Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of highly functionalized 2-thiaspiro[4.5]deca-6,8-dienes *via* atom efficient tandem Michael addition/Thorpe-Ziegler cyclization

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SUPPLEMENTARY CONTENT

Experimental

General

Melting point of the products was measured on Sigma melting point apparatus, Sl. No. 71281, watts-250, volts-230 AC. Open capillary tubes were used for the measurements and are uncorrected. The ^{1}H,^{13}C, DEPT, H,H-COSY, C,H-COSY and HMBC spectra were recorded on Bruker (Avance) 300 MHz NMR instrument using TMS as internal standard and $CDCl_3$and/or DMSO-D_6 as a solvents. Standard Bruker software was used throughout the spectral analysis. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. Electro Spray Ionization Mass Spectrometry (ESI–MS) analyses were recorded in LCQ Fleet, Thermo Fisher Instrument in negative or positive ion mode. The collision voltage and ionization voltage were −70 V and −4.5 kV, respectively, using nitrogen as atomization and desolvation gas. The desolvation temperature was set at 300 °C. The scan range of mass spectrum was 50–1100 m/z. The relative amount of each component was determined from the LC–MS chromatogram, using the area normalization method. Infrared spectra were recorded on Shimadzu FT-IR-8400S instrument using neat samples. Elemental analyses were performed on a Perkin Elmer 2400 Series II Elemental CHNS analyzer. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of petroleum ether (60–80 °C) and ethyl acetate as the eluent. All the chemicals were purchased from Sigma-Aldrich, Alfa-Aesar or Merck and used without further purification. The entire crystallographic calculations of compound **1v** were done with Bruker AXS KAPPA APEX-2 diffractometer equipped with graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares calculations using SHELXL–2014. Reliability index (R-factor) for $F^2 > 2\sigma(F^2)$ is found to be 5.92%, which confirms the convergence of the reliable structure.

General procedure for the synthesis of 2-thiaspiro[4.5]deca-6,8-dienes 1a-x

A mixture of 2,4-bis((*Z*)-arylidene)dihydrothiophen-3(2*H*)-one **3** (1 mmol) and 2-(1-arylethylidene)malononitrile **4** (1 mmol) was taken in ethanol (10 mL) to which triethylamine (1.0 equiv.) was added. The reaction mixture was stirred at ambient temperature (28 ^{o}C) for 30 minutes and the reaction progress was monitored by TLC analysis. After completion of the reaction, the precipitate obtained was filtered and washed with cold ethanol and dried under vacuum to obtain the product **1** as yellow solid.

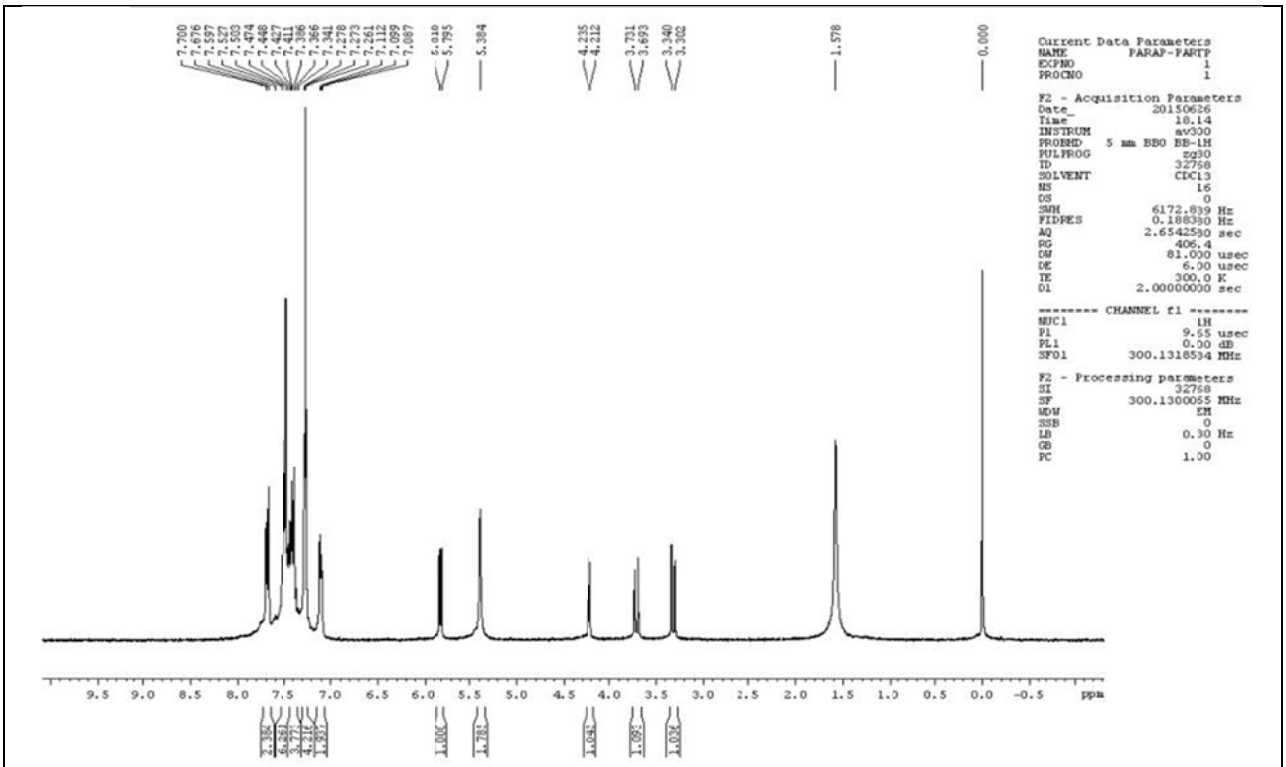

Figure 1. ^{1}H NMR spectrum of **1a**

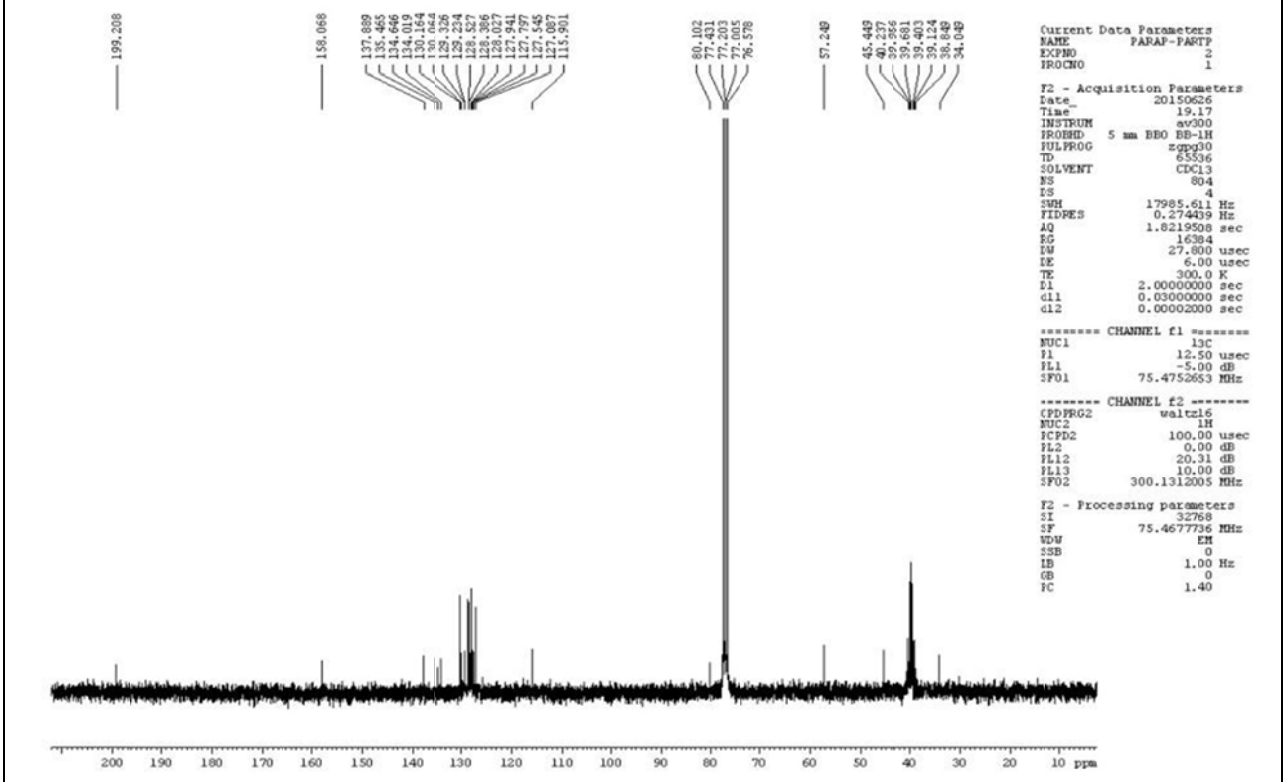

Figure 2. ^{13}C NMR spectrum of **1a**

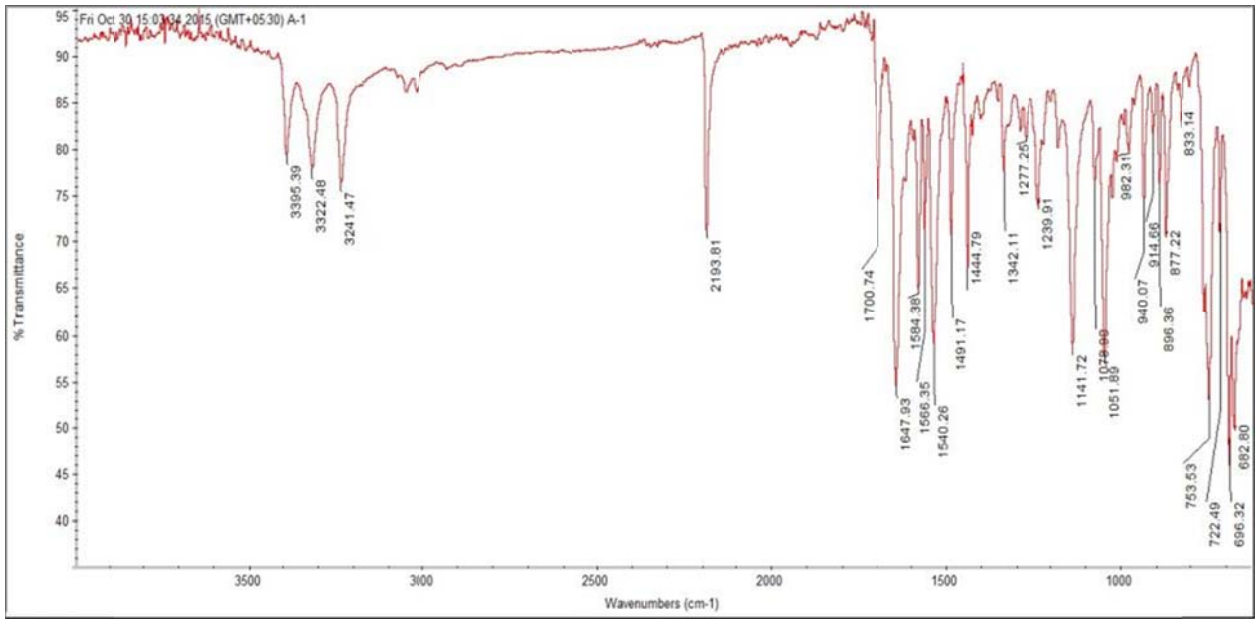

Figure 3. FT-IR spectrum of **1a**

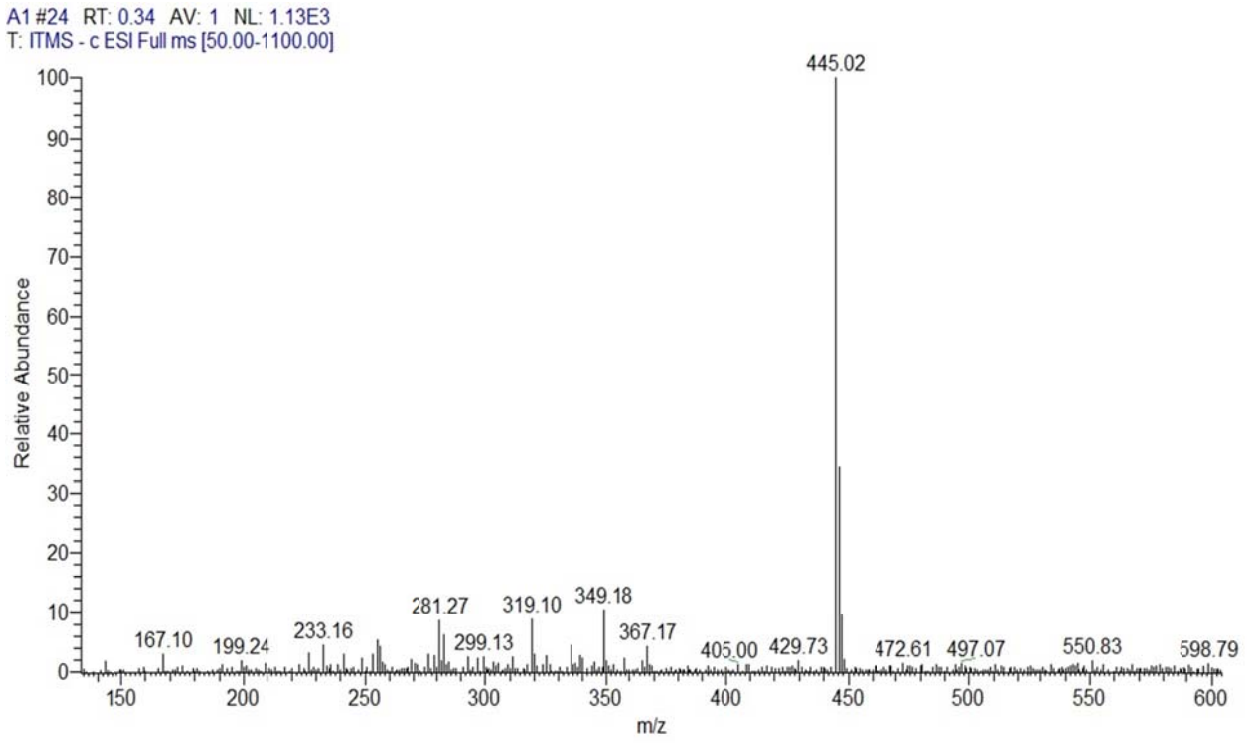

Figure 4. ESI-mass of **1a**

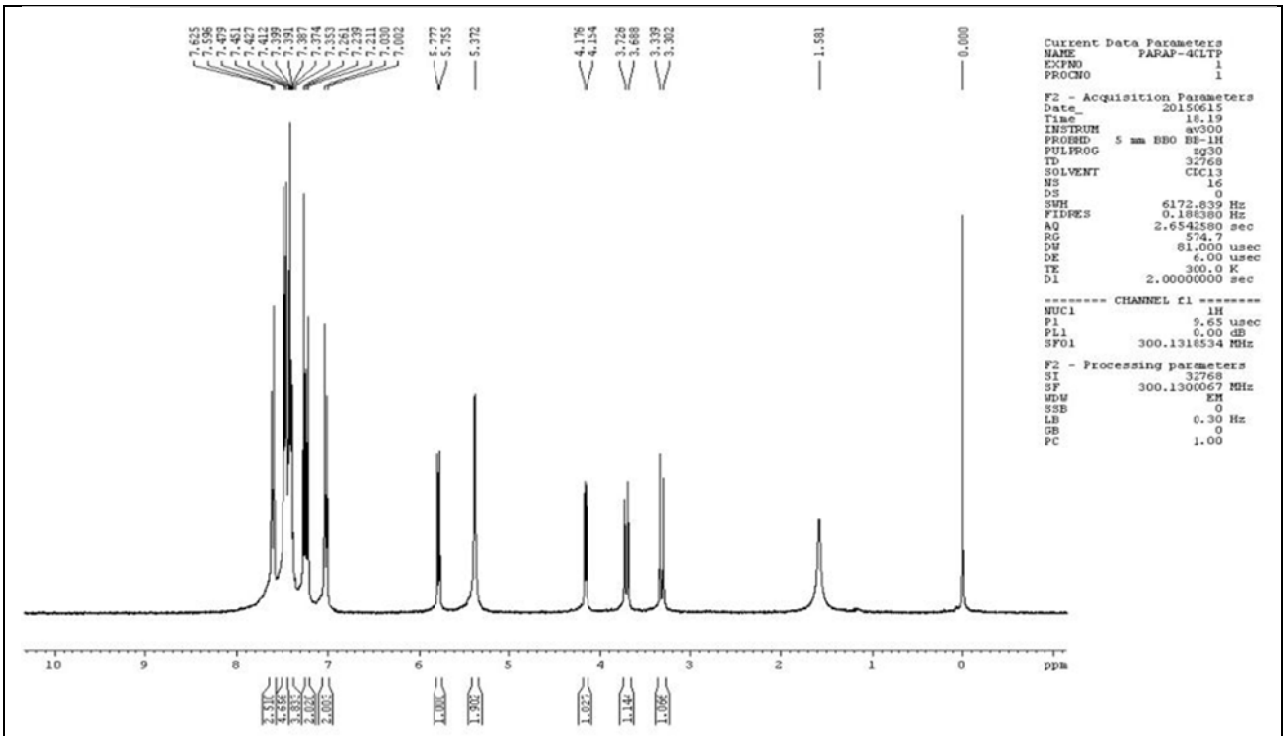

Figure 5. ^{1}H NMR spectrum of **1b**

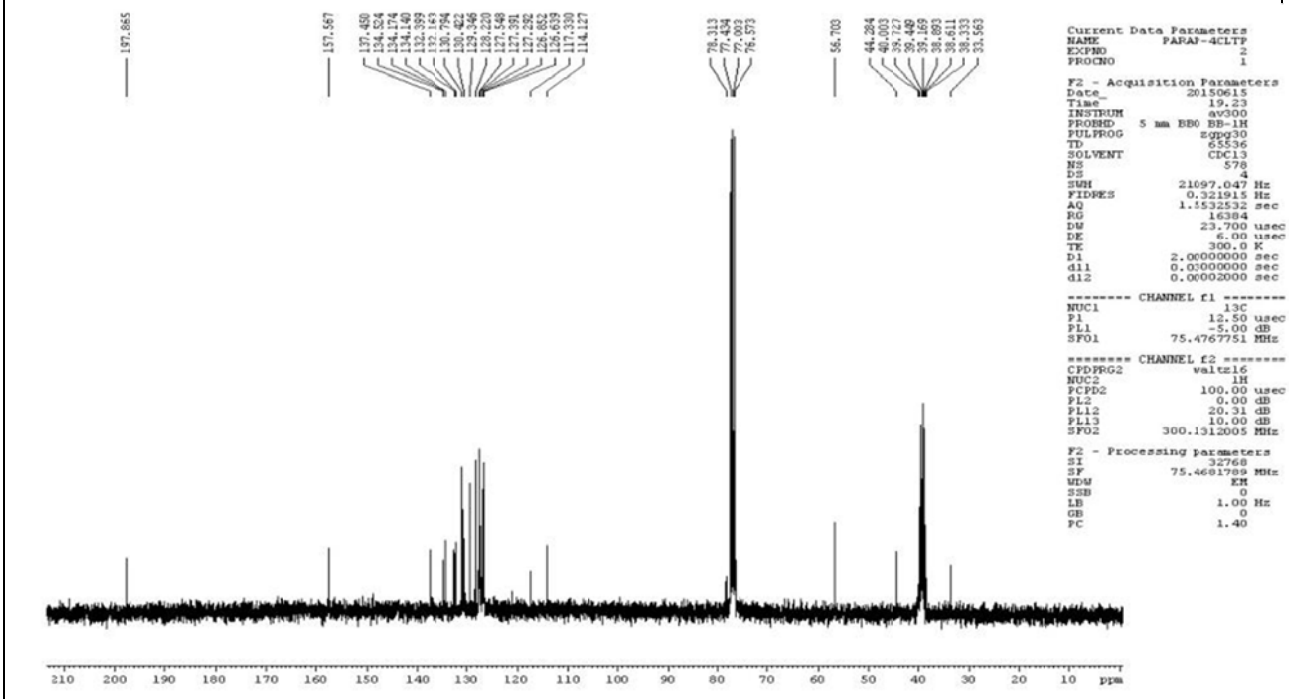

Figure 6. ^{13}C NMR spectrum of **1b**

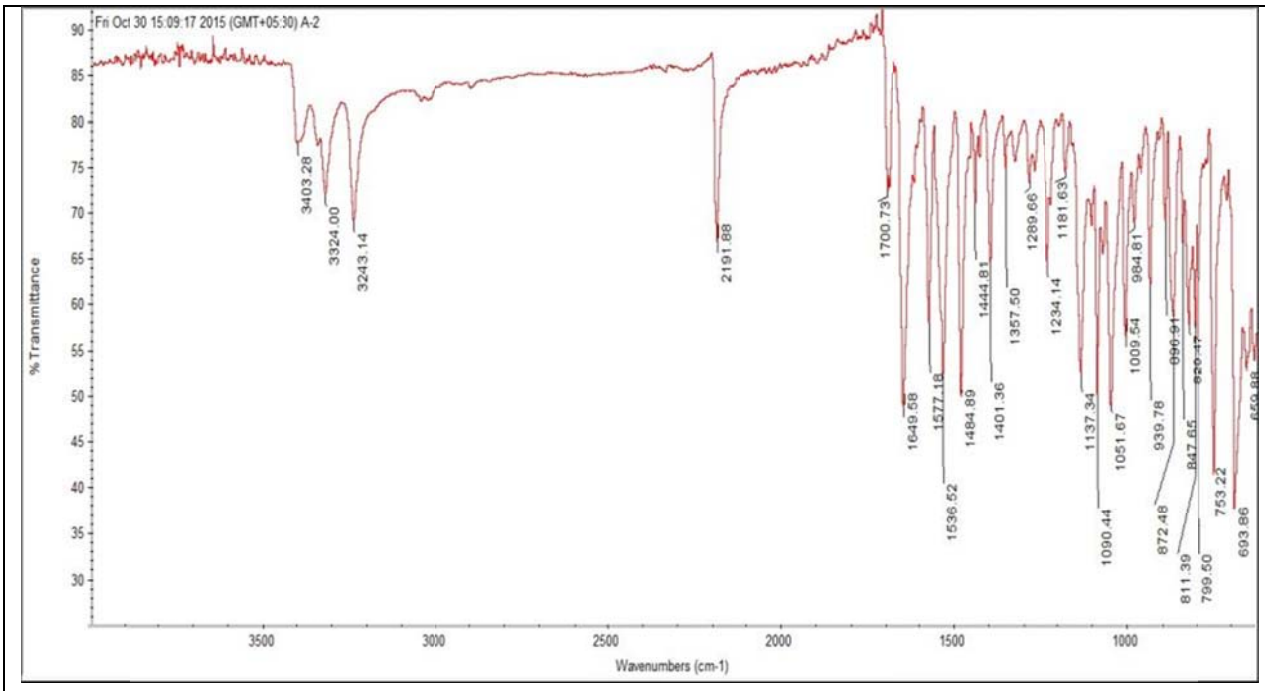

Figure 7. FT-IR spectrum of **1b**

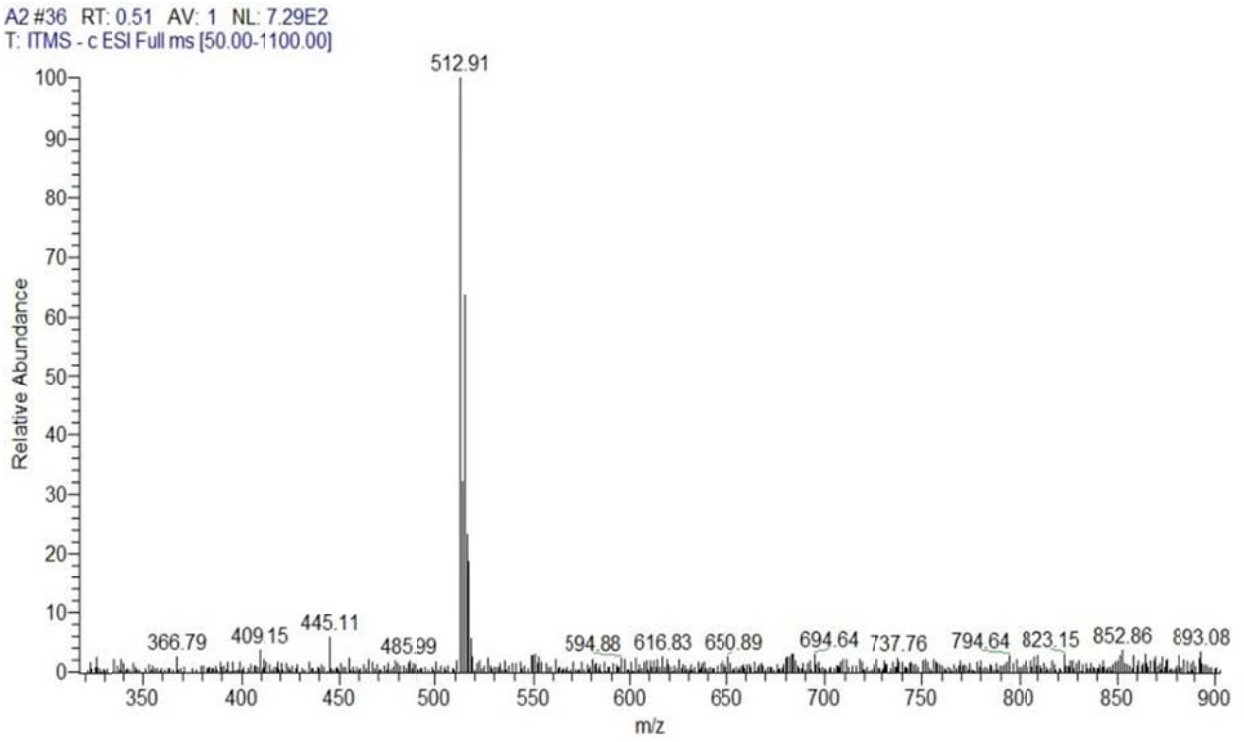

Figure 8. ESI-massof **1b**

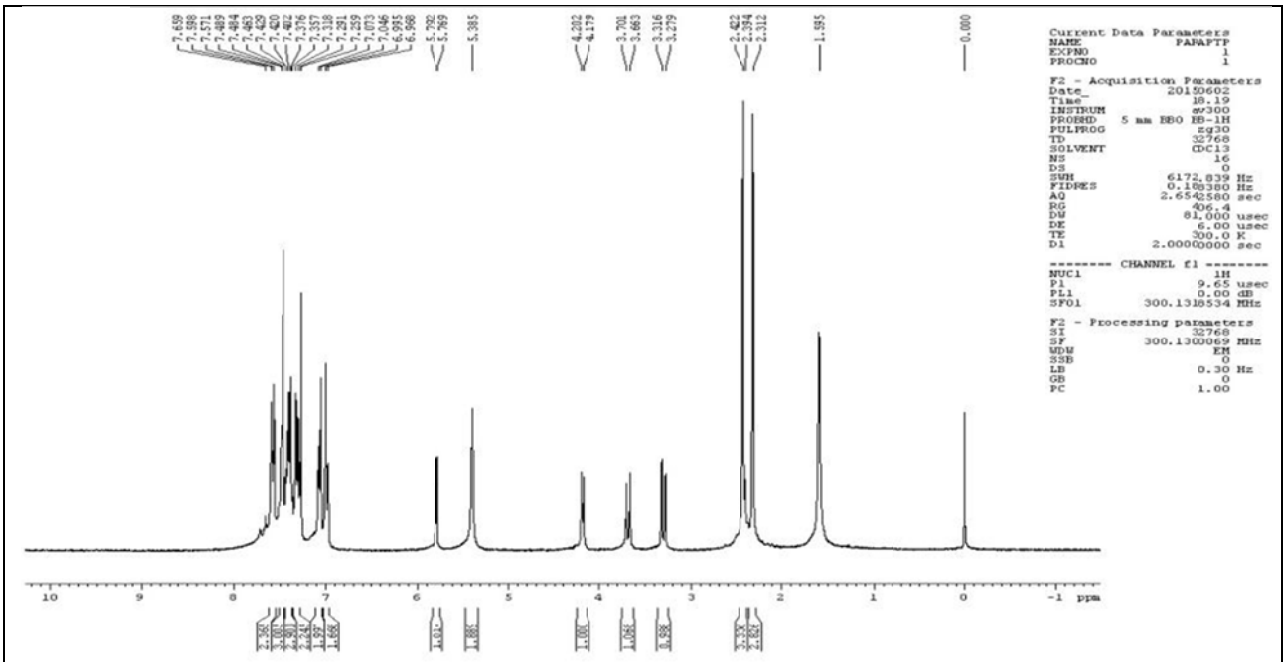

Figure 9. ^{1}H NMR spectrum of **1c**

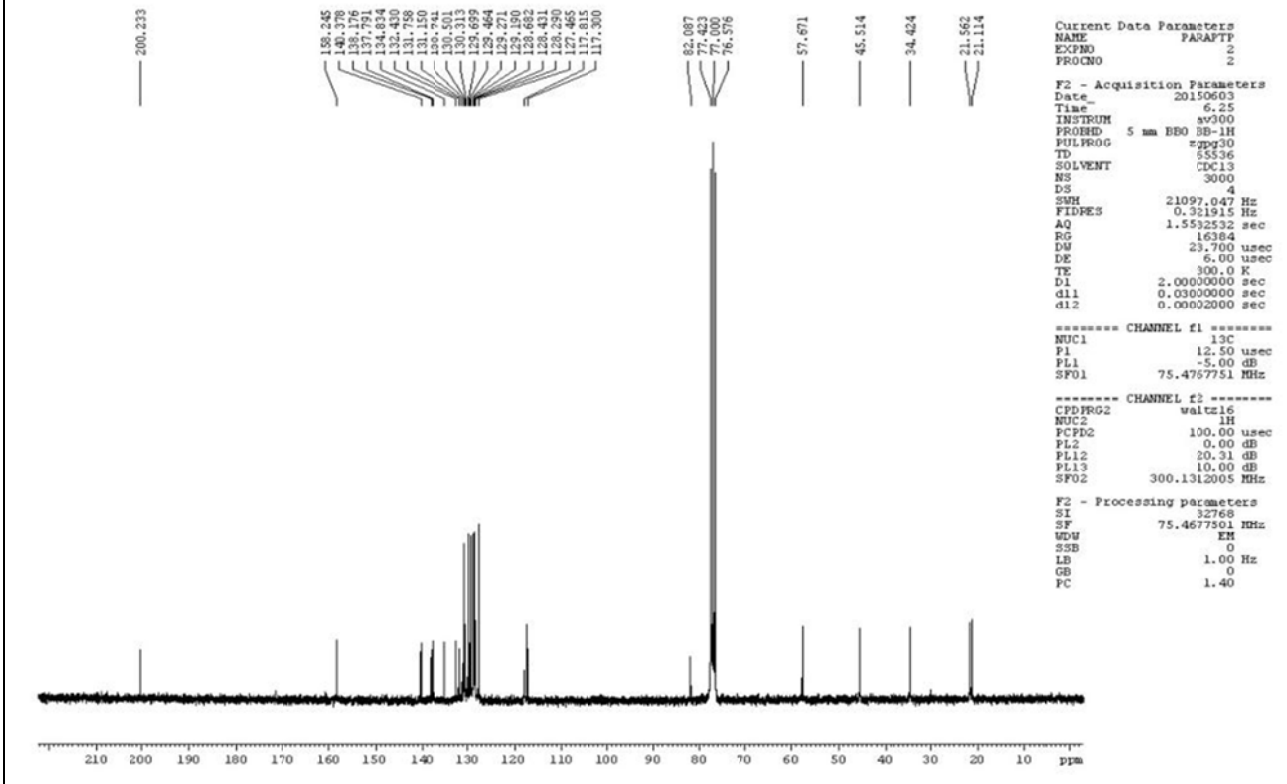

Figure 10. ^{13}C NMR spectrum of **1c**

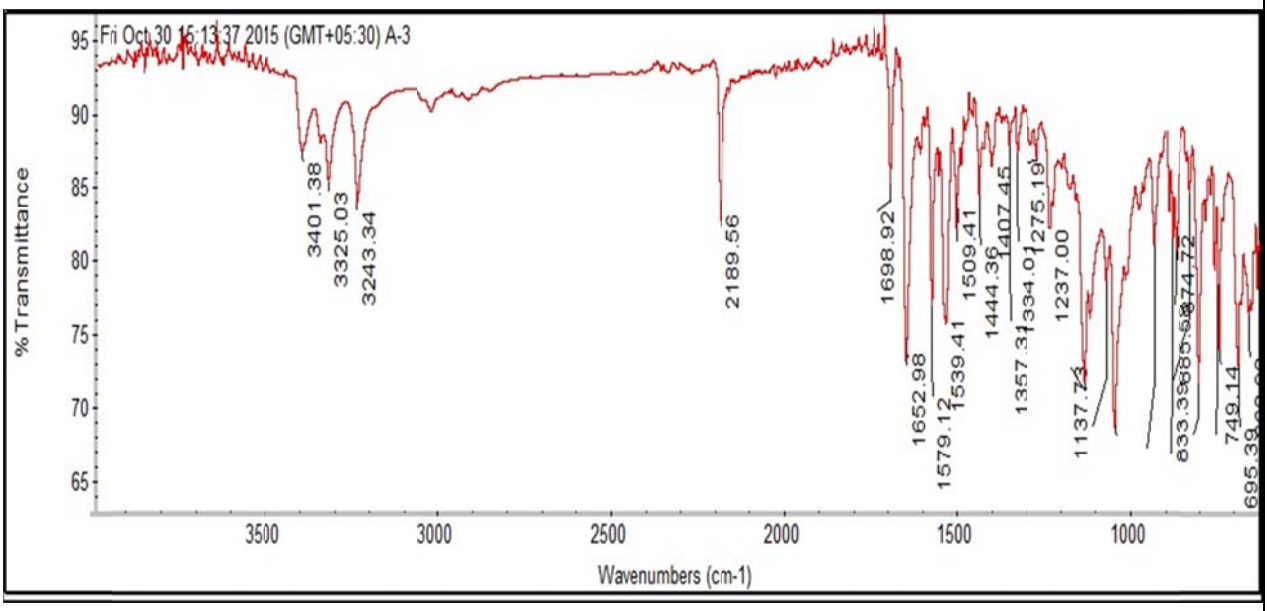

Figure 11. FT-IR spectrum of **1c**

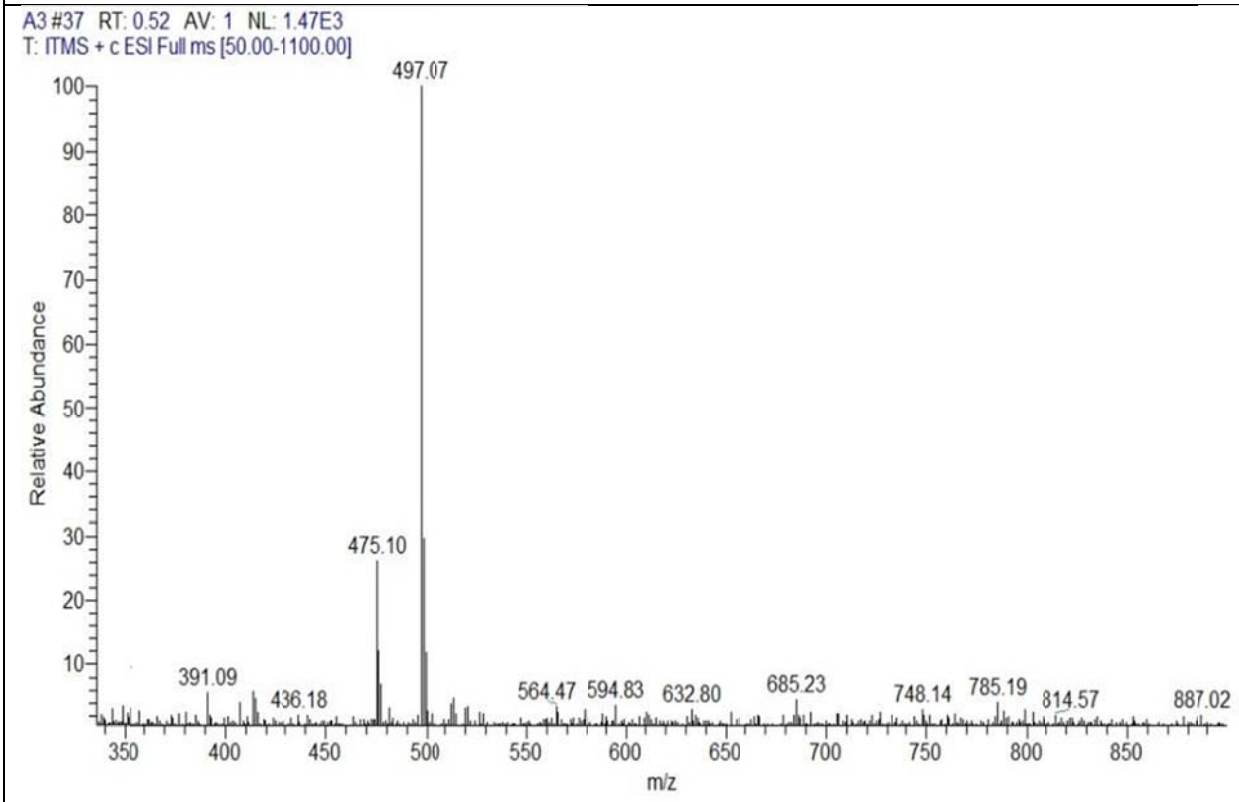

Figure 12. ESI-mass of **1c**

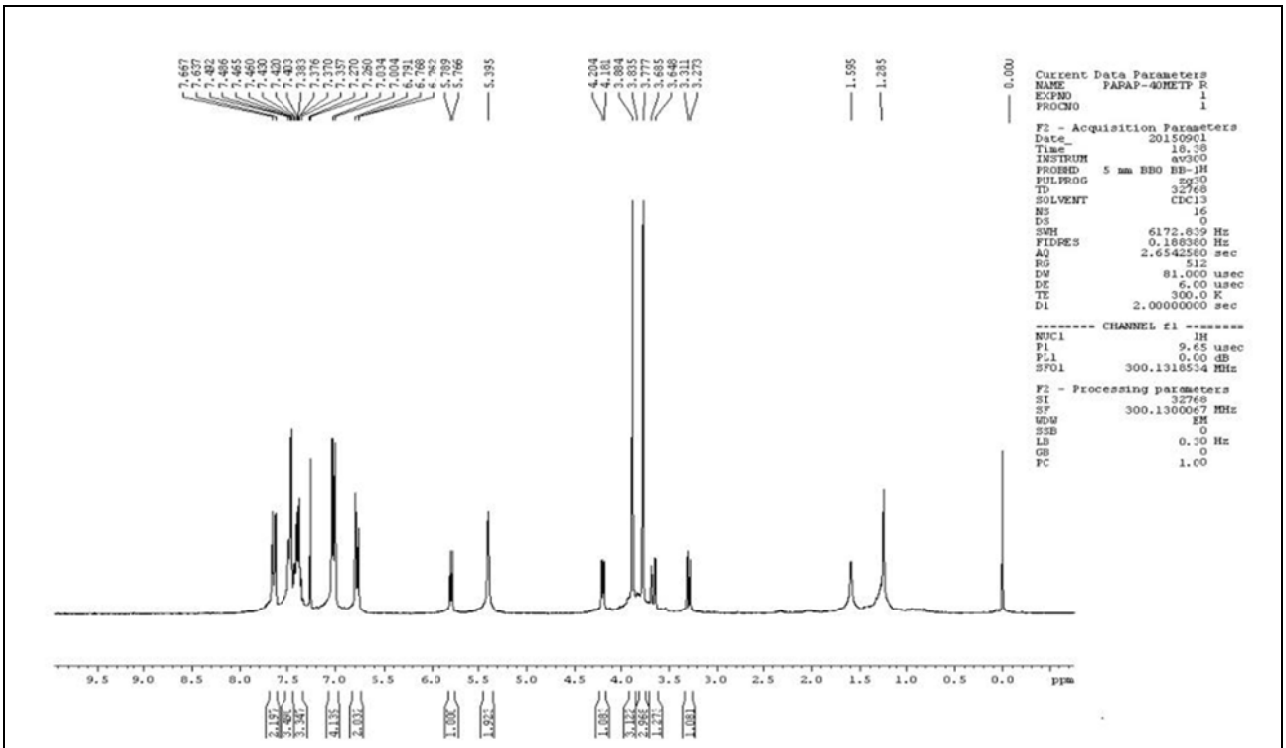

Figure 13. ^{1}H NMR spectrum of **1d**

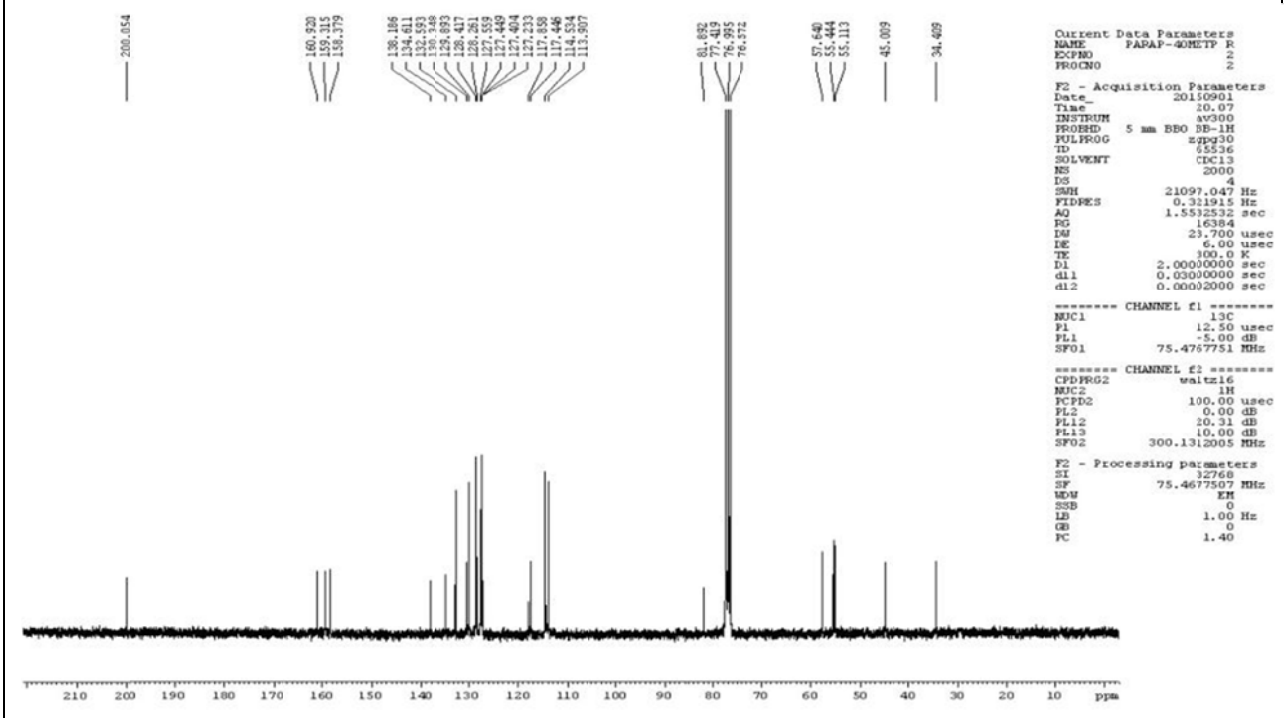

Figure 14. ^{13}C NMR spectrum of **1d**

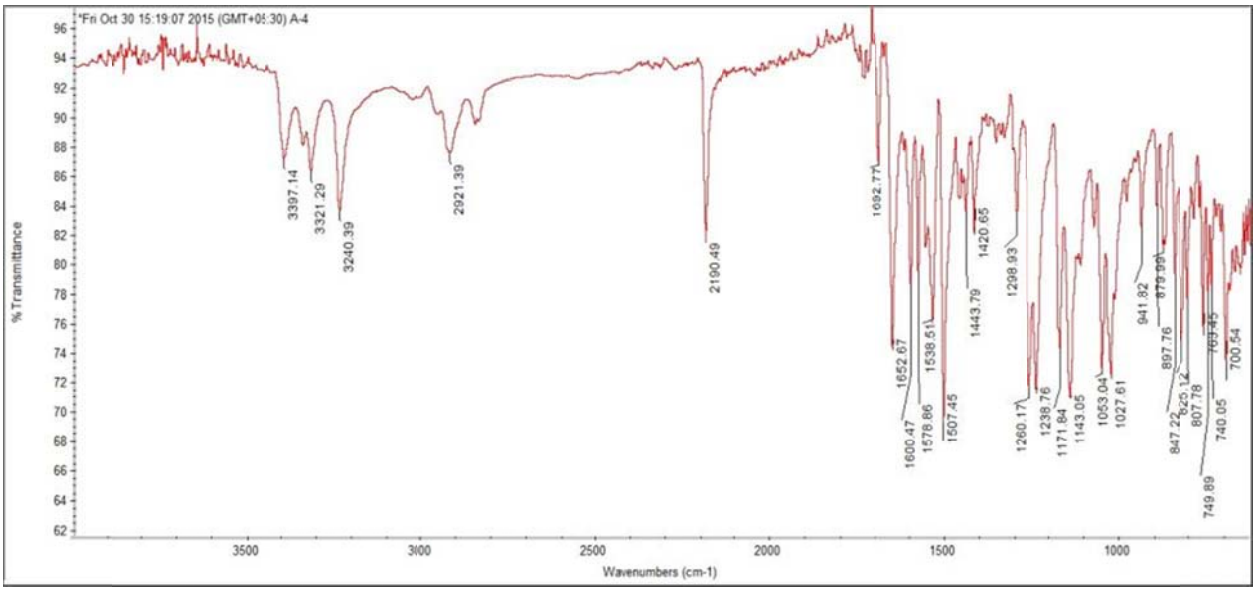

Figure 15. FT-IR spectrum of **1d**

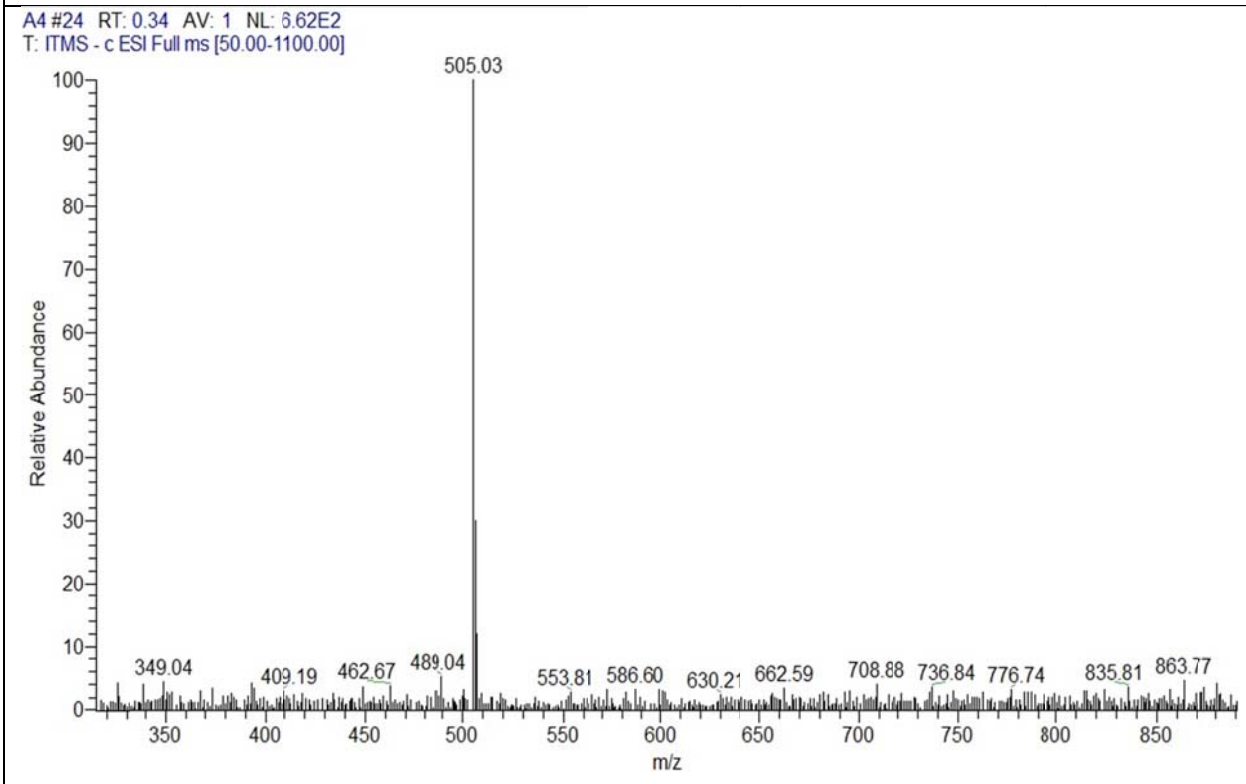

Figure 16. ESI-mass of **1d**

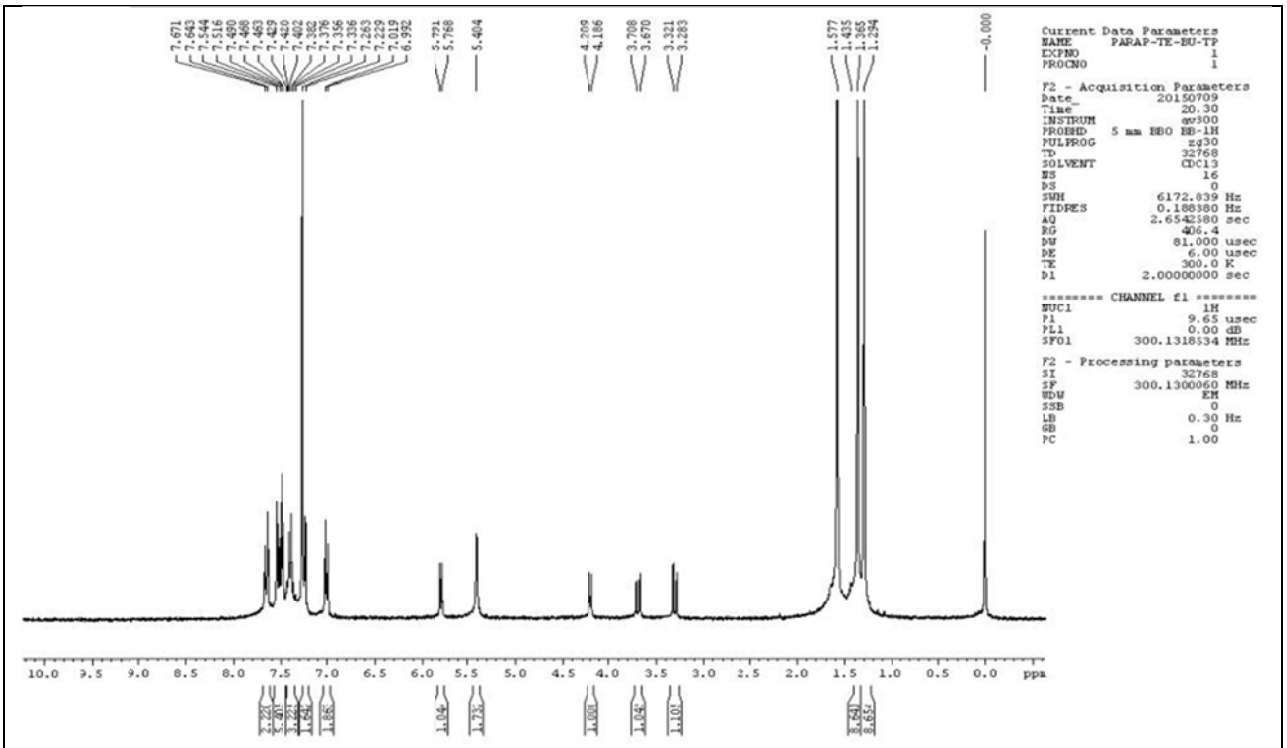

Figure 17. ^{1}H NMR spectrum of **1e**

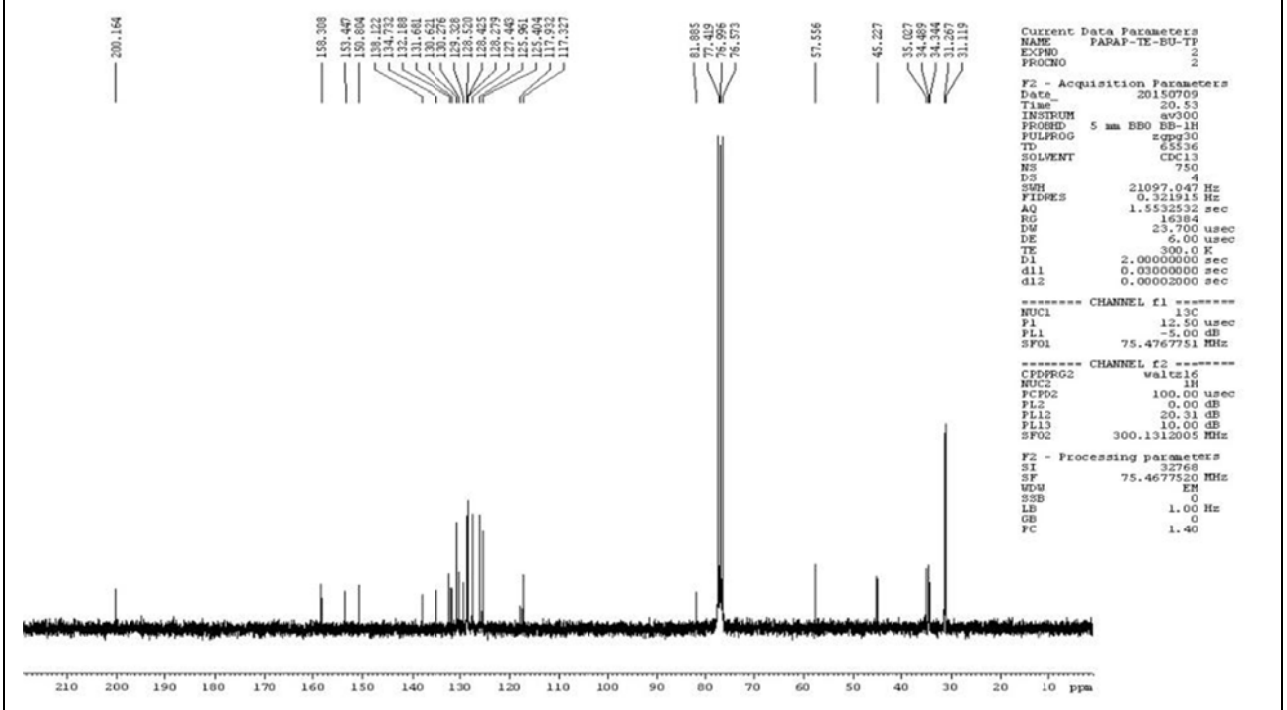

Figure 18. ^{13}C NMR spectrum of **1e**

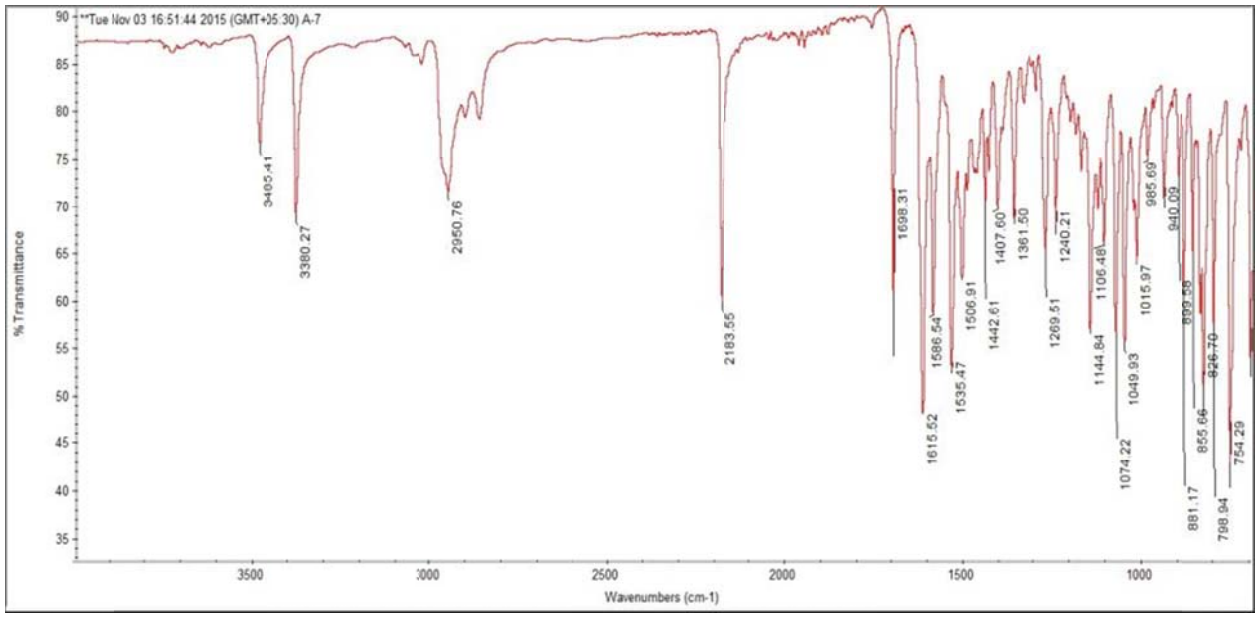

Figure 19. FT-IR spectrum of **1e**

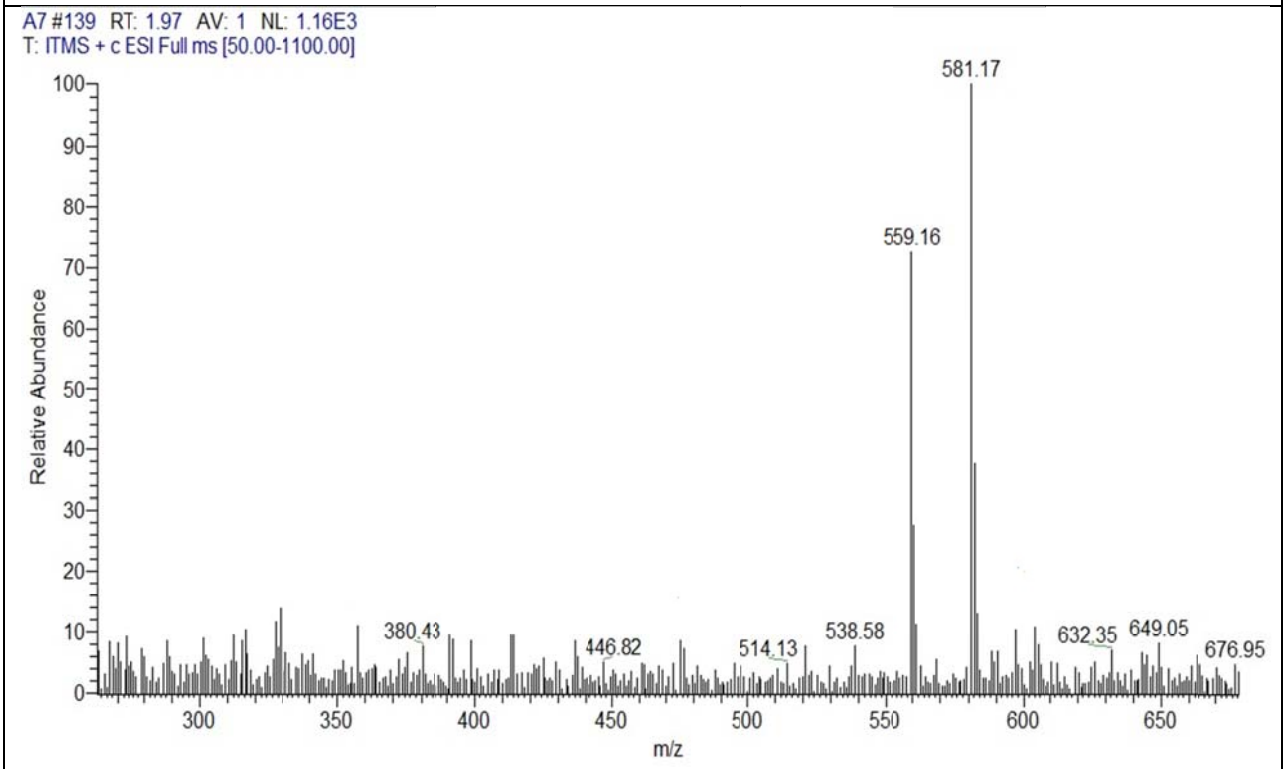

Figure 20. ESI-massof **1e**

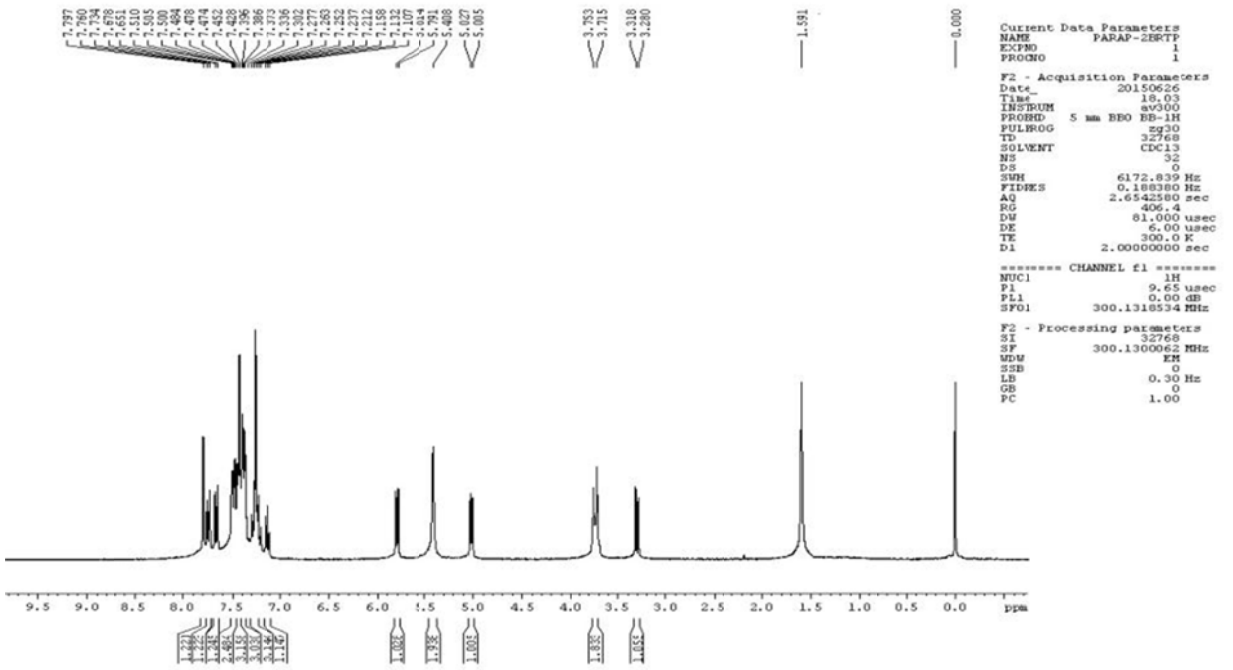

Figure 21.[1]H NMR spectrum of **1f**

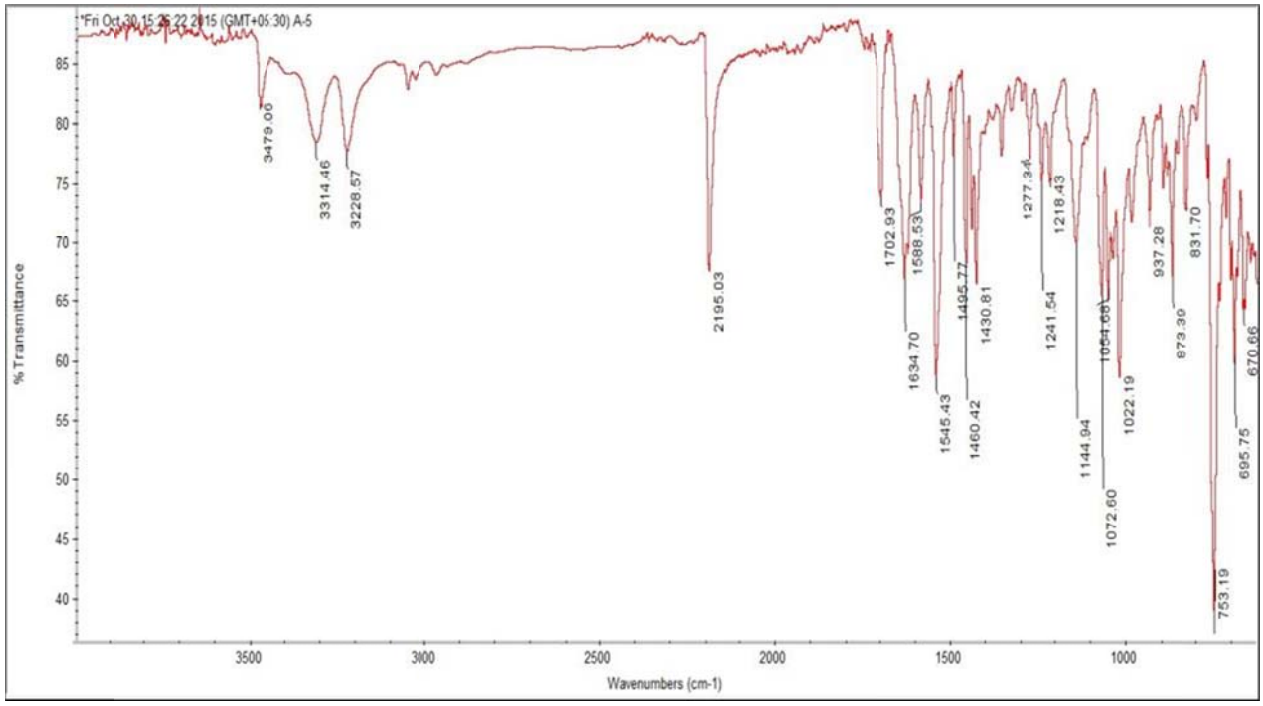

Figure 22. FT-IR spectrum of **1f**

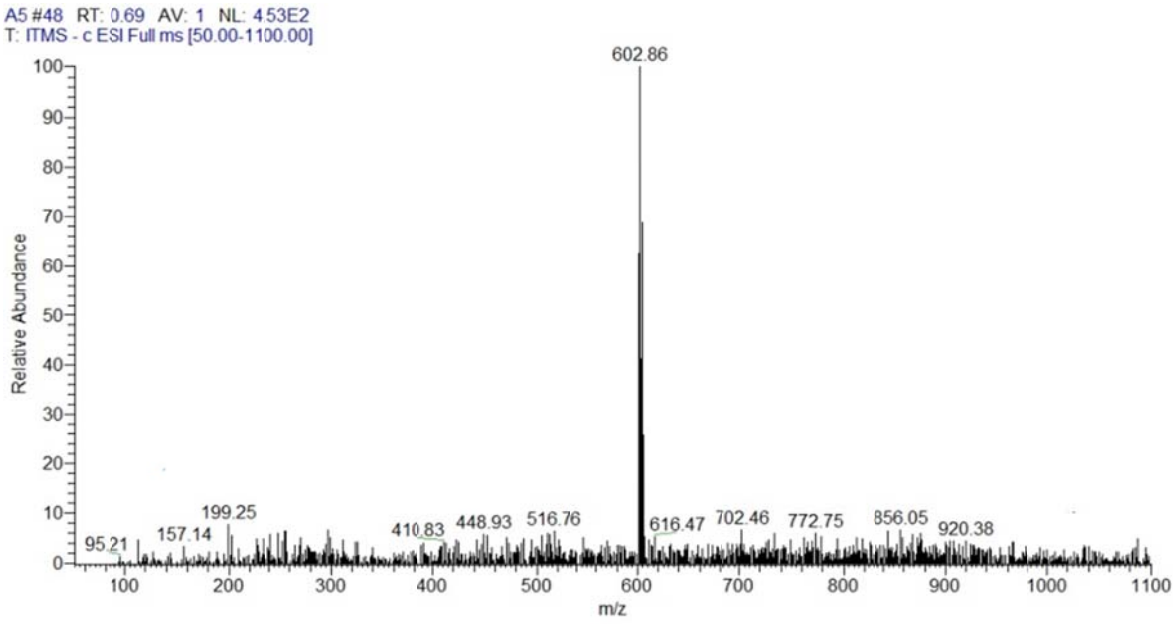

Figure 23. ESI-mass of **1f**

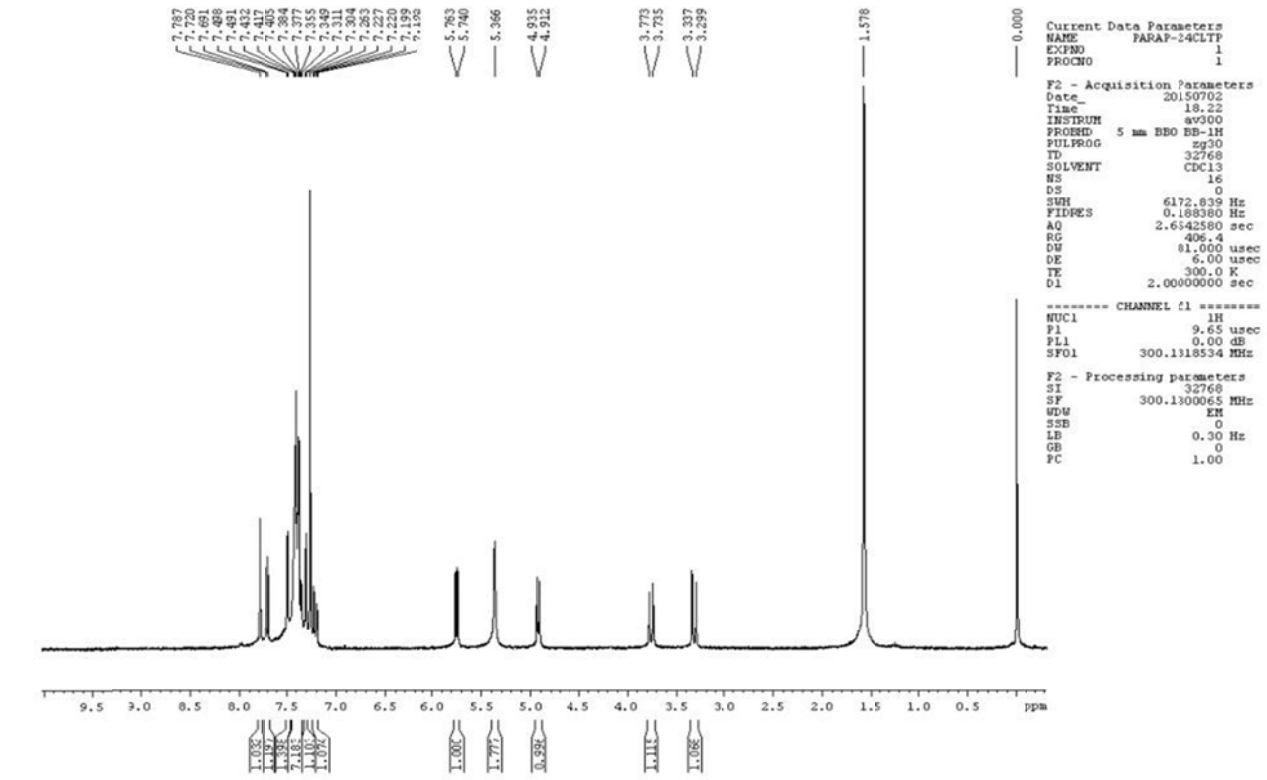

Figure 24.[1]H NMR spectrum of **1g**

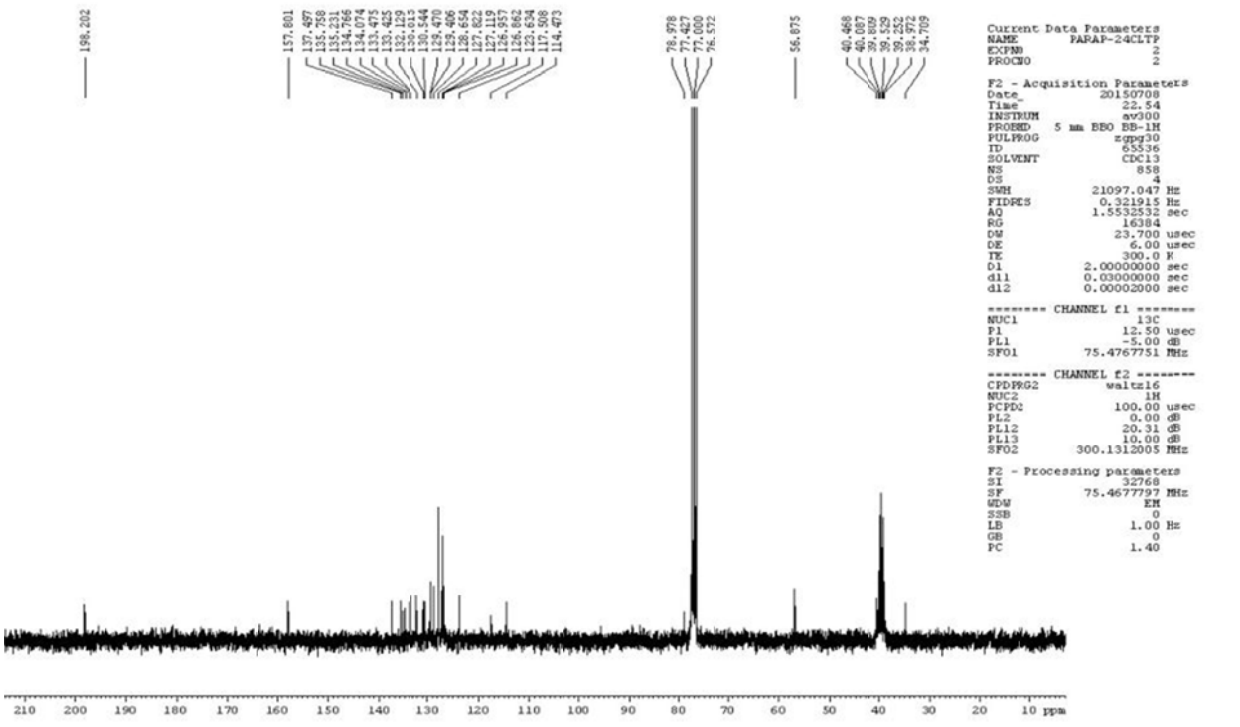

Figure 25. ^{13}C NMR spectrum of **1g**

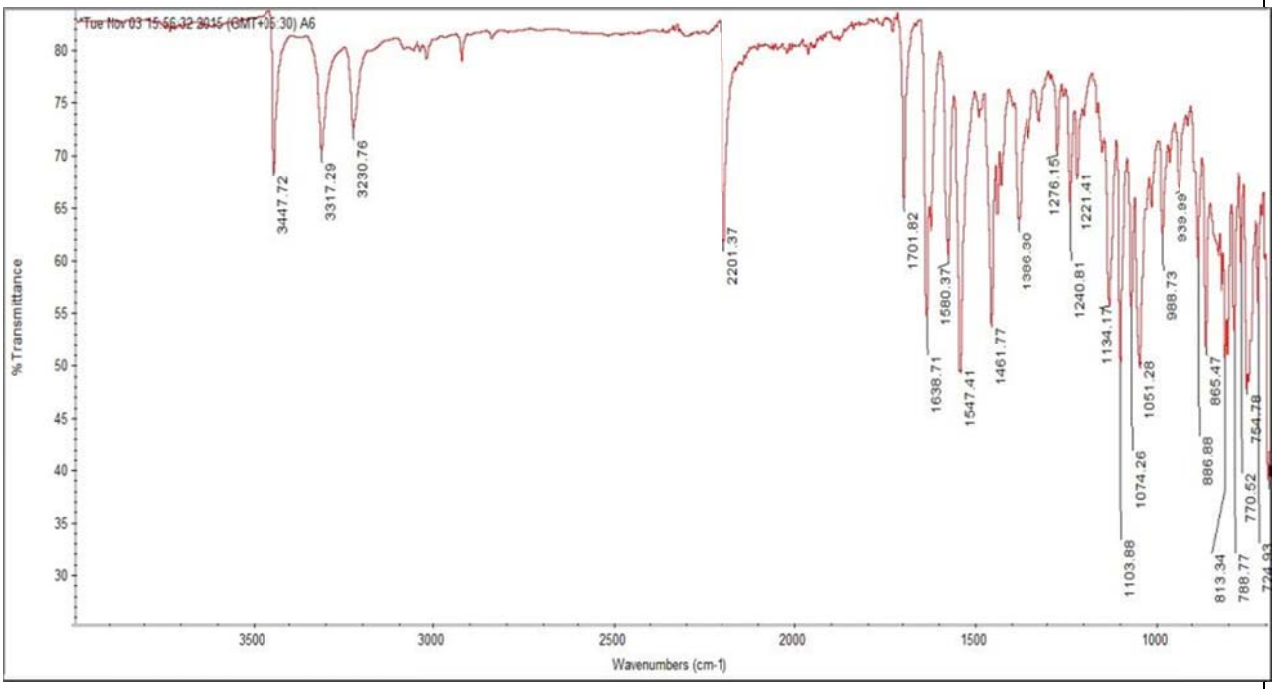

Figure 26. FT-IR spectrum of **1g**

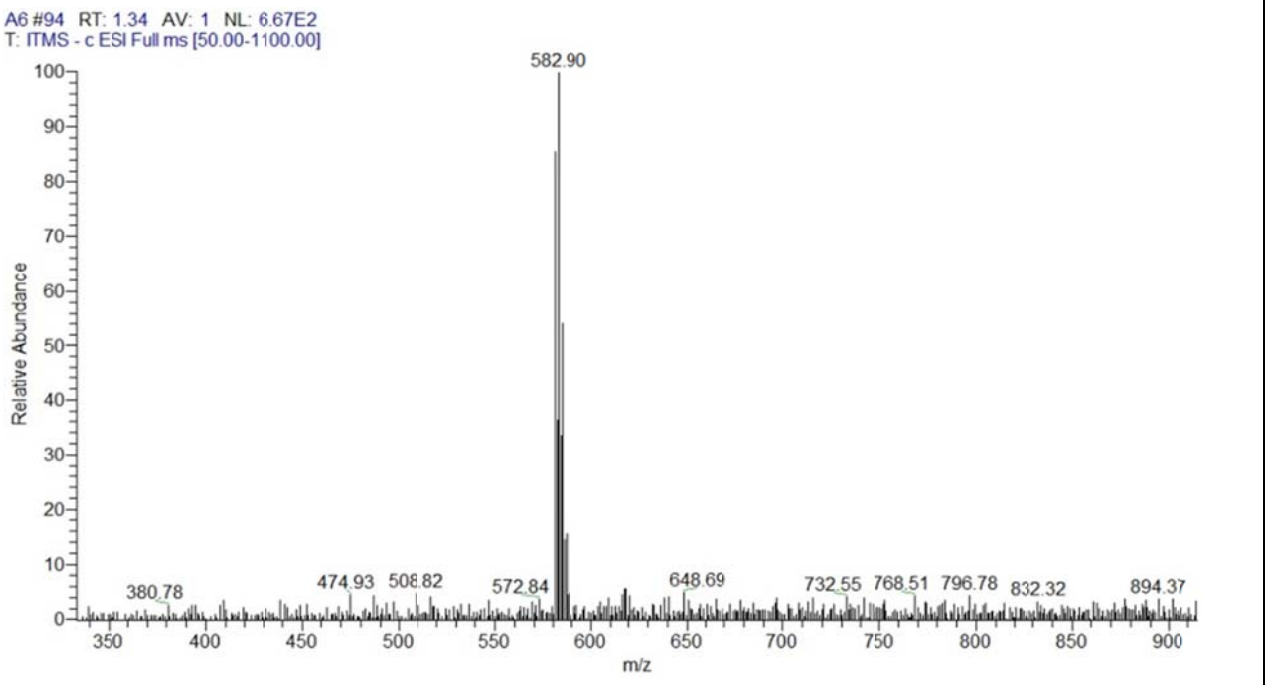

Figure 27. ESI-mass of **1g**

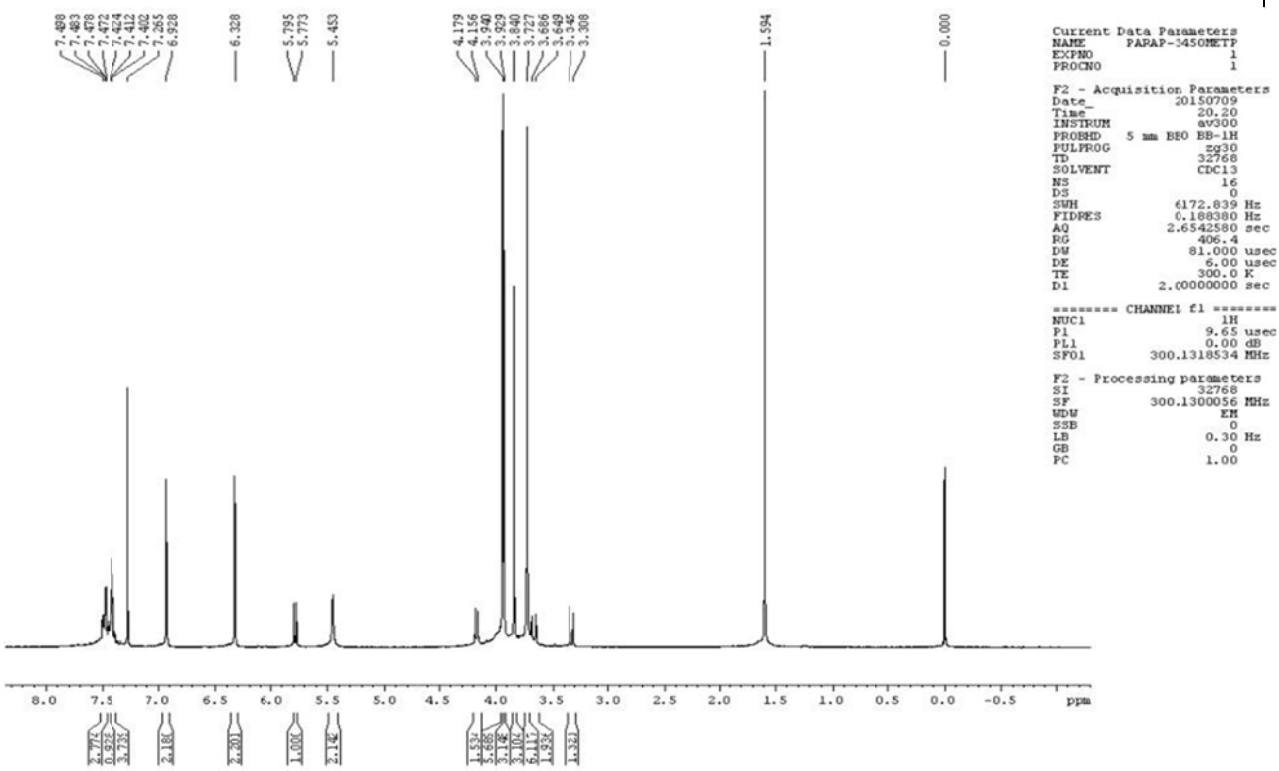

Figure 28. ^{1}H NMR spectrum of **1h**

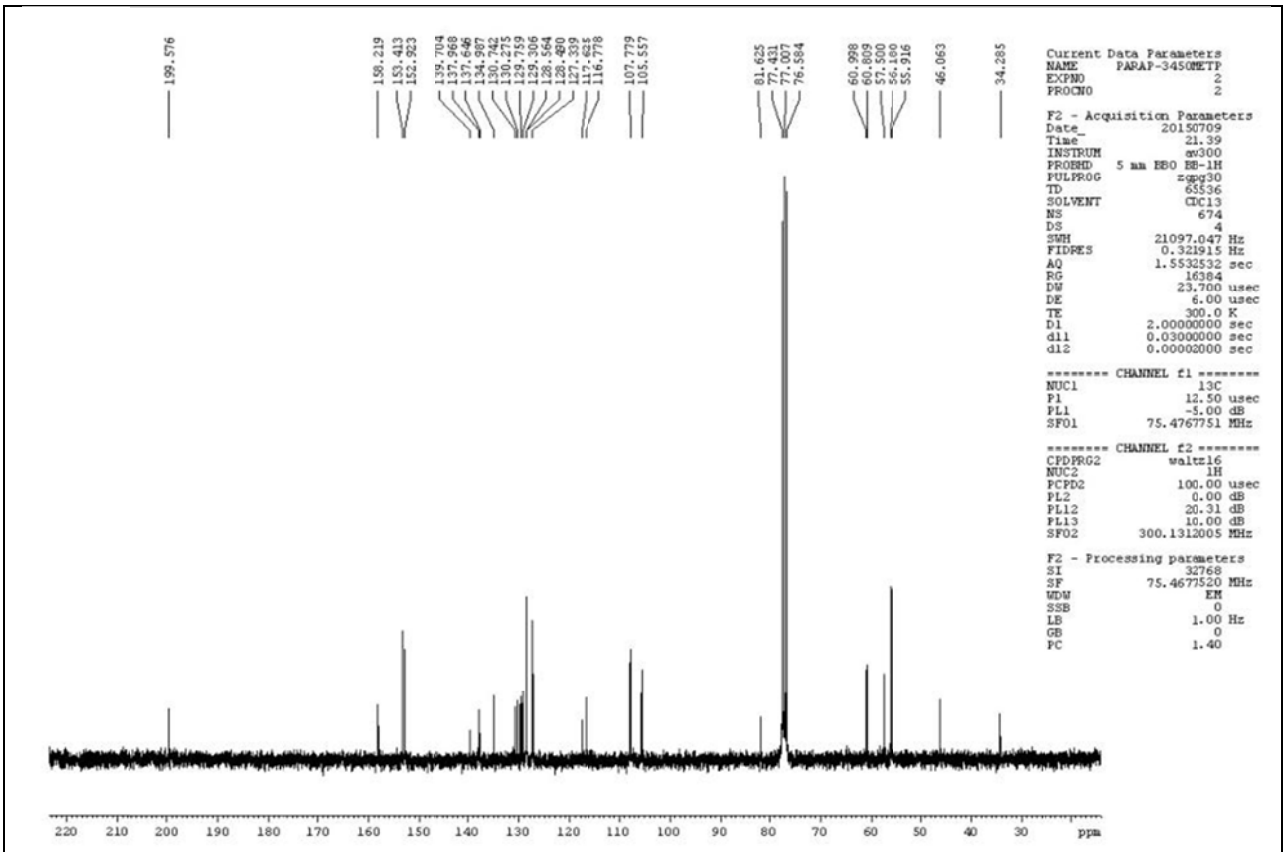

Figure 29. ^{13}C NMR spectrum of **1h**

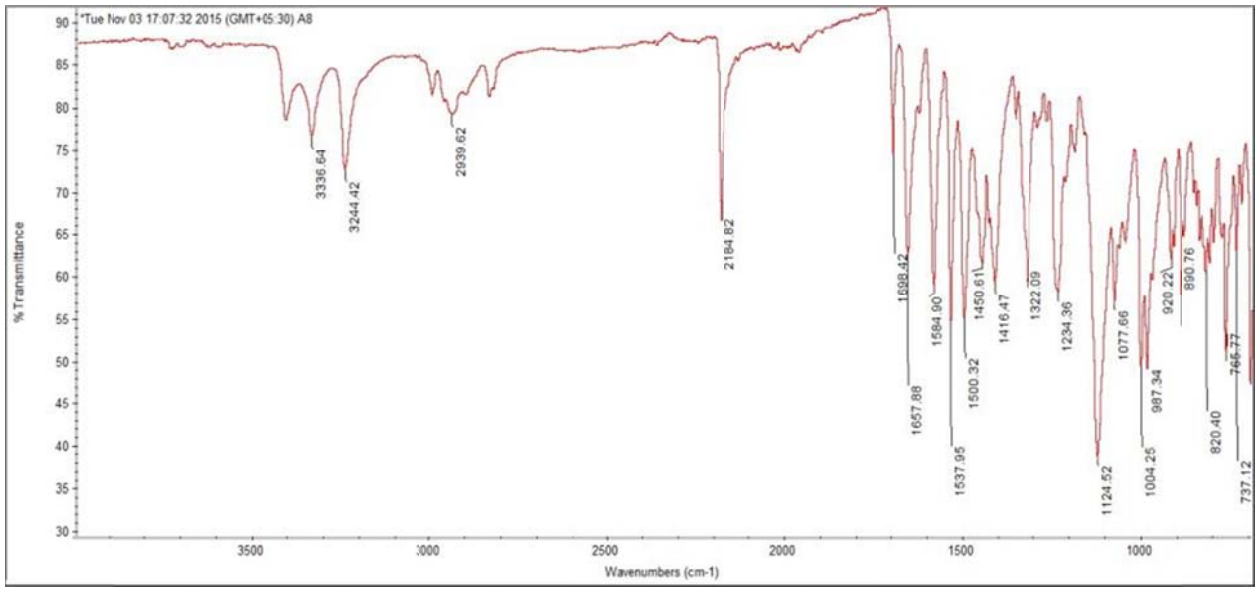

Figure 30. FT-IR spectrum of **1h**

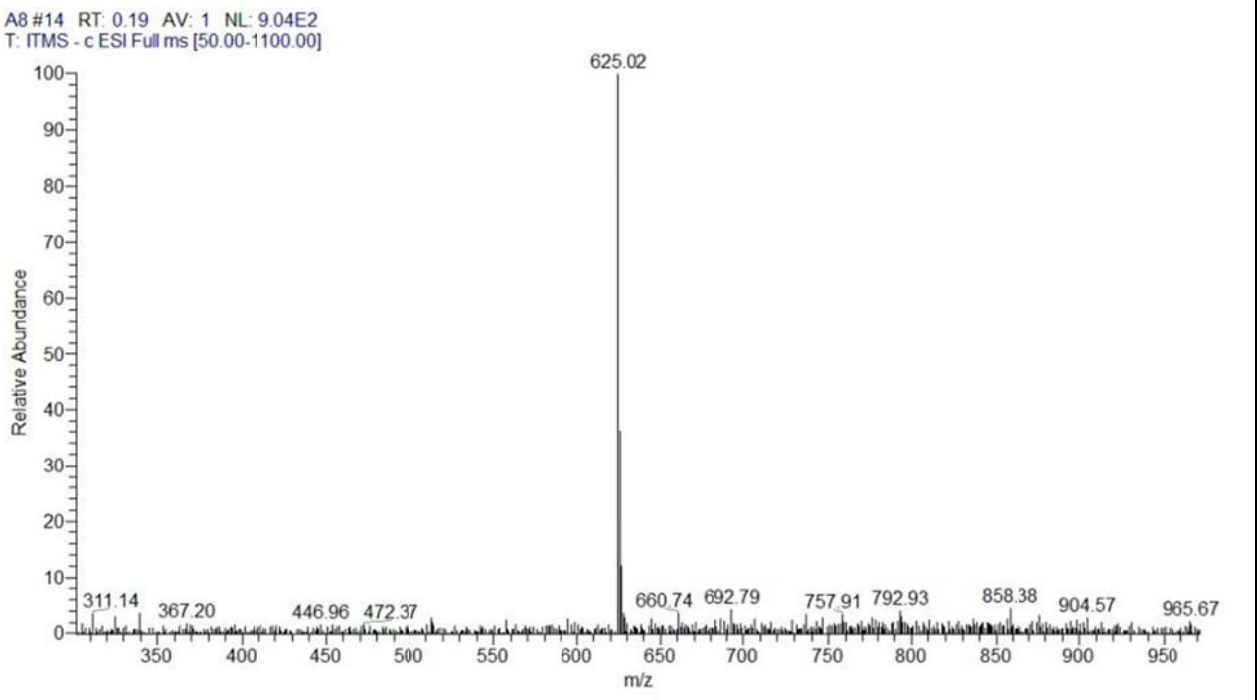

Figure 31. ESI-mass of **1h**

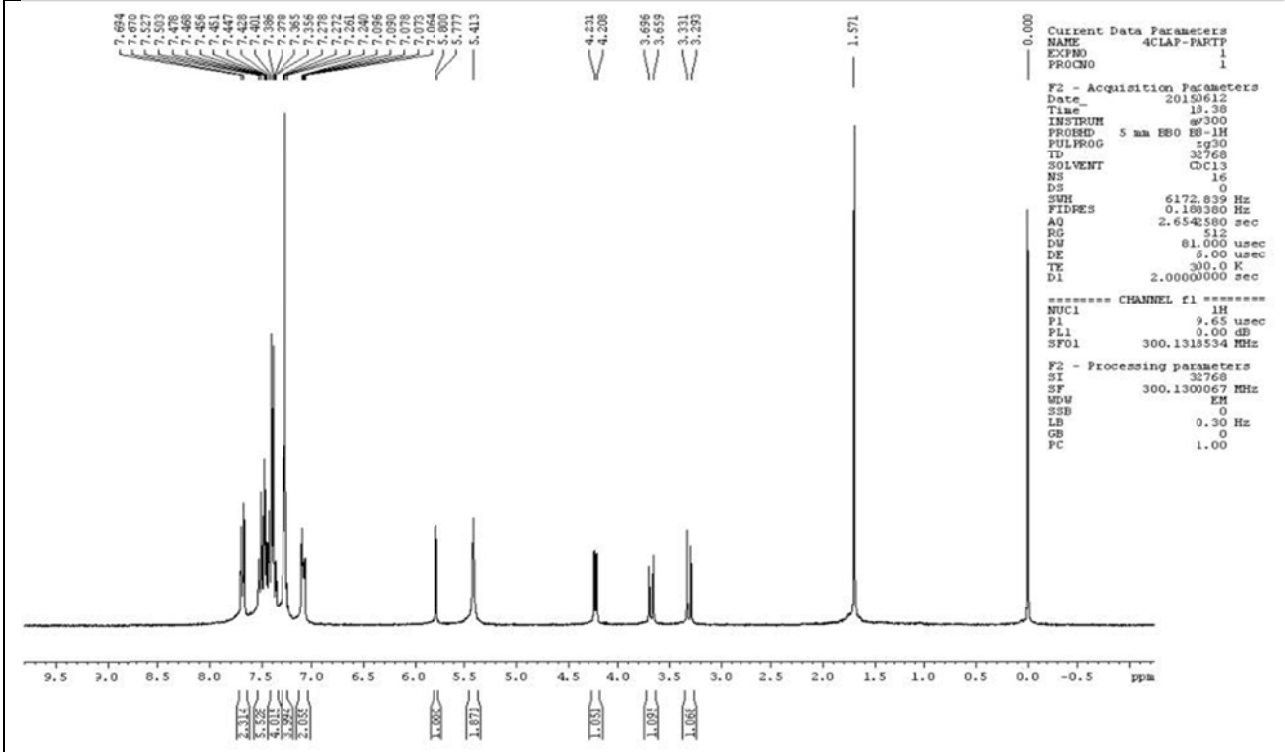

Figure 32. ^{1}H NMR spectrum of **1i**

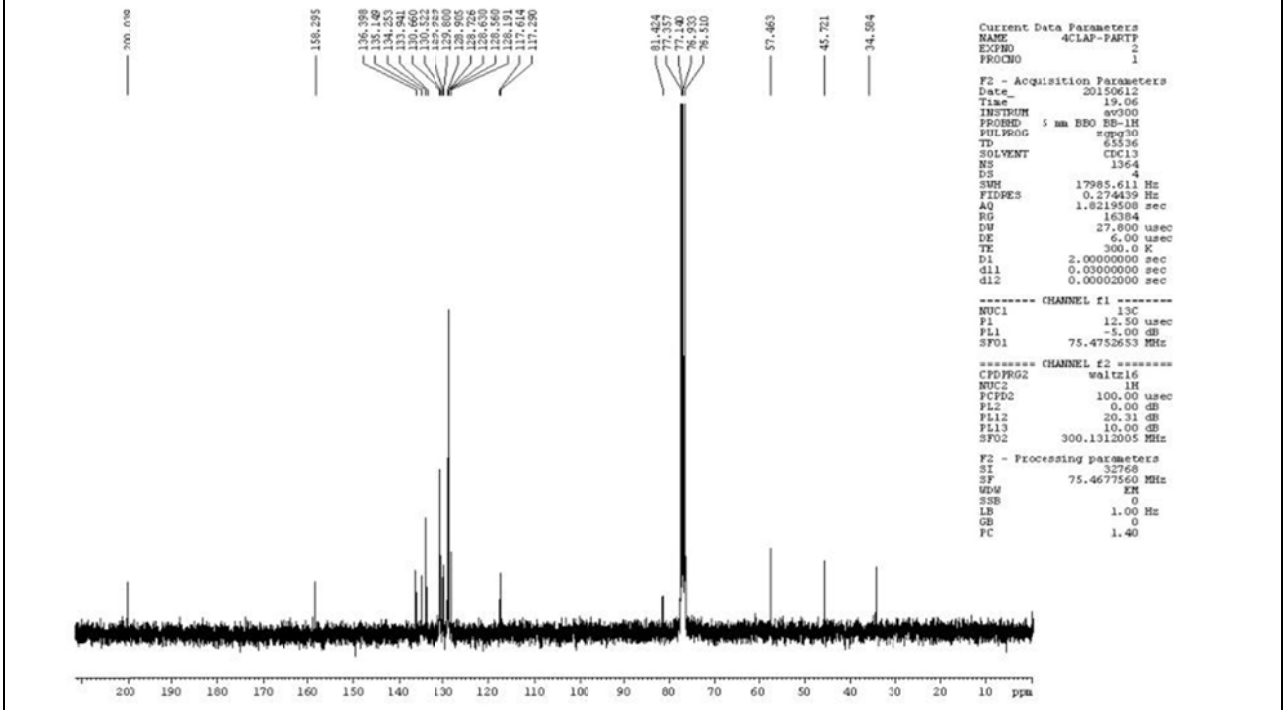

Figure 33.[13]CNMR spectrum of **1i**

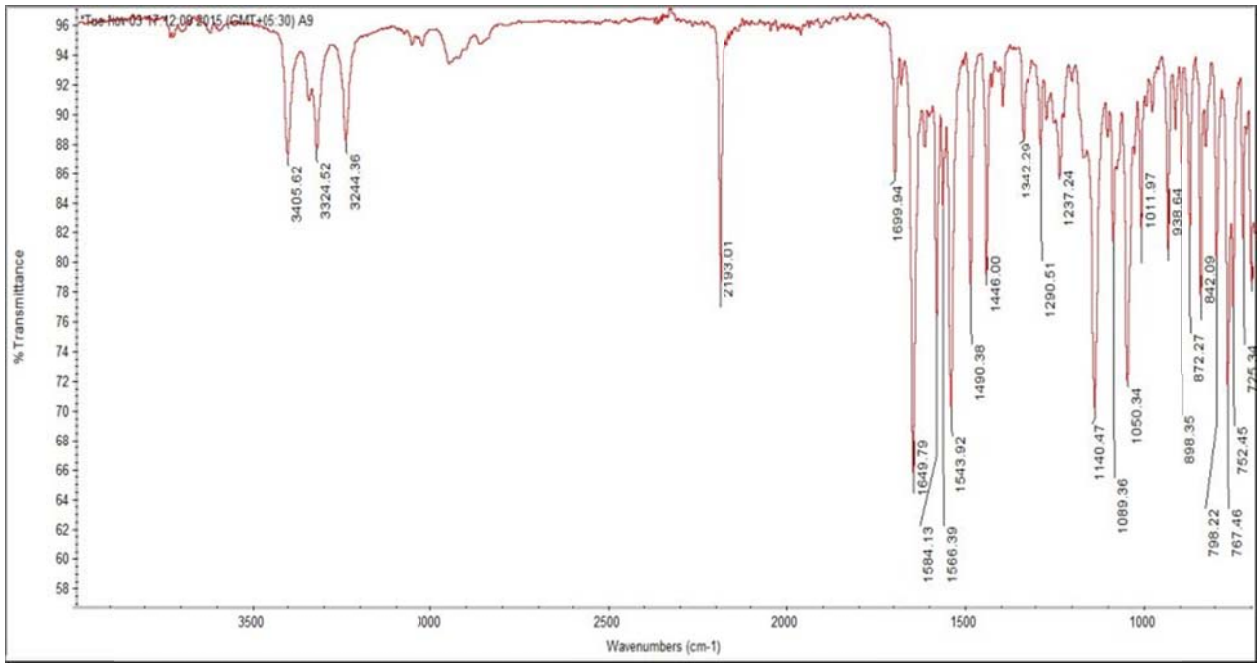

Figure 34. FT-IR spectrum of **1i**

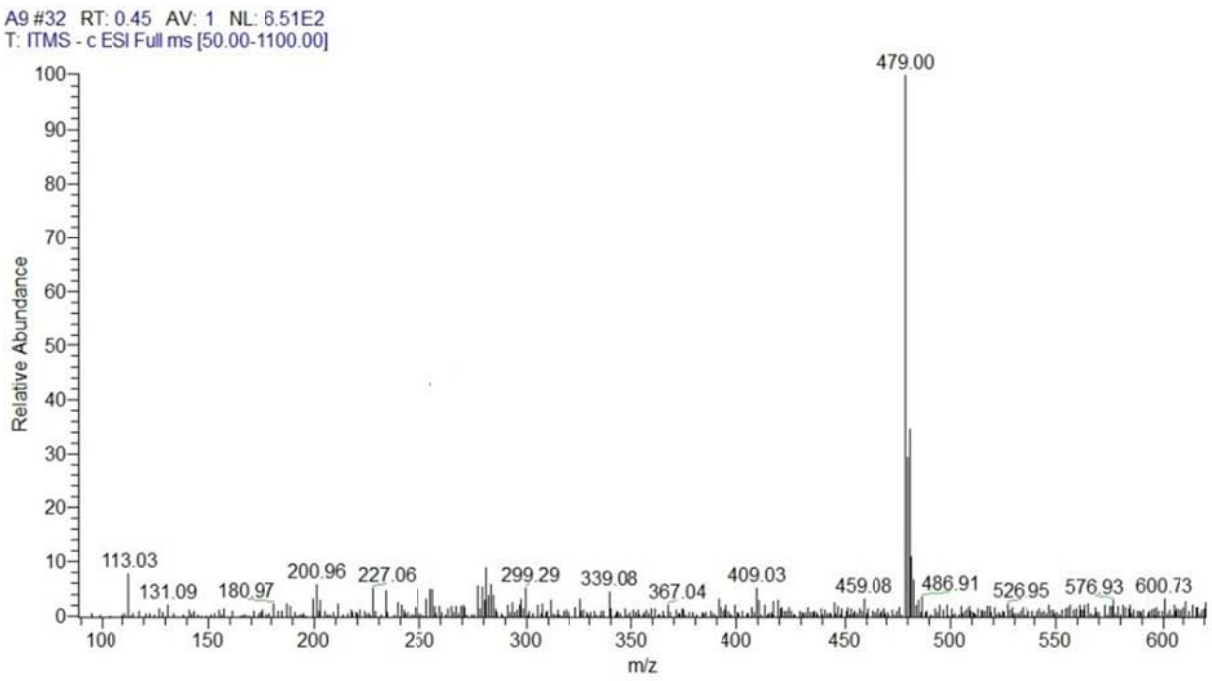

Figure 35. ESI-mass of **1i**

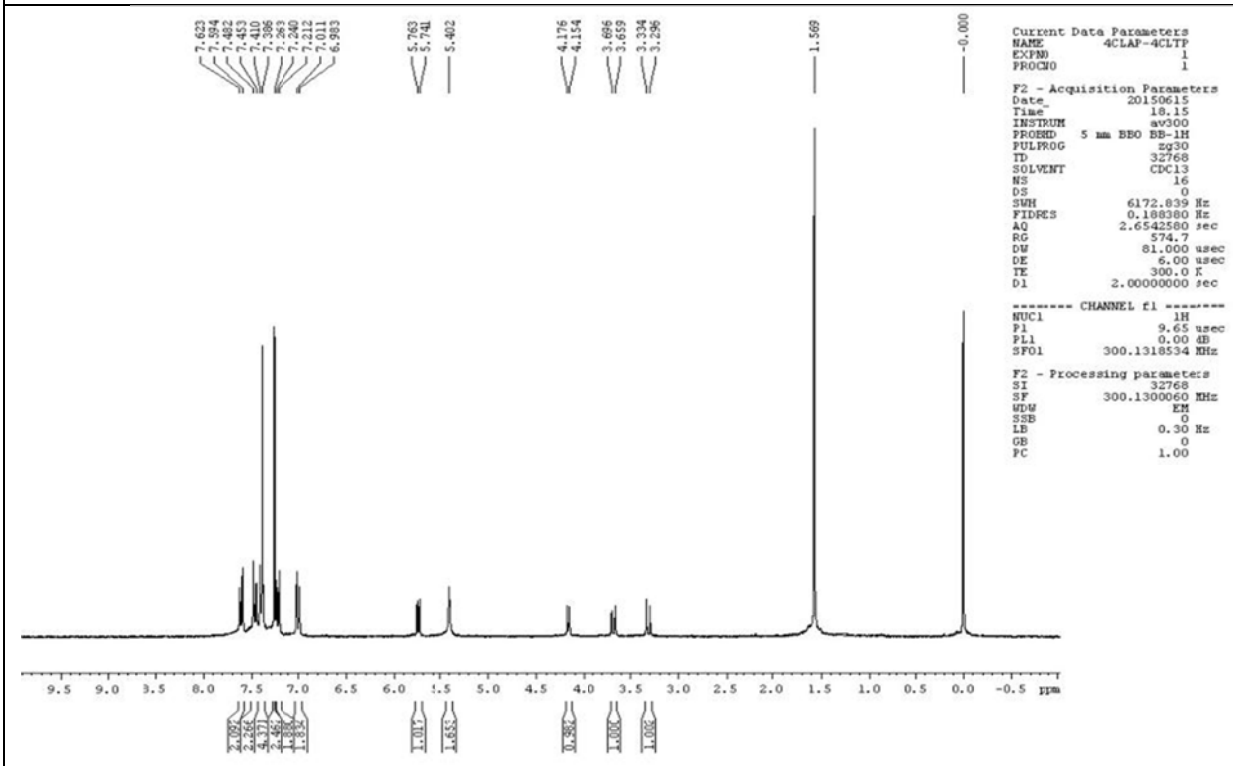

Figure 36. ^{1}H NMR spectrum of **1j**

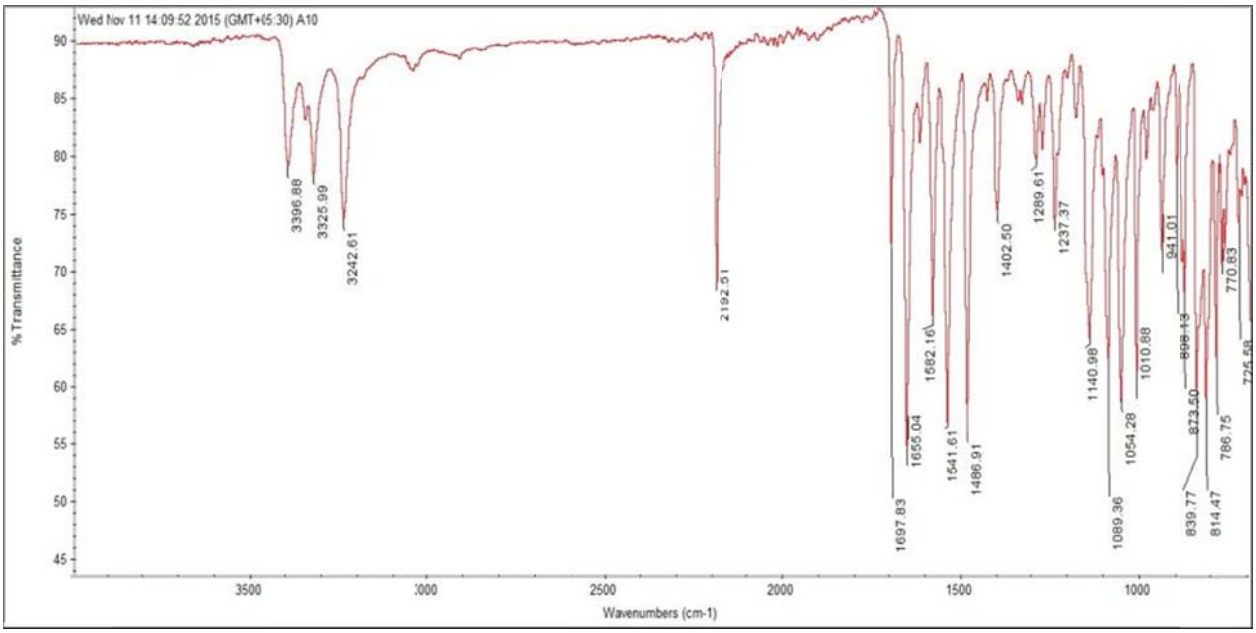

Figure 37. FT-IR spectrum of **1j**

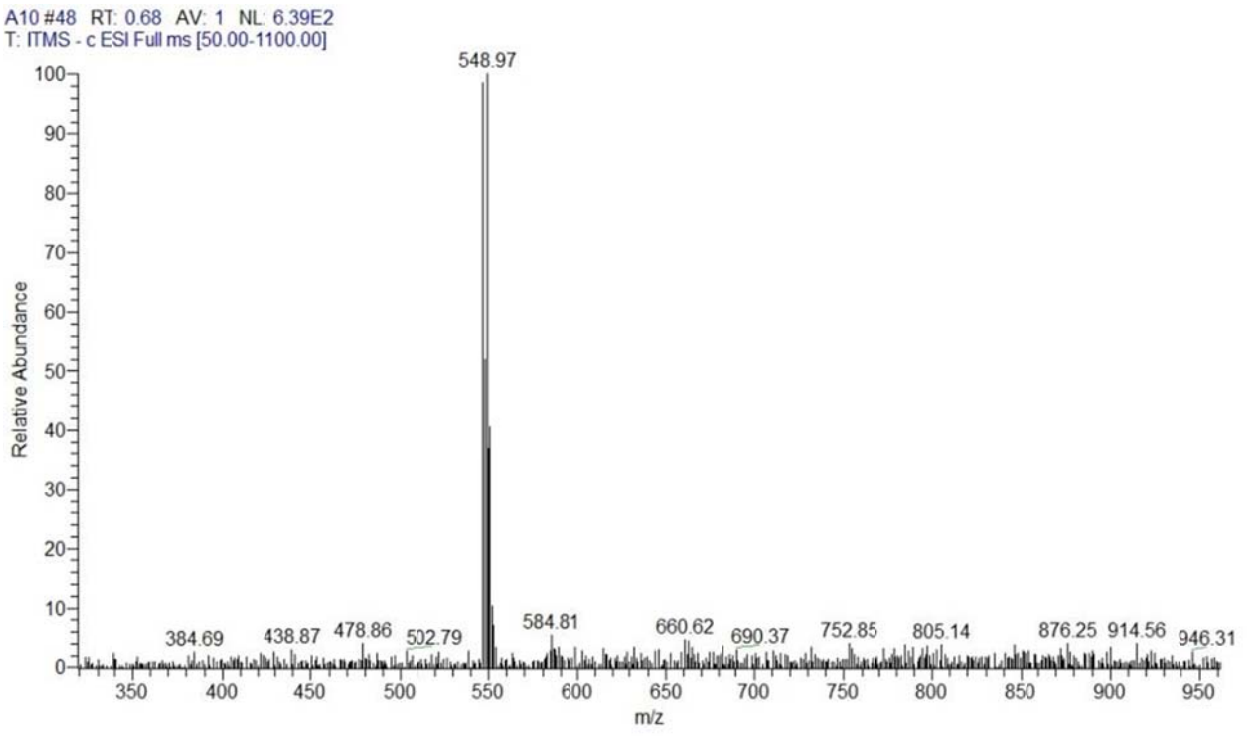

Figure 38. ESI-massof **1j**

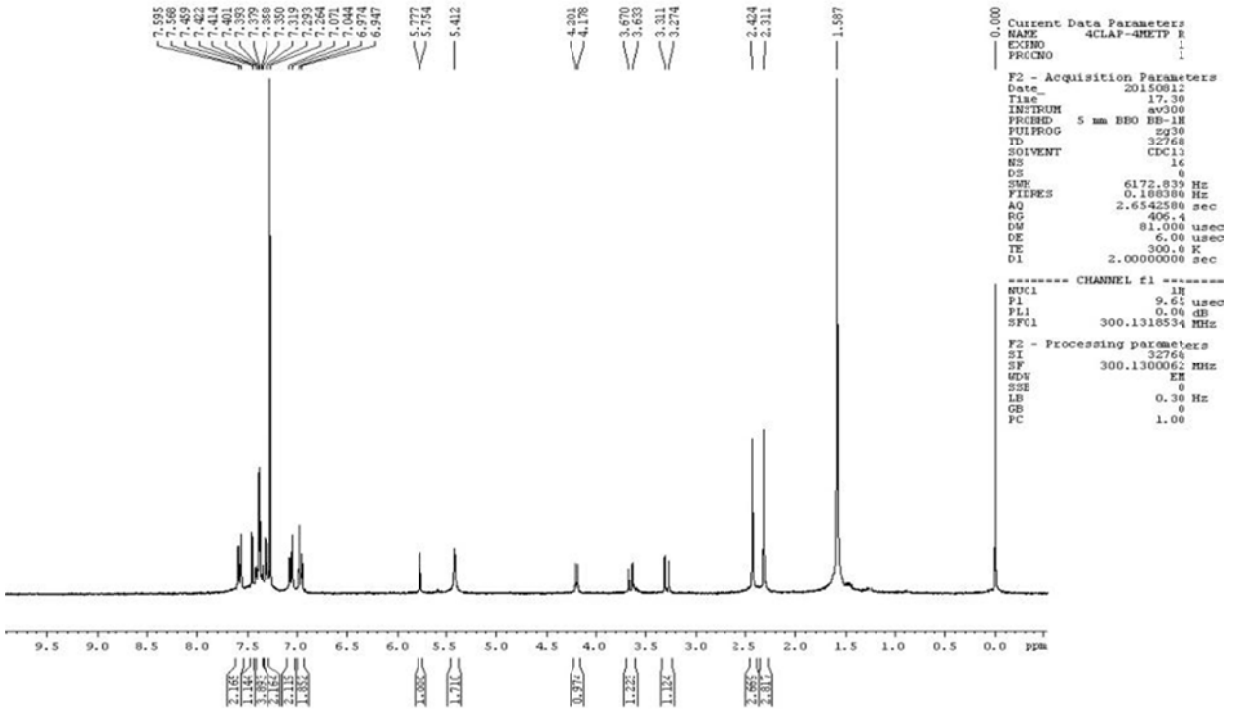

Figure 39.[1]H NMR spectrum of **1k**

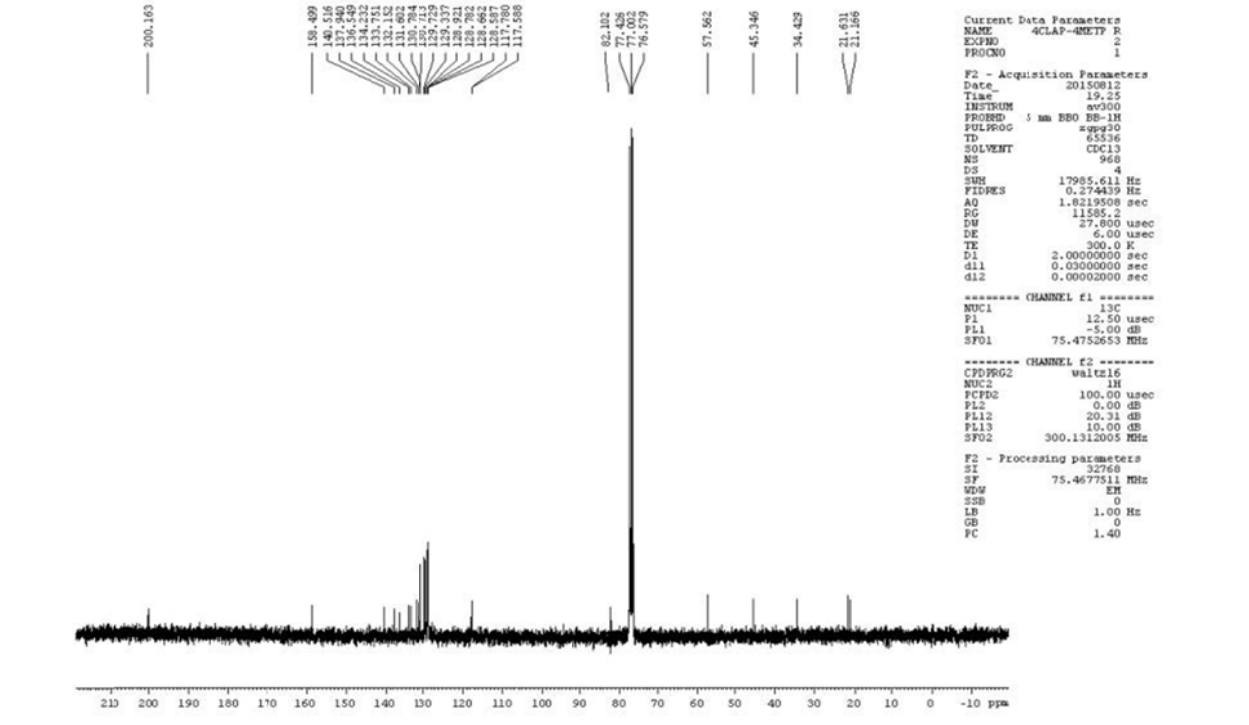

Figure 40.[13]CNMR spectrum of **1k**

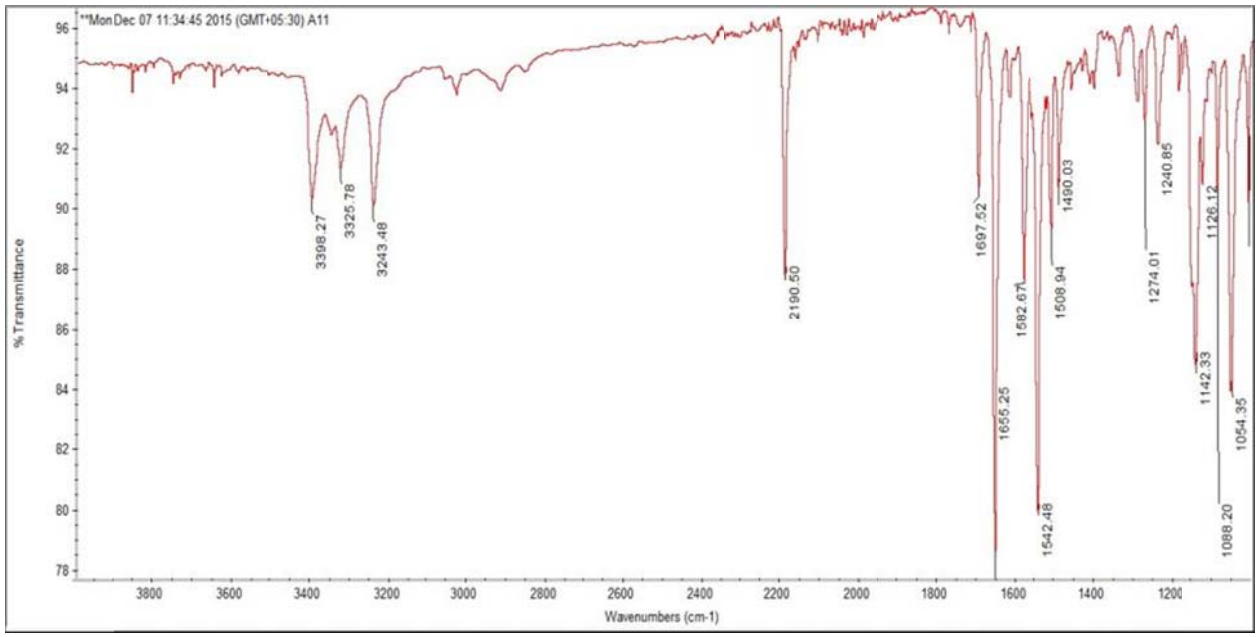

Figure 41. FT-IR spectrum of **1k**

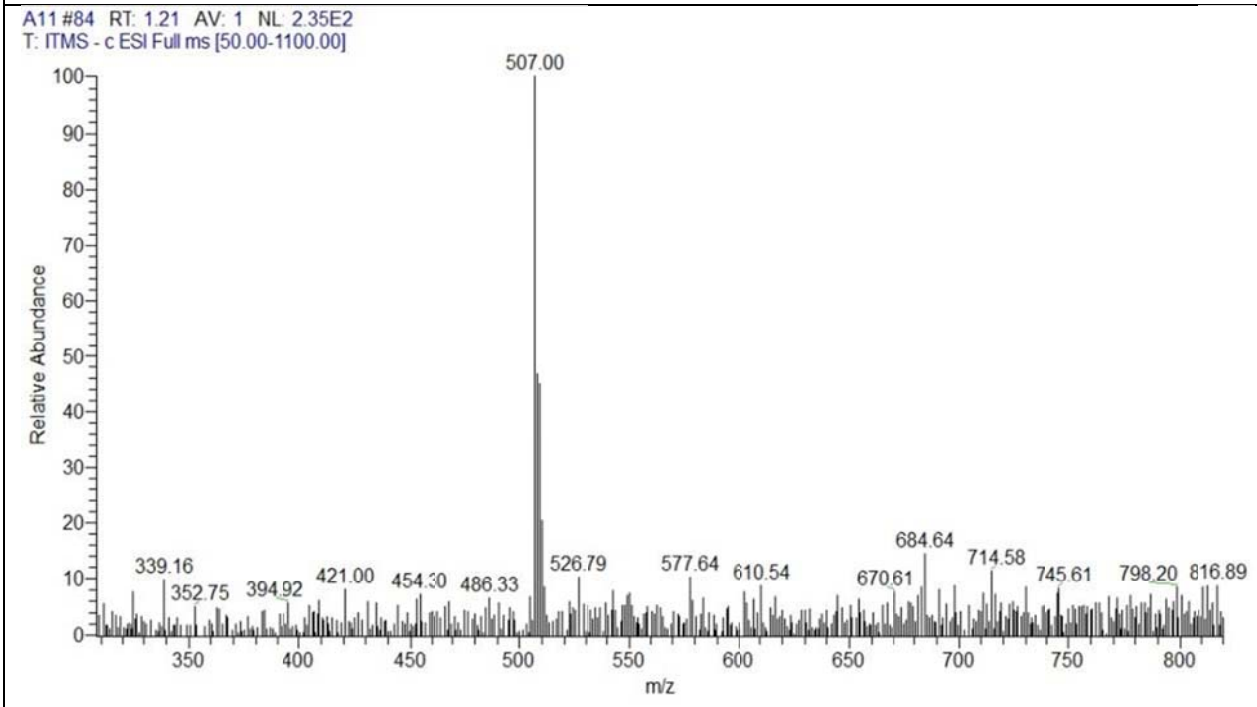

Figure 42. ESI-mass of **1k**

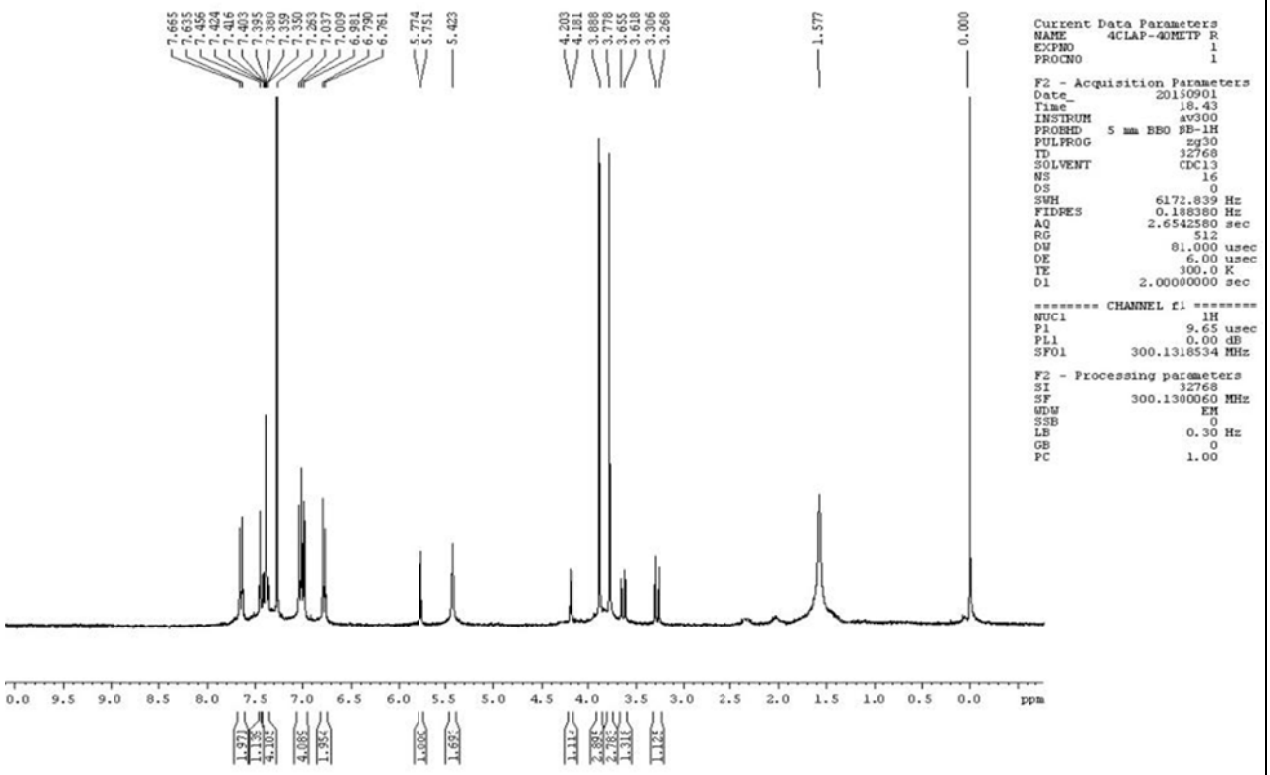

Figure 43. ^{1}H NMR spectrum of **1l**

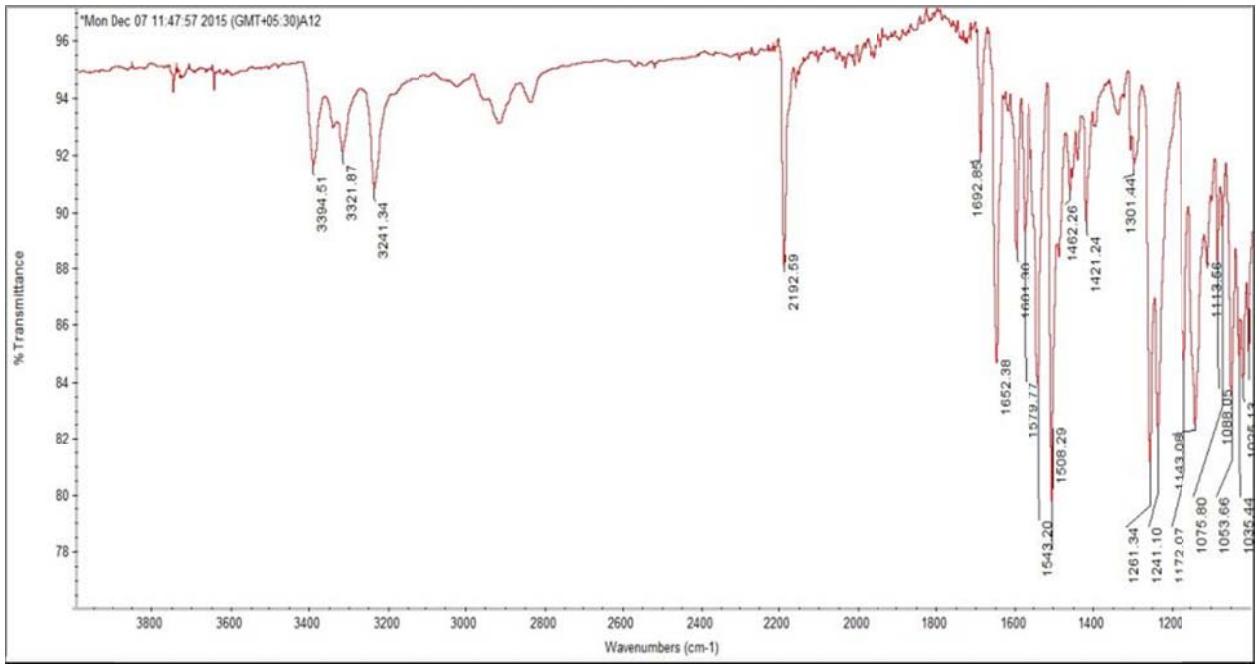

Figure 44. FT-IR spectrum of **1l**

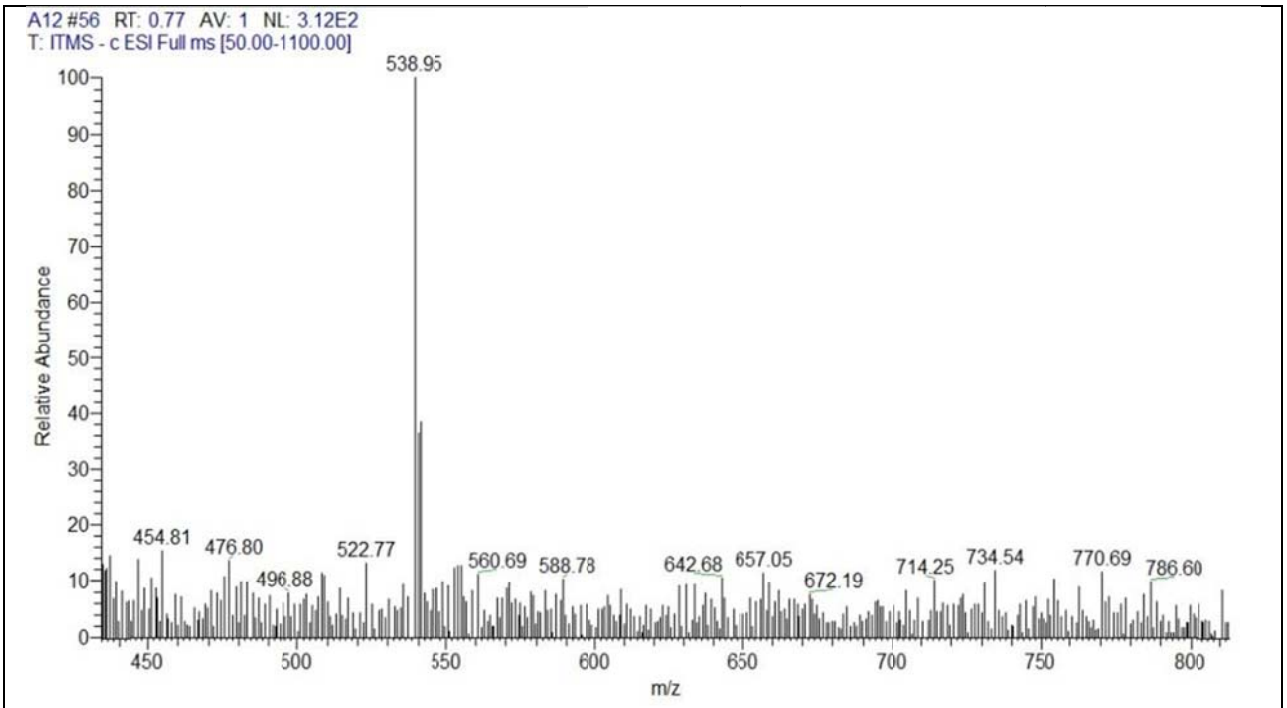

Figure 45. ESI-mass of **1l**

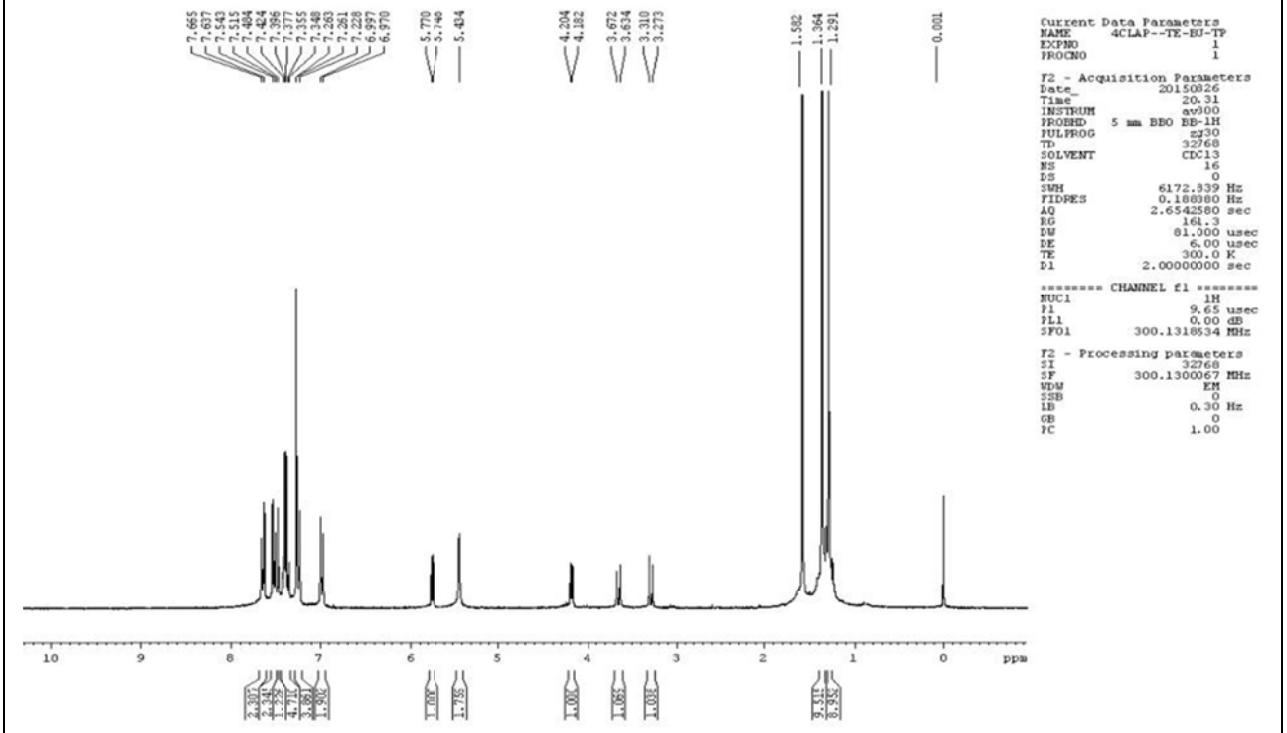

Figure 46. ^{1}H NMR spectrum of **1m**

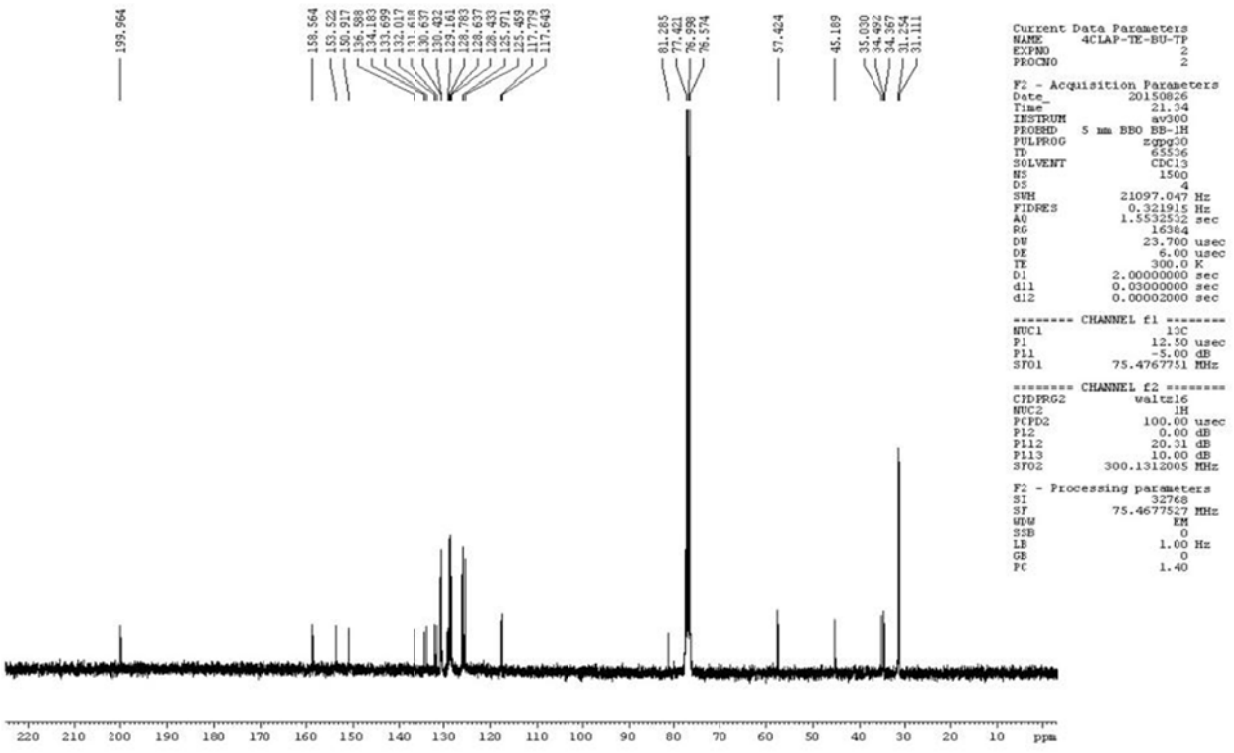

Figure 47. ^{13}CNMR spectrum of **1m**

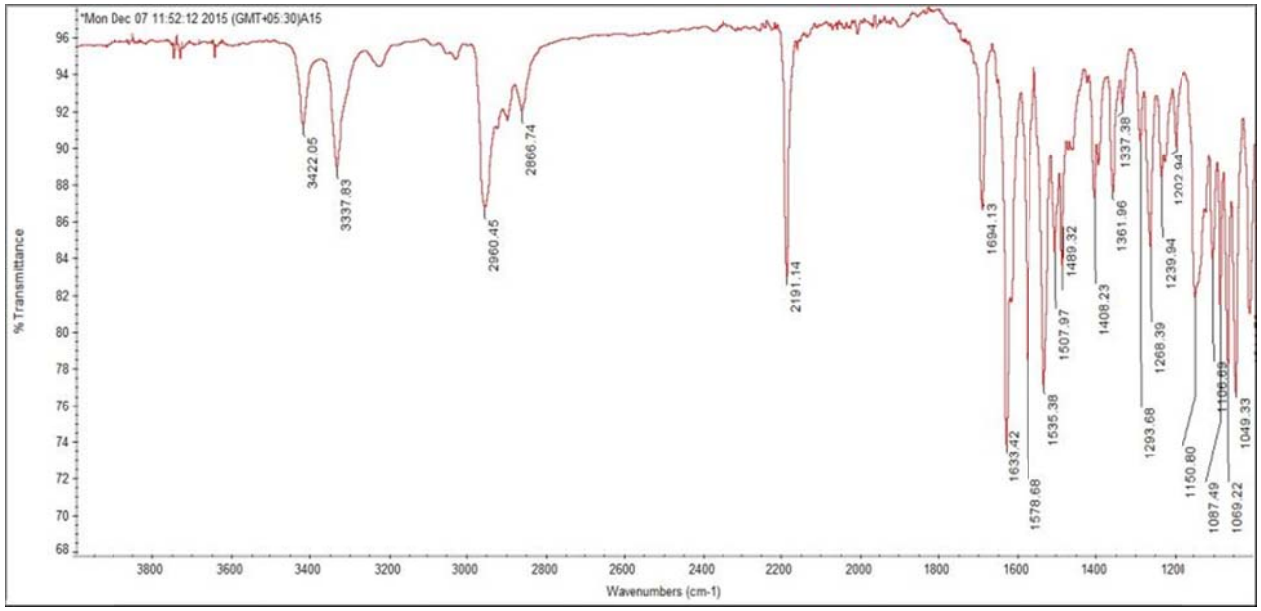

Figure 48. FT-IR spectrum of **1m**

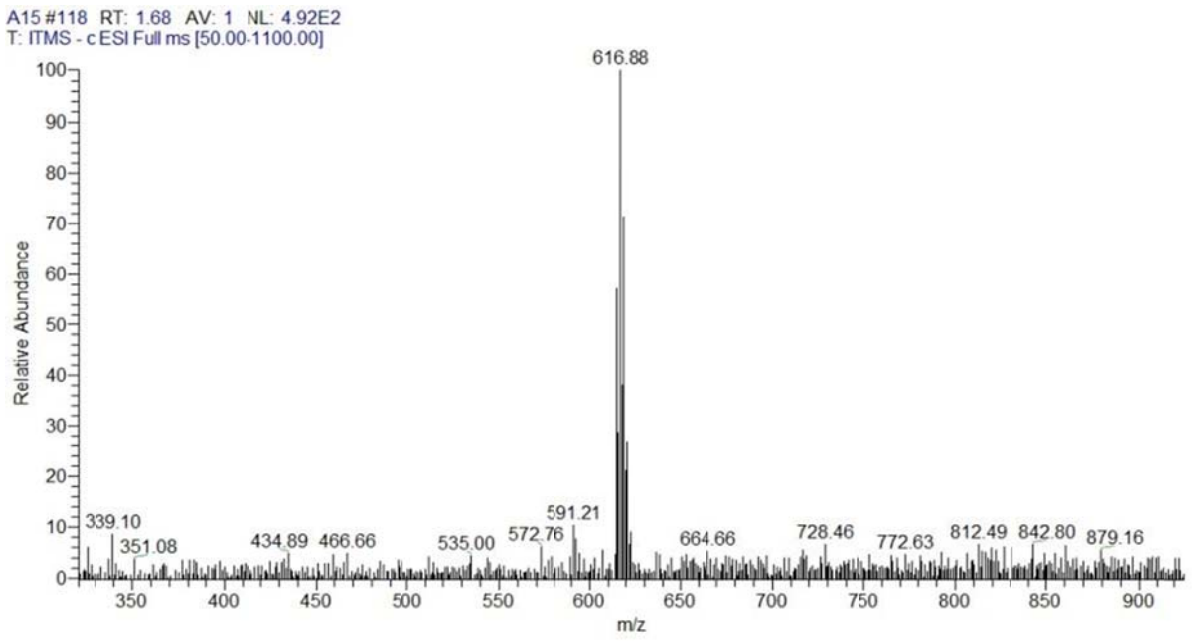

Figure 49. ESI-mass of **1m**

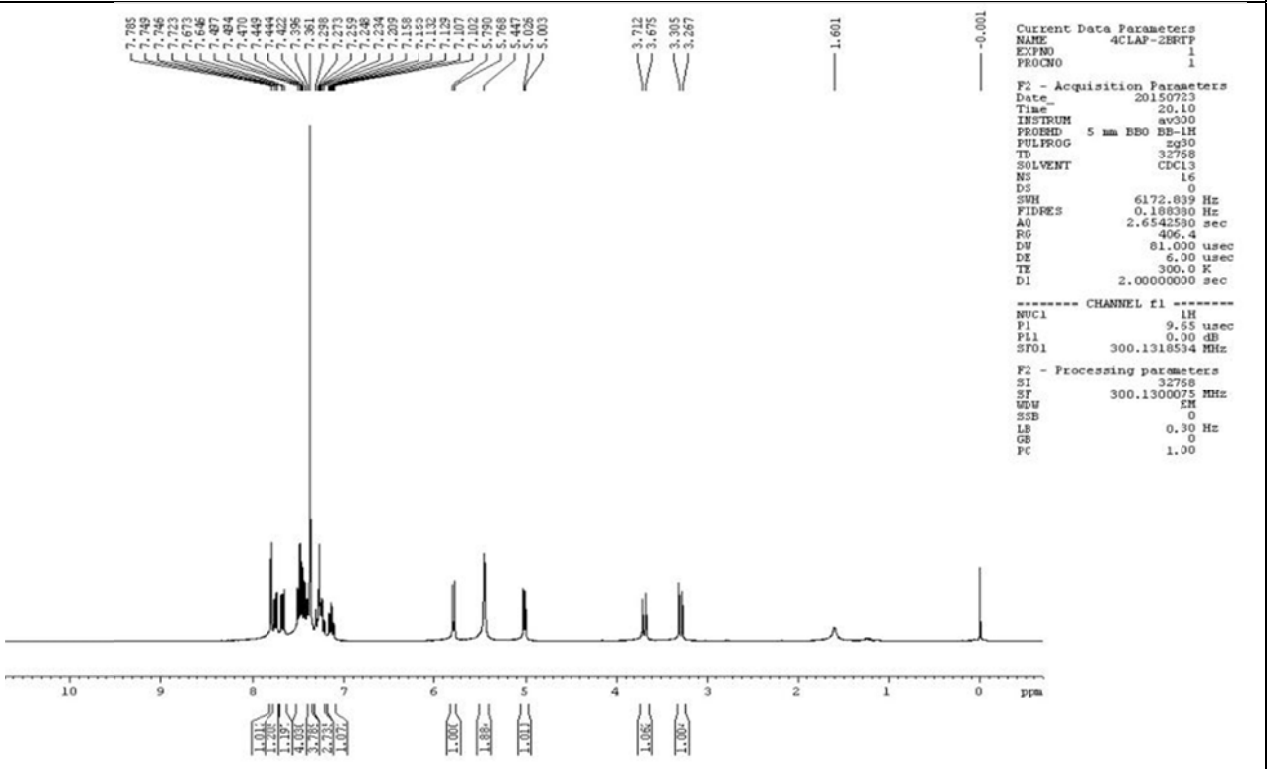

Figure 50. ^{1}H NMR spectrum of **1n**

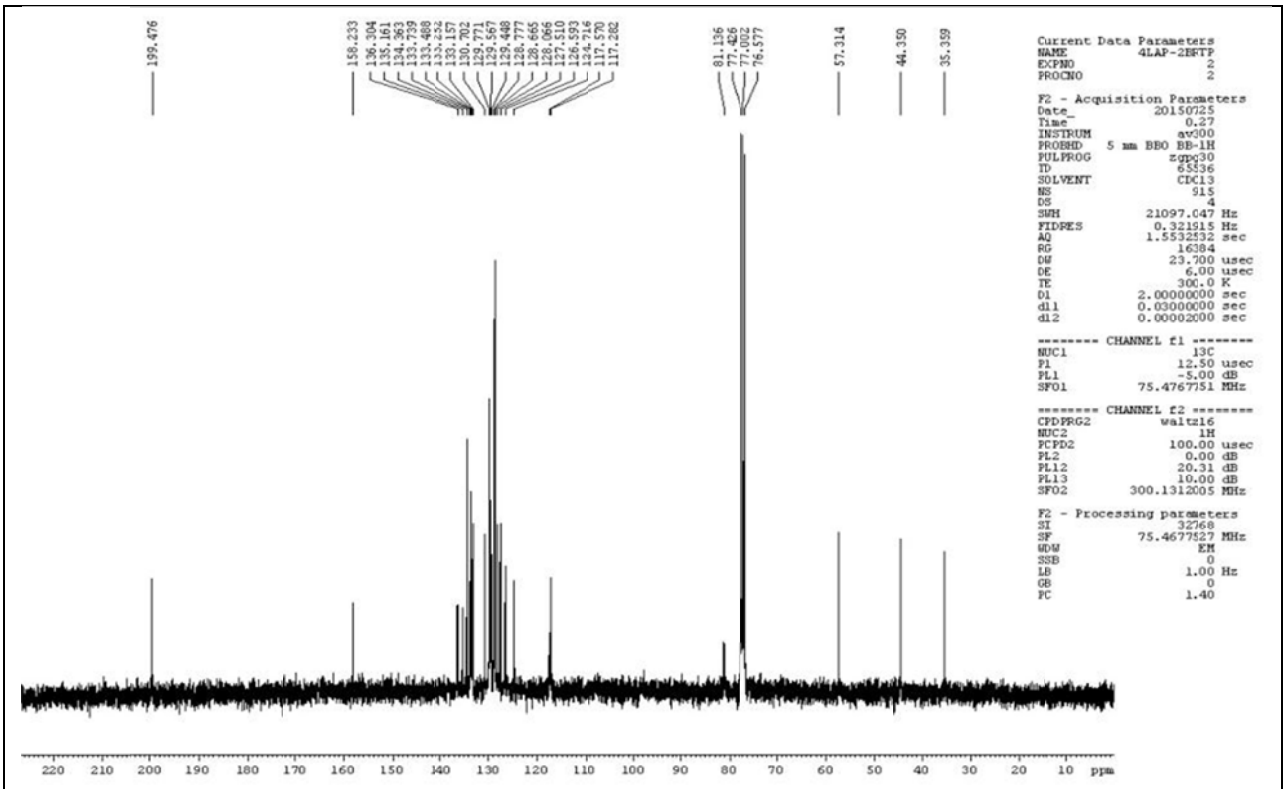

Figure 51. ^{13}CNMR spectrum of **1n**

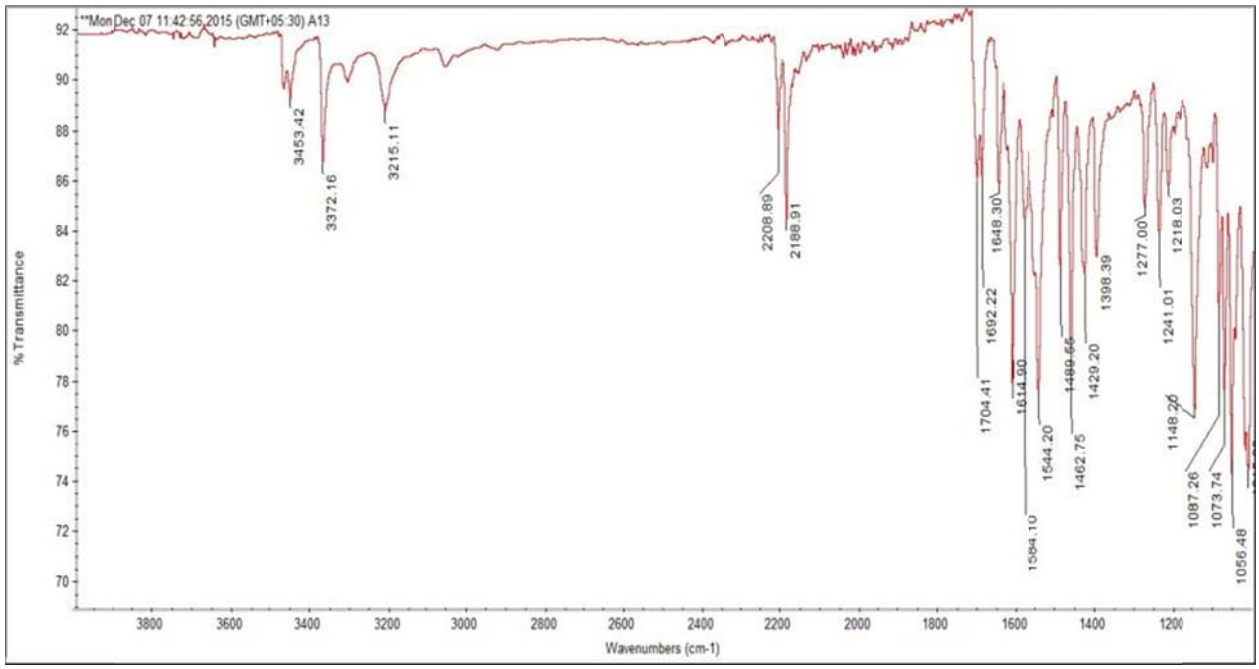

Figure 52. FT-IR spectrum of **1n**

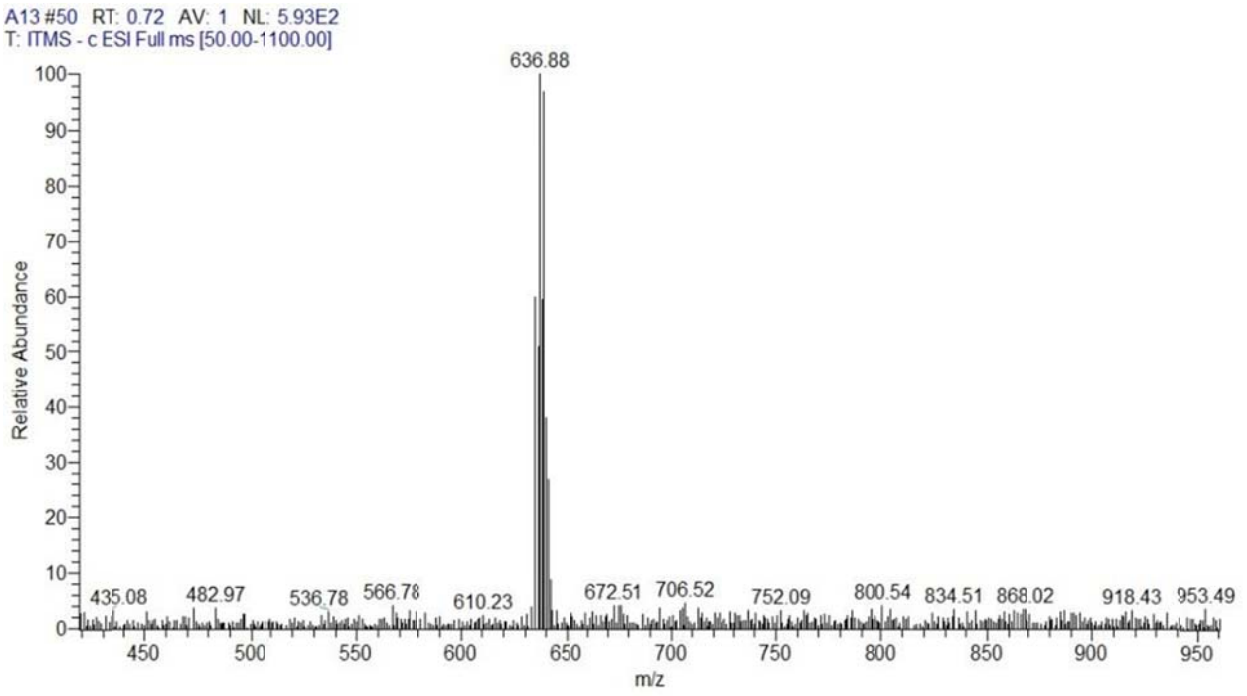

Figure 53. ESI-mass of **1n**

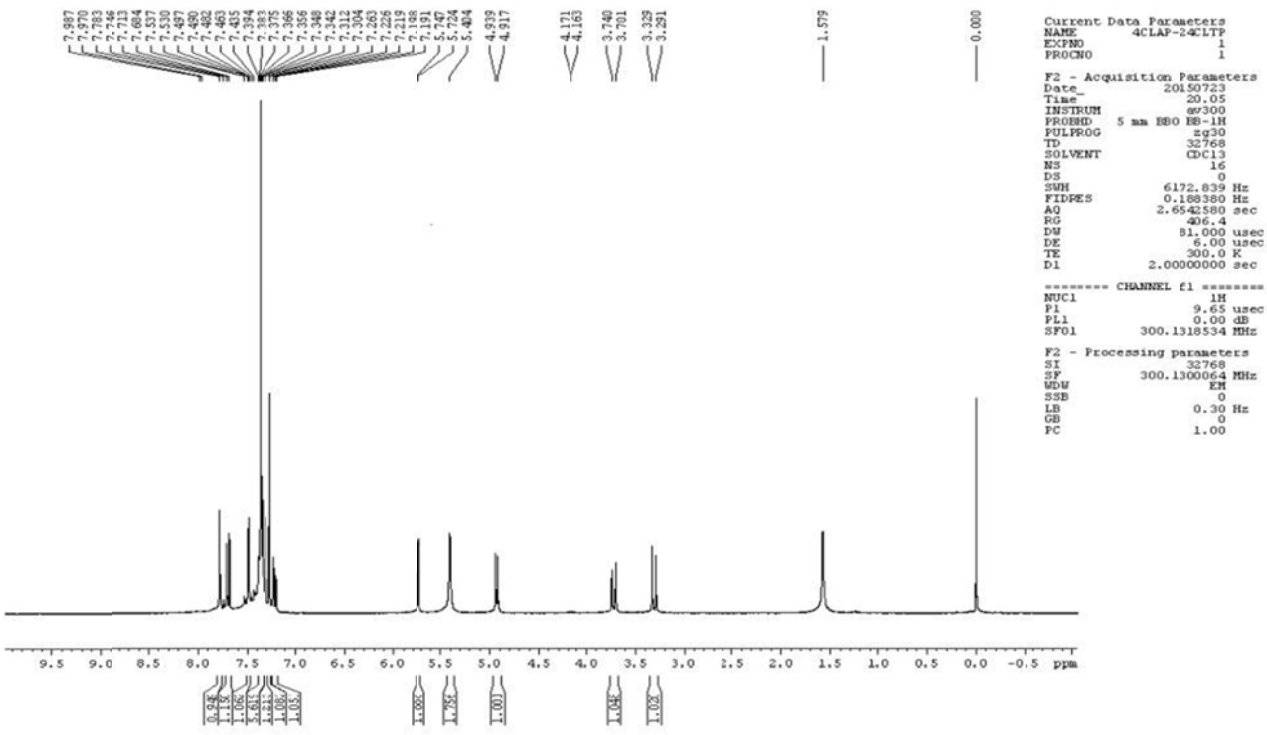

Figure 54. ^{1}H NMR spectrum of **1o**

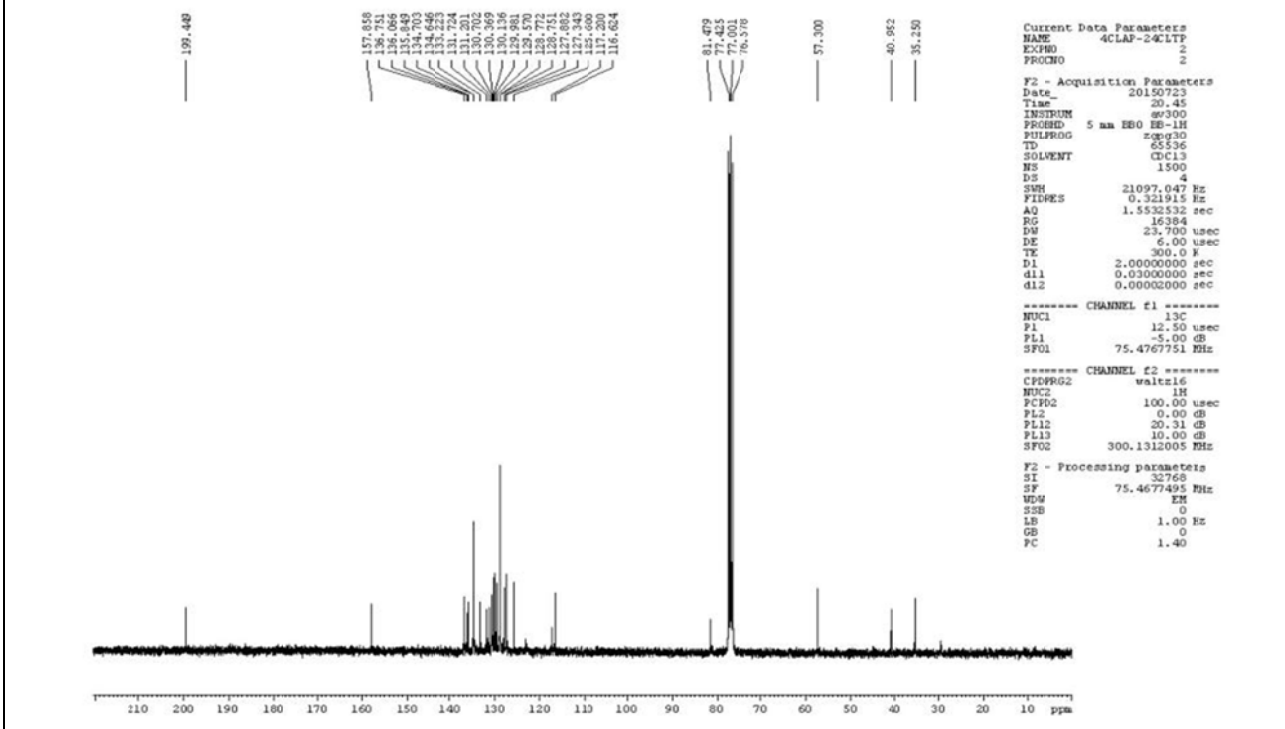

Figure 55. ^{13}CNMR spectrum of **1o**

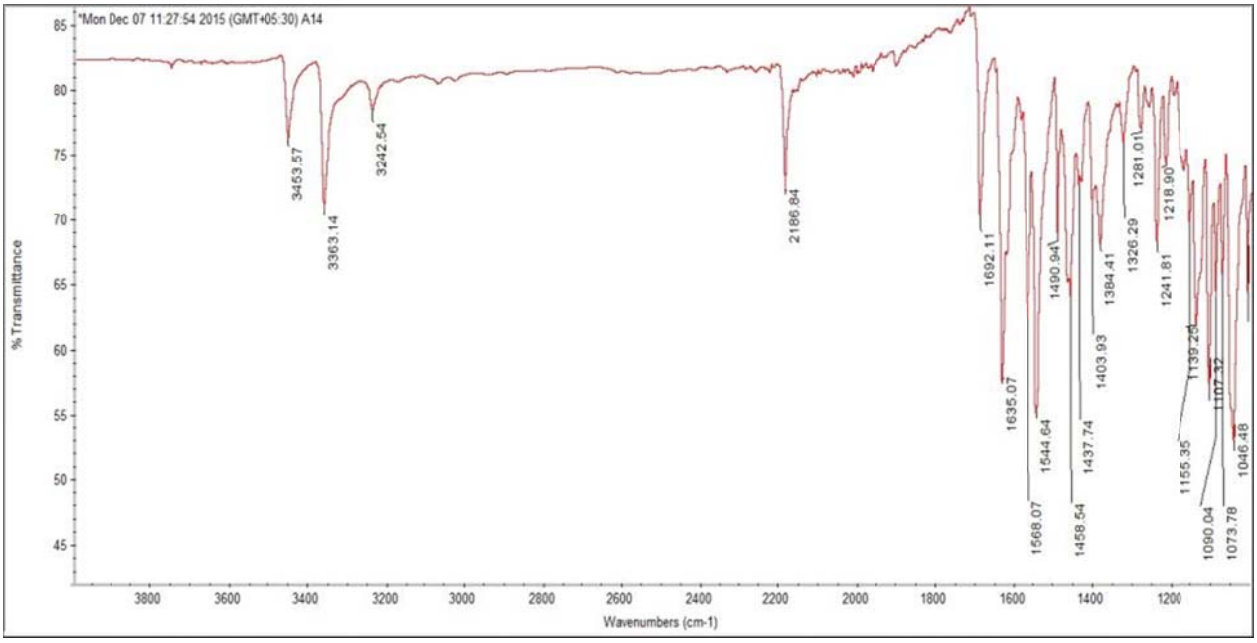

Figure 56. FT-IR spectrum of **1o**

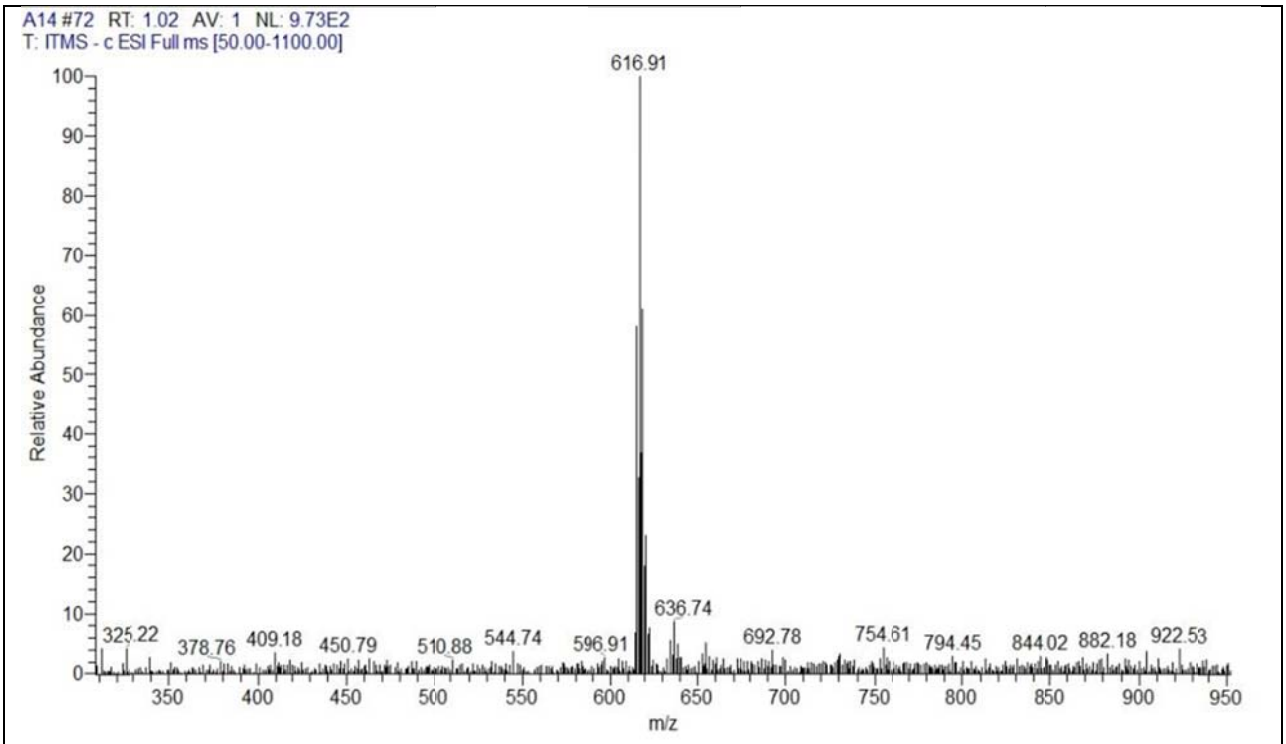

Figure 57. ESI-mass of **1o**

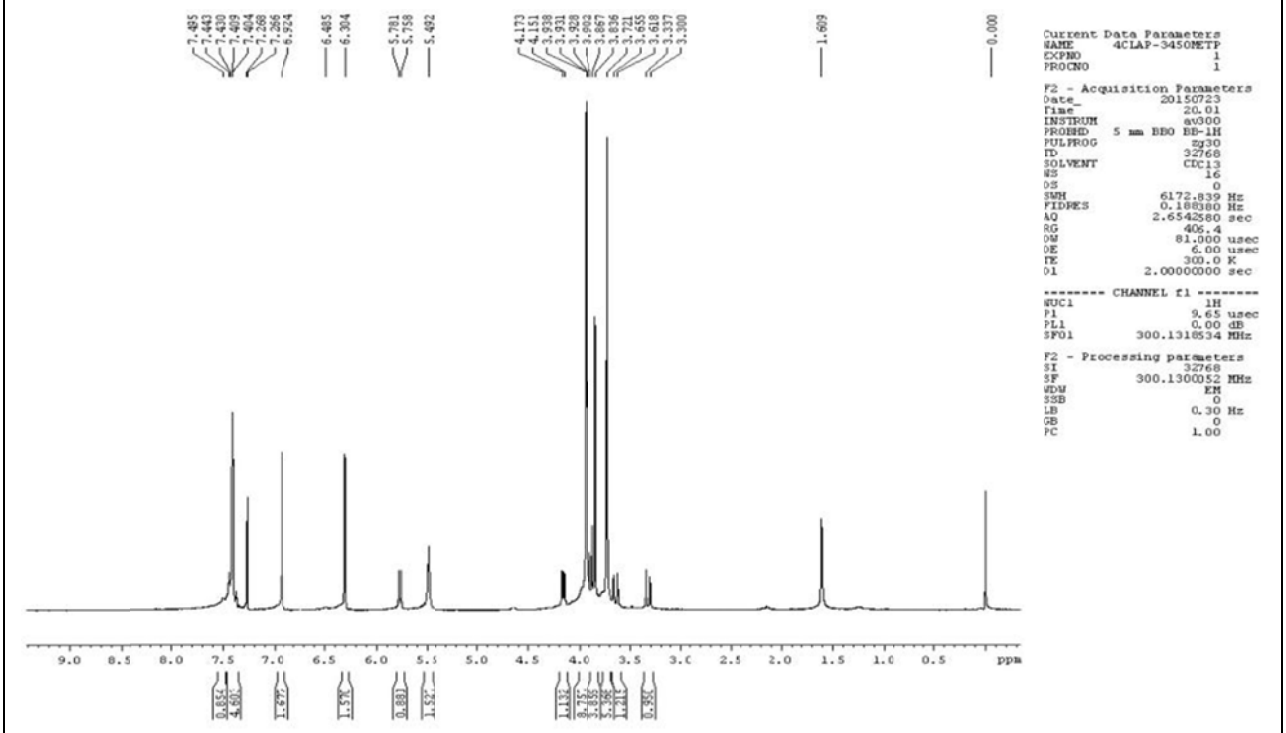

Figure 58. ^{1}H NMR spectrum of **1p**

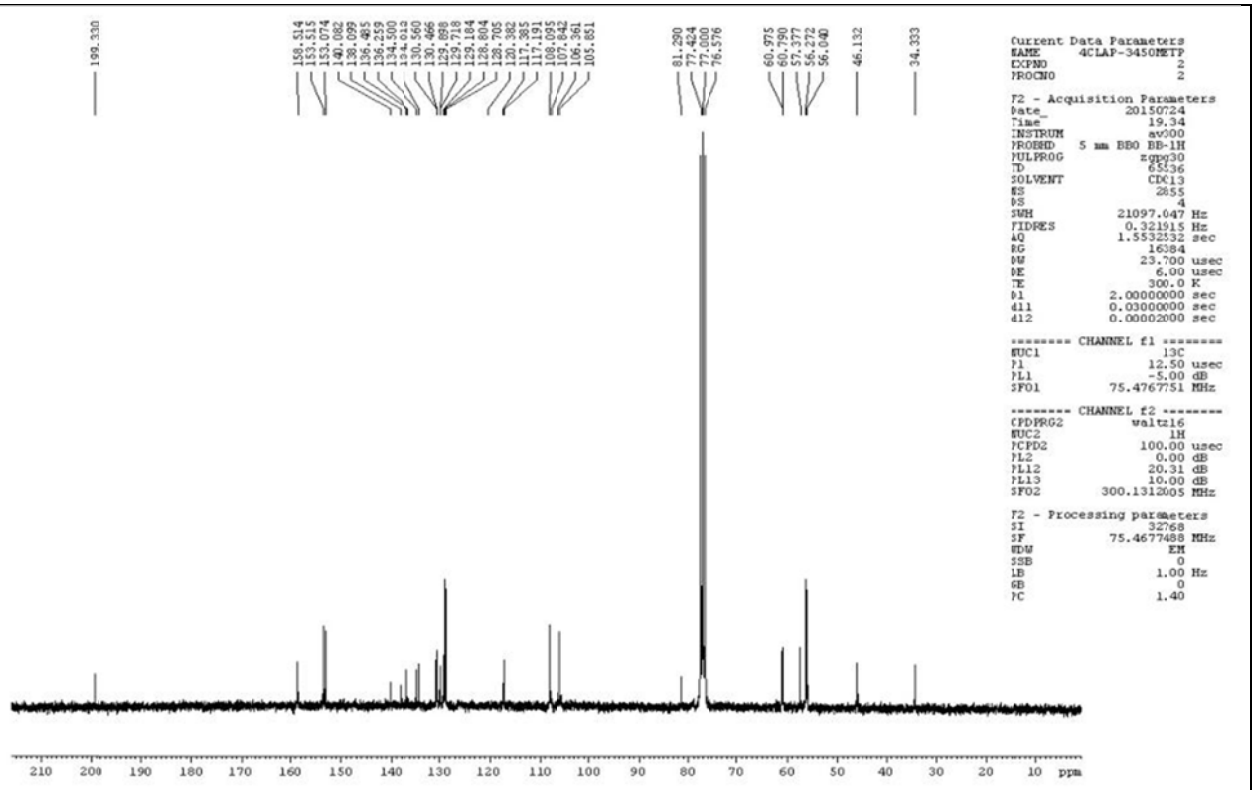

Figure 59.[13]CNMR spectrum of **1p**

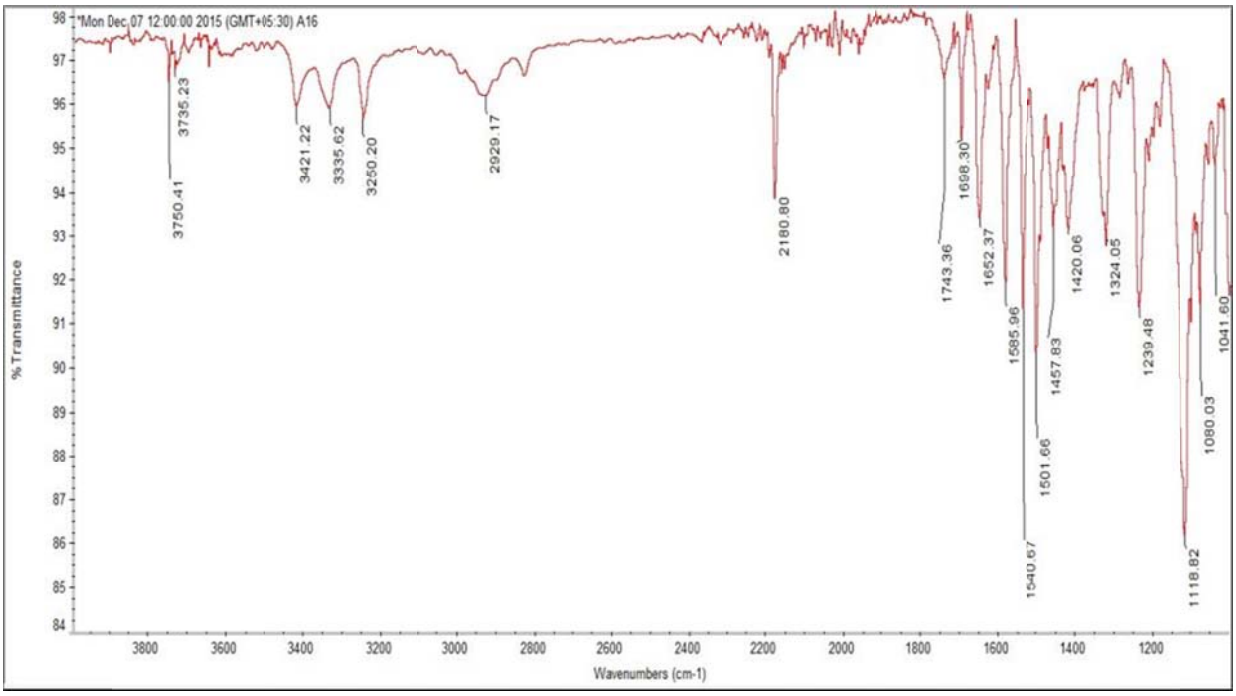

Figure 60. FT-IR spectrum of **1p**

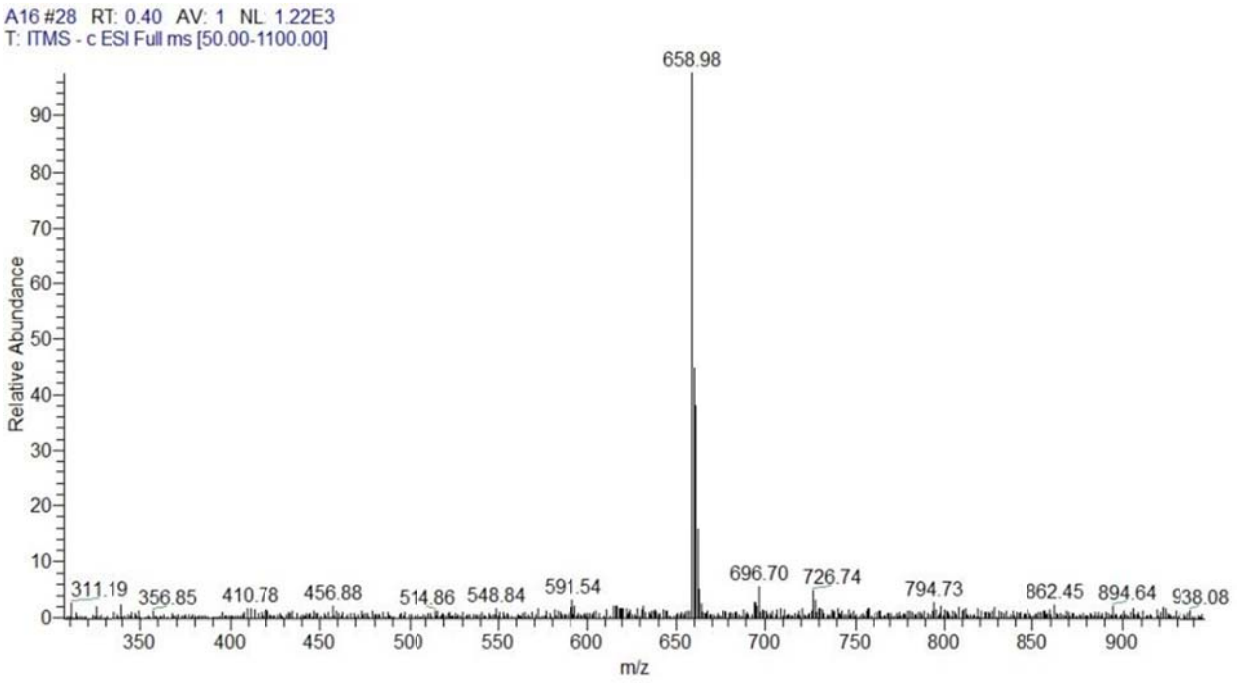

Figure 61. ESI-mass of **1p**

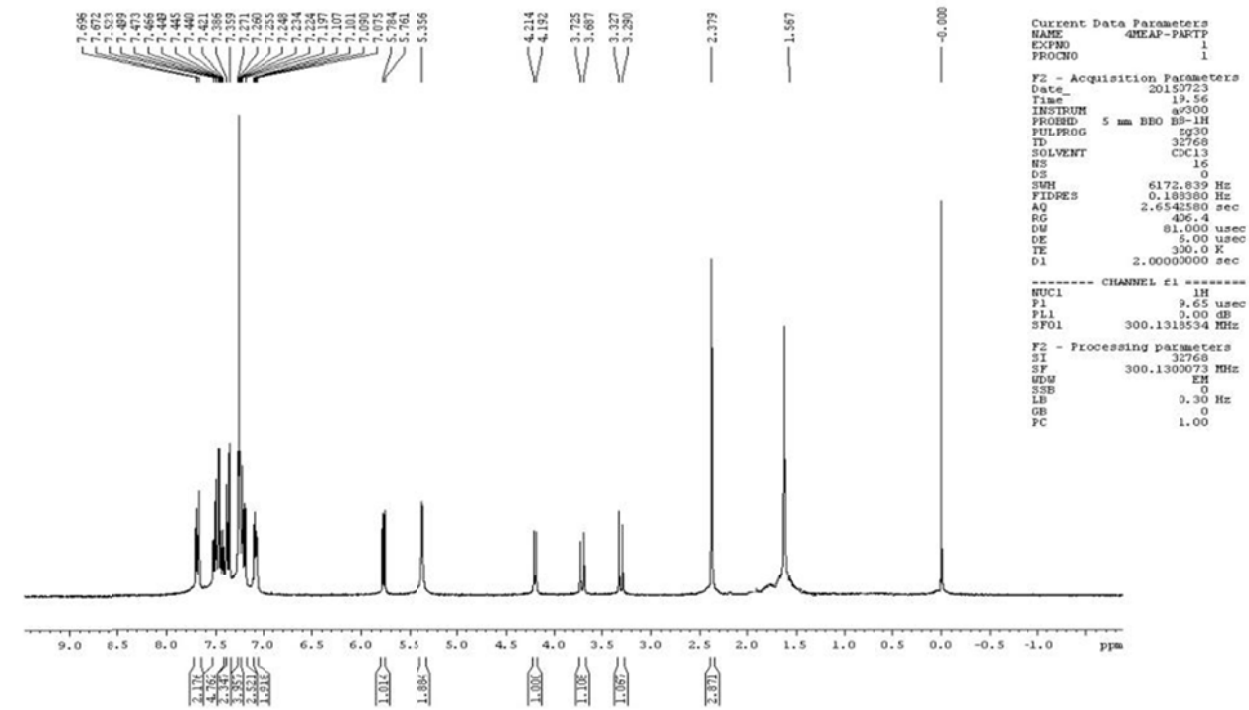

Figure 62.[1]HNMR spectrum of **1q**

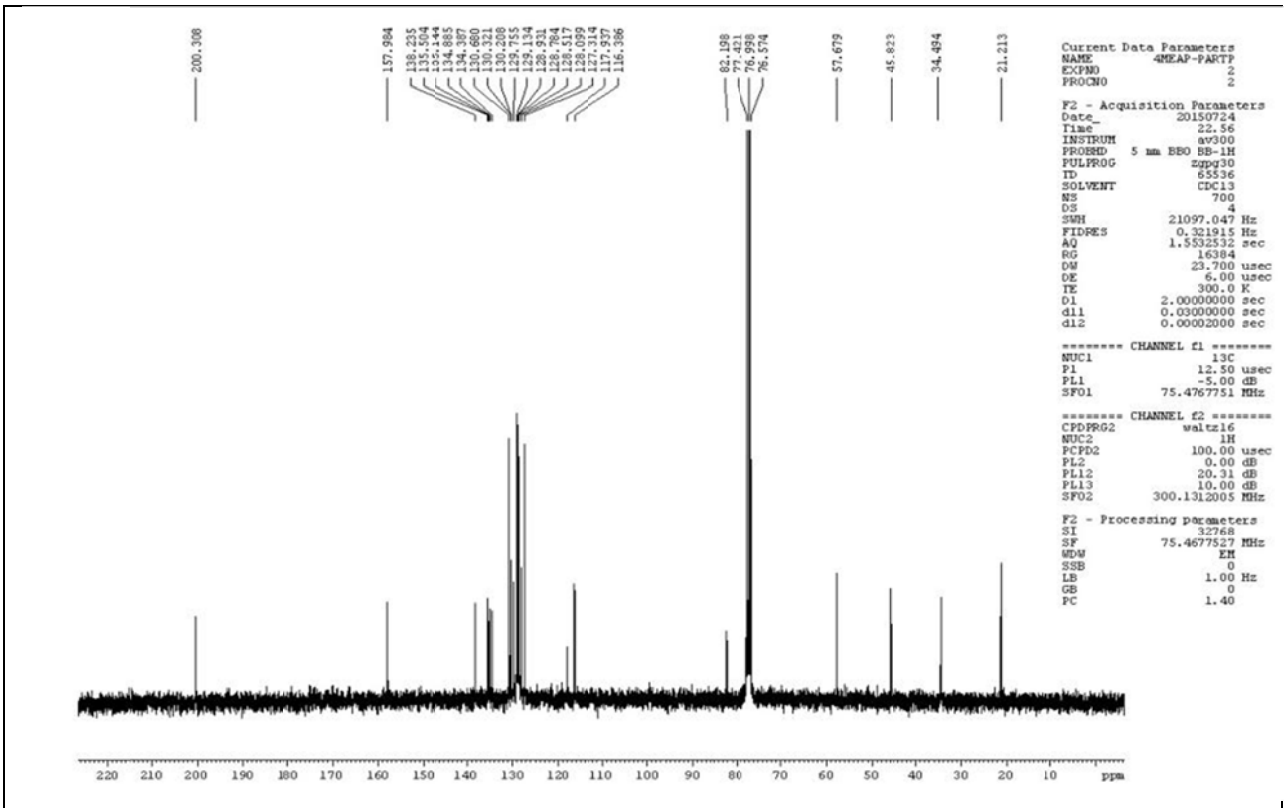

Figure 63.[13]CNMR spectrum of **1q**

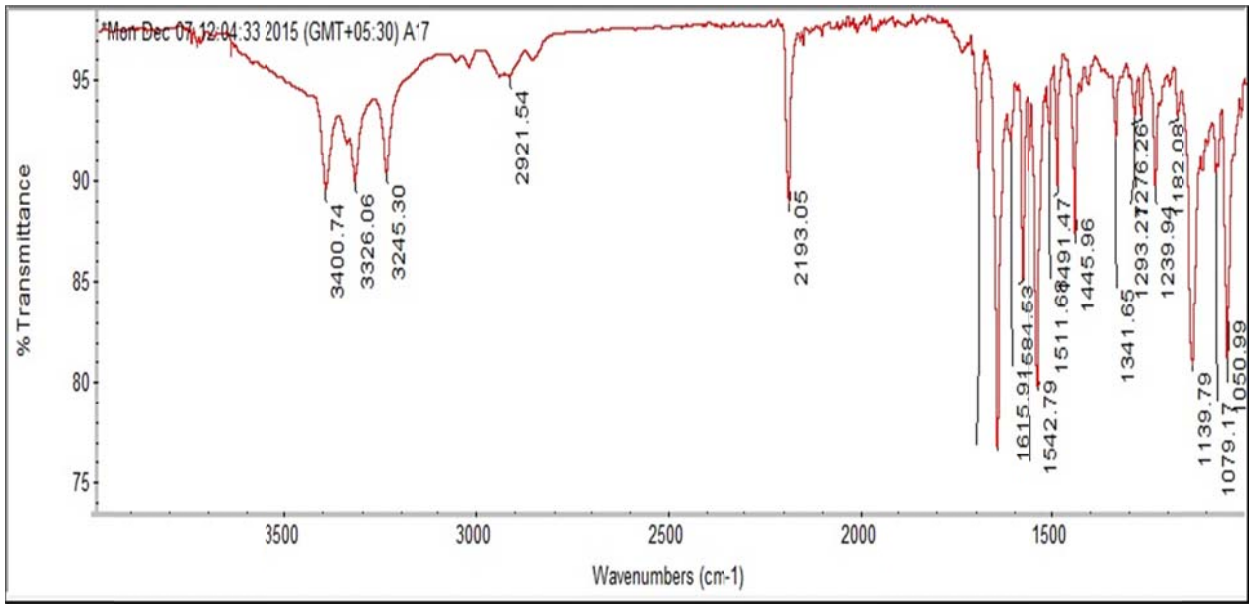

Figure 64. FT-IR spectrum of **1q**

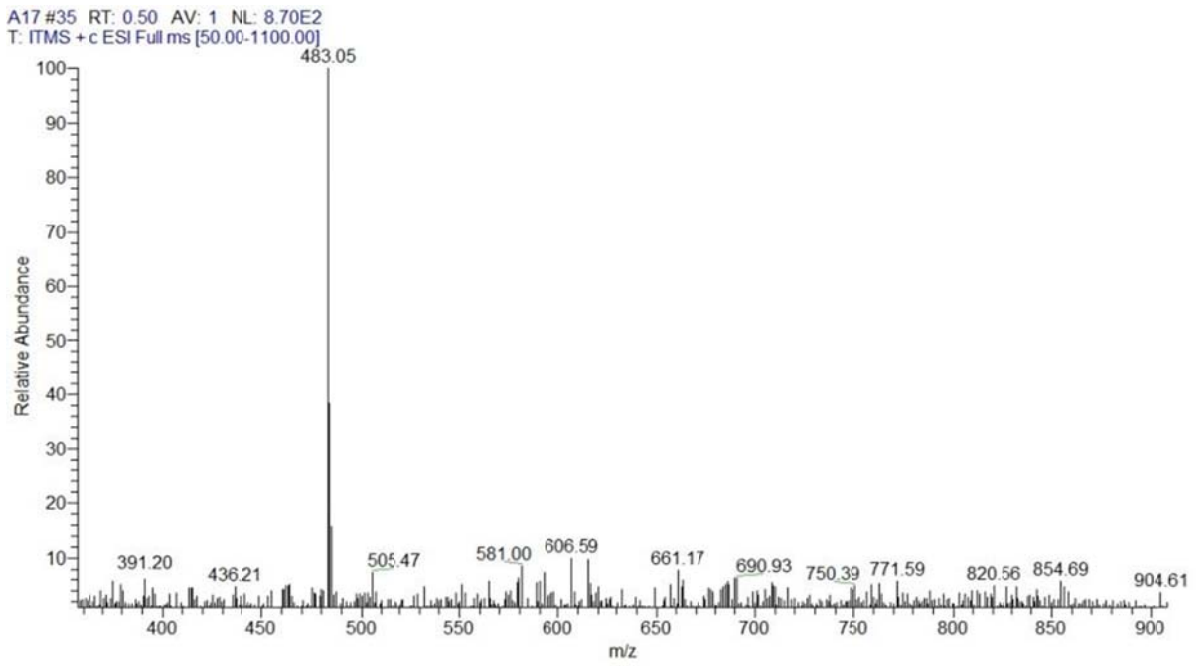

Figure 65. ESI-mass of **1q**

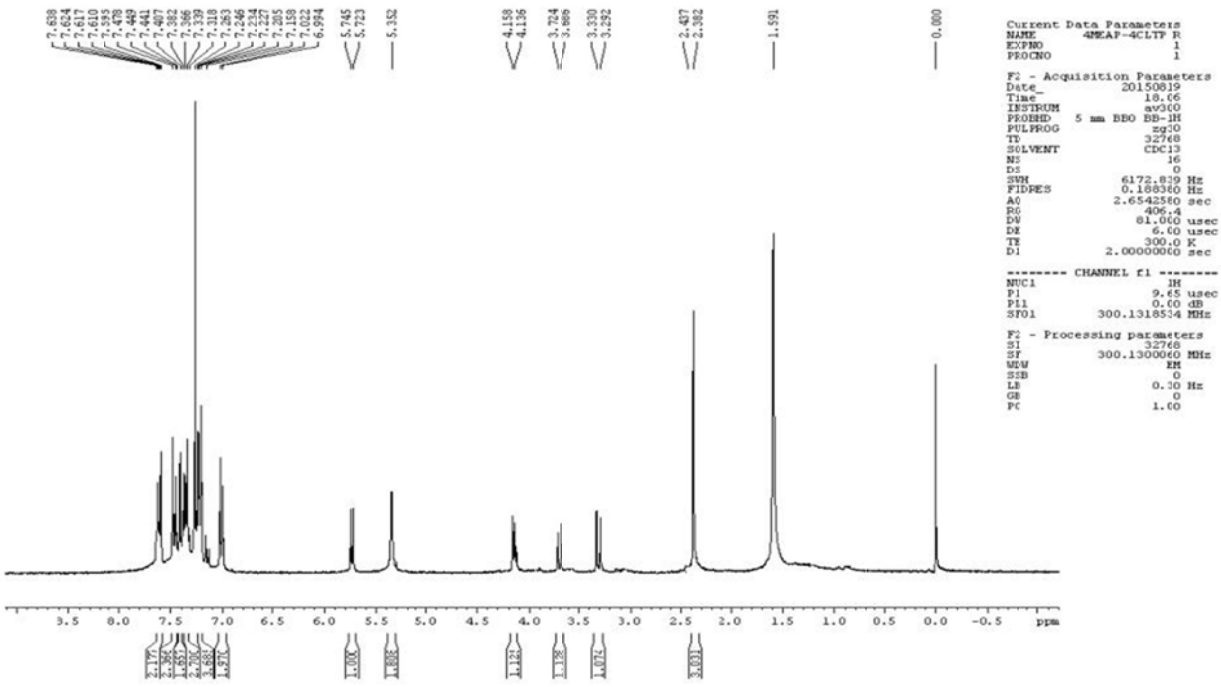

Figure 66. ^{1}H NMR spectrum of **1r**

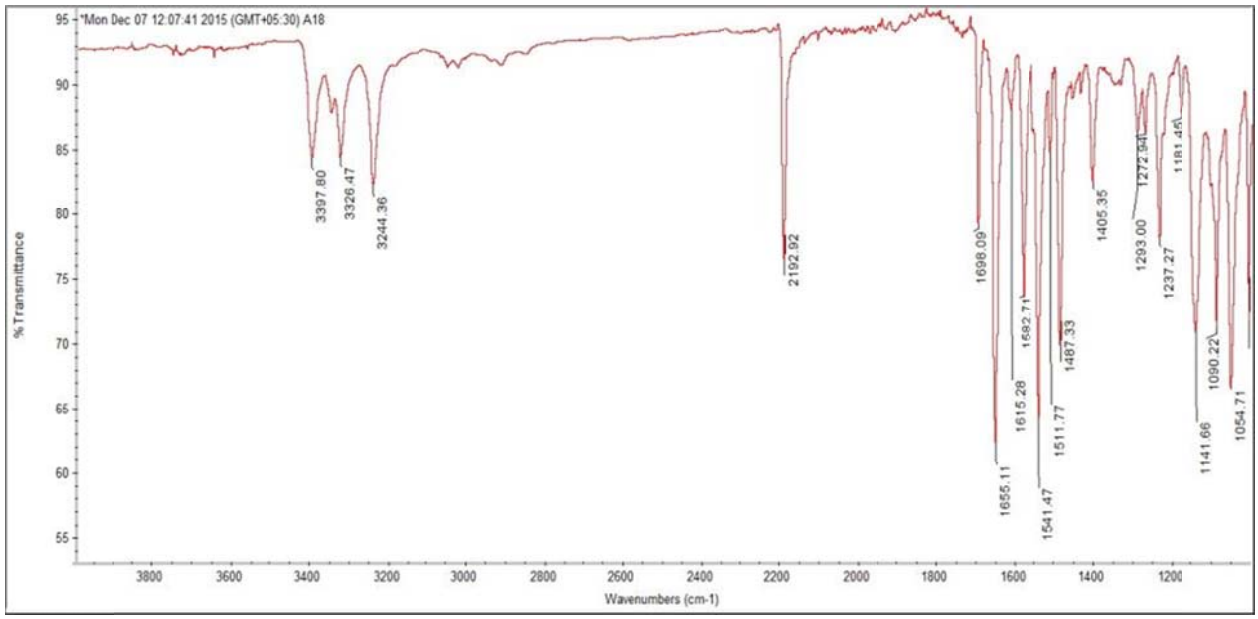

Figure 67. FT-IR spectrum of **1r**

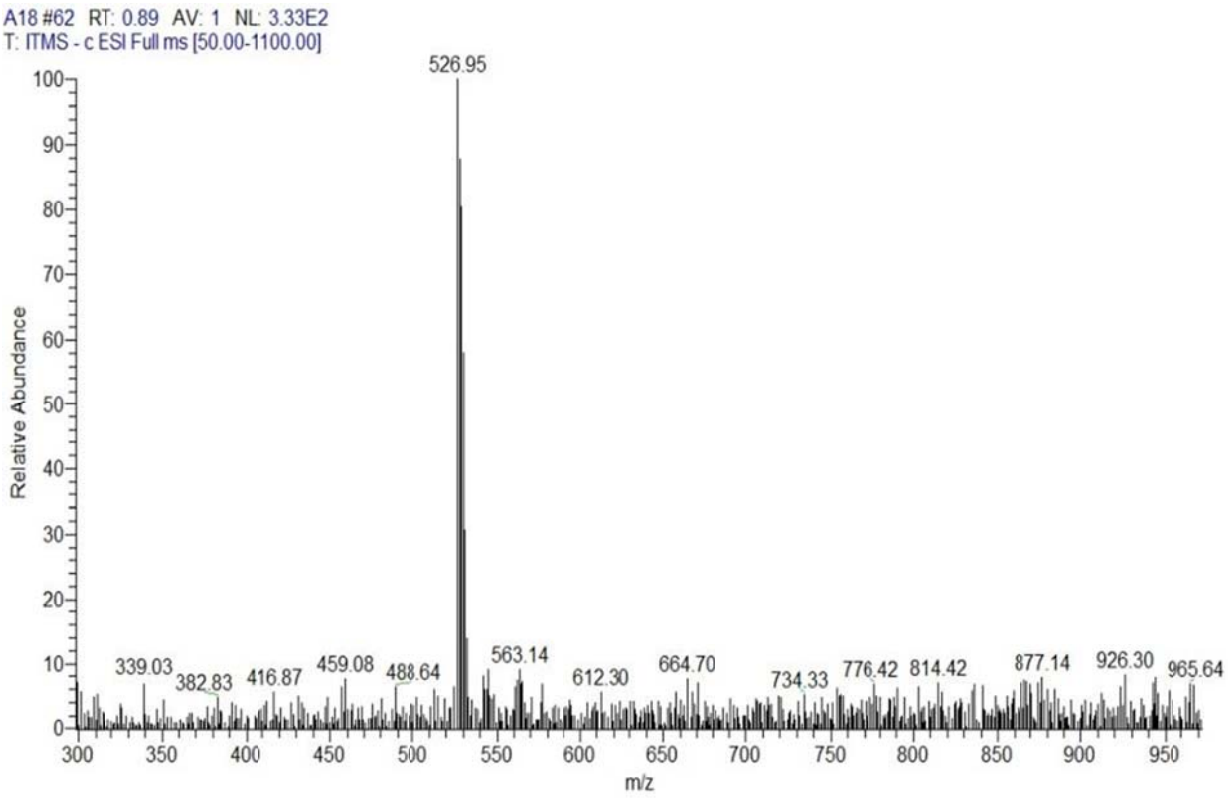

Figure 68. ESI-mass of **1r**

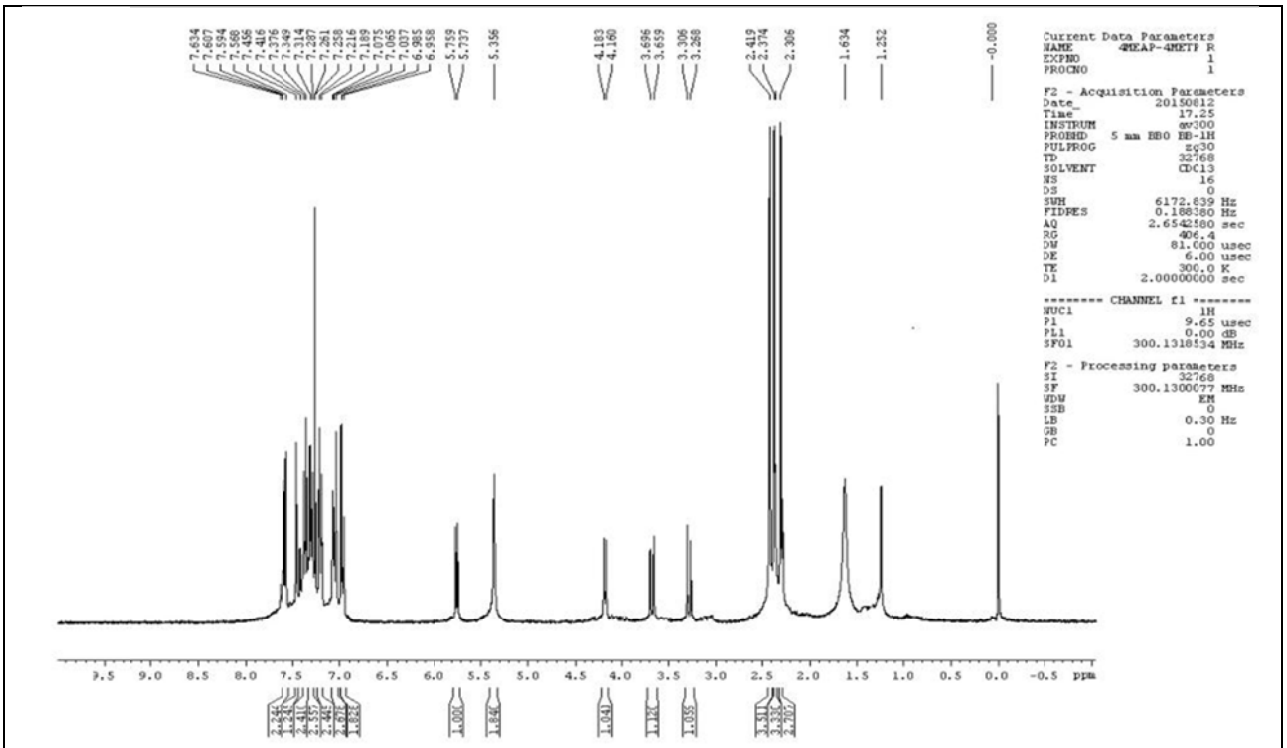

Figure 69.[1]HNMR spectrum of **1s**

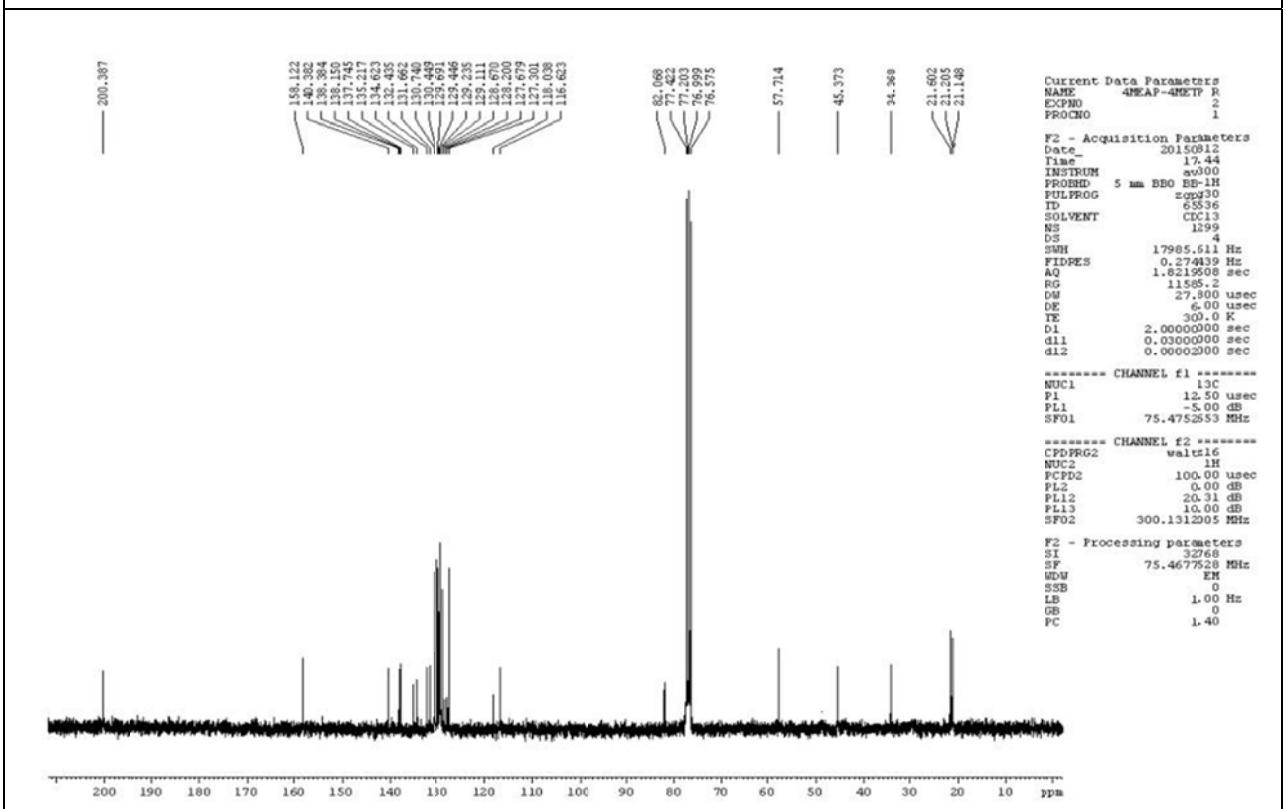

Figure 70.[13]CNMR spectrum of **1s**

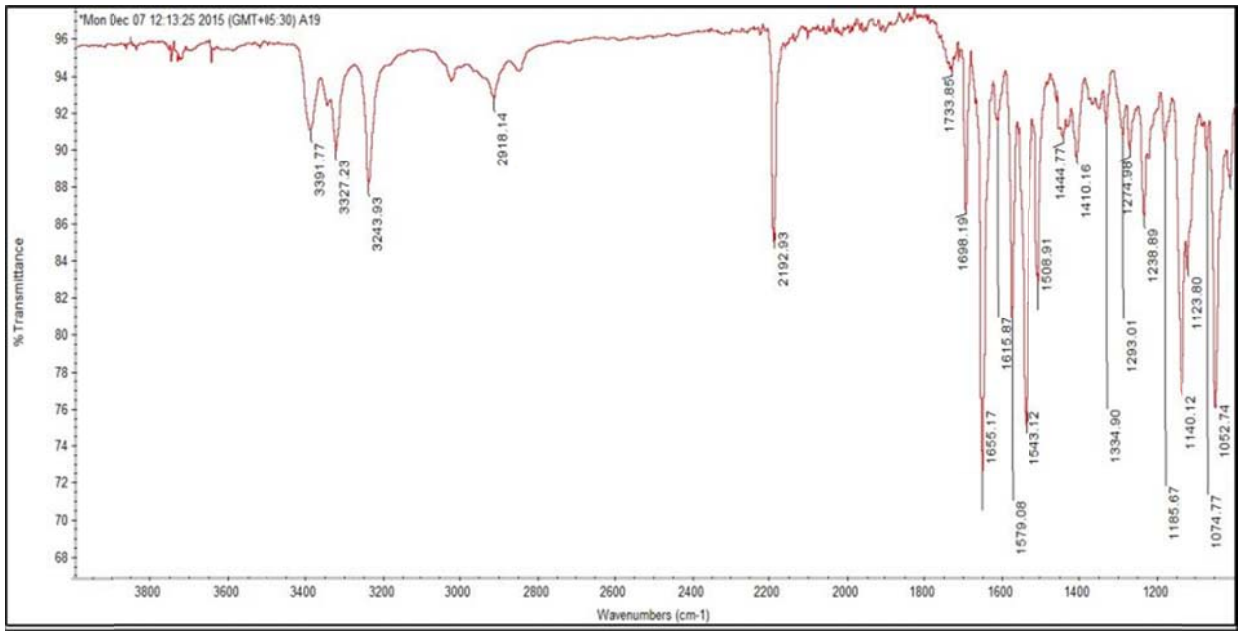

Figure 71. FT-IR spectrum of **1s**

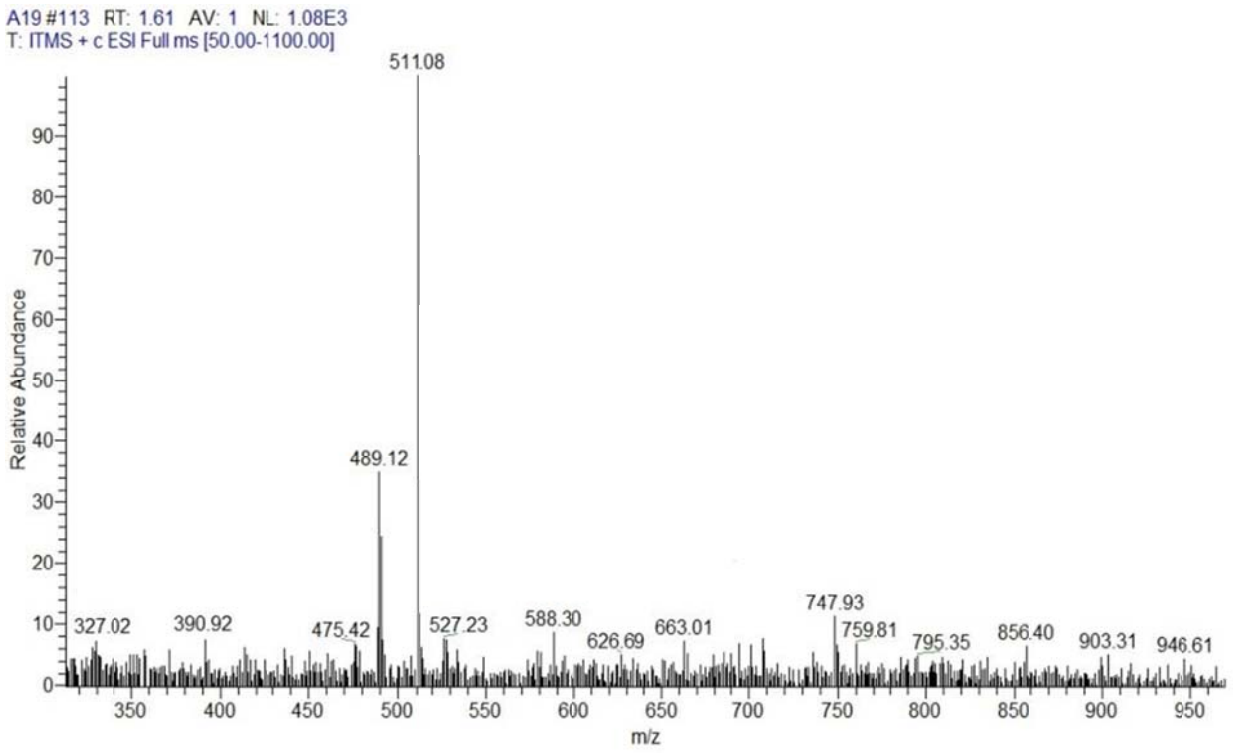

Figure 72. ESI-mass of **1s**

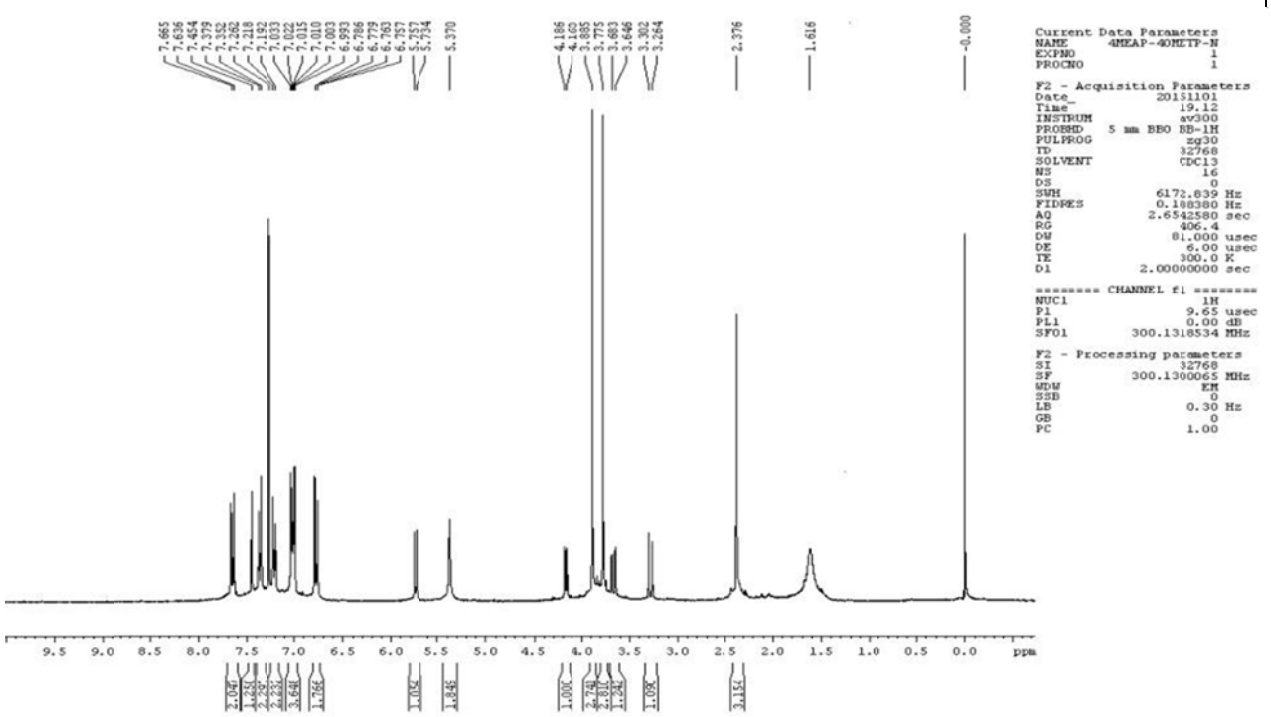

Figure 73. [1]HNMR spectrum of **1t**

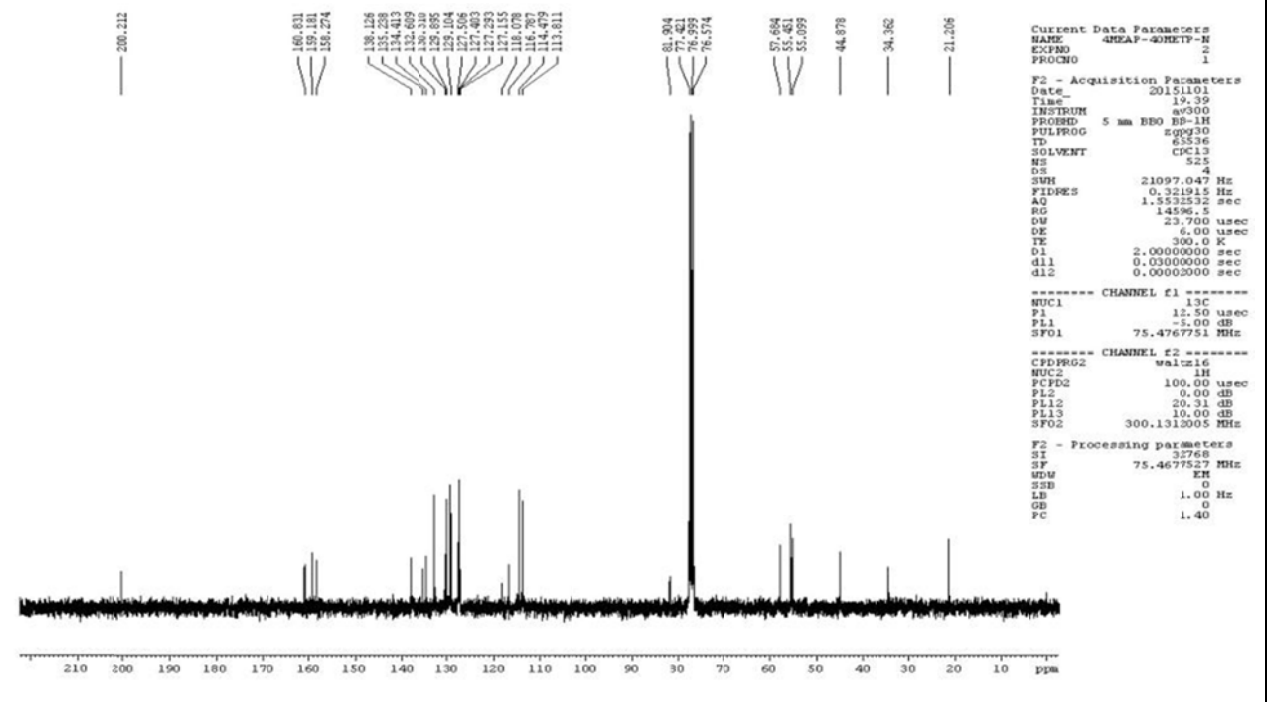

Figure 74. [13]CNMR spectrum of **1t**

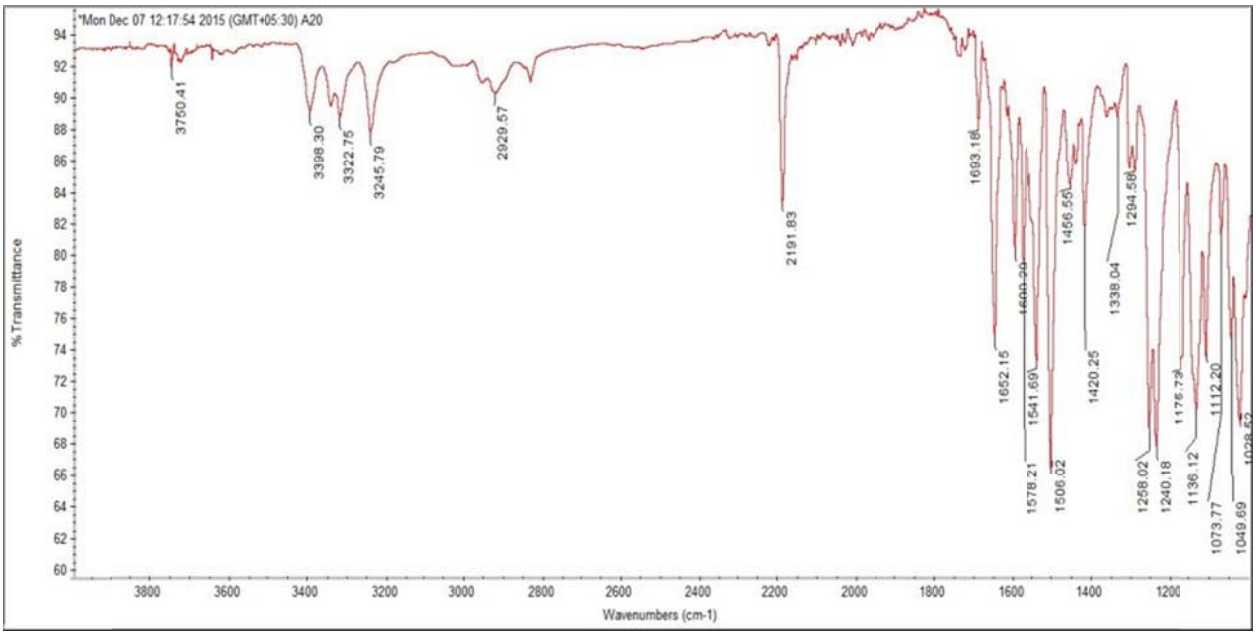

Figure 75. FT-IR spectrum of **1t**

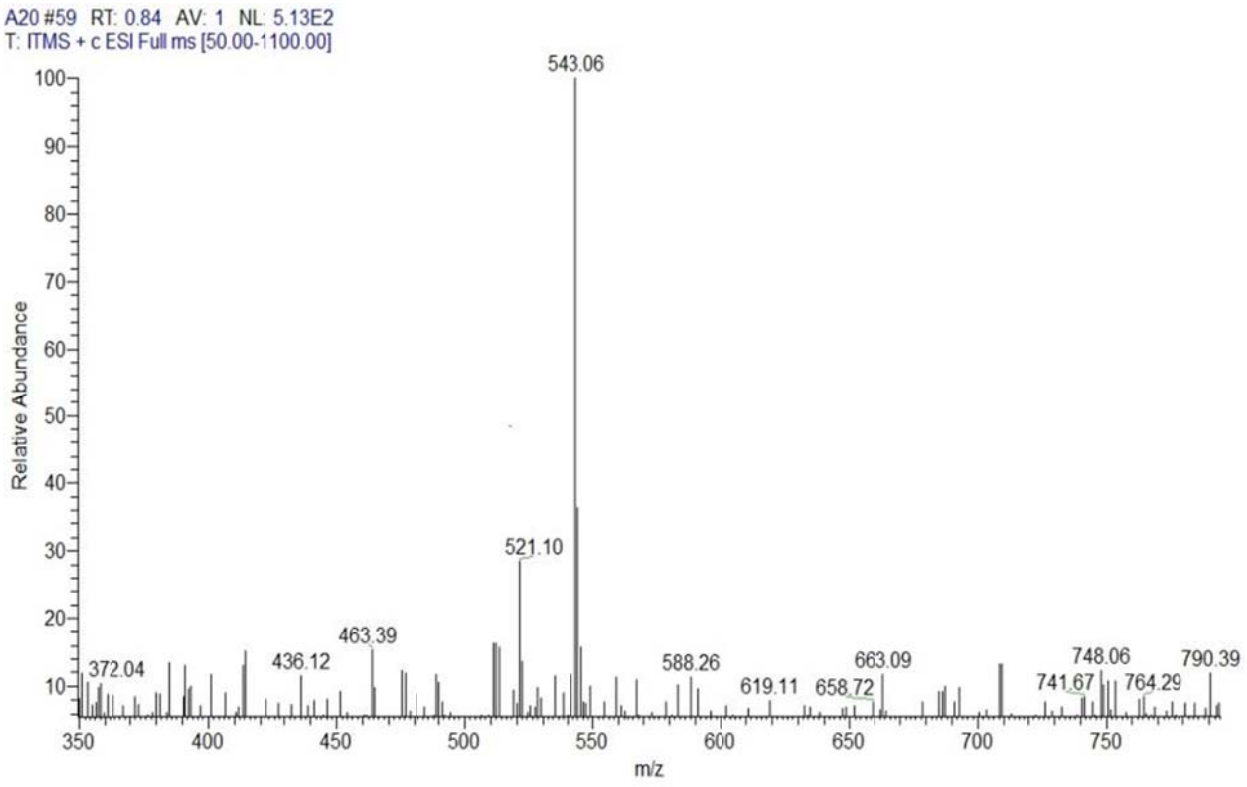

Figure 76. ESI-mass of **1t**

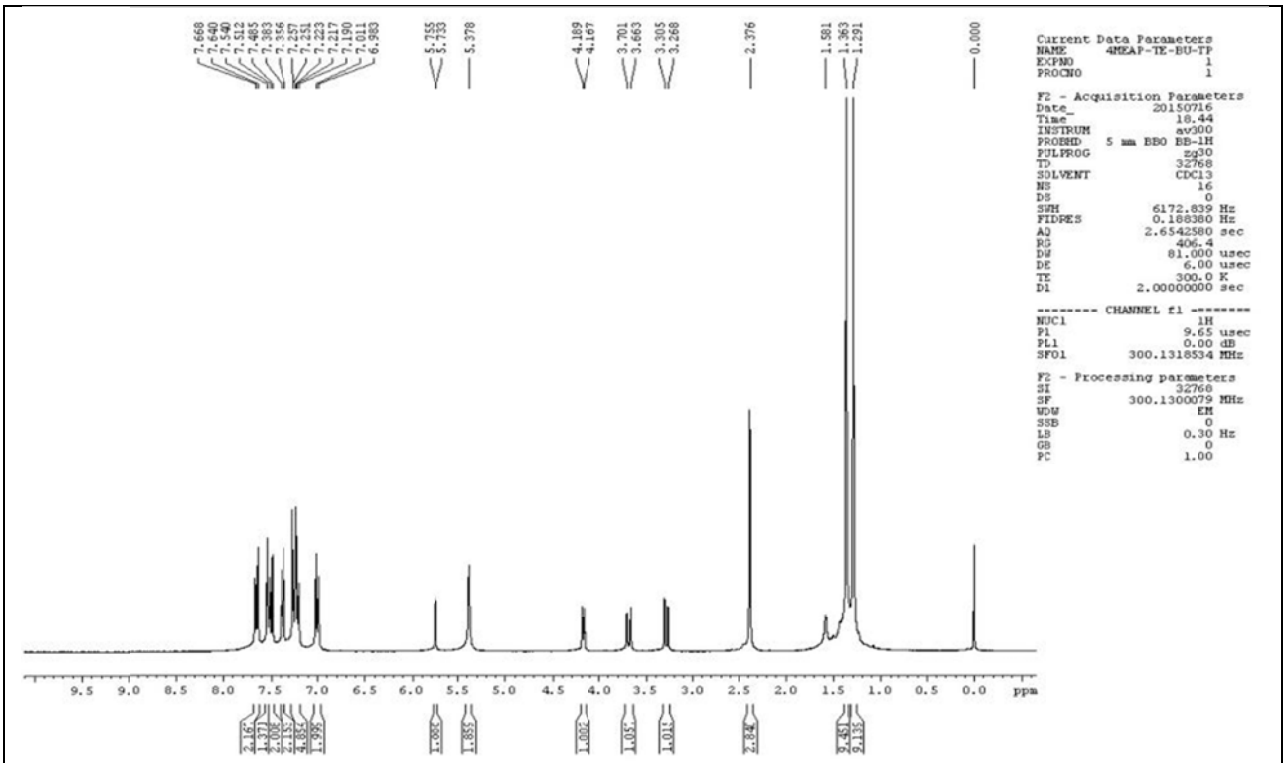

Figure 77.[1]HNMR spectrum of **1u**

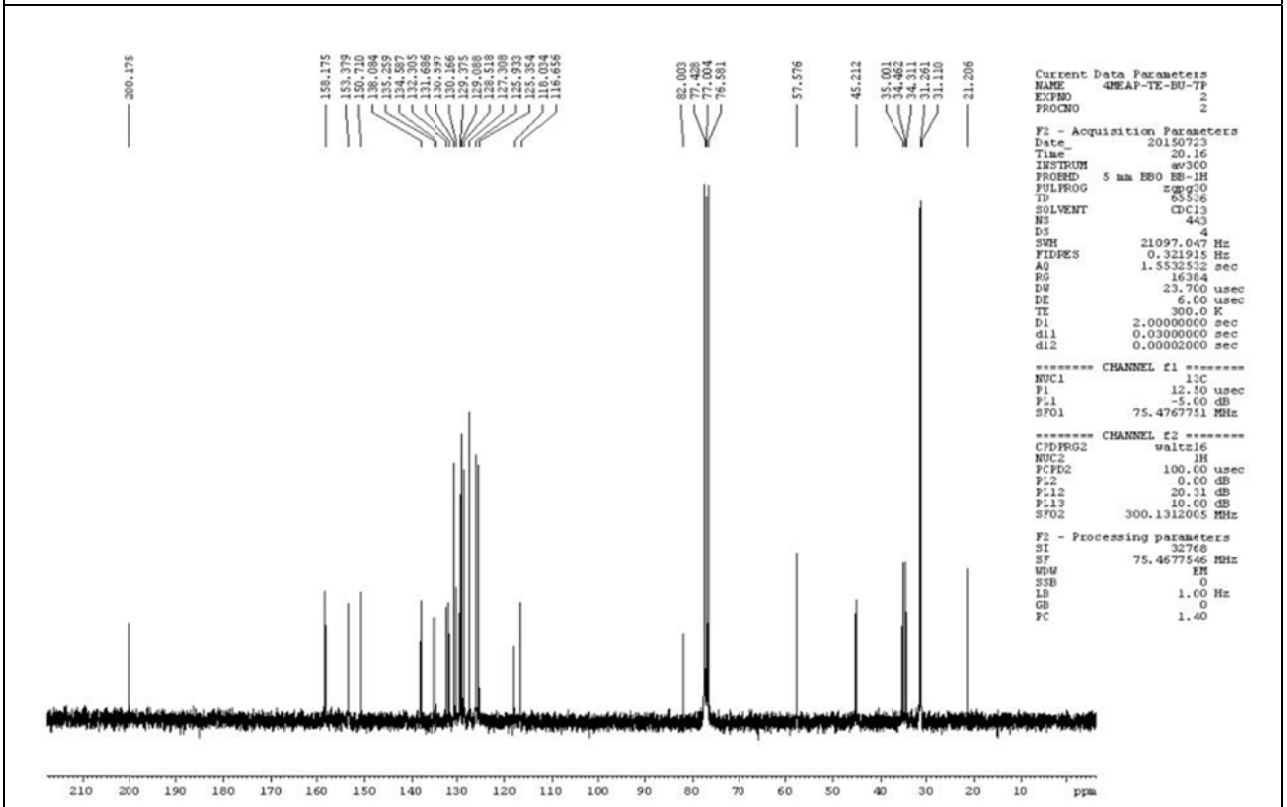

Figure 78.[13]CNMR spectrum of **1u**

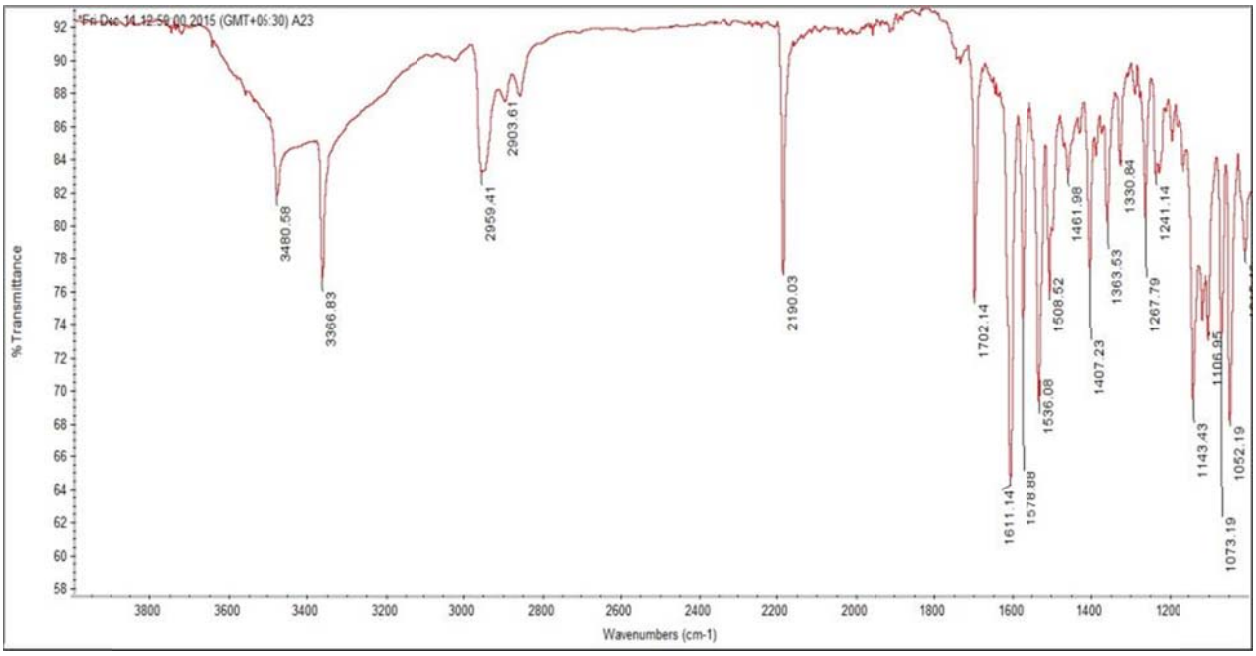

Figure 79. FT-IR spectrum of **1u**

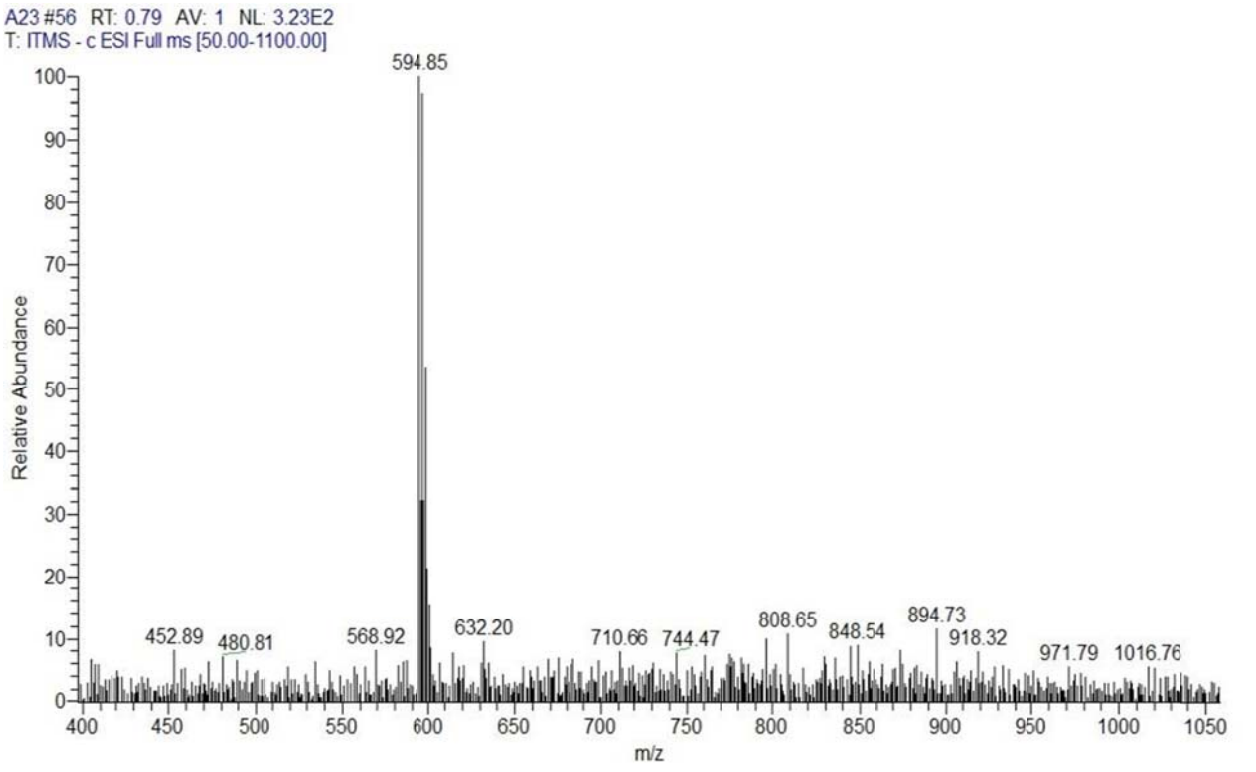

Figure 80. ESI-massof **1u**

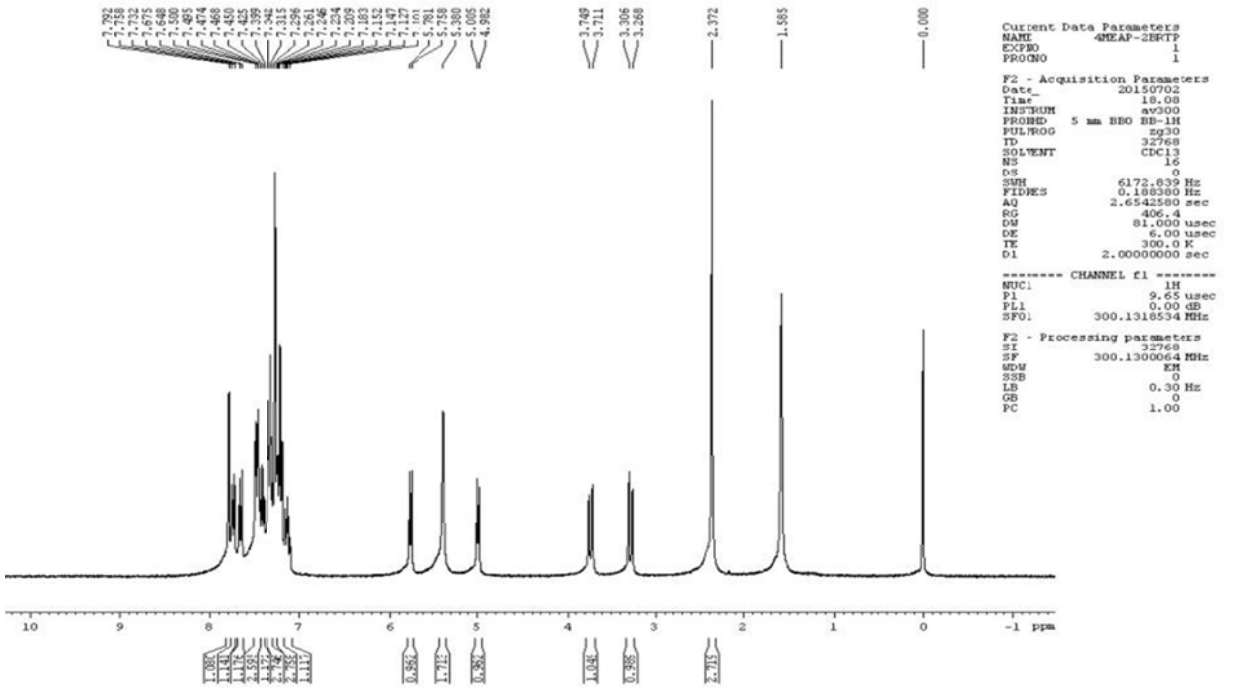

Figure 81. [1]HNMR spectrum of **1v**

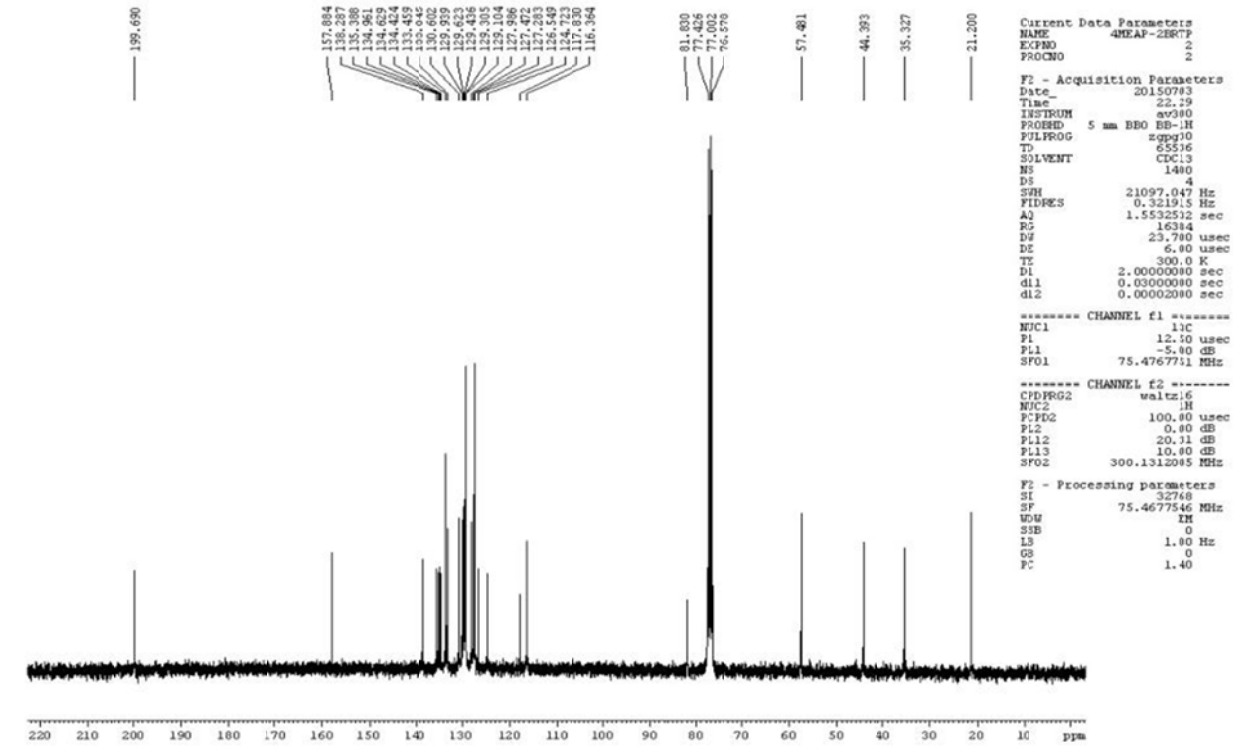

Figure 82. [13]CNMR spectrum of **1v**

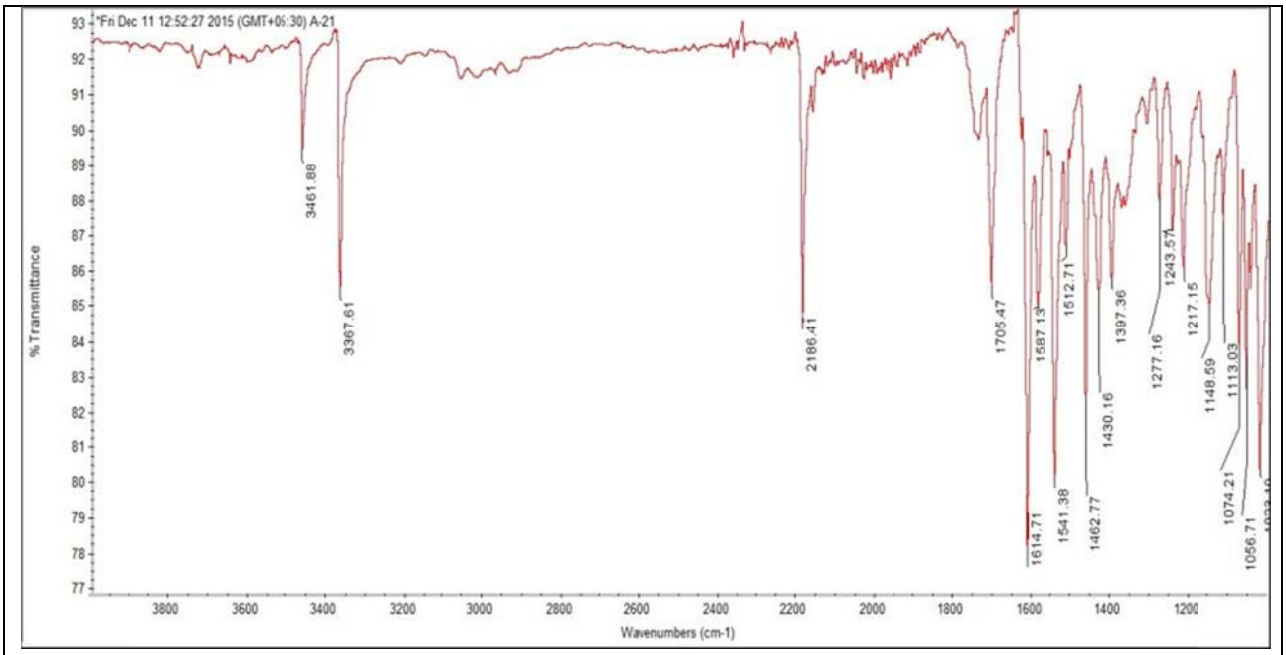

Figure 83. FT-IR spectrum of **1v**

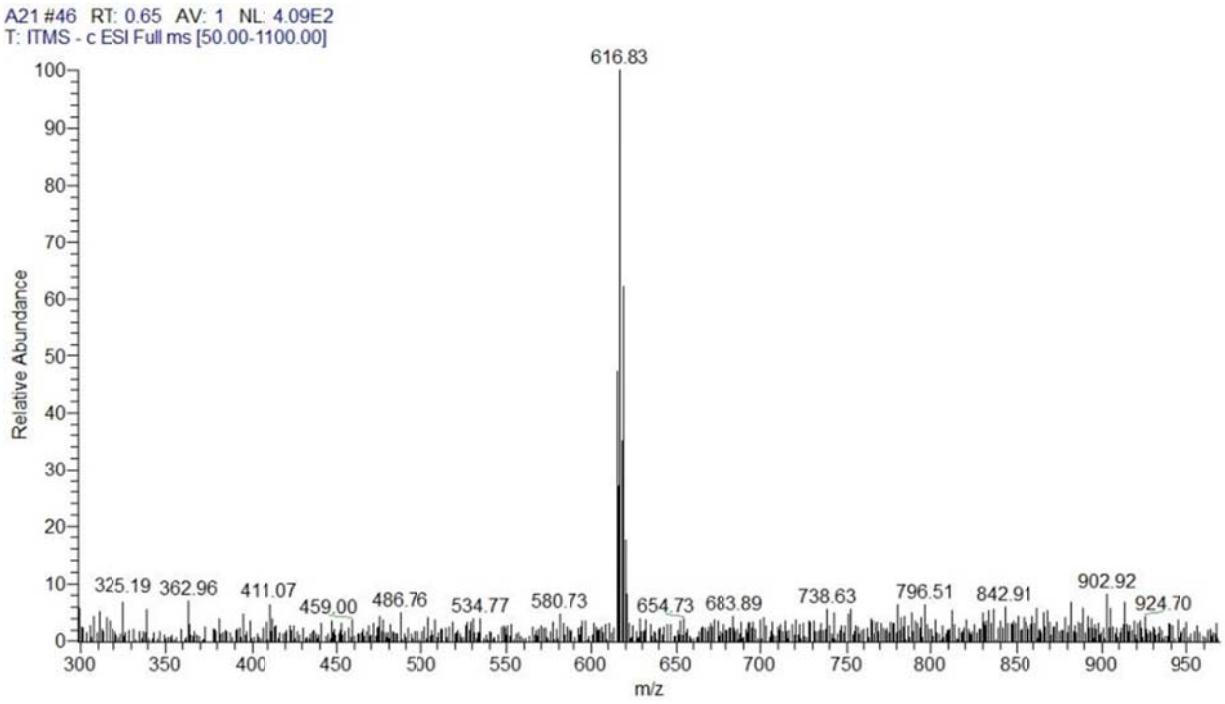

Figure 84. ESI-mass of **1v**

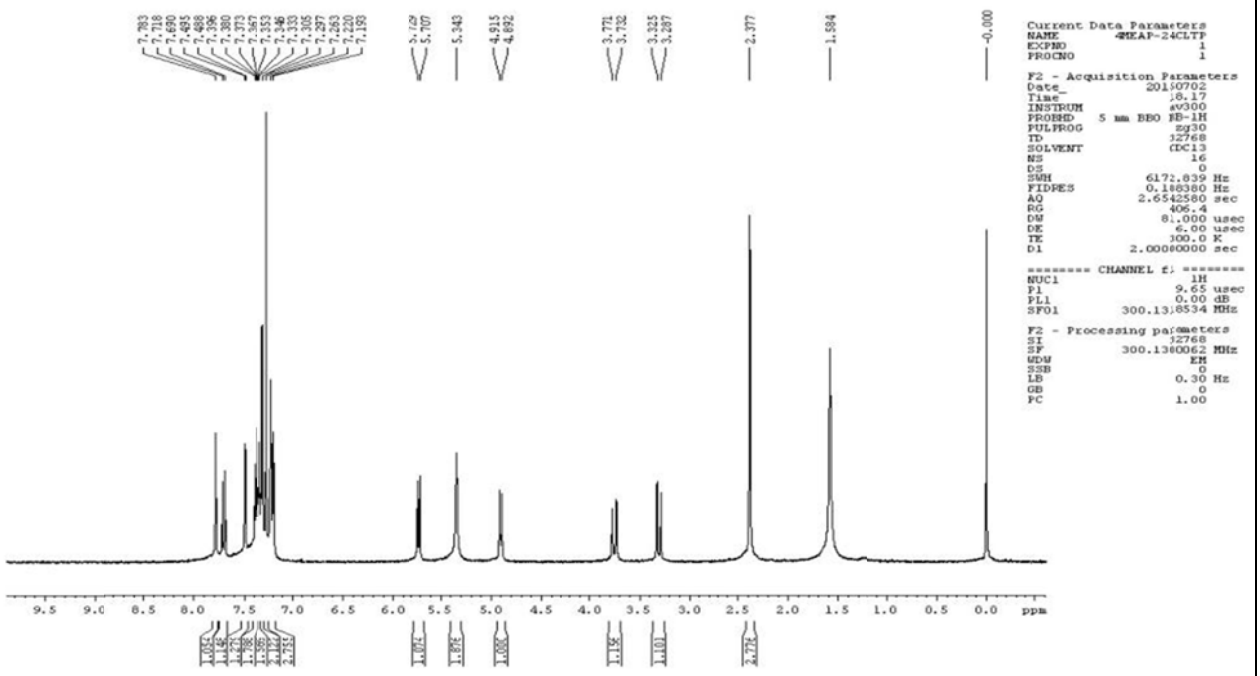

Figure 85. ^{1}HNMR spectrum of **1w**

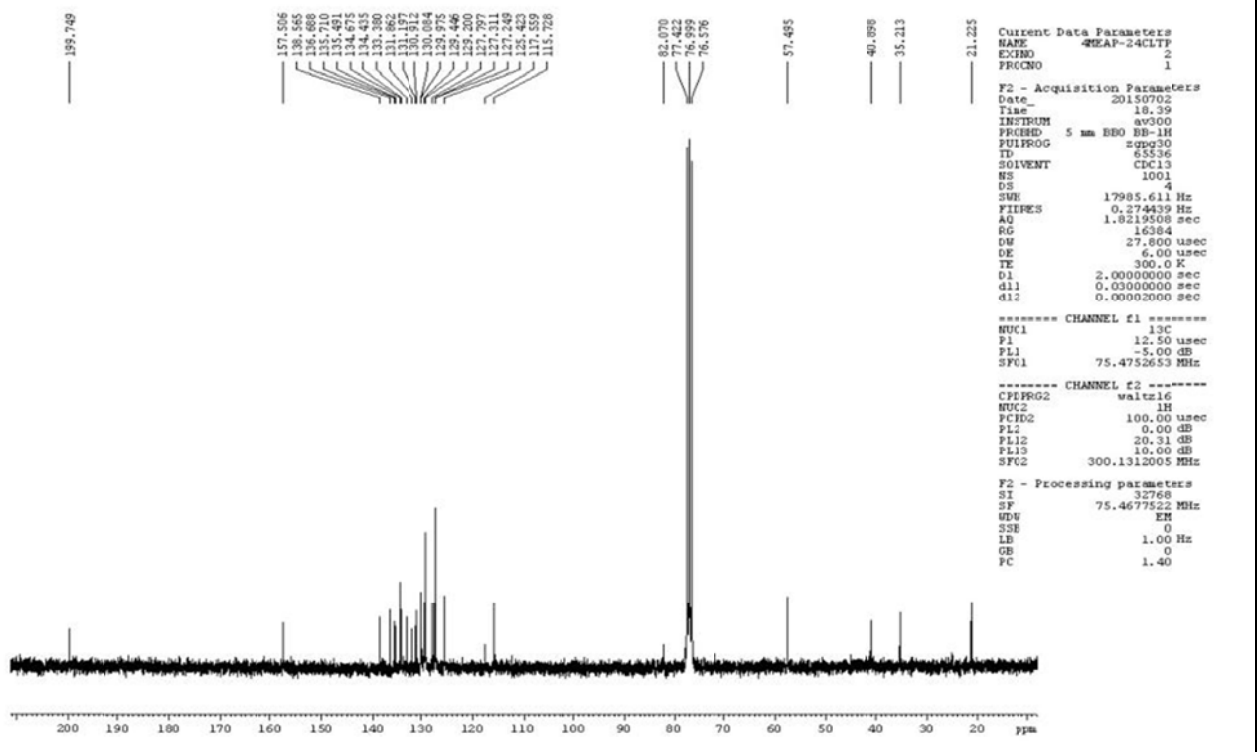

Figure 86. ^{13}CNMR spectrum of **1w**

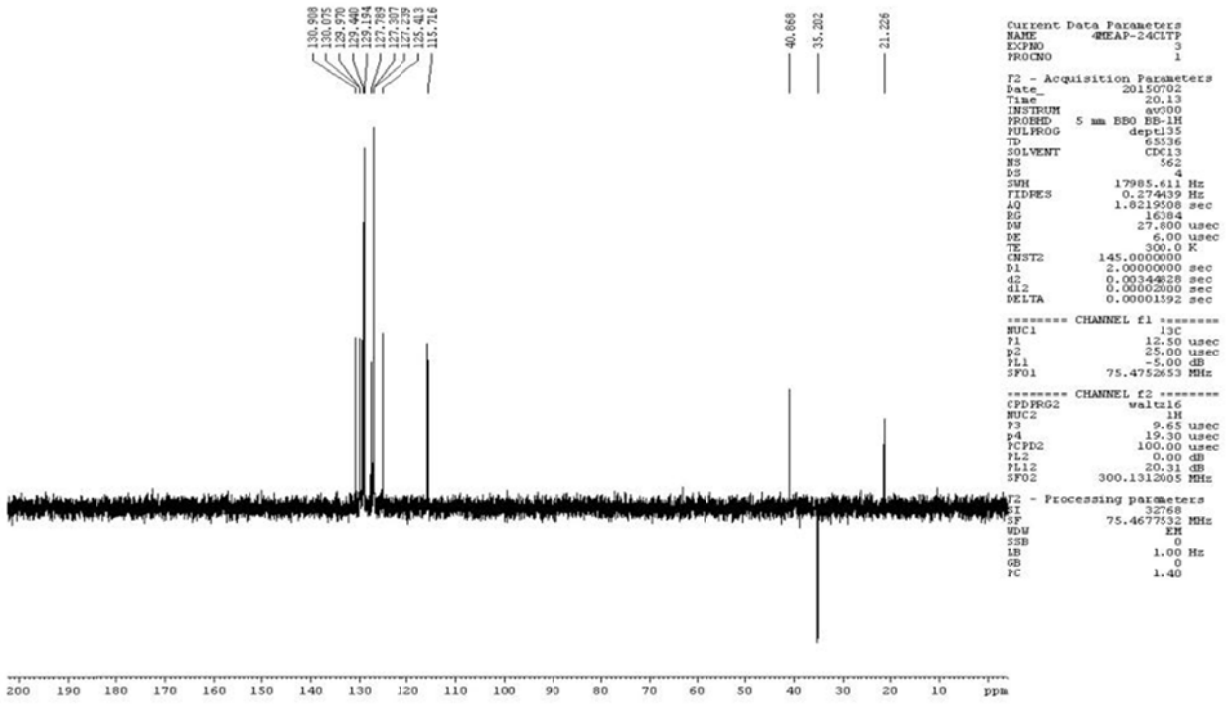

Figure 87. DEPT spectrum of **1w**

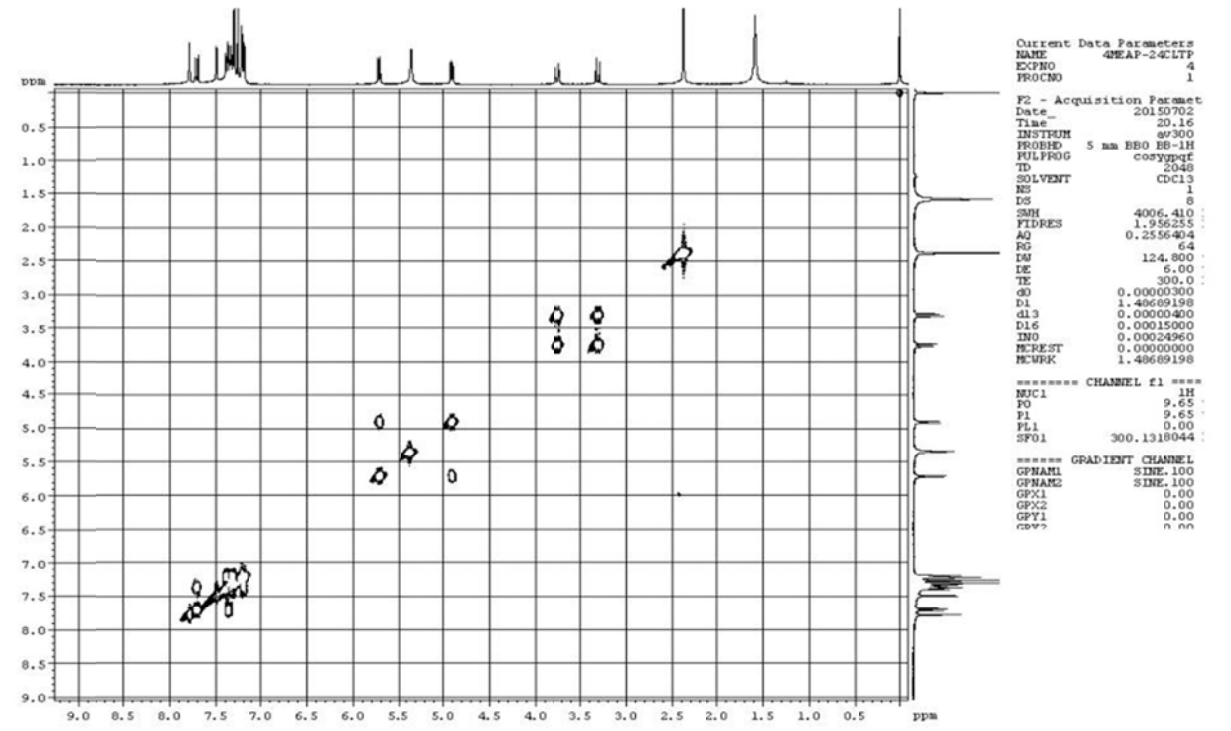

Figure 88. H-H COSY spectrum of **1w**

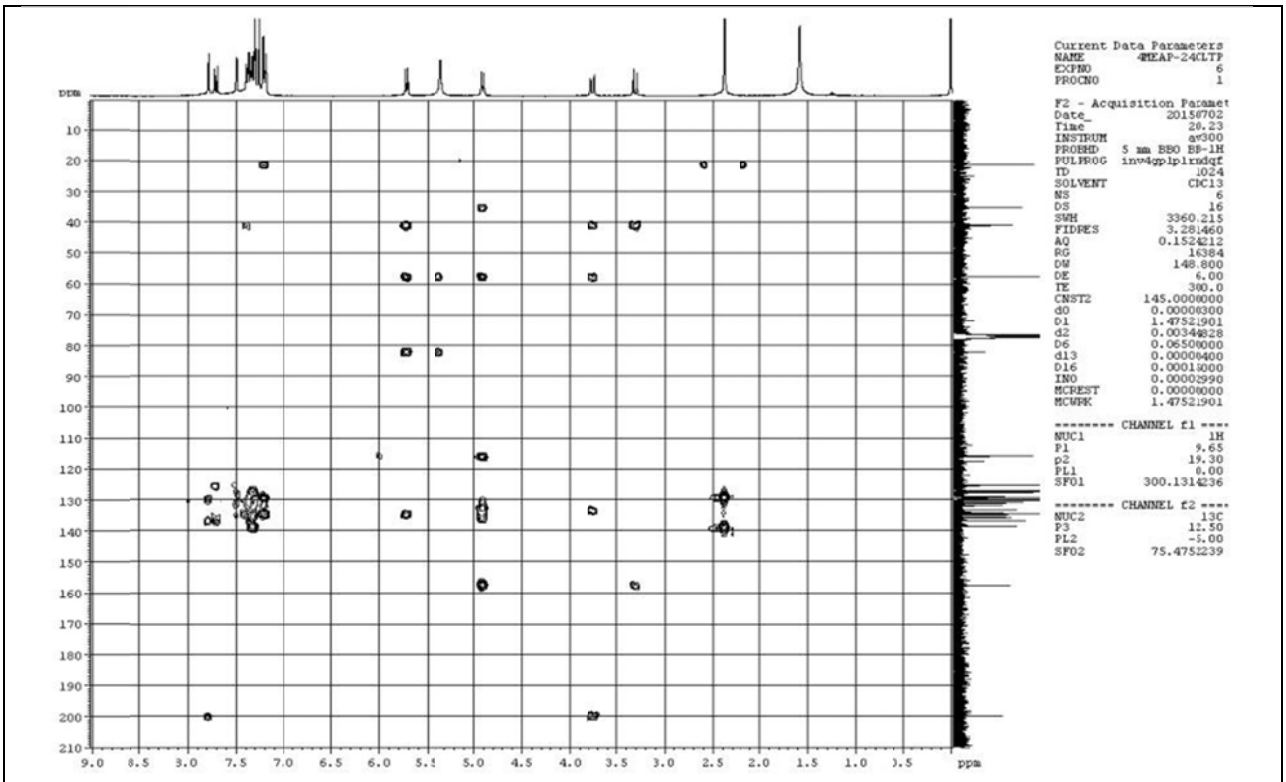

Figure 89. HMBC spectrum of **1w**

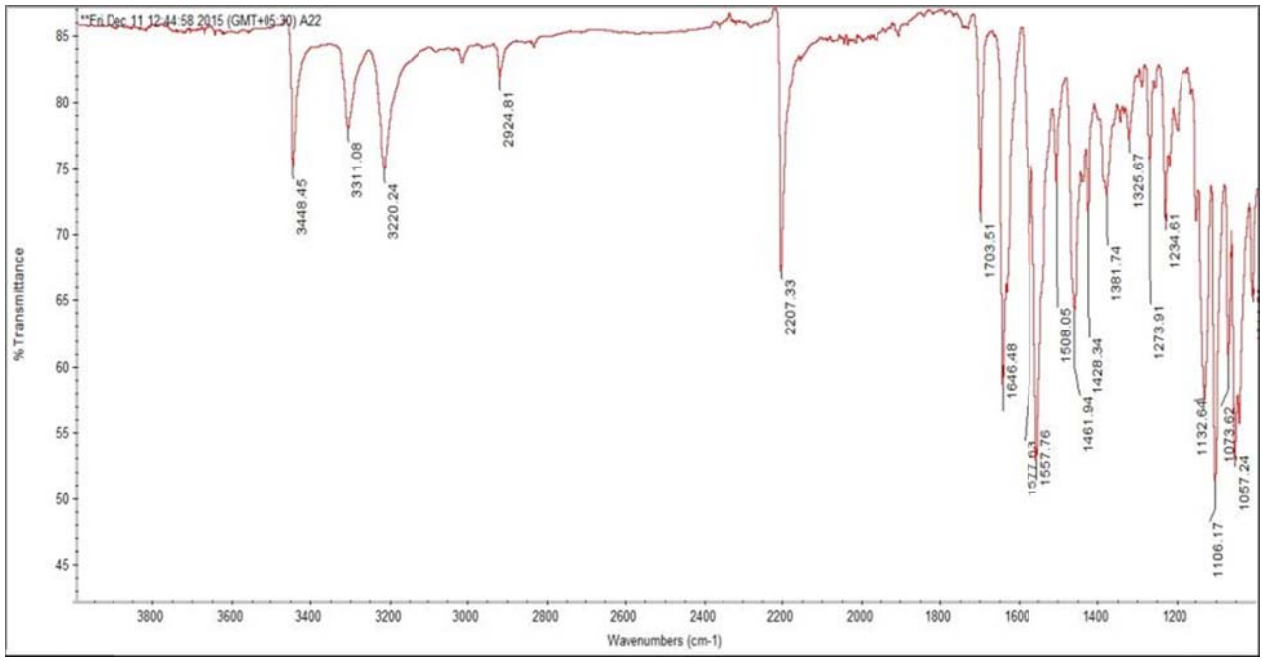

Figure 90. FT-IR spectrum of **1w**

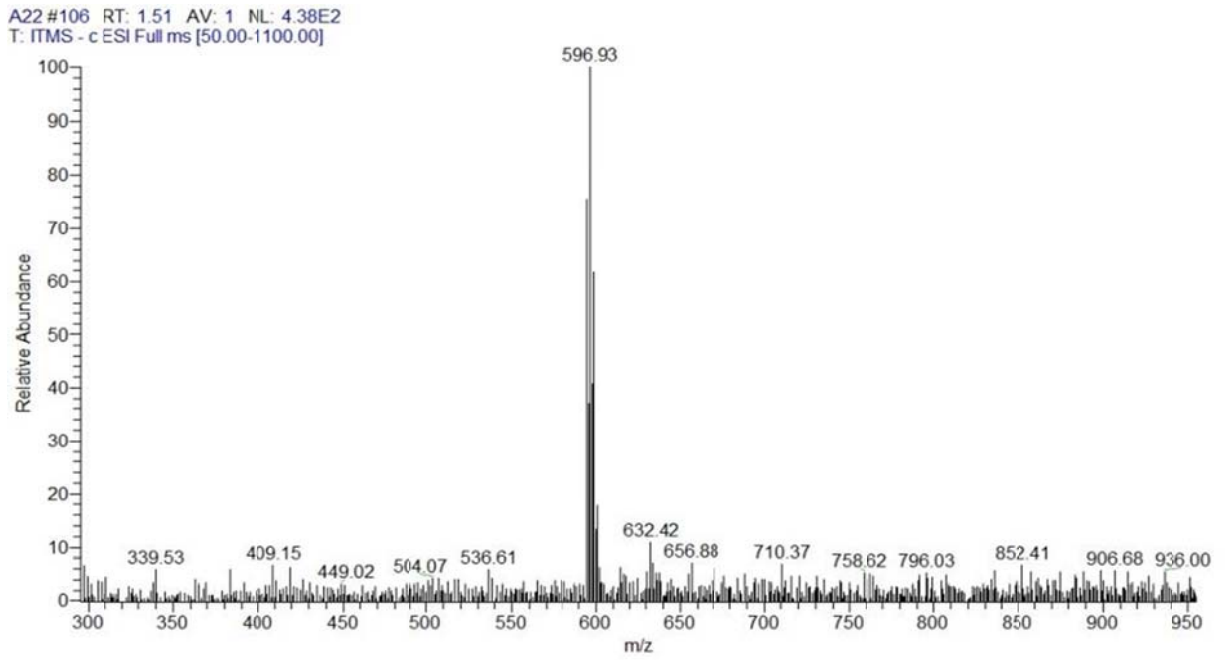

Figure 91. ESI-mass of **1w**

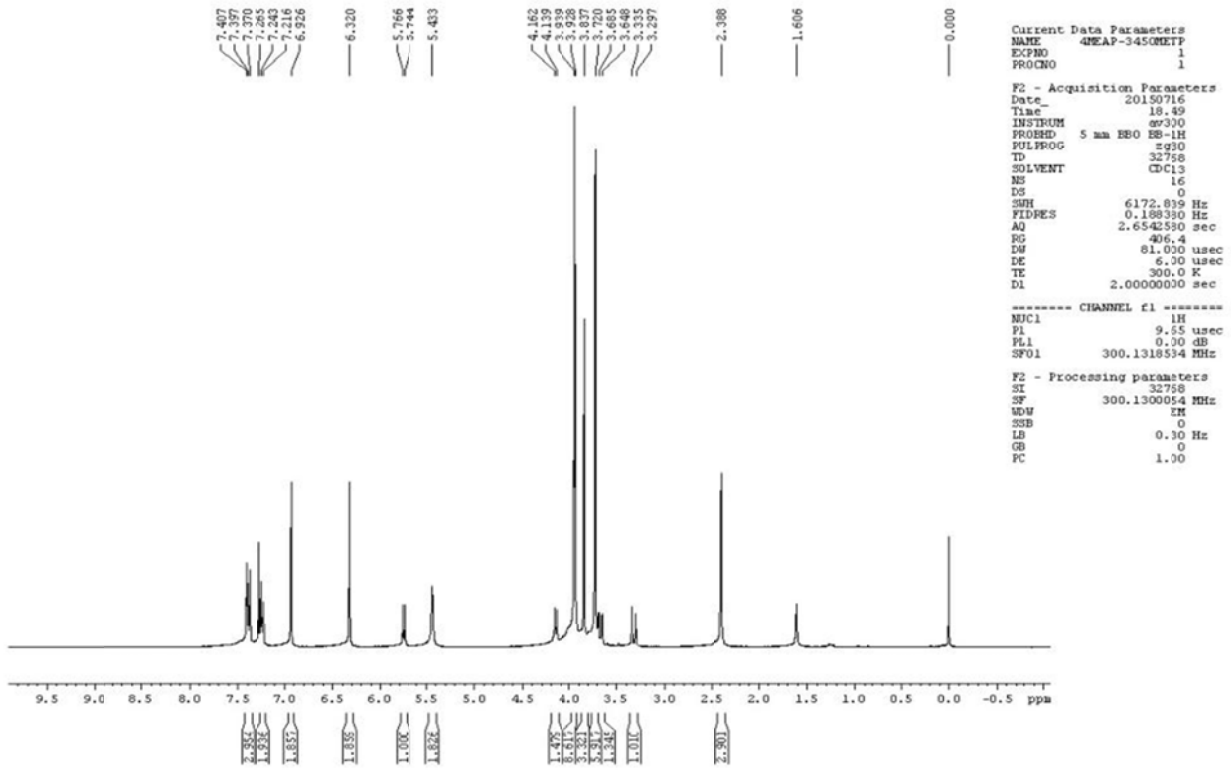

Figure 92.[1]H NMR spectrum of 1**x**

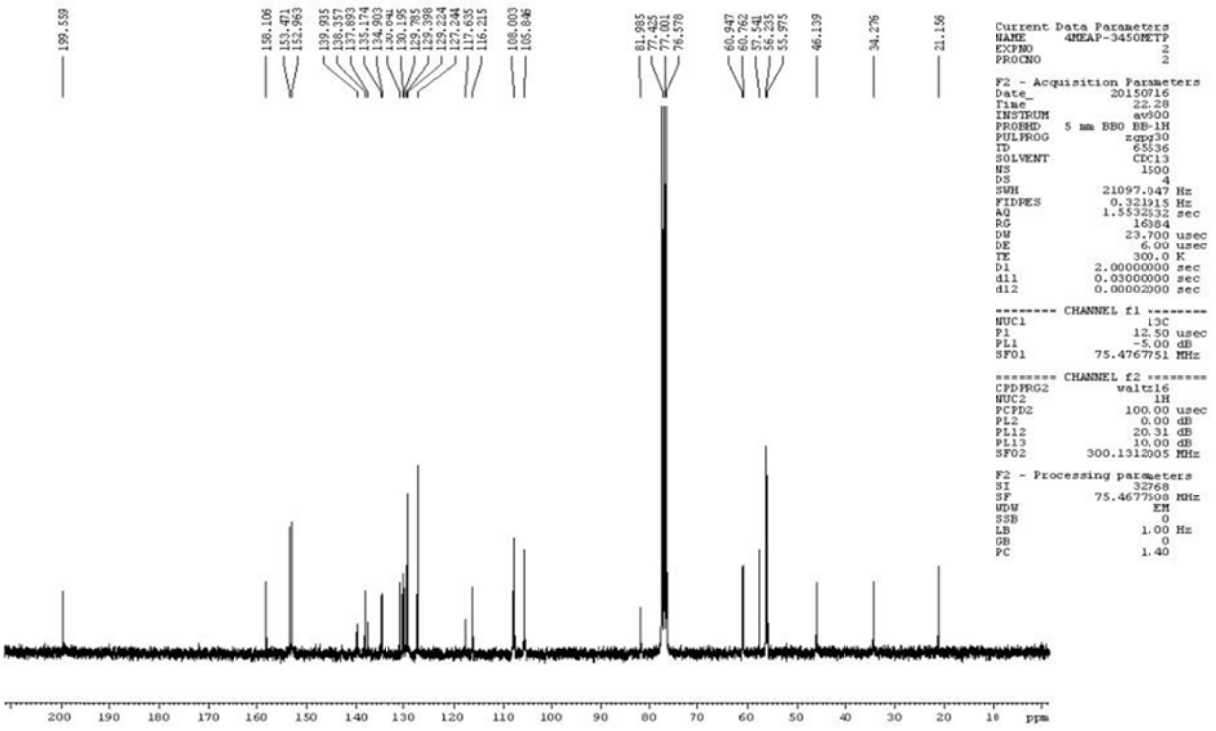

Figure 93. ^{13}C NMR spectrum of **1x**

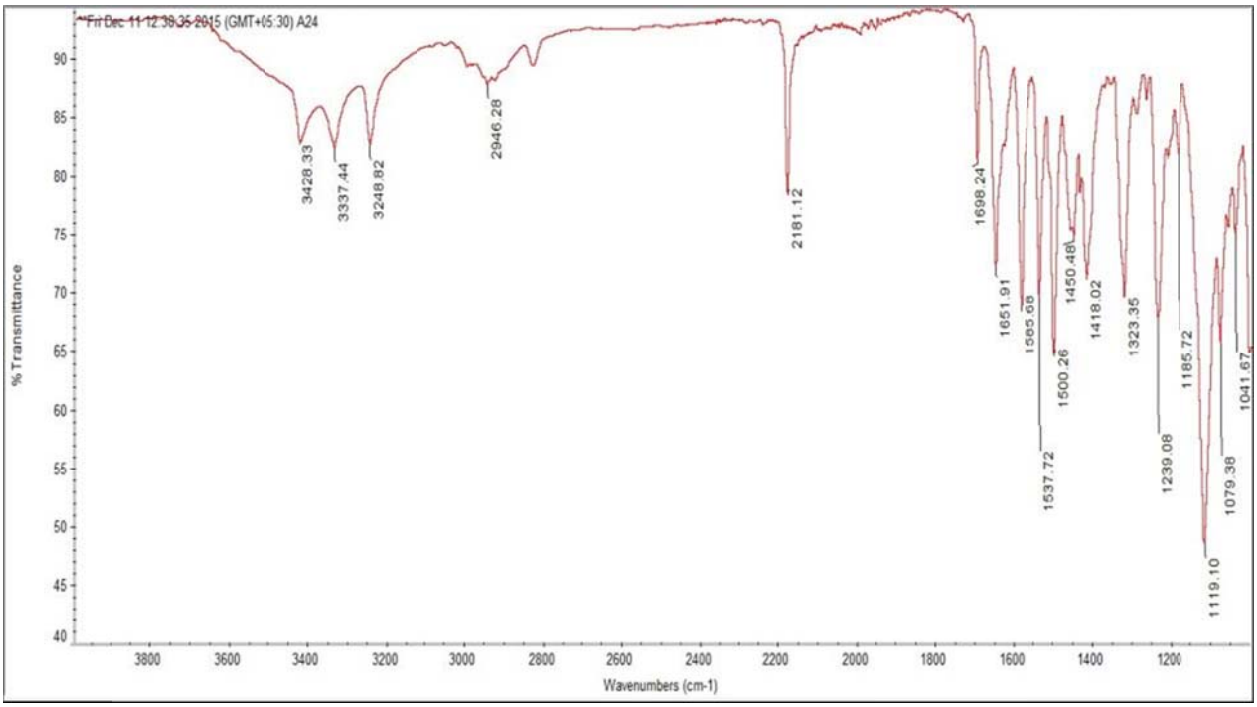

Figure 94. FT-IR spectrum of **1x**

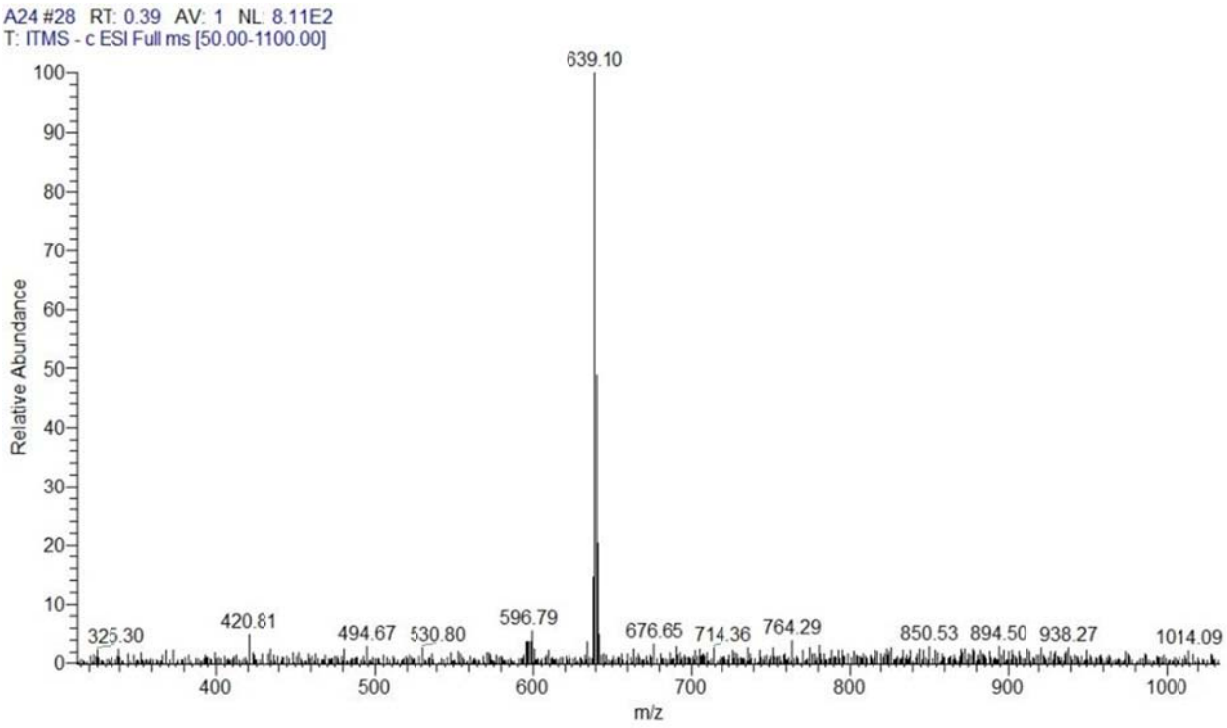

Figure 95. ESI-massof **3x**

Crystallographic data of 1v

The compound **1v** crystallized in the triclinic crystal system with two molecules in the unit cell (**Table 1**). The 2-bromobenzylidene and 2-bromophenyl rings are oriented with an angle of 75.9(1)° and the p-tolyl is making angles of 73.3(1) and 80.5(1)° with 2-bromobenzylidene and 2-bromophenyl rings, respectively. The molecular structure features an intramolecular N-H...O hydrogen bond which gives the conformational stability for the molecule (**Table 2**). Further, the crystal packing is stabilized through weak N–H···S and C-H...Br interactions. One of the C-H...S interaction in the crystal lattice leads to an infinite chain C(5) motif extending along the *a*-axis of the unit cell. One of the C-H...Br interaction leads to ring $R_2^2(24)$ motif. (**Figures 96** and **97**)

Table 1. Crystallographic data of **1v**

Empirical formula	C_{30} H_{22} Br_2 N_2 O S
Formula weight	618.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.8301(4) Å α = 76.797(9) °
	b = 9.9382(6) Å β = 83.778(8)°
	c = 18.0845(11) Å γ = 77.976(6)°
Volume	1337.29(15) $Å^3$
Z, Calculated density	2, 1.536 Mg/m^3
Absorption coefficient	3.135 mm^{-1}
F(000)	620
Crystal size	0.22 x 0.16 x 0.18 mm^3
Theta range for data collection	2.144 to 24.995°
Limiting indices	$-9 \leq h \leq 9$, $-11 \leq k \leq 11$, $-21 \leq l \leq 21$
Reflections collected / unique	25914 / 4709 [R(int) = 0.0313]
Completeness to theta = 25.242°	97.4%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4709 / 0 / 326
Goodness-of-fit on F^2	1.120
Final R indices [I>2sigma(I)]	R1 = 0.0592, wR2 = 0.2033
R indices (all data)	R1 = 0.0713, wR2 = 0.2136
Largest diff. peak and hole	4.038 and -0.472 e. $Å^{-3}$

Table 2. Hydrogen bonds geometry of **1v**

D-H...A (Å, °)	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)
C(2)-H(2)...Br(2)#1	0.93	2.96	3.750(6)	143.1
C(11)-H(11B)...Br(1)#2	0.97	3.13	3.670(6)	117.0
N(1)-H(1A)...S(1)#3	0.86	2.88	3.535(6)	134.4
N(1)-H(1B)...O(1)	0.86	2.41	2.830(8)	110.5
N(1)-H(1B)...S(1)#2	0.86	3.03	3.748(6)	142.9

Equivalent positions: #1 -x+2,-y,-z+1 #2 -x+1,-y+1,-z+1 #3 x-1,y,z

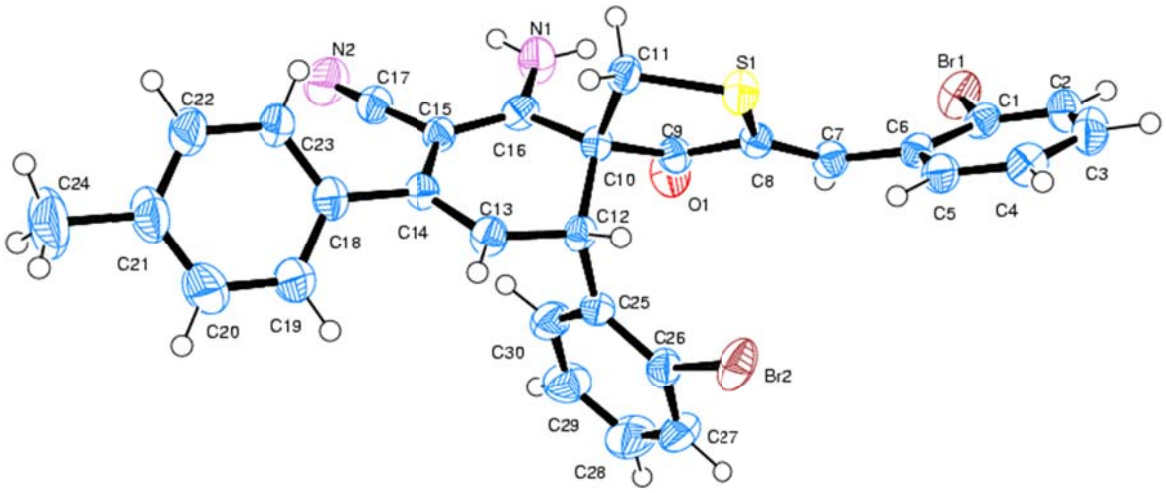

Figure 96. The molecular structure of compound **1v** with the numbering scheme for the atoms and 50% probability displacement ellipsoids

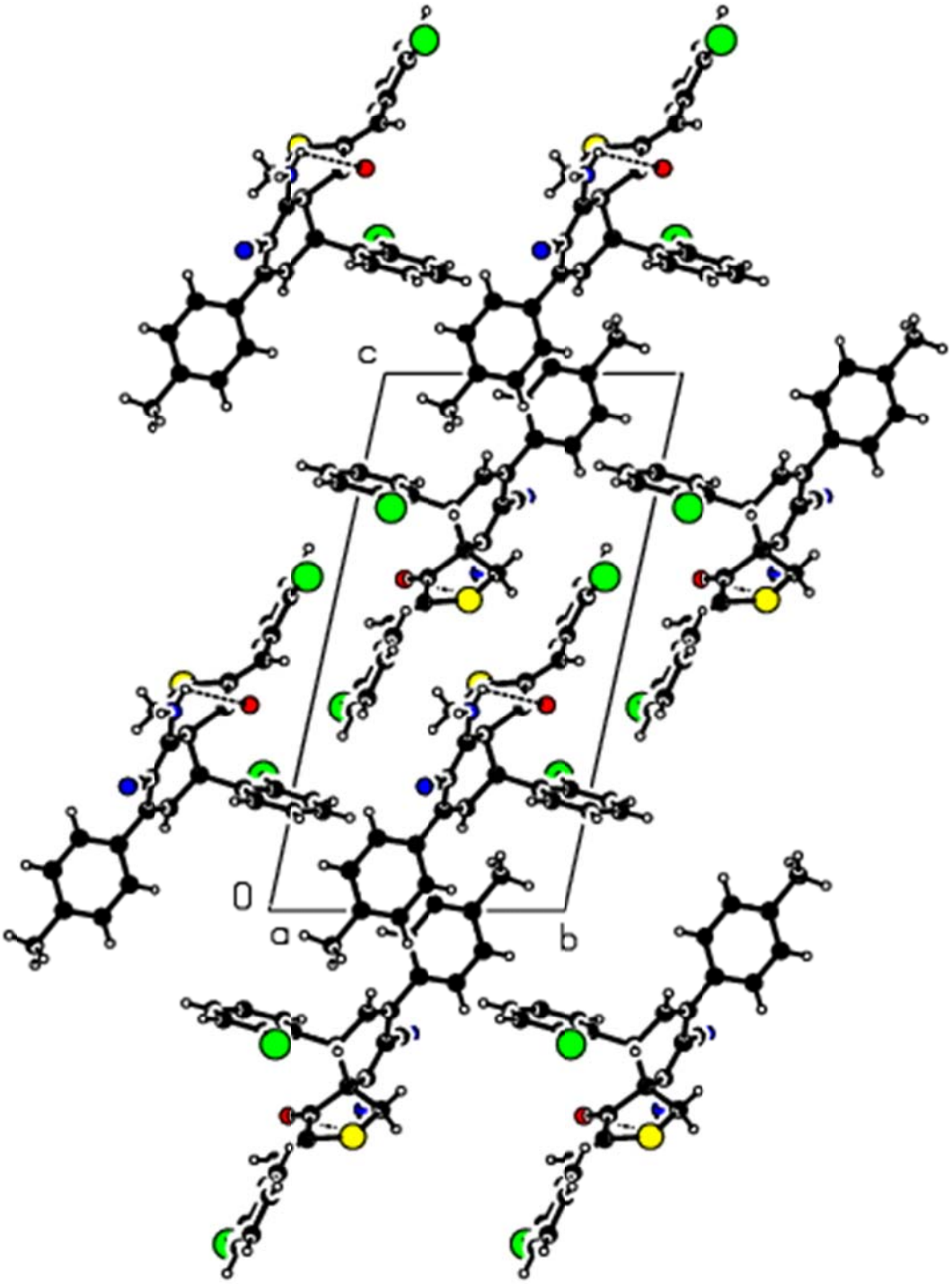

Figure 97. Packing diagram of **1v**