Electronic Supplementary Material (ESI) for RSC Advances.

Palladium Anchored Donor Flexible Pyridylidene Amide (PYA) Electrocatalysts for CO_2 Reduction

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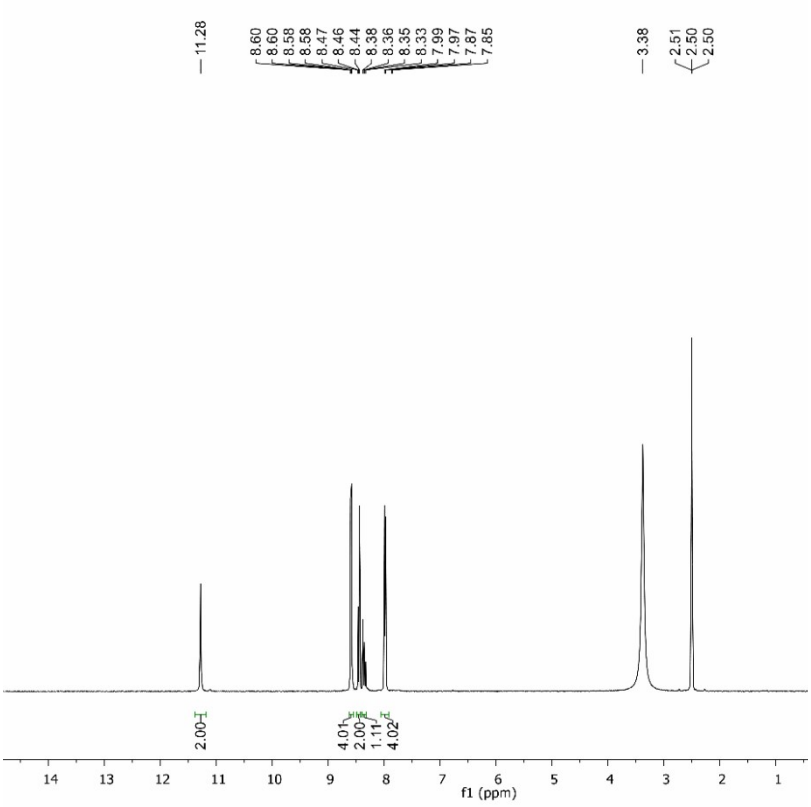


Figure 1.1 ^{1}H NMR spectrum of **1**

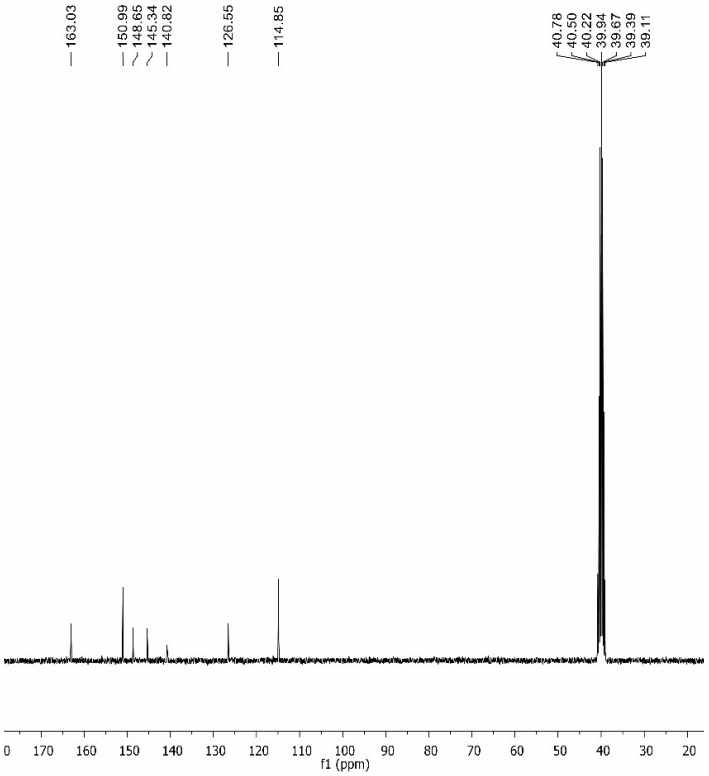


Figure 1.2 ^{13}C NMR spectrum of **1**

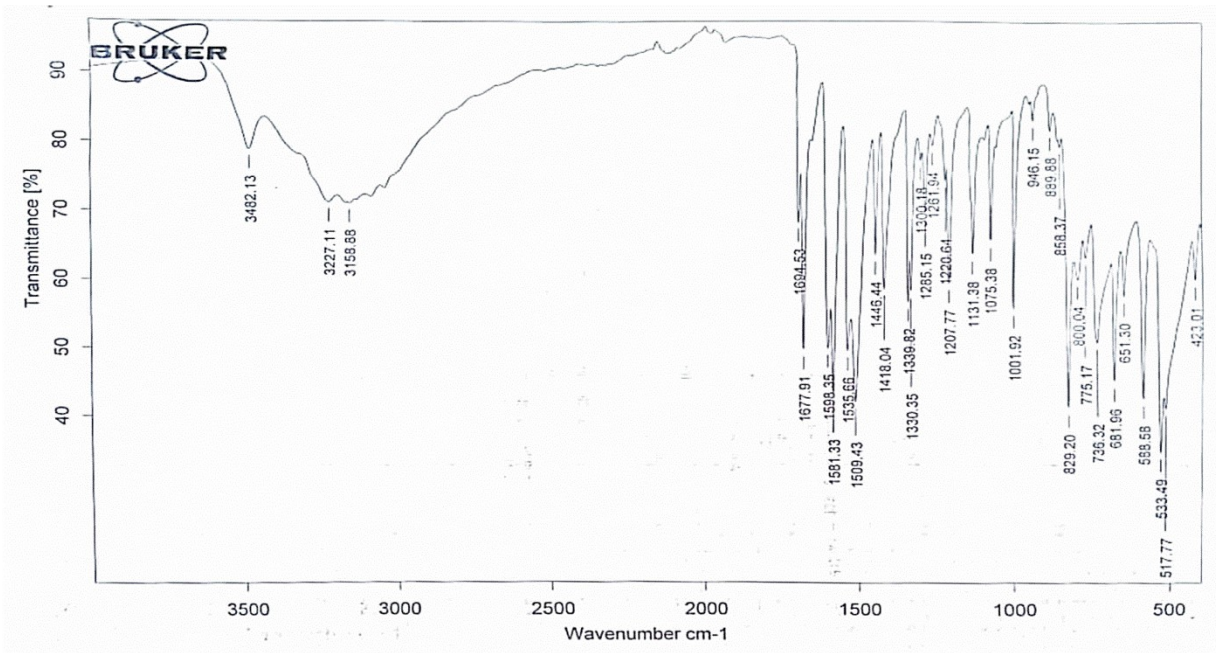


Figure 1.3. Representative FT-IR spectrum of **1**

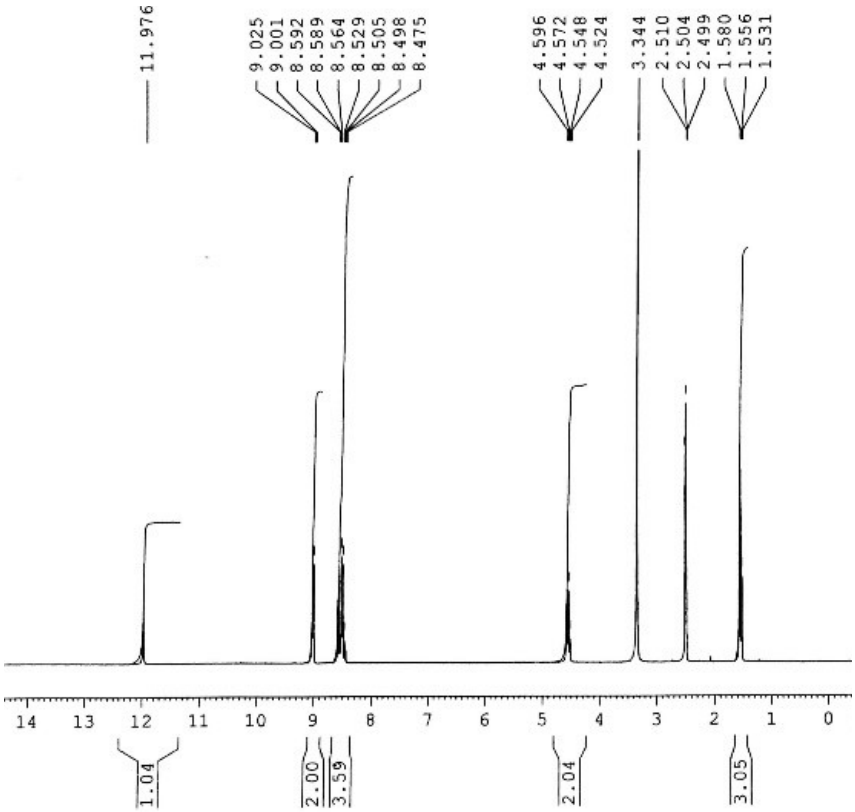


Figure 2.1 ^{1}H NMR spectrum of **2**

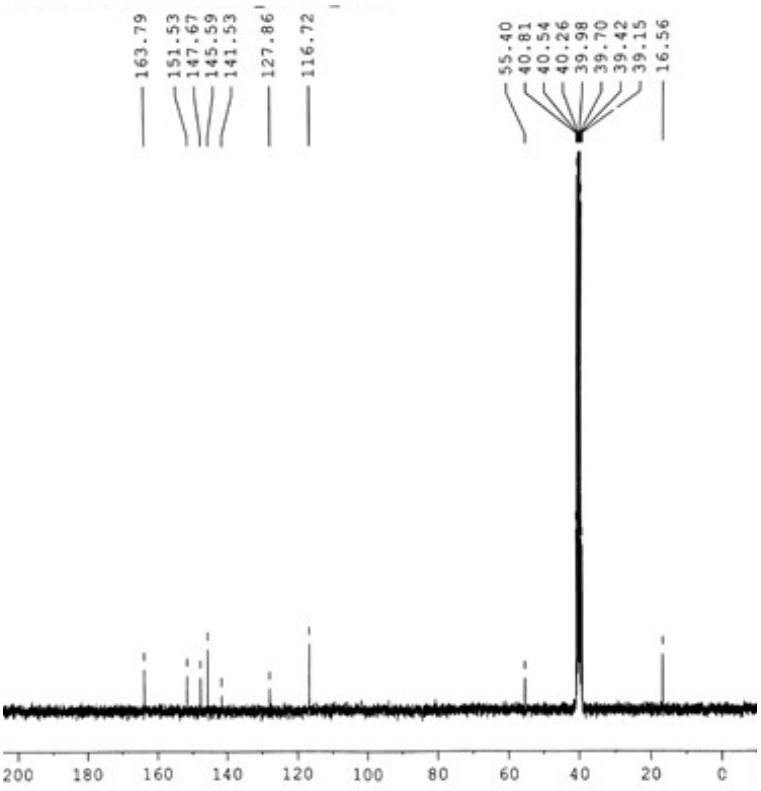


Figure 2.2 ^{13}C NMR spectrum of **2**

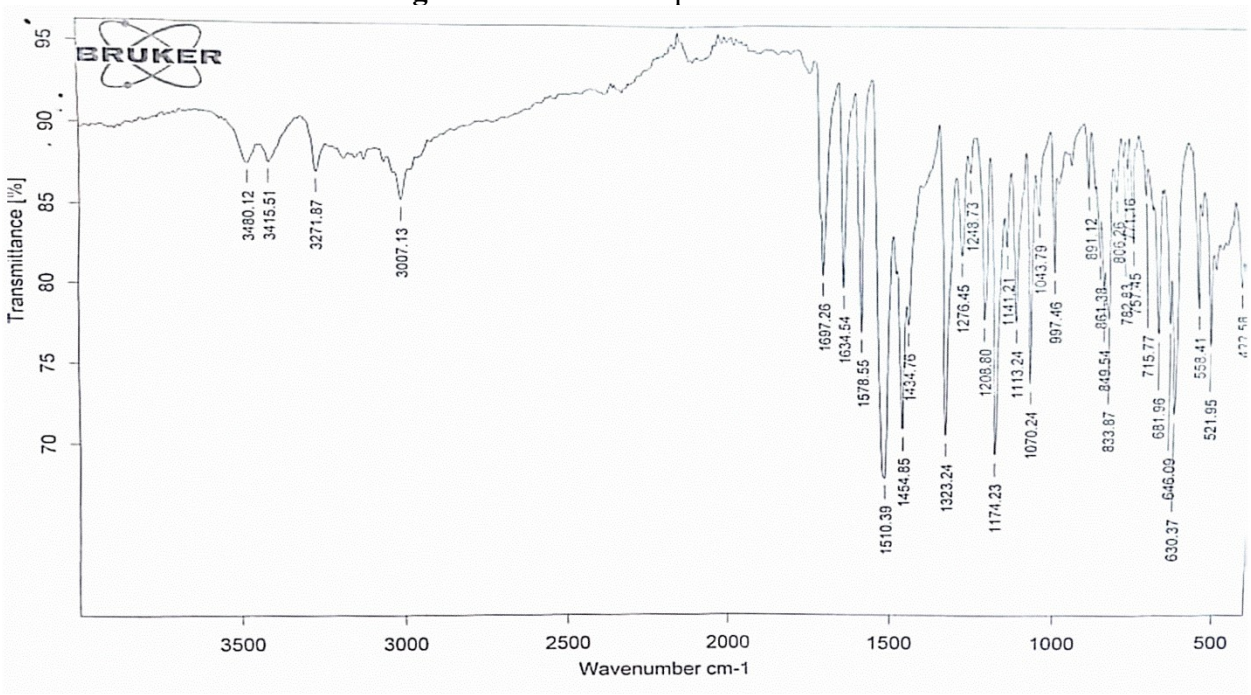


Figure 2.3. Representative FT-IR spectrum of **2**

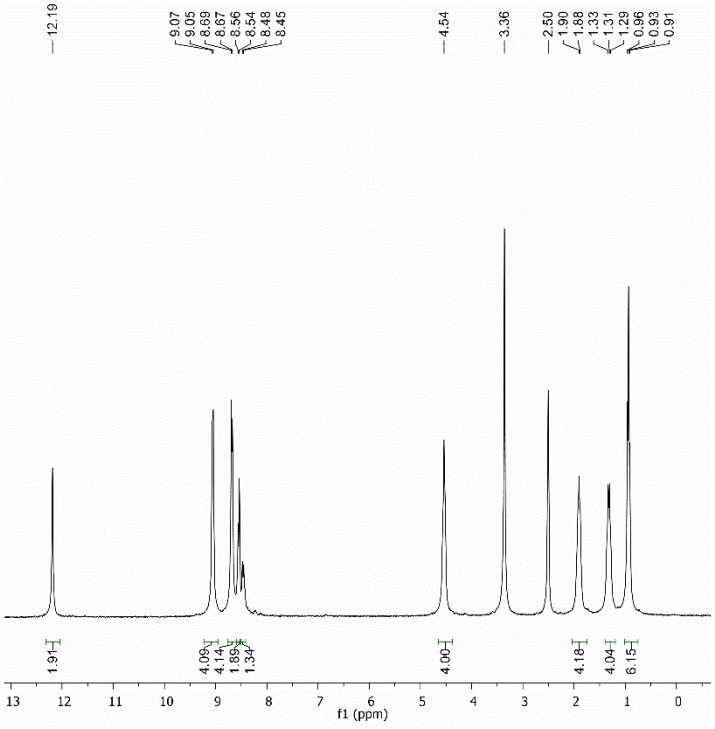


Figure 3.1. ^{1}H NMR spectrum of **3**

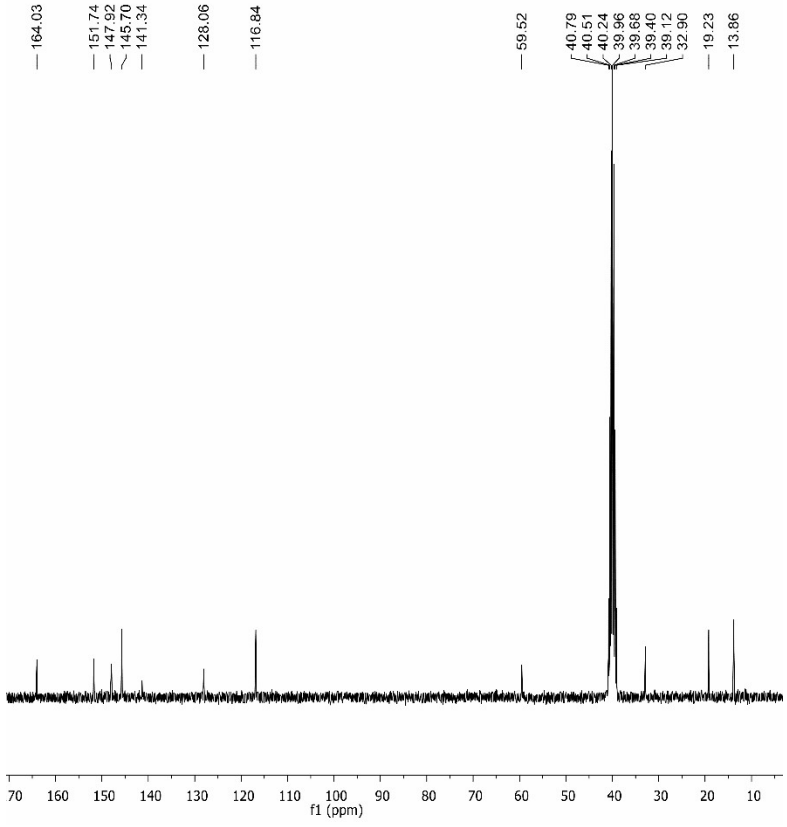


Figure 3.2. ^{13}C NMR spectrum of **3**

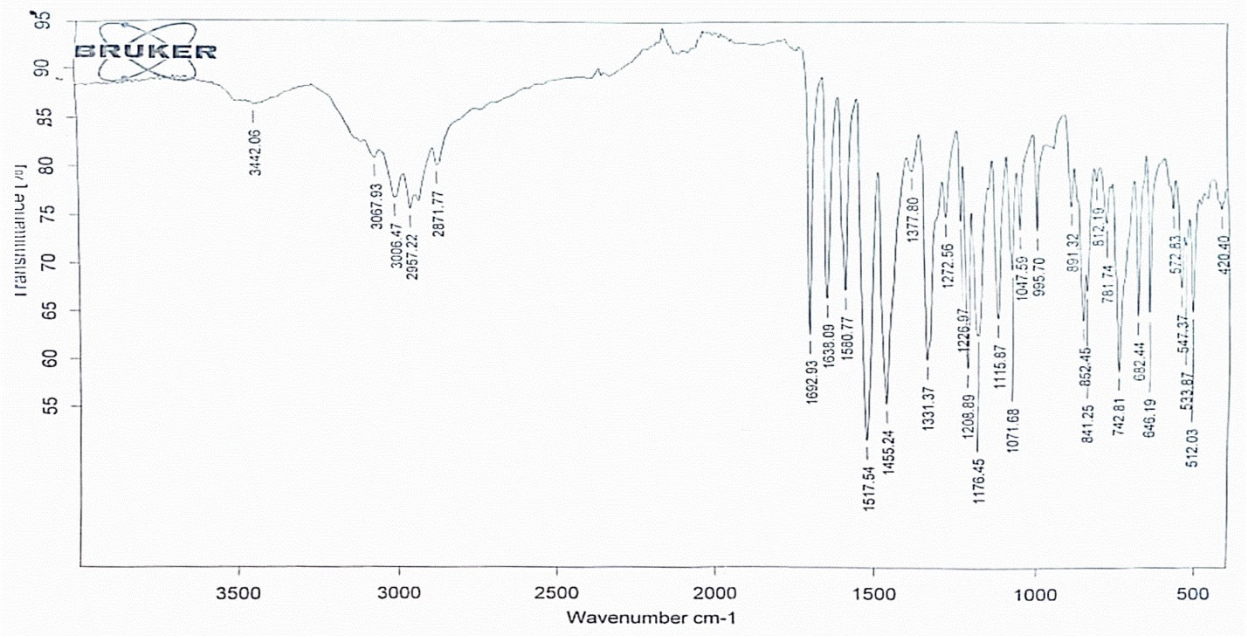


Figure 3.3. Representative FT-IR spectrum of **3**

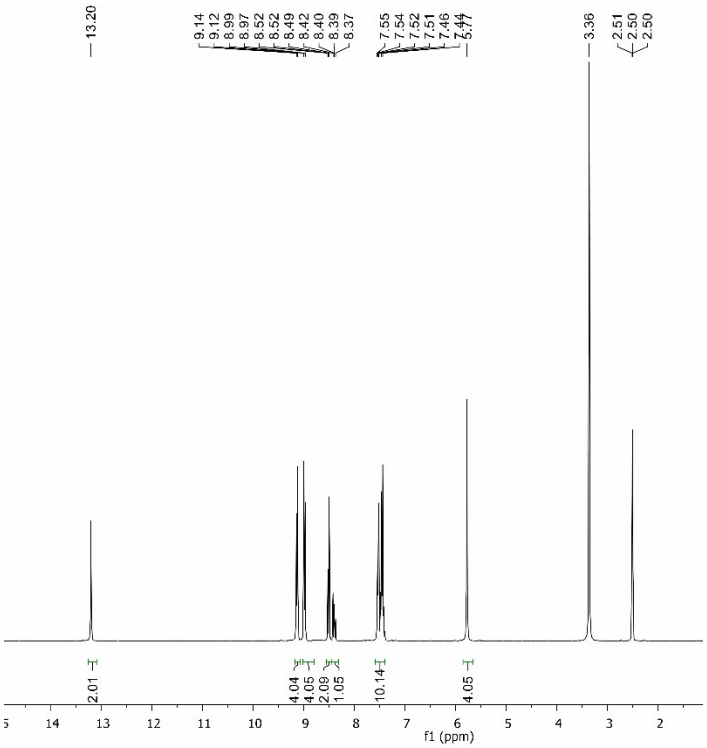


Figure 4.1. ^{1}H NMR spectrum of **4**

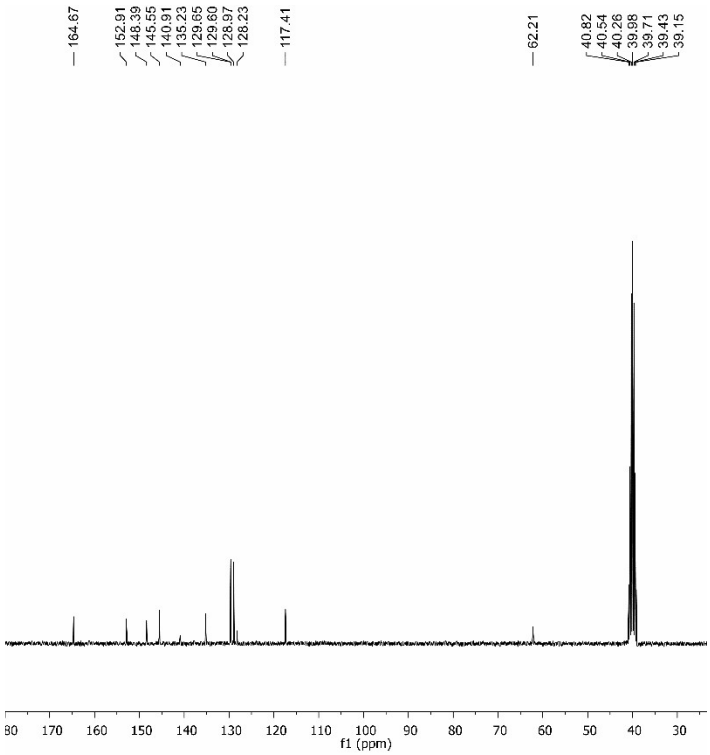


Figure 4.2. ^{13}C NMR spectrum of **4**

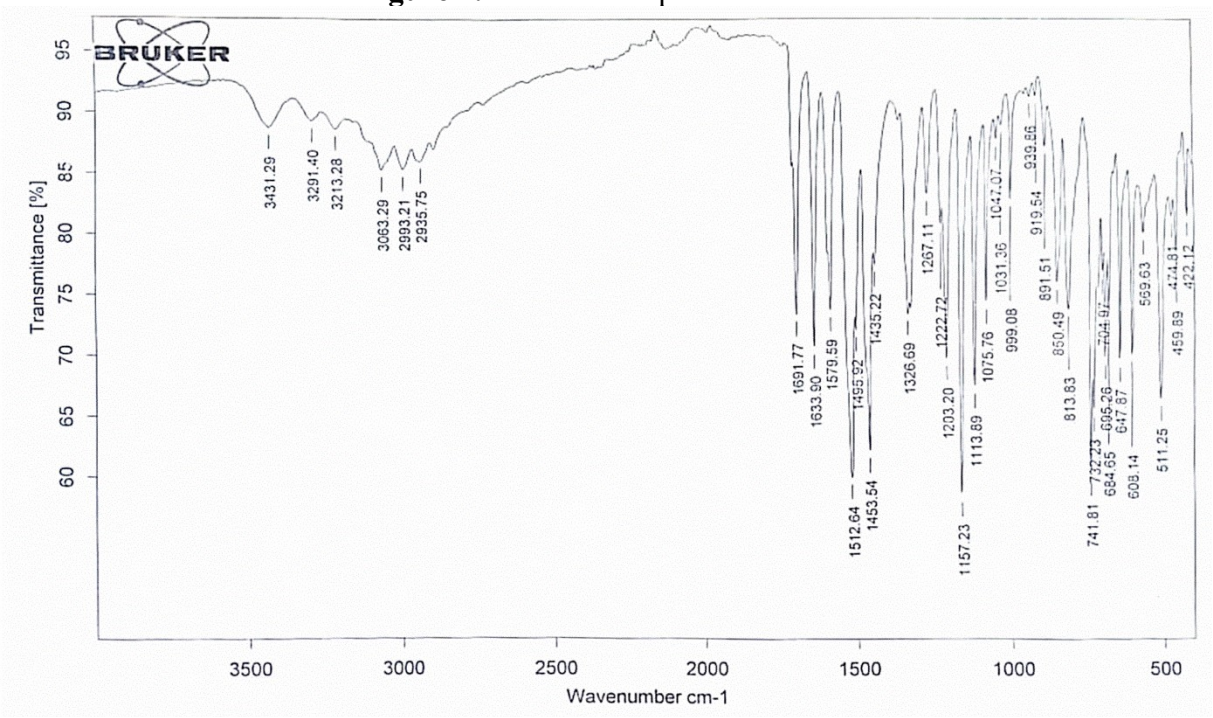


Figure 4.3. Representative FT-IR spectrum of **4**

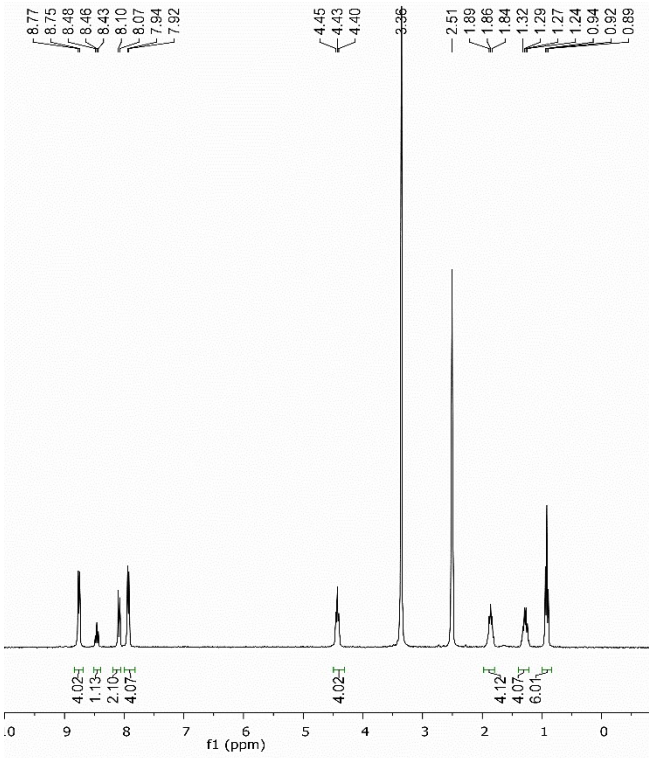


Figure 5.1. ^{1}H NMR spectrum of **5**

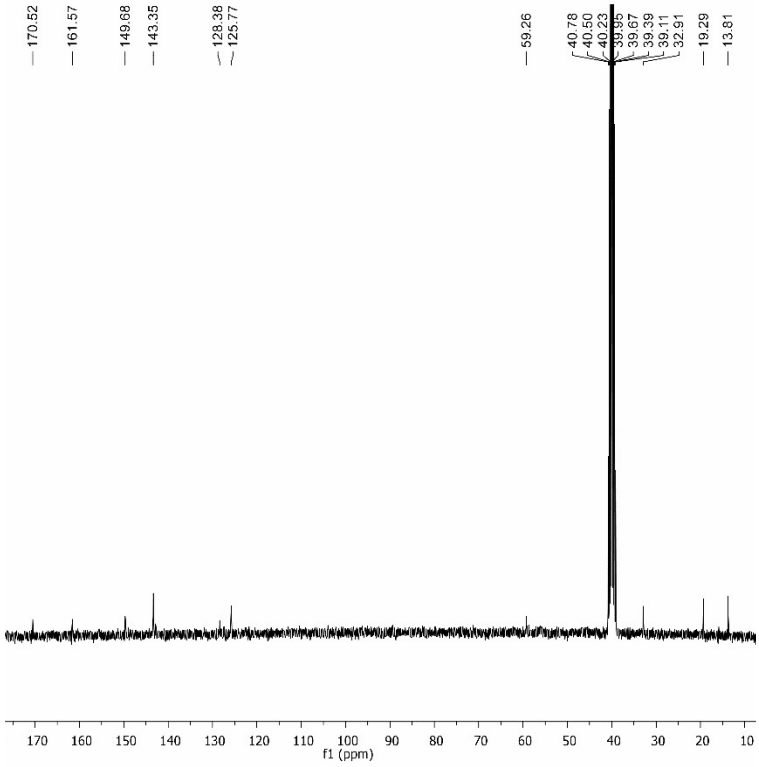


Figure 5.2. ^{13}C NMR spectrum of **5**

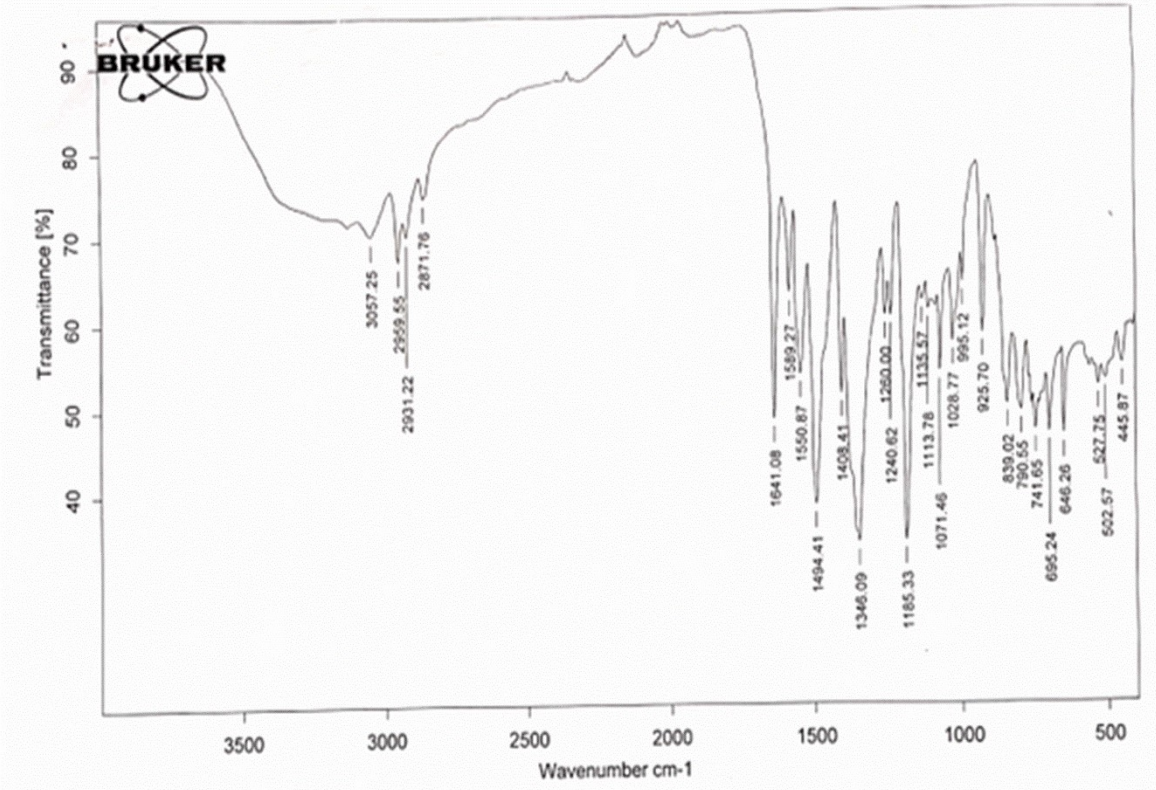


Figure 5.3. Representative FT-IR spectrum of **5**

Figure 6.1. ^{1}H NMR spectrum of **6**

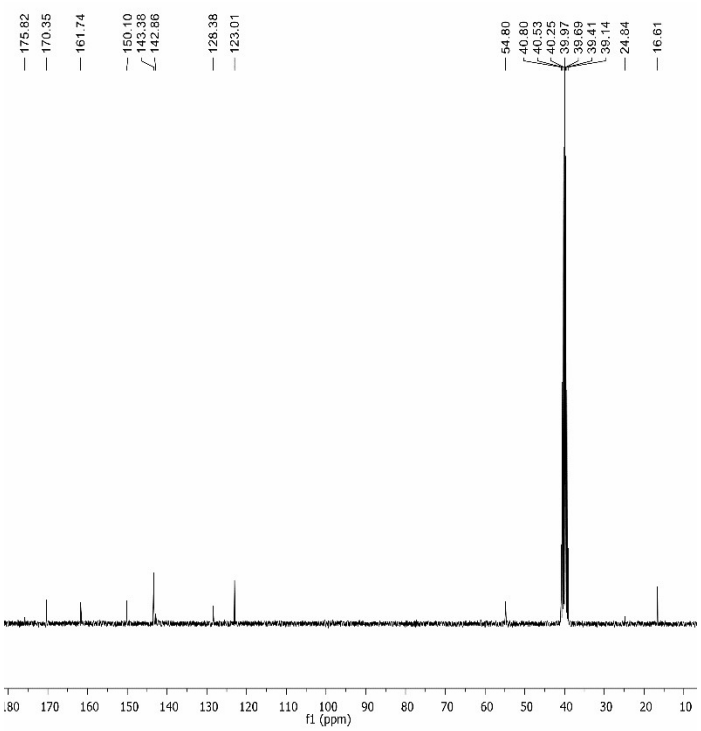


Figure 6.2. ^{13}C NMR spectrum of **6**

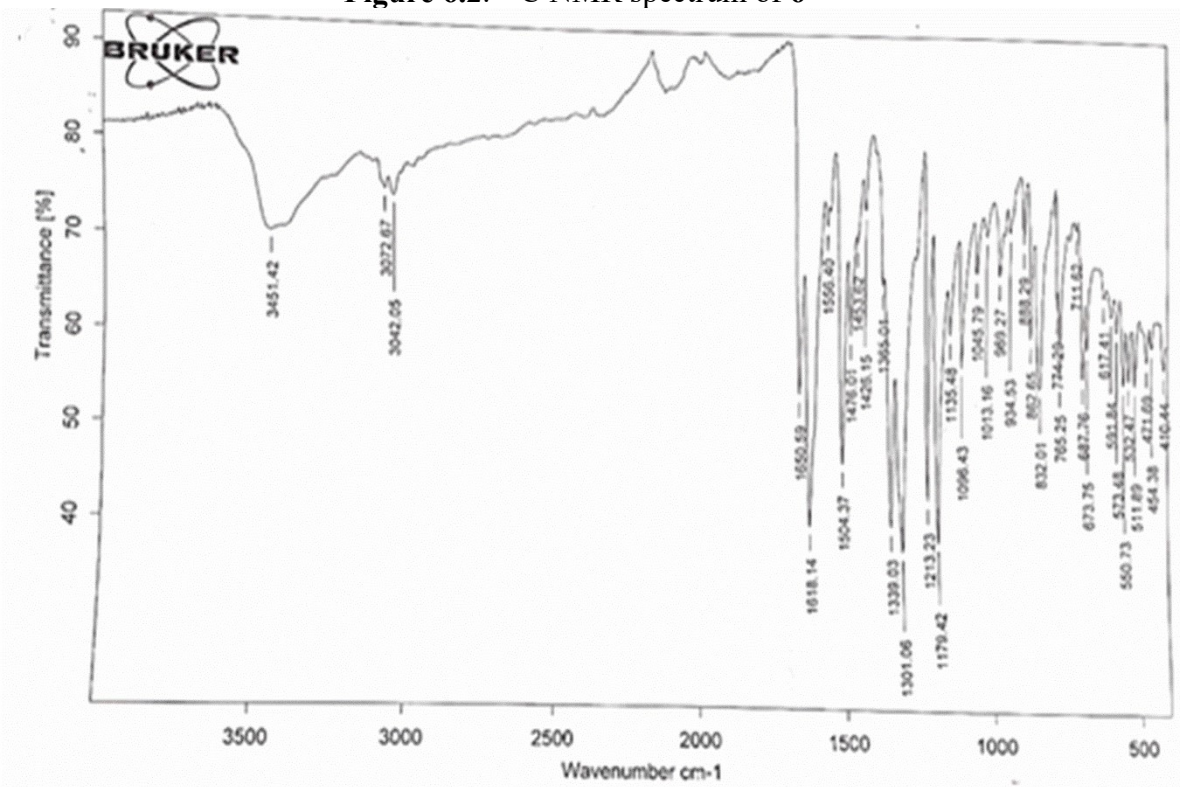


Figure 6.3. Representative FT-IR spectrum of **6**

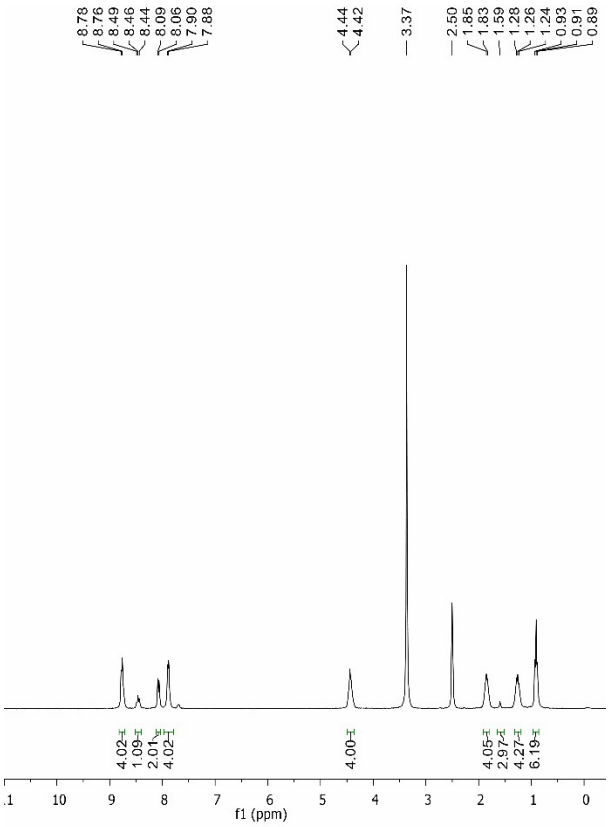


Figure 7.1. ^{1}H NMR spectrum of **7**

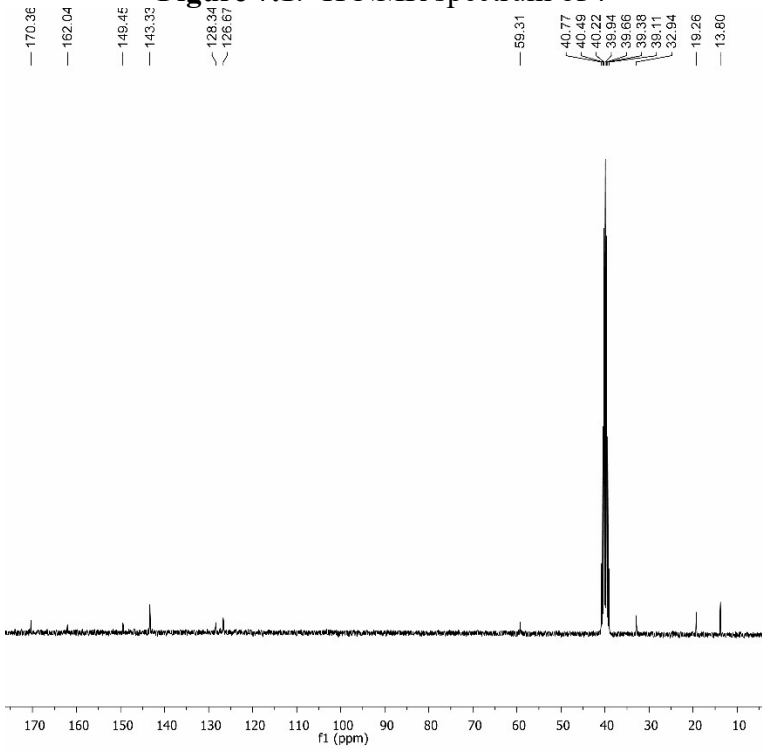


Figure 7.2. ^{13}C NMR spectrum of **7**

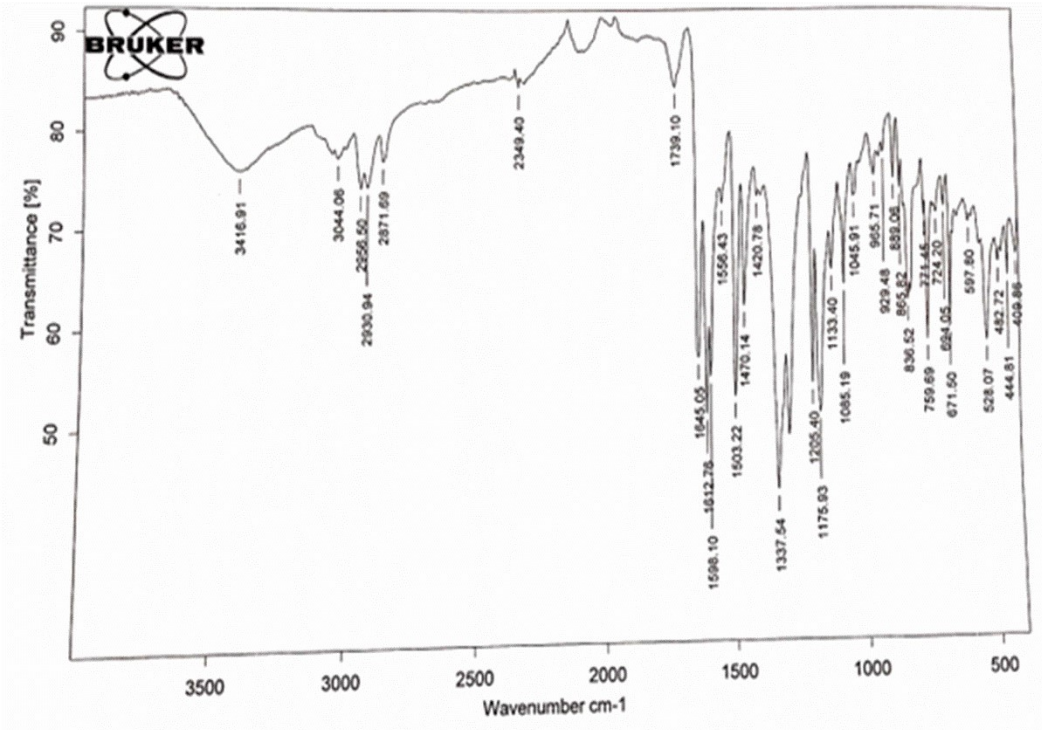


Figure 7.3. Representative FT-IR spectrum of **7**

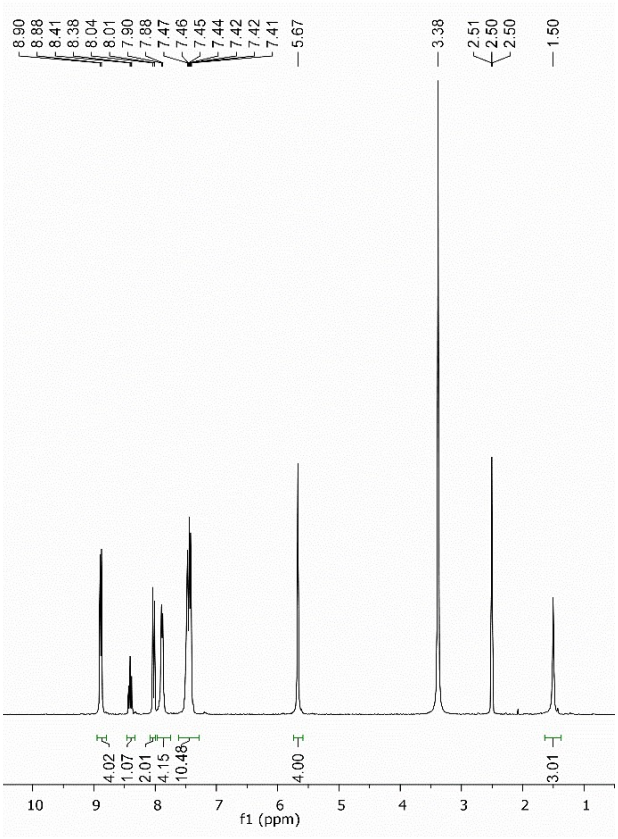


Figure 8.1. ^{1}H NMR spectrum of **8**

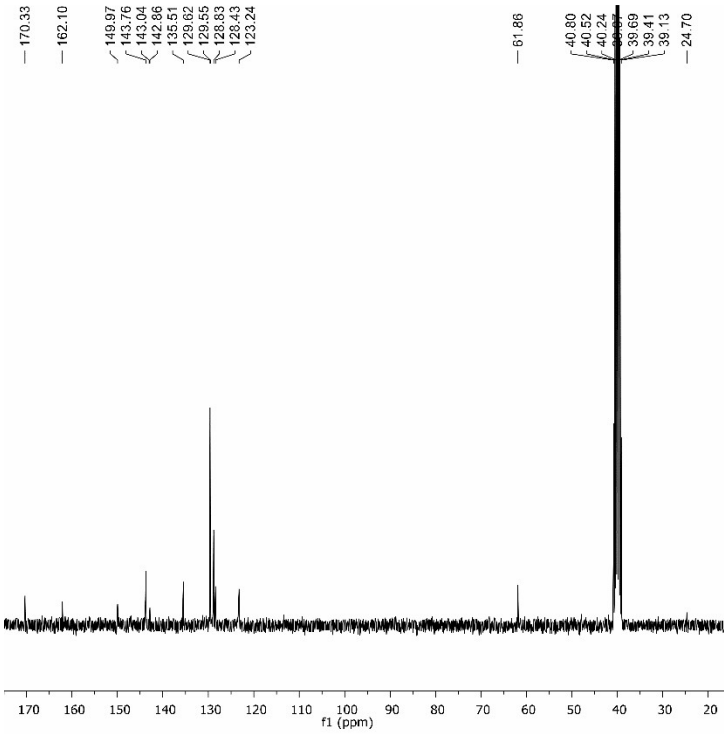


Figure 8.2. ^{13}C NMR spectrum of **8**

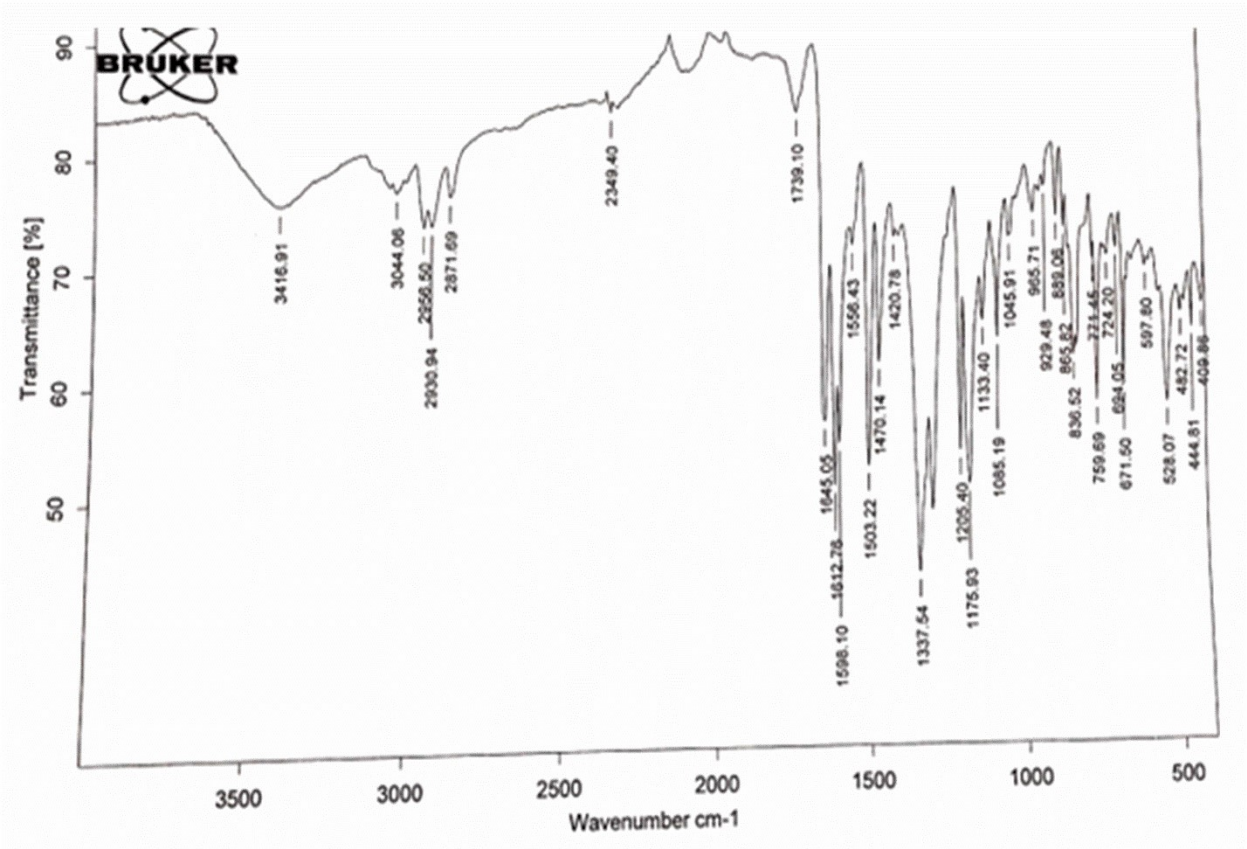


Figure 8.3. Representative FT-IR spectrum of **8**

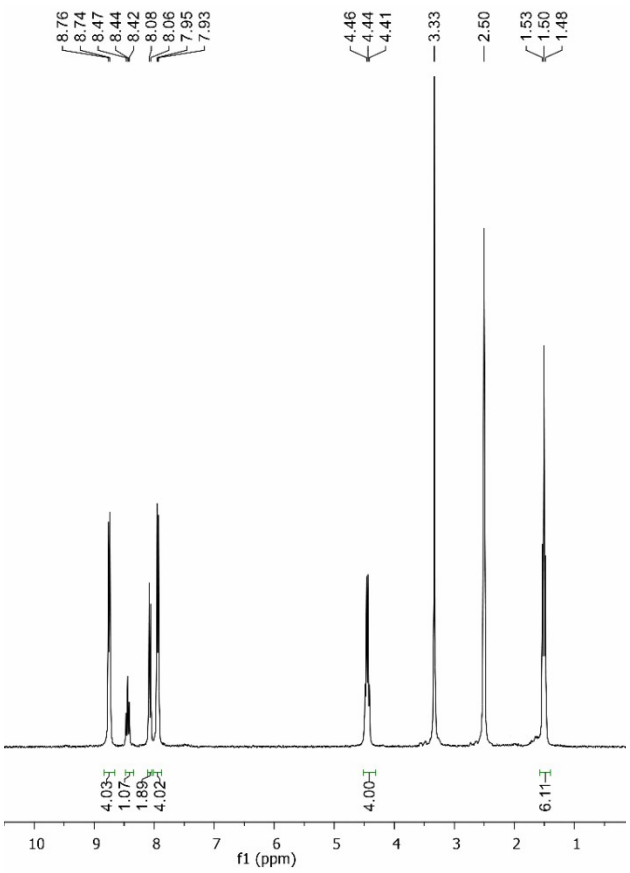


Figure 9.1. ^{1}H NMR spectrum of **9**

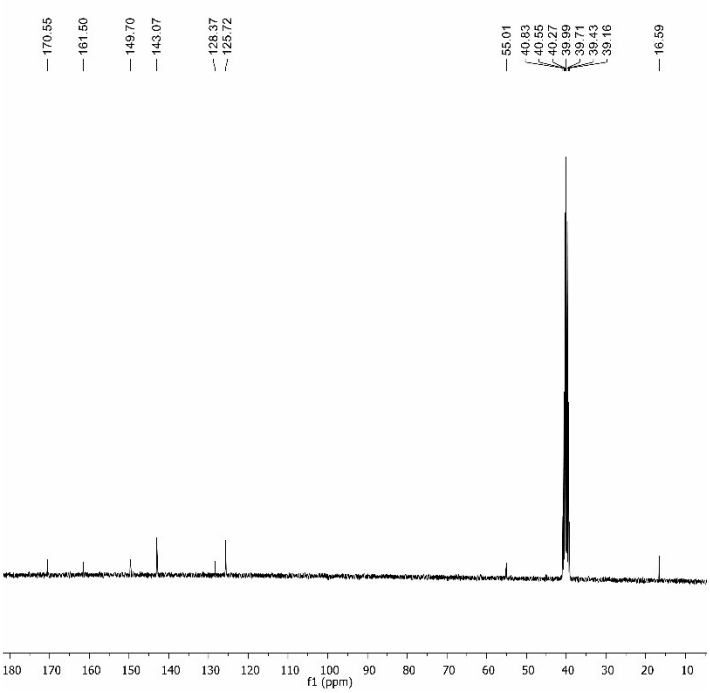


Figure 9.2. ^{13}C NMR spectrum of **9**

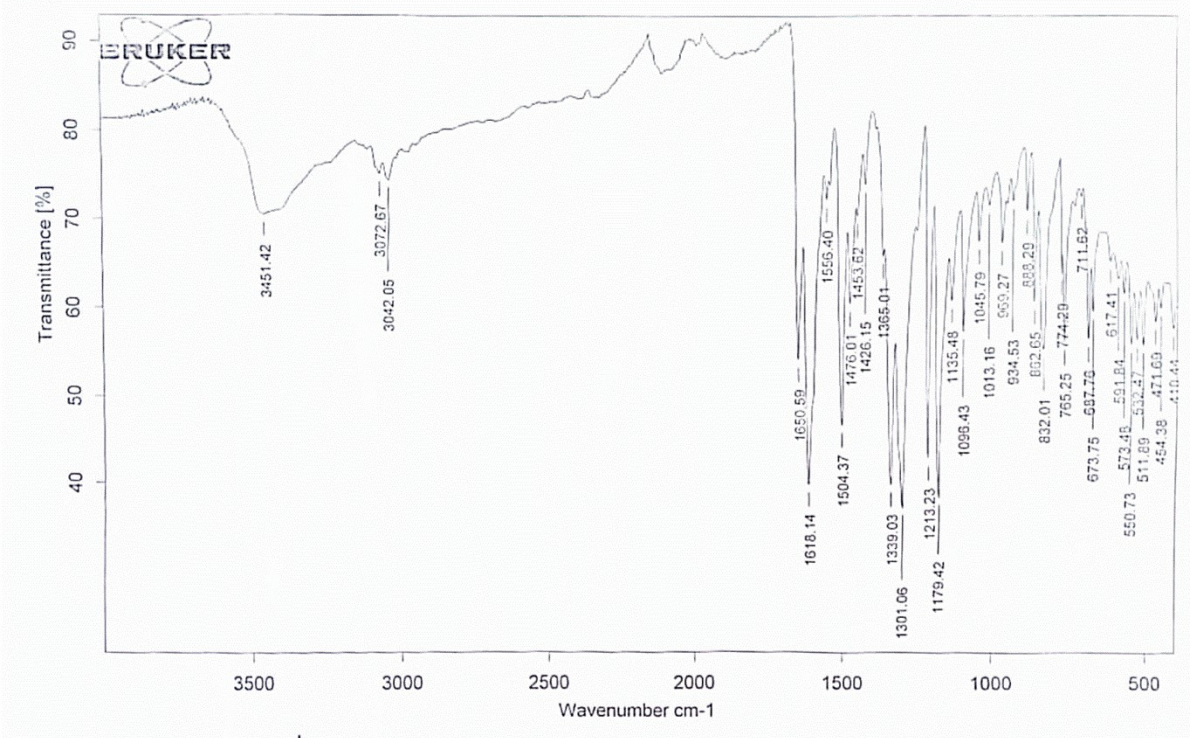


Figure 9.3. Representative FT-IR spectrum of **9**

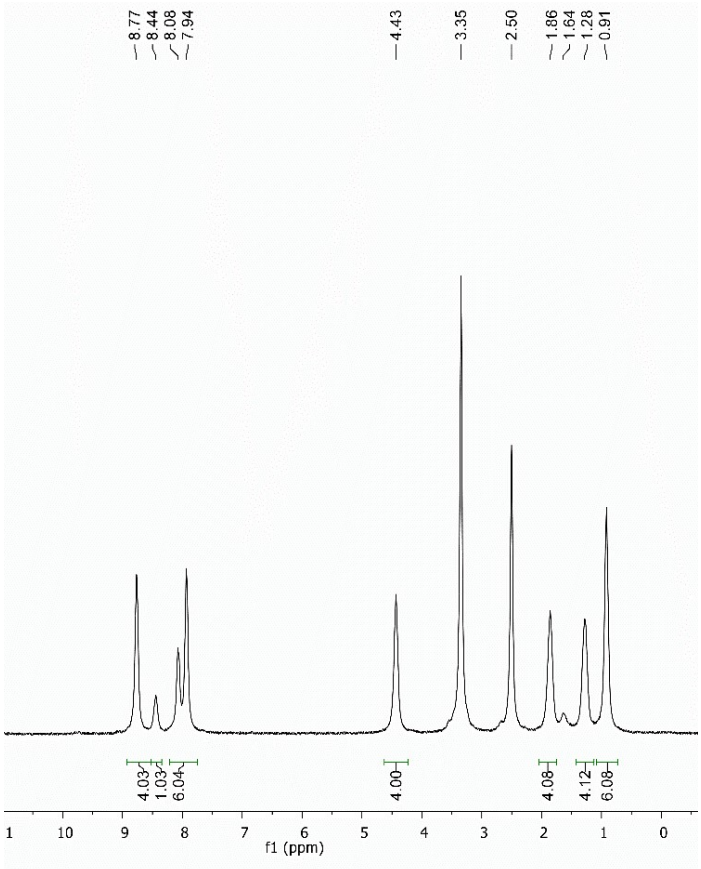


Figure 10.1. ^{1}H NMR spectrum of **10**

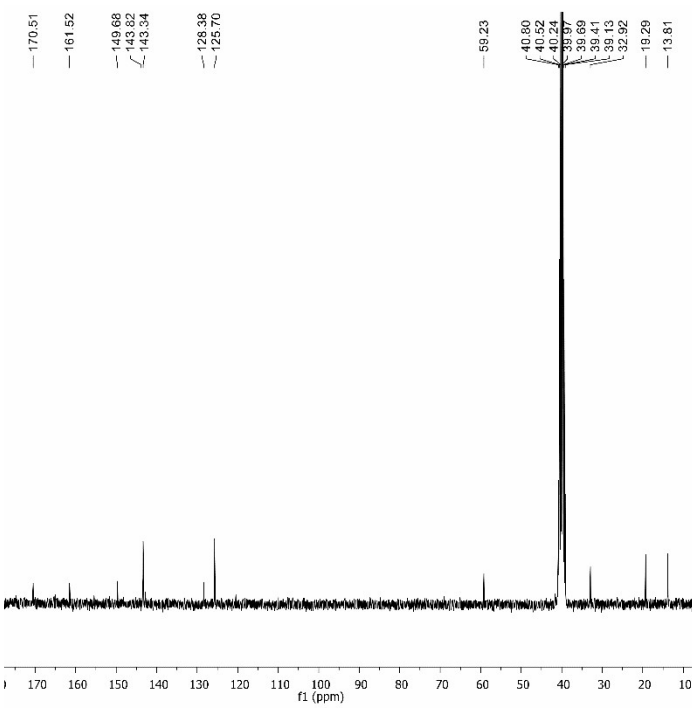


Figure 10.2. ^{13}C NMR spectrum of **10**

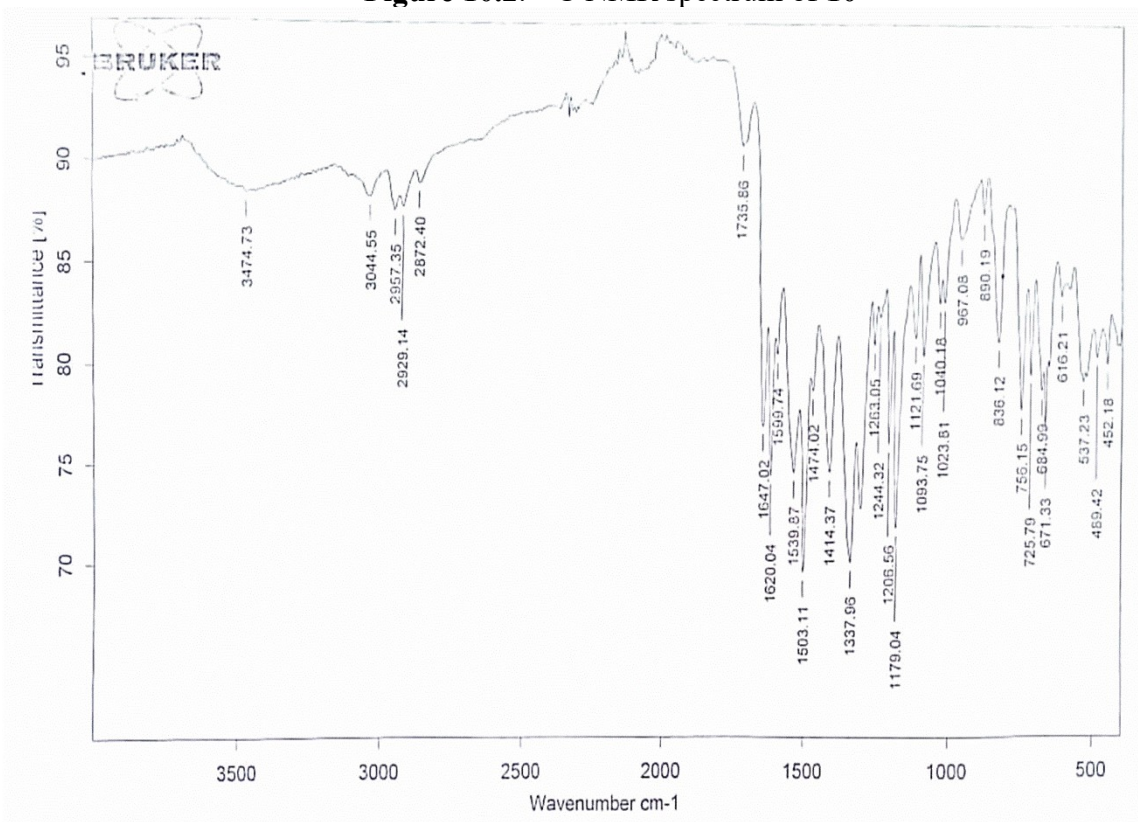


Figure 10.3. Representative FT-IR spectrum of **10**

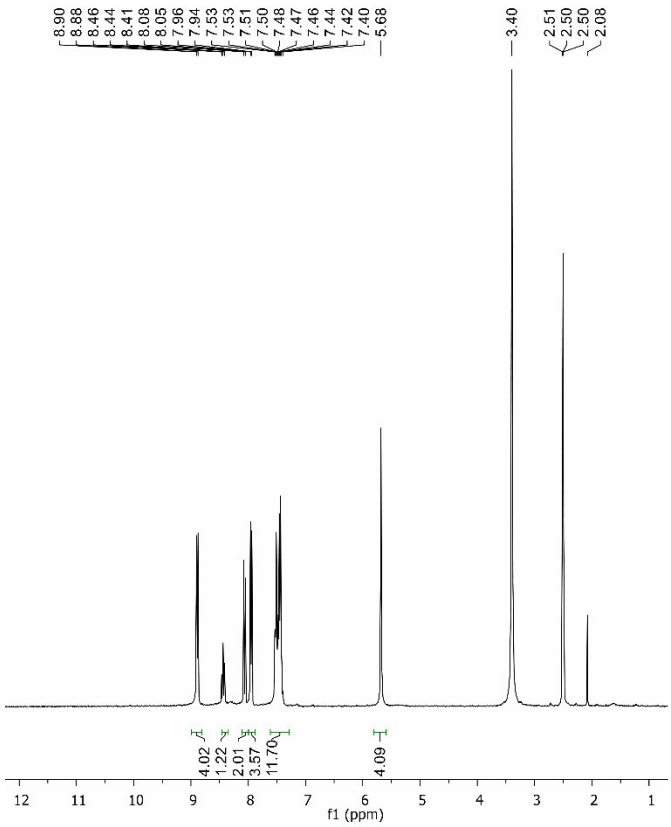


Figure 11.1. ^{1}H NMR spectrum of **11**

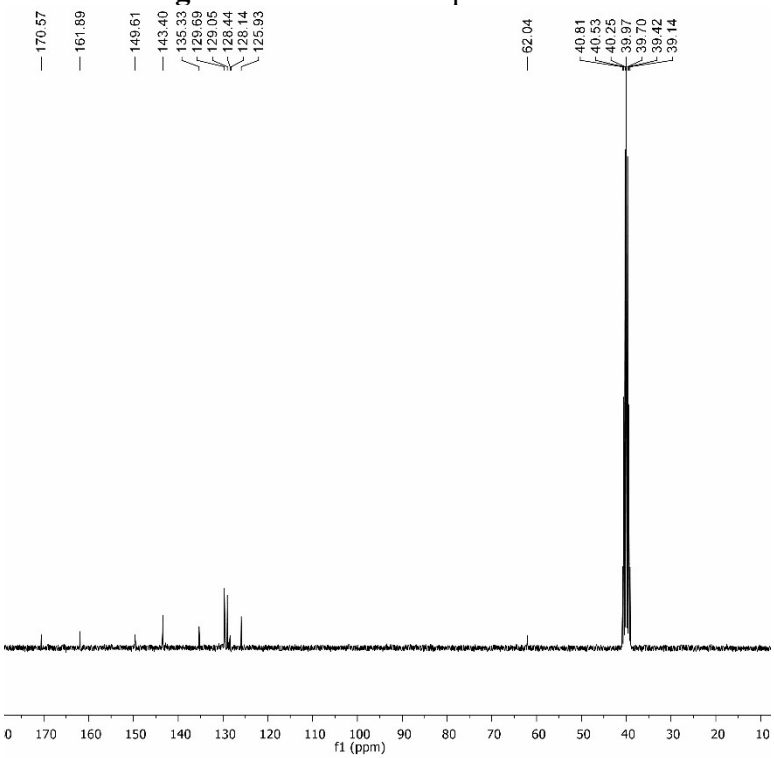


Figure 11.2. ^{13}C NMR spectrum of **11**

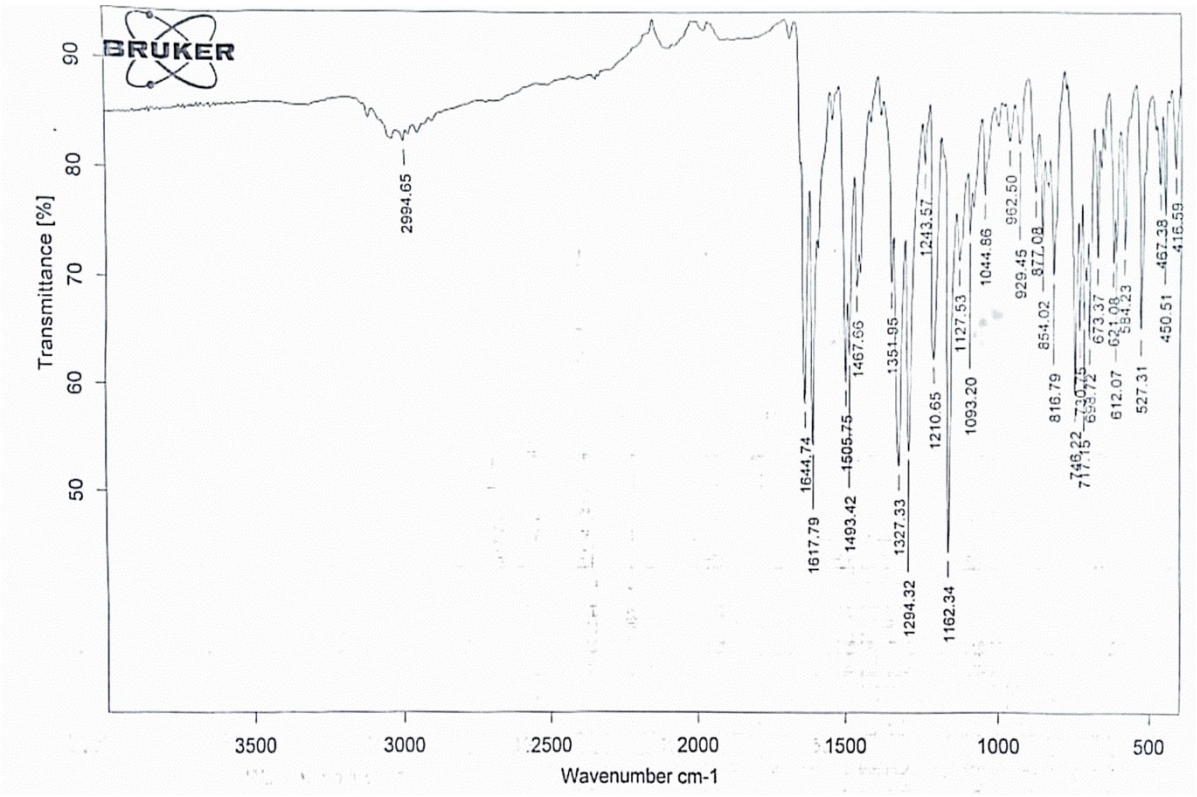
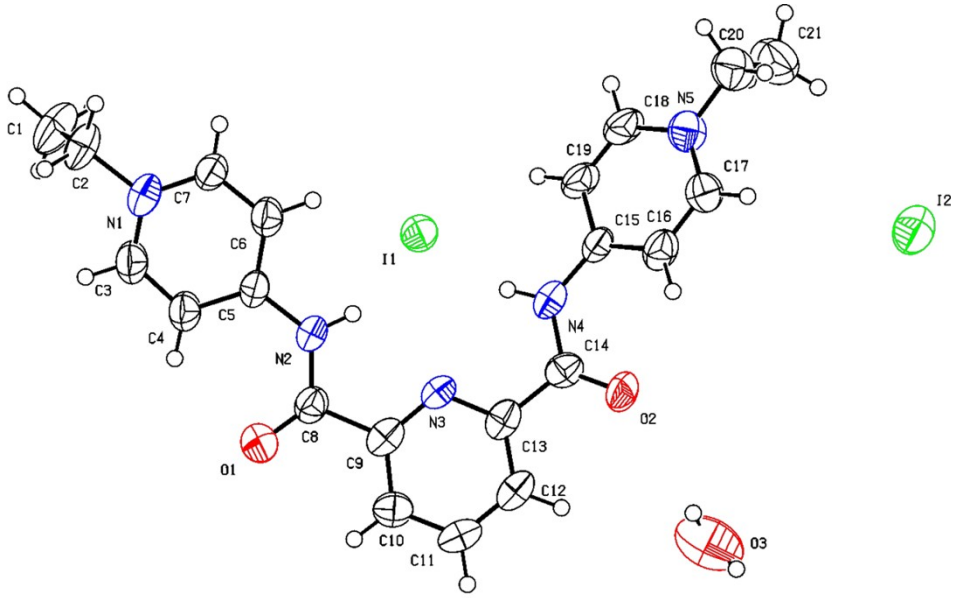
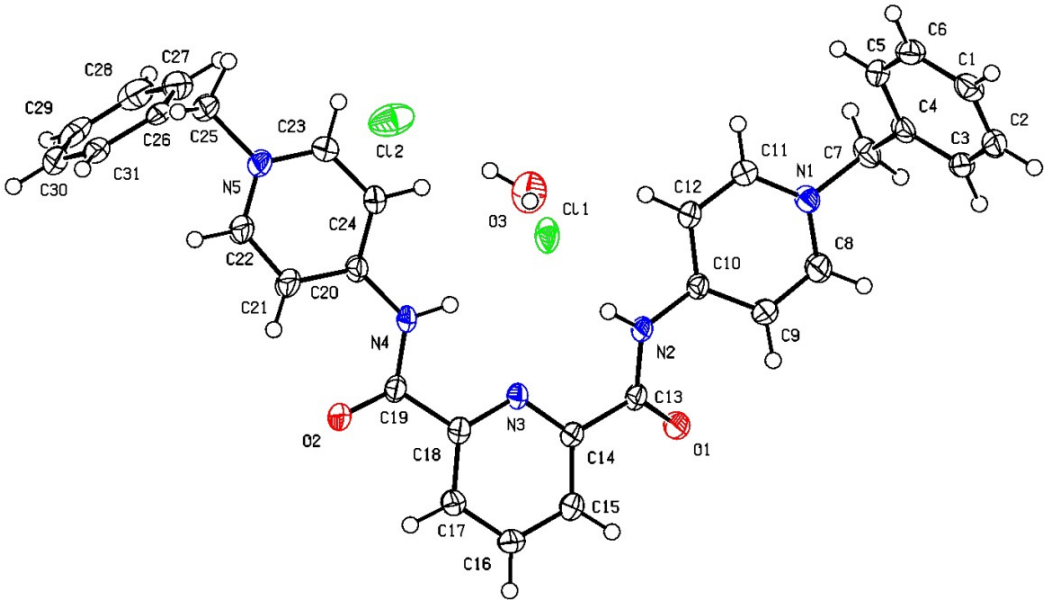


Figure 11.3. Representative FT-IR spectrum of **11**

Crystallographic Data: CCDC numbers of **2, 4** and **11** are 2281737, 2281738, 2281739.

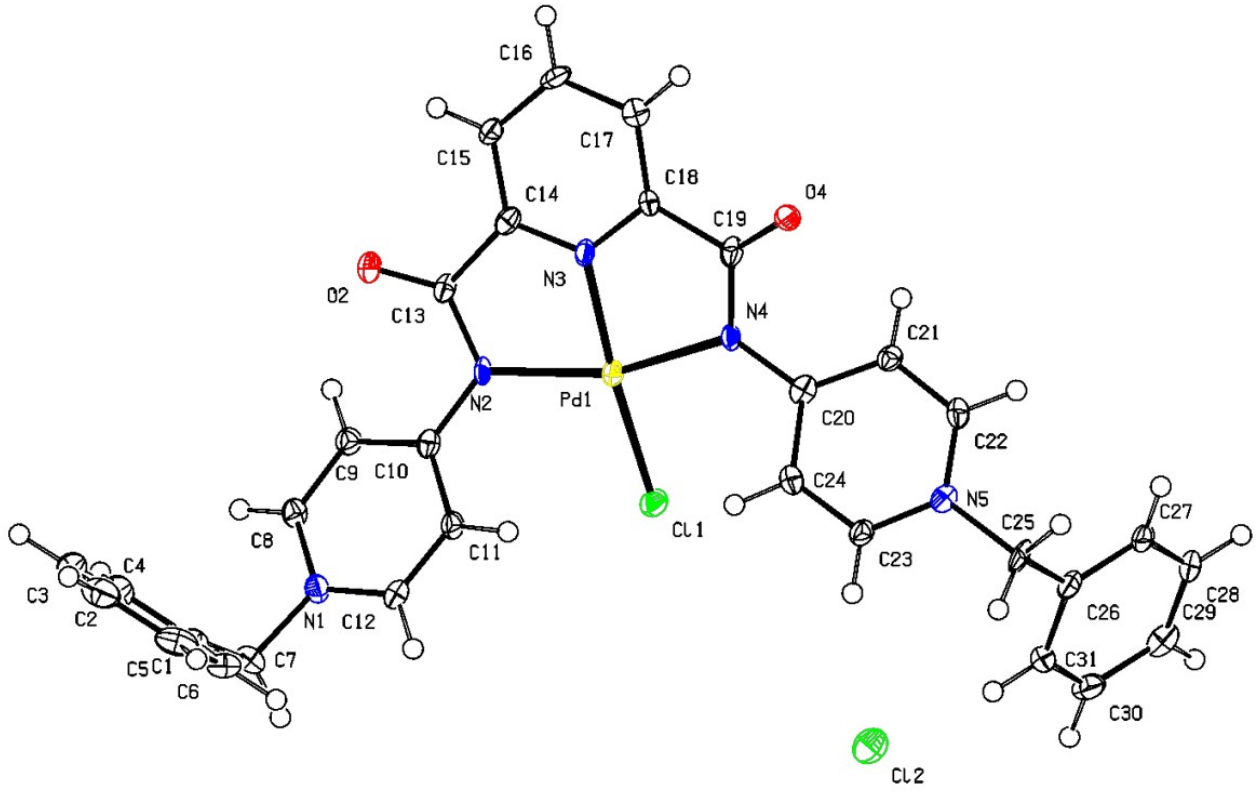


2



4

Figure S12. ORTEP diagrams of **2** and **4**



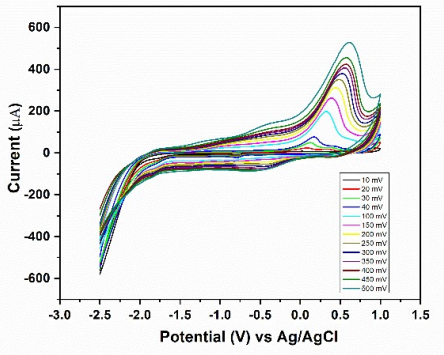
11

Figure S13. ORTEP diagrams of **11**

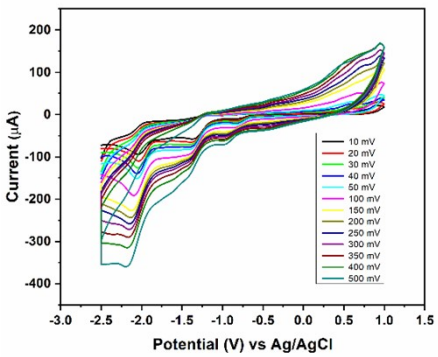
Single crystals of **2** and **4** suitable for x-ray diffraction analysis, were obtained *via* slow evaporation method. **2** was recrystallized from saturated mixture of water, methanol and acetonitrile. **4** was crystallized out from methanol. ORTEP diagrams of **2** and **4** are given in Figure S12 which evaluates the successful ethylation and benzylation of **1** respectively. The C-N bond distance of N2-C5 and N4-C15 were 1.378(1) Å and 1.385(2) Å respectively in **2** while in **4,** C20-N4 and C10-N2 were 1.382(5) Å and 1.391(6) Å respectively, which is closed to C-N bond length 1.47 Å[1]. In **2** the bond lengths of O1-C8 and O2-C14 were 1.227(2) Å and C14 1.202(2) Å respectively while in **4** the bond lengths of C13-O1 and C19-O2 were 1.218(4) Å and 1.214(6) Å respectively, representing carbon oxygen double bond character.

Single crystal of **11** suitable for x-ray diffraction analysis was grown in mixture of acetonitrile, methanol and water *via* slow evaporation method. An ORTEP and packing diagram of **11** is given in Figure S12. It has $P2_1/n$ space group and two molecules packed in unit cell. The C20-N4 and C10-N2 bond lengths extended from 1.382(5) Å to 1.388(8) Å and 1.391(6) Å to 1.394(6) Å in contrast to its respective proligand **4**, due to the shifting of electron density from nitrogen to the palladium. Palladium coordinated with three nitrogen atoms (N2, N3 and N4) of ligand and one chlorine atom (Cl1). The angle between palladium and the three nitrogen atoms (N2-Pd1-N3) and (N3-Pd1-N4) were 80.8(2)° and 80.7(2)° respectively. This distorted square planner geometry of the complex may be due to the rigidity of tridentate ligand.

Electrochemical Activity:



CV of **7** at different scan rate under N_2

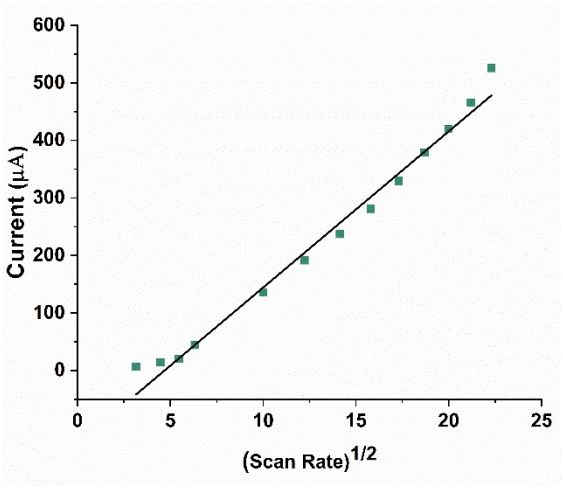


CV of **7** at different scan rate under CO_2

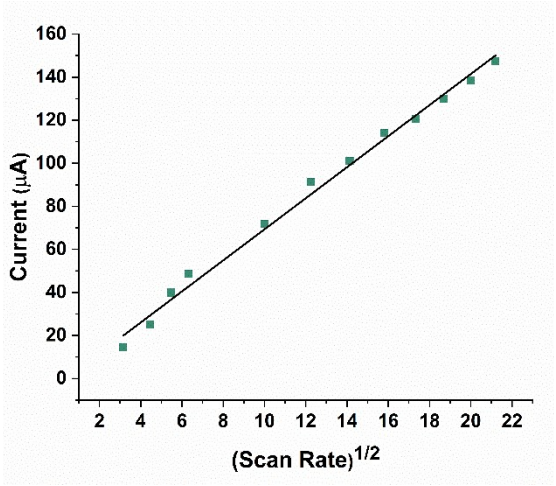
Figure S14. Cyclic voltammograms of **7** under nitrogen, CO_2 at different scan rates. All experiments were performed at 100 mVs^{-1} scan rate in DMF and 0.1 M supporting electrolyte [n Bu_4N]PF_6.

Plots of Peak Current vs. (Scan Rate)$^{1/2}$

Randles-Sevcik equation describes that the peak current is directly proportional to the square root of the scan rate in an electrochemical redox reaction. A linear plot of the peak current *vs* the square root of the scan rate demonstrates that the electroactive species in a redox reaction are freely diffusing. Randles-Sevcik plots of the 2 mM complexes (**7**) under an inert atmosphere and CO_2 are given in Figure S15.



Linear plot of **7** at different scan rate under N_2



Linear plot of **7** at different scan rate under CO_2

Figure S15. Current *vs* (scan rate)$^{1/2}$ plots of **7** under nitrogen, CO_2 at different scan rates. All experiments were performed at 100 mVs^{-1} scan rate in DMF and 0.1 M supporting electrolyte [n $Bu_4N]PF_6$.

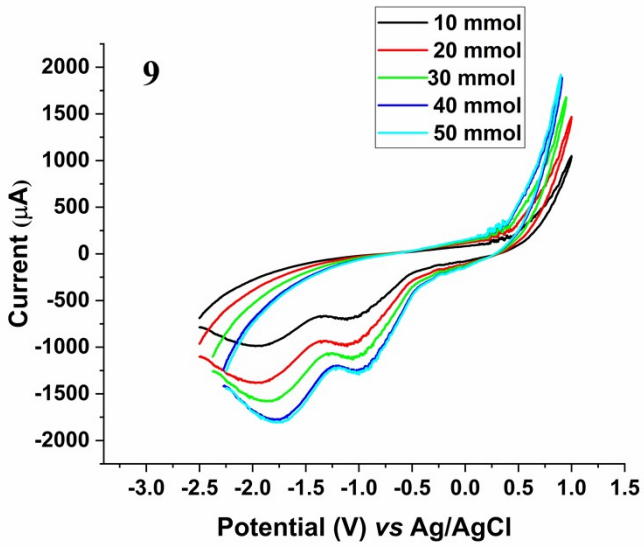


Figure S16. Cyclic voltammograms of **9** under CO_2 + TFA at different concentrations. All experiments were performed at 100 mVs^{-1} scan rate in DMF and 0.1 M supporting electrolyte ([n $Bu_4N]PF_6$)

References:

1. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R., Tables of bond lengths determined by X-ray and neutron diffraction. Part 1. Bond lengths in organic compounds. *Journal of the Chemical Society, Perkin Transactions 2* **1987,** (12), S1-S19.