Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Ag-doped Nano Magnetic γ-Fe_2O_3@DA Core–Shell Hollow Spheres: an efficient and recoverable heterogeneous catalyst for A^3, KA^2 Coupling Reactions and [2+3] cycloaddition

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1. General information

The process for the preparation of the magnetic Fe_2O_3@DA/Ag hollow sphere catalyst is schematically described in scheme 1. The nano magnetic Fe_2O_3@DA/Ag hollow sphere was prepared from commercially inexpensive available materials and fully characterized using, the corresponding data, provided by FT-IR, FE-SEM, TEM, XRD, TGA, and VSM techniques.

1.1. General details

All chemicals, including $FeCl_3 \cdot 6H_2O$, trisodium citrate dihydrate, sodium acetate trihydrate, ethanol, ethylene glycol (EG), PVP, urea, dopamine, $AgNO_3$ and $NH_3 \cdot H_2O$, were analytical grade reagents, purchased from Sigma-Aldrich, and used without further purification. The progress of reaction was 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 using a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. magnetic-Fe_2O_3@DA/Ag hollow sphere was characterized by; FT-IR spectra were obtained with potassium bromide pellets in the range of 400–4000 cm^{-1} using a Shimadzu 8400s spectrometer; X-ray diffraction (XRD) was detected by Philips using Cu-Ka radiation of wavelength 1.54Å; Scanning electron Microscopy, FE-SEM-EDX, analysis was performed using Tescanvega II XMU Digital Scanning Microscope. Samples were coated with gold at 10 mA for 2 min prior to analysis; the magnetic properties were characterized using a vibrating sample magnetometer (VSM, Lakeshore7407) at room temperature. Thermo-gravimetric

analyses (TGA) were analyzed with a LINSEIS modele STS PT 16000 thermal analyzer under air atmosphere at a heating rate of 5 °C min^{-1}.

2. Characterizations of Catalyst

2.1. FT-IR analysis

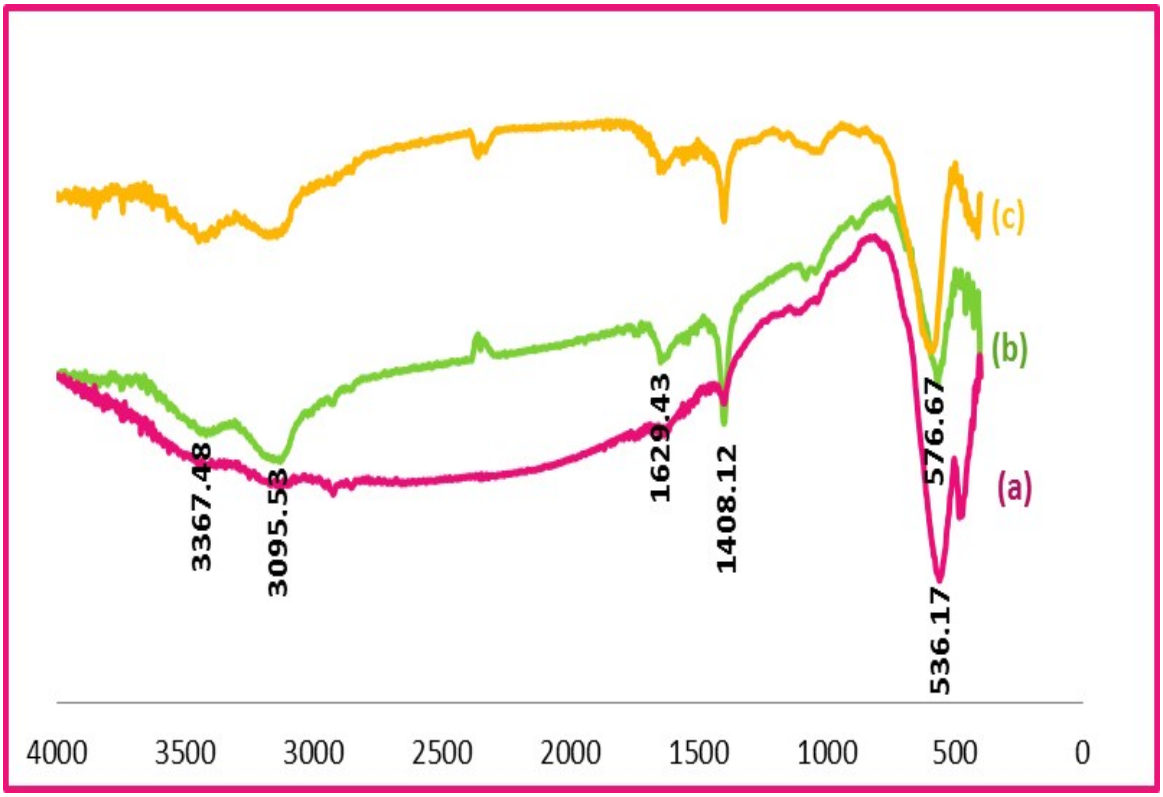


Figure 1. The FT-IR spectra of (a) h-Fe_2O_3, (b) h-Fe_2O_3@DA and (c) h-Fe_2O_3@DA/Ag.

2.2. X-ray diffraction spectra

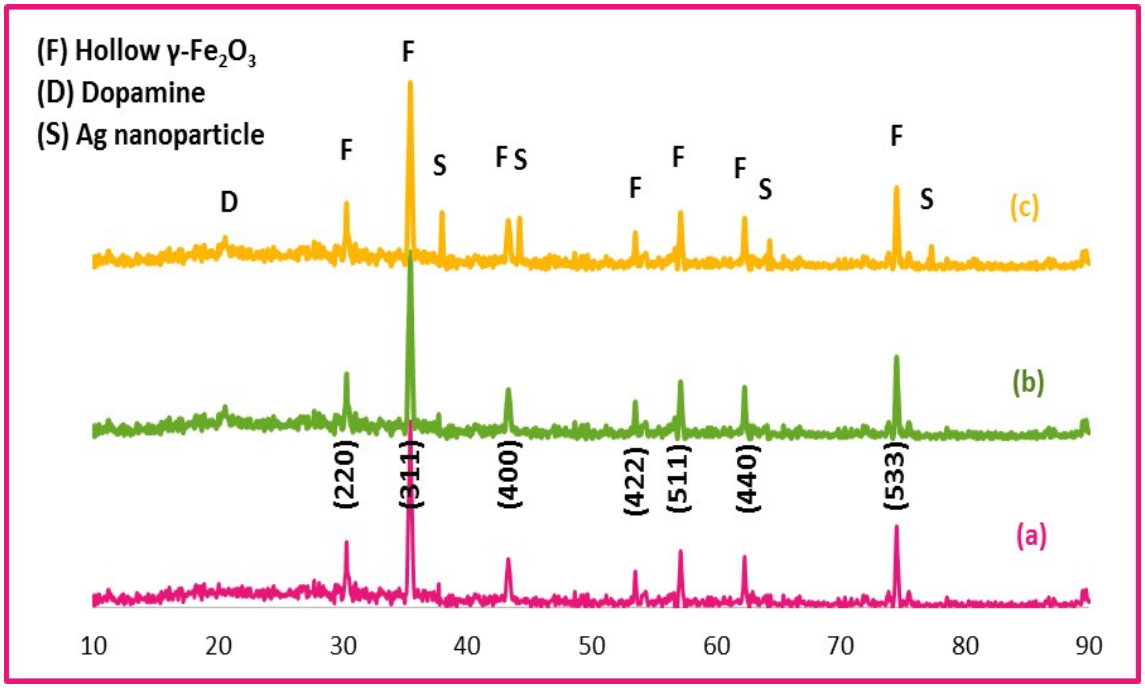


Figure 2. XRD pattern of (a) h-Fe_2O_3, (b) h-Fe_2O_3@DA and (c) h-Fe_2O_3@DA/Ag

2.3. X-ray diffraction spectra

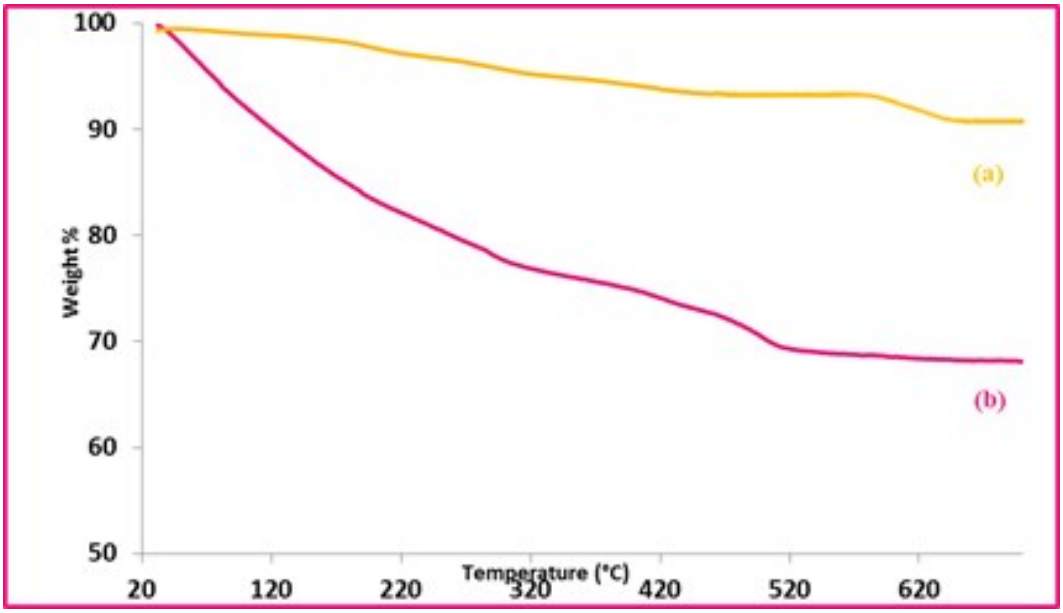


Figure 3. TGA analysis of (a) h-Fe_2O_3 and (b) h-Fe_2O_3@DA/Ag.

2.4. VSM analysis

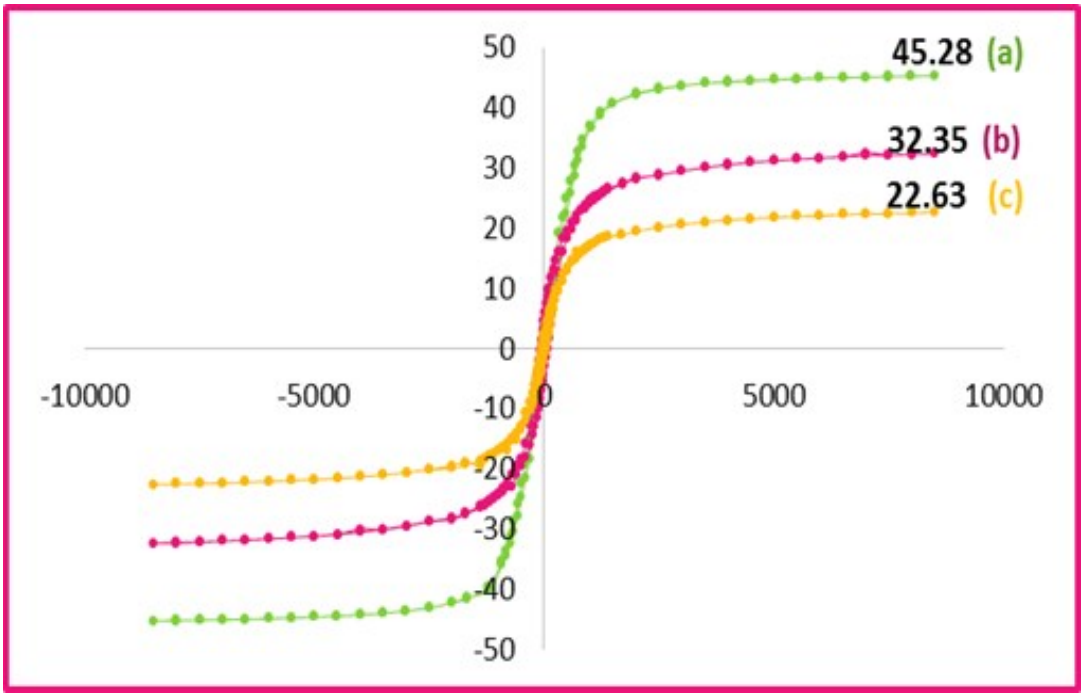


Figure 4. The magnetization curves of (a) h-Fe_2O_3, (b) h-Fe_2O_3@DA and (c) h-Fe_2O_3@DA/Ag.

2.5. FE-SEM-EDS analysis

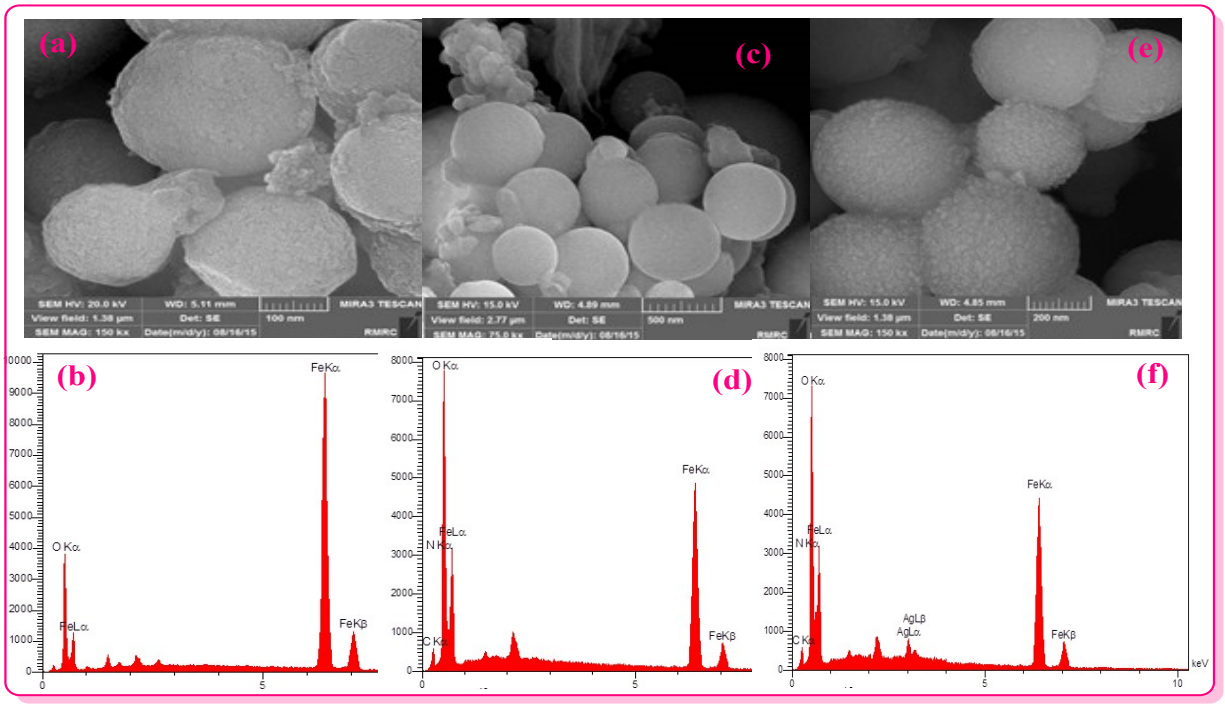


Figure 5. The FEG-SEM-EDS analysis of (a,b) h-Fe_2O_3, (c,d) h-Fe_2O_3@DA and (e,f) h-Fe_2O_3@DA/Ag.

2.6. TEM image

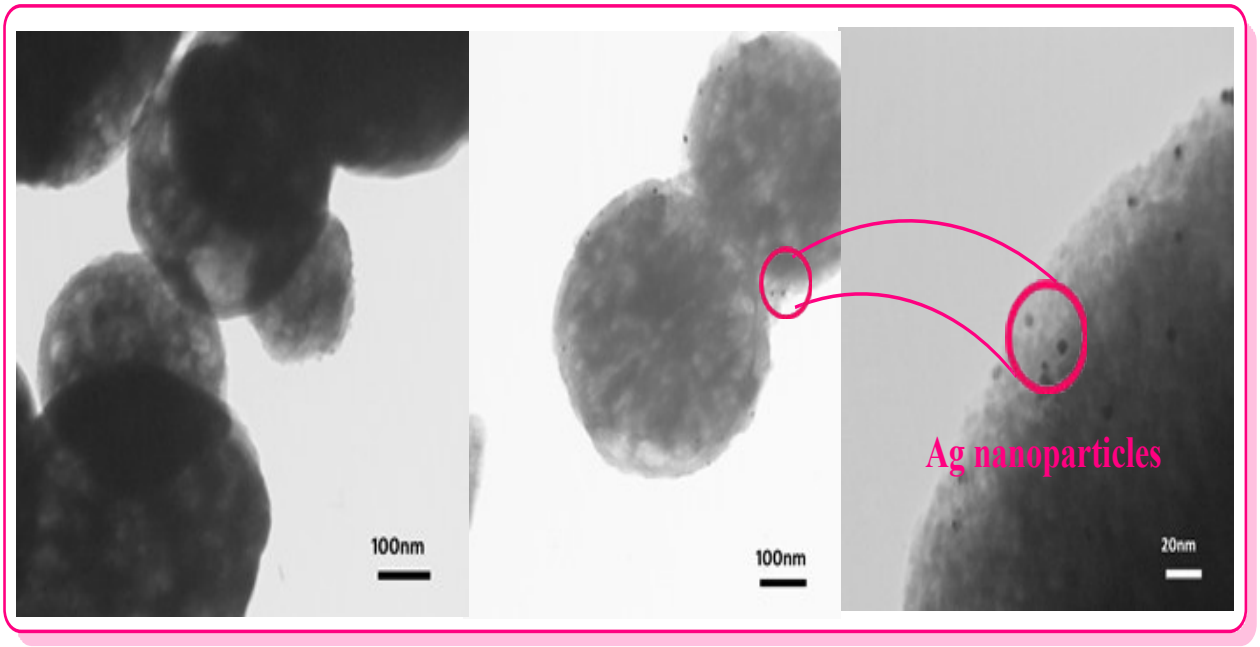
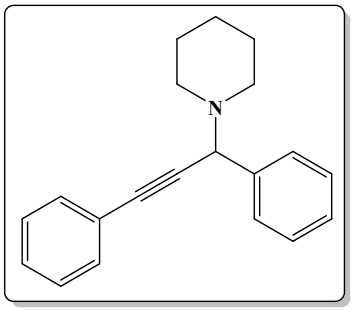
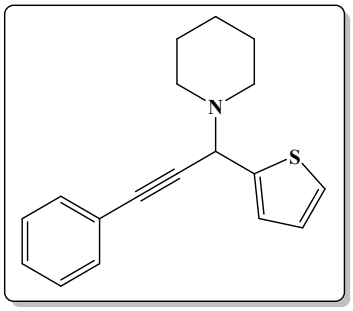


Figure 6. The TEM image of h-Fe_2O_3@DA/Ag.

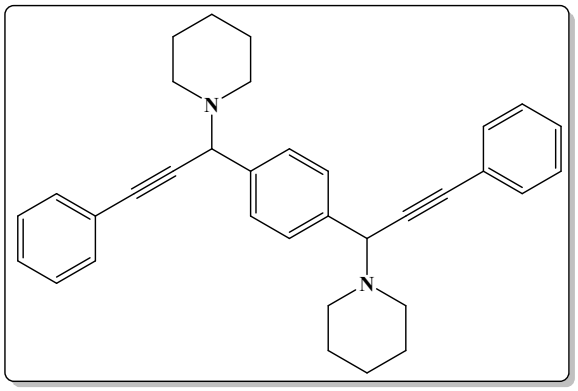
3. Spectral data for selected compounds



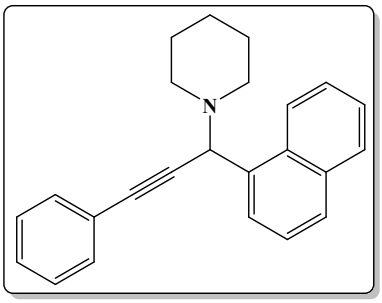
1-(1,3-diphenylprop-2-ynyl)piperidine (table 1, 5a): Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.45-1.49 (m, 2H), 1.58-1.65 (m, 4H), 2.59 (t, 4H), 4.81 (s, 1H), 7.31-7.40 (m, 6H), 7.53-7.55 (m, 2H), 7.65-67 (d, J=7.6 Hz, 2H).



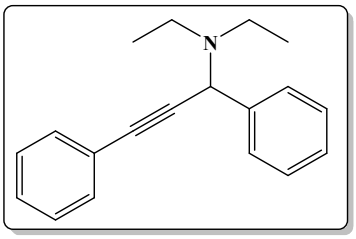
1-(3-phenyl-1-(thiophen-2-yl)prop-2-ynyl)piperidine (table 1, 5g): Yellow solid; mp 50-51 ^{o}C (Lit.[1] 52-53 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.48-1.52 (m, 2H), 1.63-1.70 (m, 4H), 2.62-2.71 (m, 4H), 5.03 (s, 1H), 7.00 (dd, J^1=J^2=3.6 Hz, 1H), 7.25-7.30 (m, 1H), 7.31 (d, J=4.4 Hz, 2H). 7.36-7.38 (m, 3H), 7.54-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 24.4, 26.1, 50.6, 58.2, 85.3, 86.9, 123, 125.3, 125.8, 126.2, 128.2, 128.3, 131.8, 144.



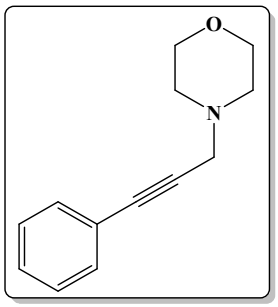
1-(3-phenyl-1-(4-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)phenyl)prop-2-ynyl)piperidine (table 1, 5h): White solid; mp 157-159 ^{o}C (Lit.[1] 158-160 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.47 (m, 2H), 1.59-1.63 (m, 4H), 2.59 (m, 4H), 4.81 (s, 1H), 7.33-7.35 (m, 3H), 7.52-7.55 (m, 2H), 7.63 (s, 2H).



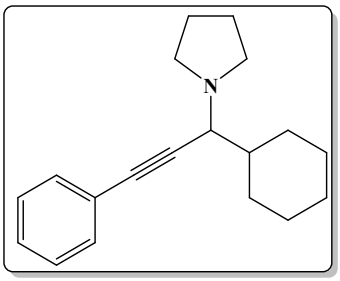
1-(1-(naphthalen-3-yl)-3-phenylprop-2-ynyl)piperidine (table 1, 5i): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.47-1.51 (m, 2H), 1.60-1.67 (m, 4H), 2.64 (t, 4H), 4.97 (s, 1H), 7.36-7.40 (m, 3H), 7.48-7.52 (m, 2H), 7.58-7.61 (m, 2H), 7.79 (dd, J^1=J^2=8.4 Hz, 1H), 7.85-7.91 (m, 3H), 8.11 (s, 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 1, 5r): 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).

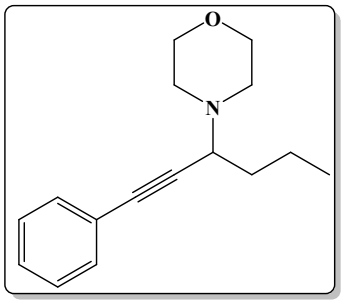


4-(3-phenylprop-2-ynyl)morpholine (table 1, 6c): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.64-2,67 (m, 6H), 3.52 (s, 3H), 3.69-3.71 (m, 1H), 3.77-3.79 (m, 6H), 7.28-7.31 (m, 4H), 7.43-7.46 (m, 2H).

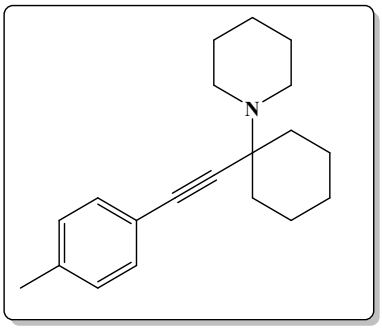


1-(1-cyclohexyl-3-phenylprop-2-ynyl)pyrrolidine (table 1, 6i): Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.05-1.36 (m, 5H), 1.56-1.63 (m, 2H), 1.75-1.79 (m, 6H), 1.82-2.10 (m, 4H), 2.5-2.98 (m, 4H), 3.36-3.38 (d, J =7.6 Hz, 1H), 7.14-7.33 (m,

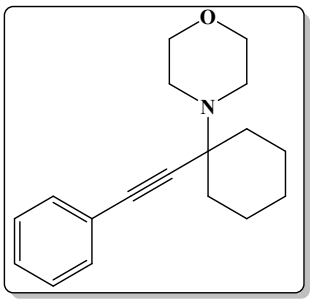
3H), 7.50-7.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 24.9, 26.9, 27.1, 28.3, 32.7, 33, 42.9, 51.1, 61.1, 86.1, 88.9, 125.9, 128.9, 129.8, 132.6.



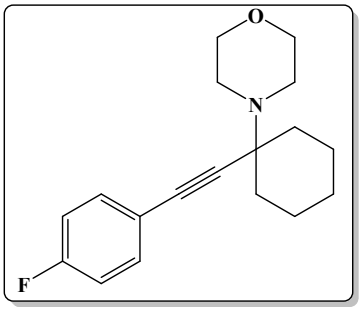
4-(1-phenylhex-1-yn-3-yl)morpholine (Table 1, 6m): Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 0.97 (m, 3H), 1.45-1.75 (m, 4H), 2.67−2.70 (m, 2H), 2.79−2.83 (m, 2H), 3.82-4.13 (m, 1H), 4.15-4.17 (m, 4H), 7.46−7.50 (m, 3H), 7.62−7.64 (m, 2H).



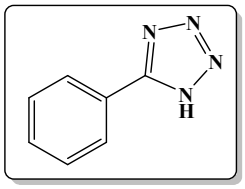
1-(1-(2-p-tolylethynyl)cyclohexyl)piperidine (Table 2, 8e): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.39-1.93 (m, 16H), 2.17-2.20 (m, 2H), 2.53 (s, 3H), 2.73-2.83 (m, 2H), 7.26-7.27 (m, 3H), 7.46-7.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 21.32, 23.4, 24.4, 25, 26.7, 37.6, 47.9, 58.8, 85.4, 92.1, 123, 127.6, 128.3, 133.



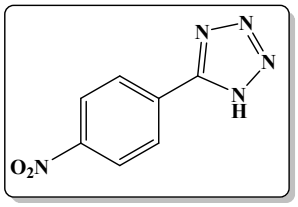
4-(1-(2-phenylethynyl)cyclohexyl)morpholine (Table 2, 8f): Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.28-1.30 (m, 1H), 1.52 (m, 2H), 1.63-1.67 (m, 3H), 1.73 (br.s, 2H), 2.03-2.05 (m, 2H), 2.74 (br.s, 4H), 3.78 (br.s, 4H), 7.27 (m, 3H), 7.44-7.45 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, 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.



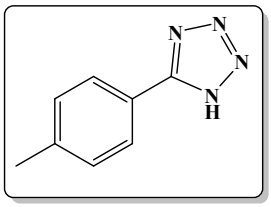
4-(1-((4-fluorophenyl)ethynyl)cyclohexyl)morpholine (Table 2, 8i): Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 1.26-1.34 (m, 1H), 1.57-1.62 (m, 2H), 1.69-1.78 (m, 3H), 1.80-1.86 (m, 2H), 2.00-2.02 (m, 2H), 2.78 (s, 4H), 3.70 (br.t, J = 4.2 Hz, 4H), 6.97-7.00 (t, J = 8.6 Hz, 2H), 7.32-7.40 (m, 2H).



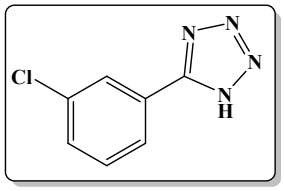
5-Phenyl-1*H*-tetrazole (Table 3, 9a): White solid; mp 213–215 ^{o}C (Lit.[2] 214–215 ^{o}C); ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.68 (s, 3H, Ph), 7.92 (s, 2H, Ph); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 126.6, 128.6, 130.3, 134.6, 155.



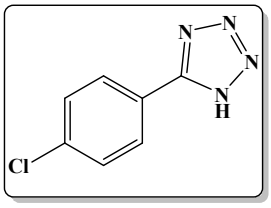
5-(4-Nitrophenyl)-1H-tetrazole (Table 3, 9b): Yellow solid; mp 218–219 °C (Lit.[2] 220-222 °C); ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 8.30 (d, 2H, *J* 8.4, Ph), 8.39 (d, 2H, *J* 8.8, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 127.6, 129.1, 131, 149.5.



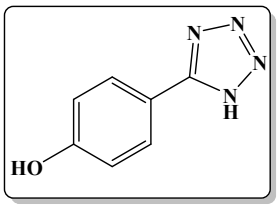
5-(4-Methylphenyl)-1H-tetrazole (Table 3, 9c): White solid; mp 249-251 °C (Lit.[2] 247-249 °C); ^{1}H NMR (250 MHz, DMSO-d_6, ppm) δ 2.35 (s, 3H, CH_3), 7.37 (d, 2H, *J* 7.6 Hz, Ph), 7.90 (d, 2H, *J* 7.5 Hz, Ph).



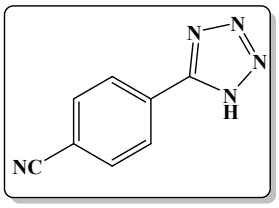
5-(3-Chlorophenyl)-1H-tetrazole (Table 3, 9g): White solid; mp 138-140 °C (Lit.[3]137-139 °C); ^{1}H NMR (250 MHz, DMSO-d_6, ppm) δ 7.55 (m, 2H, Ph), 7.96 (d, 1H, *J* 7.6, Ph), 7.99, (s, 1H); ^{13}C NMR (62.9 MHz, DMSO-d_6, ppm) δ 125.4, 126.2, 126.4, 130.7, 131.1, 133.9, 154.6.



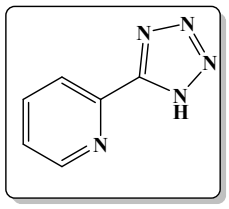
5-(4-Chlorophenyl)-1H-tetrazole (Table 3, 9h): White solid; mp 251-253 °C (Lit.[2] 251-252 °C); ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.61 (d, 2H, *J* 8.4, Ph), 8.09 (d, 2H, *J* 8.8, Ph).



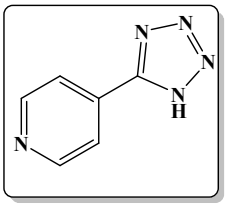
5-(4-Hydroxyphenyl)-1H-tetrazole (Table 3, 9j): White solid; mp 235 °C (Lit.[2] 233-234 °C); ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 6.91 (d, 2H, *J* 8.4, Ph), 7.58 (d, 2H, *J* 8.4, Ph), 10.11 (s broad, OH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 116.1, 117.4, 128.8, 153.2, 159.8.



4-(1H-tetrazol-5-yl)-benzonitrile (Table 3, 9k): White solid; mp 257-259 °C (Lit. [4] 258-260 °C); ^{1}H NMR (250 MHz, DMSO-d_6, ppm) δ 8.06 (d, 2H, *J* 7.1, Ph), 8.19 (d, 2H, *J* 8.6, Ar-H); ^{13}C NMR (62.9 MHz, DMSO-d_6, ppm) δ 113.3, 118.1, 127.6, 128.7, 133.1, 155.2, 162.2.



2-(1H-tetrazol-5-yl)pyridine (Table 3, 9l): White solid; mp 210-213 °C (Lit.[5] 211-212 °C); ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.75 (s, 1H, Ph), 8.07 (s, 1H, Ph), 8.20 (d, 1H, *J* 8.4 Ph), 8.63 (s, 1H).



4-(1H-tetrazol-5-yl)pyridine (Table 3, 9m): White solid; mp 256-258 °C (Lit.[6] 256-258 °C); ^{1}H NMR (250 MHz, DMSO-d_6, ppm) δ 8.10 (d, 2H, *J* 6.0, Ph), 8.77 (d, 2H, *J* 6.5, Ph); ^{13}C NMR (62.9 MHz, DMSO-d_6, ppm) δ 120.9, 121.3, 133.8, 149.9, 165.7.

3.1. Copies of 1H and 13C NMR for selected products

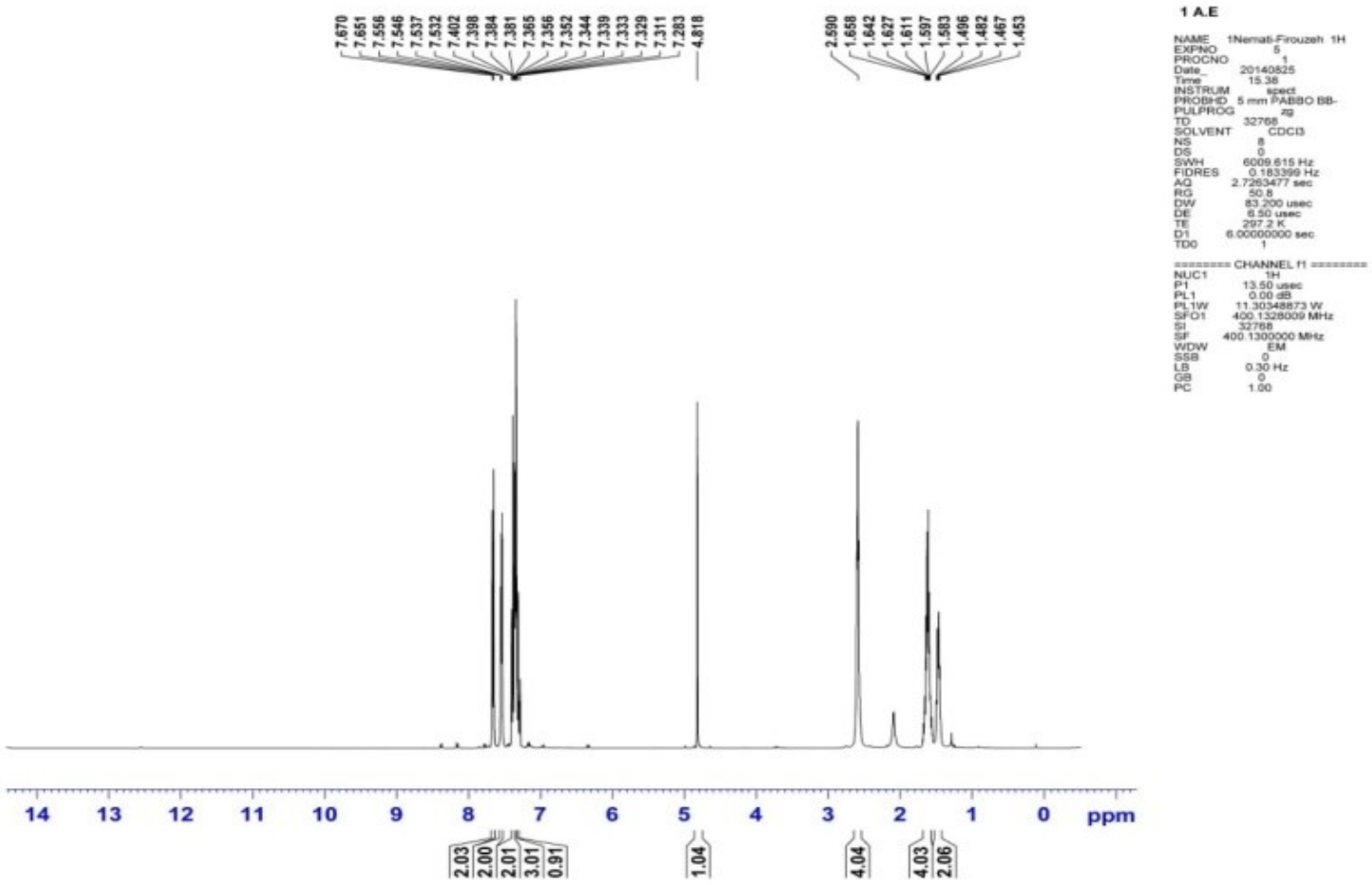
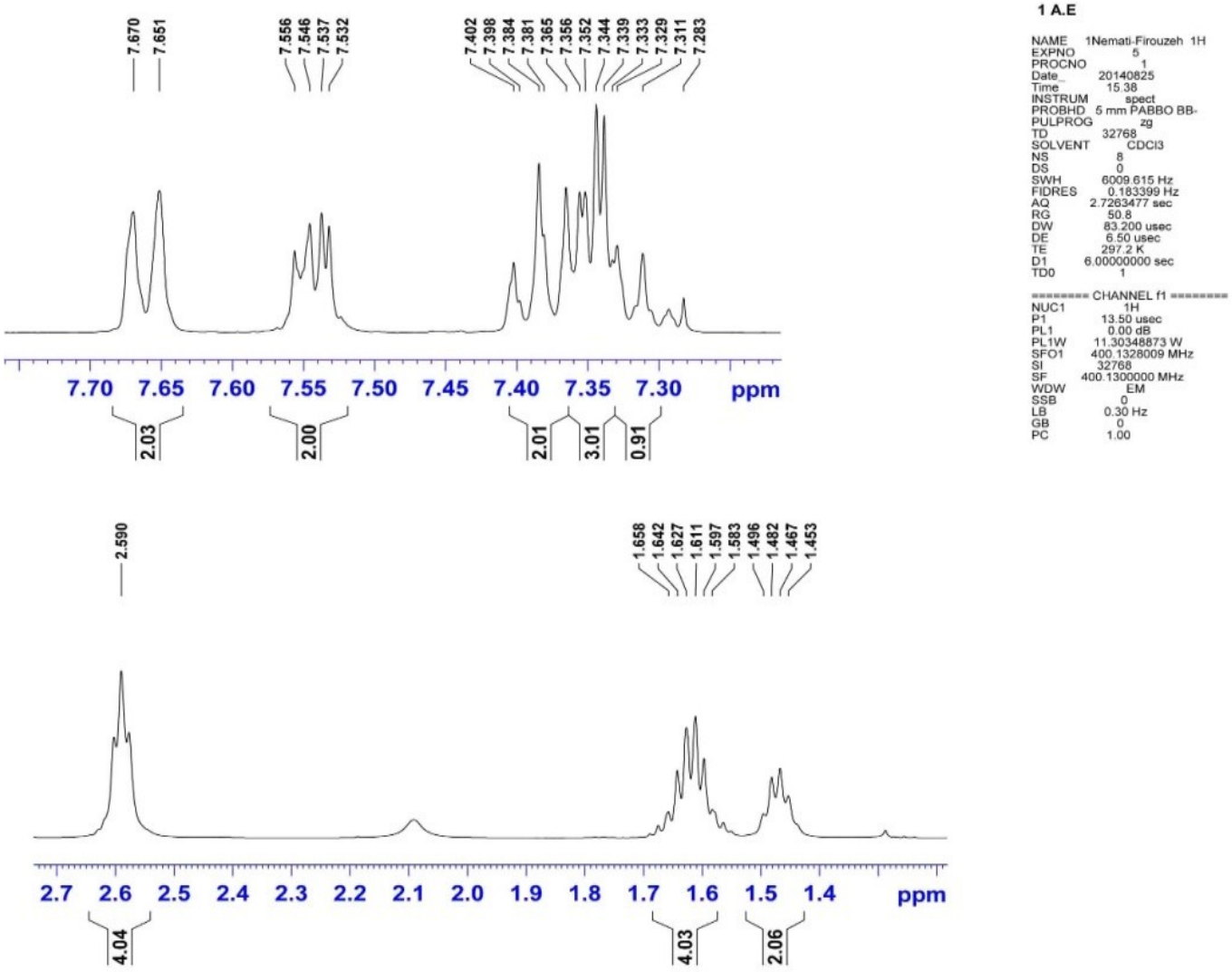


Figure 7. ^{1}H NMR spectrum of **(table 1, 5a)**



1 A.E

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TD0 1

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SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 8. ^{1}H NMR, Expand spectrum of **(table 1, 5a)**

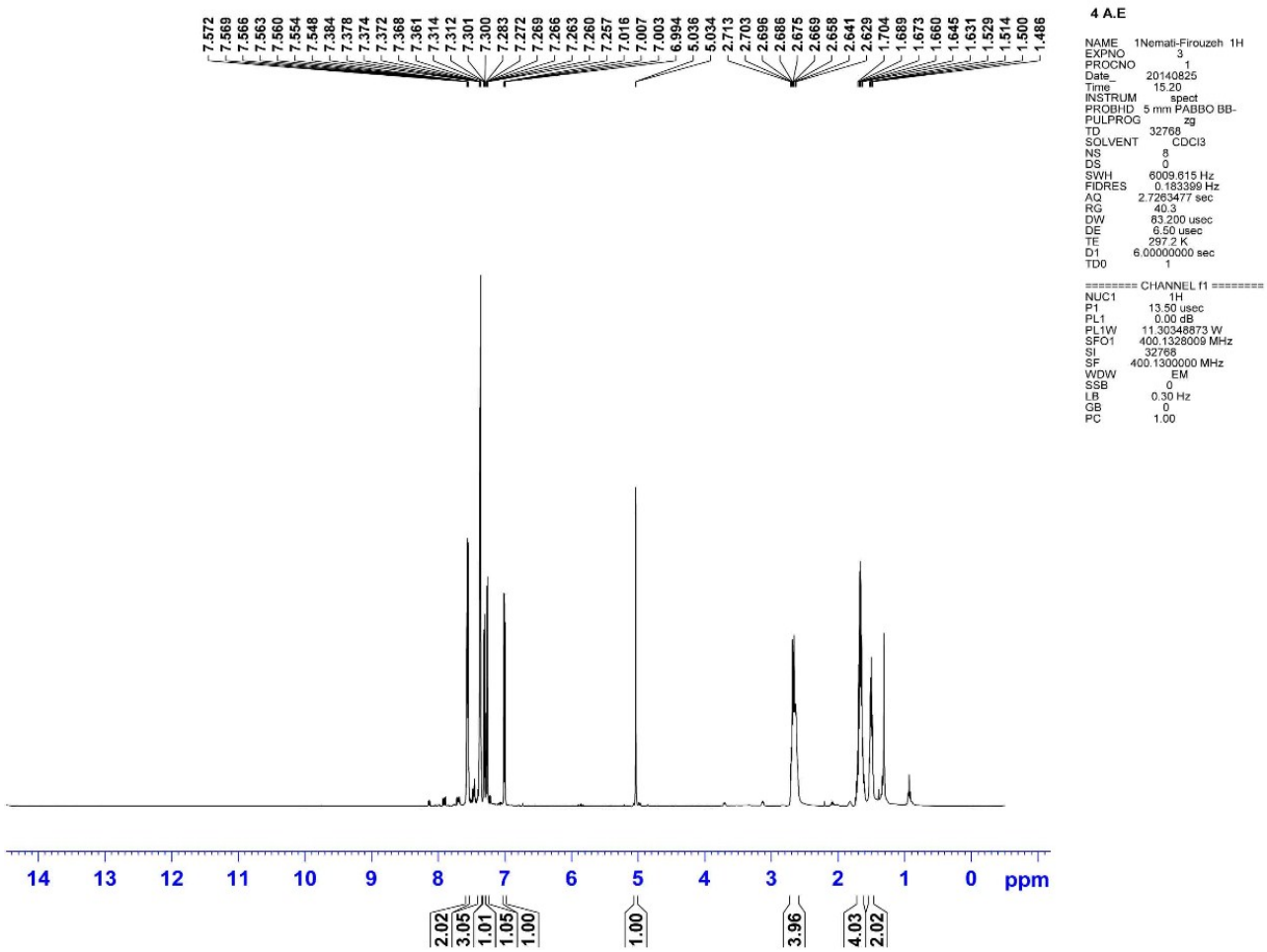


Figure 9. ^{1}H NMR, spectrum of **(table 1, 5g)**

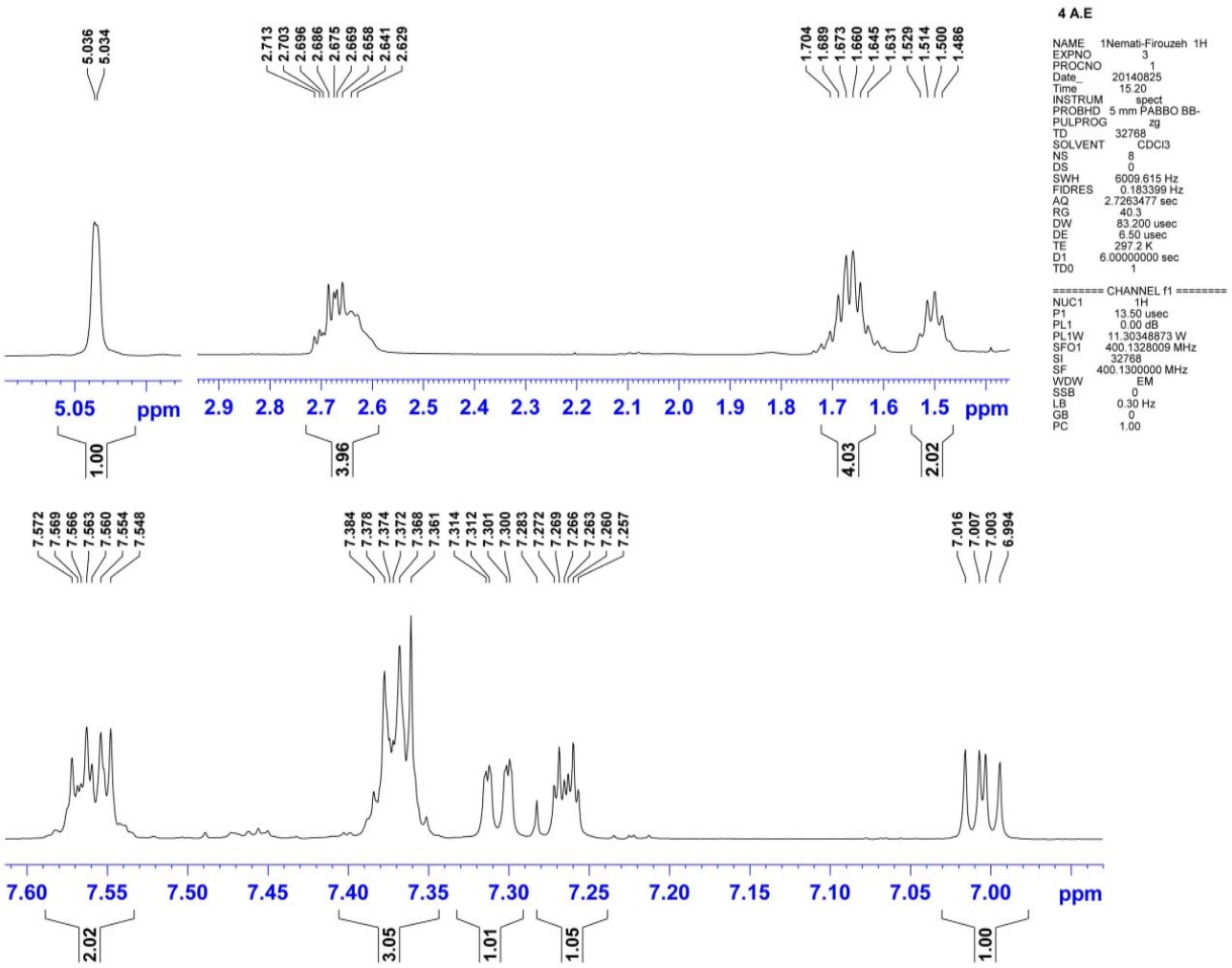


Figure 10 ^{1}H NMR, Expand spectrum of **(table 1, 5g)**

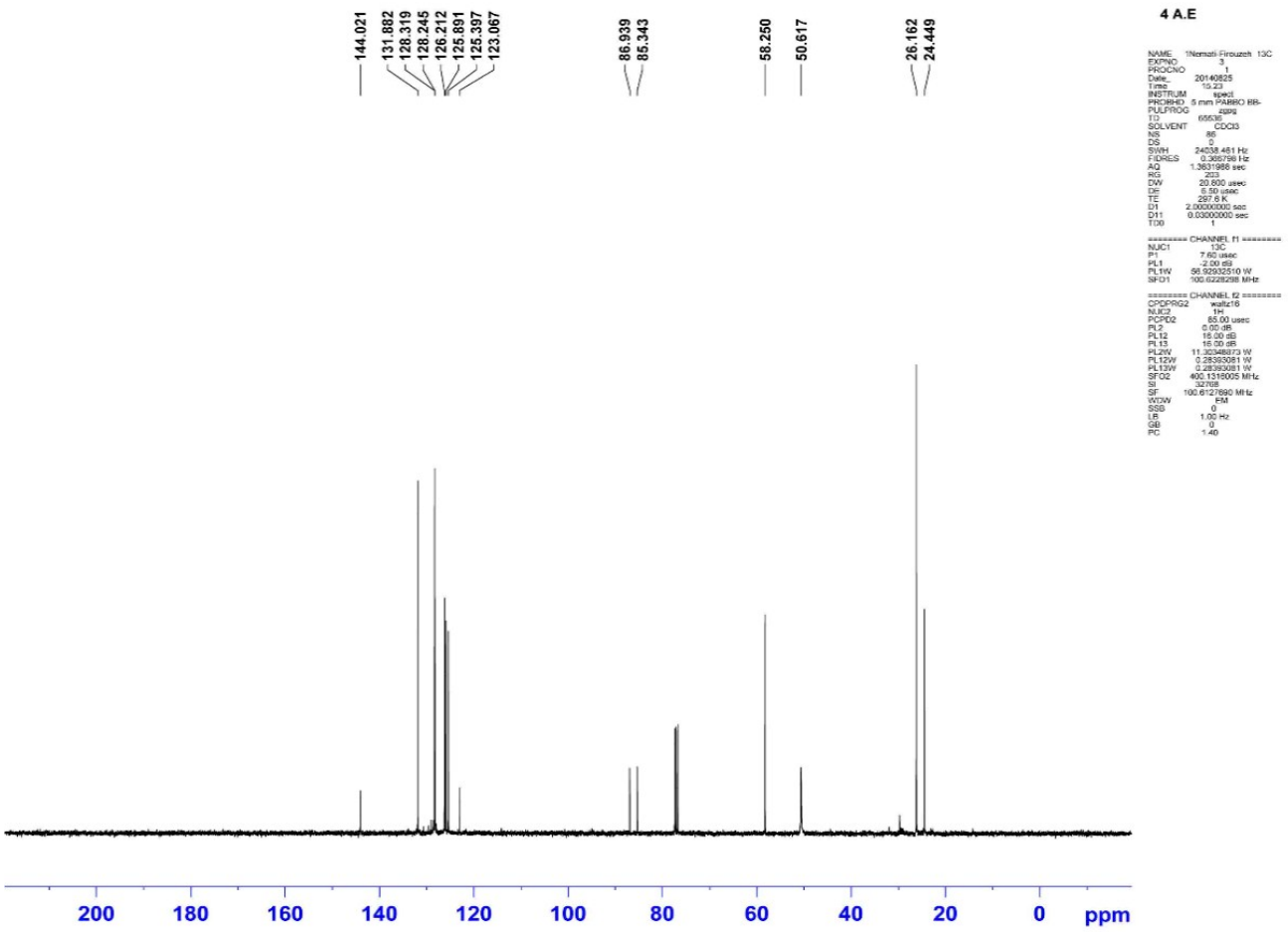


Figure 11 ^{13}C NMR, Expand spectrum of **(table 1, 5g)**

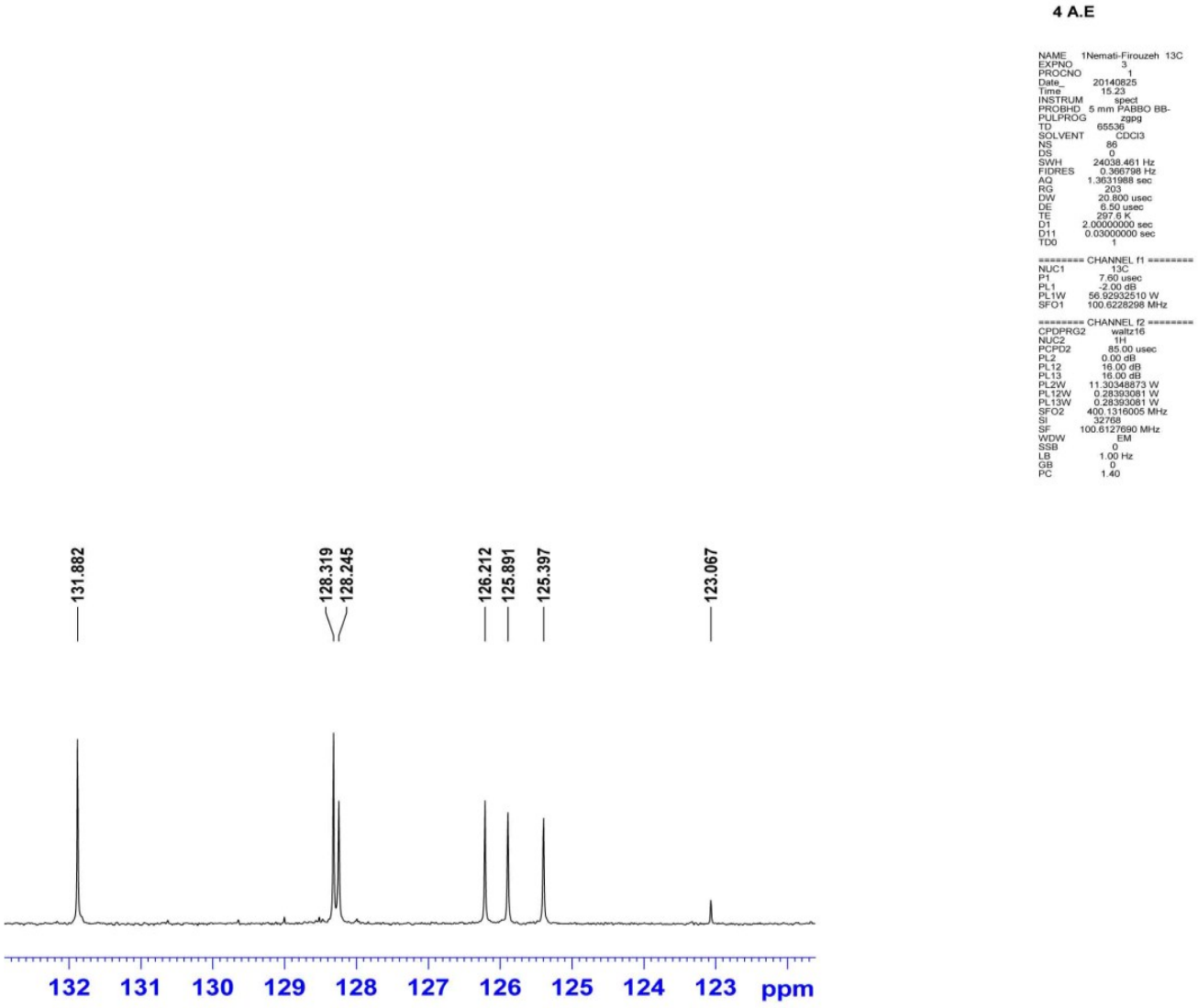


Figure 12 ^{13}C NMR, Expand spectrum of **(table 1, 5g)**

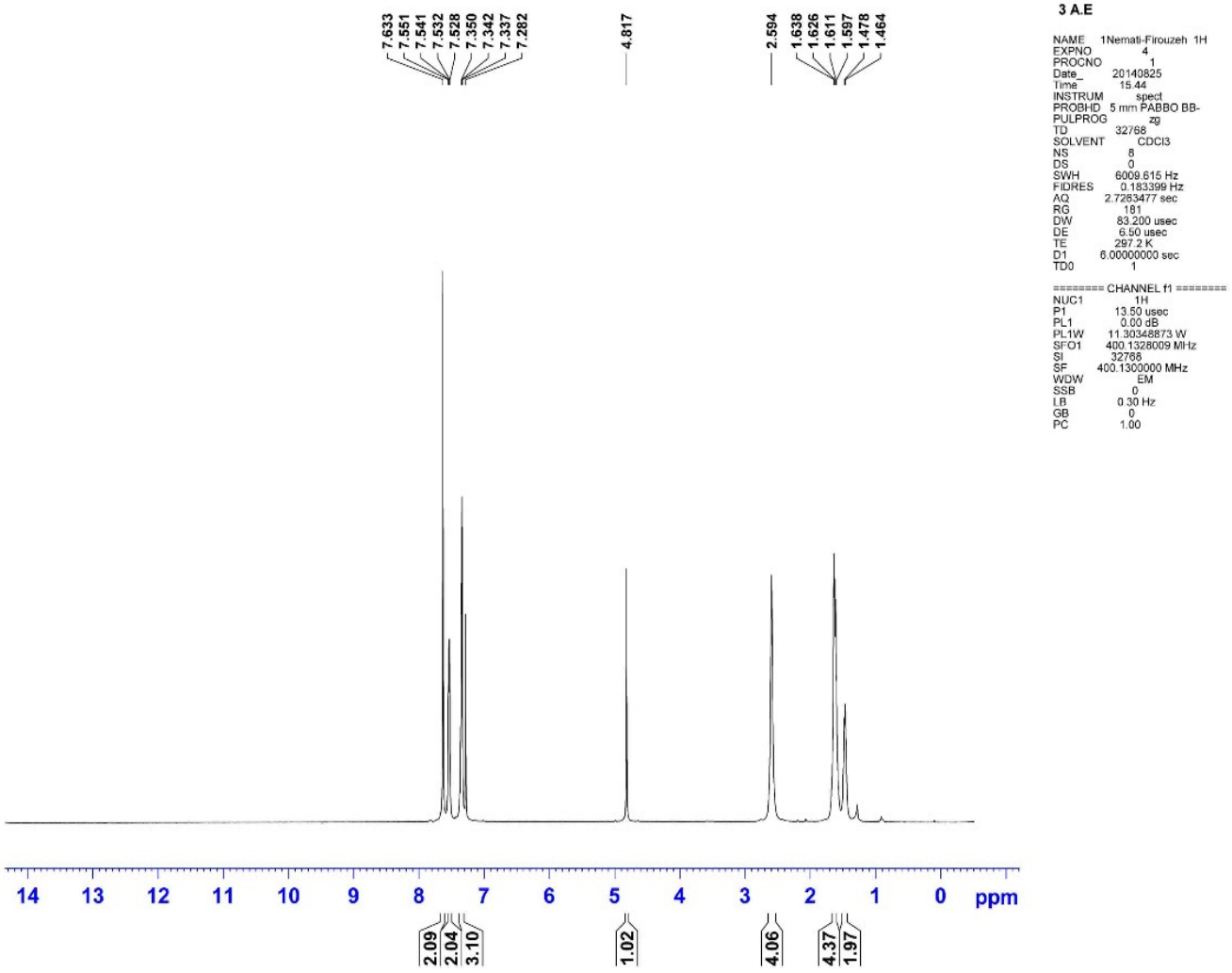
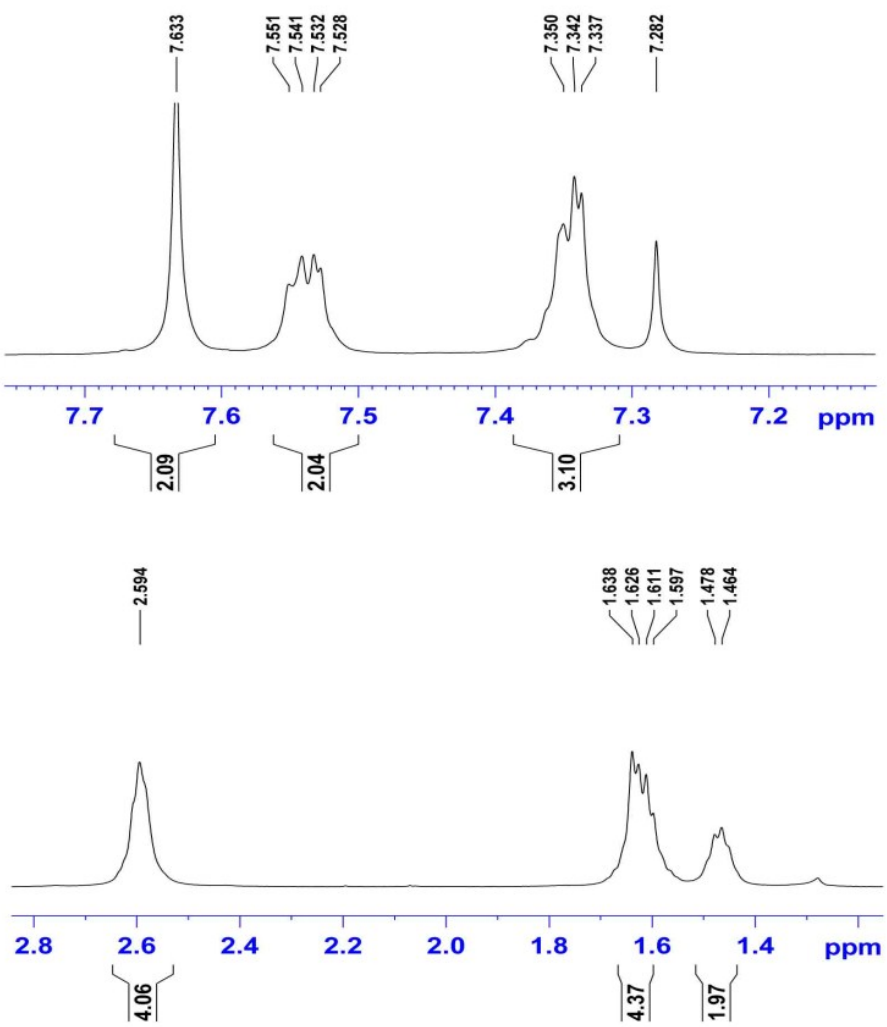


Figure 13 ^{1}H NMR, spectrum of **(table 1, 5h)**



3 A.E

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PROCNO 1
Date_ 20140825
Time 15.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 32768
SOLVENT CDCl3
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DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 181
DW 83.200 usec
DE 6.50 usec
TE 297.2 K
D1 6.00000000 sec
TD0 1

======== CHANNEL f1 ========
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P1 13.50 usec
PL1 0.00 dB
PL1W 11.30348873 W
SFO1 400.1328009 MHz
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SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure 14 ^{1}H NMR, Expand spectrum of **(table 1, 5h)**

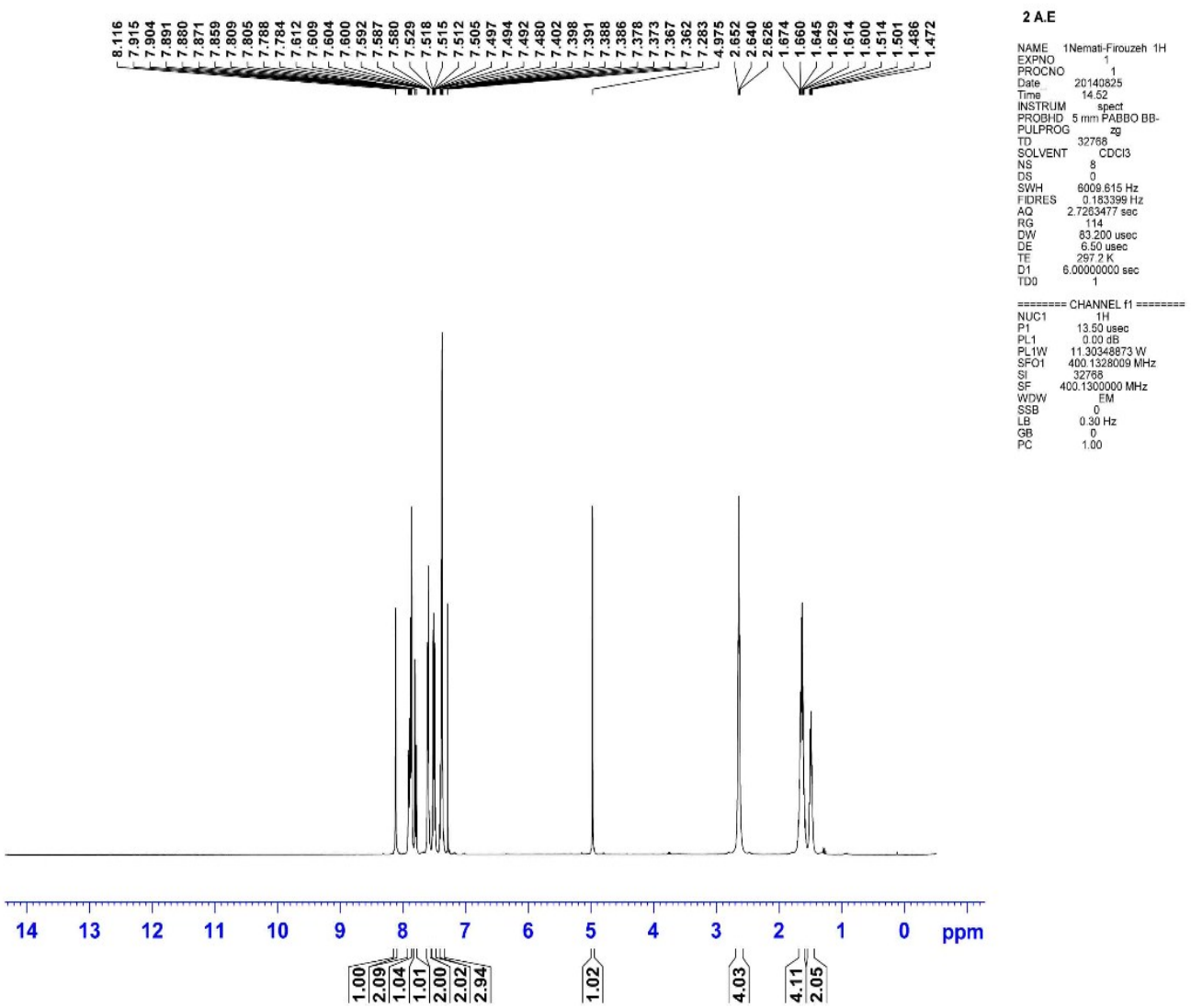

Figure 15 ^{1}H NMR, spectrum of **(table 1, 5i)**

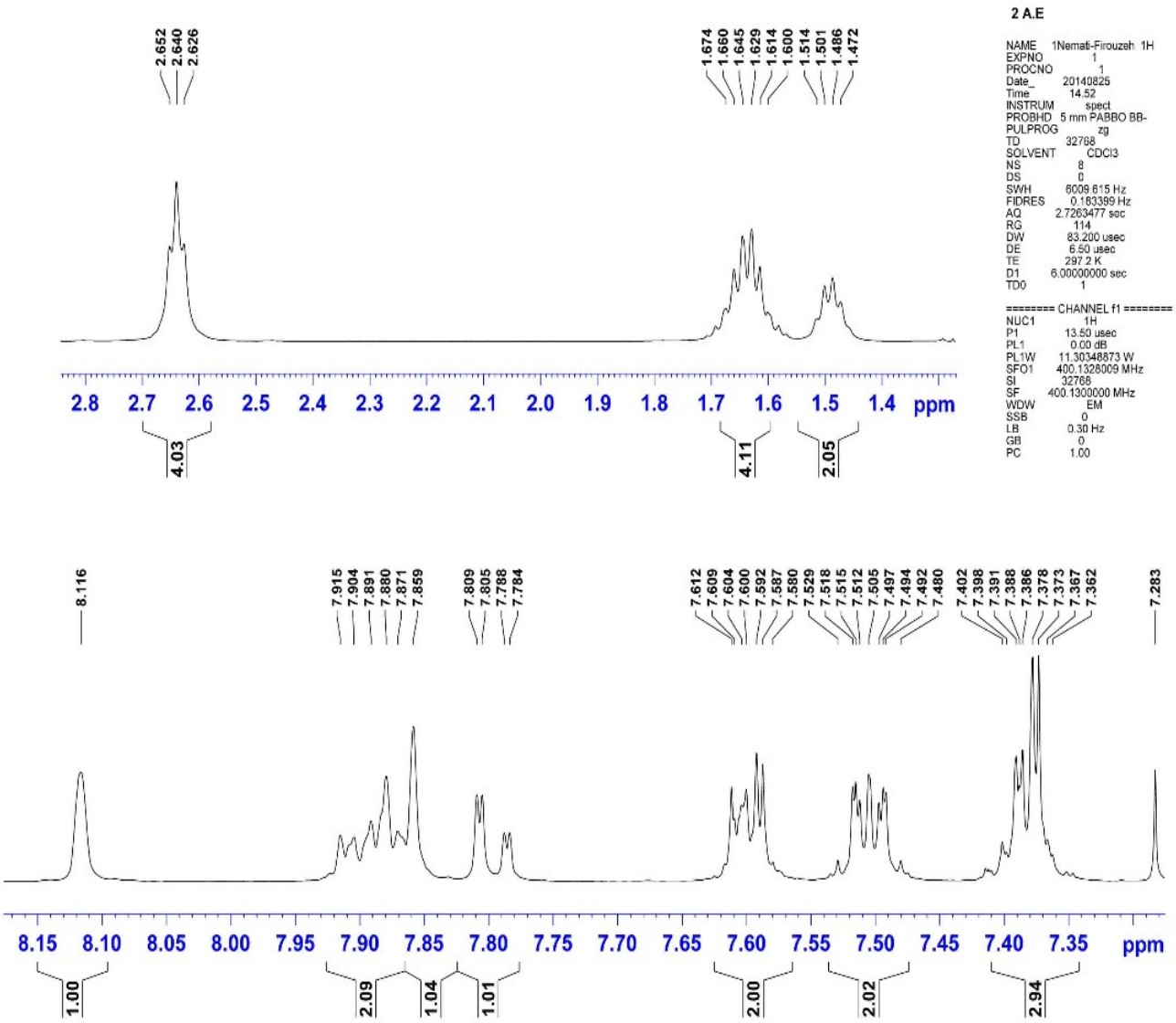

Figure 16 ^{1}H NMR, Expand spectrum of **(table 1, 5i)**

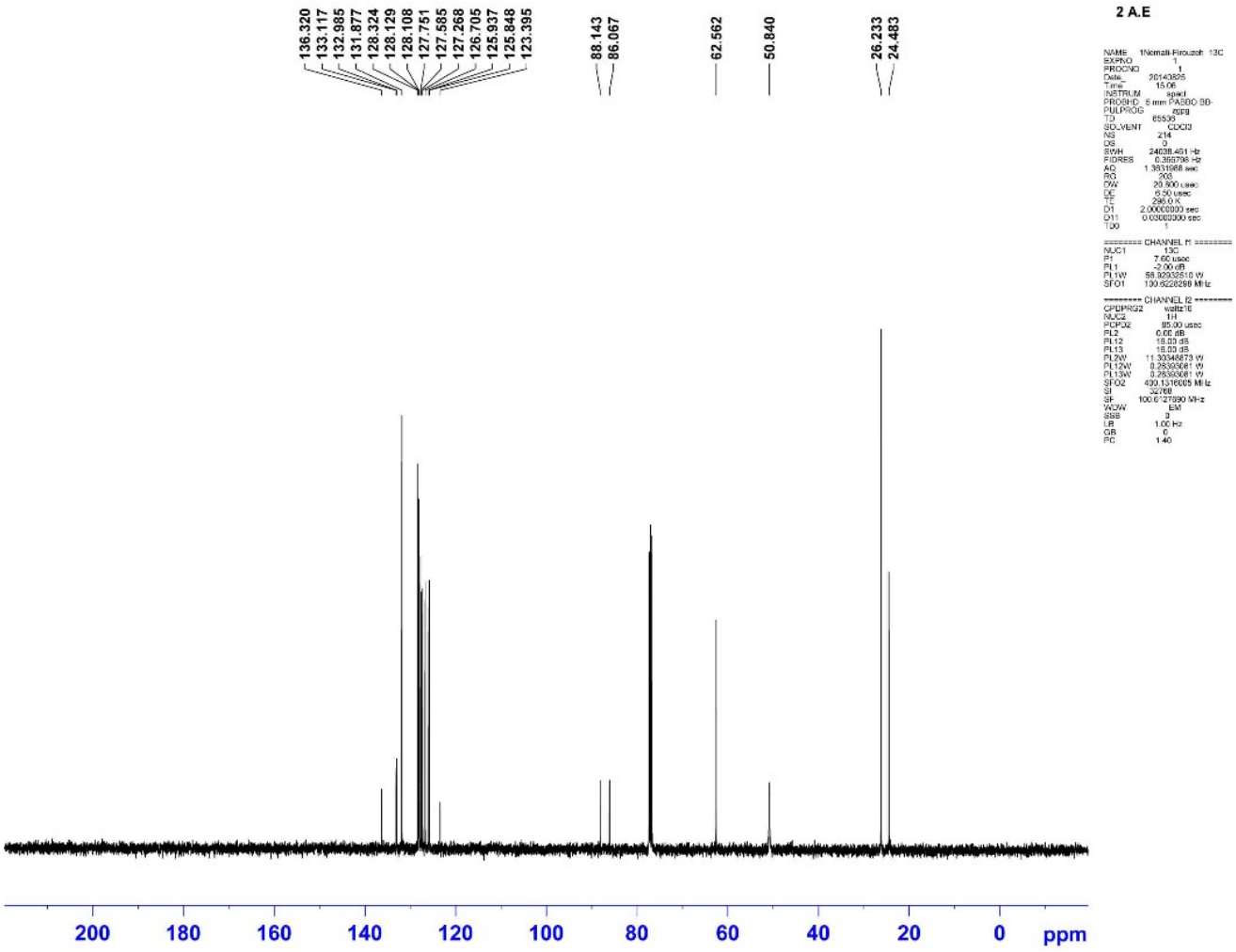

Figure 17 ^{13}C NMR, spectrum of **(table 1, 5i)**

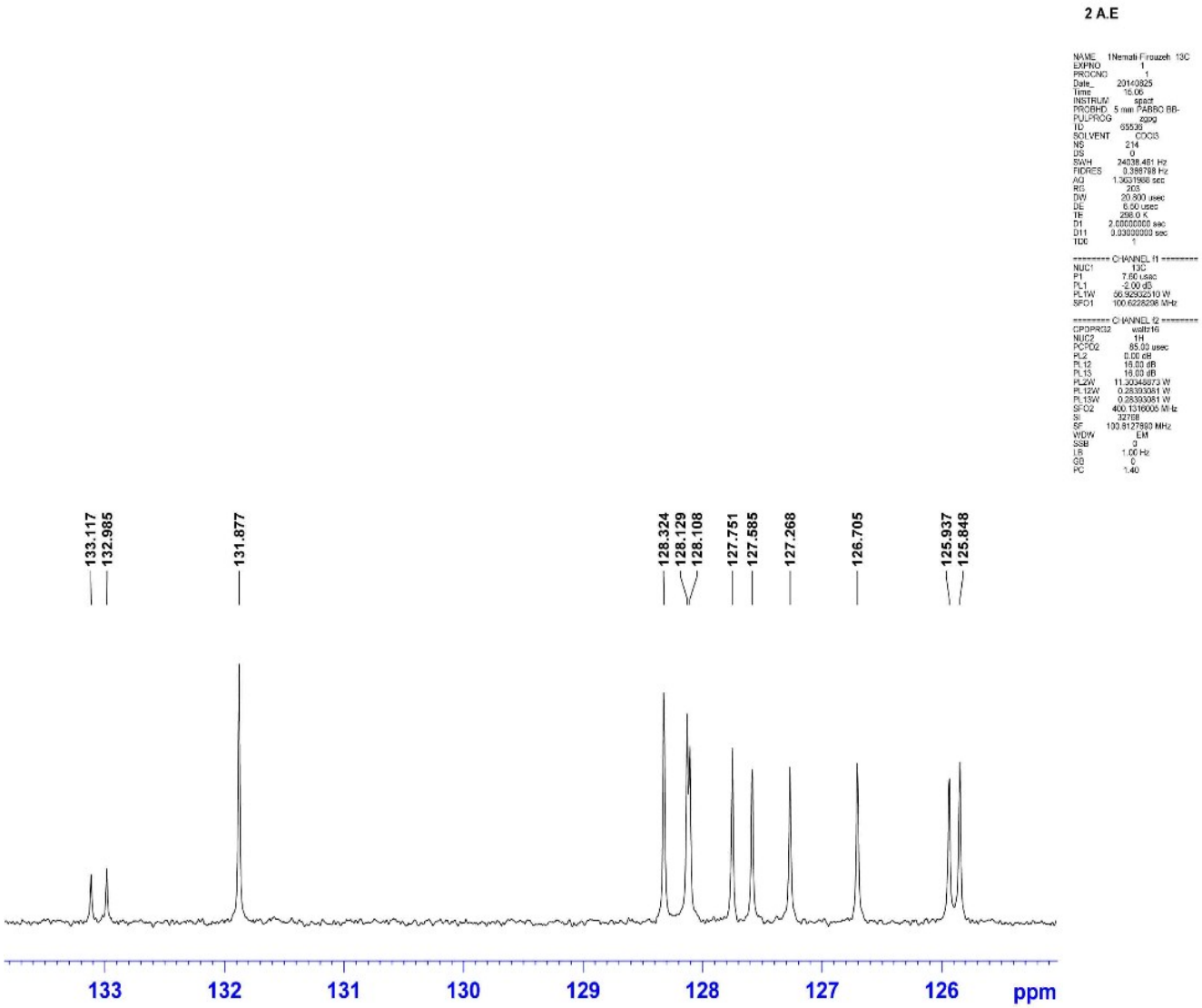

Figure 18 ^{13}C NMR, Expand spectrum of **(table 1, 5i)**

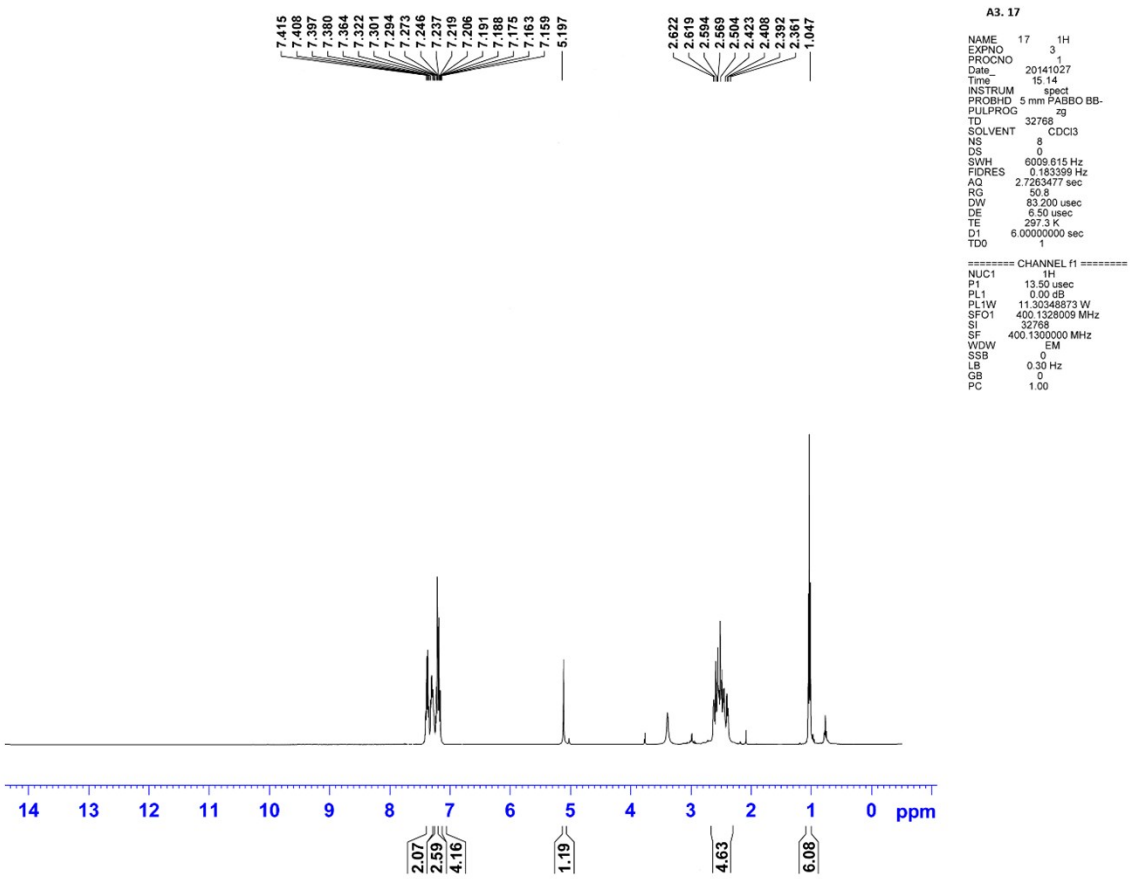

Figure 19 ^{1}H NMR, spectrum of **(table 1, 5r)**

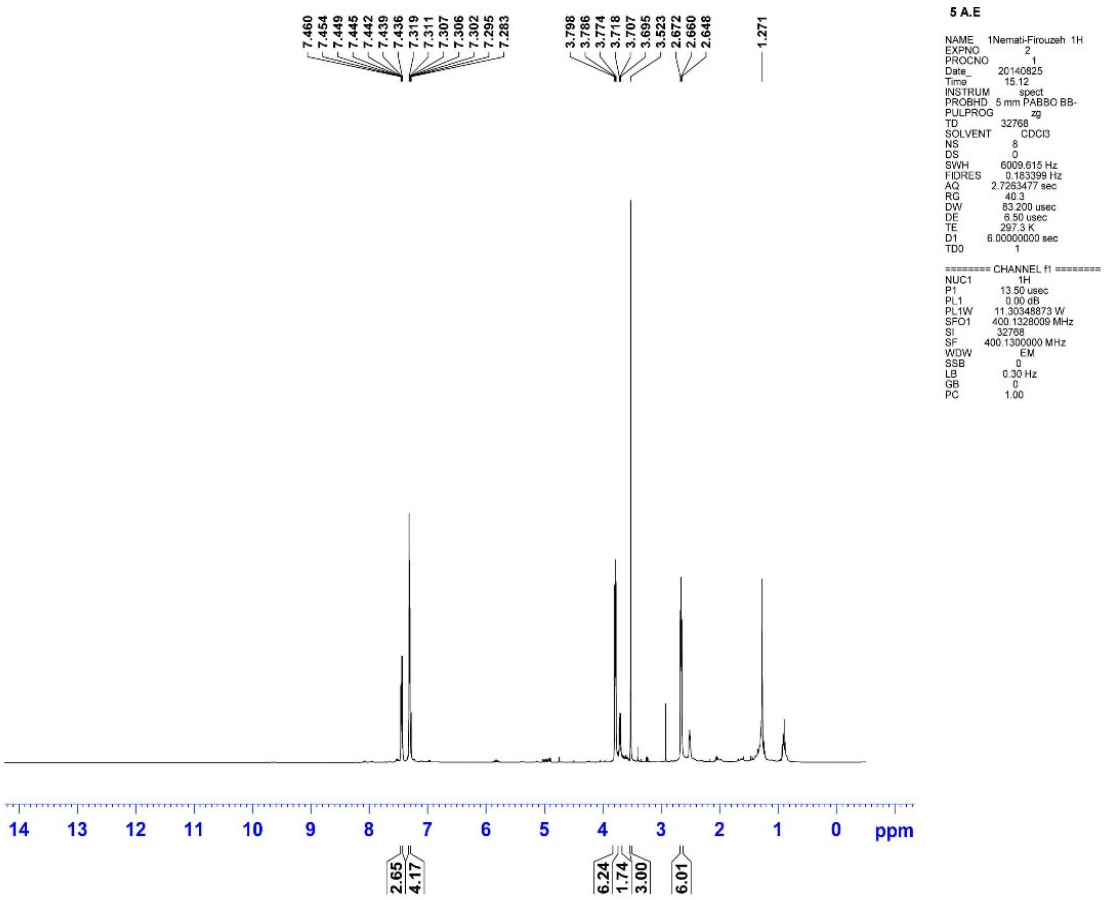

Figure 20 ^{1}H NMR, spectrum of **(table 1, 6c)**

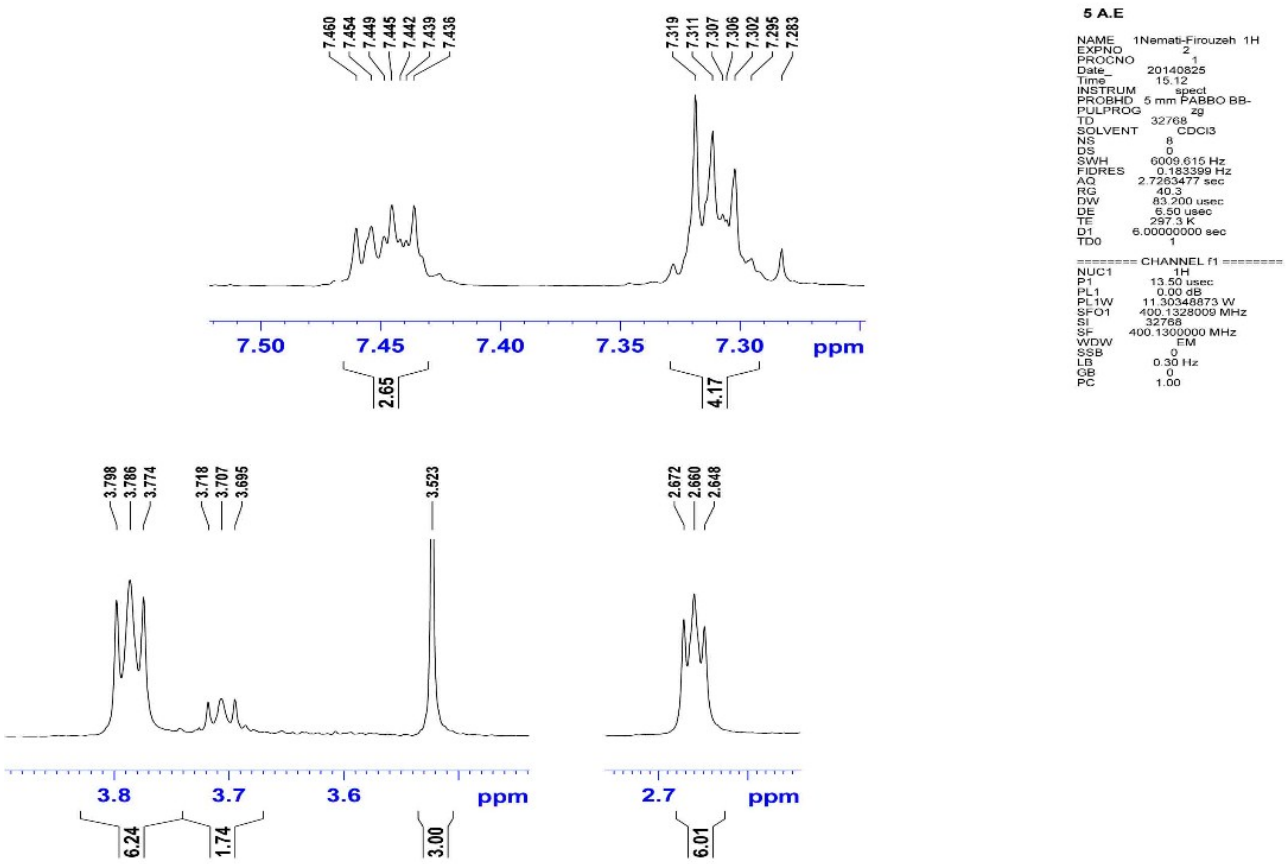

Figure 21 ^{1}H NMR, Expand spectrum of **(table 1, 6c)**

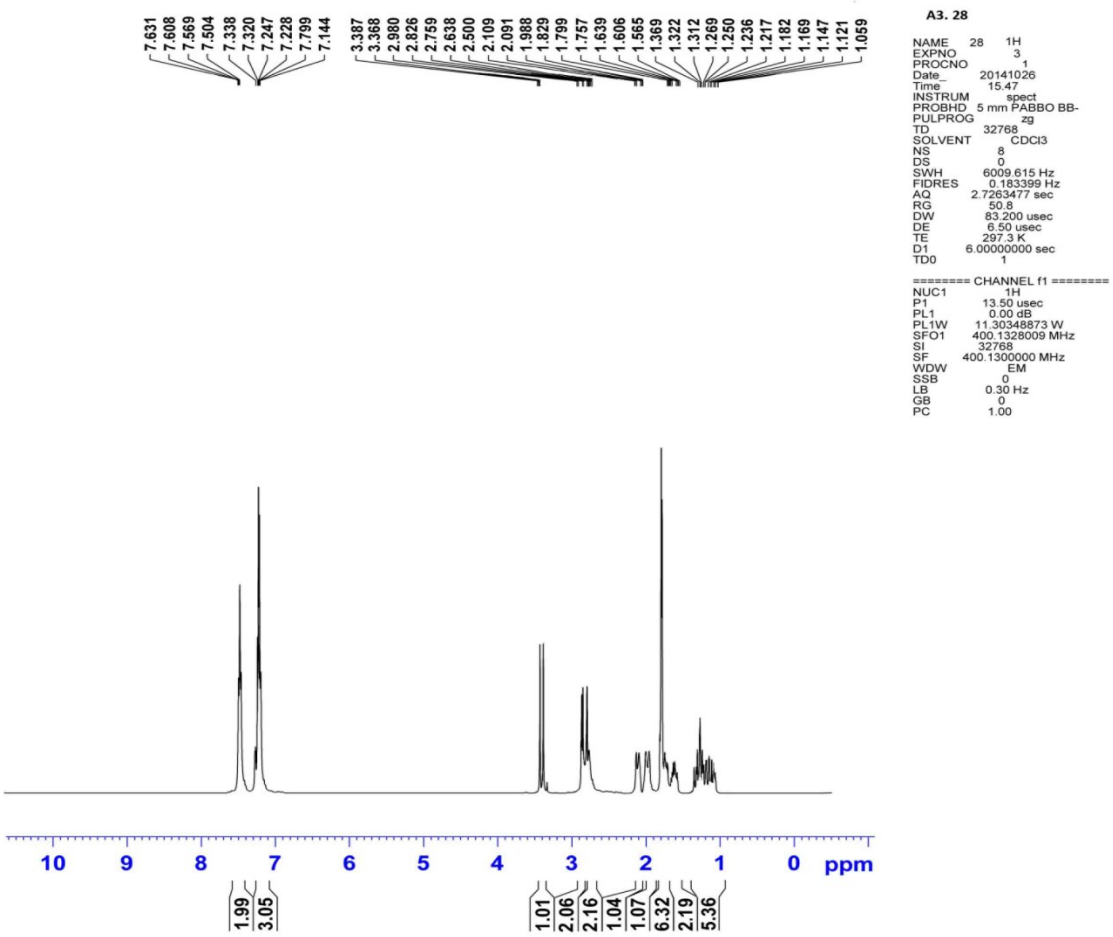

Figure 22 ^{1}H NMR, spectrum of **(table 1, 6i)**

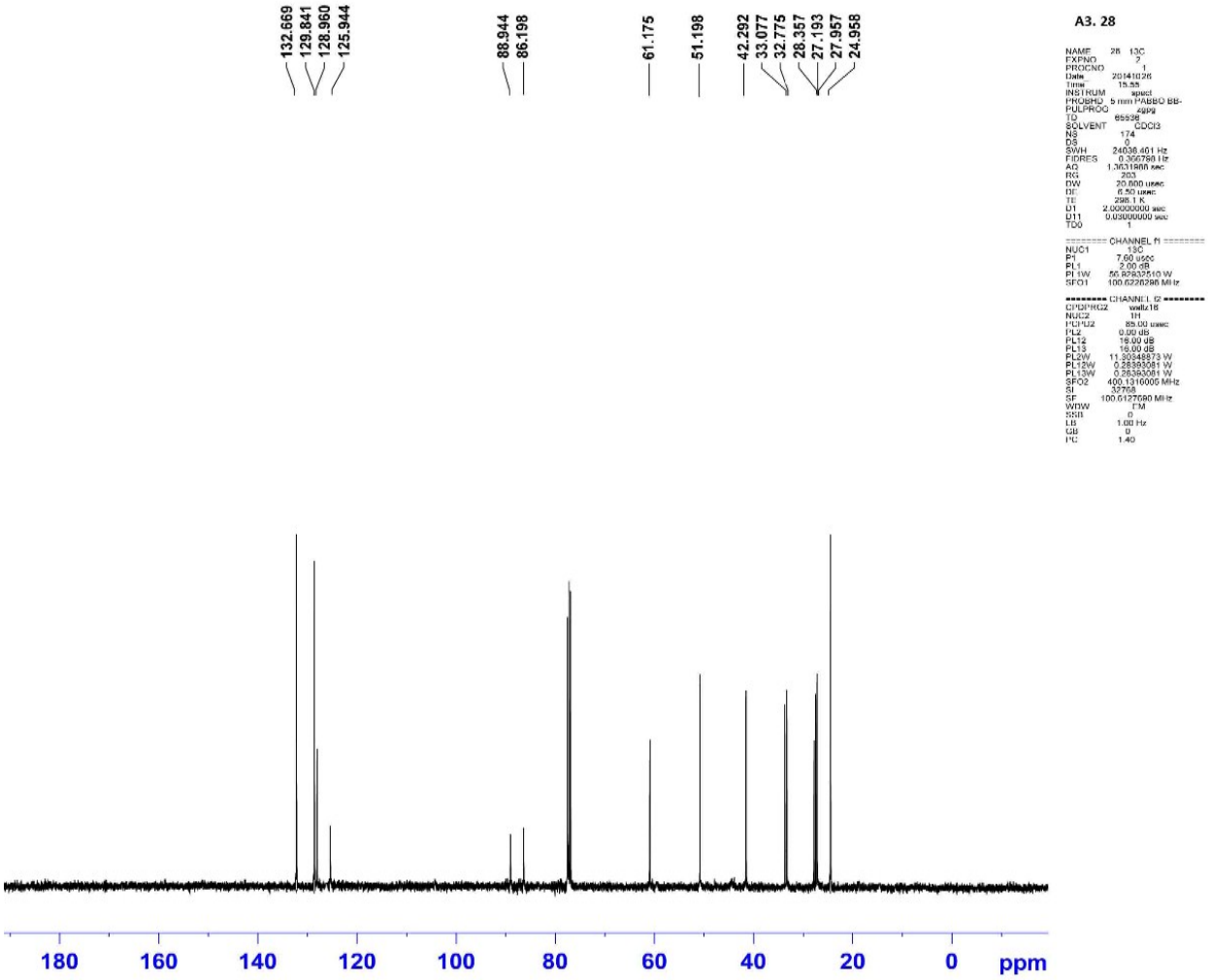

Figure 23 ^{13}C NMR, spectrum of **(table 1, 6i)**

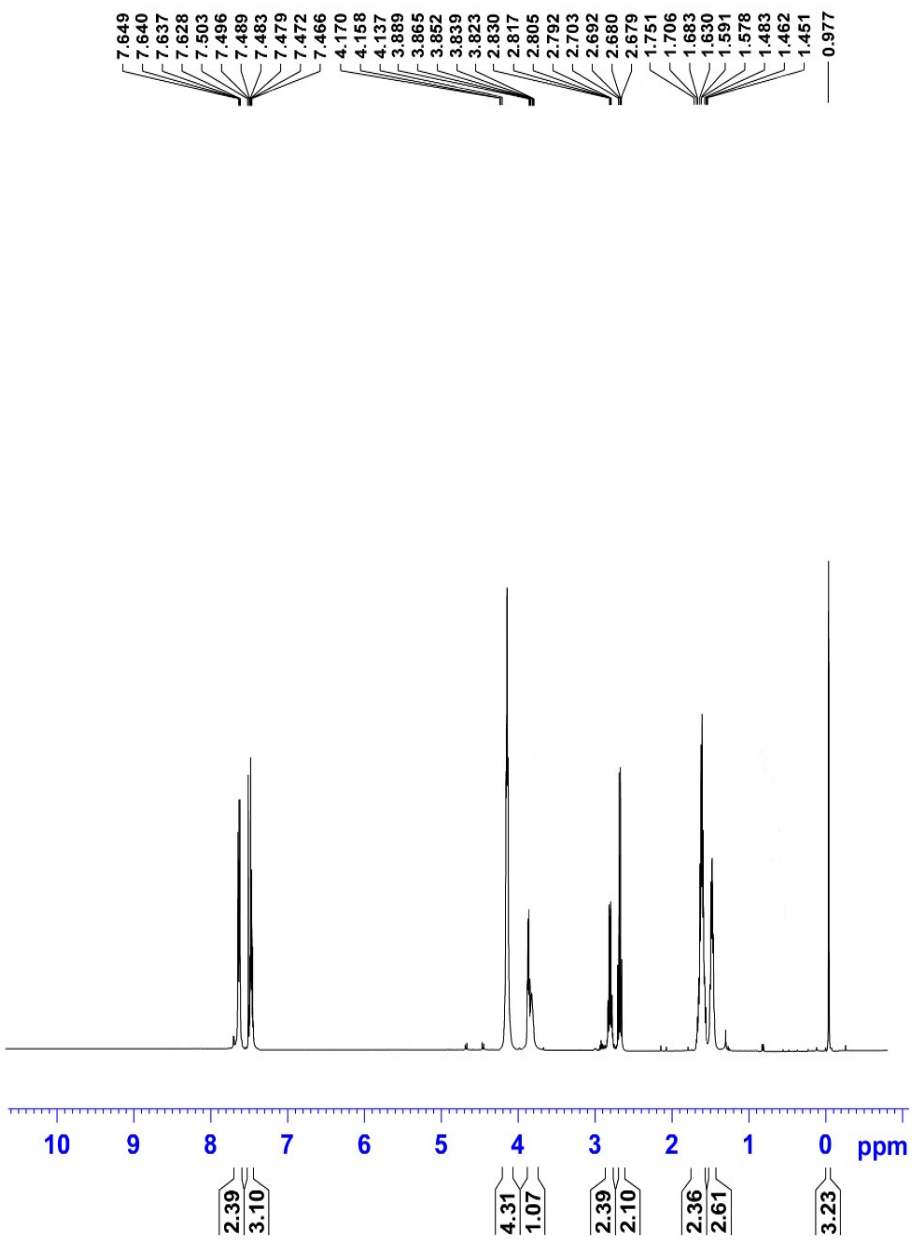

Figure 24 ^{1}H NMR, spectrum of **(table 1, 6m)**

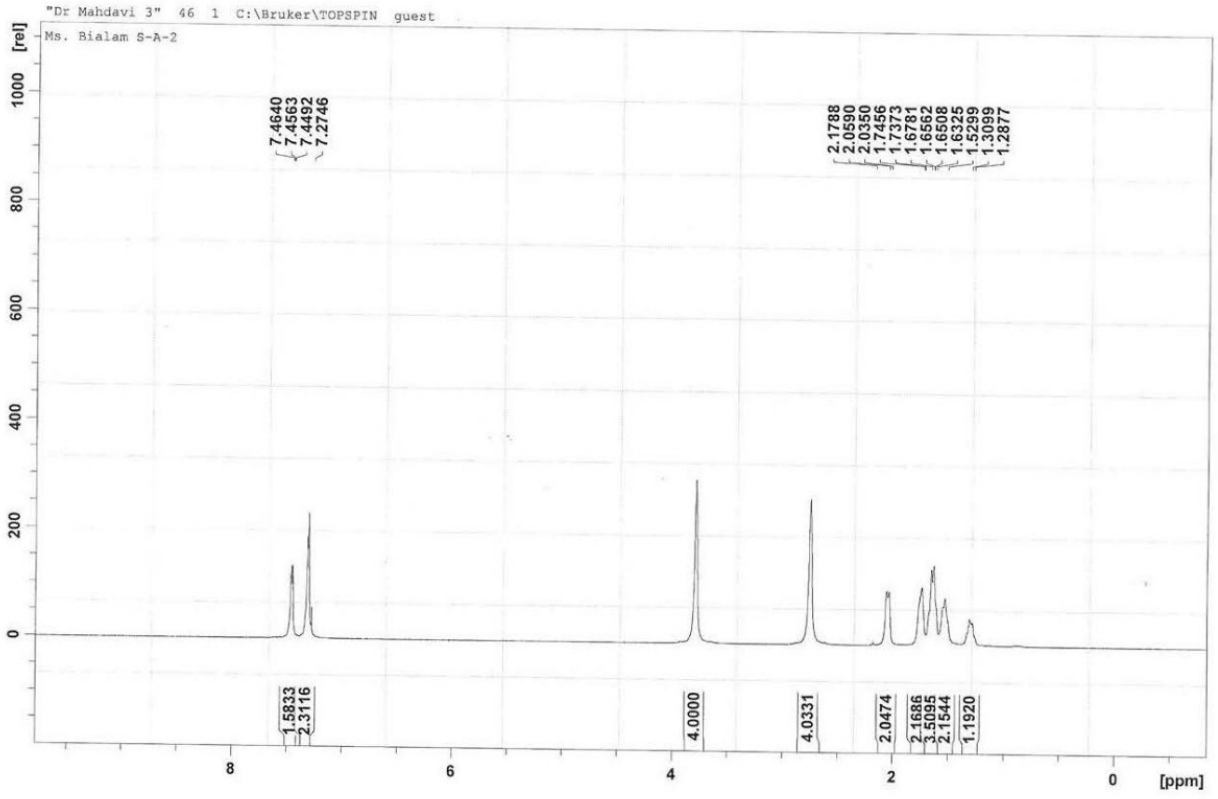

Figure 25 ^{1}H NMR, spectrum of **(table 2, 8e)**

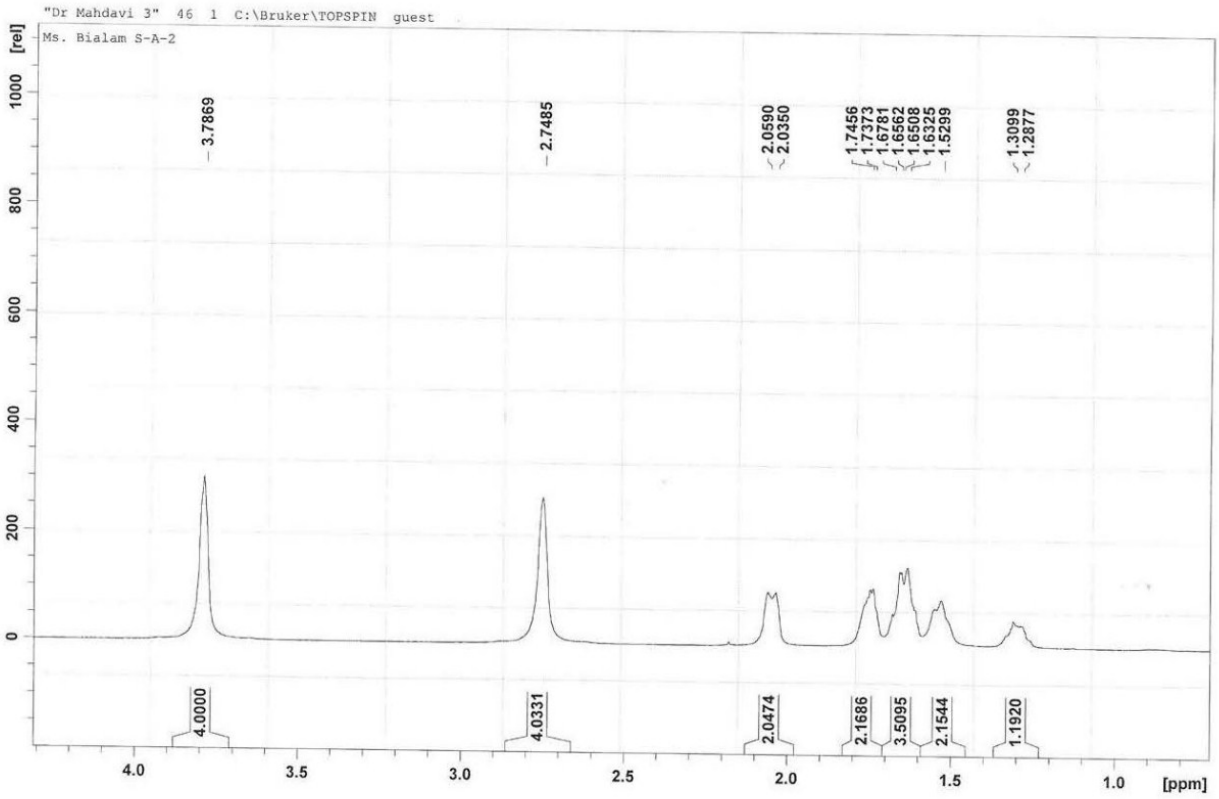

Figure 26 ^{1}H NMR, Expand spectrum of **(table 2, 8e)**

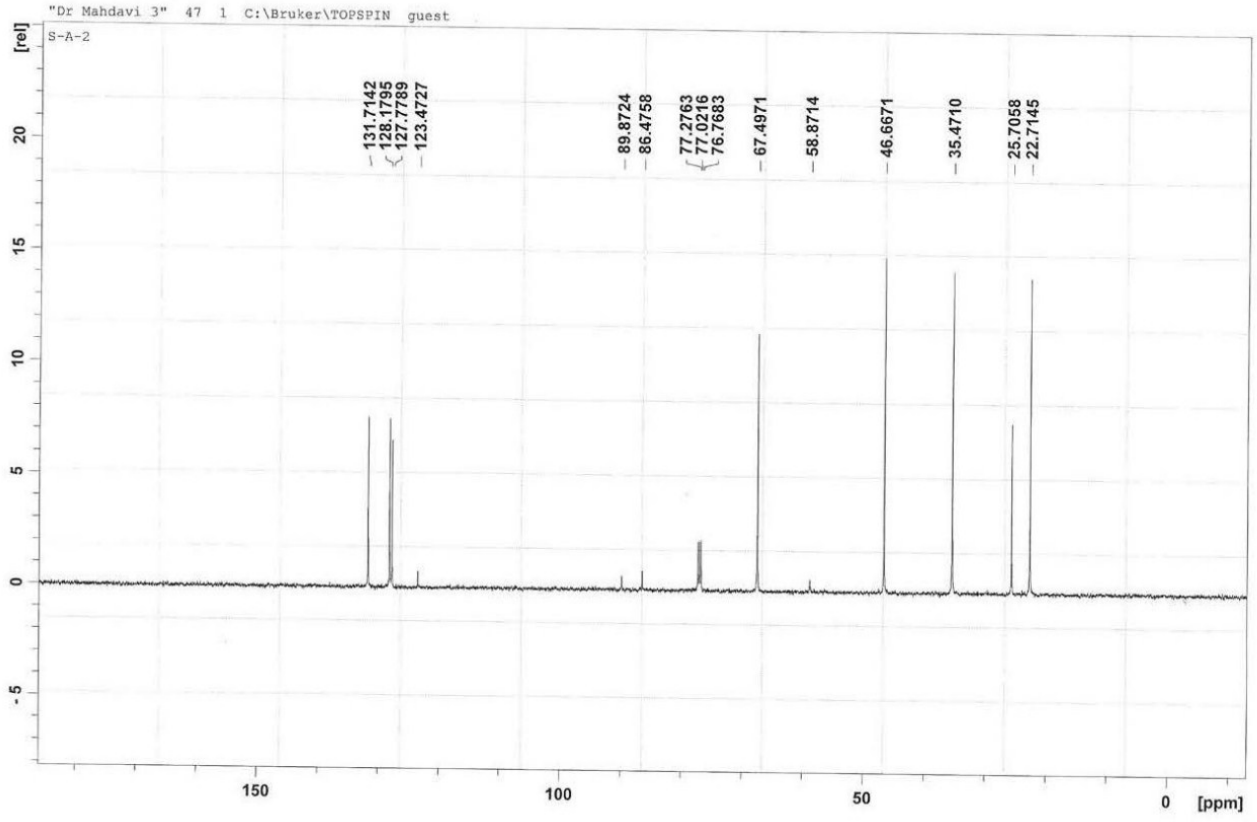

Figure 27 ^{13}C NMR, spectrum of **(table 2, 8e)**

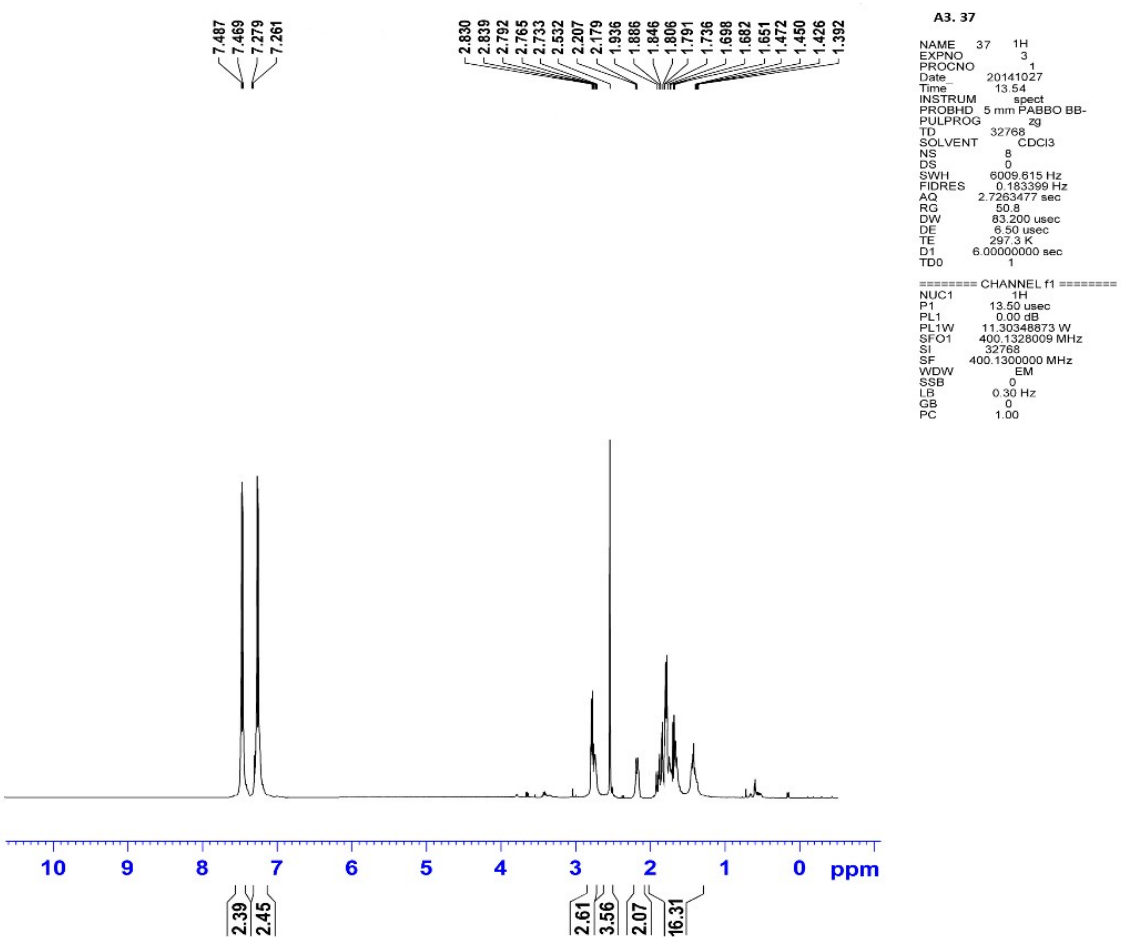

Figure 28 ^{1}H NMR, spectrum of **(table 2, 8f)**

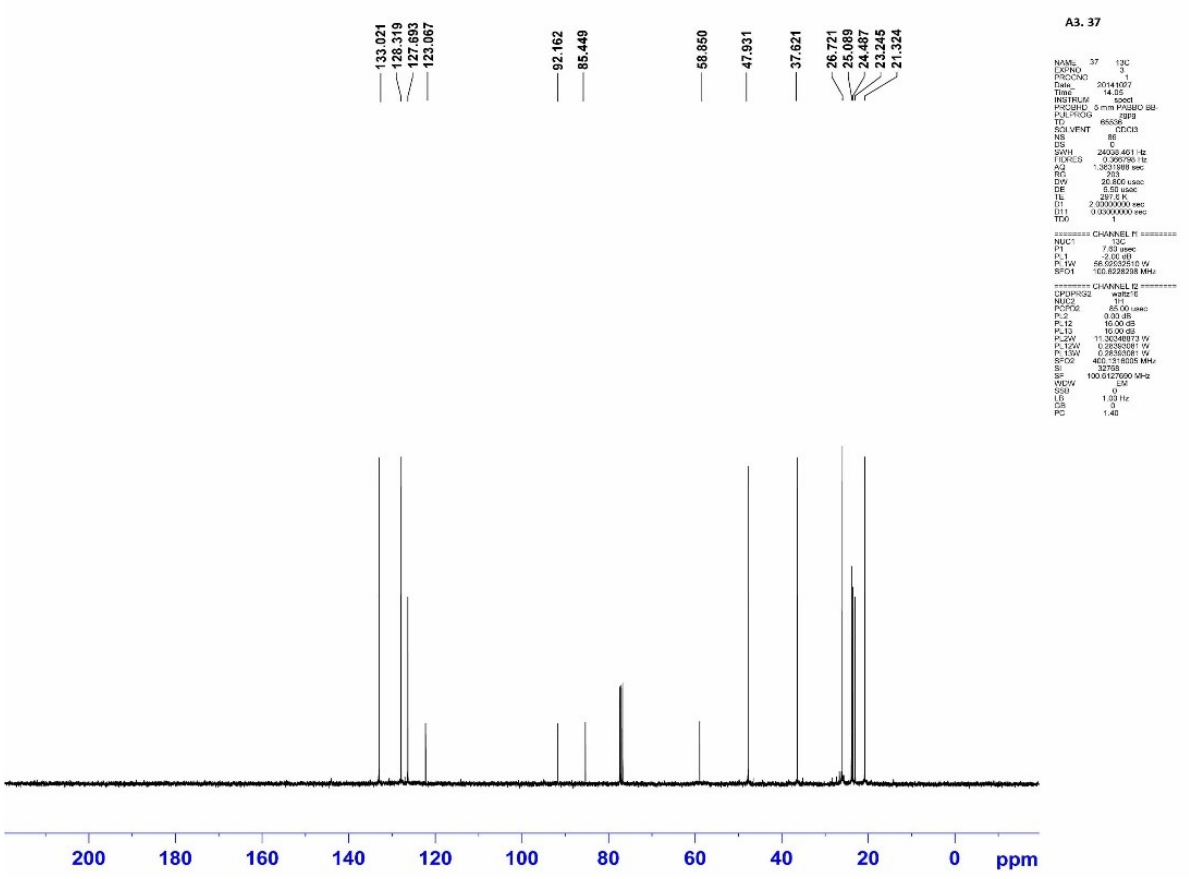

Figure 29 ^{13}C NMR, spectrum of **(table 2, 8f)**

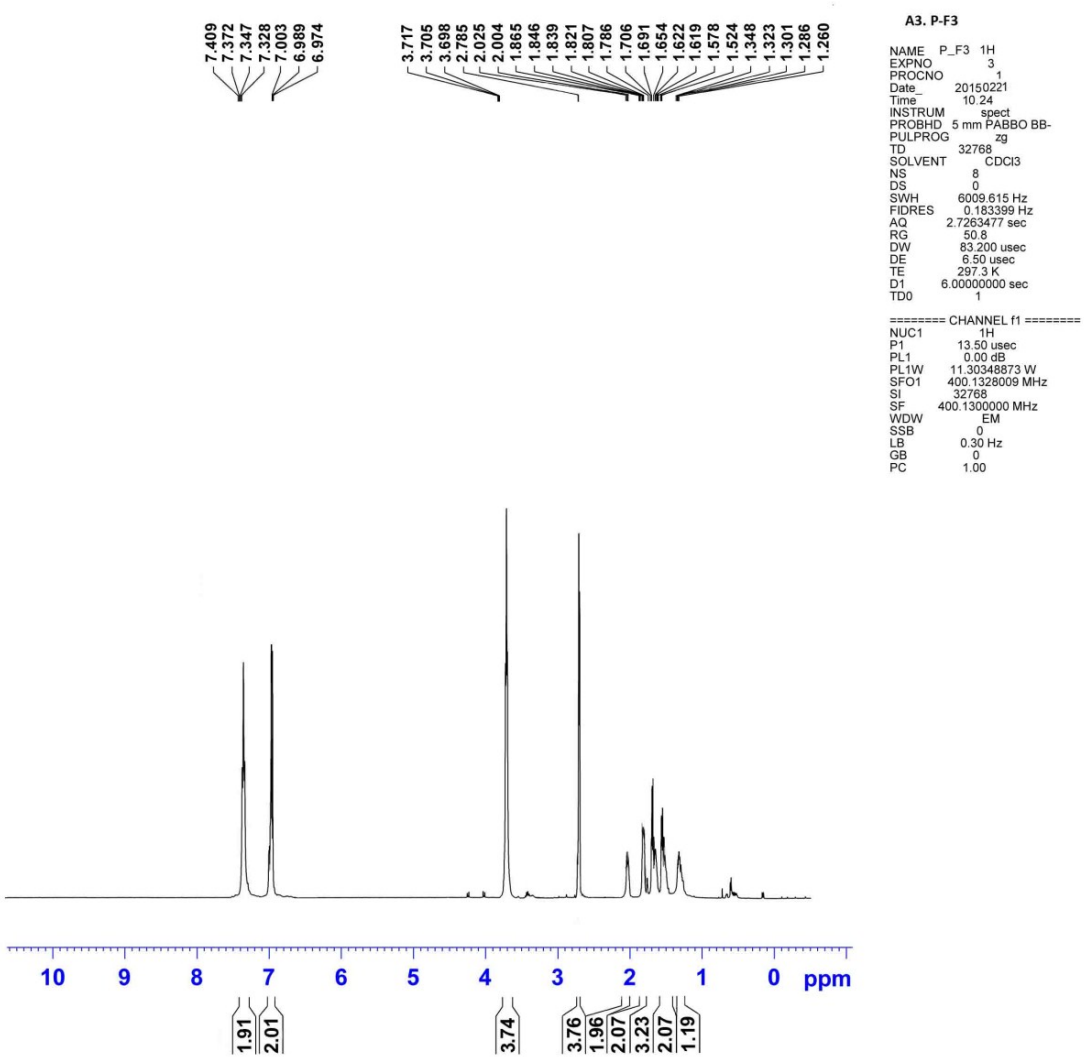

Figure 30 ^{1}H NMR spectrum of **(table 2, 8i)**

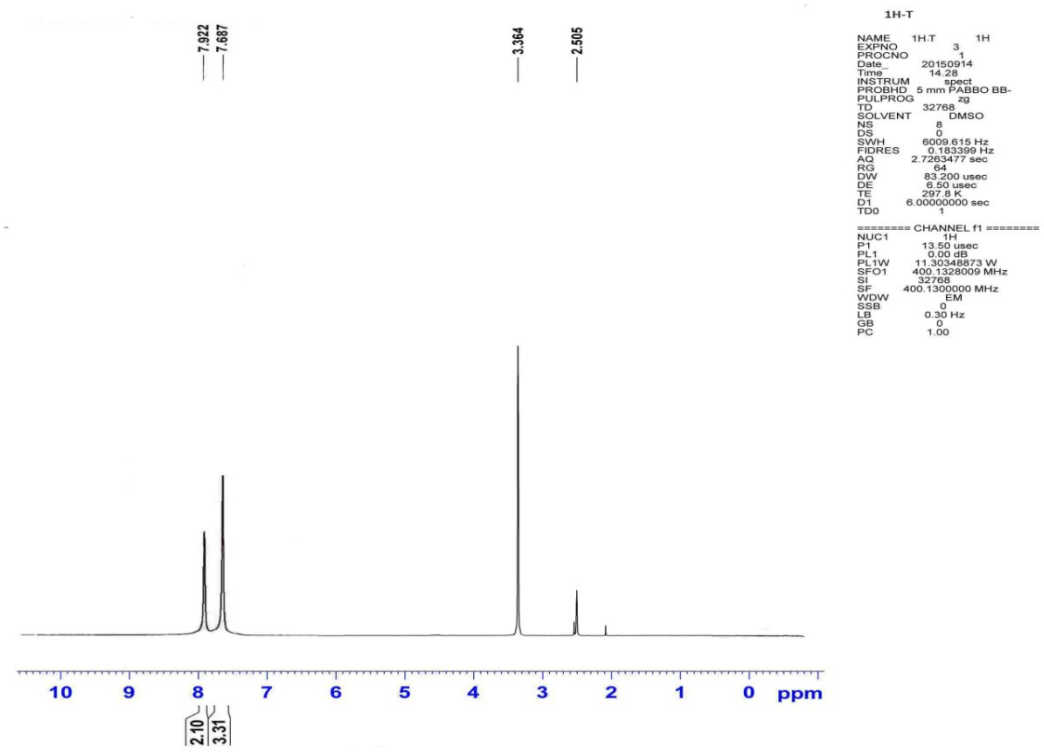

Figure 31 ^{1}H NMR spectrum of **(table 3, 9a)**

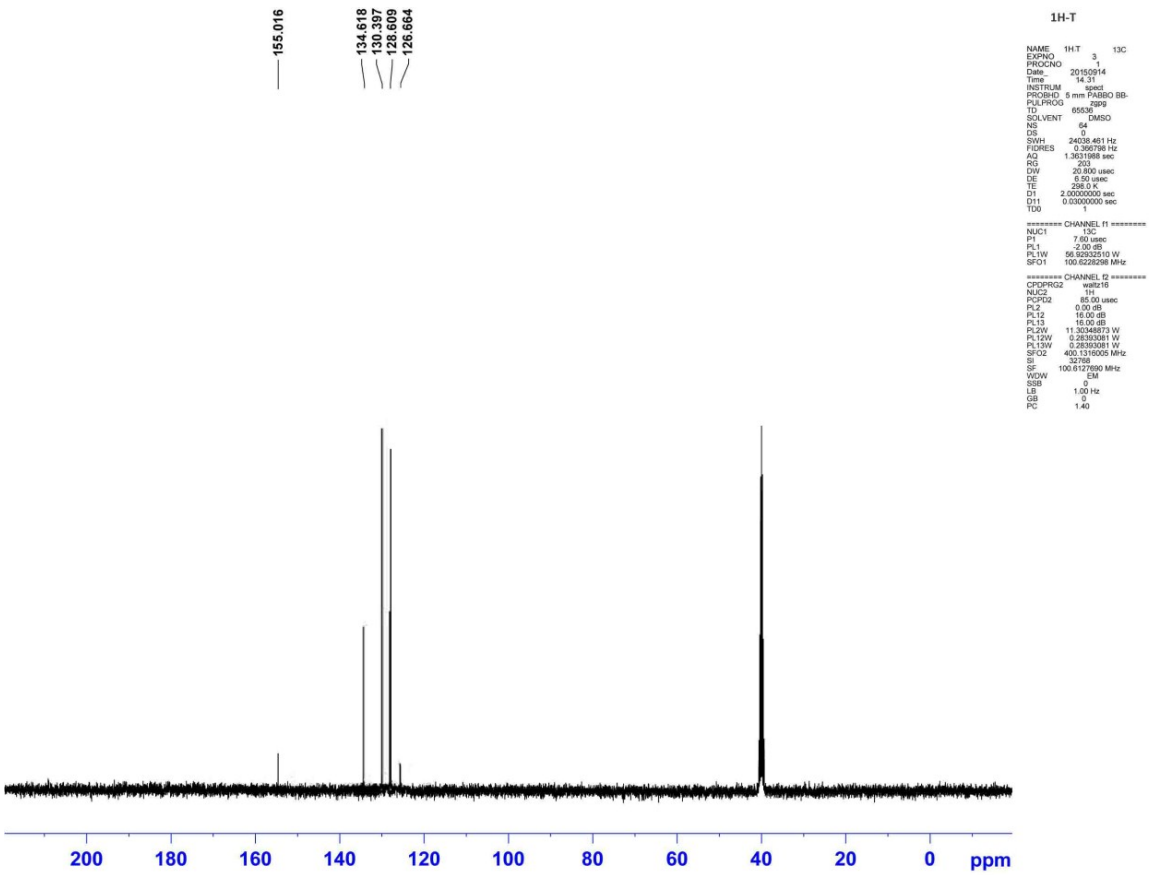

Figure 32 ^{13}C NMR spectrum of **(table 3, 9a)**

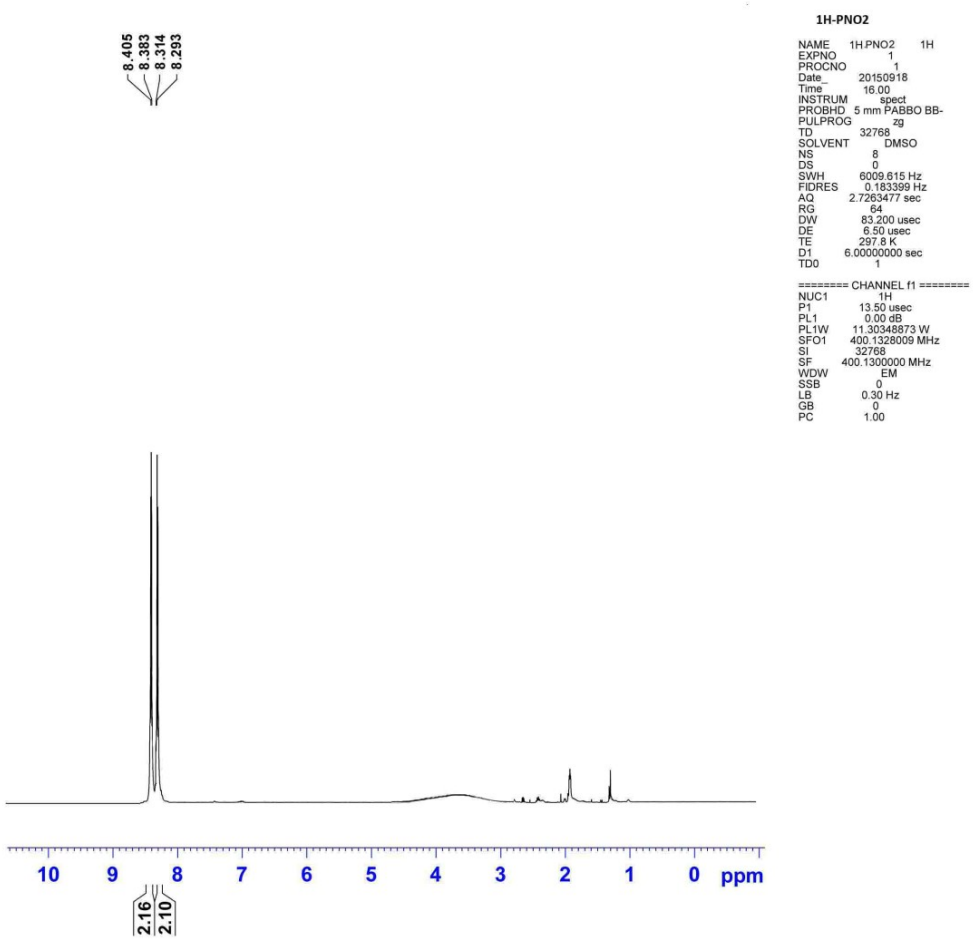

Figure 33 ^{1}H NMR spectrum of compound **(table 3, 9b)**

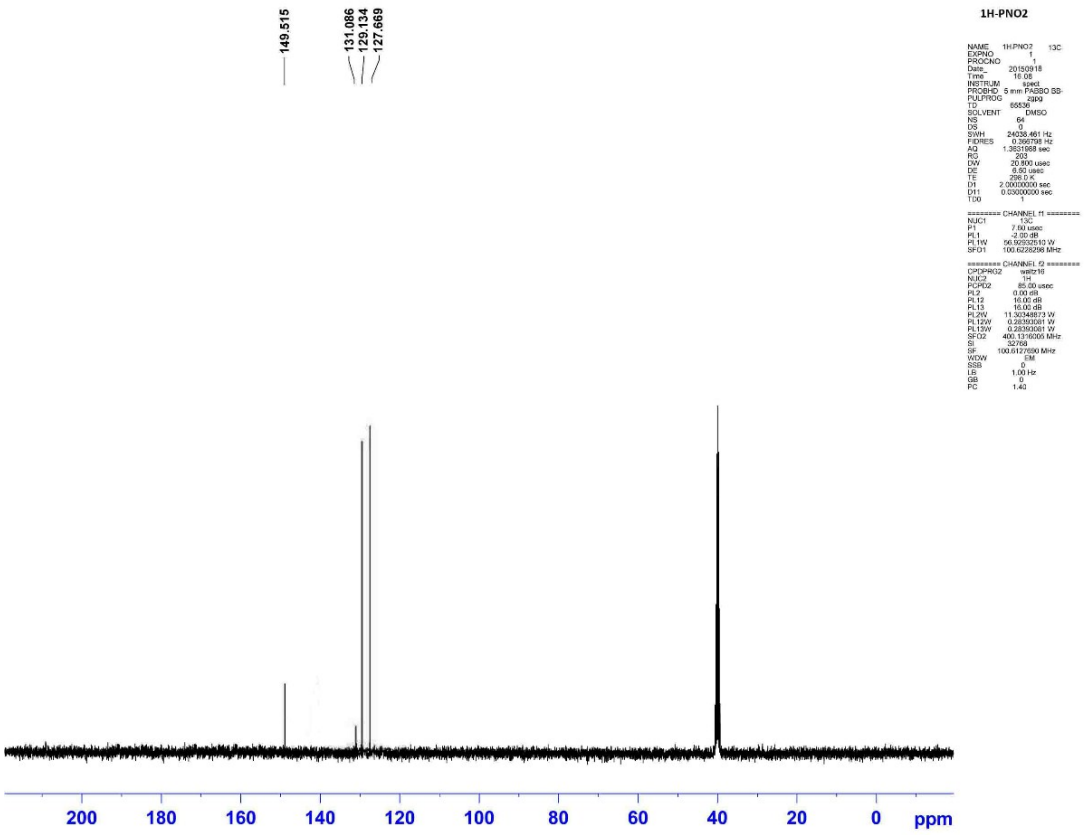

Figure 34 ^{13}C NMR spectrum of **(table 3, 9b)**

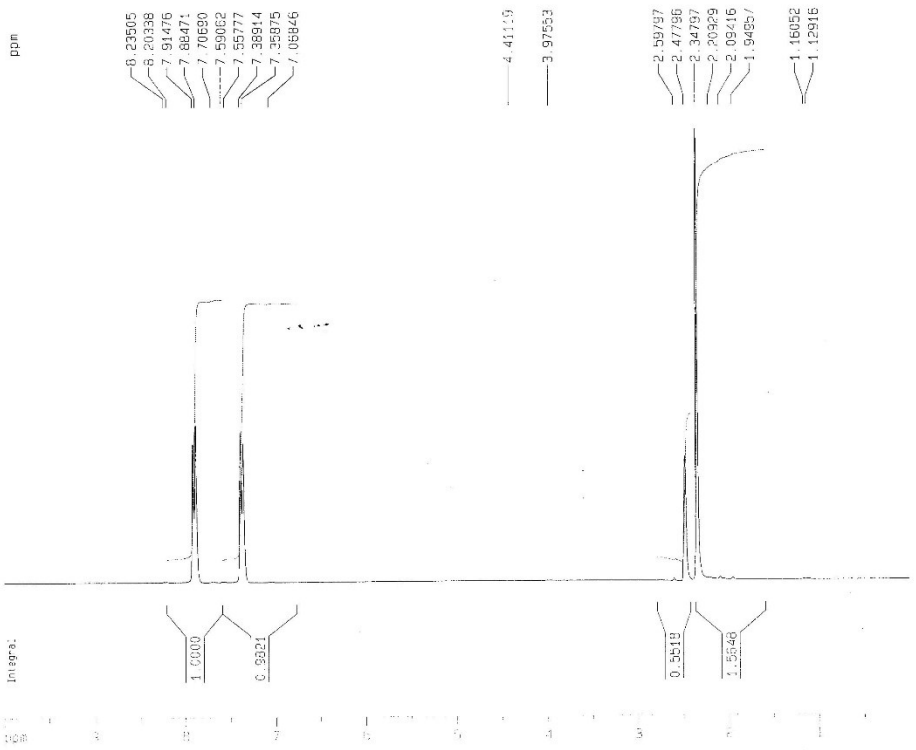

Figure 35 ^{1}H NMR spectrum of **(table 3, 9c)**

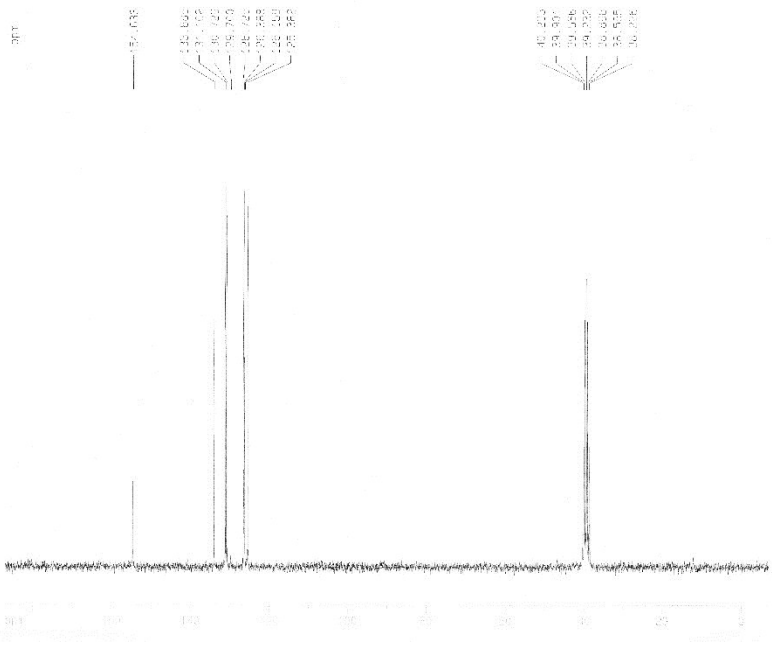

Figure 36 ^{13}C NMR spectrum of **(table 3, 9c)**

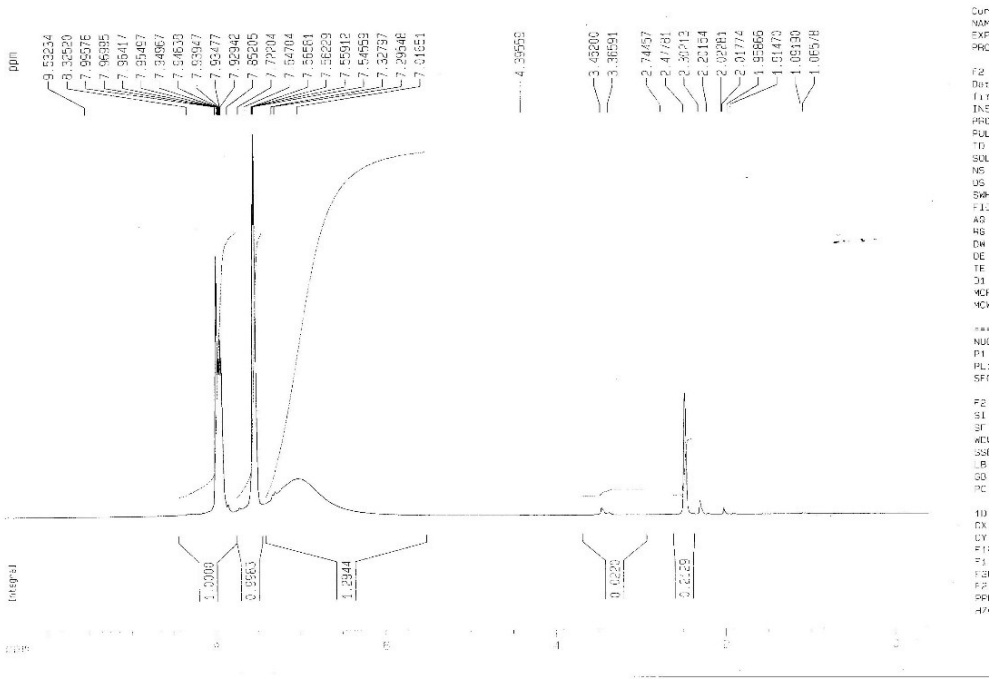

Figure 37 ^{1}H NMR spectrum of **(table 3, 9g)**

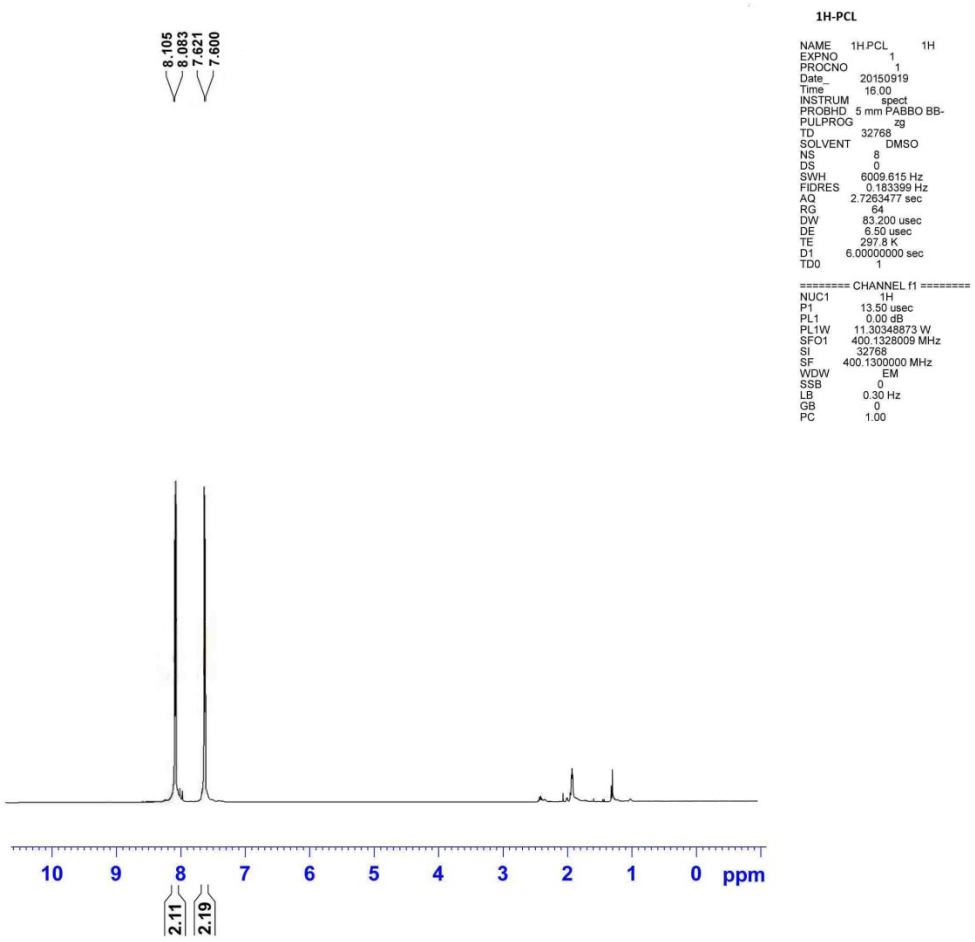

Figure 38 ^{1}H NMR spectrum of **(table 3, 9h)**

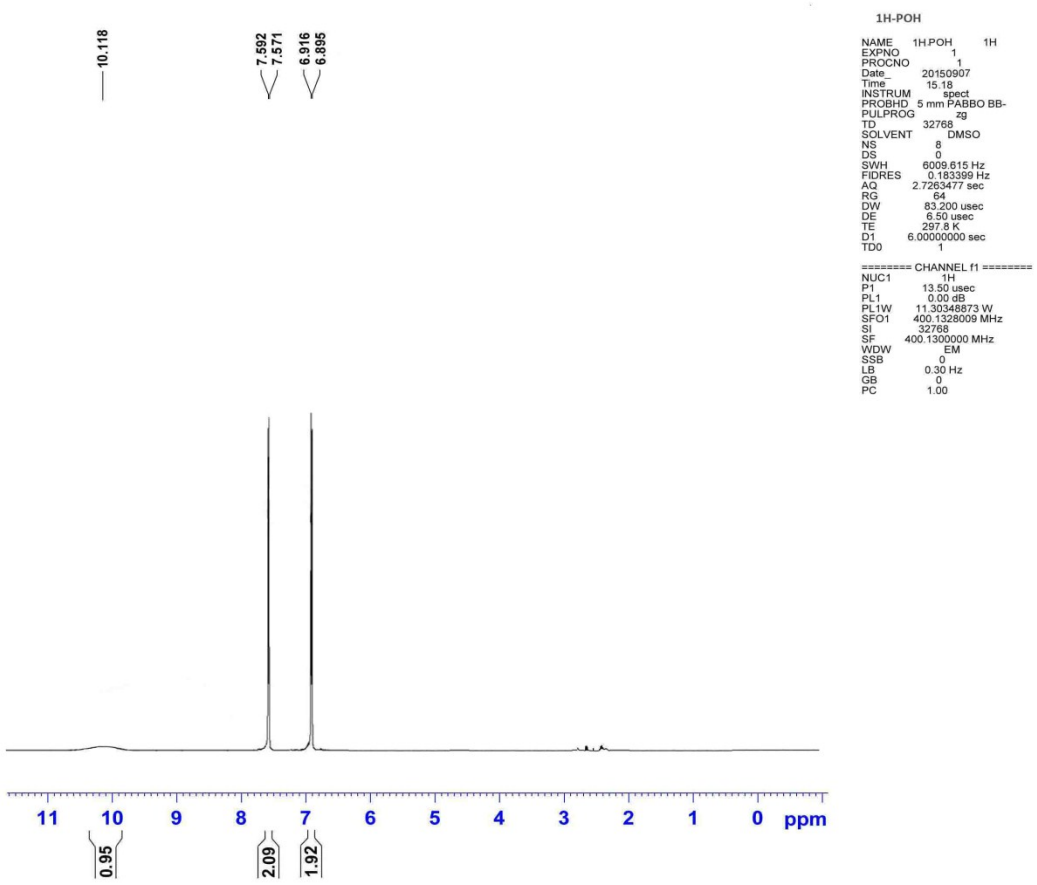

Figure 39 ^{1}H NMR spectrum of **(table 3, 9j)**

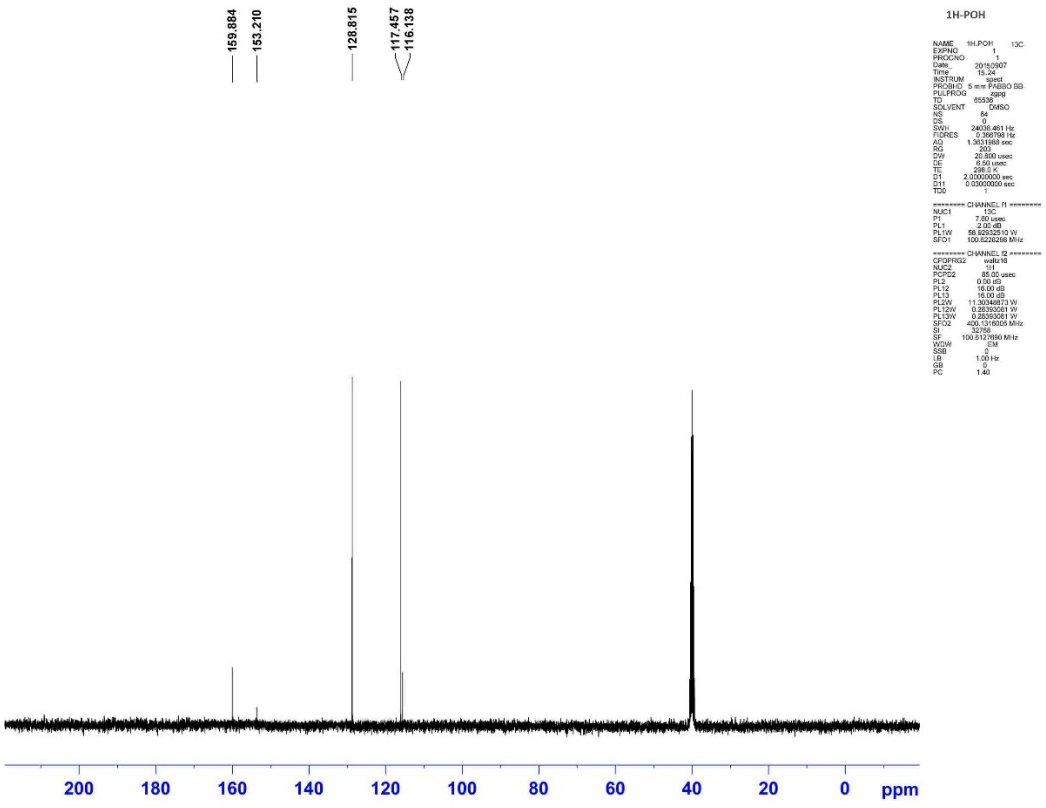

Figure 40 ^{13}C NMR spectrum of **(table 3, 9j)**

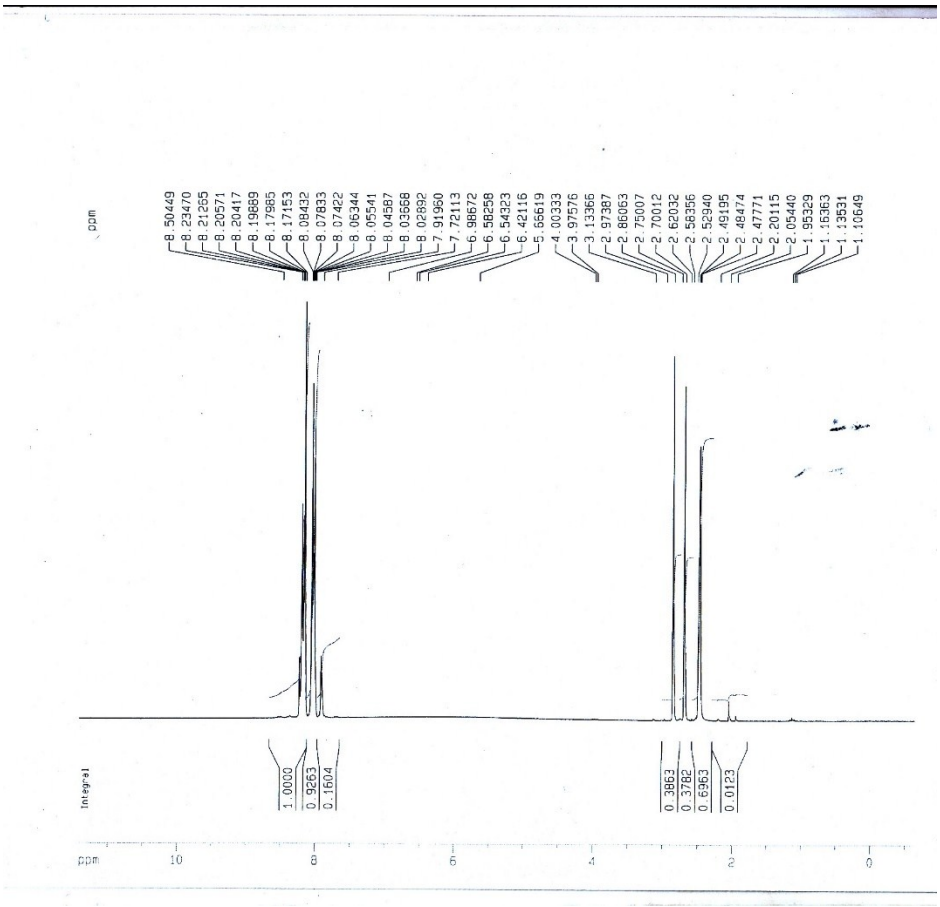

Figure 41 ^{1}H NMR spectrum of **(table 3, 9k)**

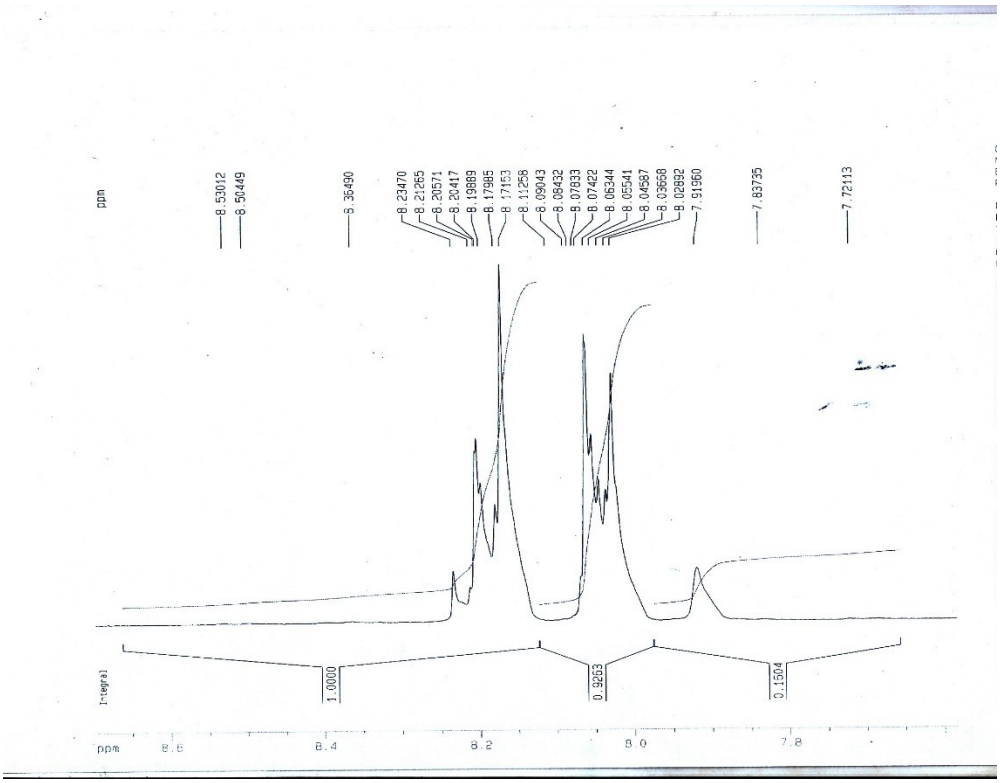

Figure 42 ^{1}H NMR expand spectrum of **(table 3, 9k)**

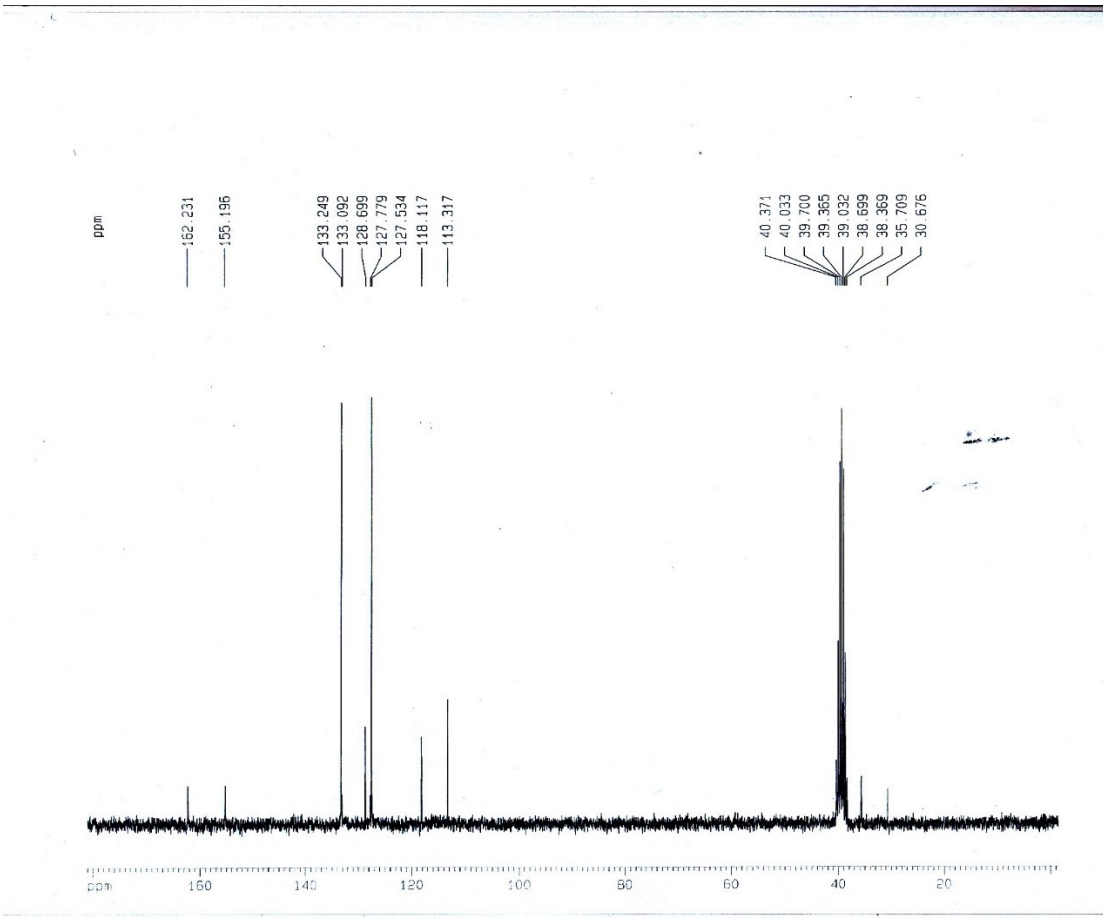

Figure 43 ^{13}C NMR spectrum of **(table 3, 9k)**

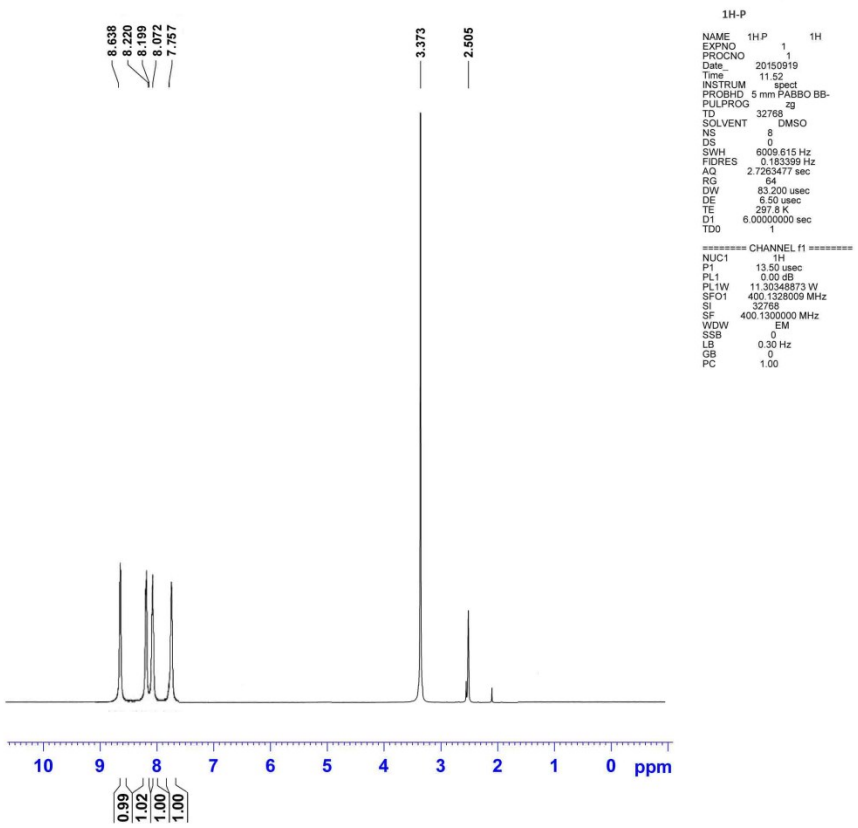

Figure 44 ^{1}H NMR spectrum of **(table 3, 9l)**

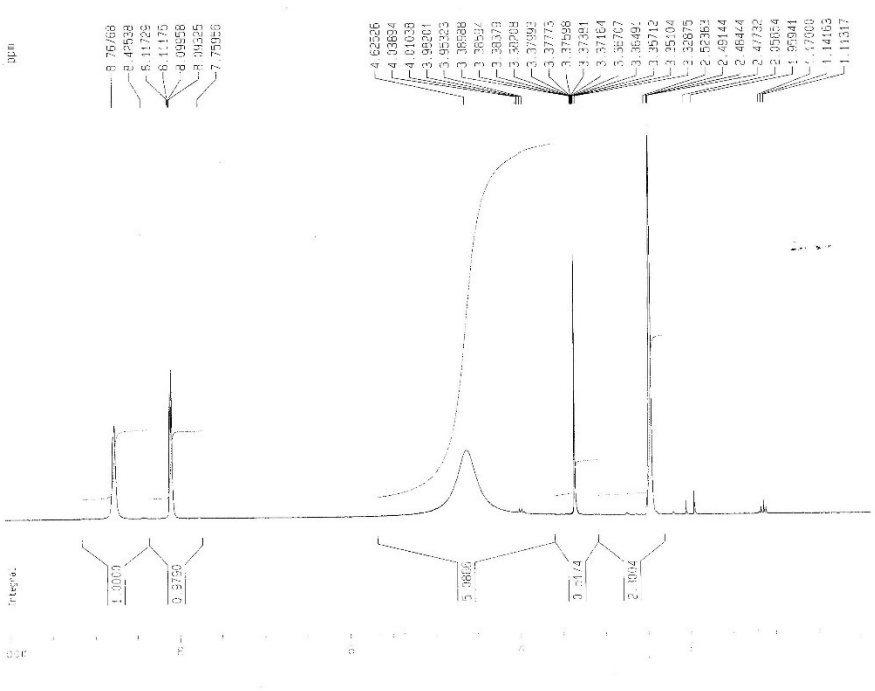

Figure 45 ^{1}H NMR spectrum of **(table 3, 9m)**

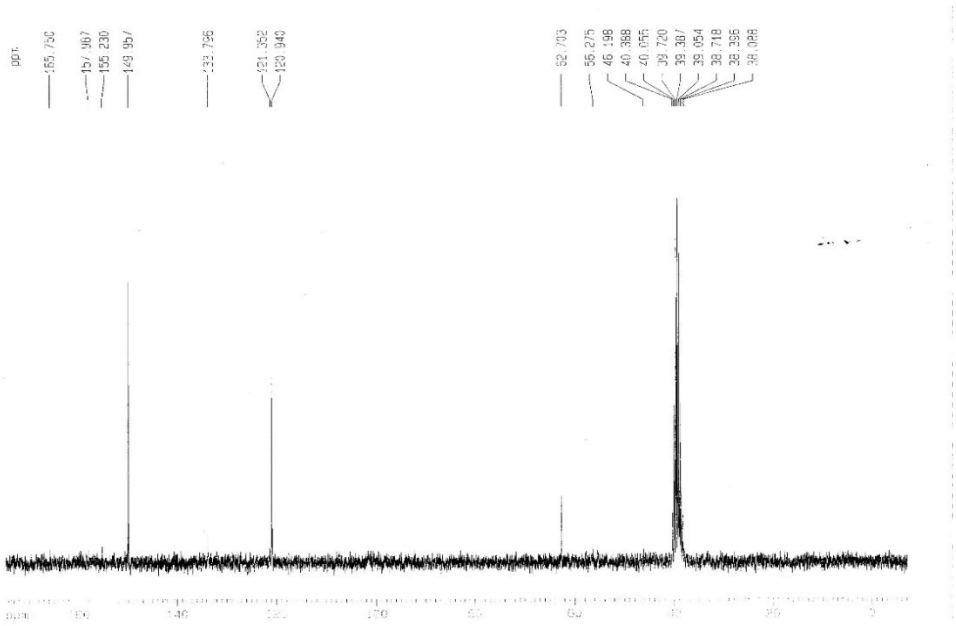

Figure 46 ^{13}C NMR spectrum of **(table 3, 9m)**

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