Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Cu@Furfural Imine-Decorated Halloysite as an Efficient Heterogeneous Catalyst for Promoting Ultrasonic-Assisted A^3 and KA^2 Coupling Reactions: A Combination of Experimental and Computational Study

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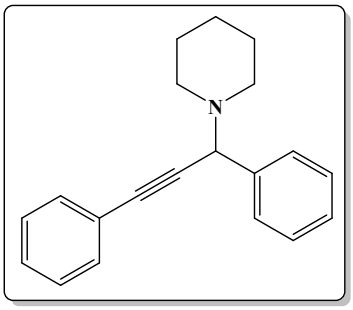
1. General information

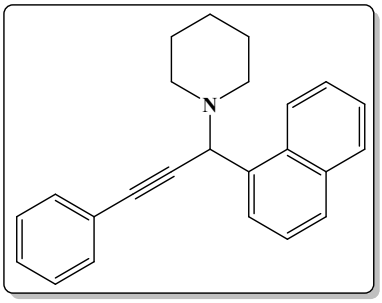
All chemicals and reagents, including aldehydes, amines, ketone, phenyl acetylene, halloysite clay, toluene, tiosemicarbazide, furfural, ethanol, (3-chloropropyl) trimethoxysilan and $Cu(OAc)_2$ were analytical grade reagents, purchased from Sigma-Aldrich, and used without further purification. The progress of the organic reactions were monitored by TLC on commercial aluminum-backed plates of silica gel 60 F254, visualized, using ultraviolet light. Melting points were determined in open capillaries using an Electrothermal 9100 without further corrections. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-400 spectrometer at 400 and 100 MHz respectively.

Catalyst characterization was carried out by applying various techniques including SEM/EDX, TGA, FTIR, XRD, BET and ICP-AES. FTIR spectra were obtained by employing PERKIN-ELMER- Spectrum 65 instrument. SEM/EDX analyses were recorded by a Tescan instrument, using Au-coated samples and acceleration voltage of 20 kV. Room temperature powder X-ray diffraction patterns were obtained by using a Siemens, D5000. CuKα radiation from a sealed tube. The BET analyses were performed using BELSORP Mini II instrument. Prior to BET analyses, the samples were degassed at 423 K for 3 h. Thermo gravimetric analysis (TGA) was performed on a METTLER TOLEDO thermo gravimetric analysis apparatus with a heating rate of 10 °C min^{-1} from 50 to 600 °C under N_2 atmosphere. The used ultrasonic apparatus for promoting the organic transformations was Bandelin HD 3200 with output power of 150 W and tip TT13.

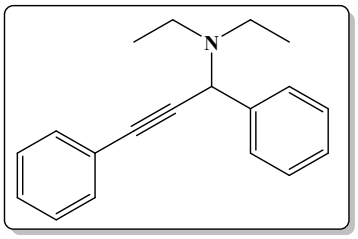
1.1. Spectral data for selected compounds



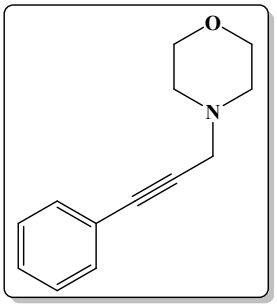
1-(1,3-diphenylprop-2-ynyl)piperidine (Table 5, 5a): Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.45-1.49 (m, 2H), 1.58-1.65 (m, 4H), 2.59 (t, 4H), 4.81 (s, 1H), 7.31-7.40 (m, 6H), 7.53-7.55 (m, 2H), 7.65-67 (d, *J*=7.6 Hz, 2H).



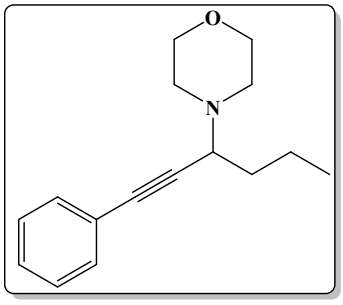
1-(1-(naphthalen-3-yl)-3-phenylprop-2-ynyl)piperidine (Table 5, 5h): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.47-1.51 (m, 2H), 1.60-1.67 (m, 4H), 2.64 (t, 4H), 4.97 (s, 1H), 7.36-7.40 (m, 3H), 7.48-7.52 (m, 2H), 7.58-7.61 (m, 2H), 7.79 (dd, J^1=J^2=8.4 Hz, 1H), 7.85-7.91 (m, 3H), 8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) d 24.4, 26.2, 50.8, 62.5, 86, 88.1, 123.3, 125.8, 125.9, 126.7, 127.2, 127.5, 127.7, 128.1, 128.12, 131.8, 132.9, 133.1, 136.3.



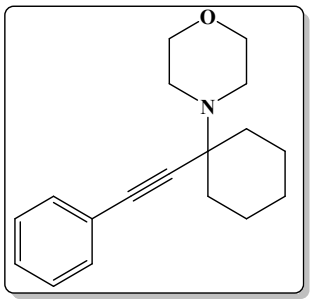
***N,N*-diethyl-1,3-diphenylprop-2-yn-1-amine (Table 5, 5q):** Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.04 (m, 6H), 2.36-2.62 (m, 4H), 5.19 (s, 1H), 7.15-7.27 (m, 4H), 7.29-7.38 (m, 3H), 7.39-7.41 (m, 2H).



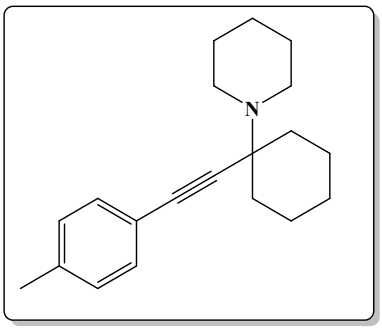
4-(3-phenylprop-2-ynyl)morpholine (Table 5, 6b): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.64-2,67 (m, 6H), 3.52 (s, 3H), 3.69-3.71 (m, 1H), 3.77-3.79 (m, 6H), 7.28-7.31 (m, 4H), 7.43-7.46 (m, 2H).



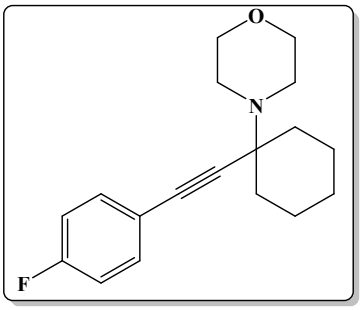
4-(1-phenylhex-1-yn-3-yl)morpholine (Table 5, 6h): Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 0.97 (m, 3H), 1.45-1.75 (m, 4H), 2.67−2.70 (m, 2H), 2.79−2.83 (m, 2H), 3.82-4.13 (m, 1H), 4.15-4.17 (m, 4H), 7.46−7.50 (m, 3H), 7.62−7.64 (m, 2H).



4-(1-(2-phenylethynyl)cyclohexyl)morpholine (Table 5, 6k): Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.28-1.30 (m, 1H), 1.52 (m, 2H), 1.63-1.67 (m, 3H), 1.73 (br.s, 2H), 2.03-2.05 (m, 2H), 2.74 (br.s, 4H), 3.78 (br.s, 4H), 7.27 (m, 3H), 7.44-7.45 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 22.7, 25.7, 35.4, 46.6, 58.8, 67.4, 86.4, 89.8, 123.4, 127.7, 128.1, 131.7.



1-(1-(2-p-tolylethynyl)cyclohexyl)piperidine (Table 5, 6m): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.39-1.93 (m, 16H), 2.17-2.20 (m, 2H), 2.53 (s, 3H), 2.73-2.83 (m, 2H), 7.26-7.27 (m, 3H), 7.46-7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 21.32, 23.4, 24.4, 25, 26.7, 37.6, 47.9, 58.8, 85.4, 92.1, 123, 127.6, 128.3, 133.



4-(1-((4-fluorophenyl)ethynyl)cyclohexyl)morpholine (Table 5, 6n): Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 1.26-1.34 (m, 1H), 1.57-1.62 (m, 2H), 1.69-1.78 (m, 3H), 1.80-1.86 (m, 2H), 2.00-2.02 (m, 2H), 2.78 (s, 4H), 3.70 (br.t, *J* = 4.2 Hz, 4H), 6.97-7.00 (t, *J* = 8.6 Hz, 2H), 7.32-7.40 (m, 2H).

2. The SEM image of pure HNTs

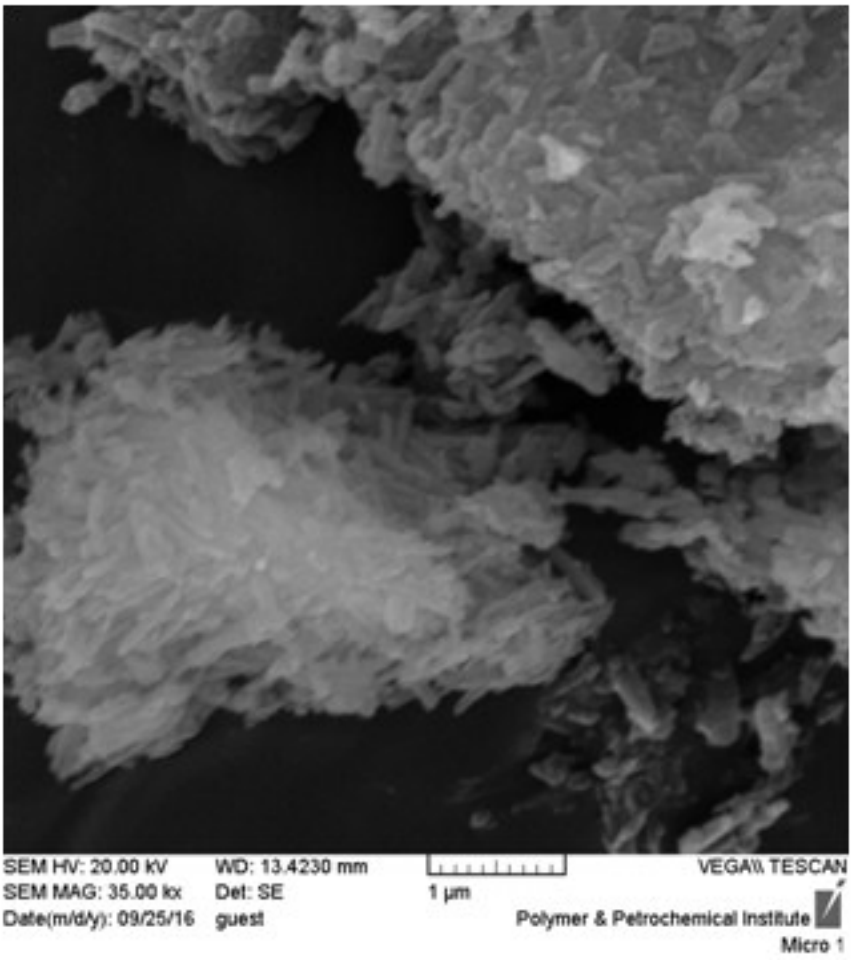


Figure 1. SEM image of pure HNTs

3. Copies of ^{1}H and ^{13}C NMR for selected products[1]

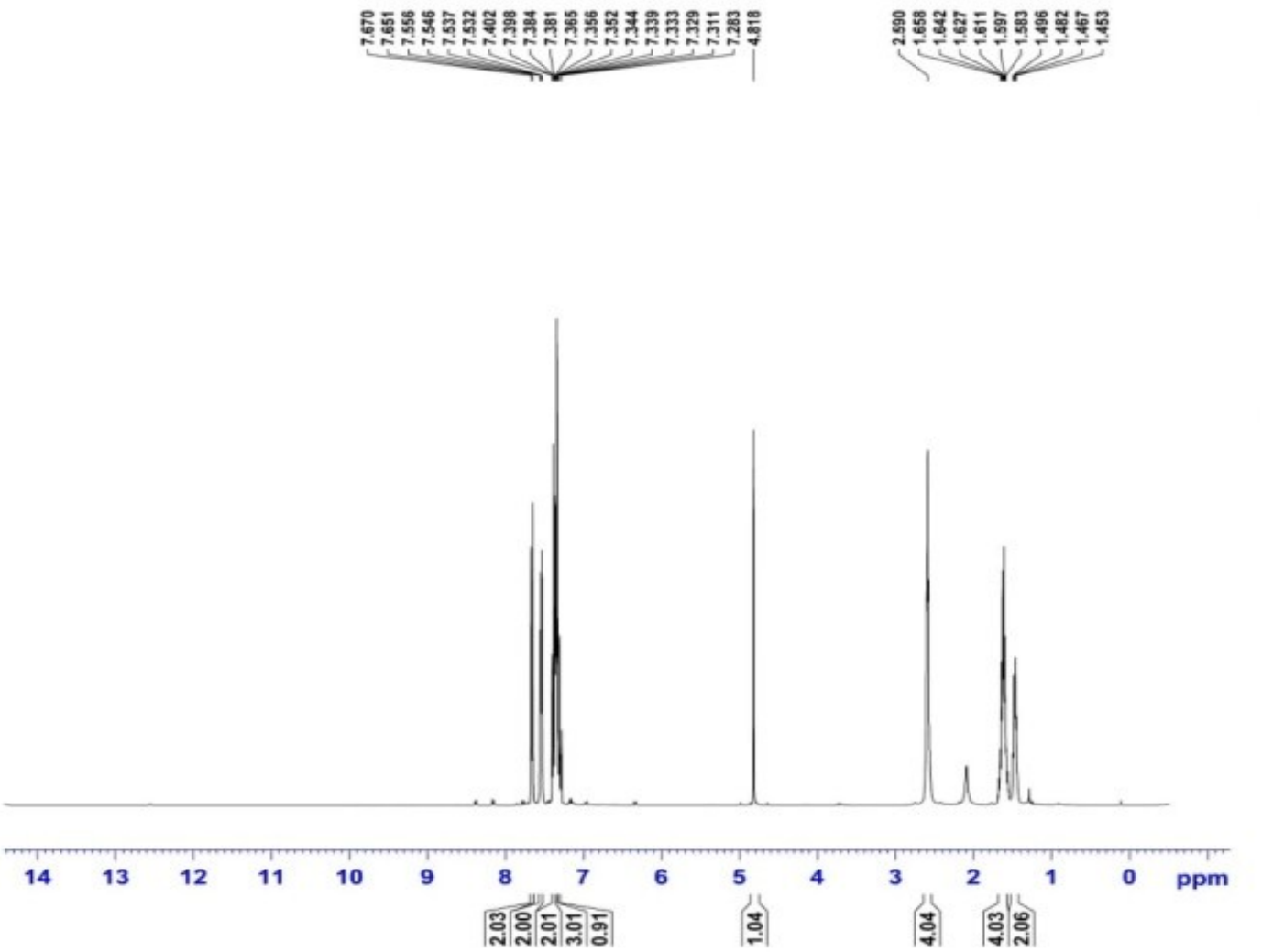


Figure 2.^{1}H NMR spectrum of **(Table 5, 5a)**

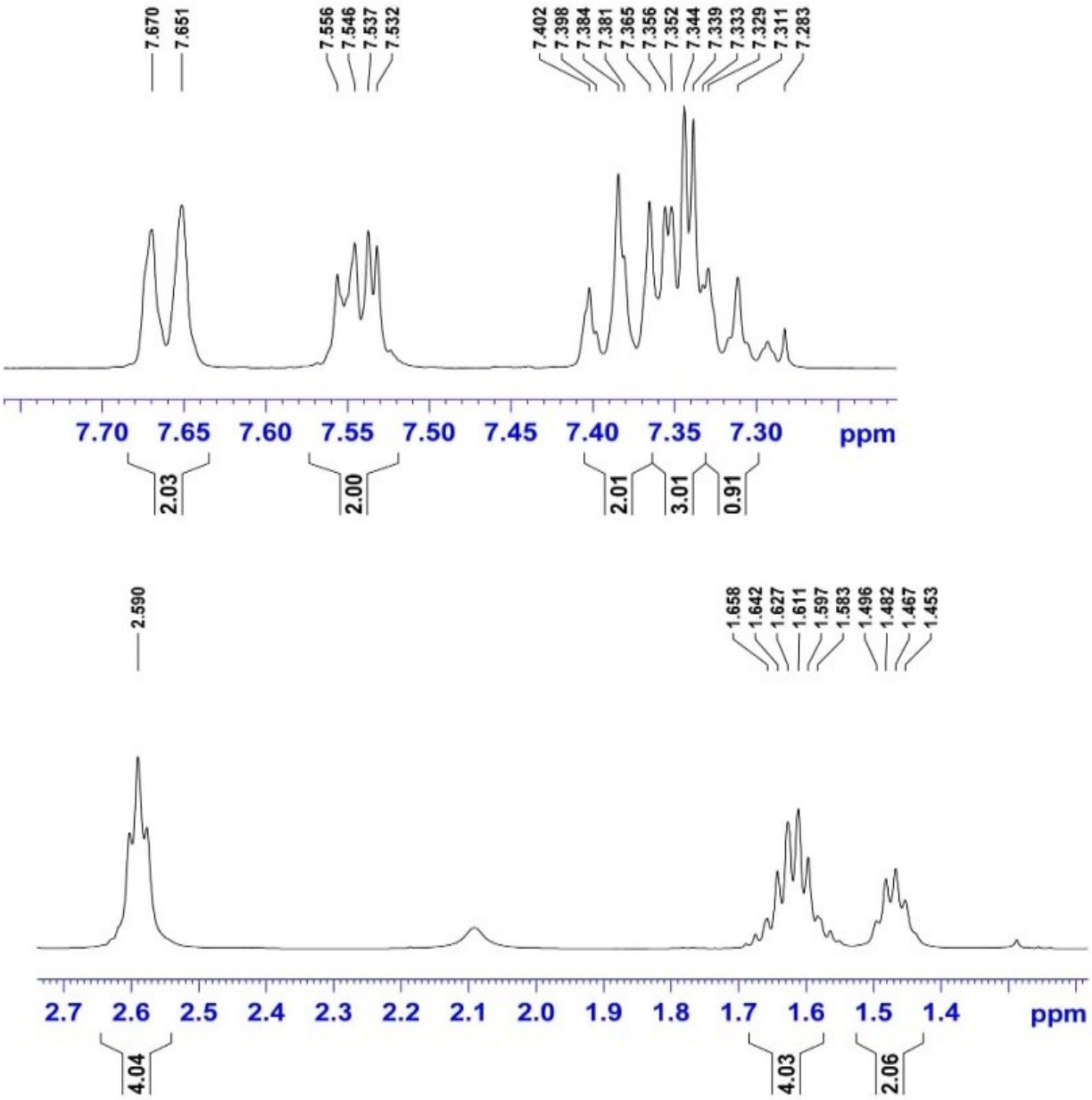


Figure 3.[1]H NMR, Expand spectrum of **(Table 5, 5a)**

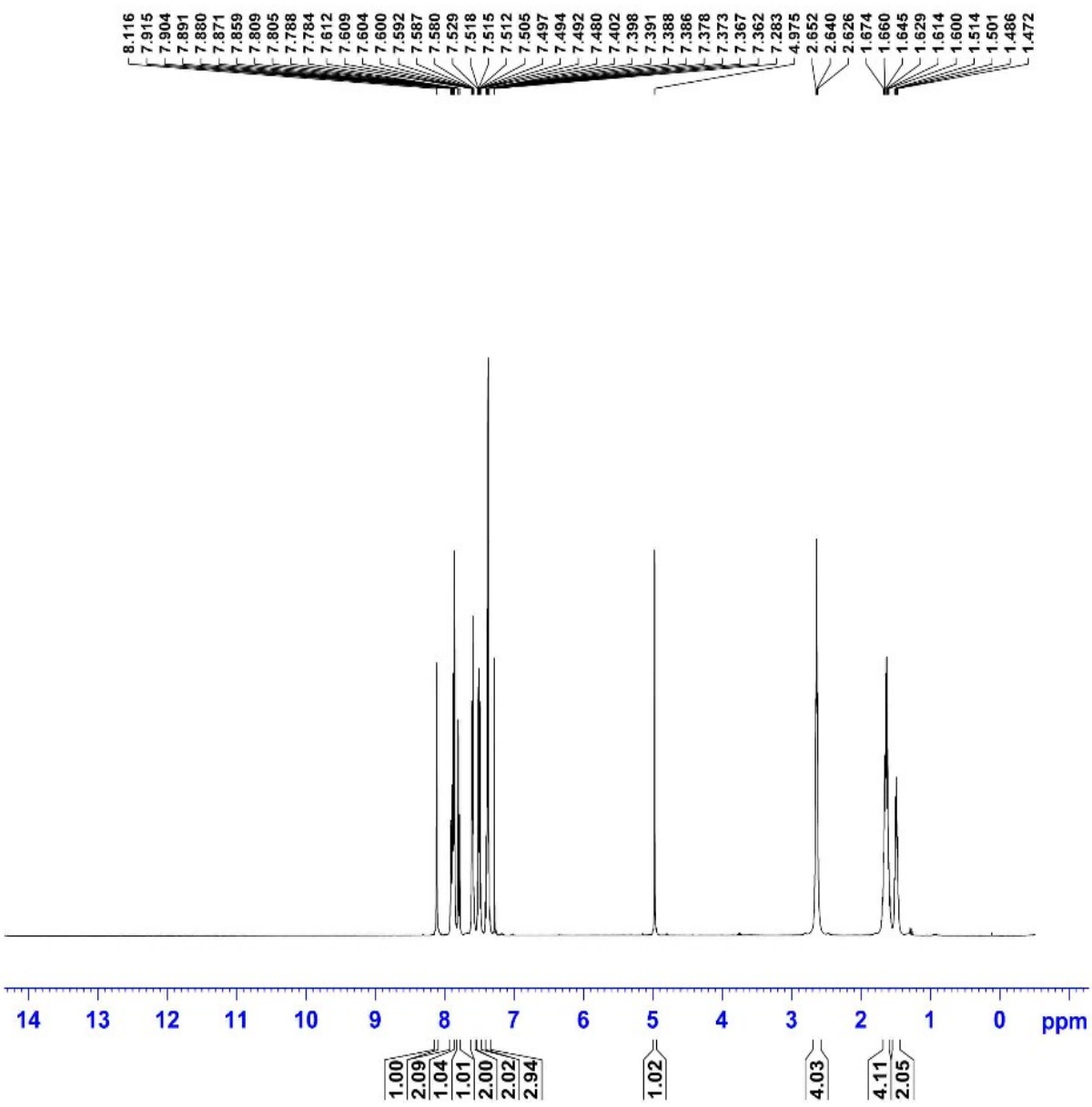


Figure 4. ^{1}H NMR, spectrum of **(Table 5, 5h)**

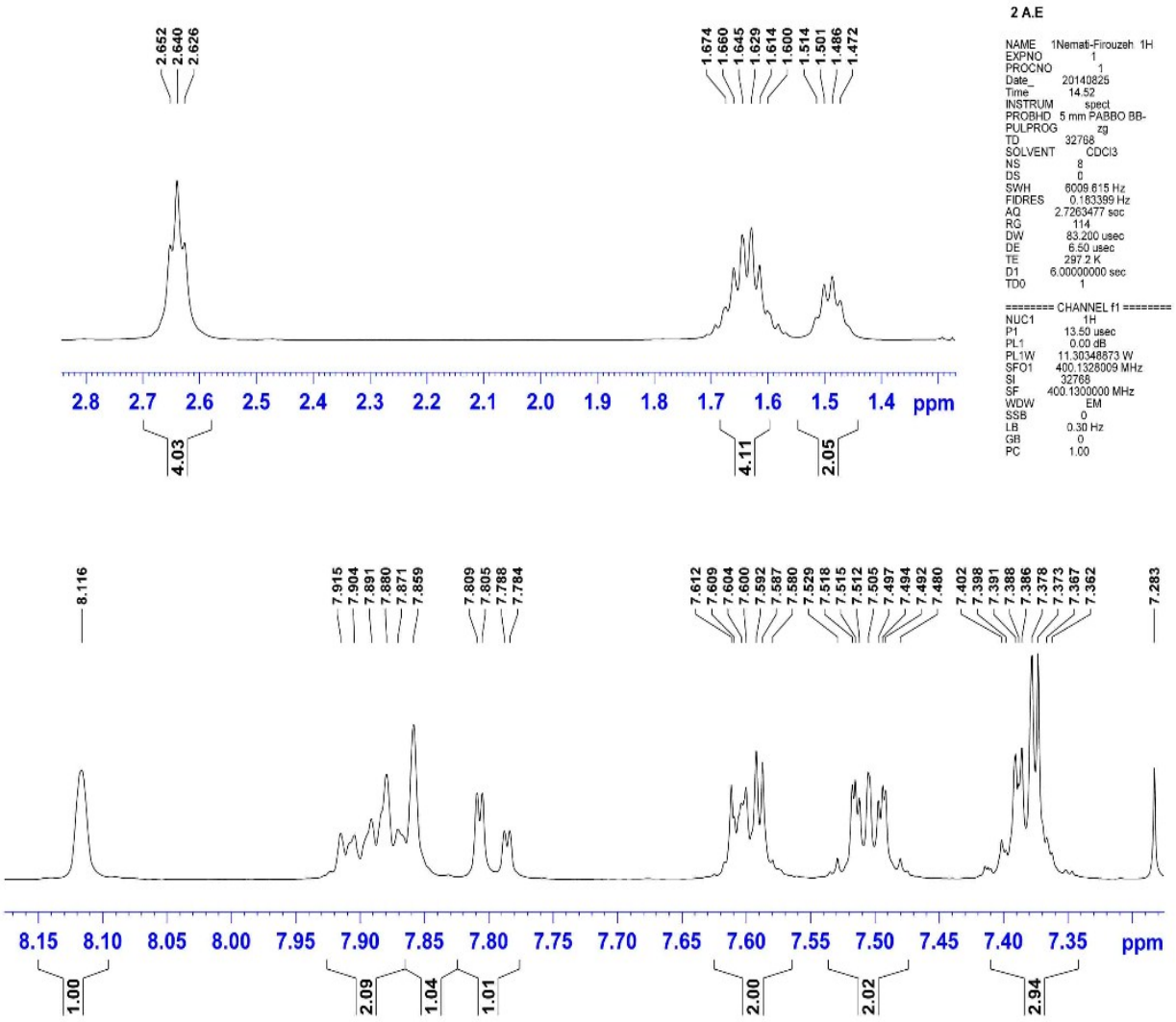


Figure 5. ^{1}H NMR, Expand spectrum of **(Table 5, 5h)**

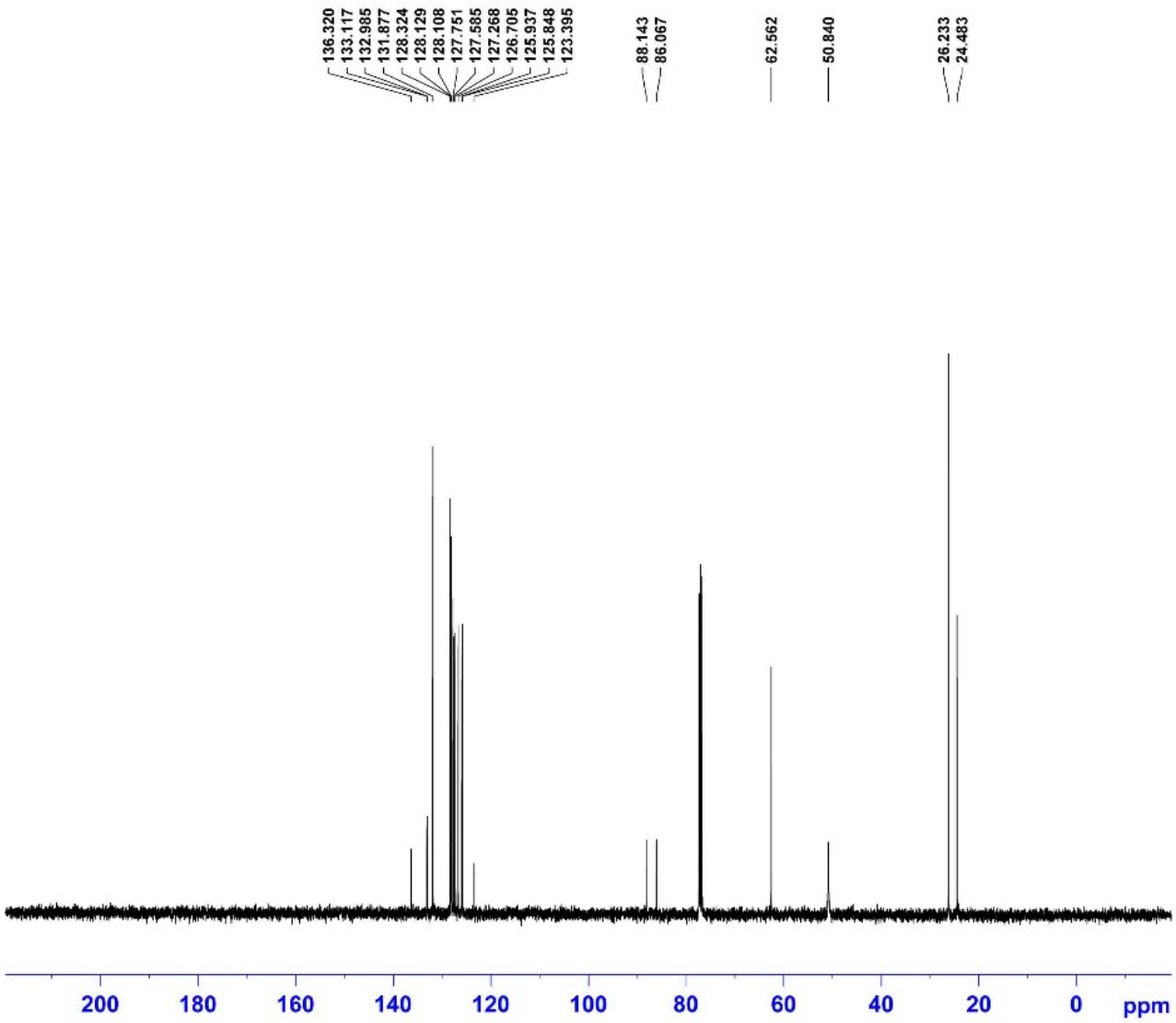


Figure 6. ^{13}C NMR spectrum of **(Table 5, 5h)**

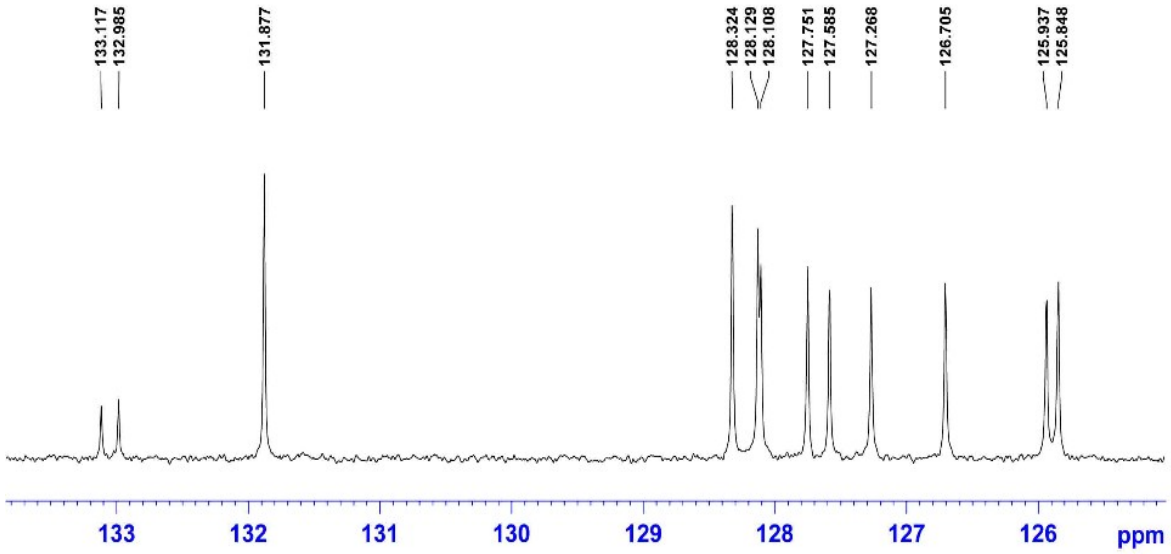


Figure 7. ^{13}C NMR, Expand spectrum of **(Table 5, 5h)**

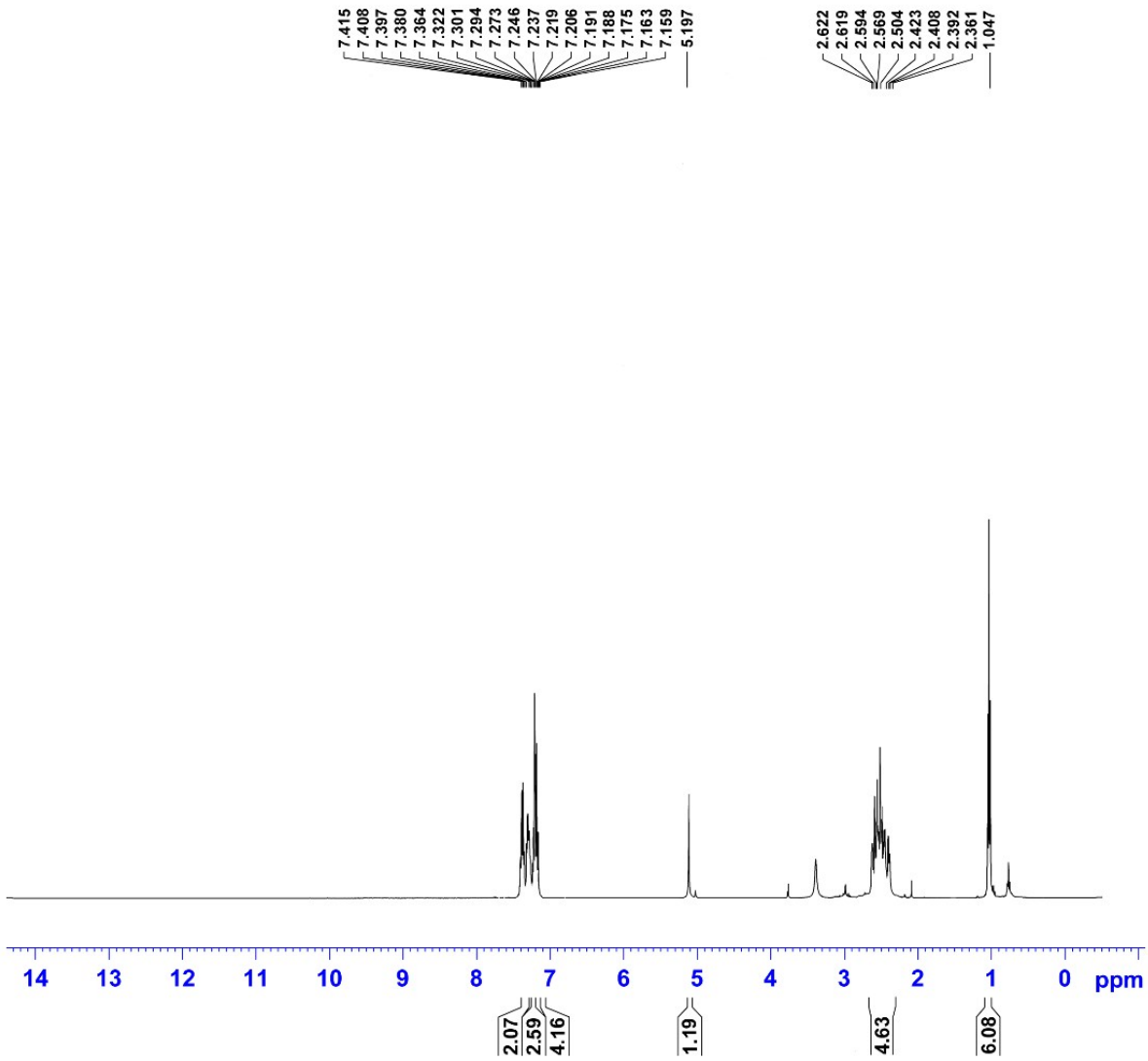


Figure 8. ^{1}H NMR, spectrum of **(Table 5, 5q)**

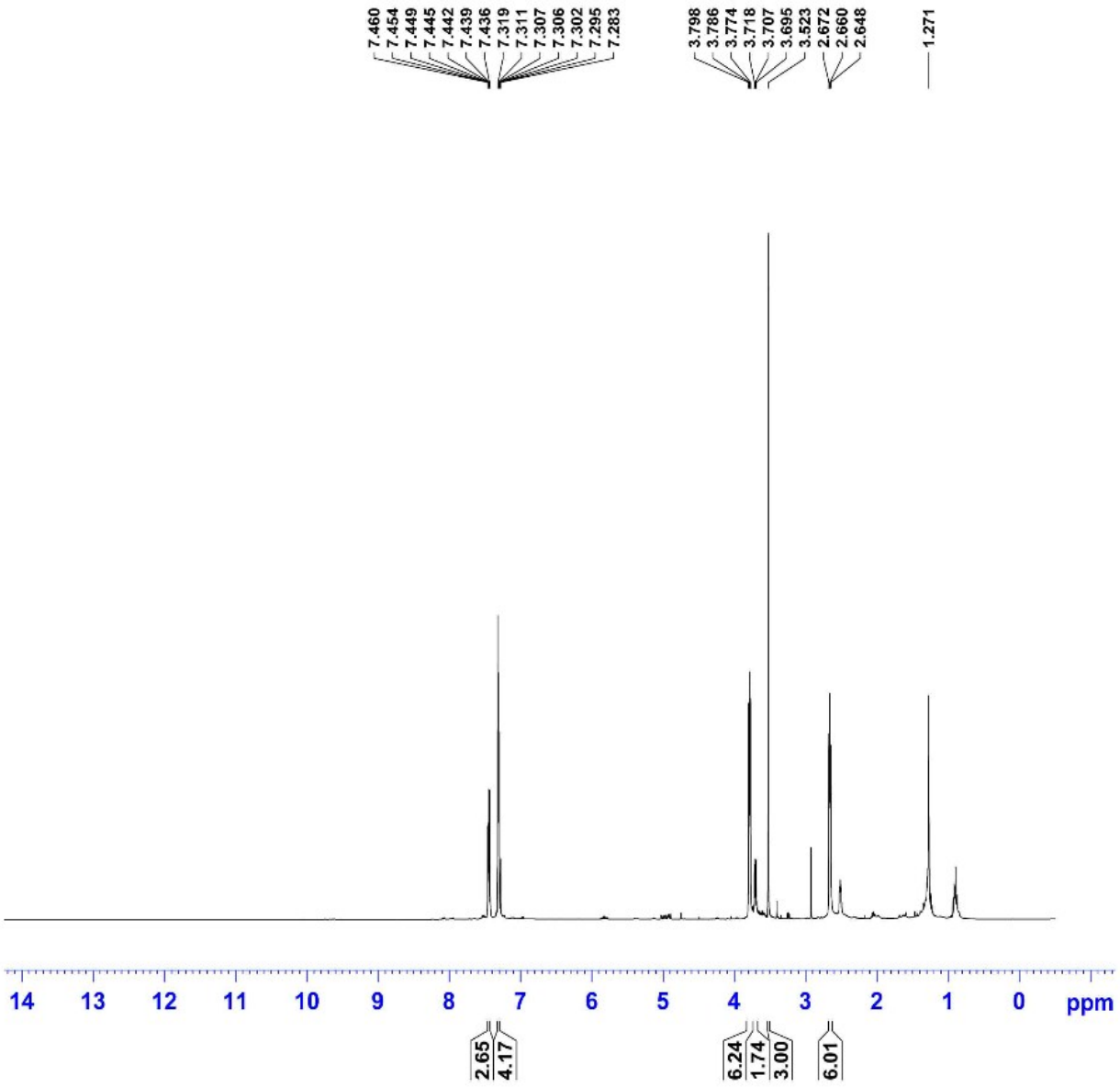


Figure 9. ^{1}H NMR, spectrum of **(Table 5, 6b)**

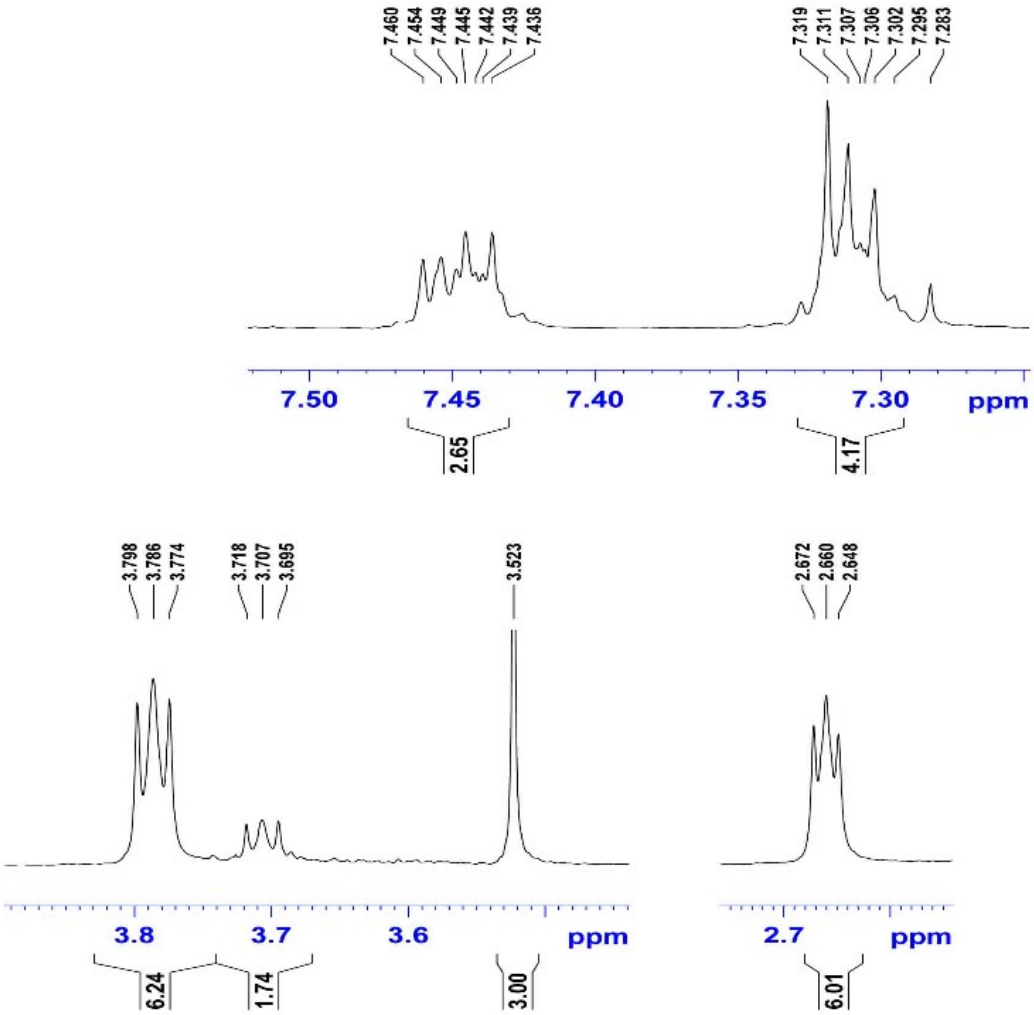


Figure 10. ^{1}H NMR, Expand spectrum of **(Table 5, 6b)**

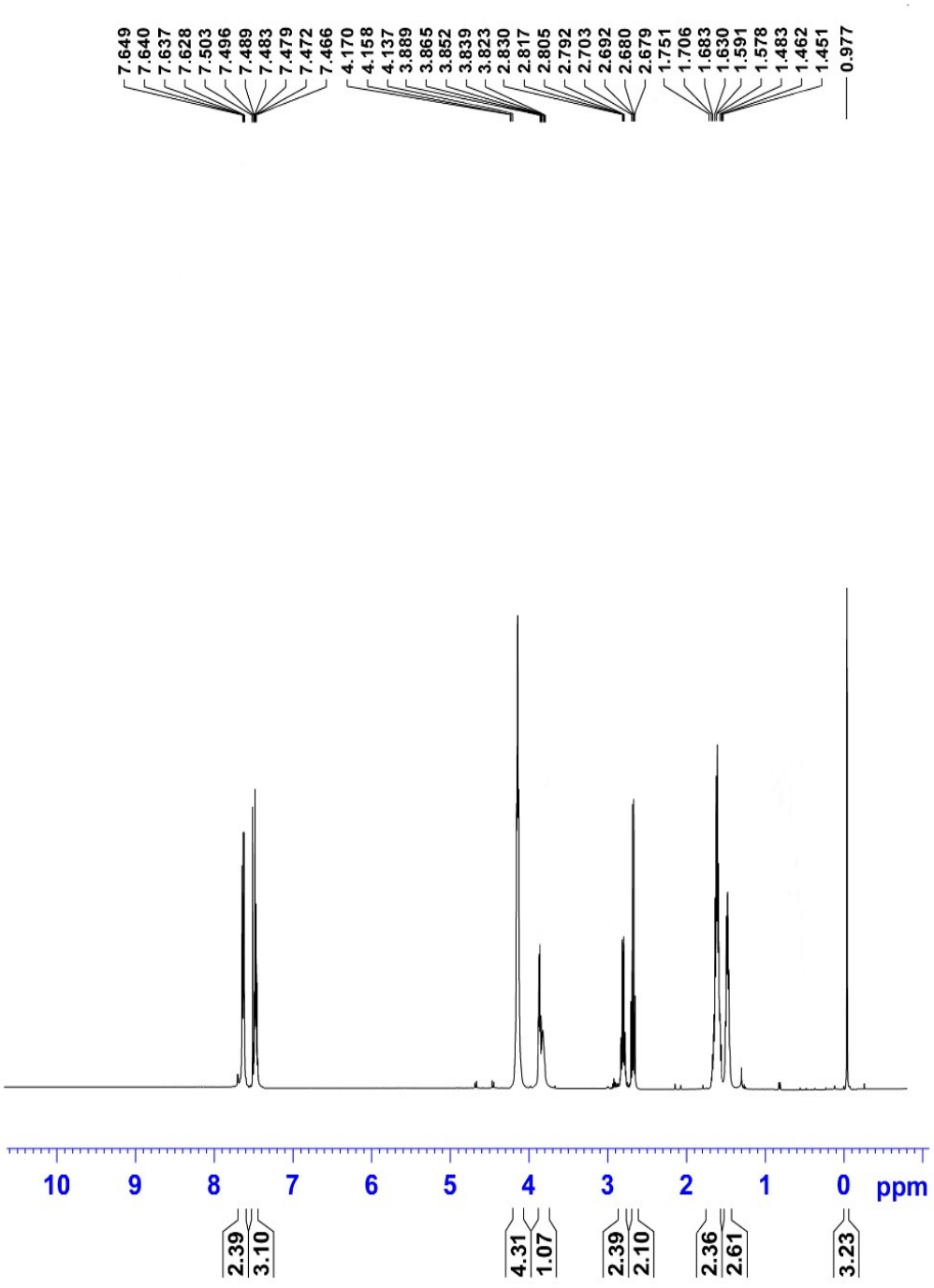


Figure 11. ^{1}H NMR, spectrum of **(Table 5, 6h)**

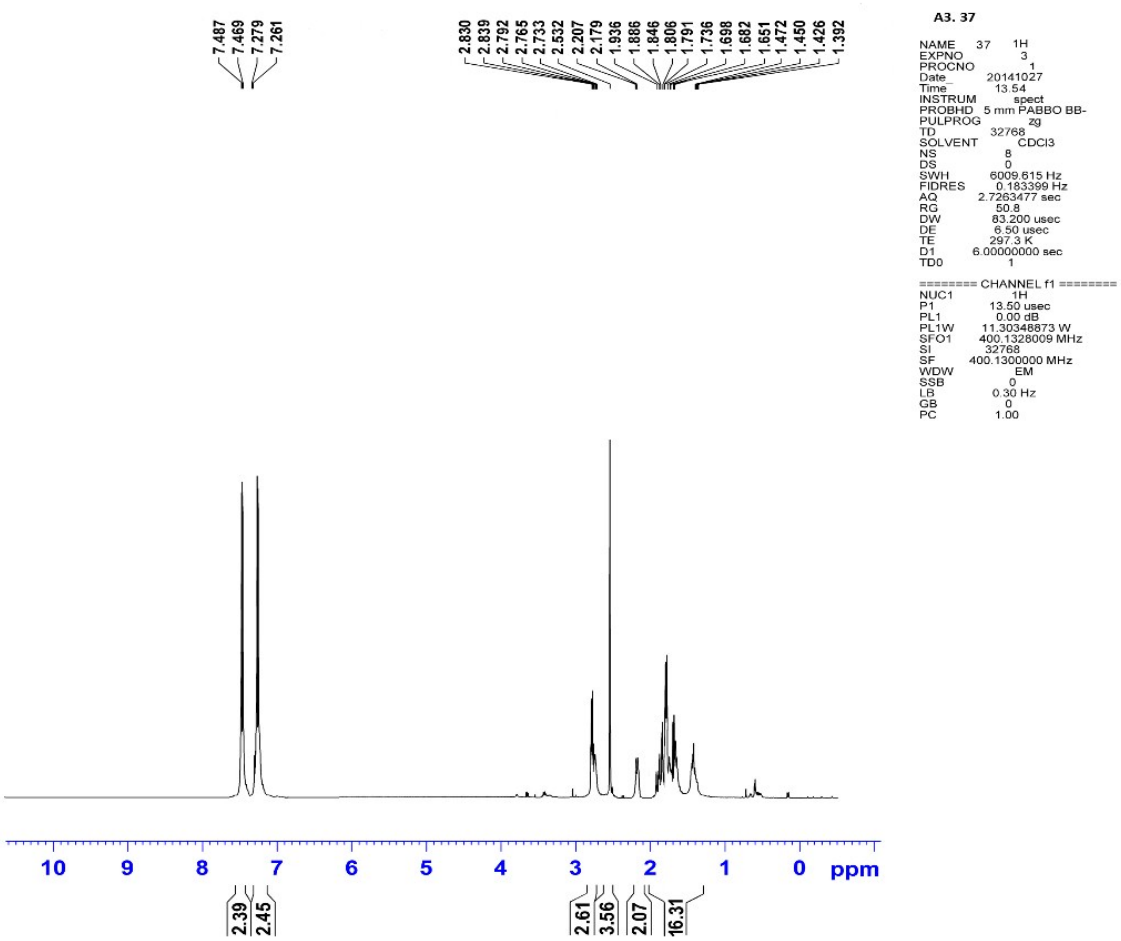


Figure 12. ^{1}H NMR spectrum of **(Table 5, 6k)**

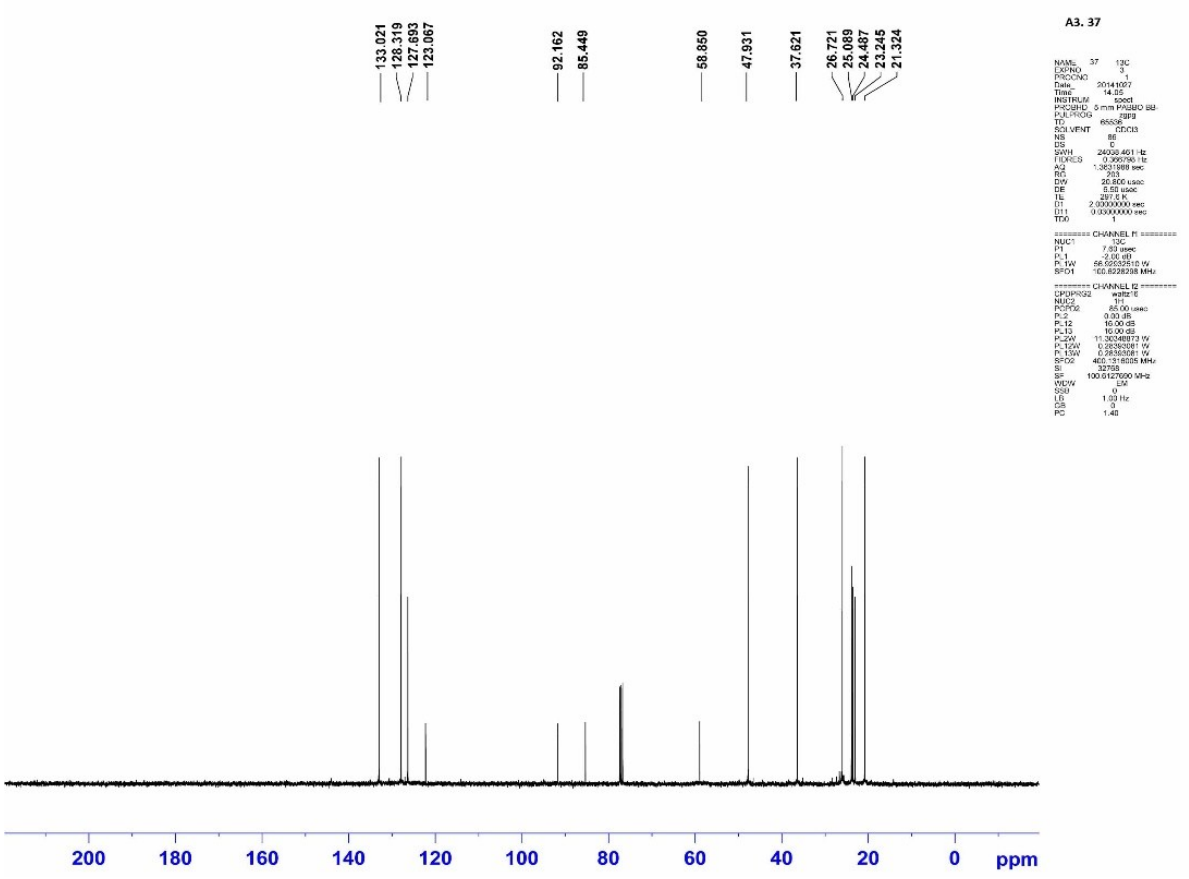


Figure 13. ^{13}C NMR spectrum of **(Table 5, 6k)**

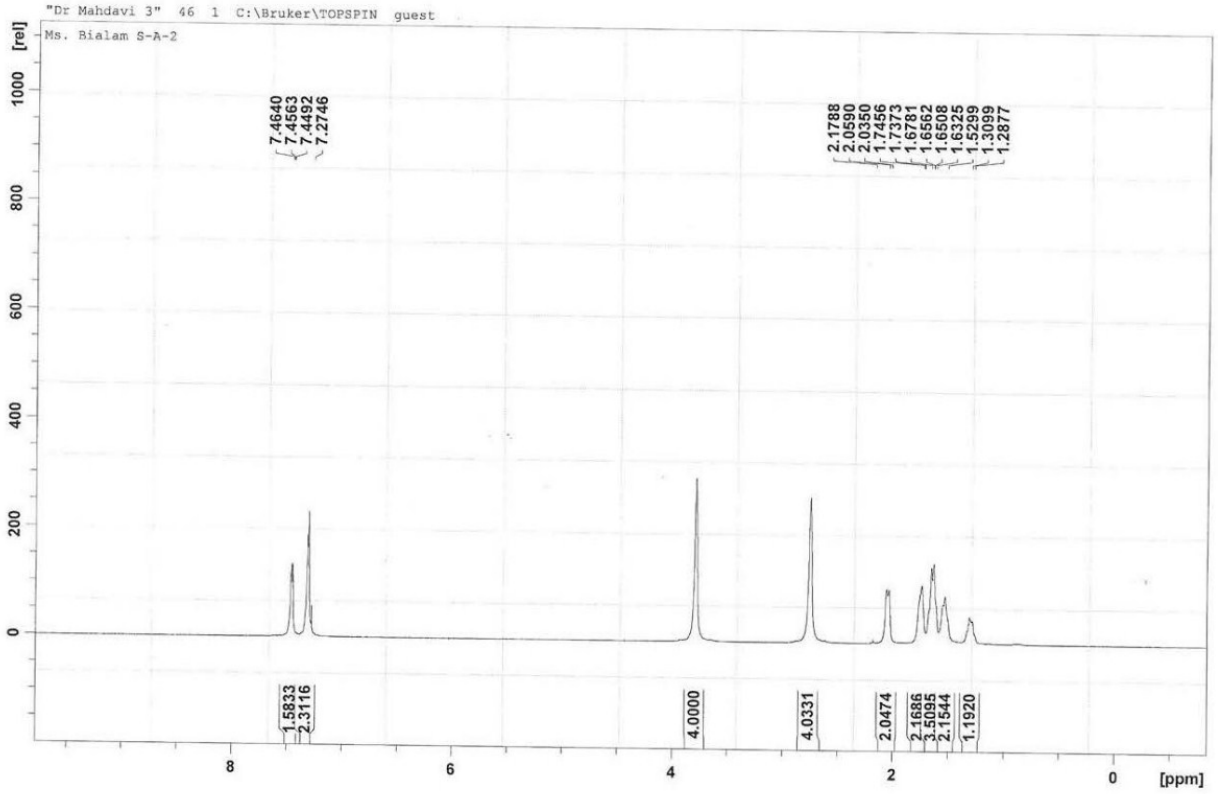


Figure 14. ^{1}H NMR spectrum of **(Table 5, 6m)**

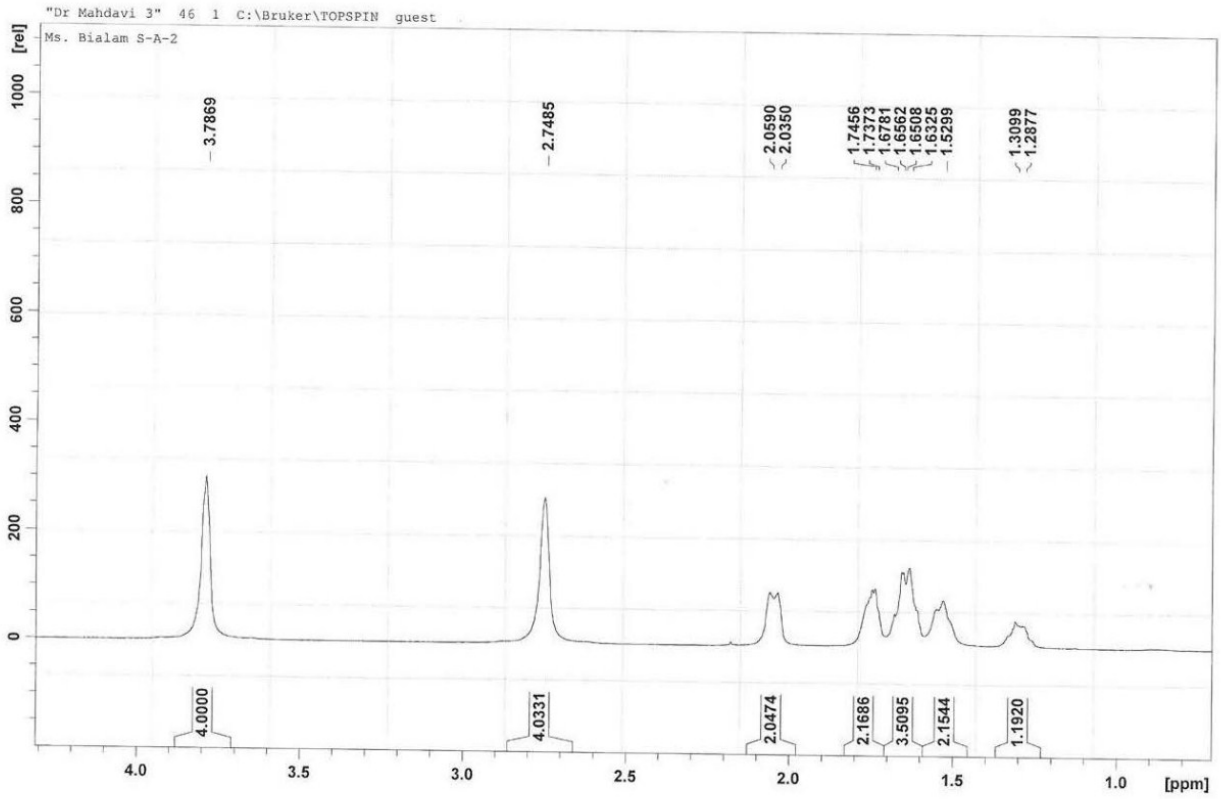


Figure 15. ^{1}H NMR Expand spectrum of **(Table 5, 6m)**

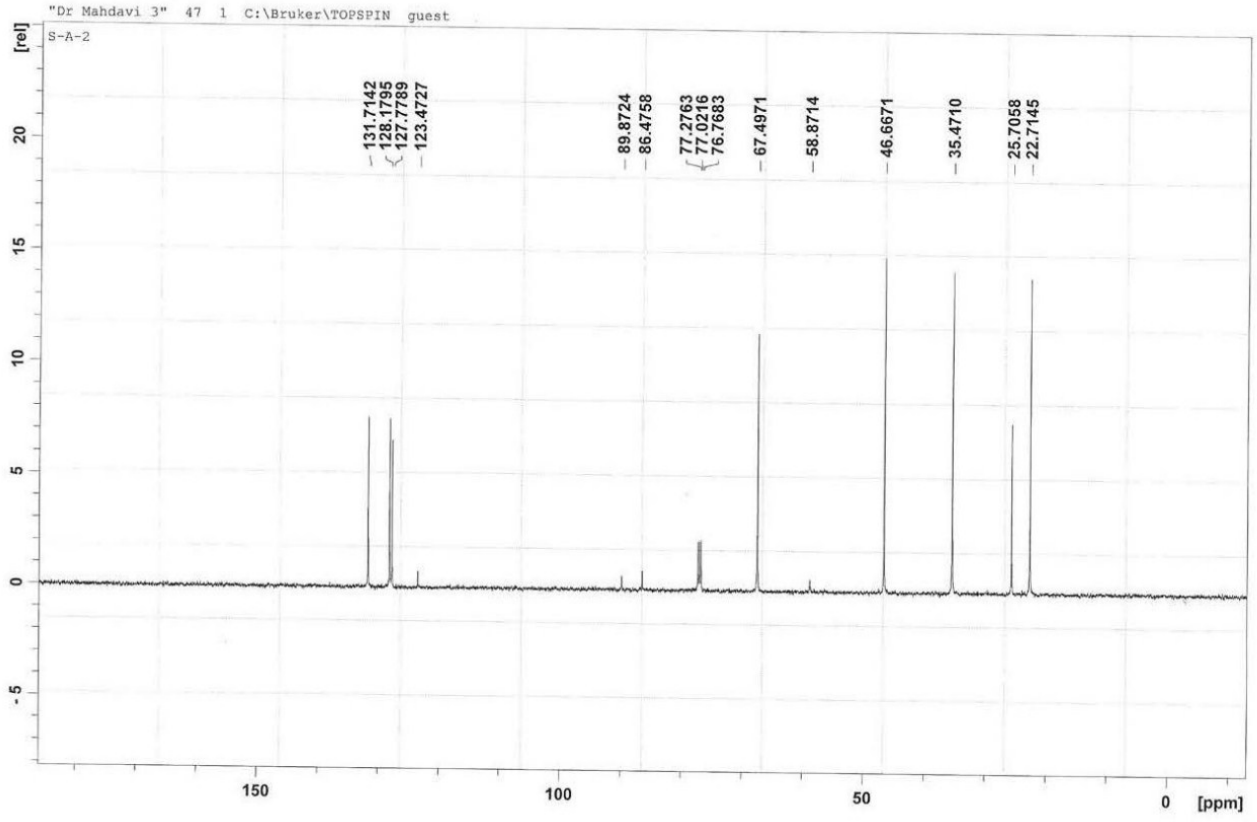


Figure 16. ^{13}C NMR spectrum of **(Table 5, 6m)**

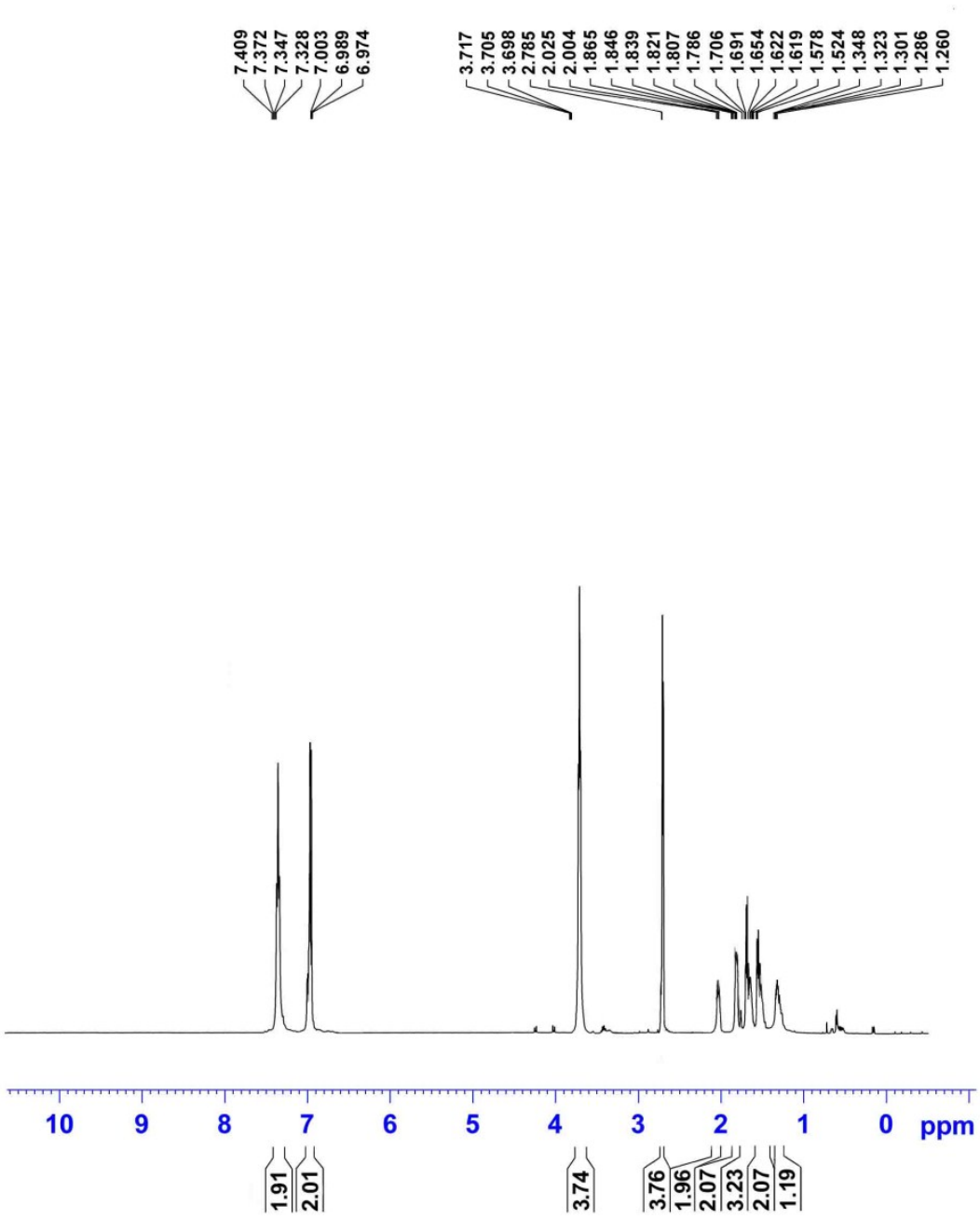


Figure 17. ^{1}H NMR spectrum of **(Table 5, 6n)**

4. References

Elhampour, A. Malmir, E. M. Kowsari, F. A. Boorboor and F. Nemati, *RSC Adv.*, 2016, 6, 96623-96634.