Ambient reductive synthesis of N-heterocyclic compounds over cellulose-derived carbon supported Pt nanocatalyst under H_2 atmosphere

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1. Experimental Section

1.1 Materials.

Cellulose, $ZnCl_2$ (99%) and acetone (99%) were acquired from Sinopharm Chemical Reagent. Phytic acid (45 wt% in water), levulinic acid (99%), aniline (99%), o-toluidine (99%), m-toluidine (99%) p-toluidine (99%), 4-fluoroaniline (98%), 4-chloroaniline (98%), 3-chloroaniline (98%), 4-bromoaniline (98%), 4-iodoaniline (99%), cyclohexylamine (99%), n-butylamine (99%), n-octylamine (99%), benzylamine (99%), 4-acetylbutyric acid (96%), 2-nitrobenzaldehyde (98%), 5-bromo-2-nitrobenzaldehyde (97%), 4-chloro-2-nitrobenzaldehyde (98%), 5-chloro-2-nitrobenzaldehyde (98%), 5-methoxy-2-nitrobenzaldehyde (98%), 6-nitroveratraldehyde (96%) and chloroplatinic acid hexahydrate (99.9%) were purchased from J&K Scientific Ltd.. Commercial Pt/C (5.0 wt% Pt loading, particle size around 2 nm, specific surface area of 1120 $m^2 \cdot g^{-1}$) was supplied by J&K Scientific Ltd.. H_2 was supplied by Beijing Analytical Instrument Factory with purity of 99.99%. All above chemicals were used without further purification.

1.2 Characterization.

The morphology of the samples was observed by field emission SEM on a scanning electron microscope (S-4800, Hitachi, Japan) and by TEM on a transmission electron microscope (JEM2100F, JEOL, Japan). The specific surface area (SSA) and pore structure were investigated with a Quantachrome Quadrasorb SI-MP porosimeter using nitrogen as the adsorbate at 77 K. Prior to determination of the isotherm, the samples were degassed at 200 °C under vacuum for at least 3 h. The value of the total pore volume was determined from the NLDFT kernel at the relative pressure $P/P_0 = 0.99$. The total SSA was calculated using the Brunauer-Emmett-Teller (BET) method from the nitrogen adsorption data in the relative pressure (P/P_0) of 0.03-0.30. X-Ray photoelectron spectroscopy (XPS) data were collected on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al-Kα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. FT-IR analysis of the samples were performed using a Bruker Optic TENSOR-37. All samples were determined in the range of 4000-400 cm^{-1} wavenumbers. Raman spectrum was detected on LabRAM HR Evolution. The elemental contents of the samples were determined using Flash EA1112 from

Thermo. Inductively coupled plasma (ICP) analysis was performed on a Jarrel-AshJ-A1100 spectrometer. The reaction systems were analysed on a gas chromatography- mass spectrometry (GC-MS, Ultra). NMR analysis was performed on a Bruker Avance 400 MHz spectrometer.

1.3 General procedures to synthesize c-C, Pt/c-C and Pt/rGO.

The synthesis of c-C was as follows: cellulose (1 g) and $ZnCl_2$ (8 g) were transferred into a flask charged with phytic acid (2 g, 45 wt% in water). Then, the system was stirred at 60 ^oC for 10 hours. Hydrogel formed when the system cooled down to room temperature. The formed hydrogel was collected and transferred into a ceramic boat, then moved to a tubular furnace for carbonization under nitrogen atmosphere with a flow rate of 100 $mL \cdot min^{-1}$. Gradient heating mode was adopted. The sample was heated with a heating rate of 10 $^oC \cdot min^{-1}$ from room temperature to 300 °C and held at this temperature for 2 h; then the temperature was further increased to 600 °C with a heating rate of 5 $°C \cdot min^{-1}$, and maintained at the final temperature for 2 h. Afterwards, the tubular furnace was allowed to cool down to room temperature under nitrogen atmosphere. The resultant mixture was ground into powder in an agate mortar, and washed with hydrochloric acid aqueous solution and deionized water at room temperature to remove the salts until there was no Cl^- detected in the supernatant. The resultant sample was dried under vacuum at 100 °C for 12 h. Similarly, using chitosan as the feedstock chitosan-derived carbon (ch-C) was prepared.

To prepare the Pt/c-C catalyst, $H_2PtCl_6 \cdot 6H_2O$ ethanol solution with a concentration of 7.432 $mg \cdot mL^{-1}$ (673 uL) was mixed with 95 mg of c-C. The mixture was dried under vacuum at 60 °C for 2 h to remove ethanol and then moved into a quartz tube for being reduced at 200 °C under H_2 + Ar atmosphere (containing 90% Ar) for 2 h. The Pt content was detected by ICP analysis to be 5.0 wt%. Similarly, using ch-C as the carbon support Pt/ch-C was prepared with Pt content ~5.0 wt%. Pt/rGO was synthesized employing reduced graphene oxide as the support under the same other conditions.

1.4 General procedures for recycling experiments

To test the recyclability of Pt/c-C, the catalyst was separated from the reaction system by filtration, washed with methanol for 4 times, and then dried under vacuum at 60 °C for 10 h. The recycled Pt/c-C was reused in the next run keeping the same catalyst consumption.

1.5 Methods to calculate the product yields.

After the reaction, mesitylene (0.33 mmol) acting as an internal standard was added to the reaction system and the mixture was determined by ^{1}H NMR after well stirring. The yield was calculated by the integral area ratio of the characteristic H peak in mesitylene and product. The characteristic H peaks of mesitylene and products (2,1-benzisoxazole, 5-methyl-1-phenylpyrrolidin-2-one) were displayed in Figure S5 and S6.

2. Characterization for the synthesized materials and reaction process, figure S1-S4, Scheme S1.

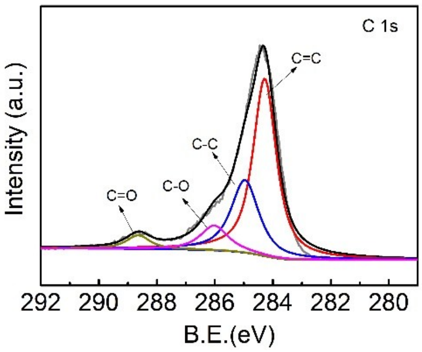


Figure S1. C 1s XPS spectrum for Pt/c-C.

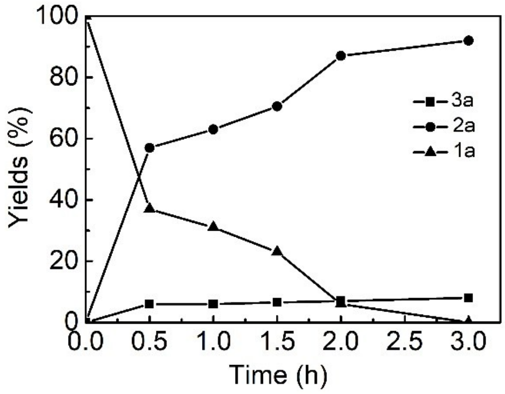


Figure S2. Time course of reductive heterocyclization of 2-nitrobenzaldehyde: 2-nitrobenzaldehyde (1a), 2,1-benzisoxazole (2a) and 2-aminobenzaldehyde (3a).

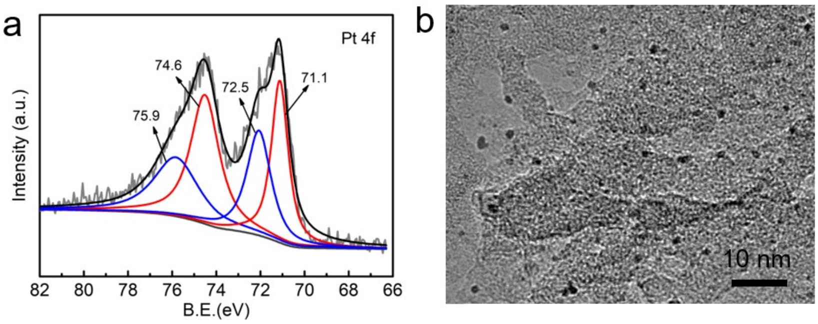
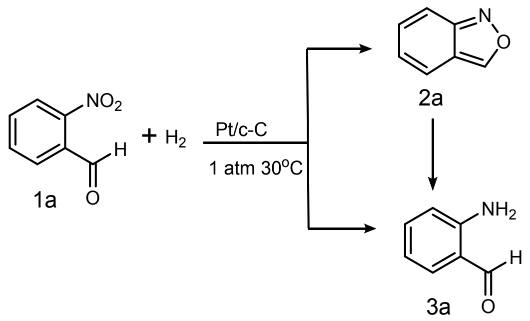


Figure S3. (a) Pt 4f XPS spectrum and (b)TEM image of reused Pt/c-C after 5 runs.



Scheme S1. Reductive heterocyclization of 2-nitrobenzaldehyde.

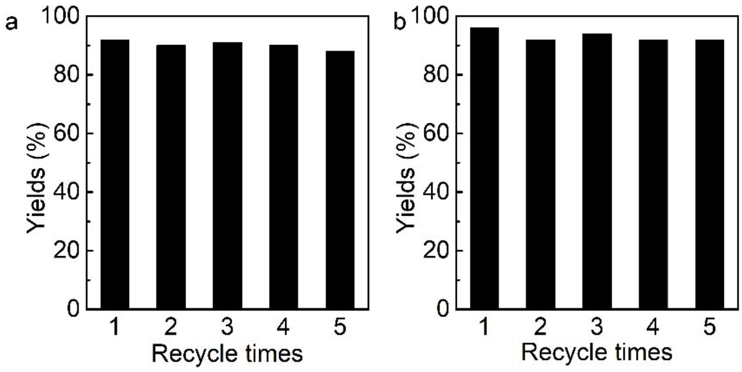


Figure S4. The results of the recycling test for reductive N-heterocyclization of (a) 2-nitrobenzaldehyde to 2,1-benzisoxazole and (b) LA with aniline to pyrrolidone.

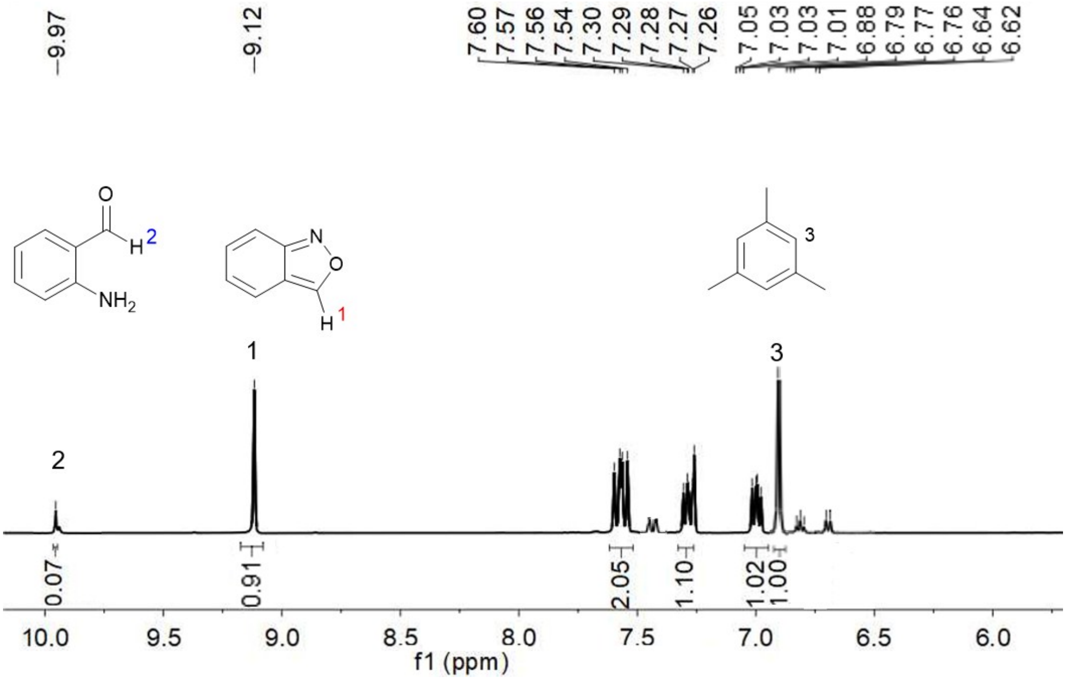


Figure S5. Typical ^1H NMR method to determine the yield of 2,1-benzisoxazole.

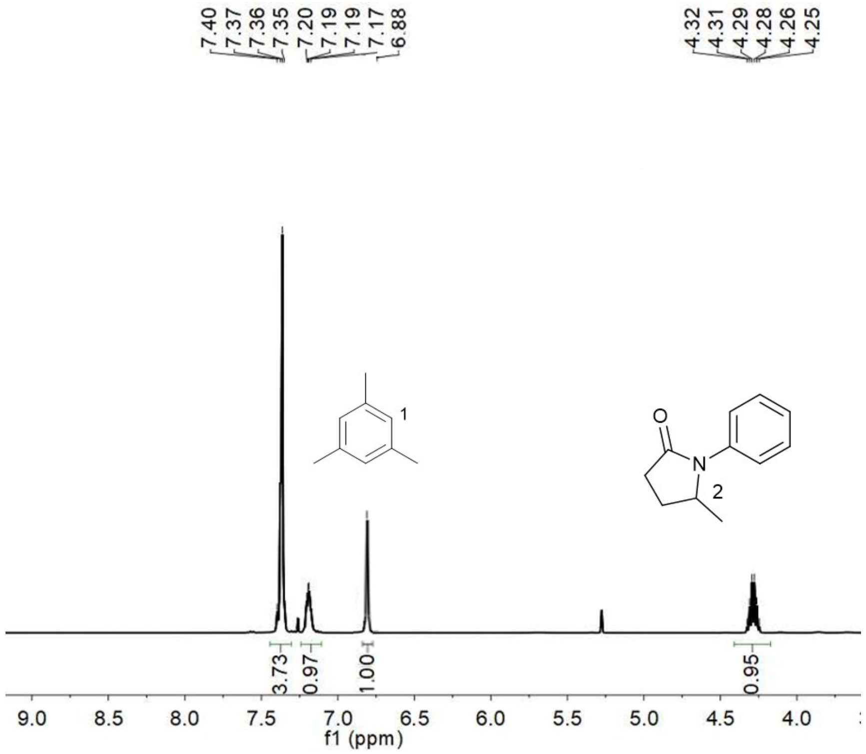


Figure S6. Typical ^{1}H NMR method to determine the yield of 5-methyl-1-phenylpyrrolidin-2-one.

3. NMR spectra for products, Figure S7 – S50.

After the reaction, the catalyst was removed from the reaction solution to collect the filtrate. To get pure NMR spectrum, the filtrate was diluted by methanol and isolated by column chromatography on silica gel (eluent: petroleum ether and EtOAc). The pure product was detected by both of ^{1}H and ^{13}C NMR as shown in Figure S7-S50.

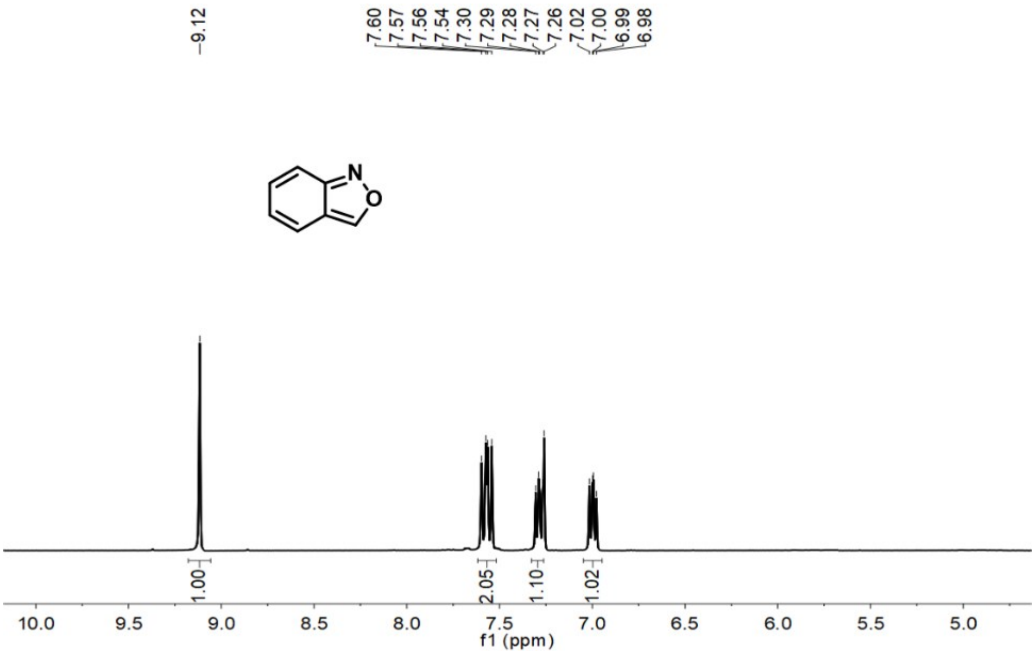


Figure S7. ^{1}H NMR spectrum for **2a**.

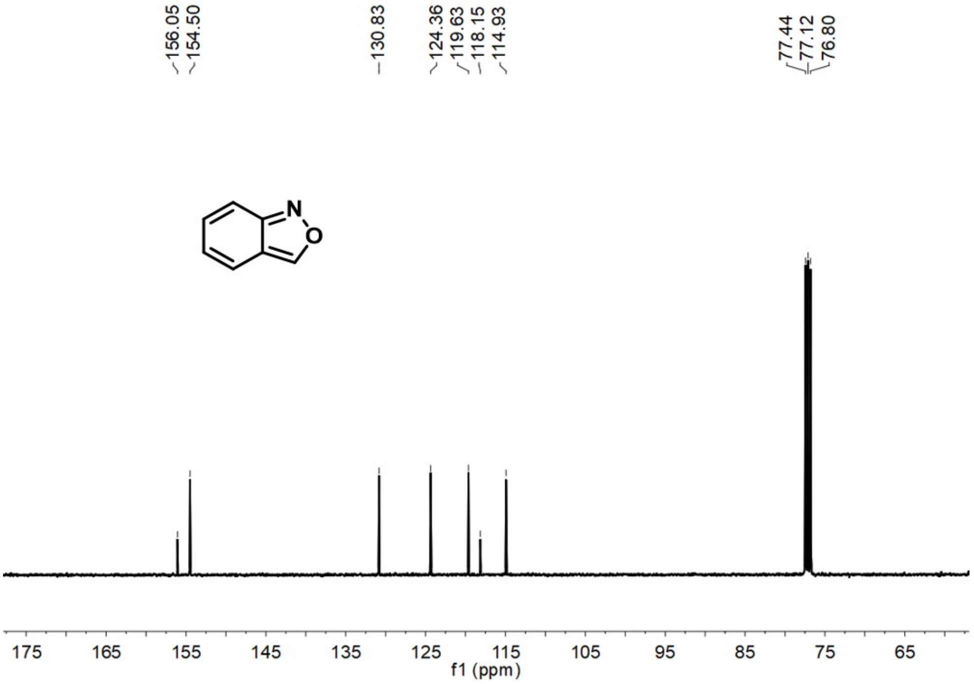


Figure S8. ^{13}C NMR spectrum for **2a**.

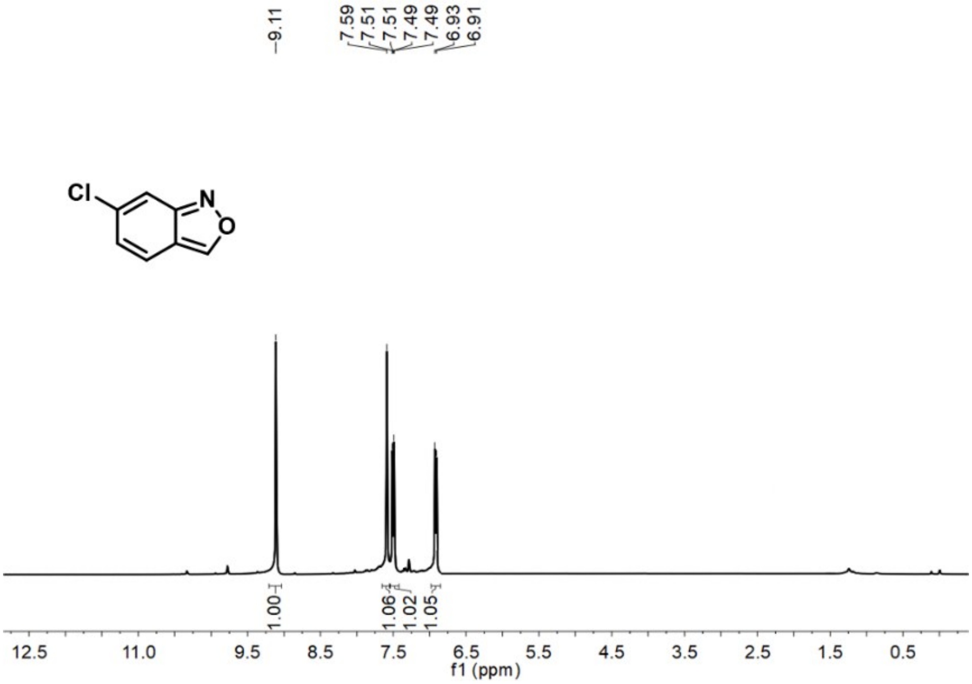


Figure S9. ^{1}H NMR spectrum for **2b**.

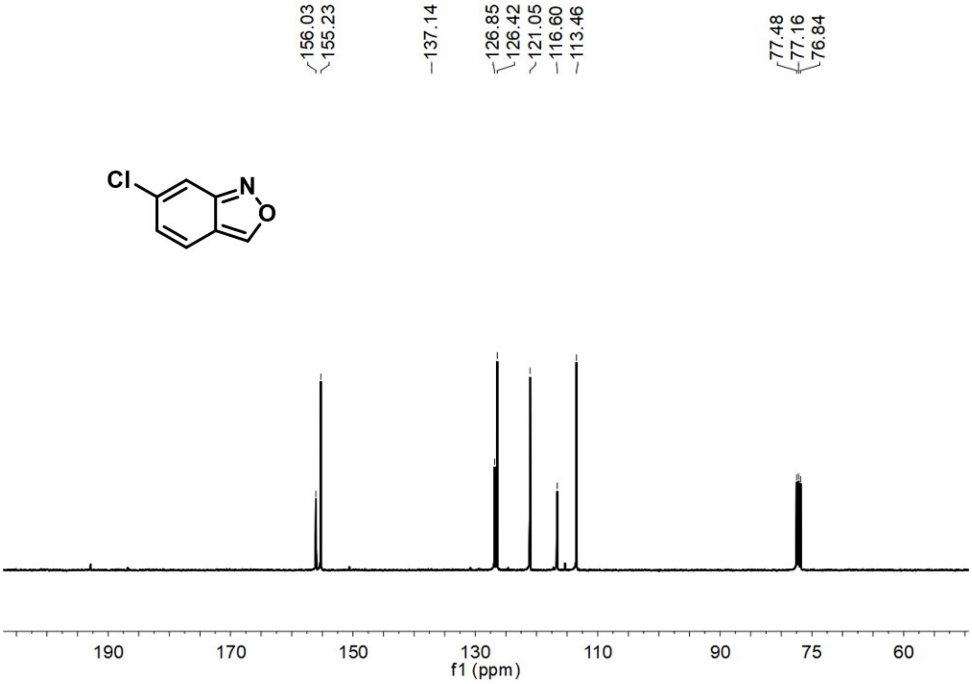


Figure S10. ^{13}C NMR spectrum for **2b**.

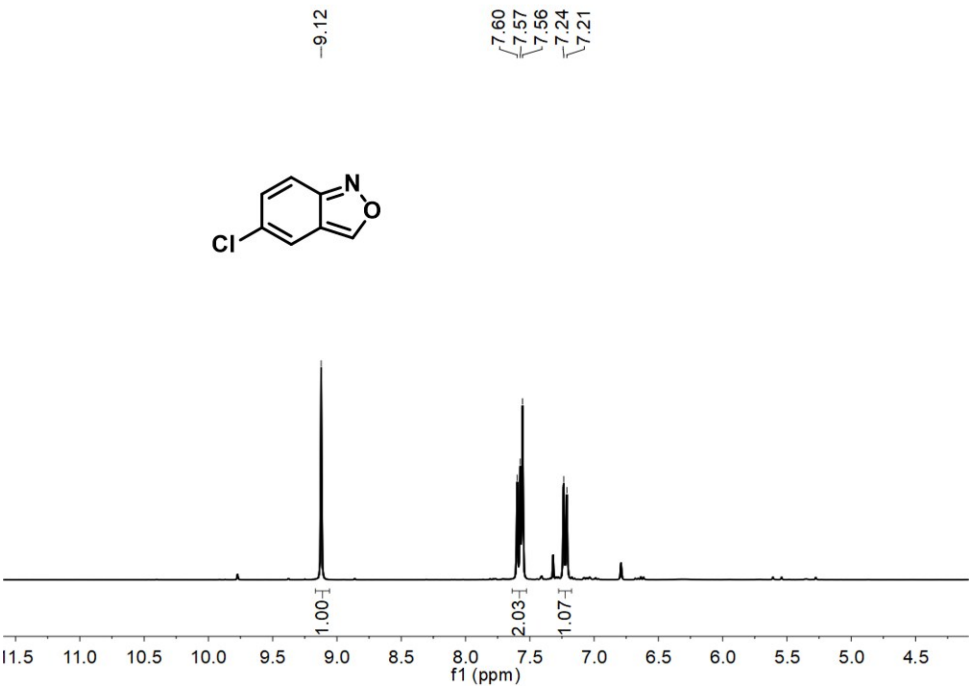


Figure S11. ^{1}H NMR spectrum for **2c**.

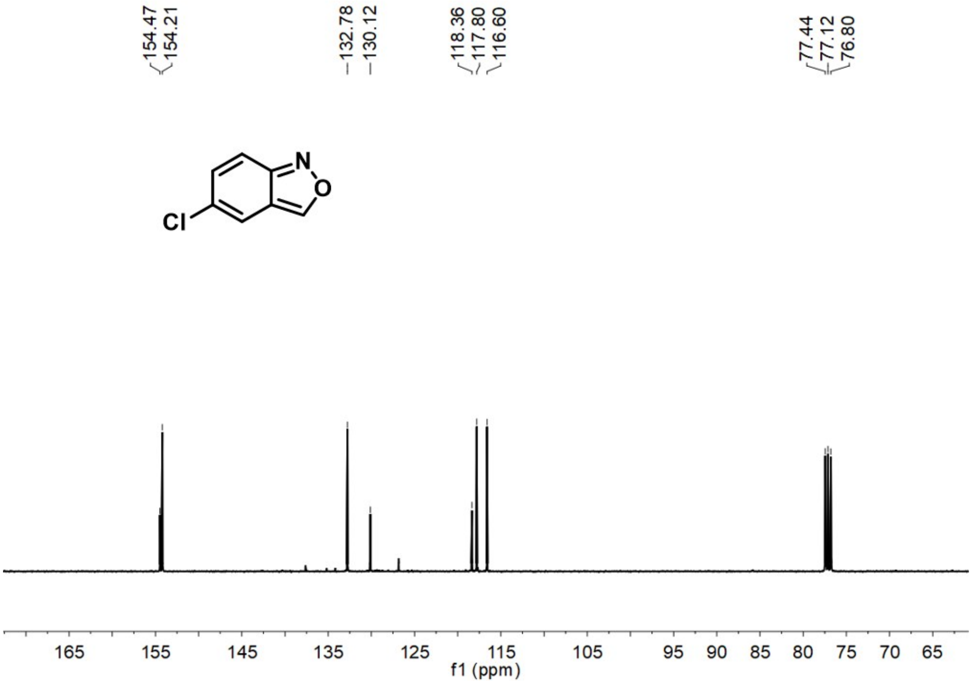


Figure S12. ^{13}C NMR spectrum for **2c**.

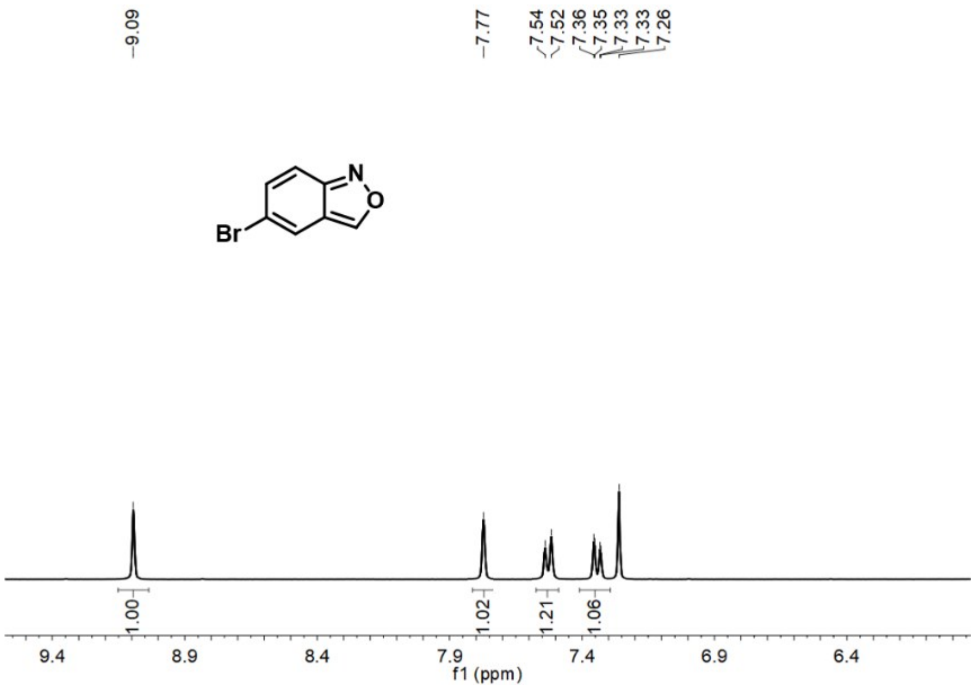


Figure S13. ^{1}H NMR spectrum for **2d**.

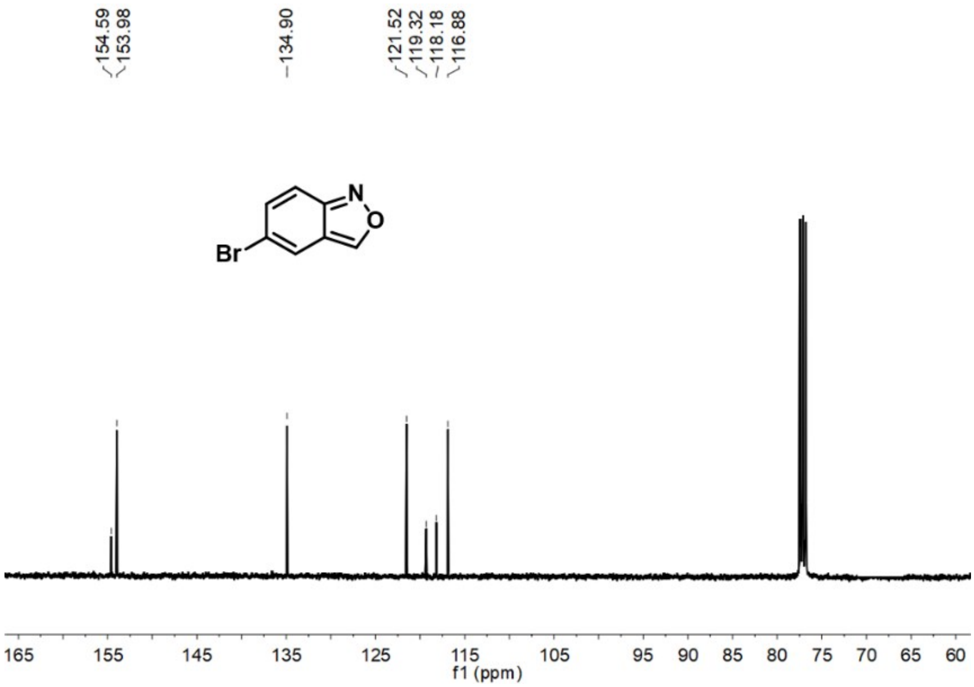


Figure S14. ^{13}C NMR spectrum for **2d**.

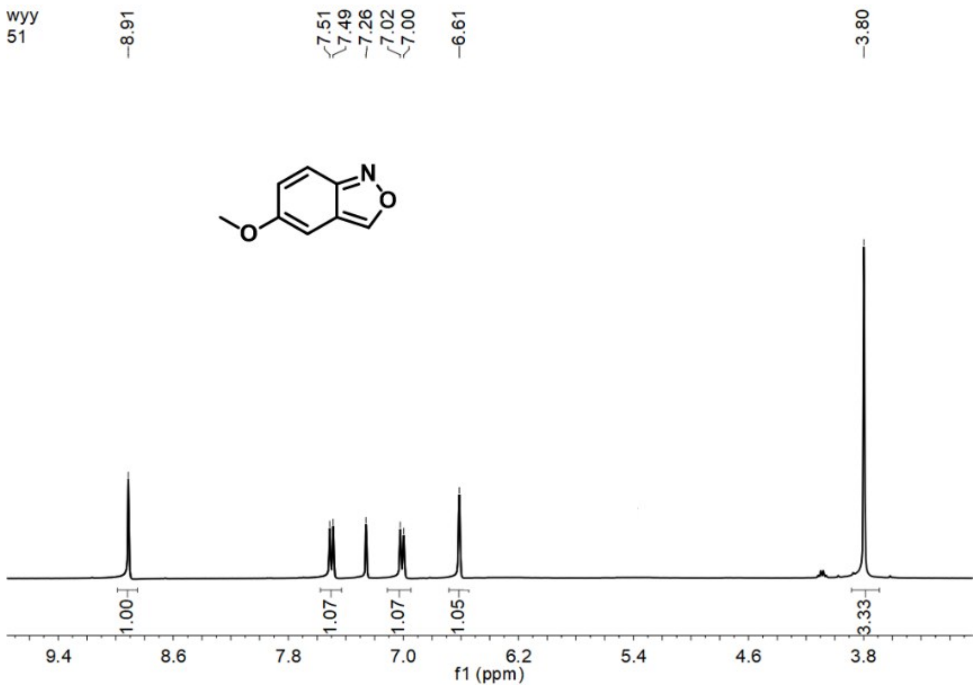


Figure S15. ^{1}H NMR spectrum for **2e**.

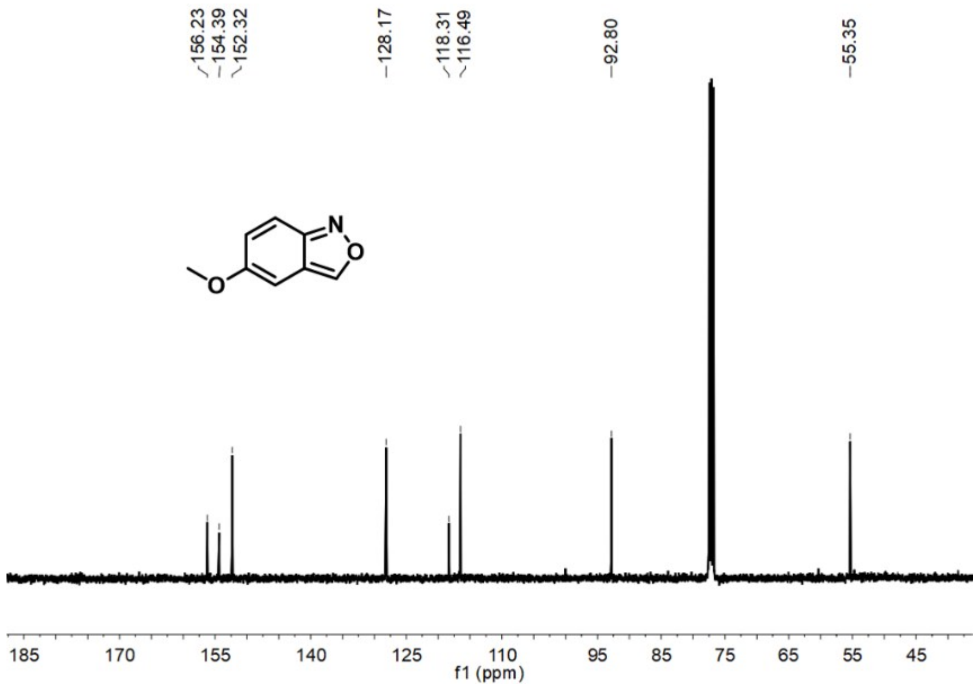


Figure S16. ^{13}C NMR spectrum for **2e**.

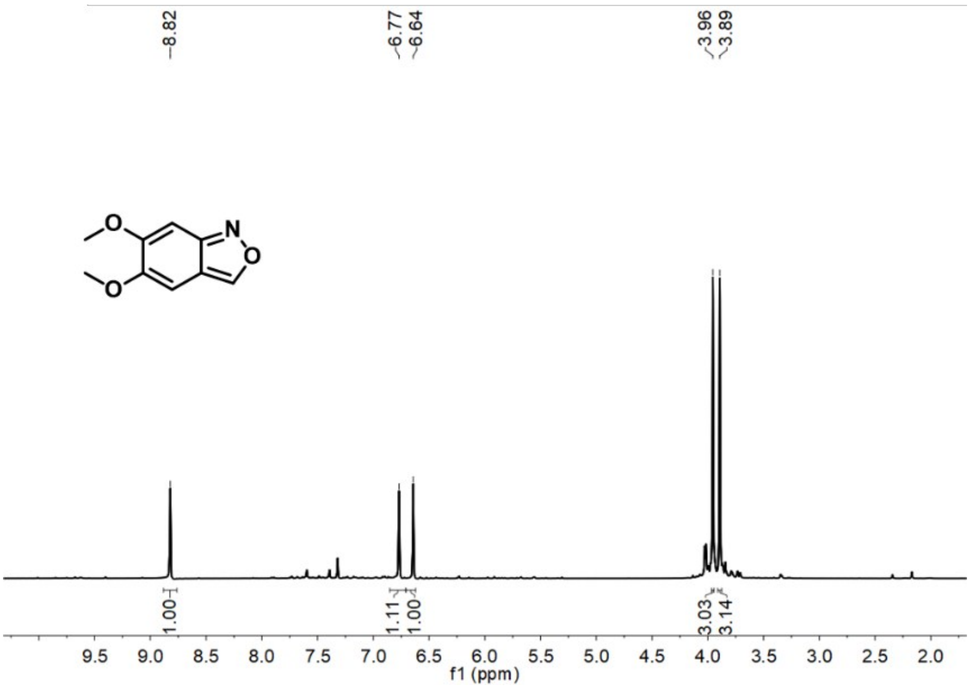


Figure S17. ^{1}H NMR spectrum for **2f**.

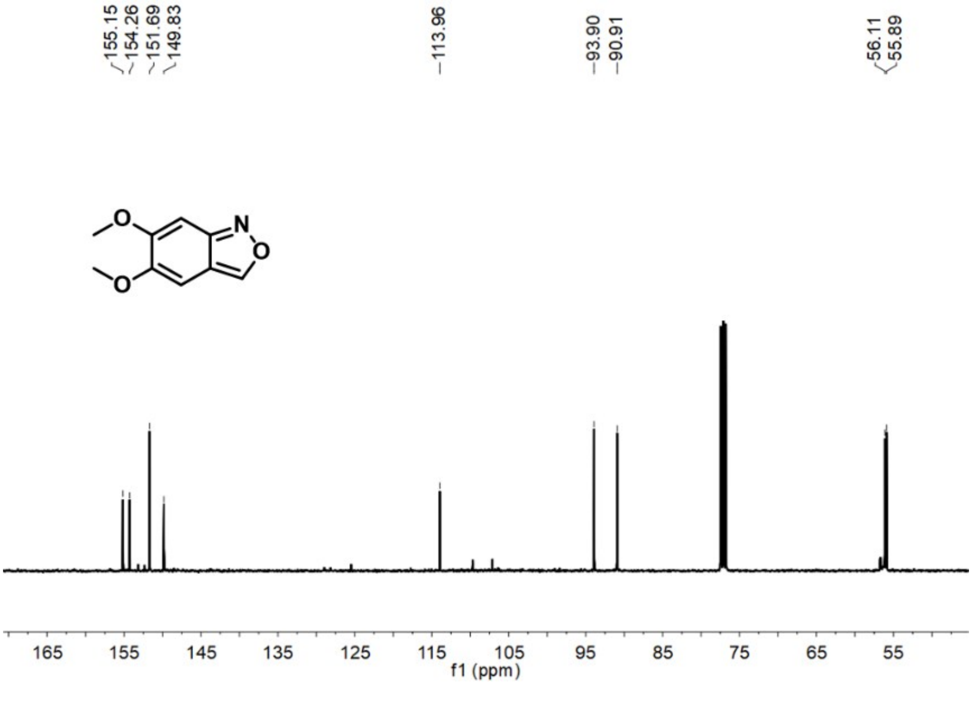


Figure S18. ^{13}C NMR spectrum for **2f**.

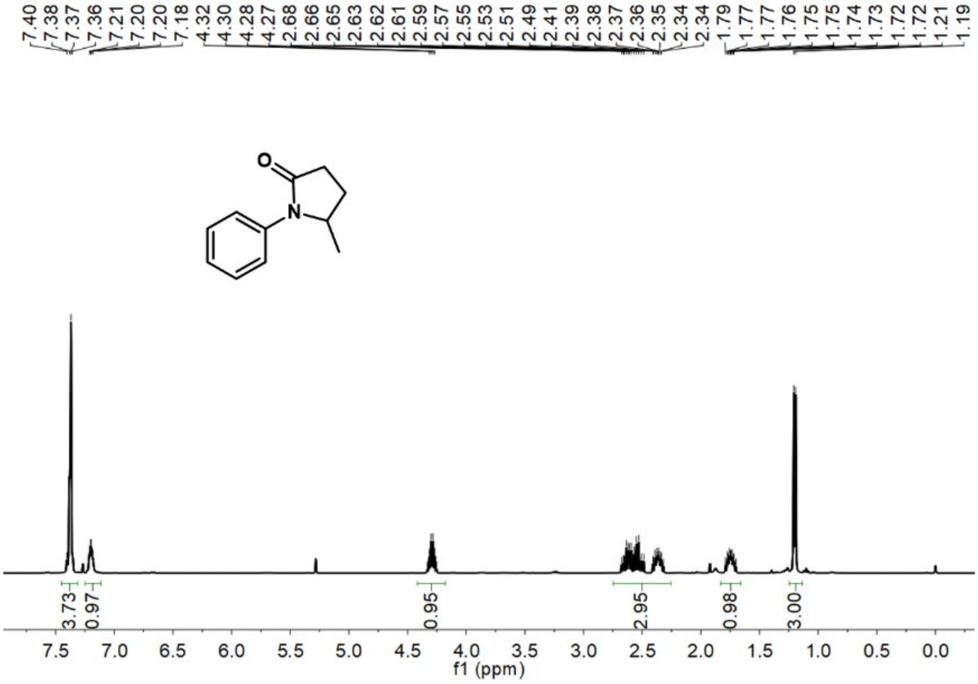


Figure S19. ^{1}H NMR spectrum for **5a**.

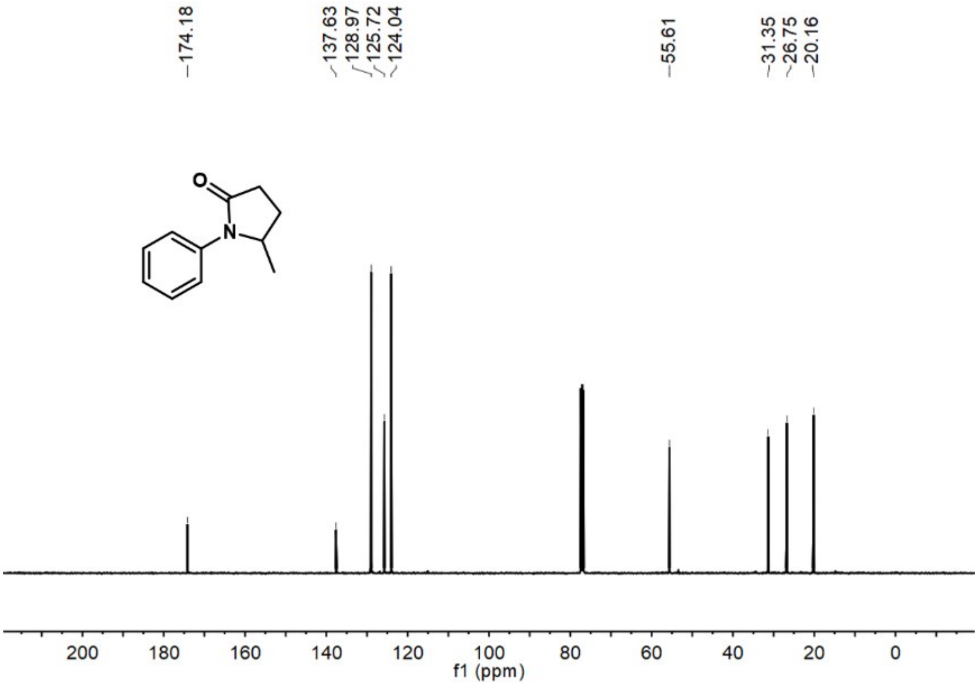


Figure S20. ^{13}C NMR spectrum for **5a**.

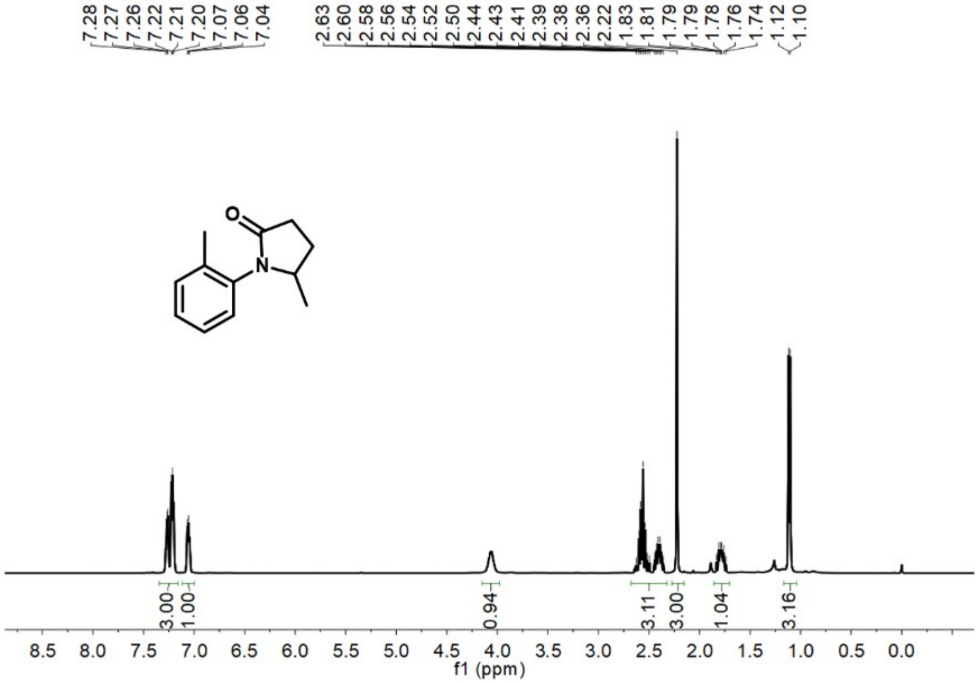


Figure S21. ^{1}H NMR spectrum for **5b**.

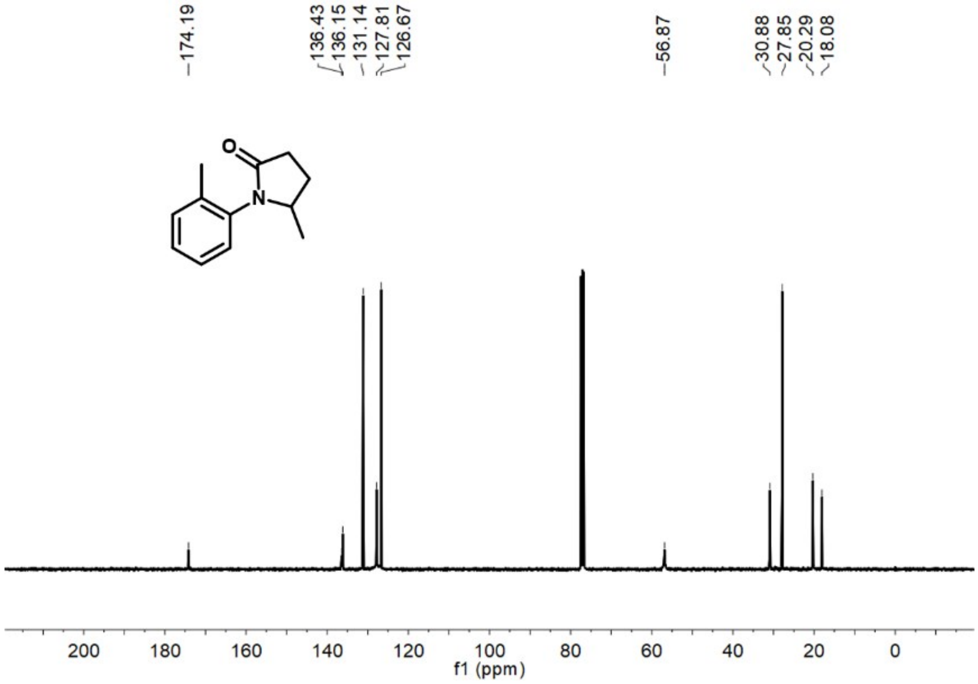


Figure S22. ^{13}C NMR spectrum for **5b**.

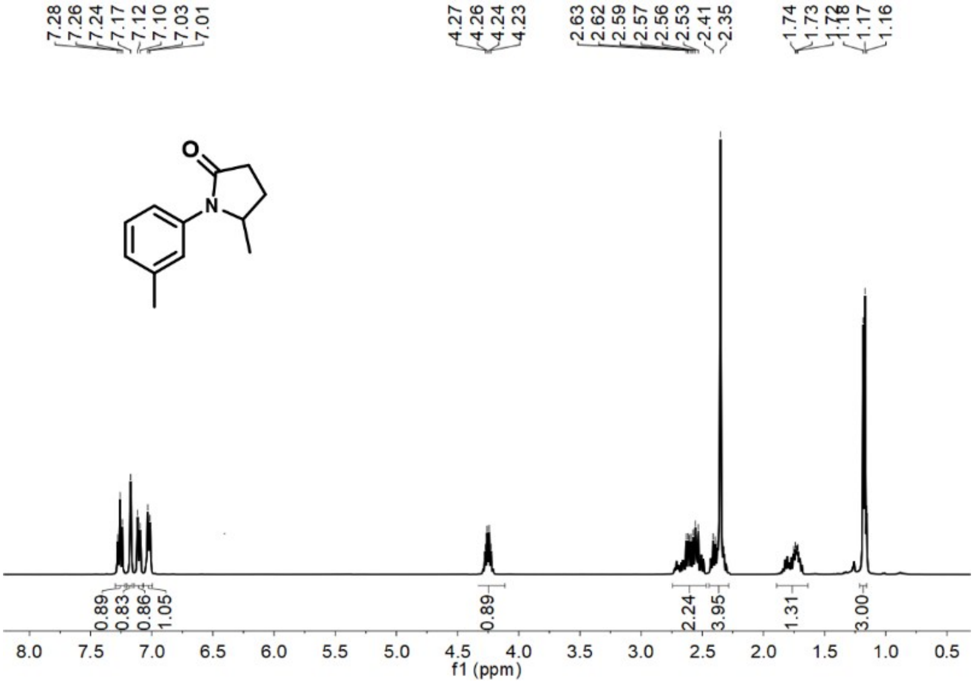


Figure S23. ^{1}H NMR spectrum for **5c**.

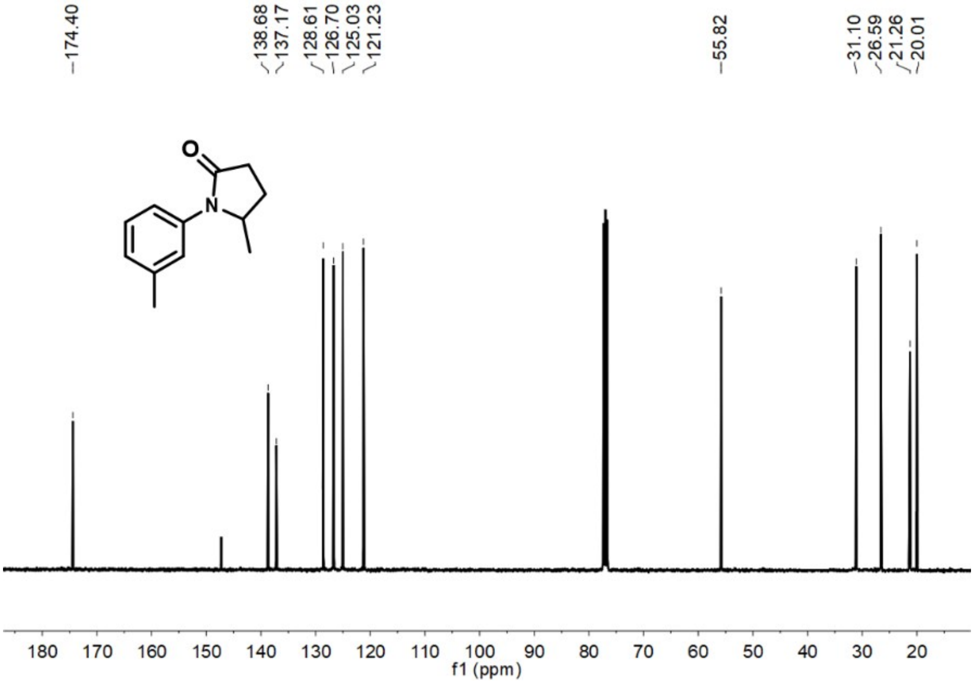


Figure S24. ^{13}C NMR spectrum for **5c**.

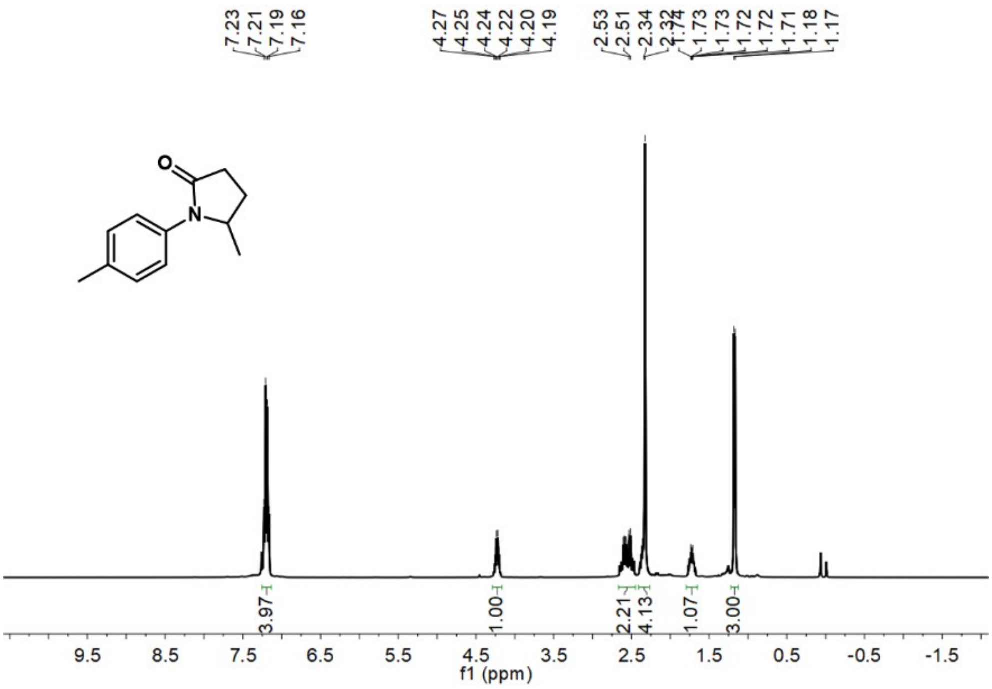


Figure S25. ^{1}H NMR spectrum for **5d**.

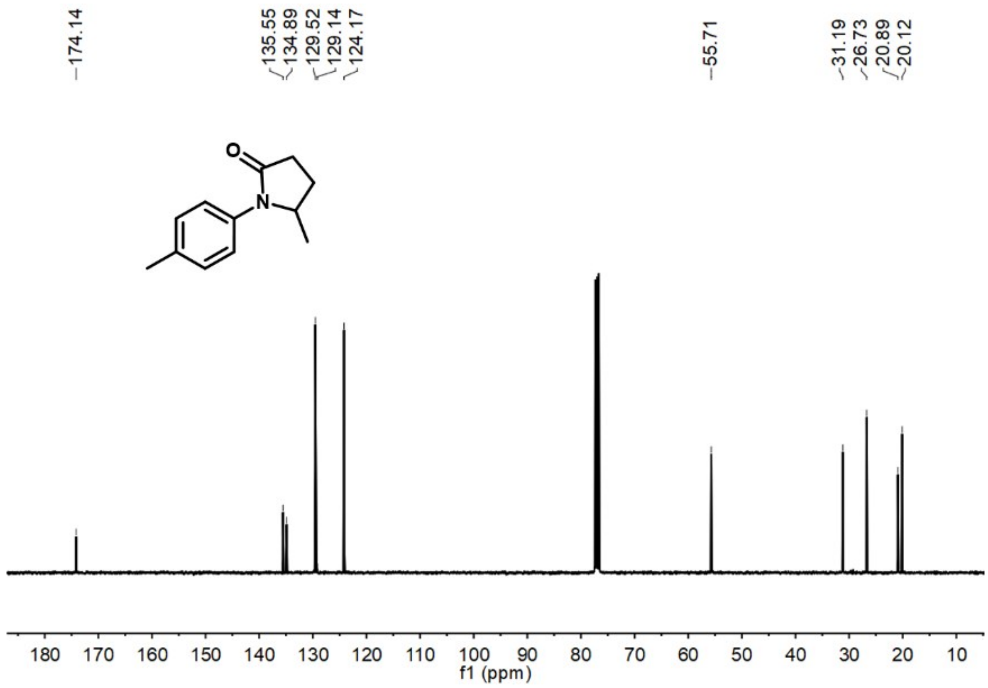


Figure S26. ^{13}C NMR spectrum for **5d**.

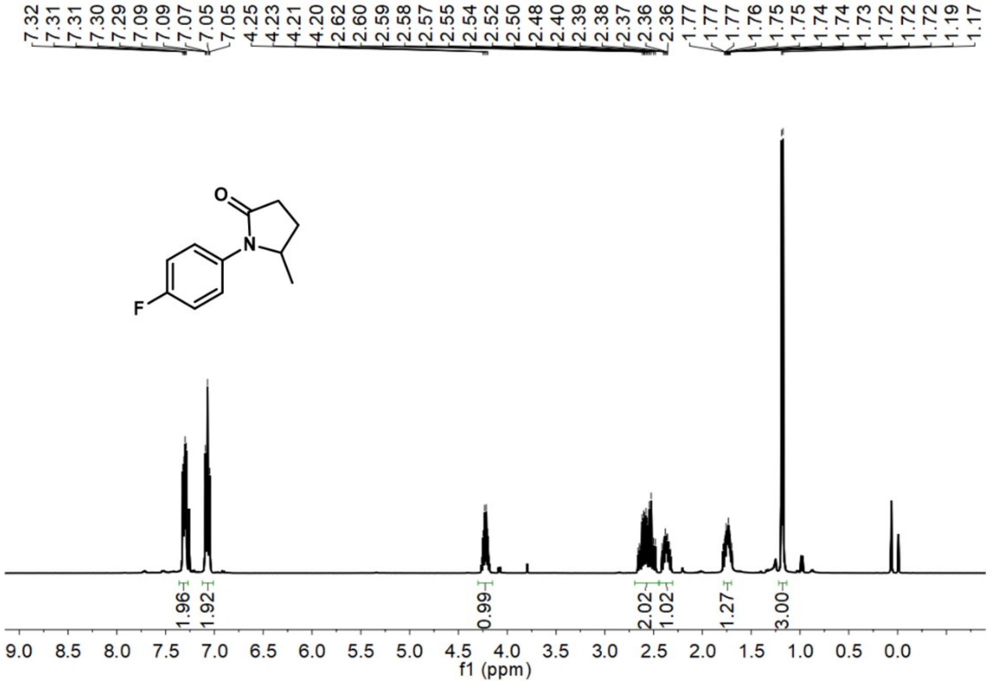


Figure S27. ^{1}H NMR spectrum for **5e**.

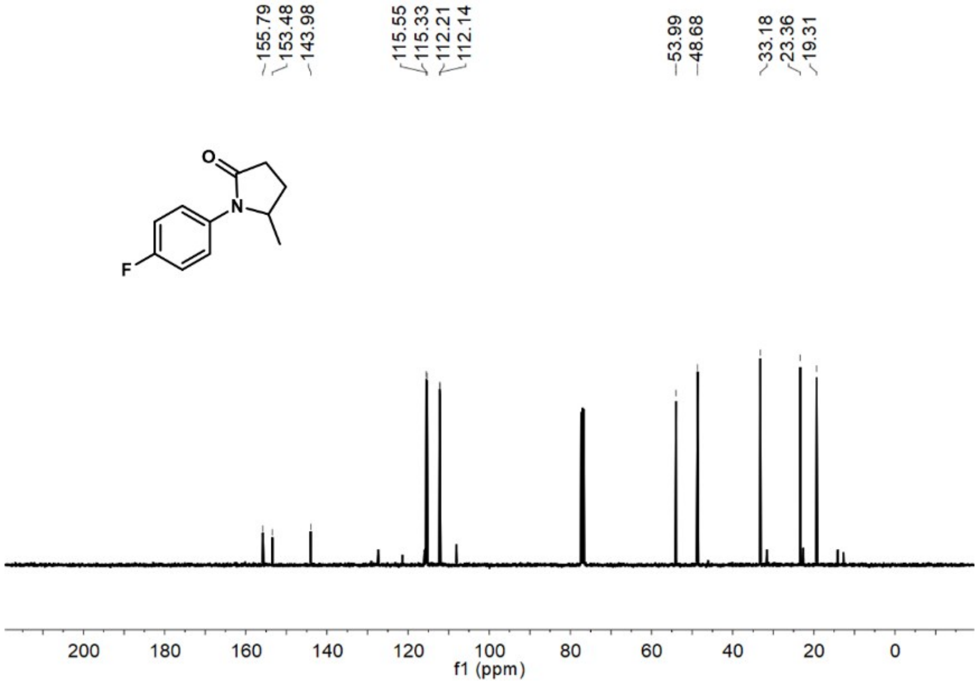


Figure S28. ^{13}C NMR spectrum for **5e**.

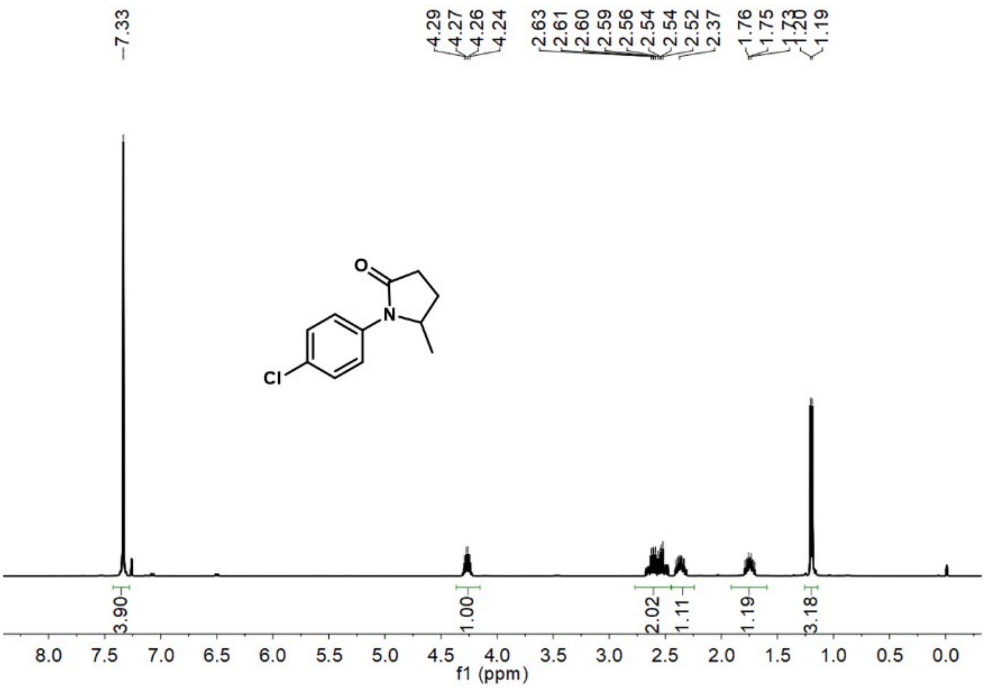


Figure S29. ^{1}H NMR spectrum for **5f**.

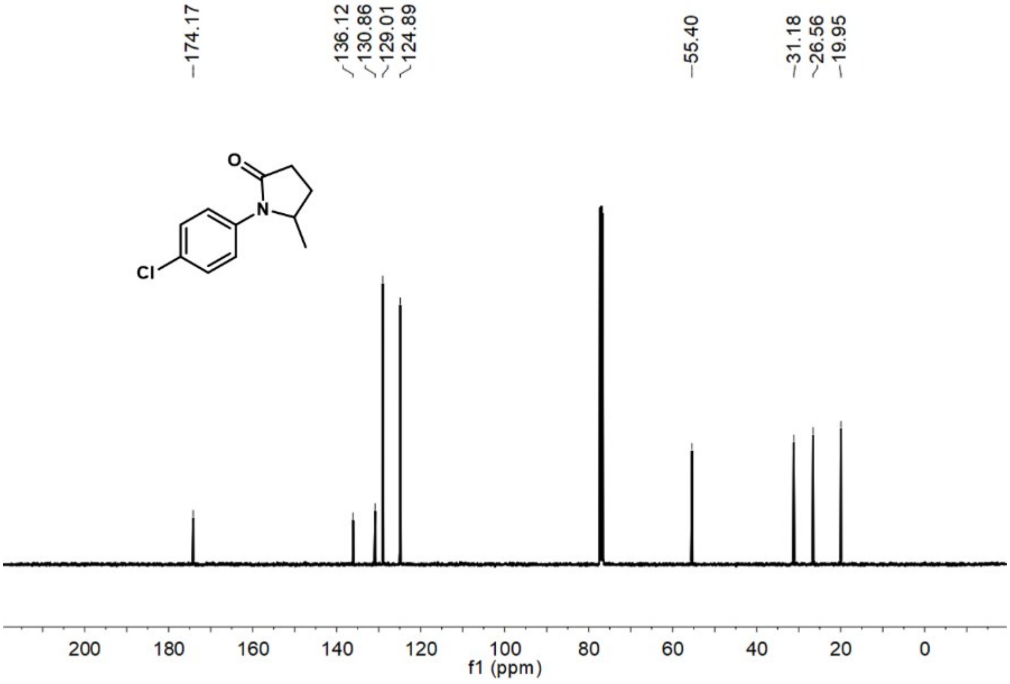


Figure S30. ^{13}C NMR spectrum for **5f**.

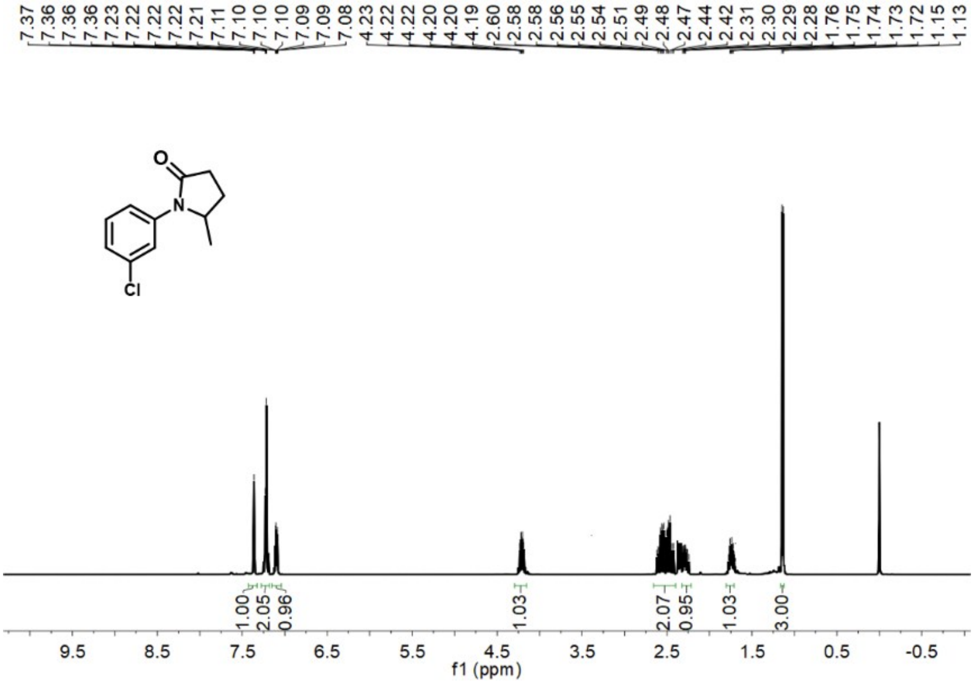


Figure S31. ^{1}H NMR spectrum for **5g**.

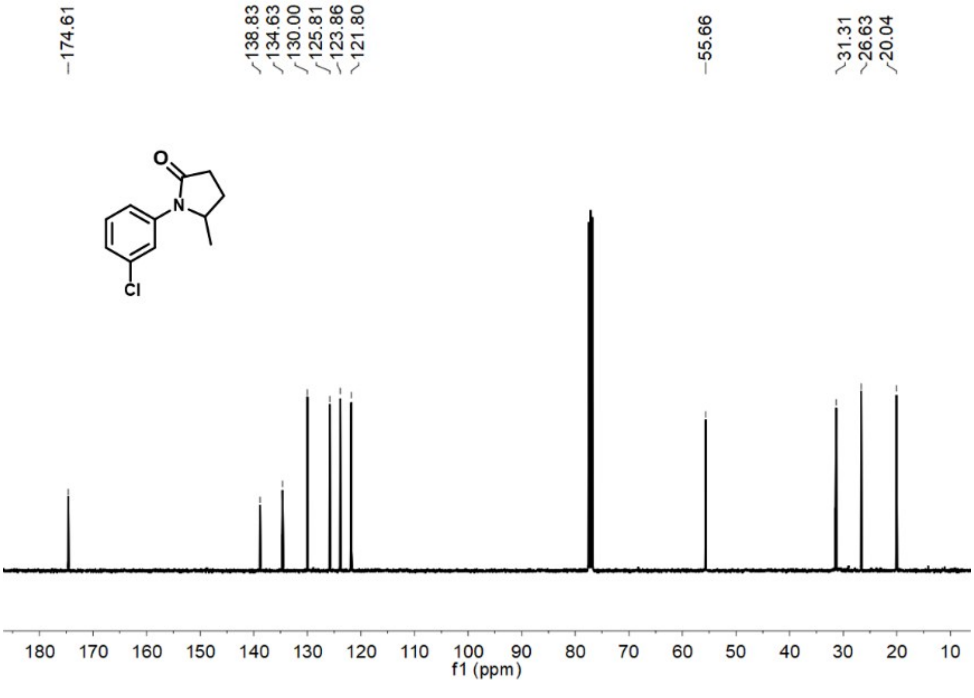


Figure S32. ^{13}C NMR spectrum for **5g**.

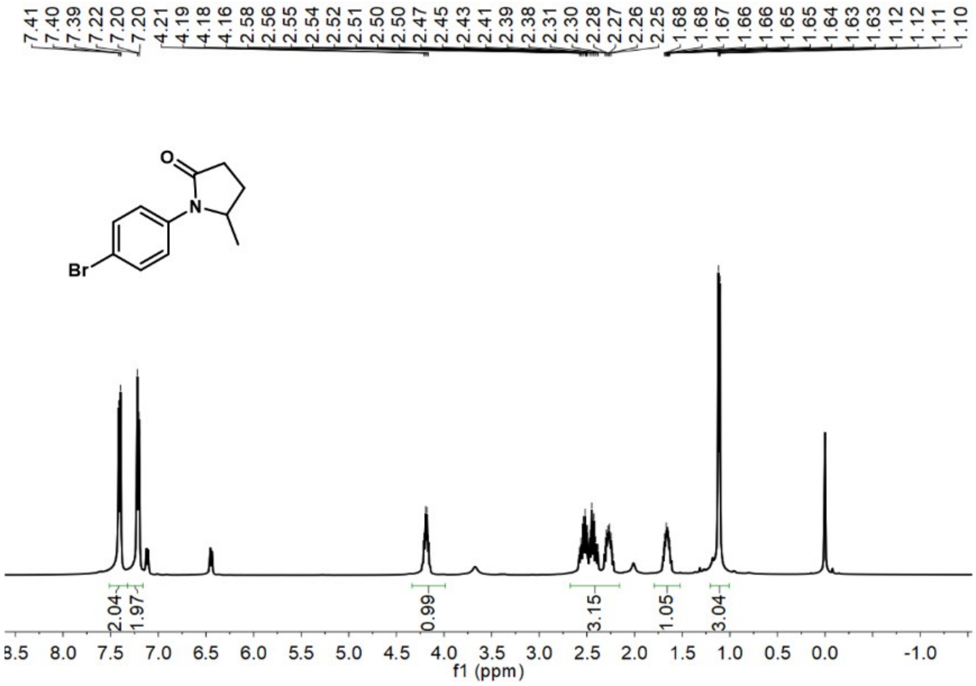


Figure S33. ^{1}H NMR spectrum for **5h**.

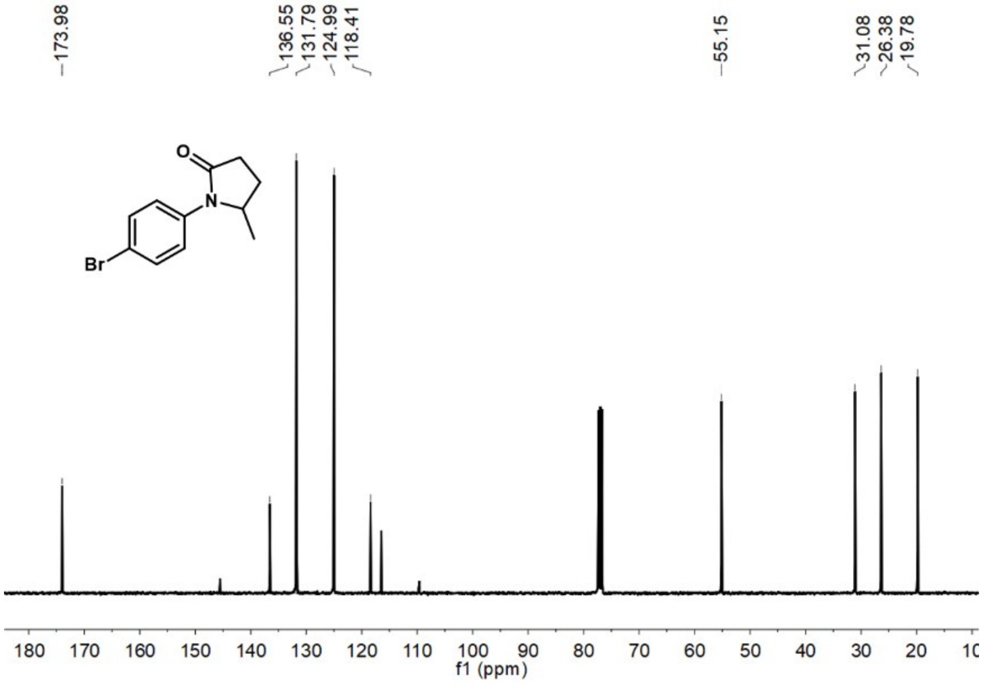


Figure S34. ^{13}C NMR spectrum for **5h**.

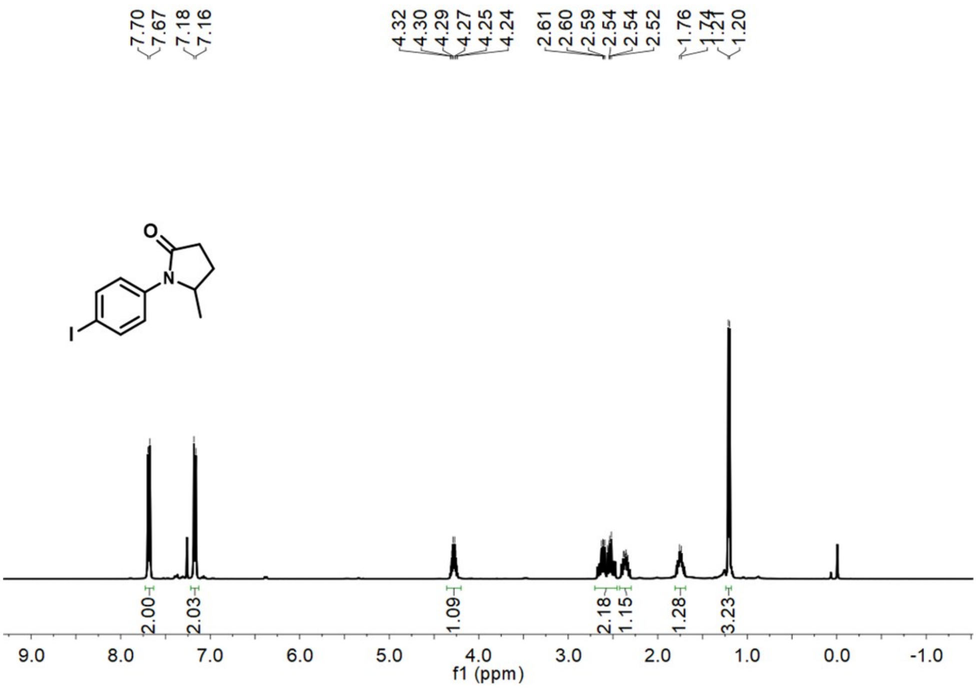


Figure S35. ^{1}H NMR spectrum for **5i**.

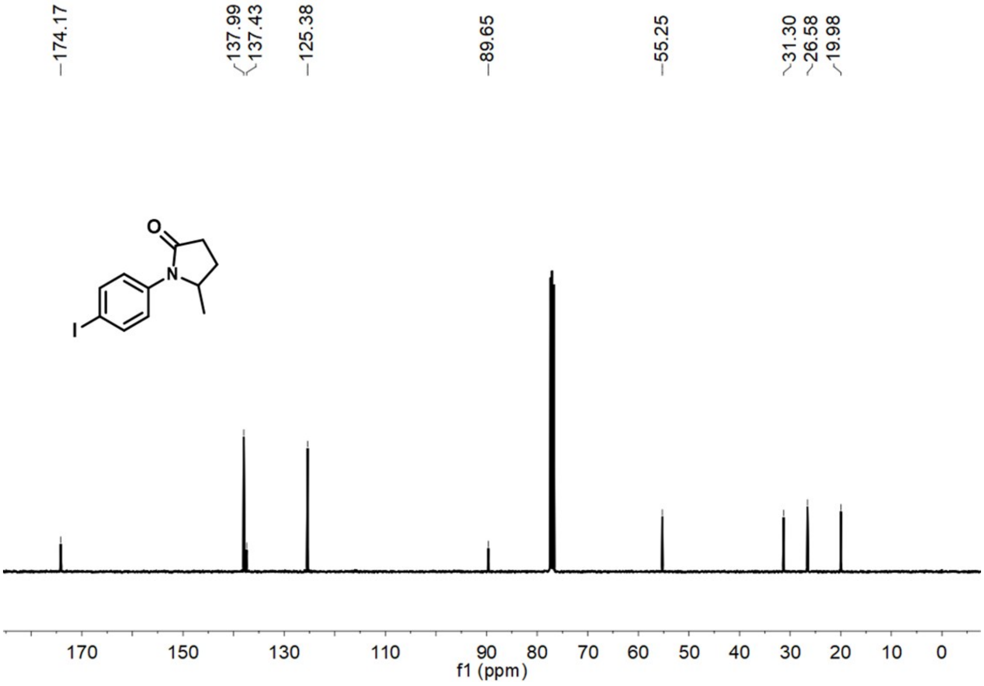


Figure S35. ^{13}C NMR spectrum for **5i**.

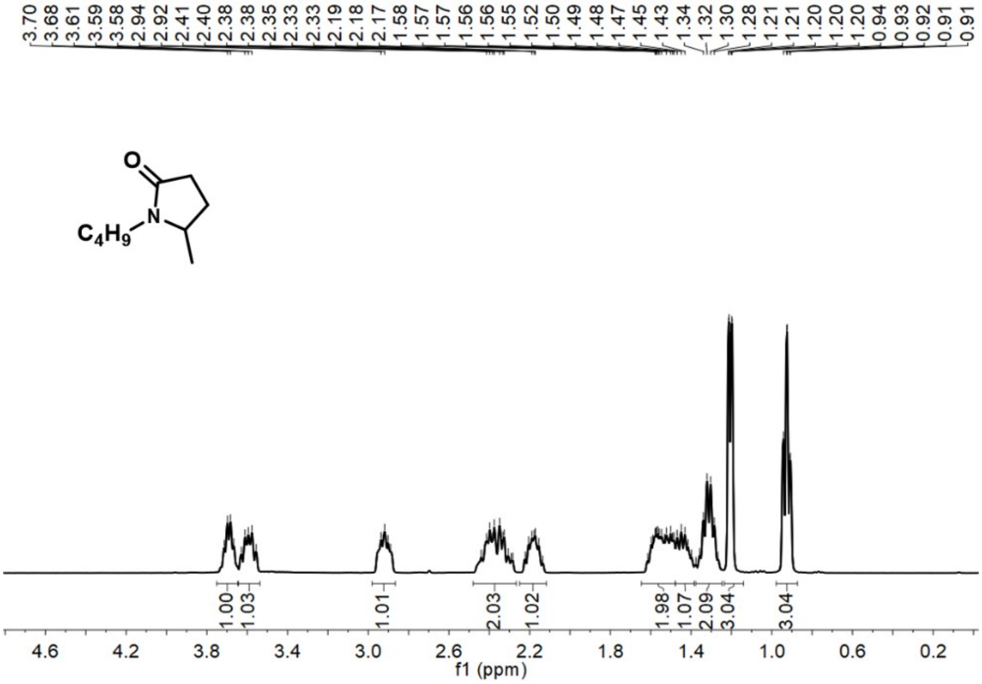


Figure S37. ^{1}H NMR spectrum for **5j**.

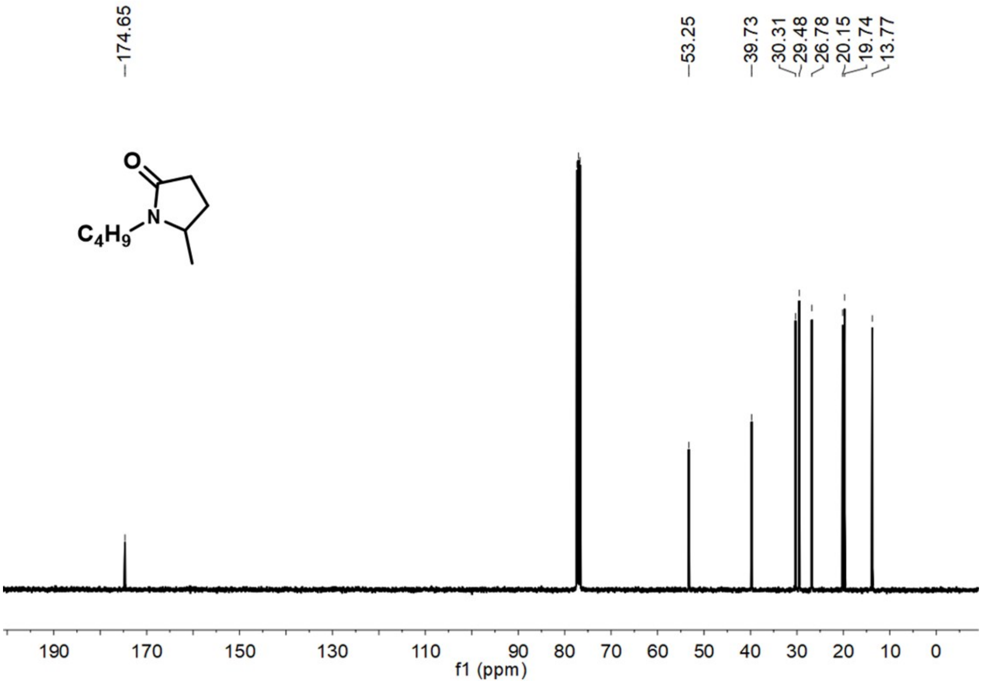


Figure S38. ^{13}C NMR spectrum for **5j**.

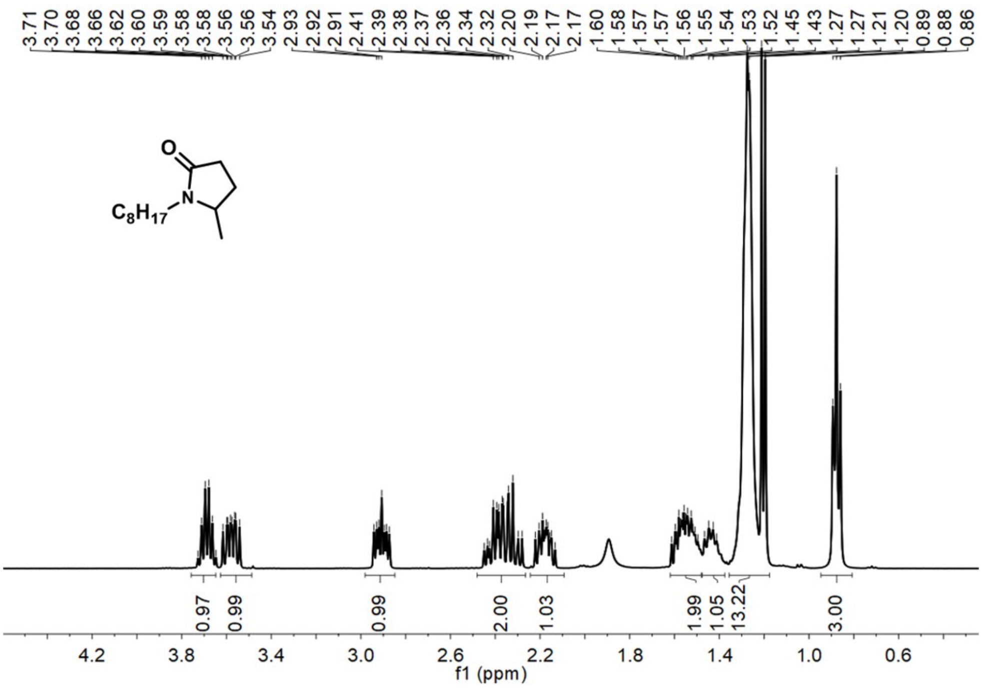


Figure S39. ^{1}H NMR spectrum for **5k**.

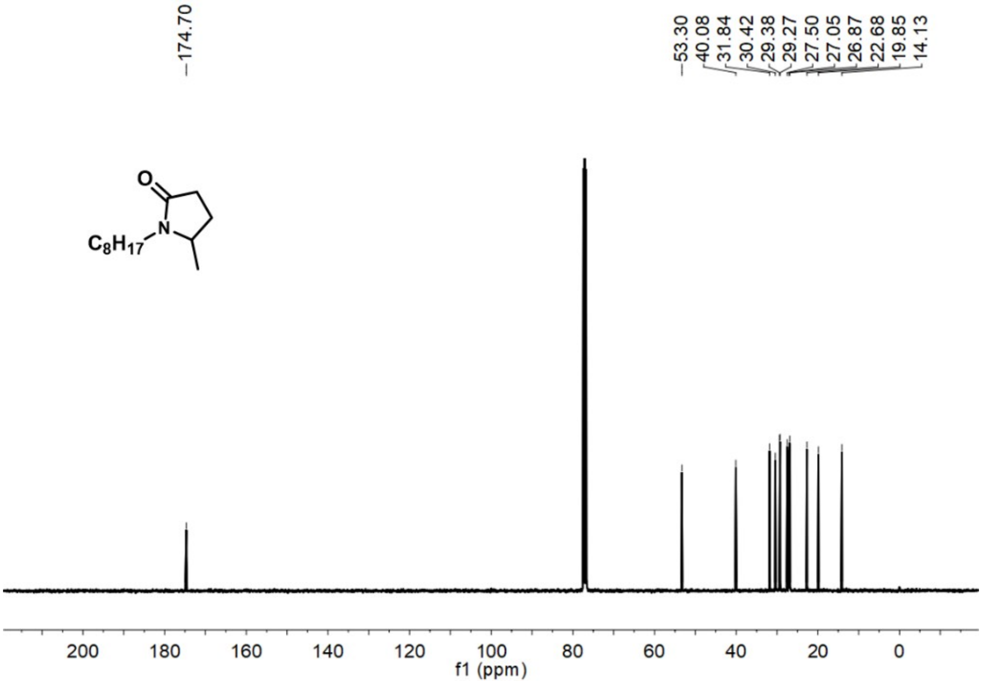


Figure S40. ^{13}C NMR spectrum for **5k**.

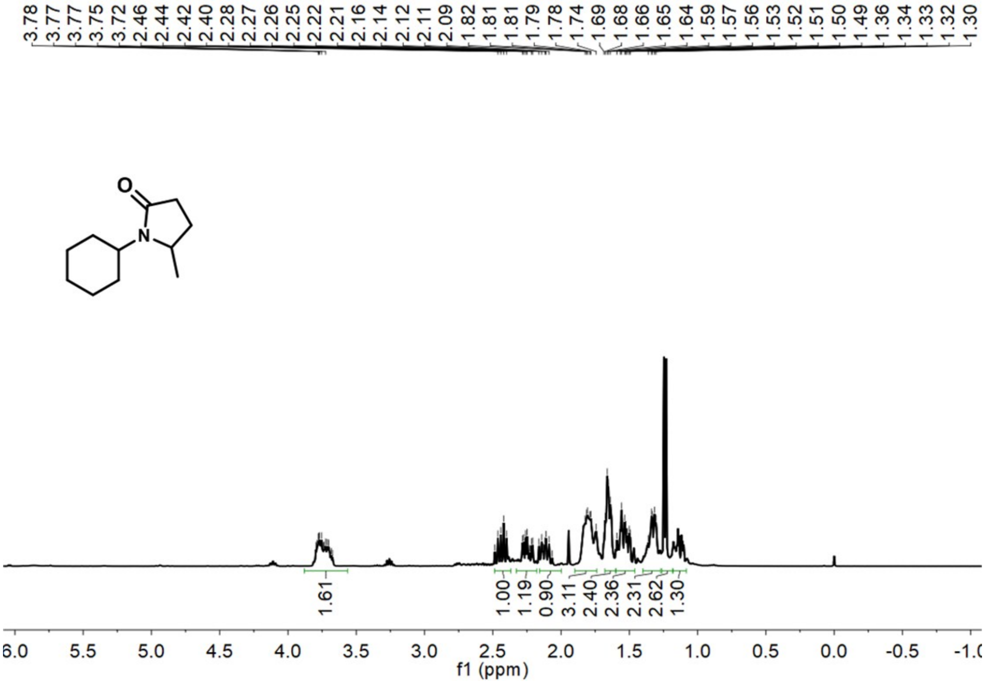


Figure S41. ^{1}H NMR spectrum for **5l**.

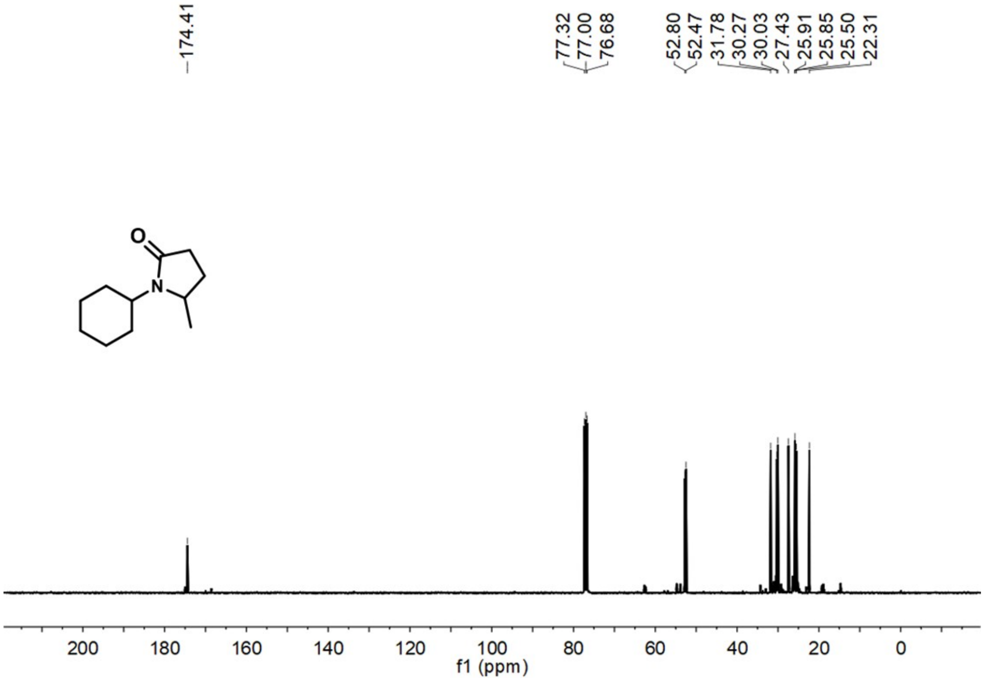


Figure S42. ^{13}C NMR spectrum for **5l**.

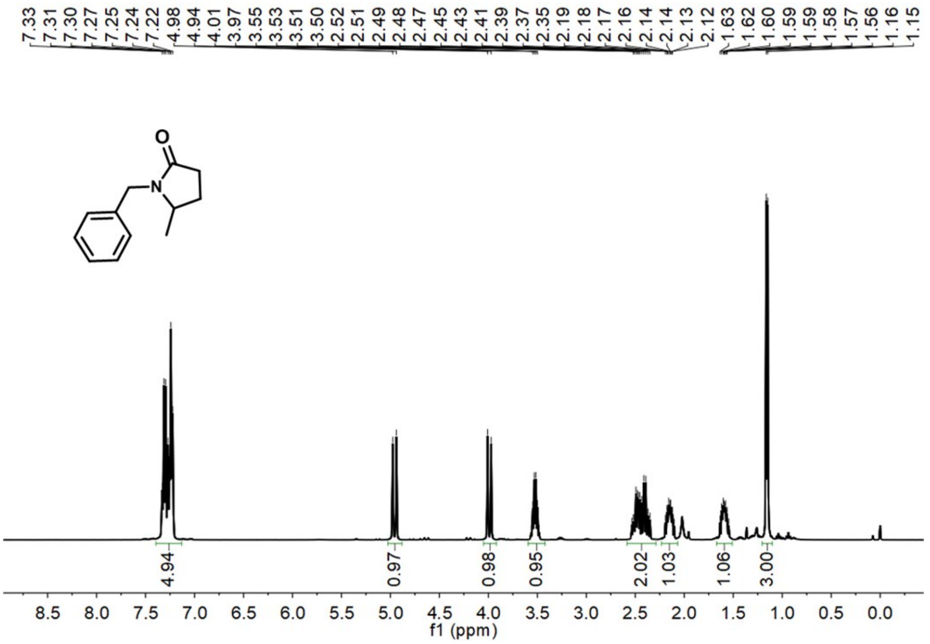


Figure S43. ^{1}H NMR spectrum for **5m**.

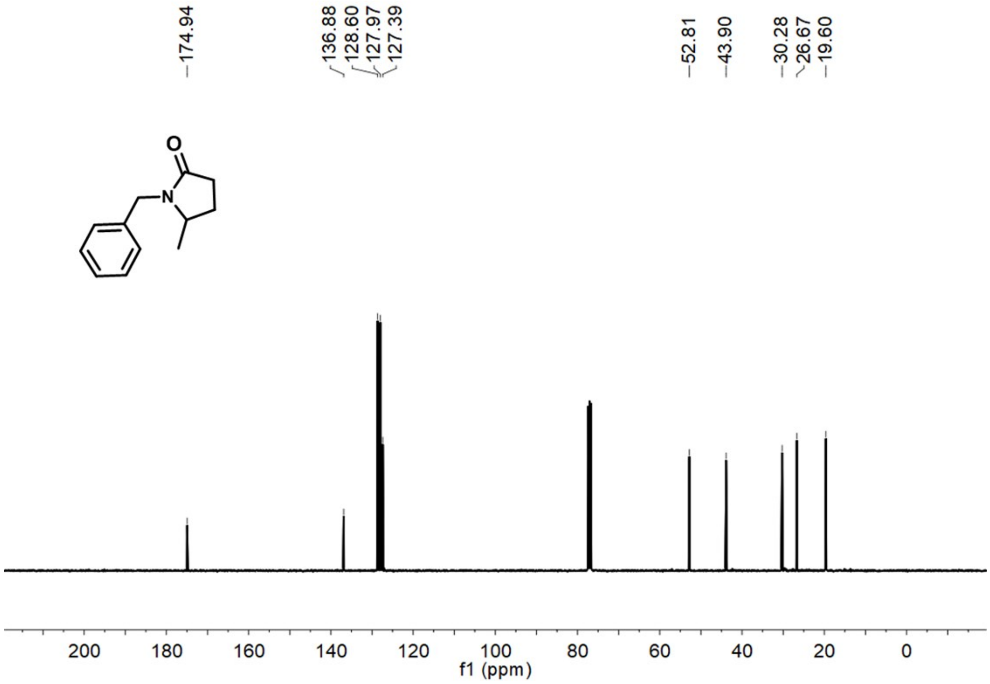


Figure S44. ^{13}C NMR spectrum for **5m**.

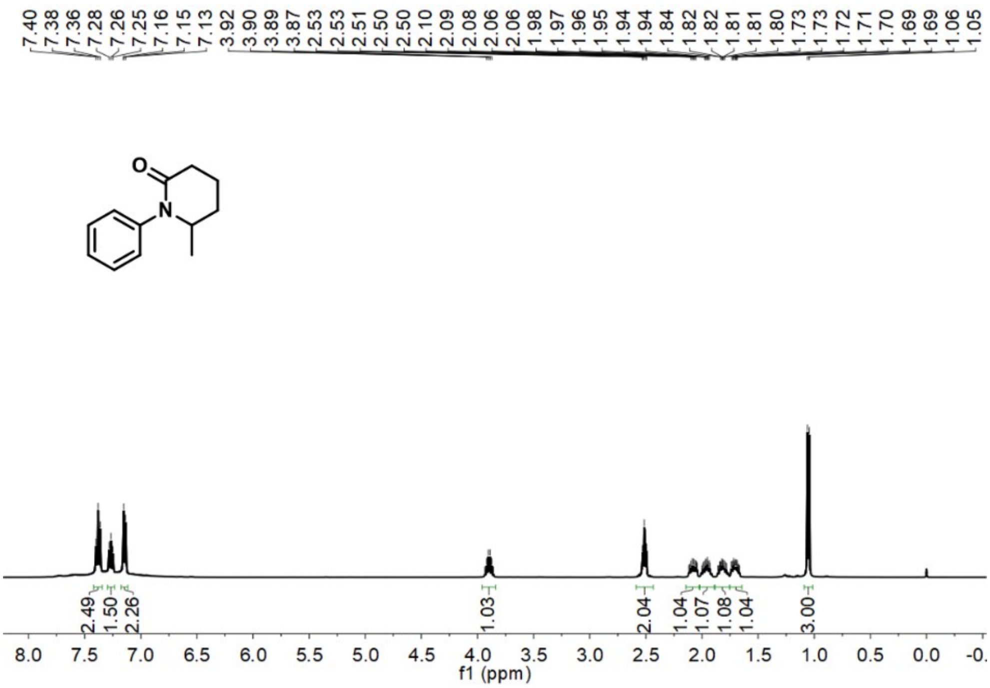


Figure S45. ^{1}H NMR spectrum for **5n**.

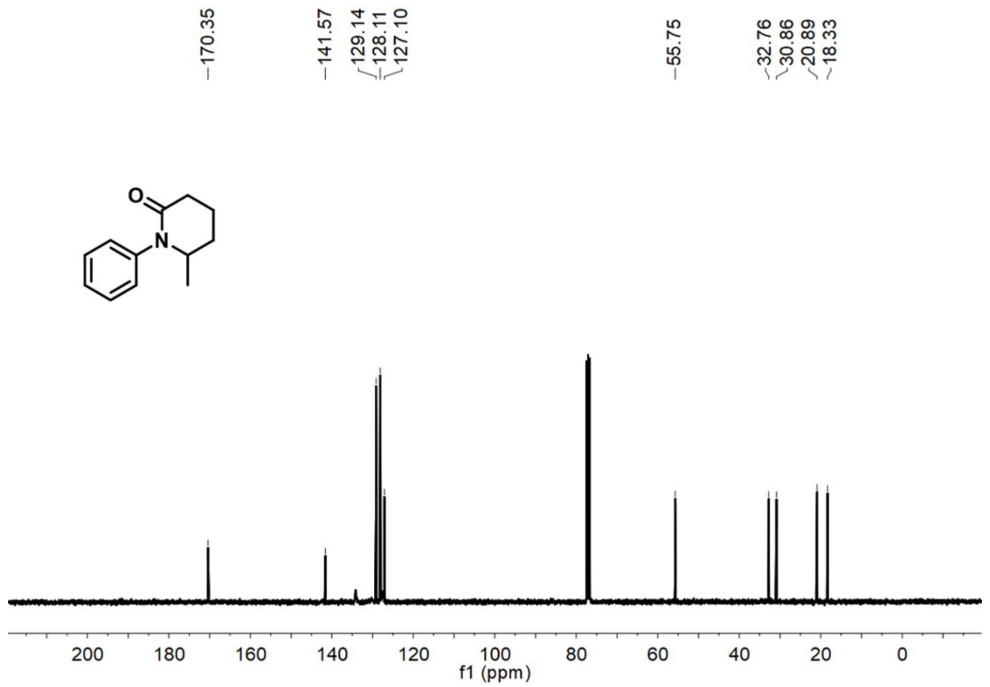


Figure S46. ^{13}C NMR spectrum for **5n**.

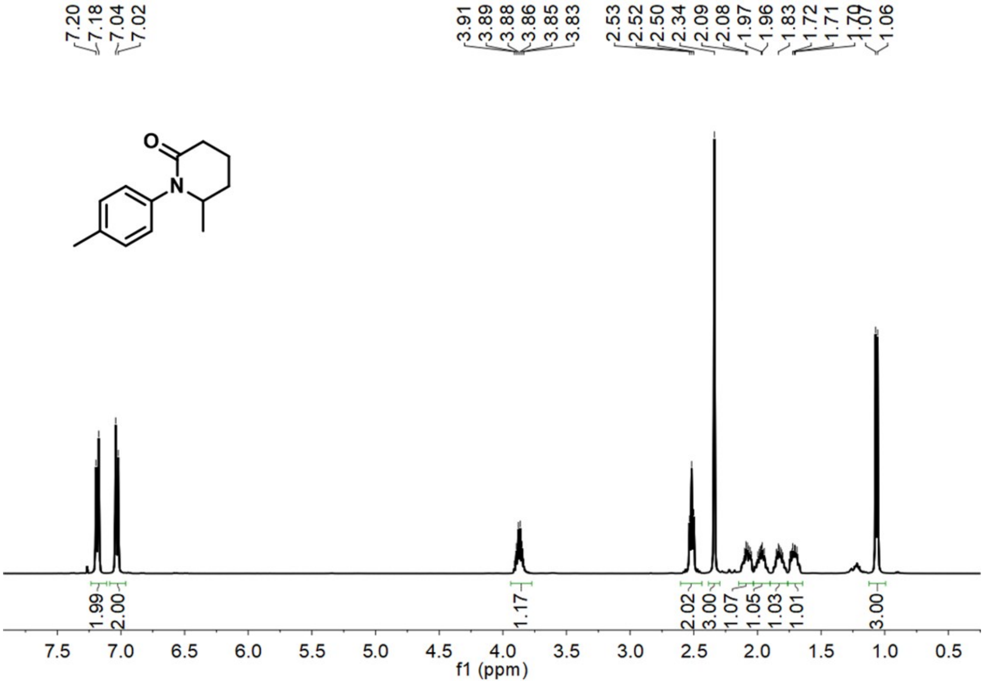


Figure S47. ^{1}H NMR spectrum for **5o**.

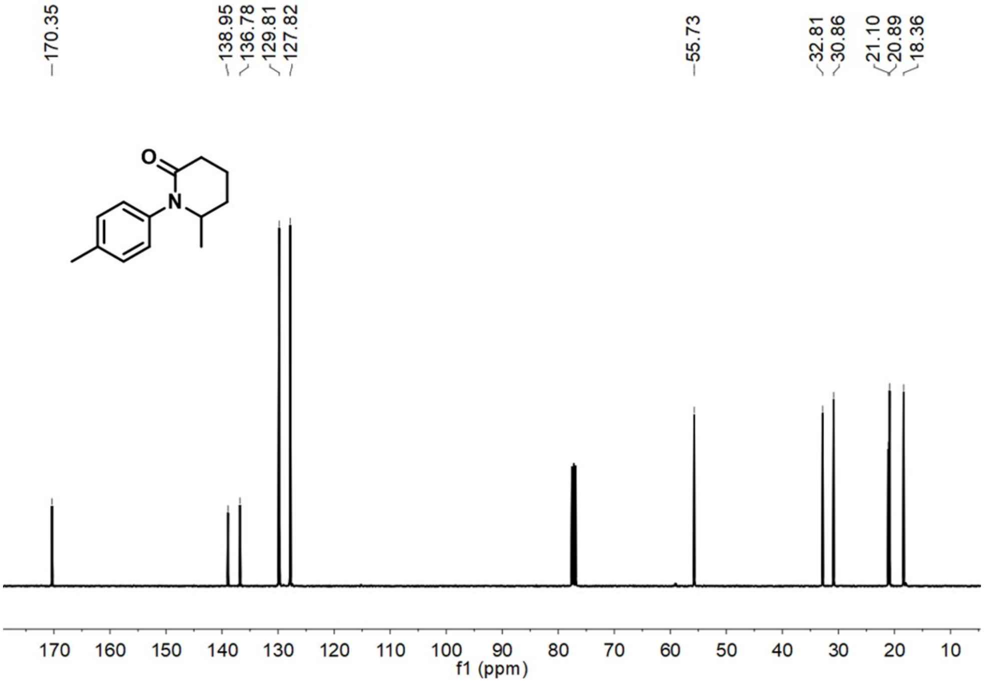


Figure S48. ^{13}C NMR spectrum for **5o**.

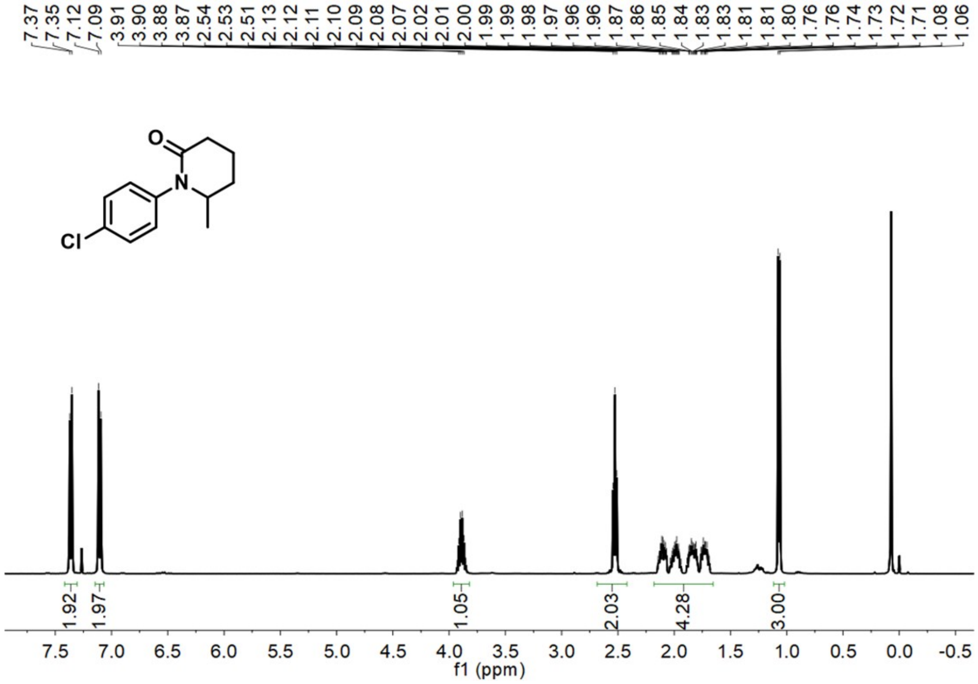


Figure S49. ^{1}H NMR spectrum for **5p**.

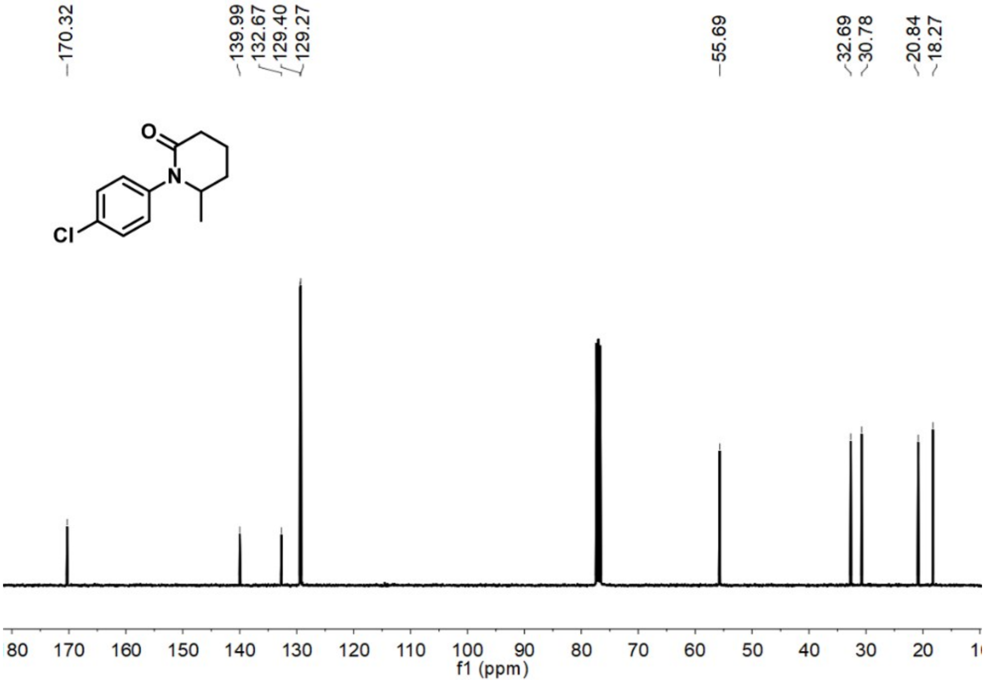


Figure S50. ^{13}C NMR spectrum for **5p.**