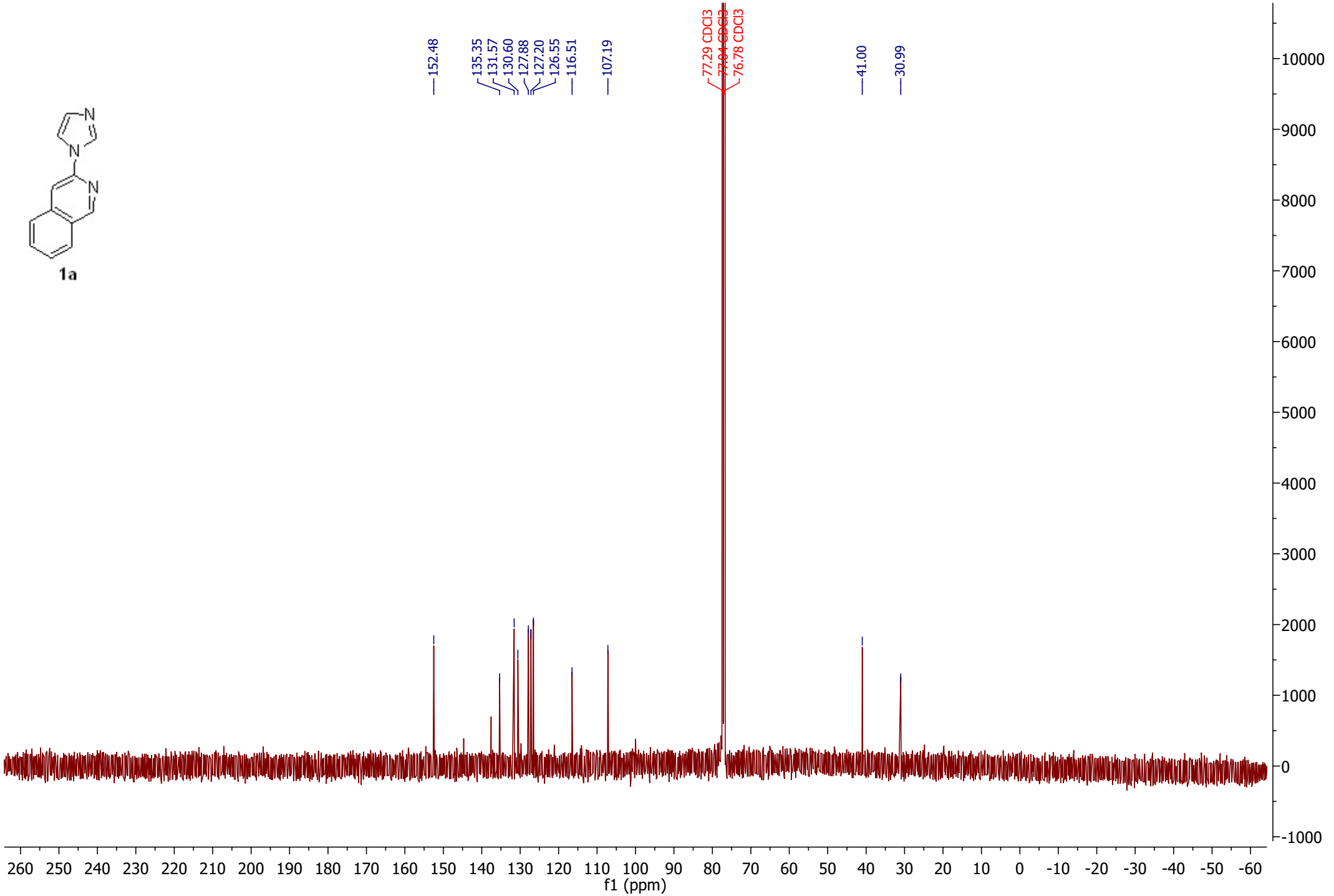

Figure S12. ^{13}C NMR Spectrum of **1a**.

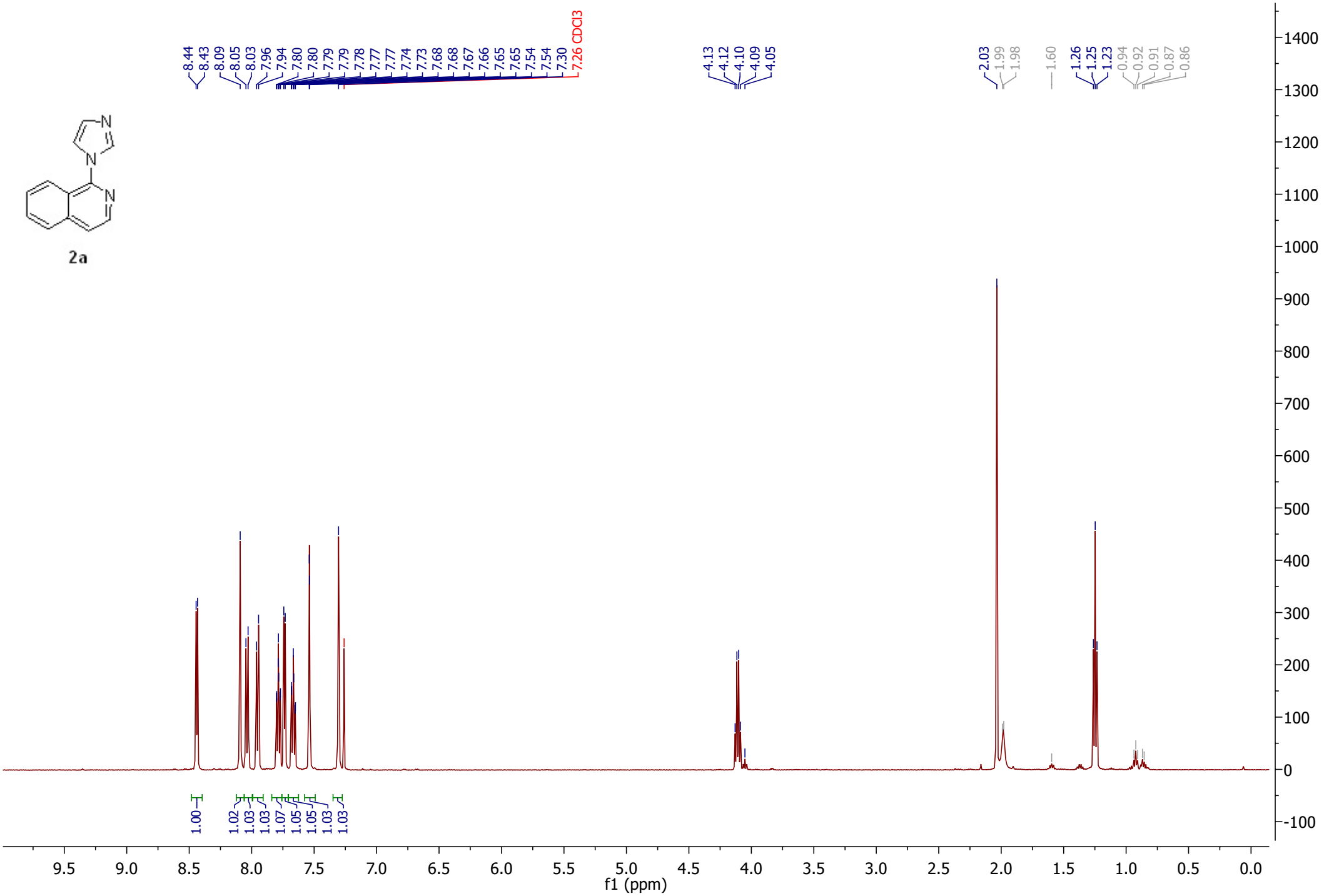

Figure S13. ^{1}H NMR Spectrum of **2a**.

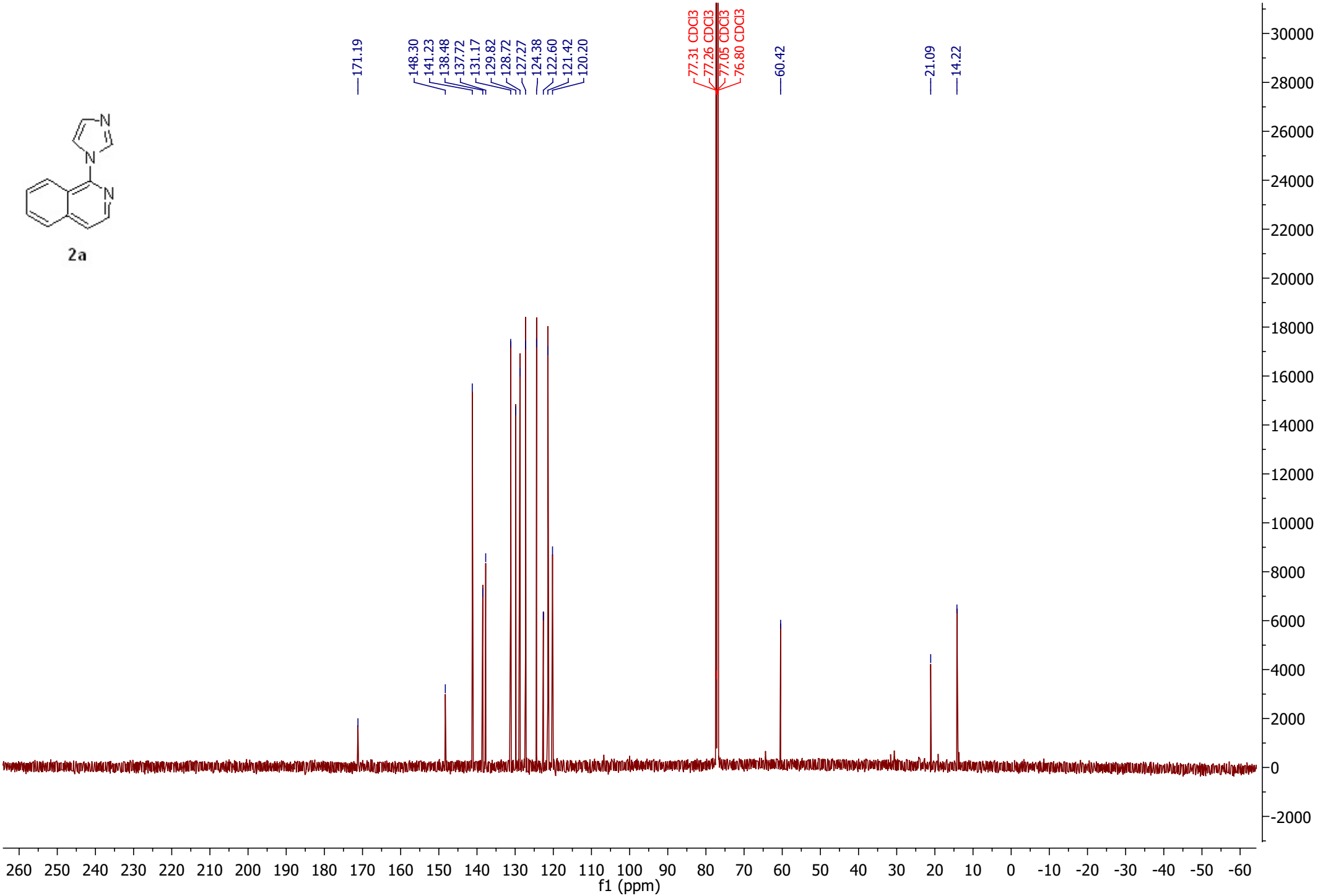

Figure S14. ^{13}C NMR Spectrum of **2a**.

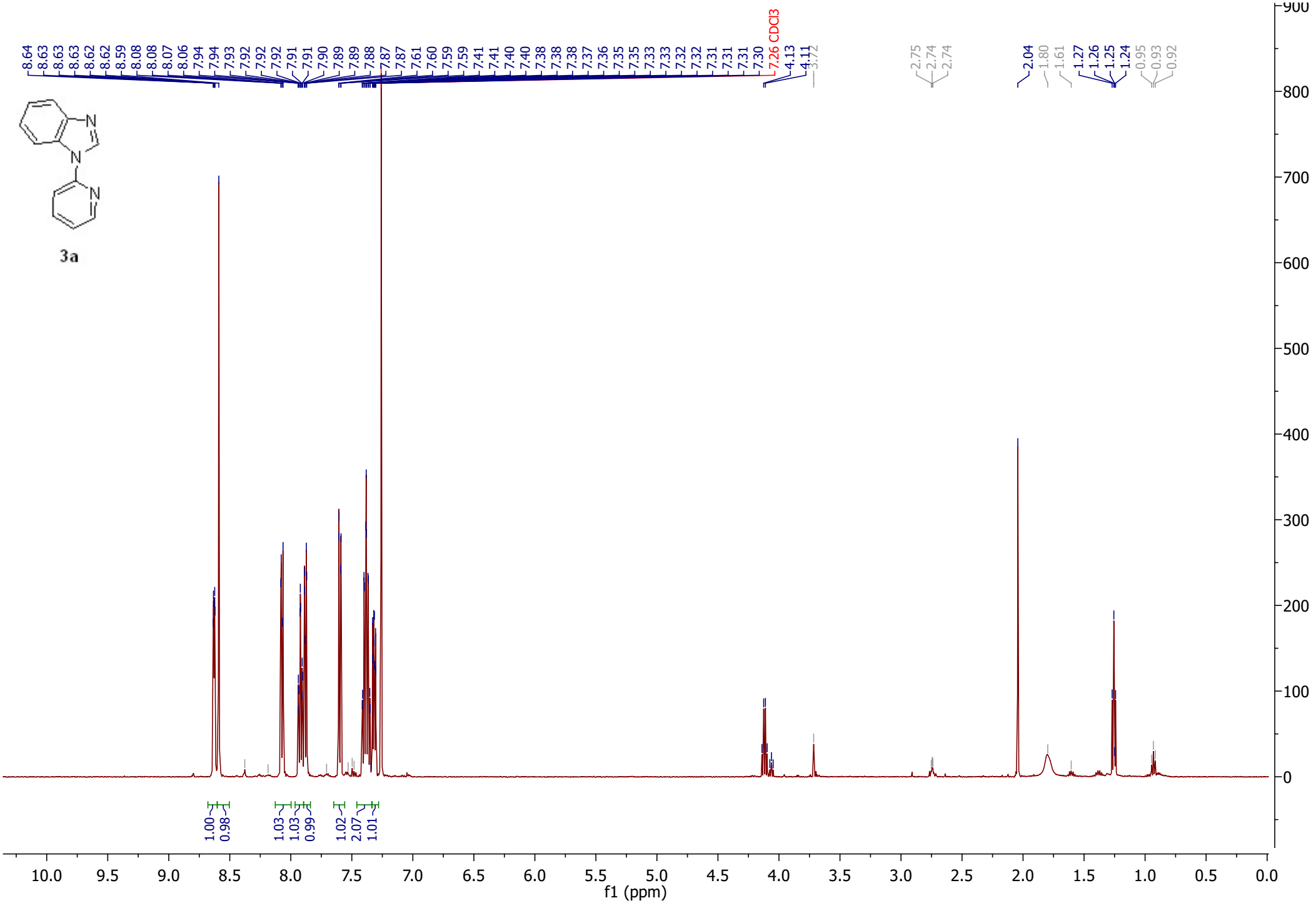

Figure S15. ^{1}H NMR Spectrum of **3a**.

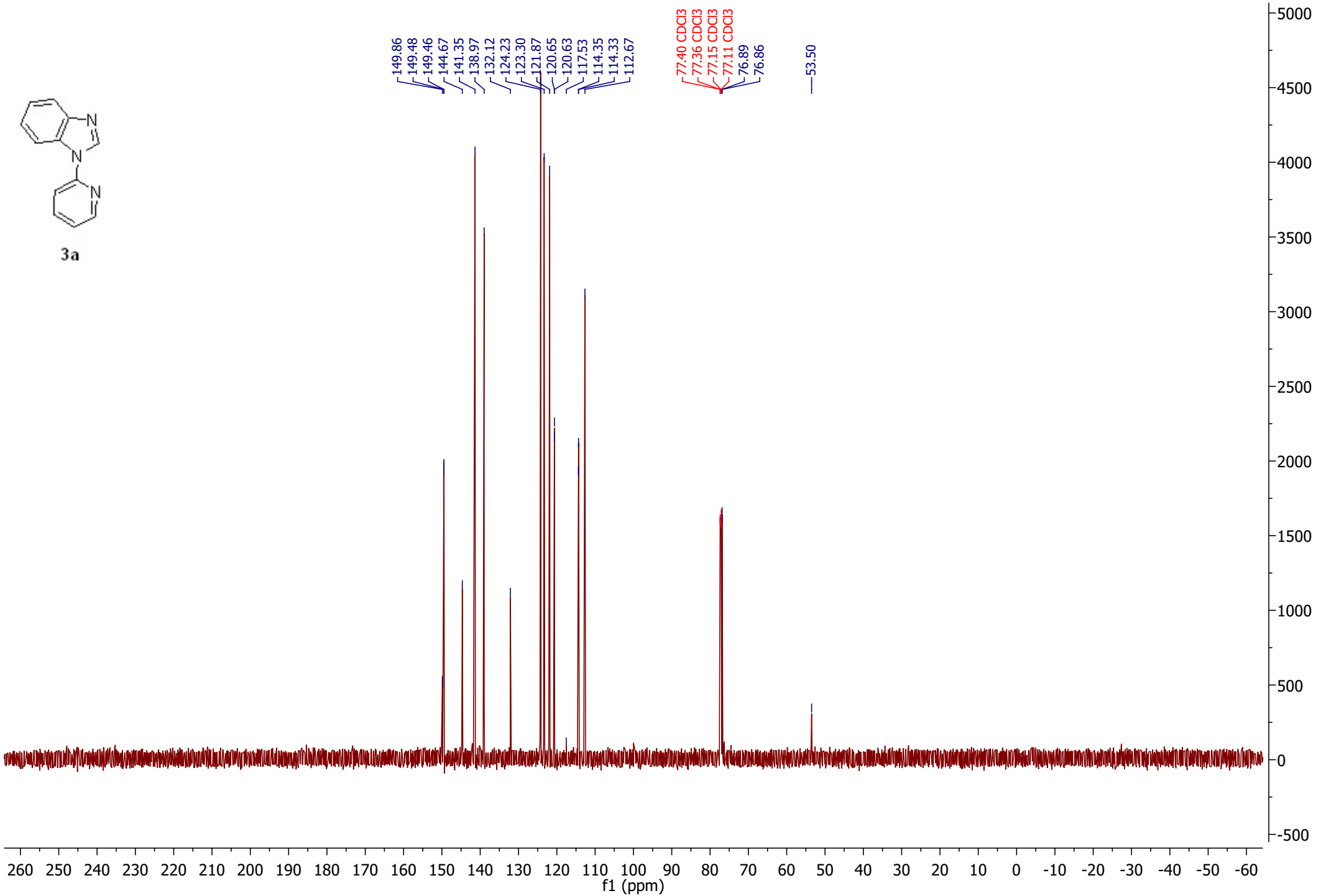

Figure S16. ^{13}C NMR Spectrum of **3a**.

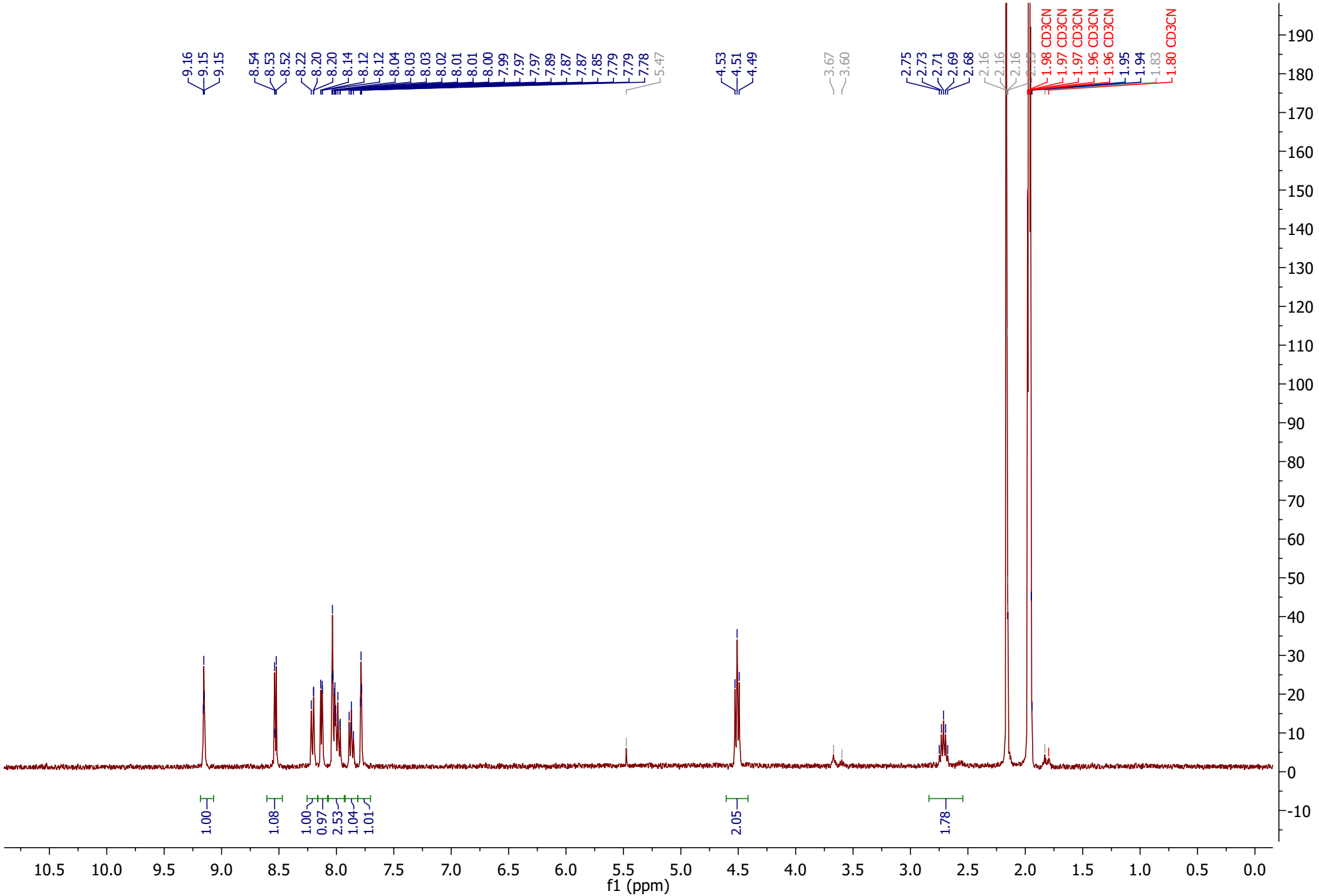

Figure S17. ^{1}H NMR Spectrum of **2b**.

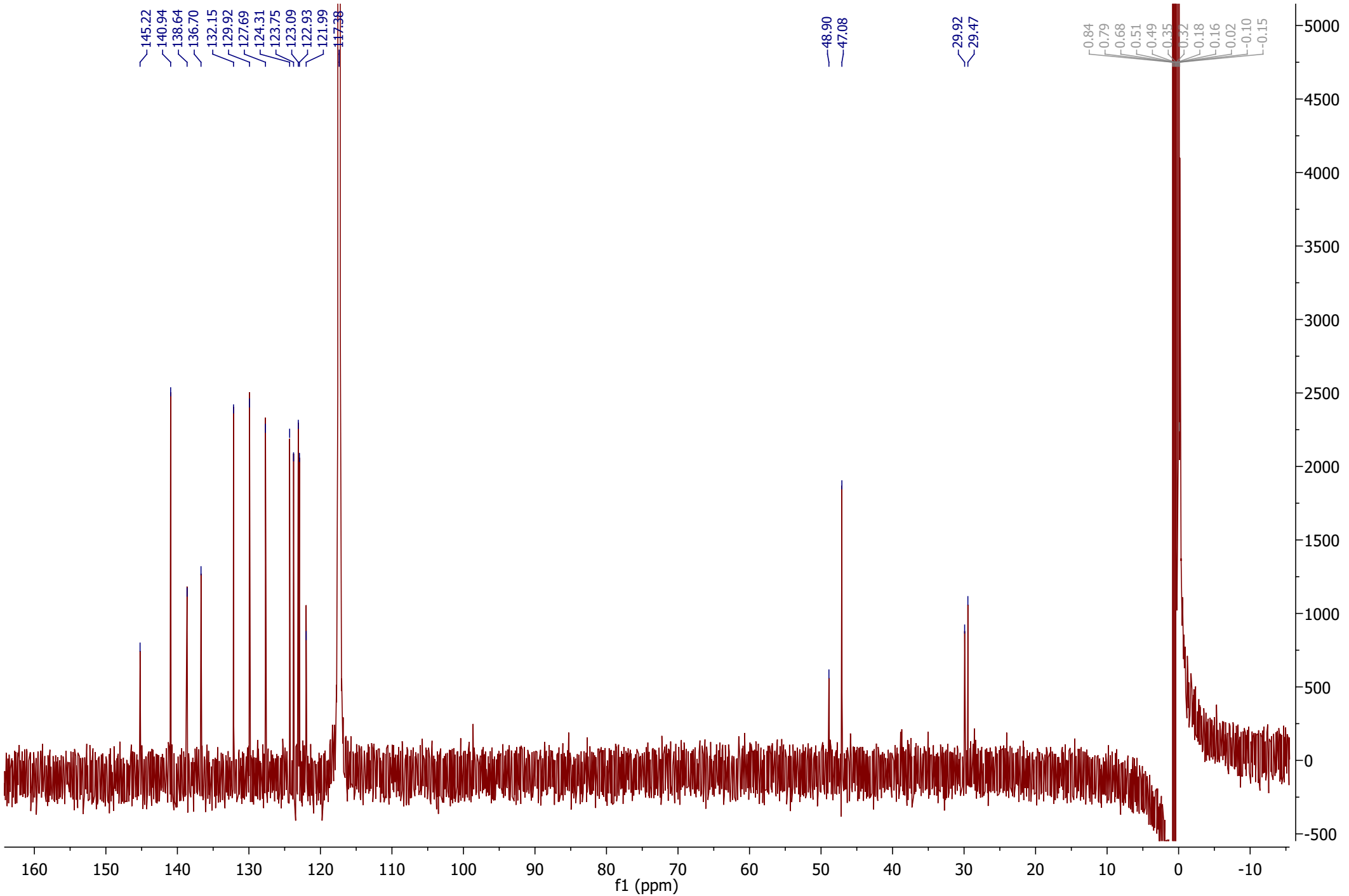

Figure S18. ^{13}C NMR Spectrum of **2b**.