Electronic Supplementary Information

Introducing tetramethylurea as a new methylene precursor: Microwave-assisted $RuCl_3$-catalyzed cross dehydrogenative coupling approach to bis(indolyl)methanes

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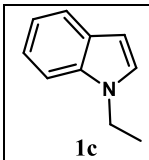
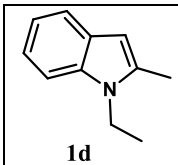
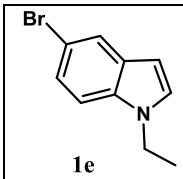
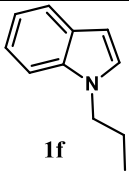
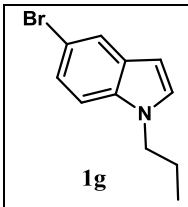
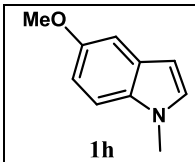
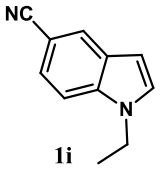
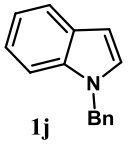
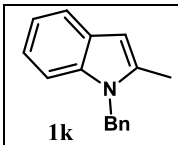
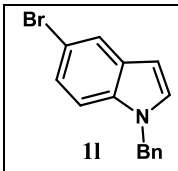
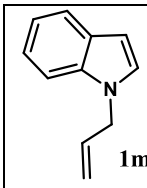
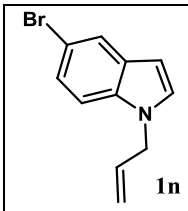
General procedure for the preparation of N-substituted indoles (1) (except 1-methylindole and 1,2-dimethylindole which were purchased):

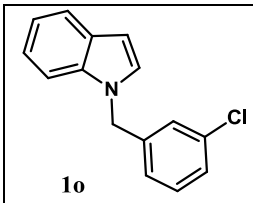
Indole (10 mmol, 1.17 g), sodium hydroxide (12 mmol, 1.2 eq., 480 mg), DMSO (3.5 mL) were taken in a round bottom flask and stirred for 20-30 minutes at room temperature. Then the flask was placed in an ice-bath. While stirring the reaction mixture, the alkyl halide (12 mmol, 1.2 eq.) was added slowly over a period of 10 minutes. Removed the ice bath and stirred the reaction mixture for 3-4 h at room temperature. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was poured into ice-water. Extracted the organic product with ethyl acetate (2 x 50 mL) and dried over anhydrous Na_2SO_4. Removed the solvent under vacuum and purified the product with column chromatography (silica gel, 100-200 mesh; hexane/ethyl acetate as eluent).

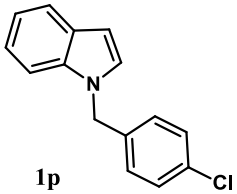
 **1c**	**1-ethyl-1H-indole (1c):**[1] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64-7.62 (m, 1H), 7.35 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.22-7.19 (m, 1H), 7.12-7.08 (m, 2H), 6.49 (dd, *J* = 3.1, 0.8 Hz, 1H), 4.17 (q, *J* = 7.3 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H).
 **1d**	**1-ethyl-2-methyl-1H-indole (1d):**[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.14-7.11 (m, 1H), 7.07-7.04 (m, 1H), 6.23 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).
 **1e**	**5-bromo-1-ethyl-1H-indole (1e):**[3] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 2.0 Hz, 1H), 7.28 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.22-7.20 (m, 1H), 7.11 (d, *J* = 3.2 Hz, 1H), 6.43 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.14 (q, *J* = 7.3 Hz, 2H), 1.45 (t, *J* = 7.3 Hz, 3H).
 **1f**	**1-propyl-1H-indole (1f):**[4] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.21-7.18 (m, 1H), 7.10-7.08 (m, 2H), 6.48 (d, *J* = 3.2 Hz, 1H), 4.07 (t, *J* = 7.0 Hz, 2H), 1.90-1.82 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

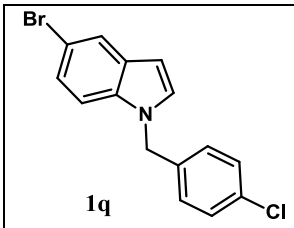
 1g	**5-bromo-1-propyl-1H-indole (1g):**[5] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 1.7 Hz, 1H), 7.27 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.20 (d, *J* = 8.7 Hz, 1H), 7.09 (d, *J* = 3.1 Hz, 1H), 6.42 (dd, *J* = 3.1, 0.6 Hz, 1H), 4.05 (t, *J* = 7.0 Hz, 2H), 1.88-1.81 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).
 1h	**5-methoxy-1-methyl-1H-indole (1h):**[6] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.9 Hz, 1H), 7.12 (d, *J* = 2.5 Hz, 1H), 7.05 (d, *J* = 3.2 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.41-6.40 (m, 1H), 3.86 (s, 3H), 3.76 (s, 3H).
 1i	**1-ethyl-1H-indole-5-carbonitrile (1i):**[4] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.36-7.29 (m, 2H), 7.15 (d, *J* = 3.2 Hz, 1H), 6.47 (d, *J* = 3.1 Hz, 1H), 4.09 (q, *J* = 7.3 Hz, 2H), 1.36 (t, *J* = 7.3 Hz, 3H).
 1j	**1-benzyl-1H-indole (1j):**[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.31-7.25 (m, 4H), 7.18-7.17 (m, 1H), 7.15 (d, *J* = 3.1 Hz, 1H), 7.12-7.09 (m, 3H), 6.56 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.33 (s, 2H).
 1k	**1-benzyl-2-methyl-1H-indole (1k):**[2] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56-7.55 (m, 1H), 7.27-7.19 (m, 4H), 7.11-7.07 (m, 2H), 6.97 (d, *J* = 6.9 Hz, 2H), 6.33 (s, 1H), 5.30 (s, 2H), 2.36 (s, 3H).
 1l	**1-benzyl-5-bromo-1H-indole (1l):**[7] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 1.5 Hz, 1H), 7.31-7.26 (m, 3H), 7.23 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.13-7.12 (m, 2H), 7.08-7.06 (m, 2H), 6.49 (dd, *J* = 3.1, 0.8 Hz, 1H), 5.29 (s, 1H).

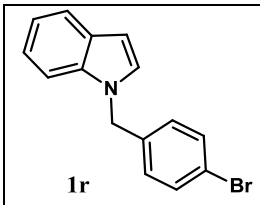
 1m	**1-allyl-1H-indole (1m):**[8] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64-7.62 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.21-7.18 (m, 1H), 7.12-7.09 (m, 2H), 6.52-6.51 (m, 1H), 6.04-5.93 (m, 1H), 5.20-5.16 (m, 1H), 5.10-5.05 (m, 1H), 4.73-4.72 (m, 2H).

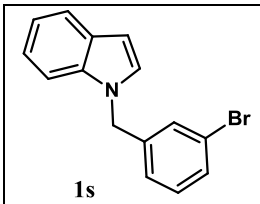
 1n	**1-allyl-5-bromo-1H-indole (1n):**[9] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 1.4 Hz, 1H), 7.27 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 6.45 (d, *J* = 3.1 Hz, 1H), 6.00-5.93 (m, 1H), 5.21-5.19 (m, 1H), 5.07-5.02 (m, 1H), 4.71-4.69 (m, 2H).

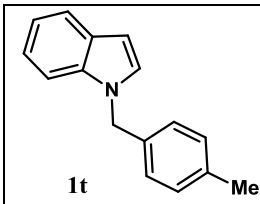
 1o	**1-(3-chlorobenzyl)-1H-indole (1o):**[10] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.29-7.25 (m, 1H), 7.25-7.22 (m, 2H), 7.21-7.16 (m, 2H), 7.12 (d, *J* = 3.1 Hz, 2H), 6.95-6.93 (m, 1H), 6.57 (d, *J* = 3.2 Hz, 1H), 5.29 (s, 2H).

 1p	**1-(4-chlorobenzyl)-1H-indole (1p):**[11] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.26-7.22 (m, 3H), 7.19-7.16 (m, 1H), 7.13-7.11 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.56 (m, 1H), 5.29 (s, 2H).

 1q	**5-bromo-1-(4-chlorobenzyl)-1H-indole (1q):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.27-7.21 (m, 3H), 7.10-7.06 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.49 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.24 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.5, 134.7, 133.6, 130.4, 129.3, 129.0, 127.9, 124.6, 123.5, 113.0, 111.0, 101.5, 49.6; HRMS (ESI) exact mass calculated for $C_{15}H_{11}BrClN$ $[M + H]^+$: 319.9842; found: 319.9836.

 1r	**1-(4-bromobenzyl)-1H-indole (1r):**[12] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.23-7.10 (m, 4H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.56 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.26 (s, 2H).

 1s	**1-(3-bromobenzyl)-1H-indole (1s):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.28-7.22 (m, 2H), 7.20-7.16 (m, 1H), 7.13-7.10 (m, 3H), 6.96-6.95 (m, 1H), 6.57 (d, *J* = 3.1 Hz, 1H), 5.25 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 136.1, 130.7, 130.3, 129.7, 128.7, 128.1, 125.2, 122.8, 121.9, 121.0, 119.7, 109.5, 102.1, 49.4; HRMS (ESI) exact mass calculated for $C_{15}H_{12}BrN$ $[M + H]^+$: 286.0231; found: 286.0234.

 1t	**1-(4-methylbenzyl)-1H-indole (1t):**[12] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.11-7.08 (m, 4H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.54-6.53 (m, 1H), 5.27 (s, 2H), 2.30 (s, 3H).

References

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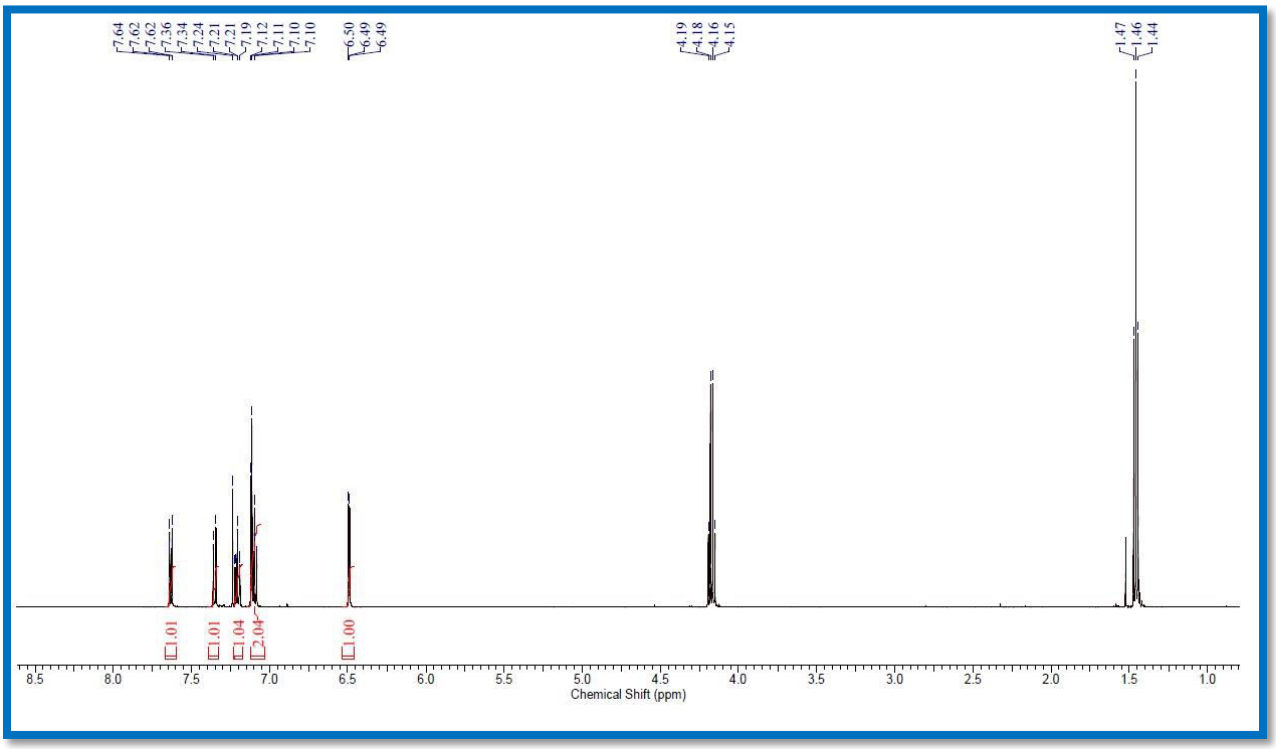
^{1}H-NMR of compound 1c



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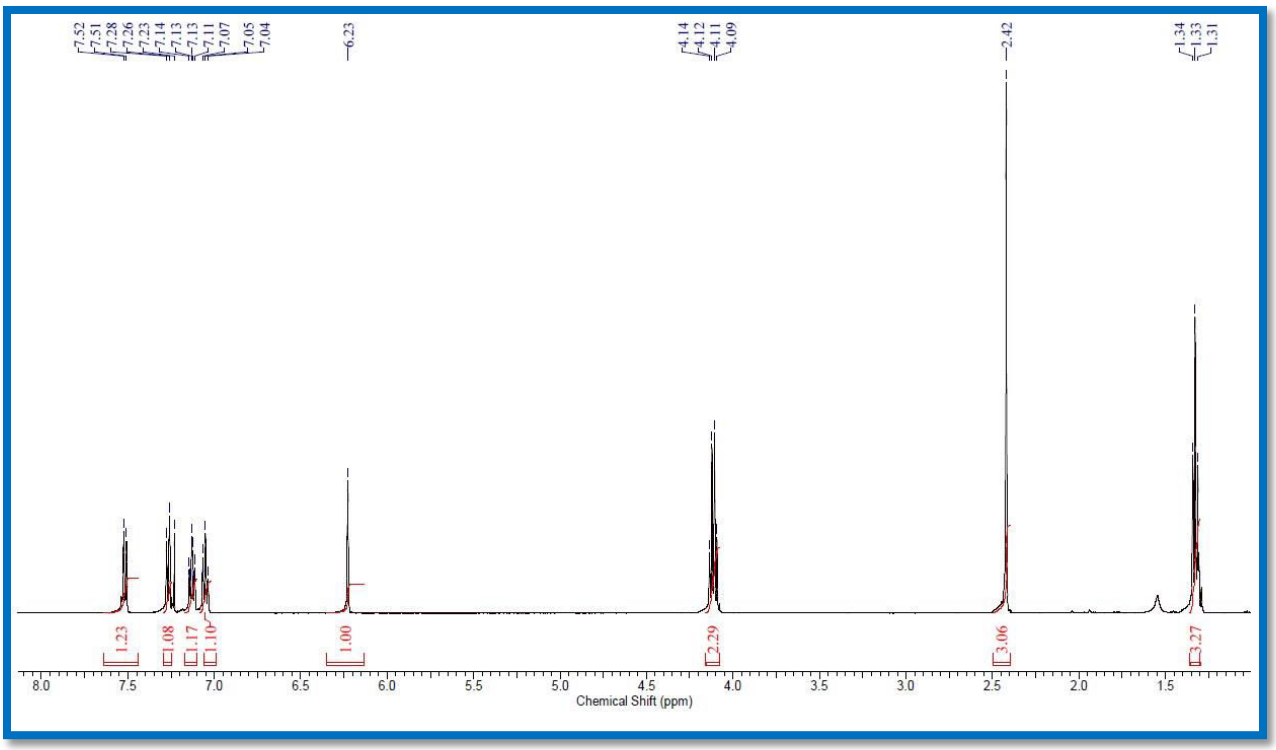

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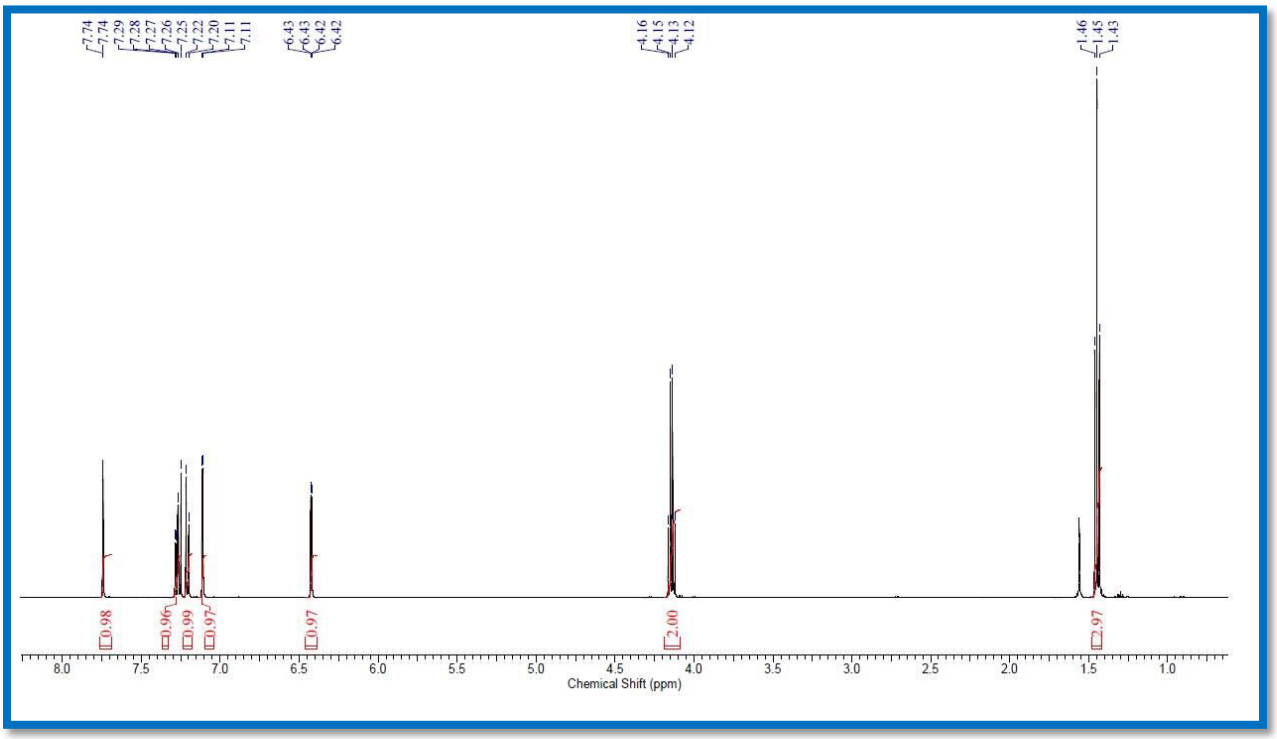

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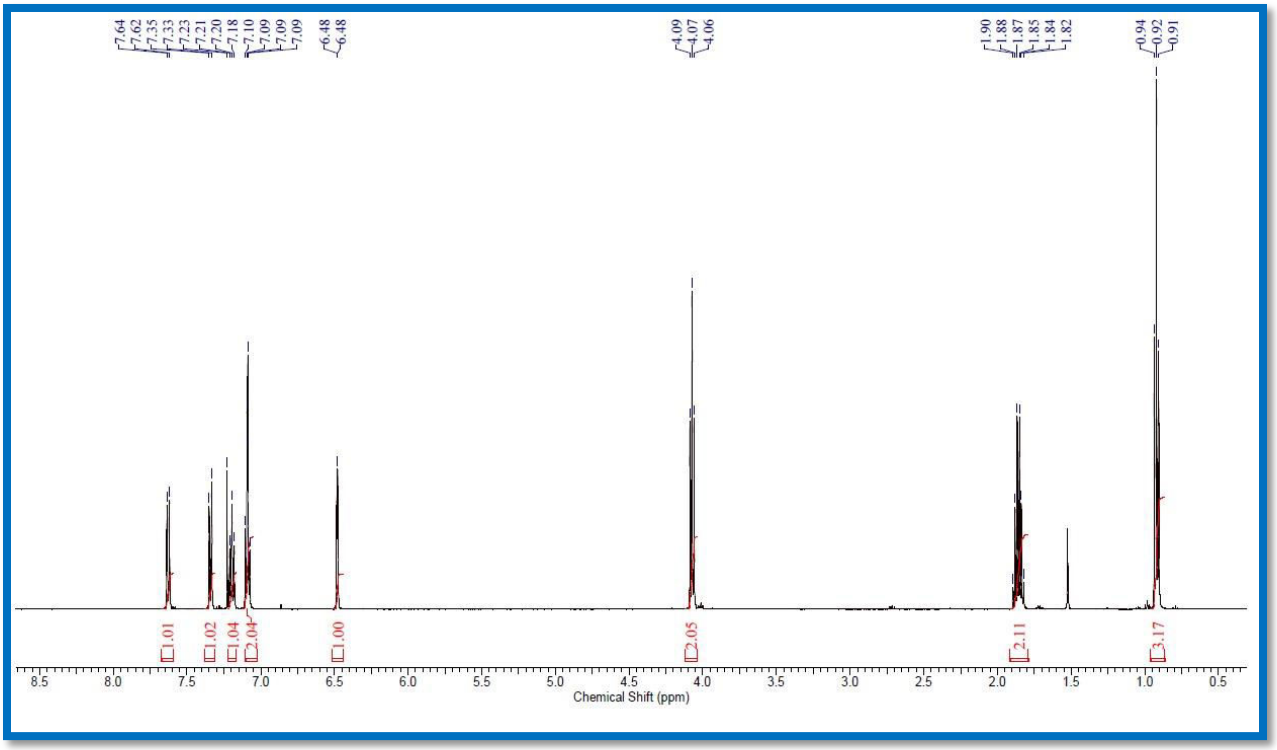

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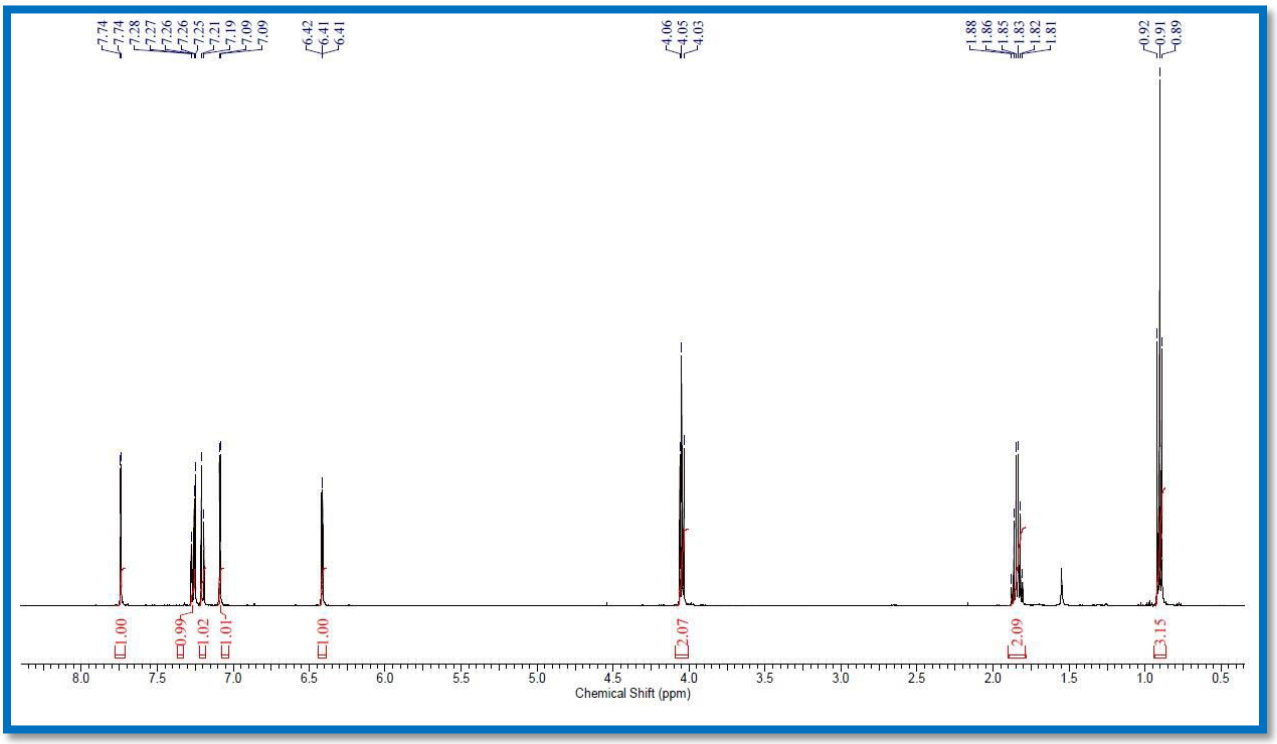

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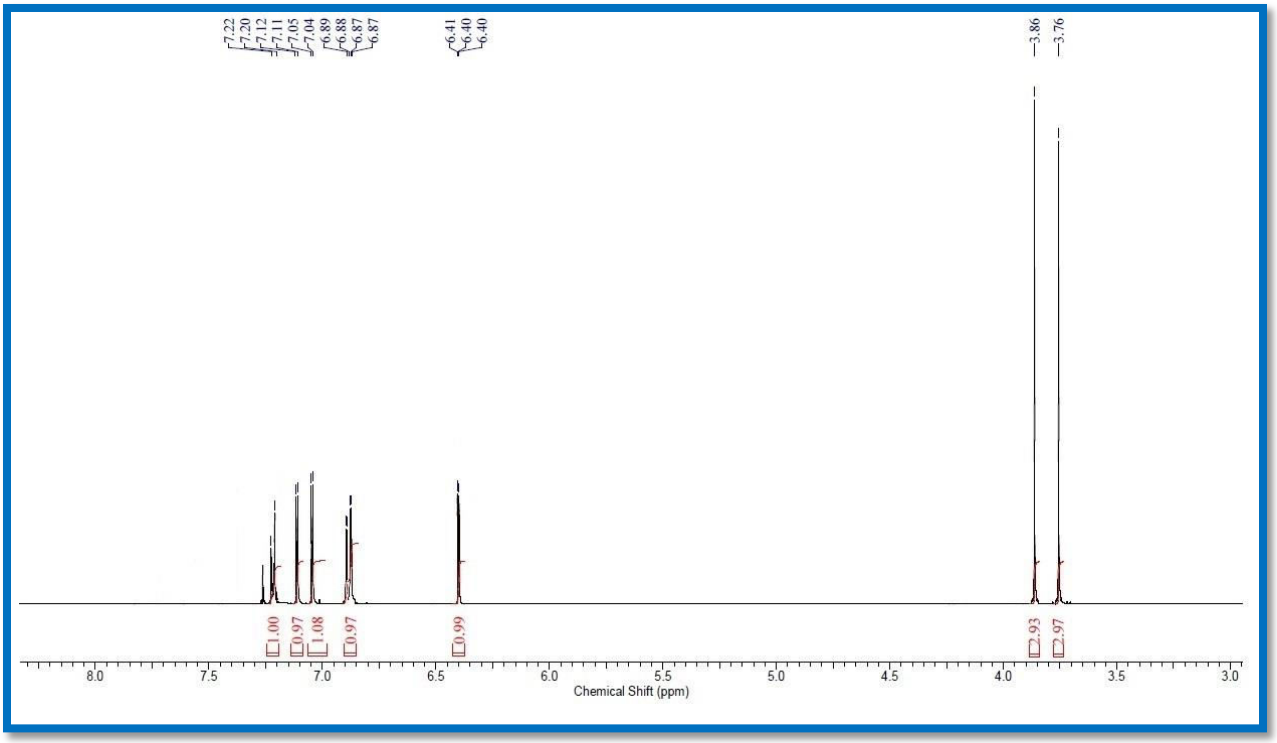

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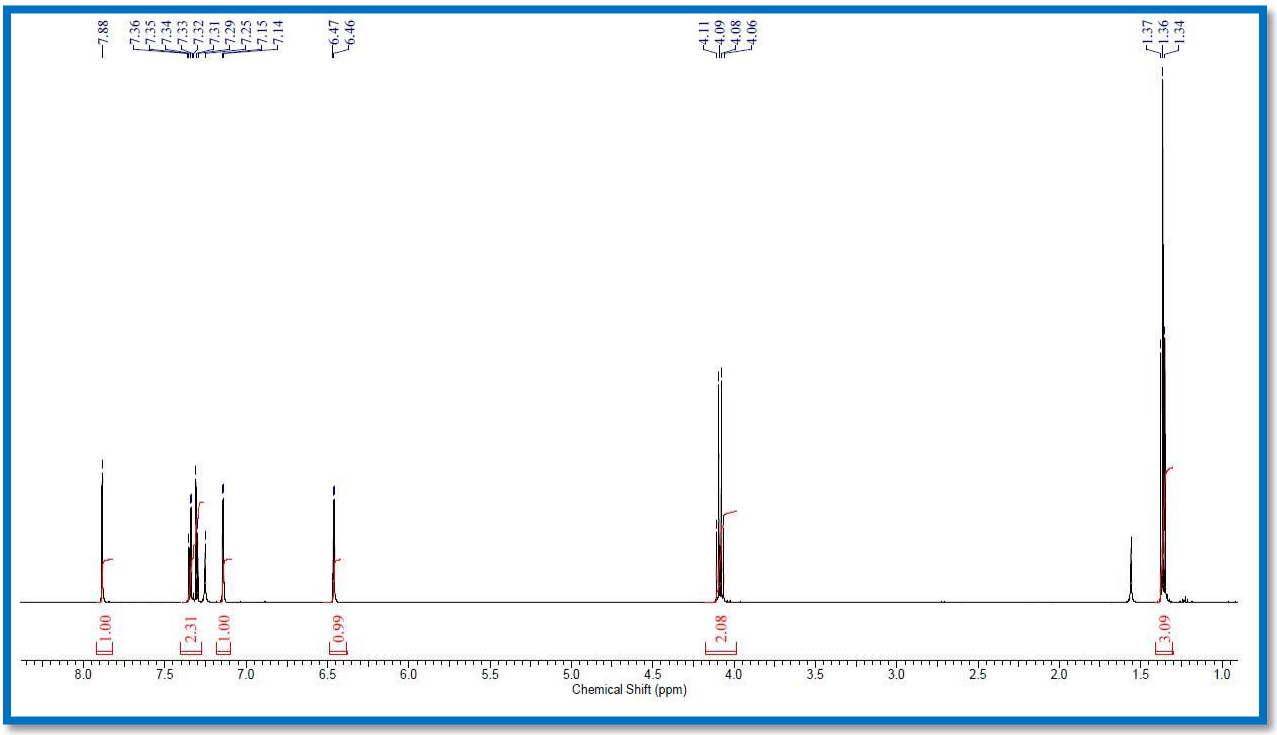

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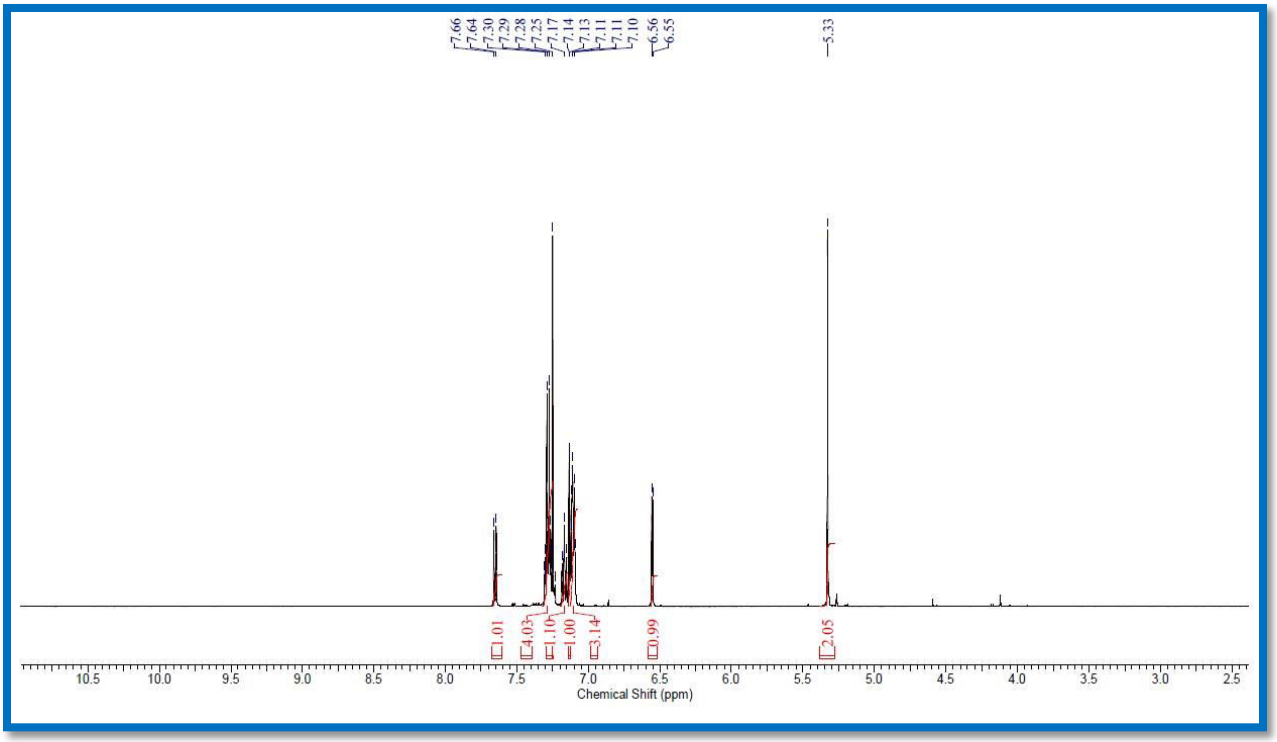

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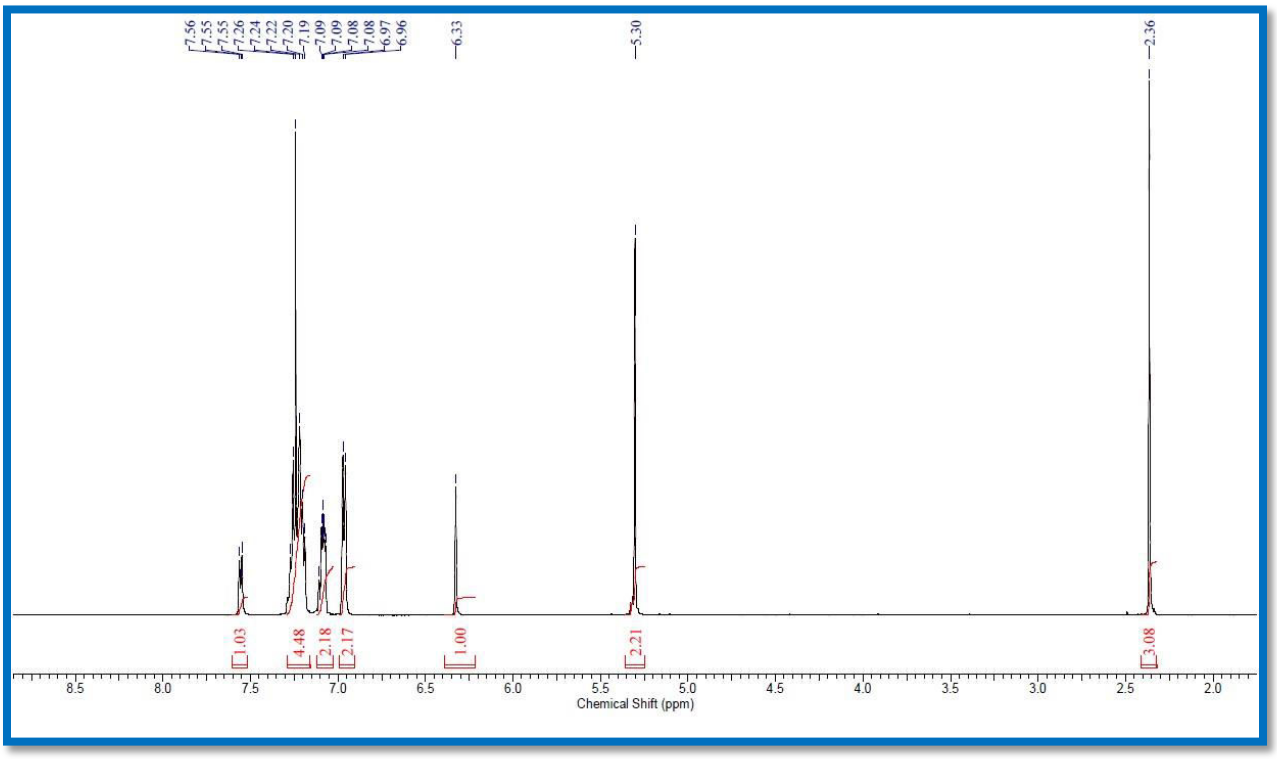

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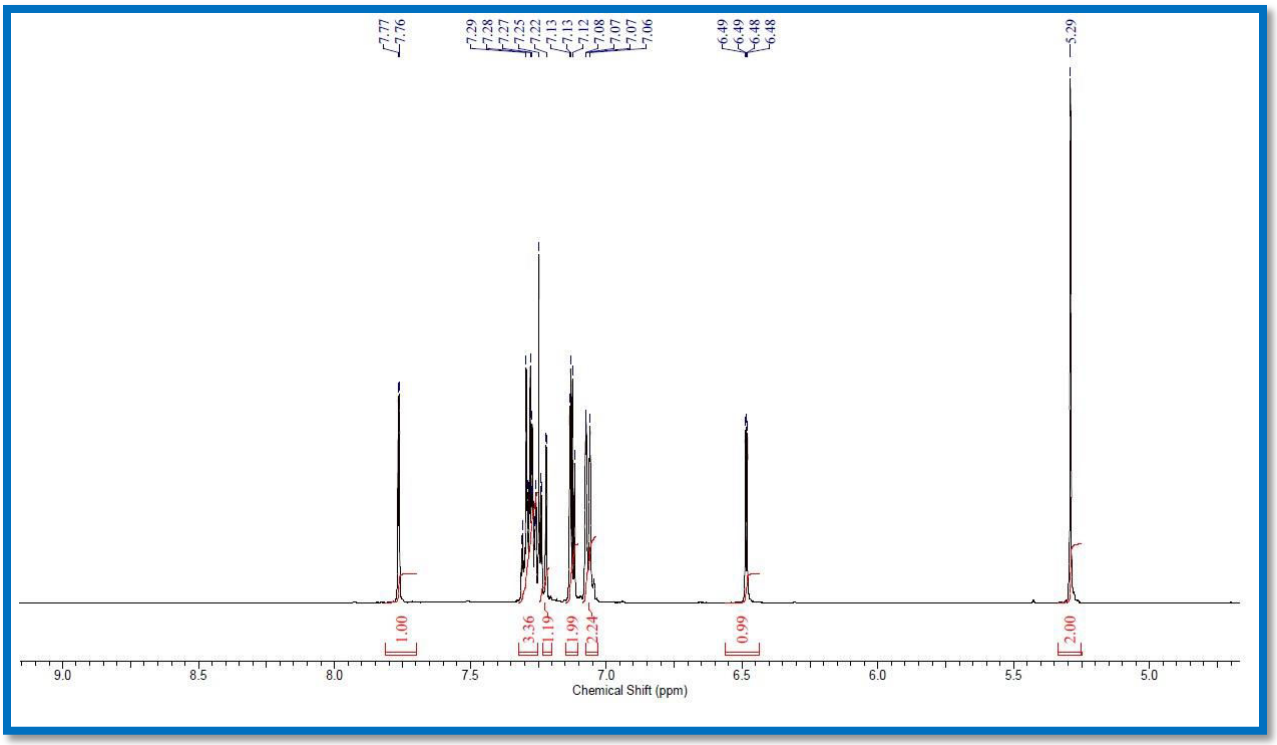

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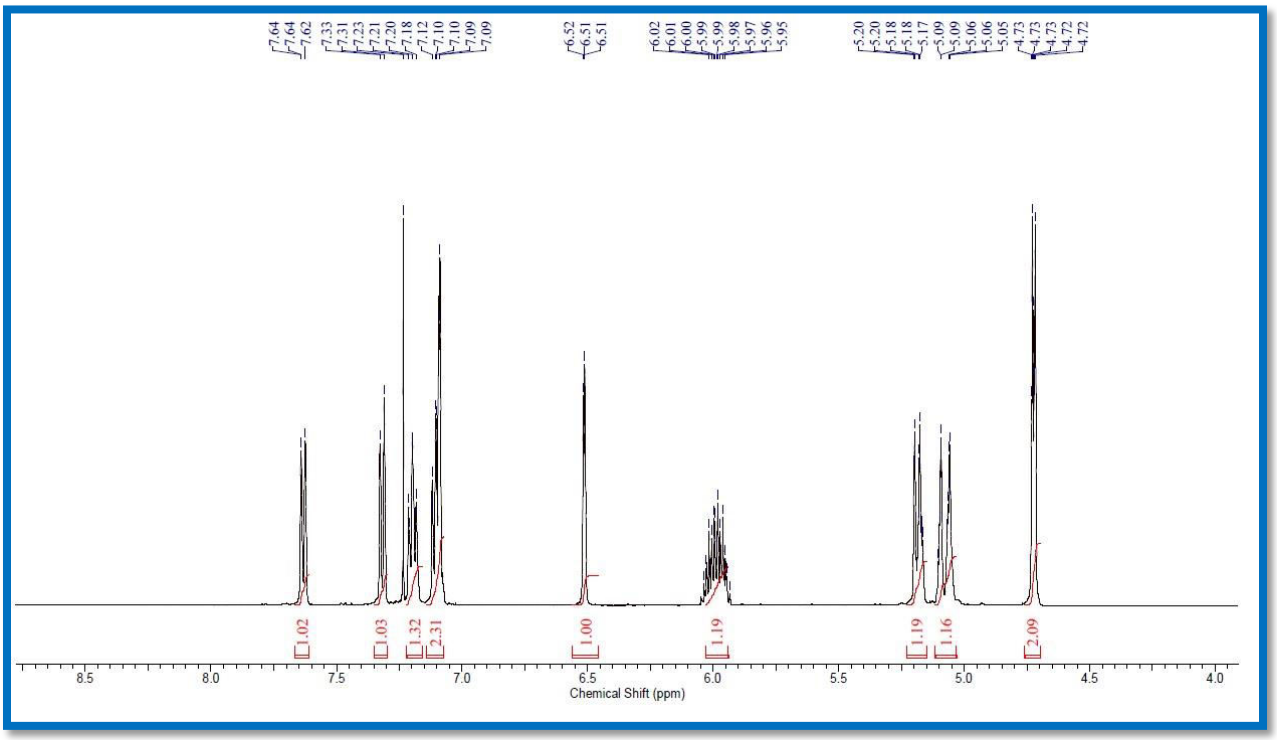

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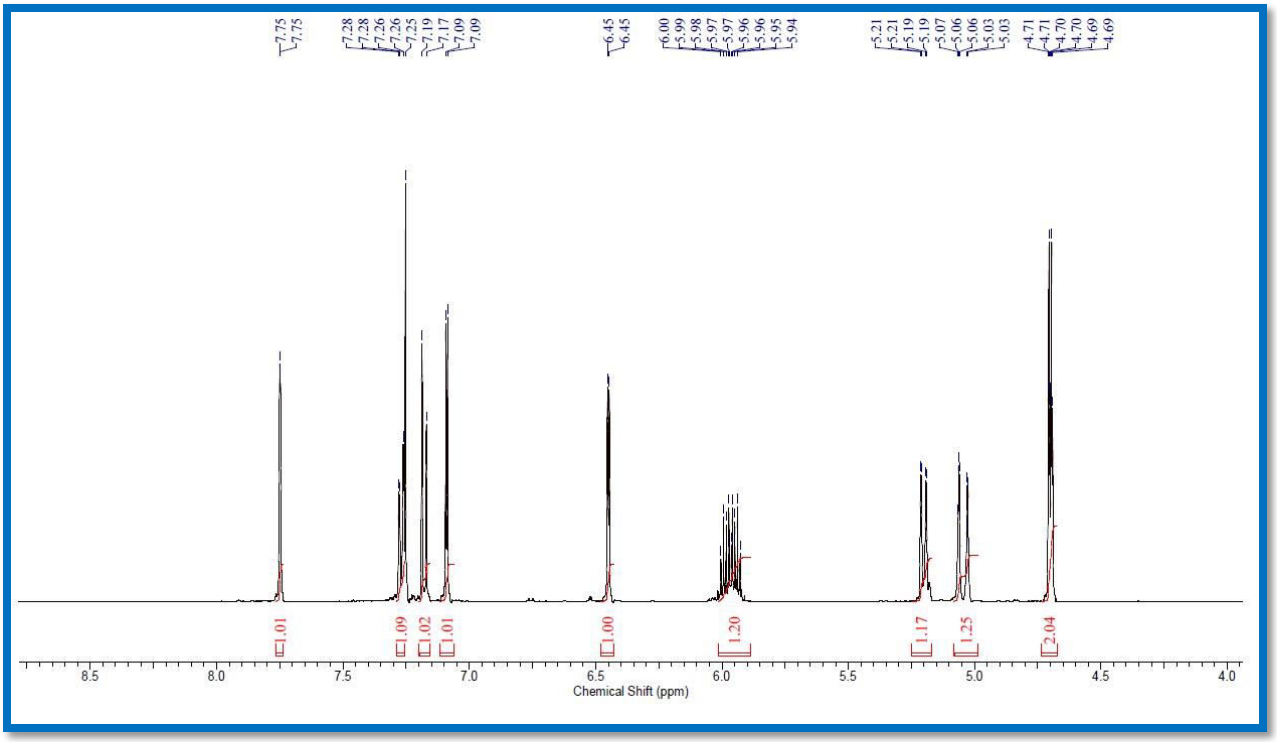

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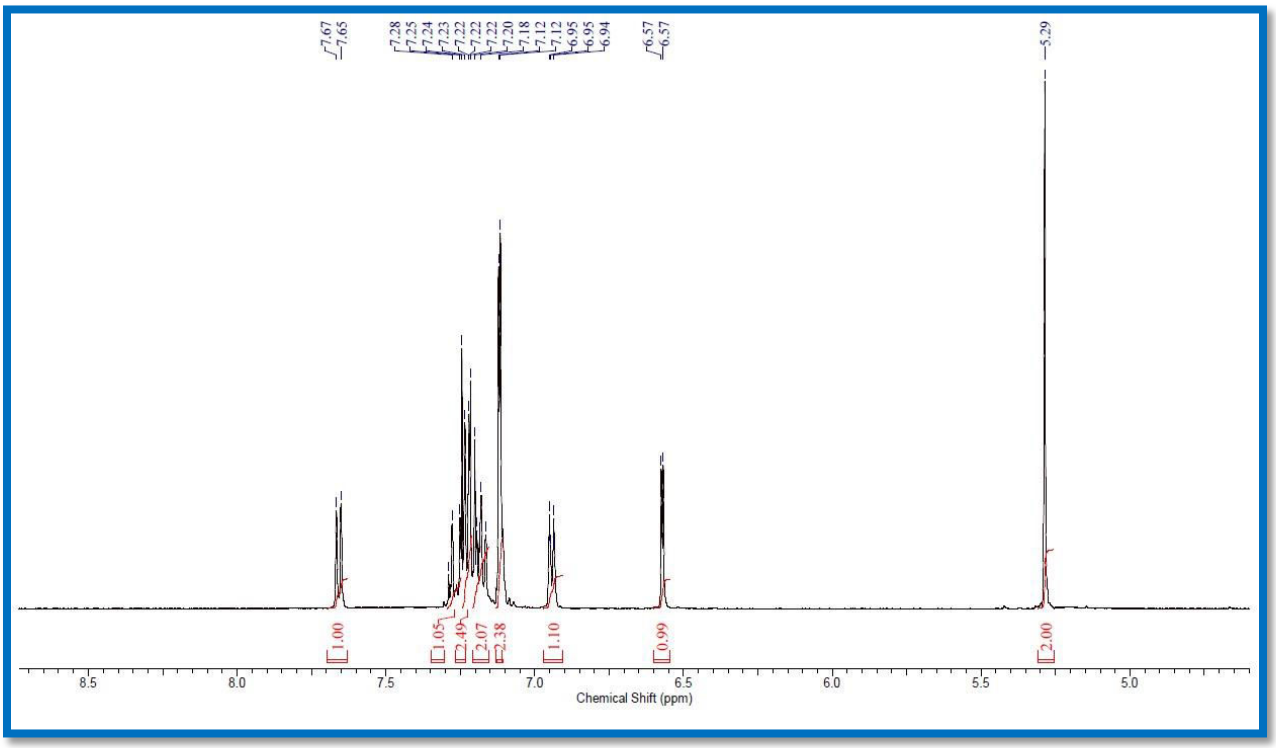
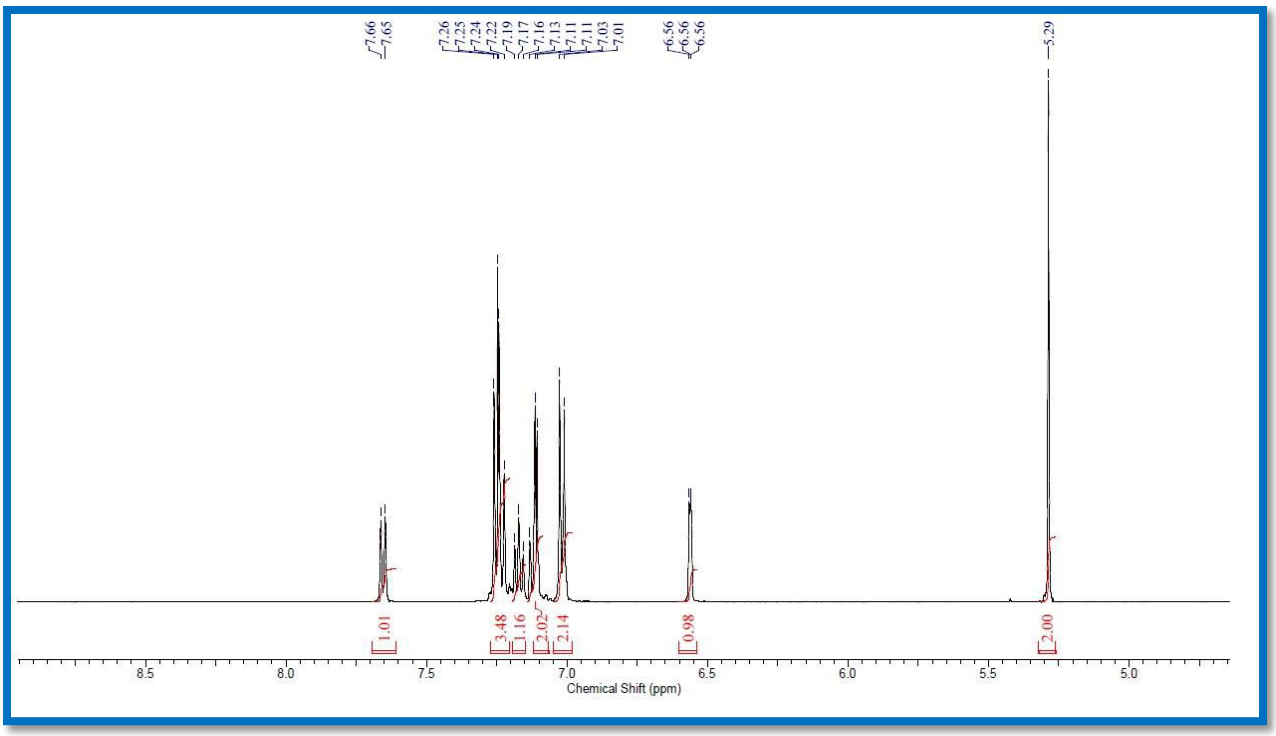
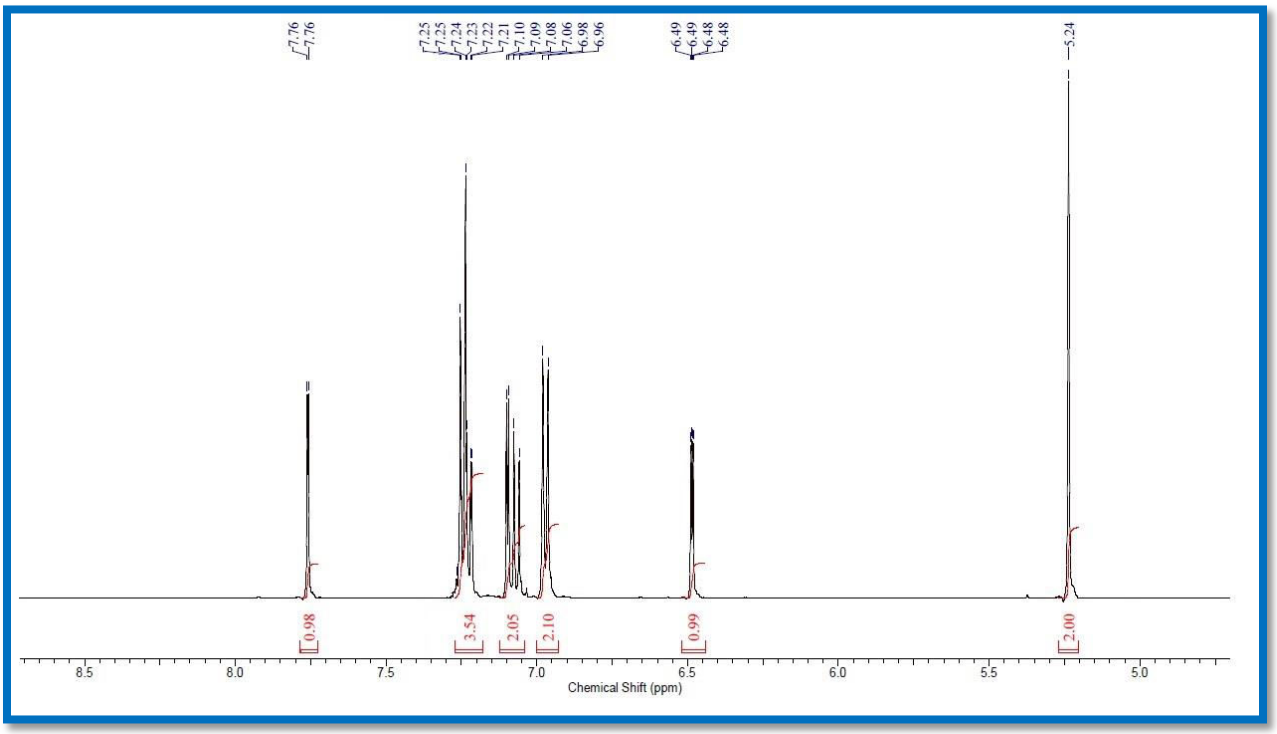


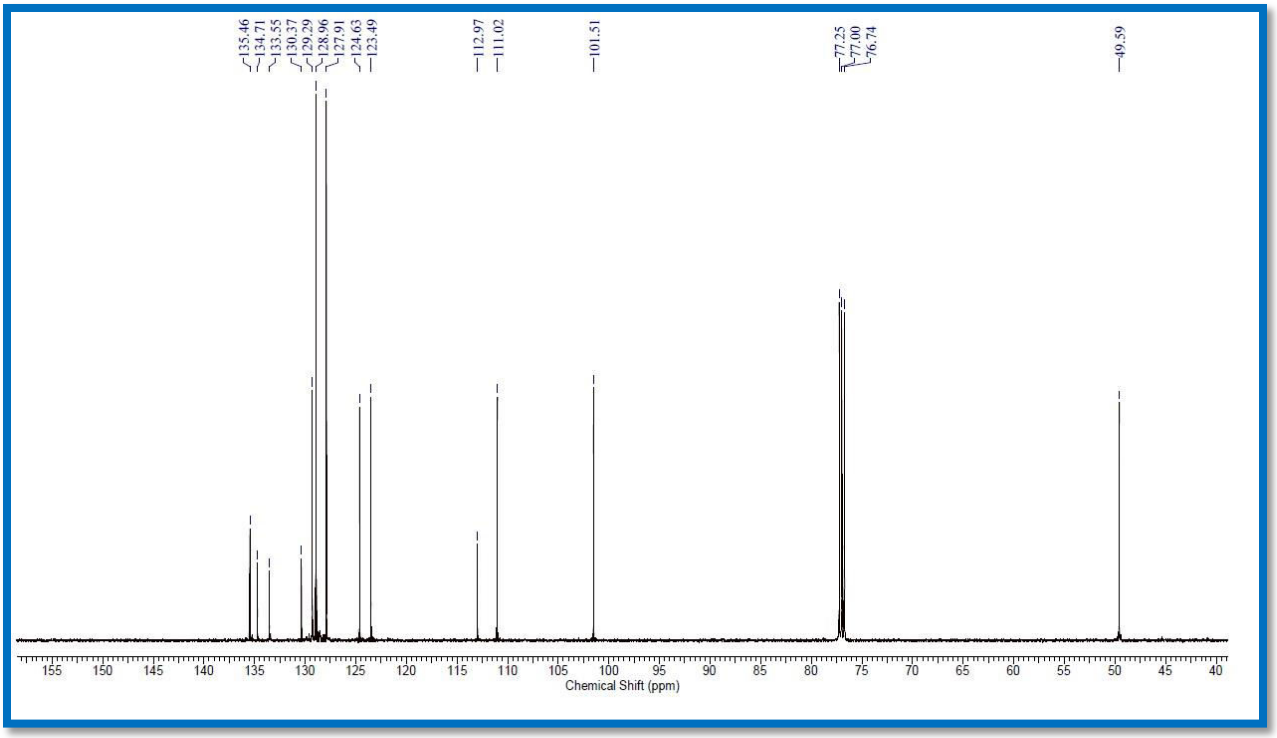
^{1}H-NMR of compound 1p



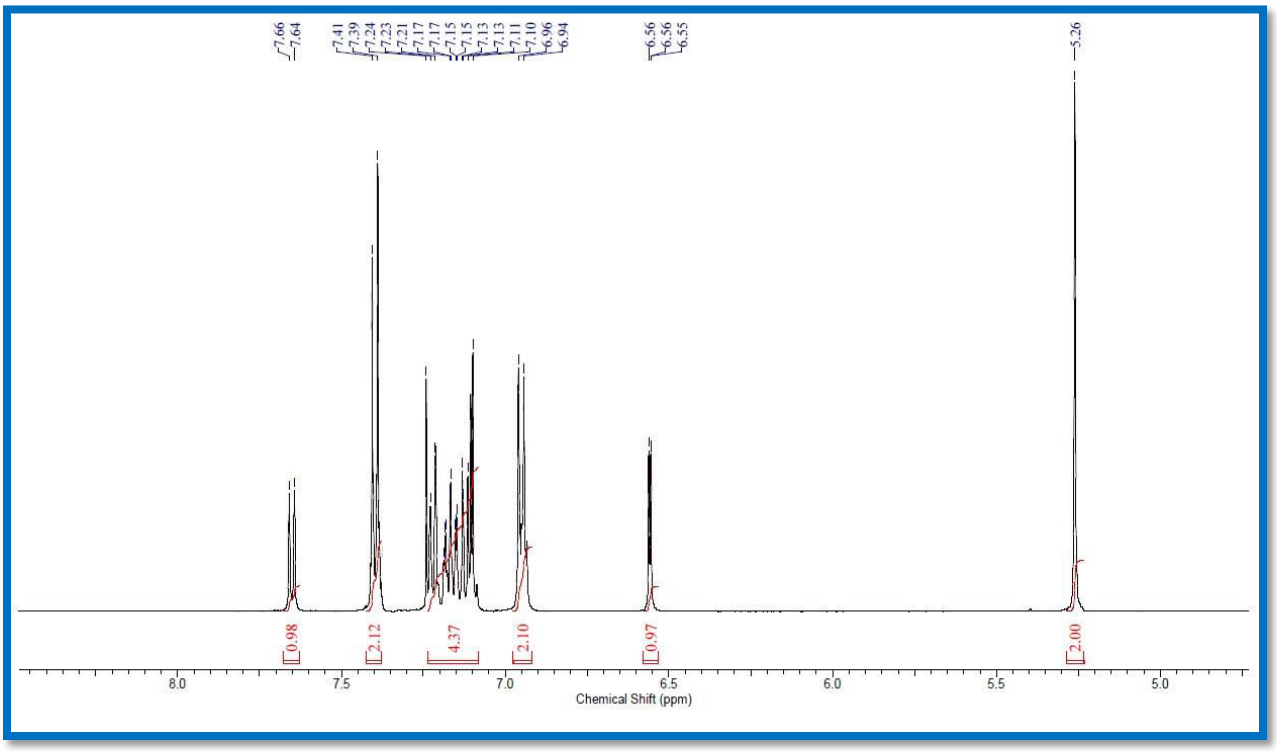
^{1}H-NMR of compound 1q



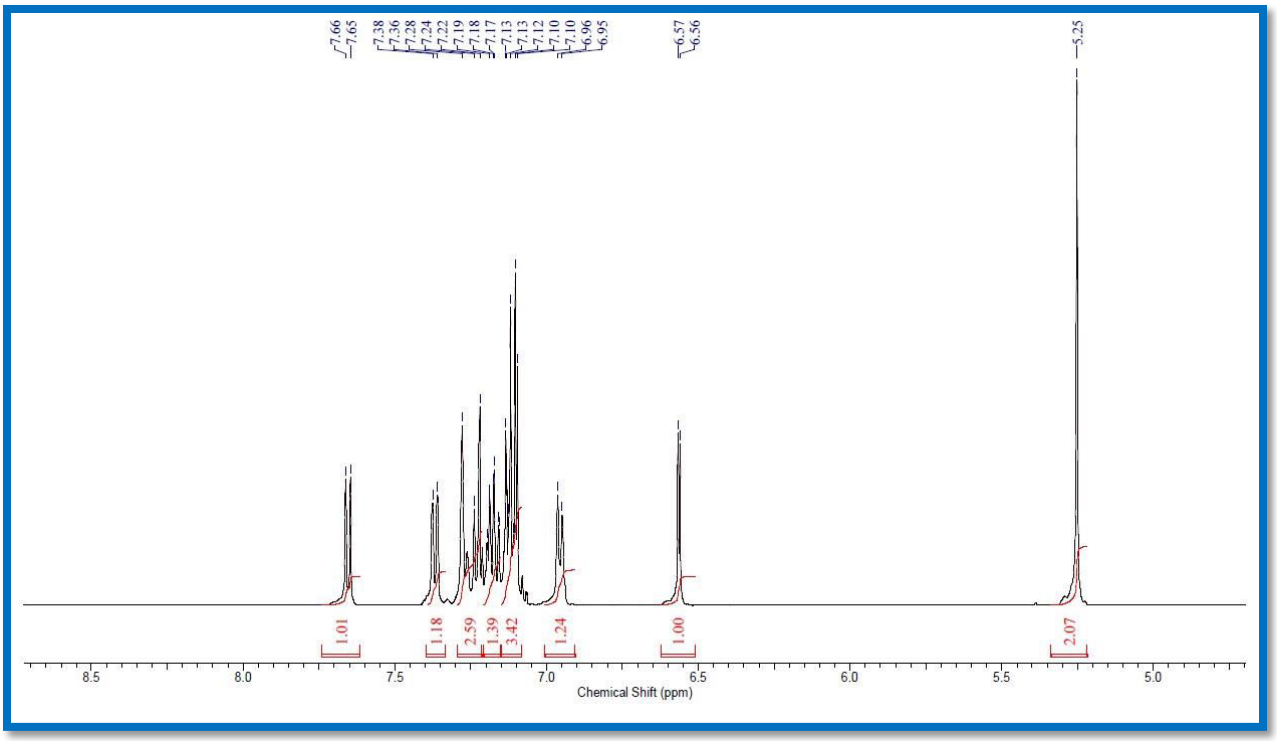
^{13}C-NMR of compound 1q



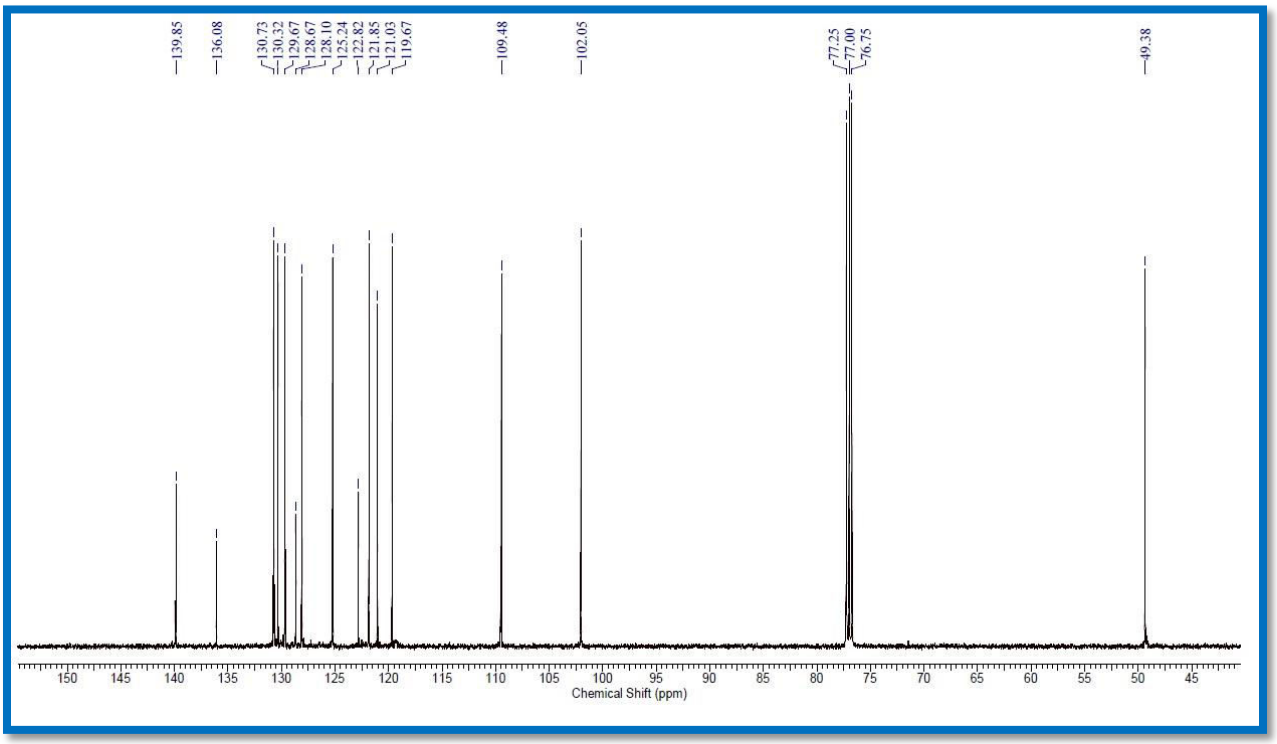
^{1}H-NMR of compound 1r



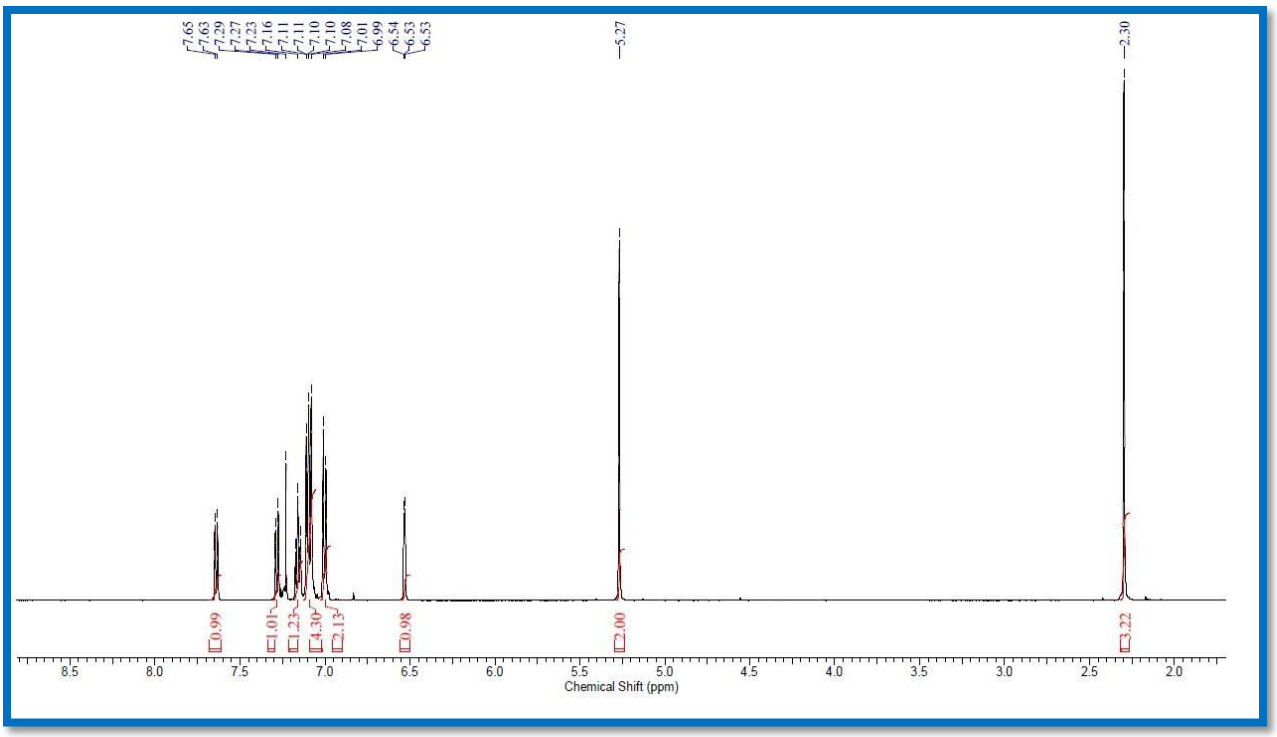
^{1}H-NMR of compound 1s



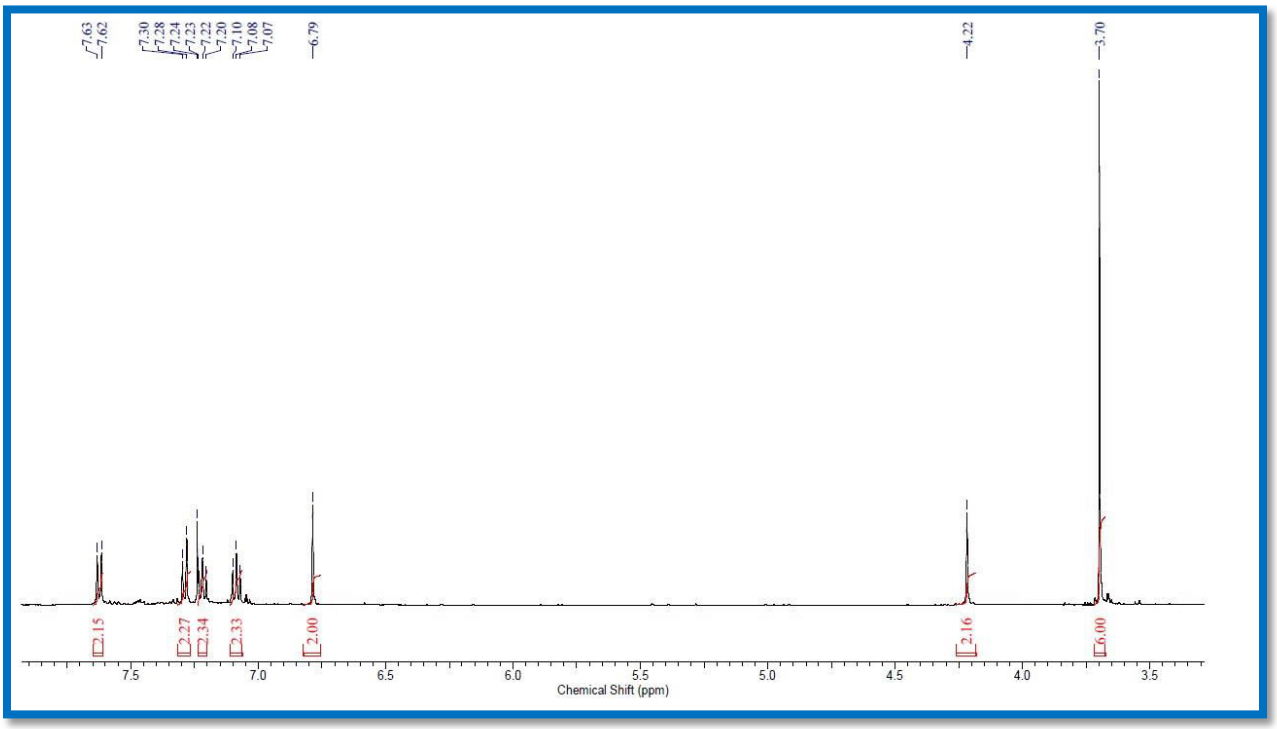
^{13}C-NMR of compound 1s



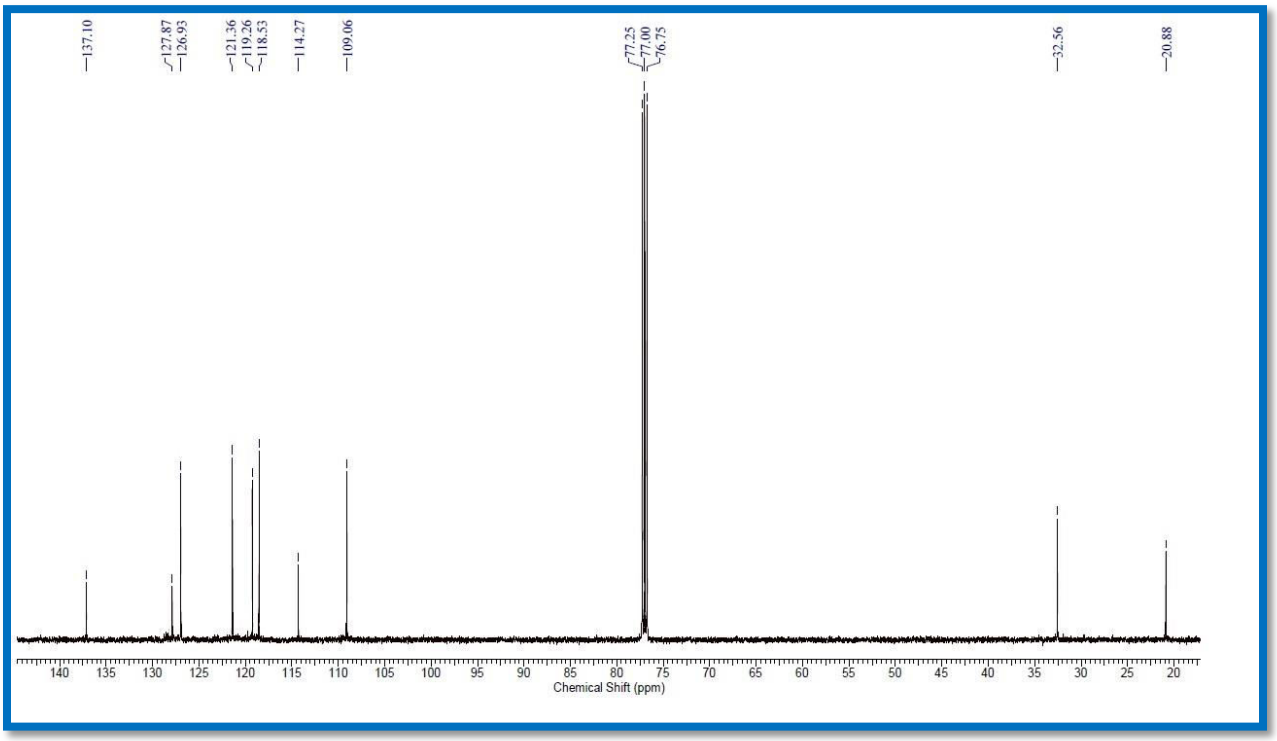
^{1}H-NMR of compound 1t



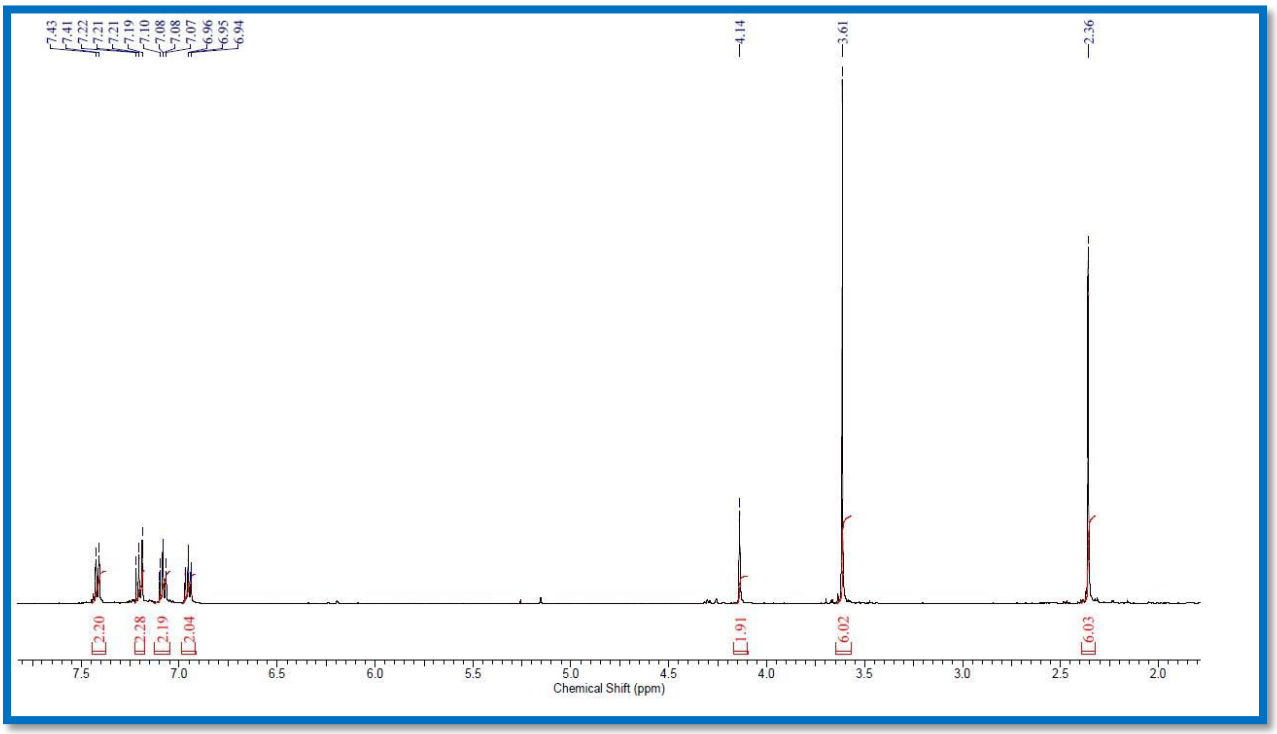
^{1}H-NMR of compound 2a



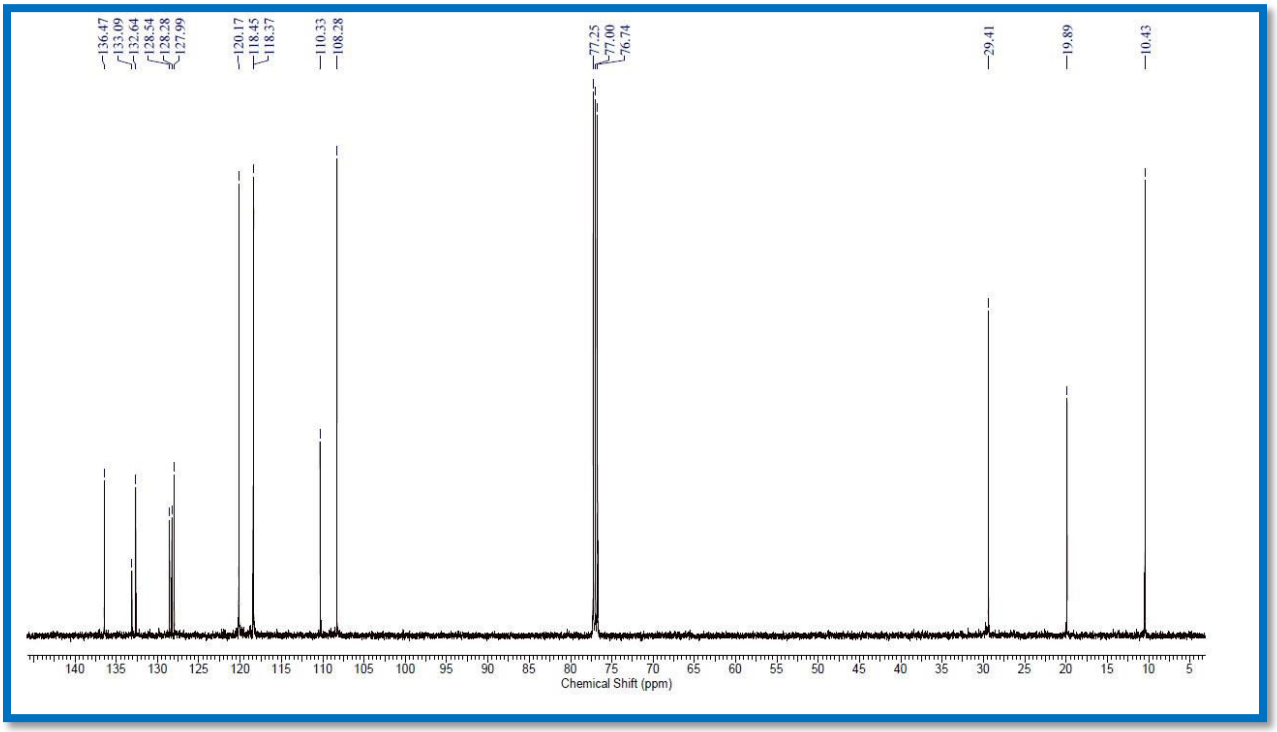
^{13}C-NMR of compound 2a



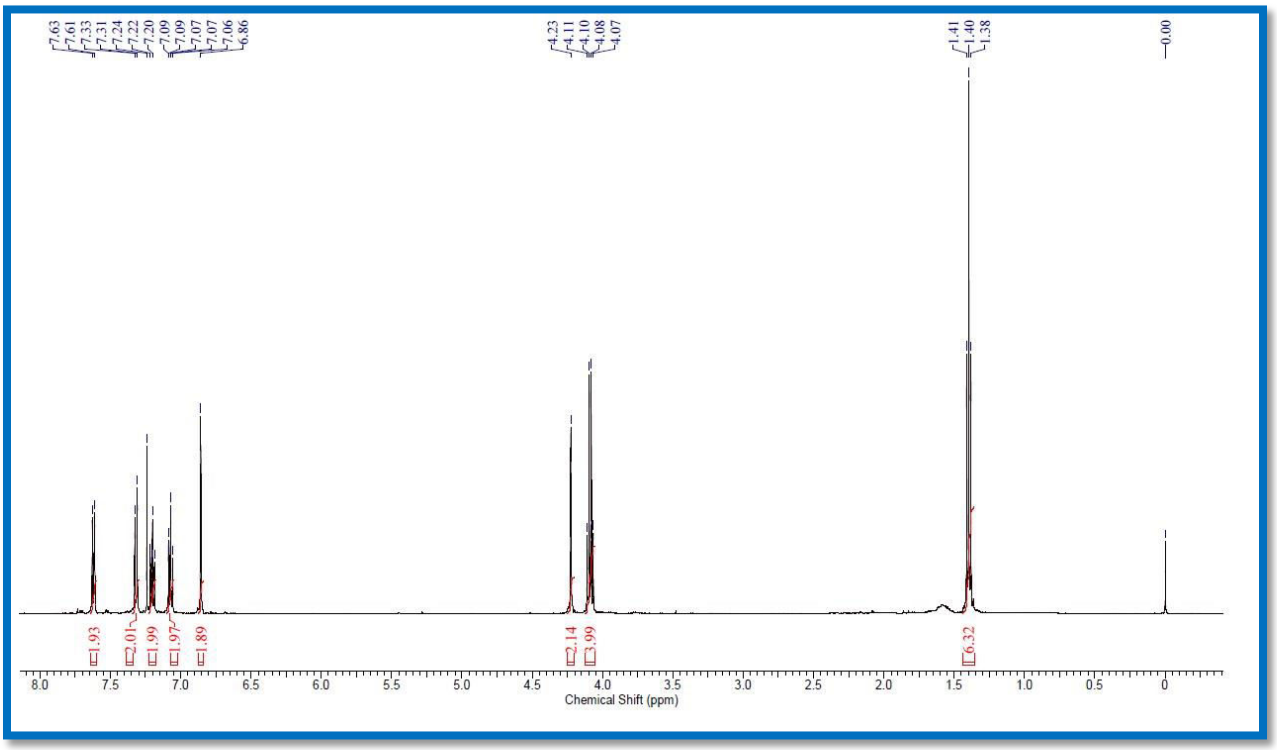
^{1}H-NMR of compound 2b



^{13}C-NMR of compound 2b



^{1}H-NMR of compound 2c



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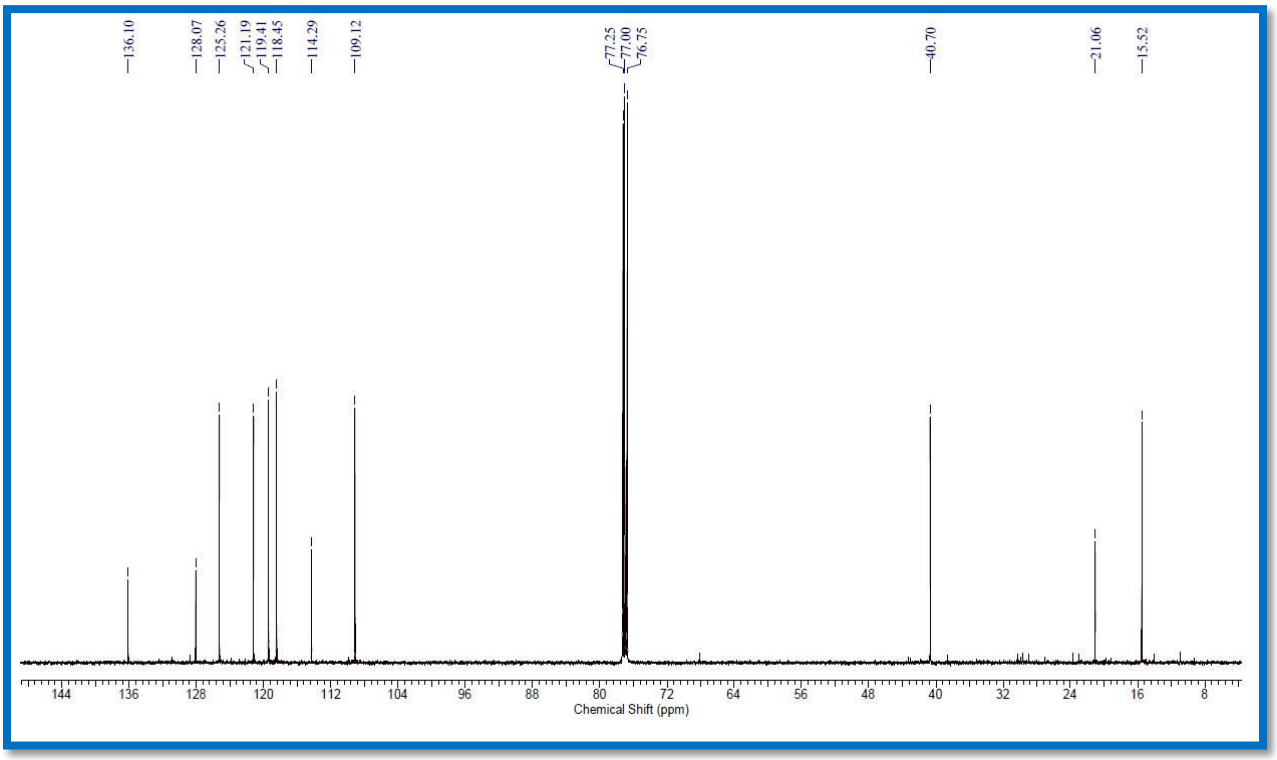
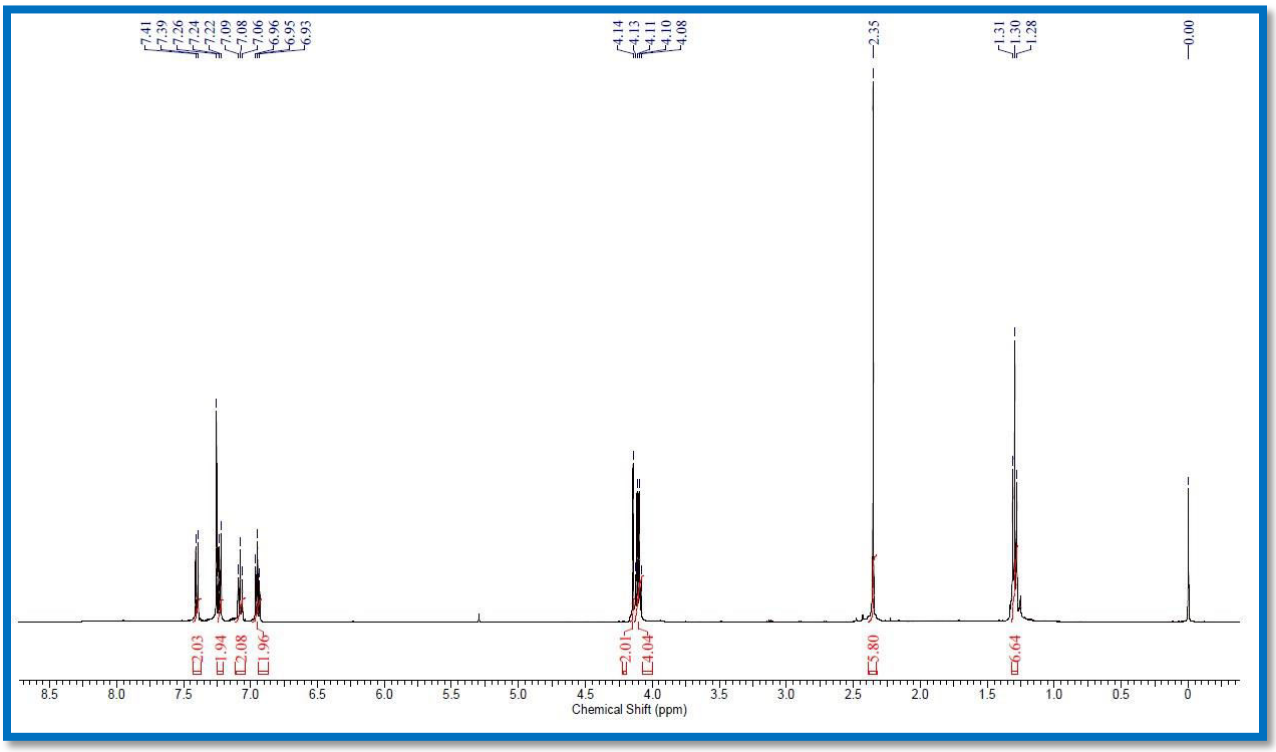


^{1}H-NMR of compound 2d



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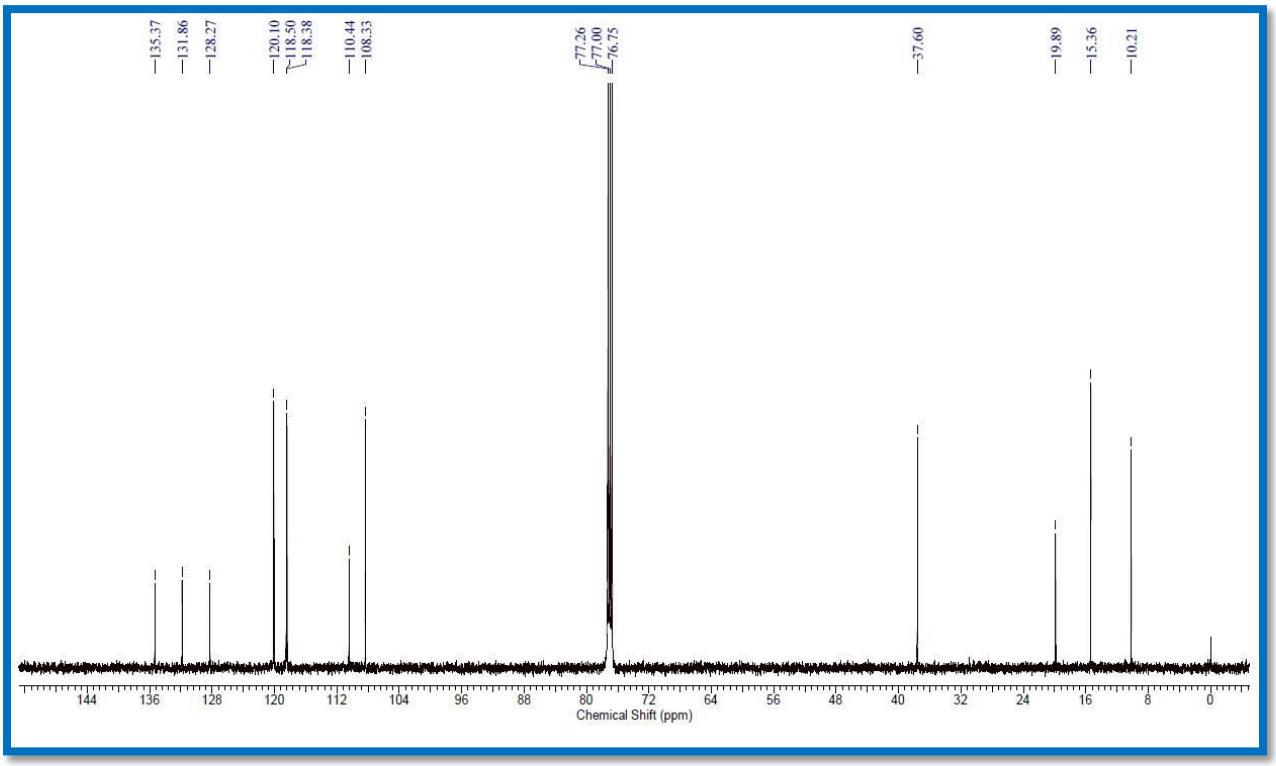
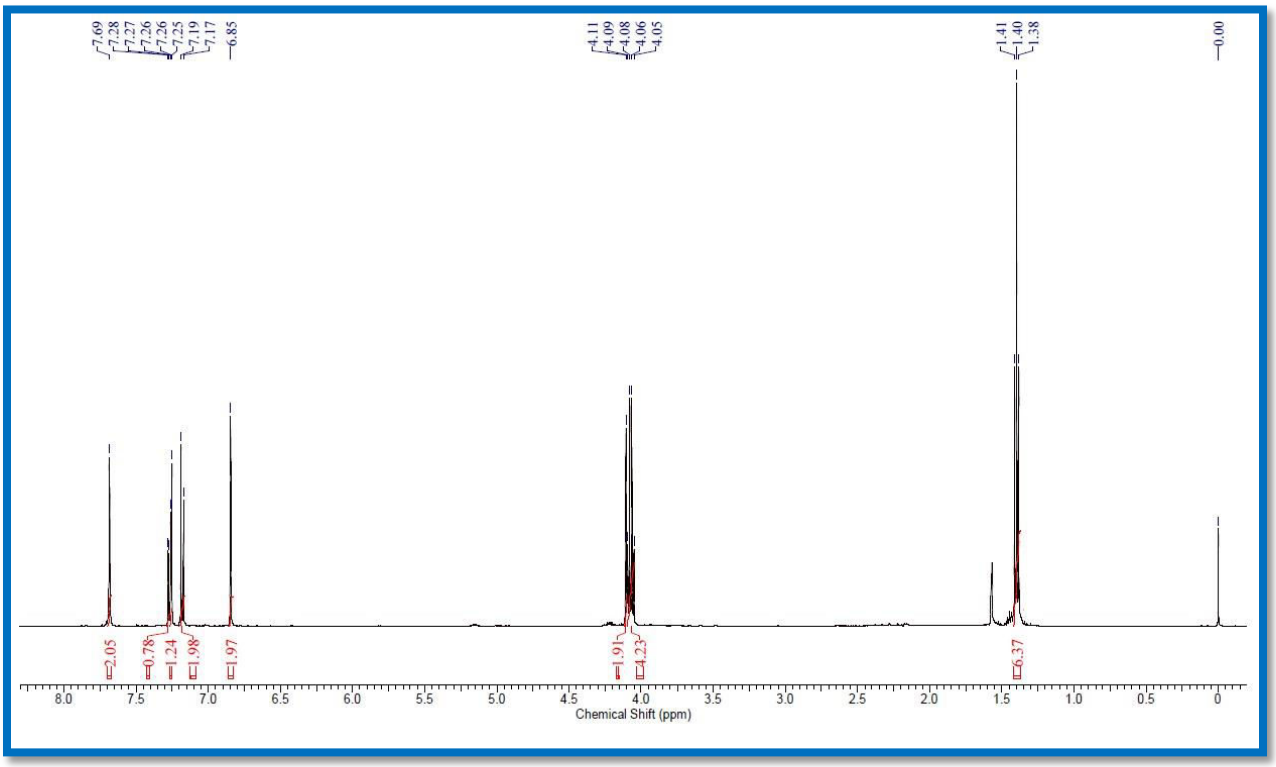
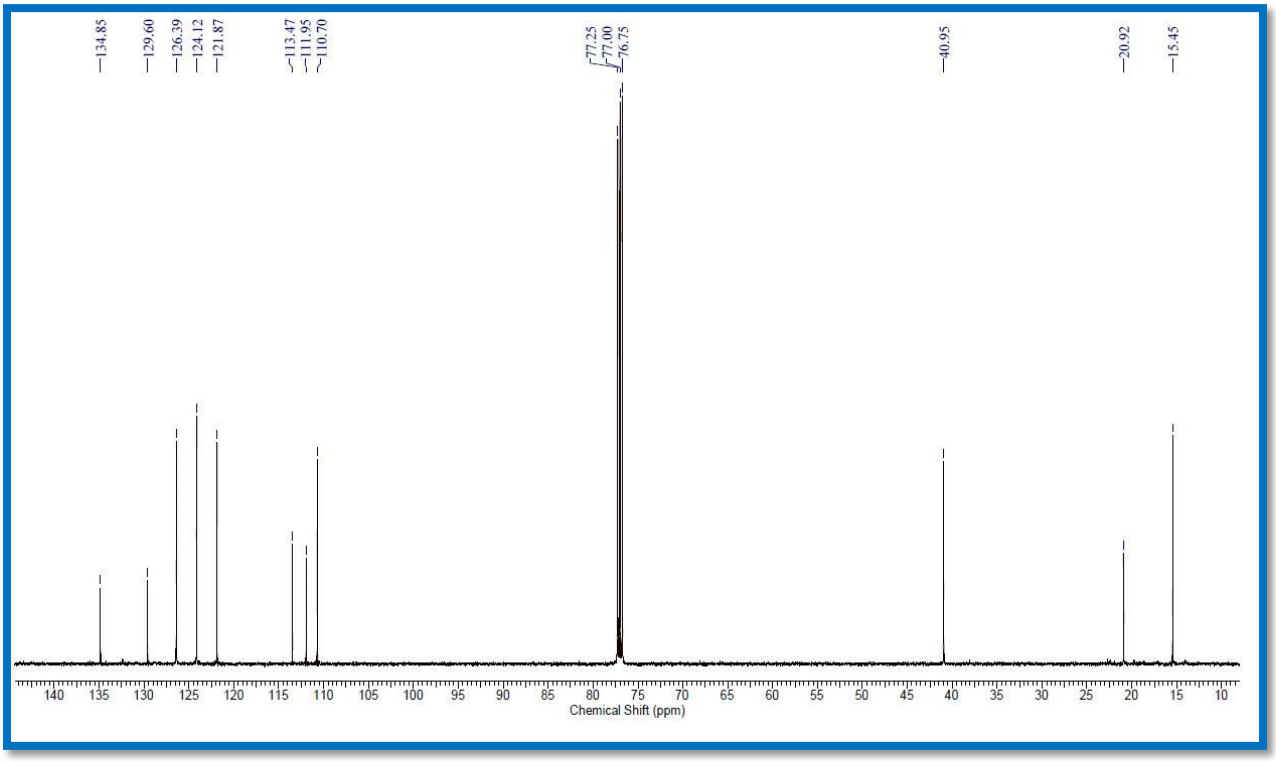


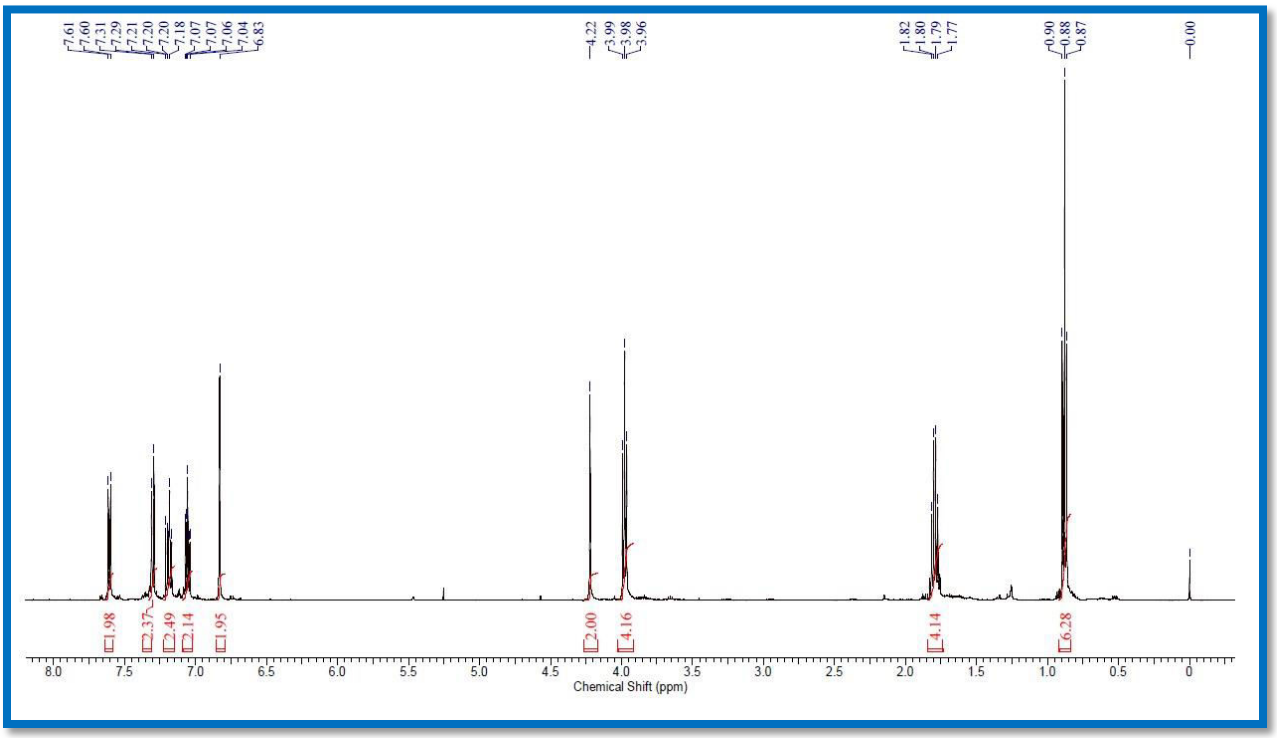
^{1}H-NMR of compound 2e



^{13}C-NMR of compound 2e



^{1}H-NMR of compound 2f



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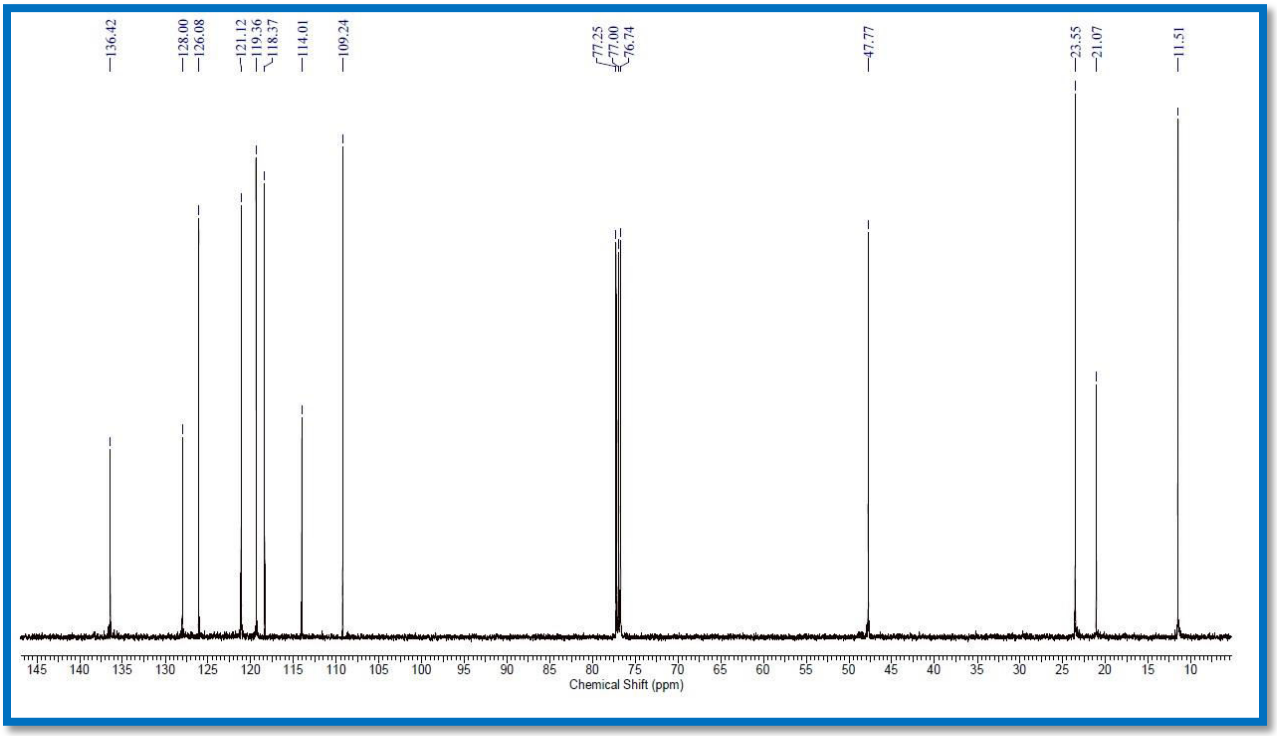

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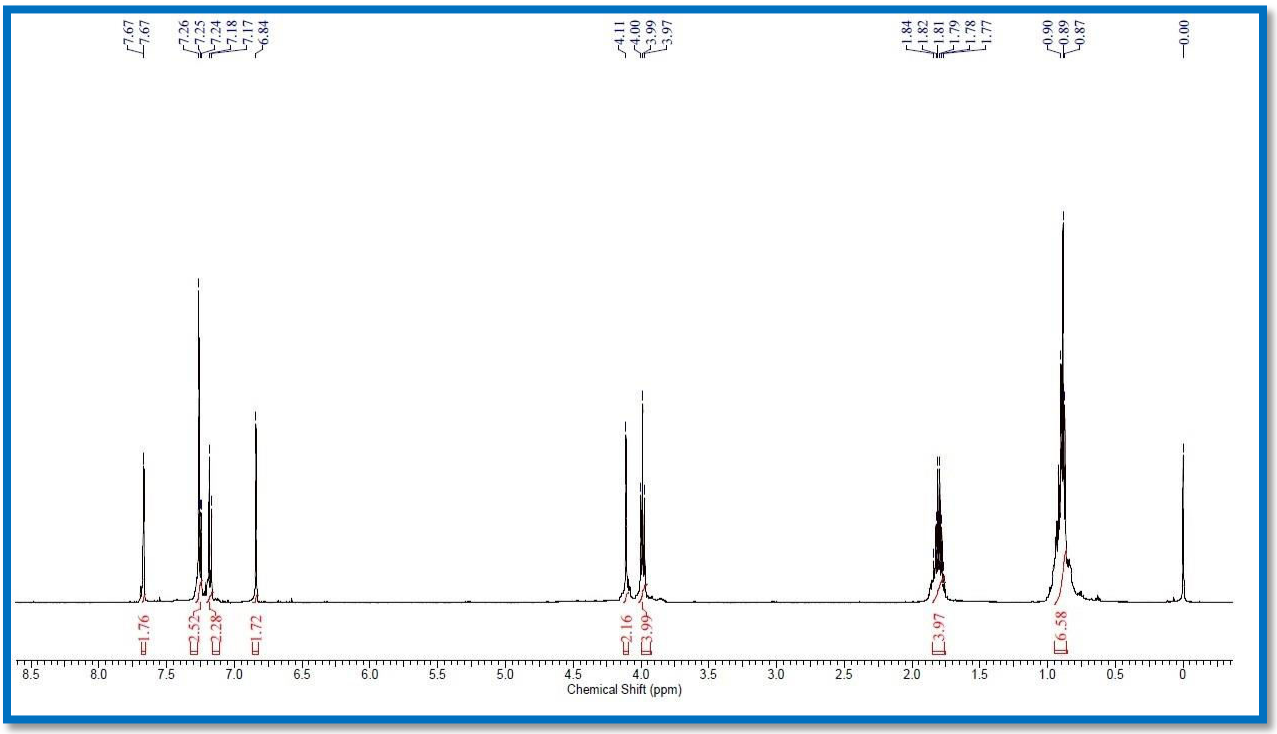

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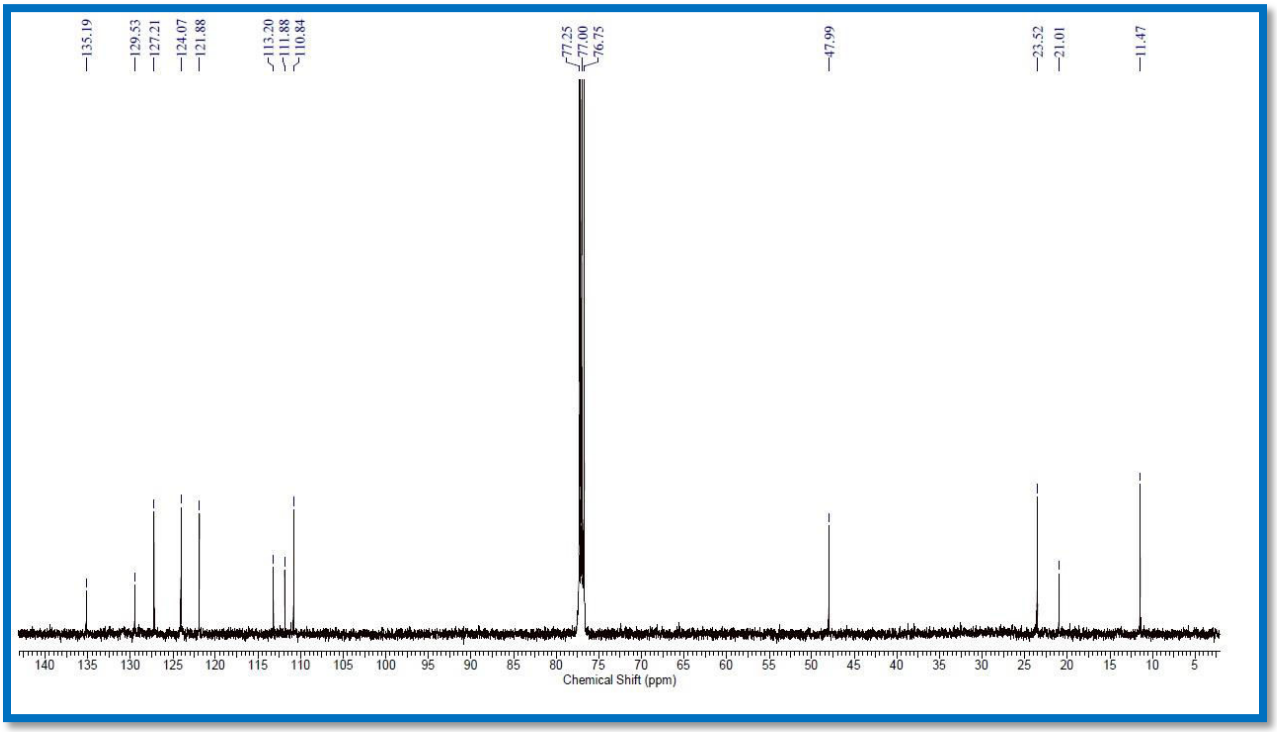
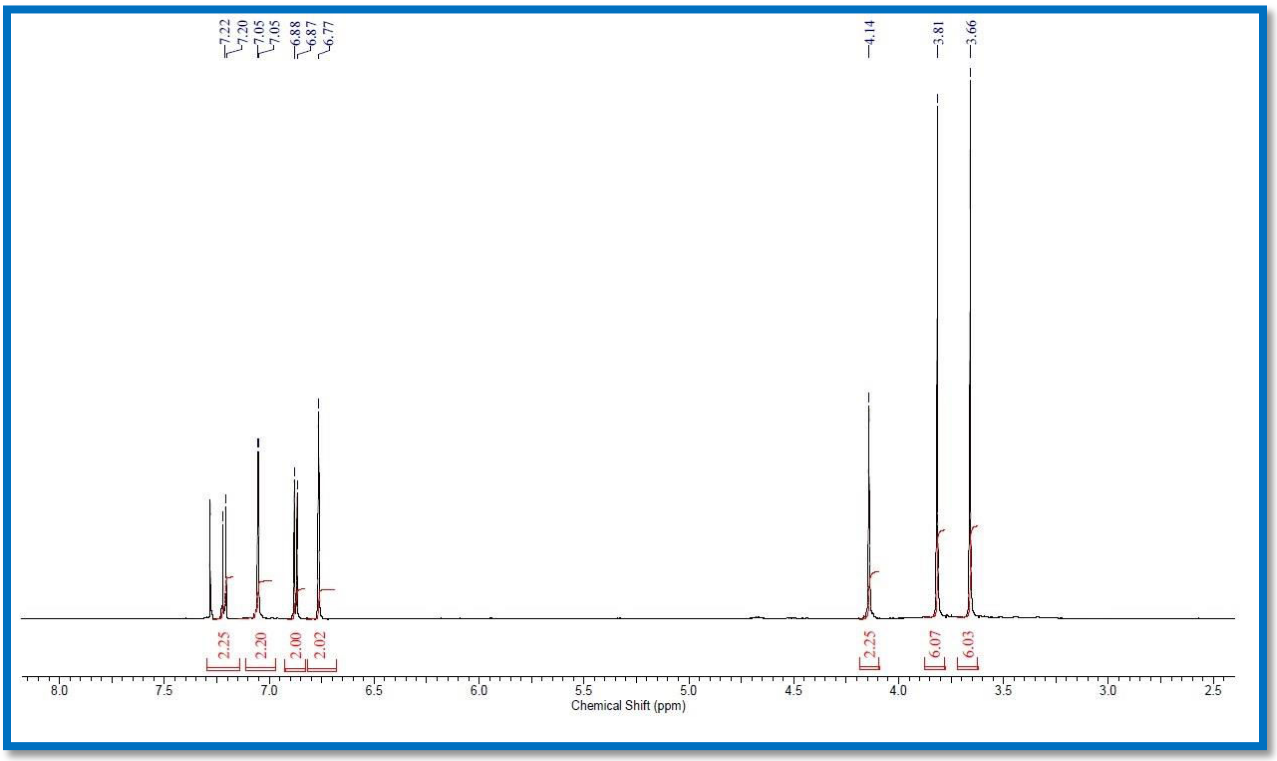
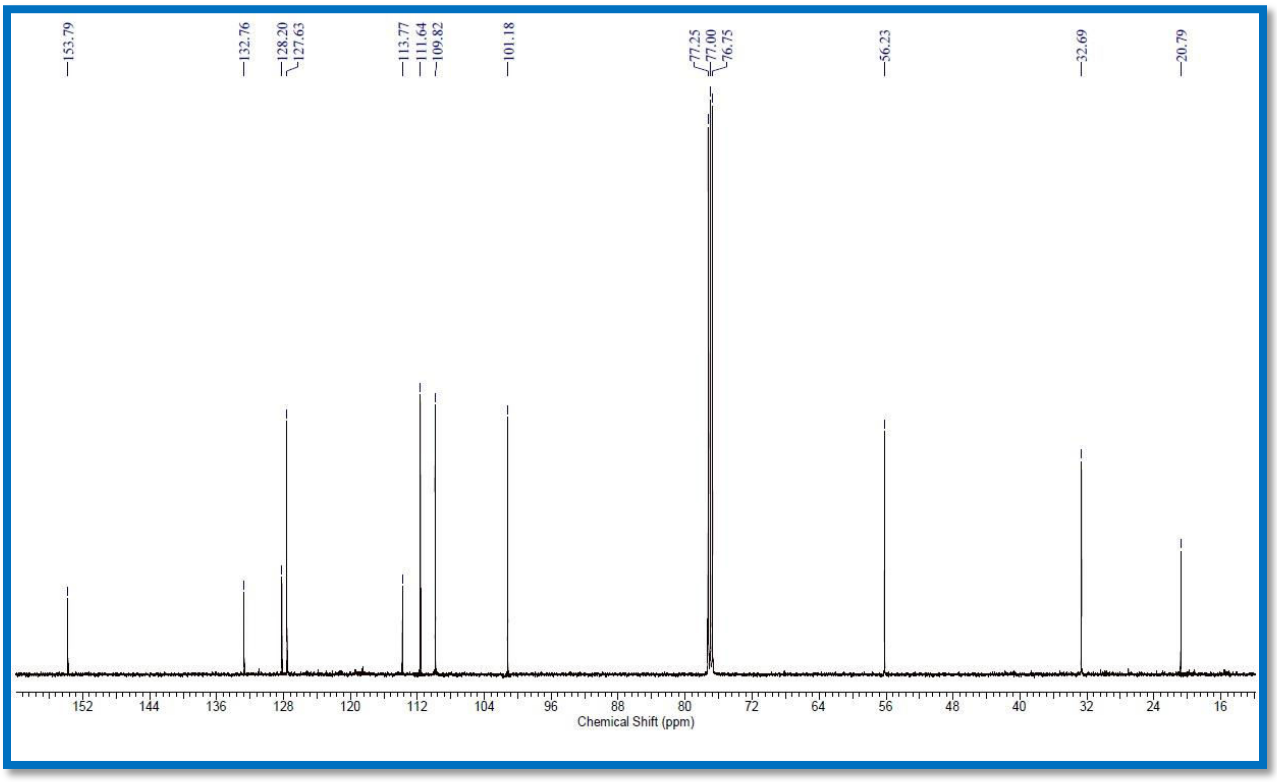


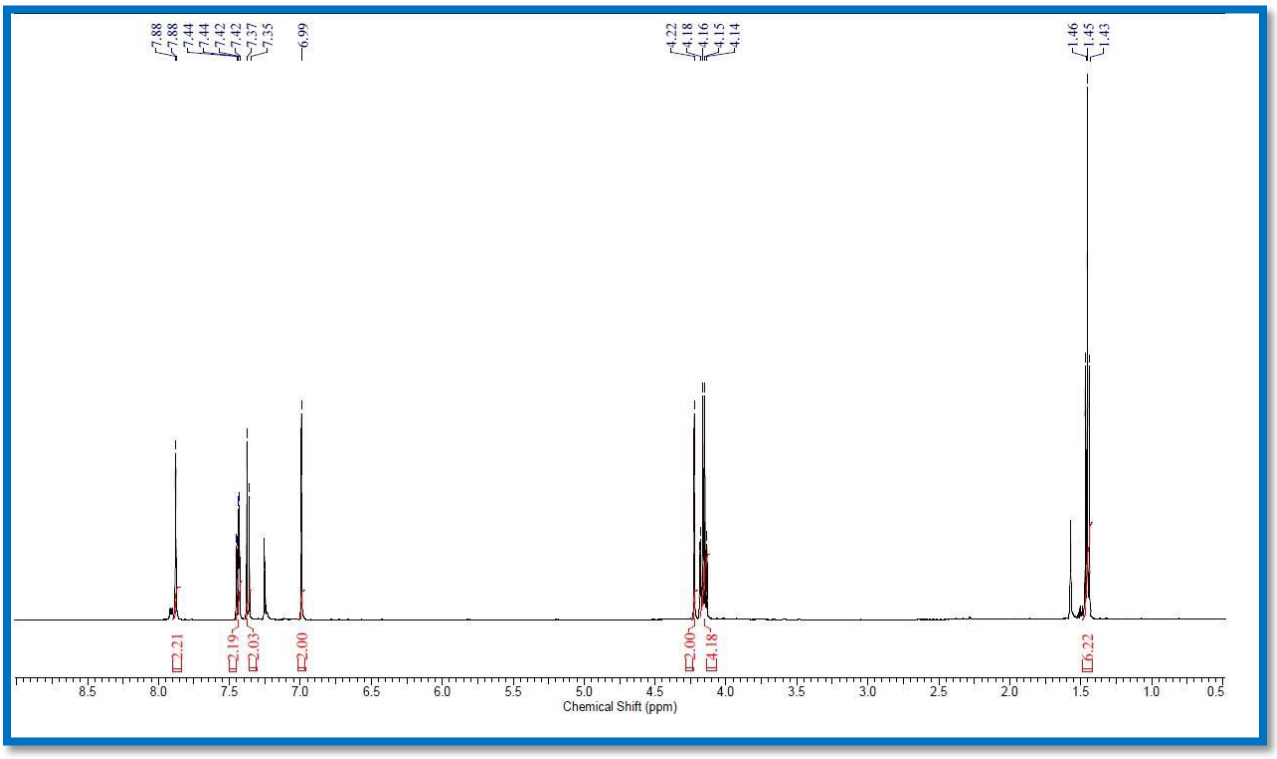
^{1}H-NMR of compound 2h



^{13}C-NMR of compound 2h



^{1}H-NMR of compound 2i



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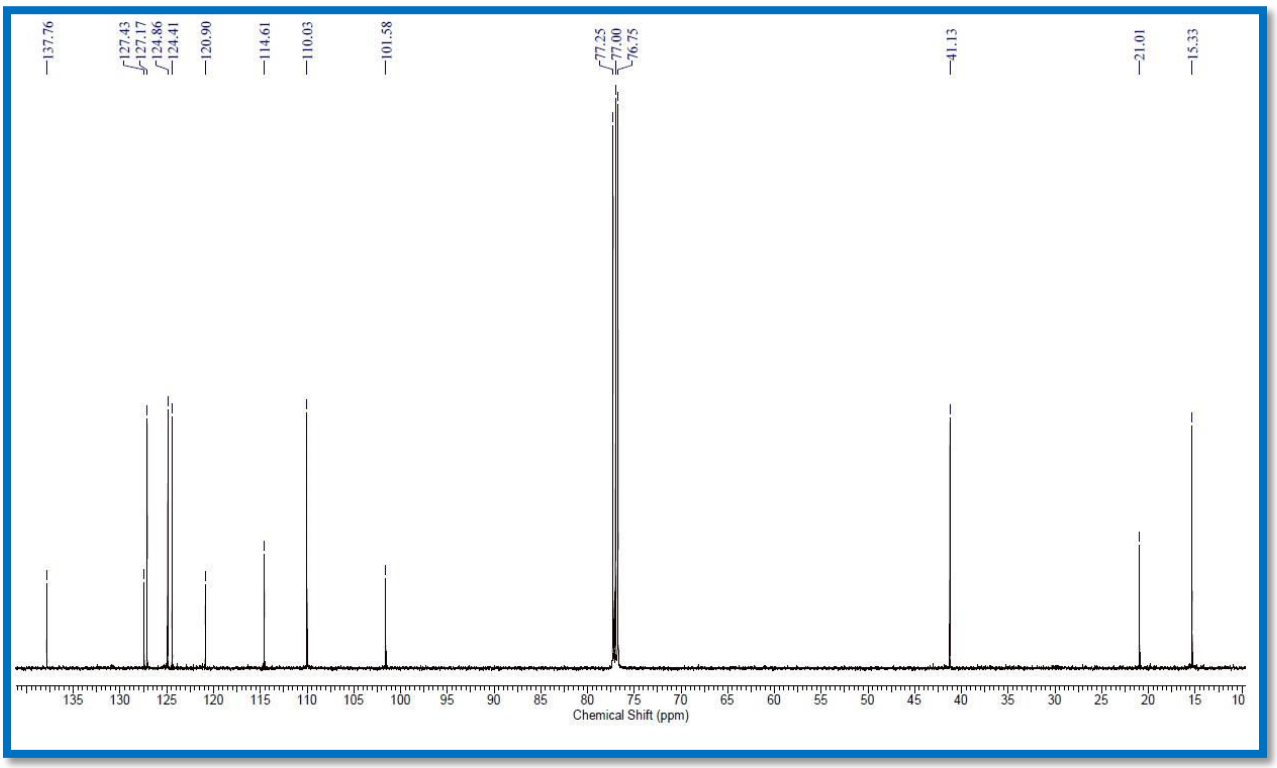

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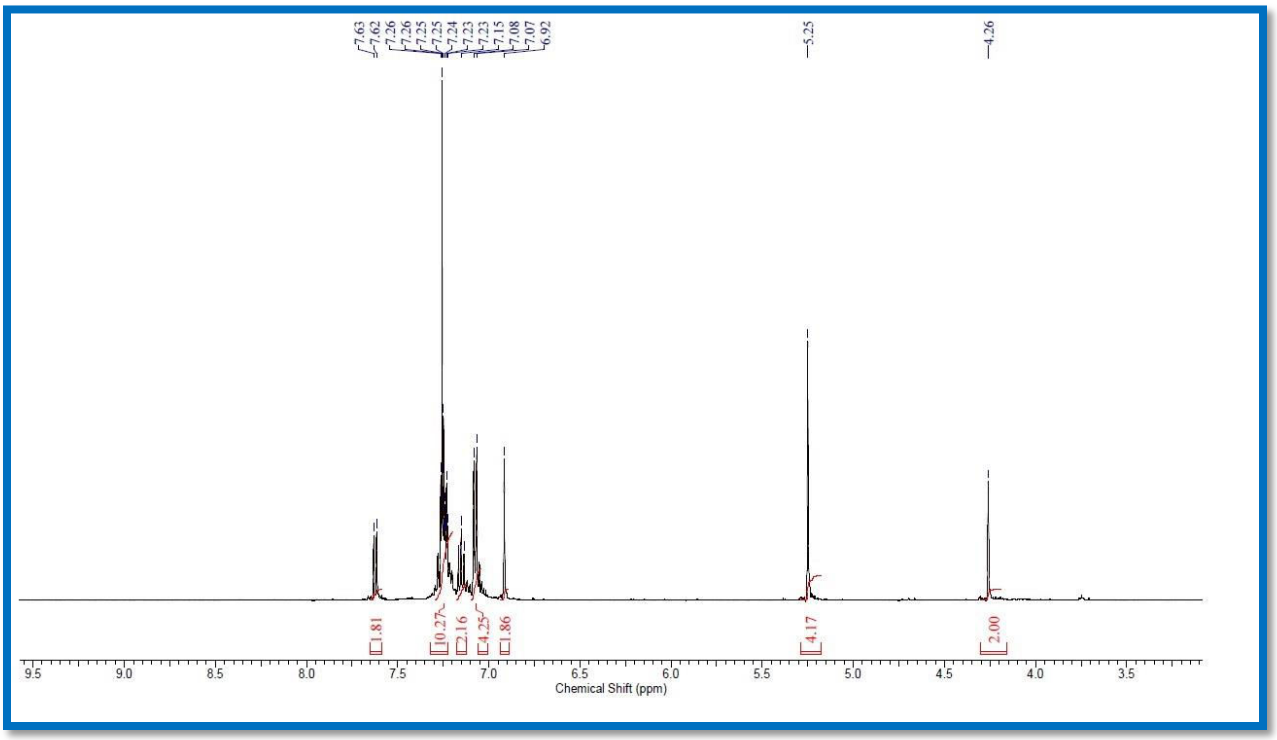

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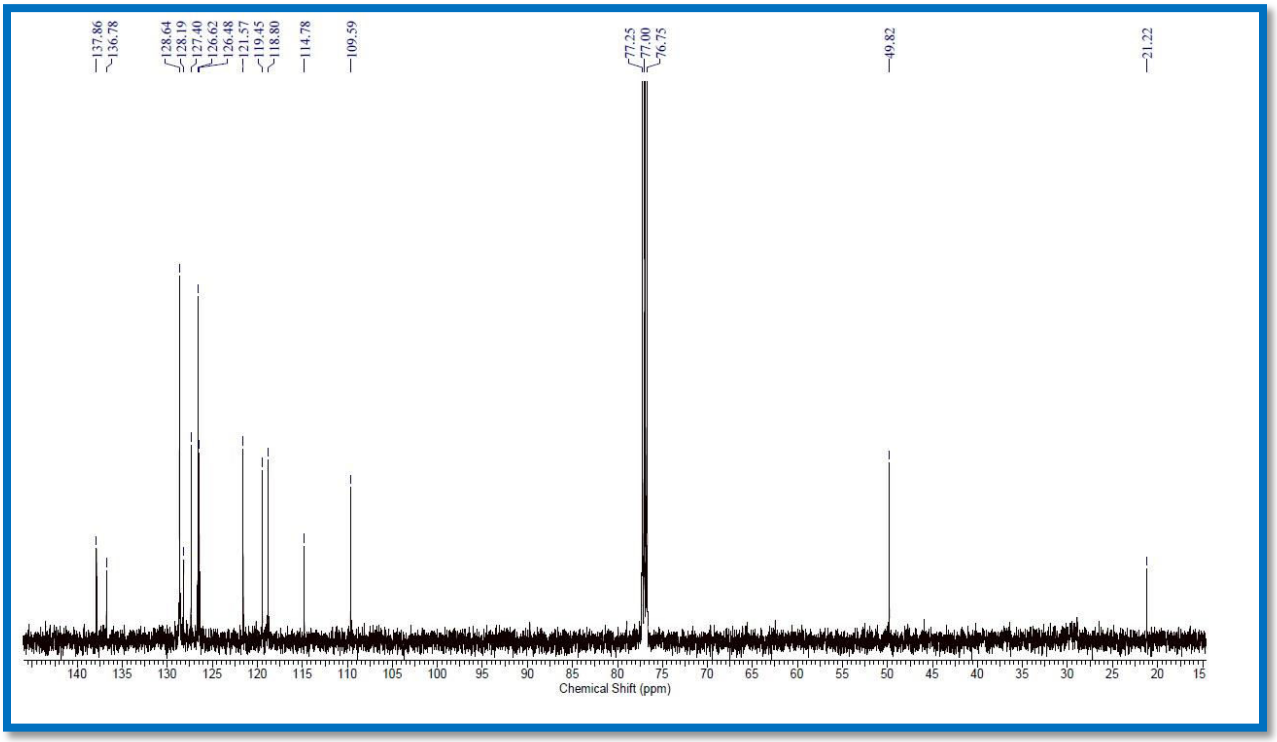
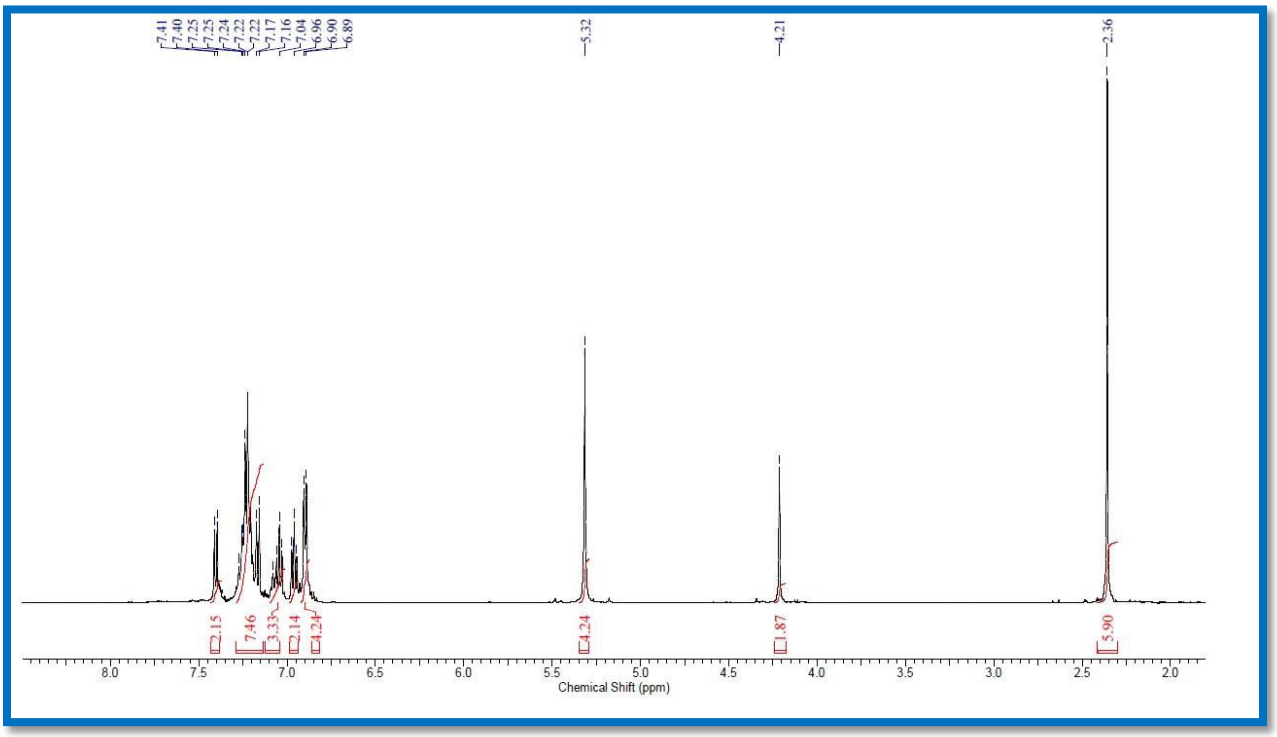


^{1}H-NMR of compound 2k



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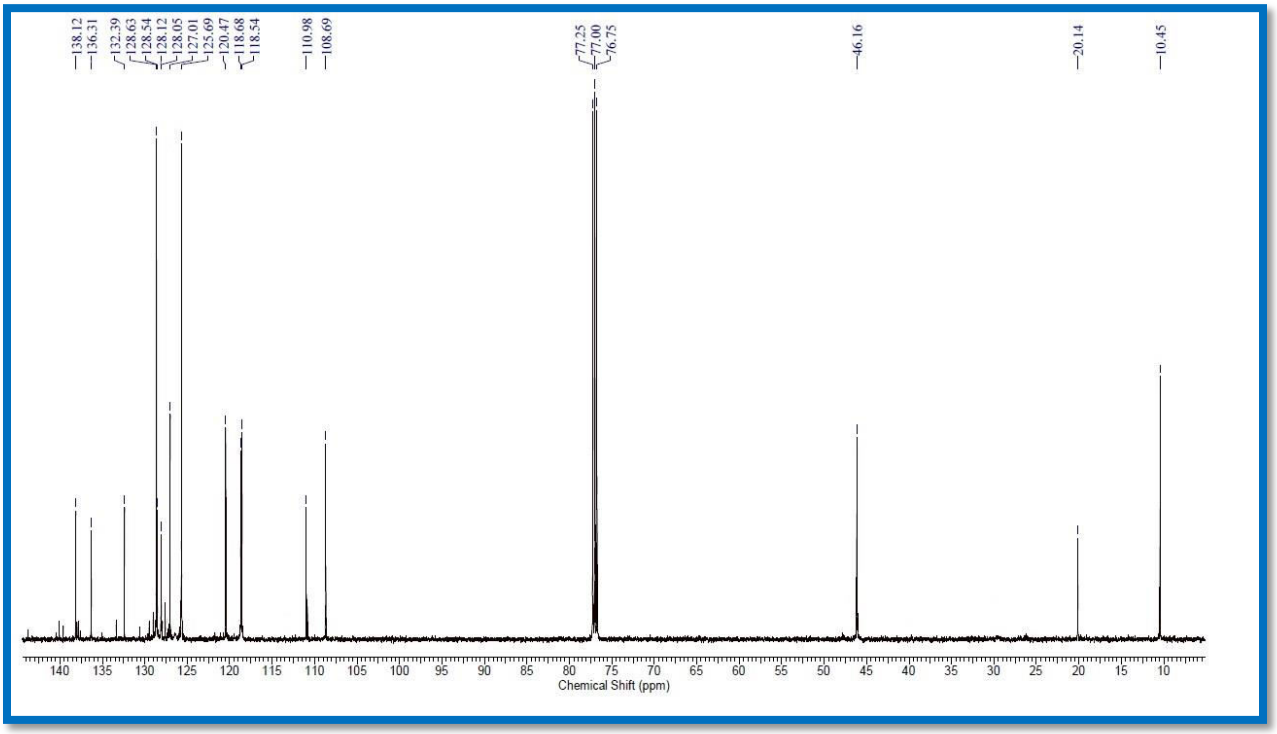

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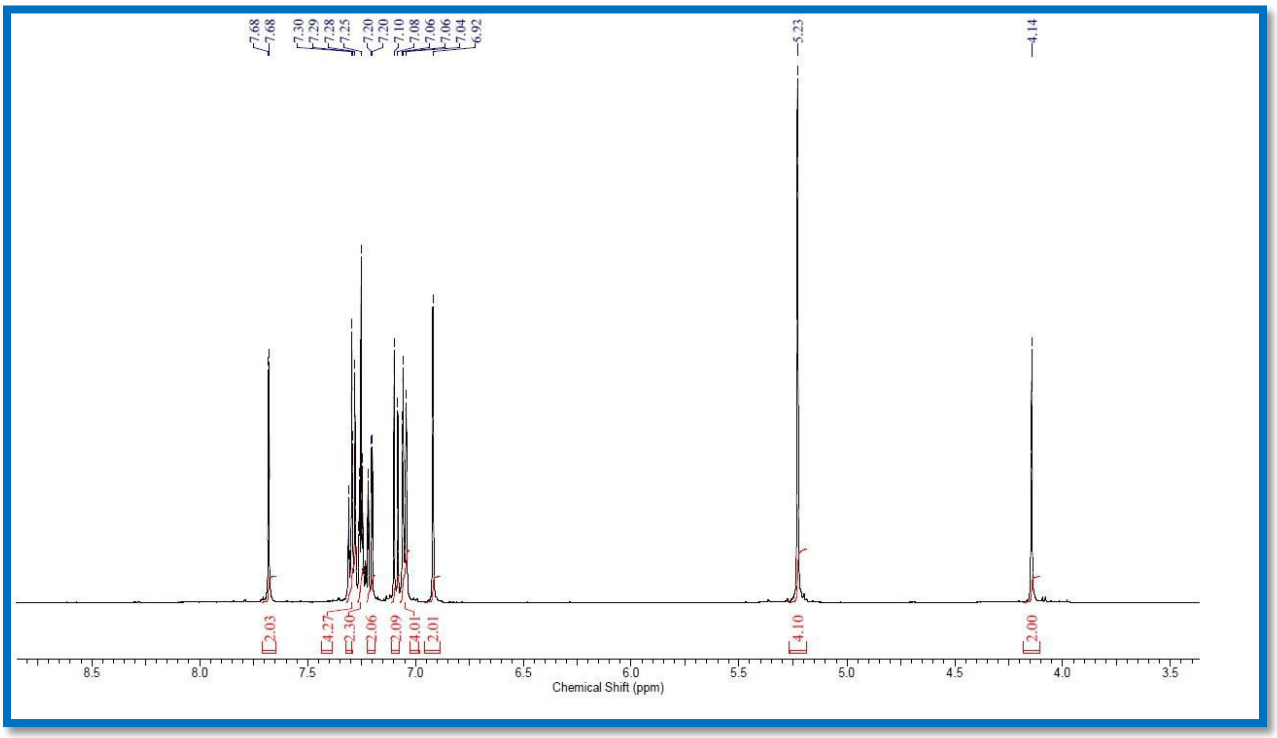

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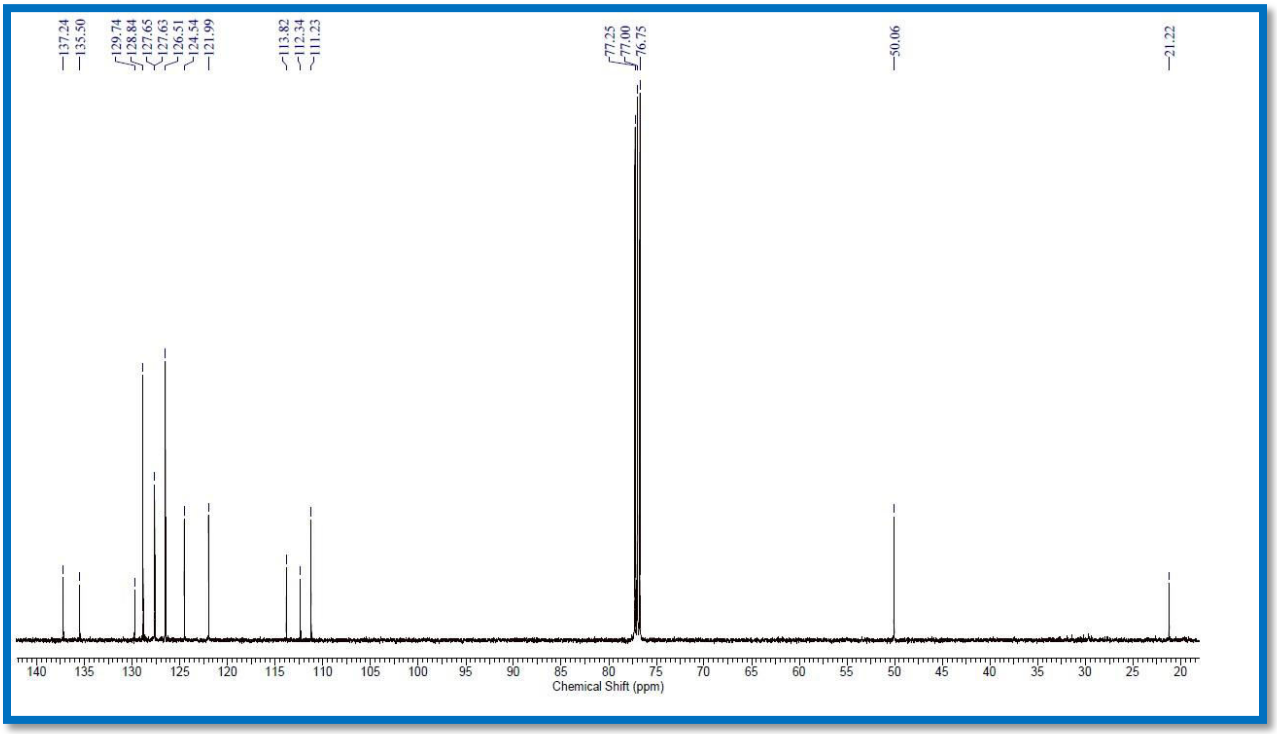
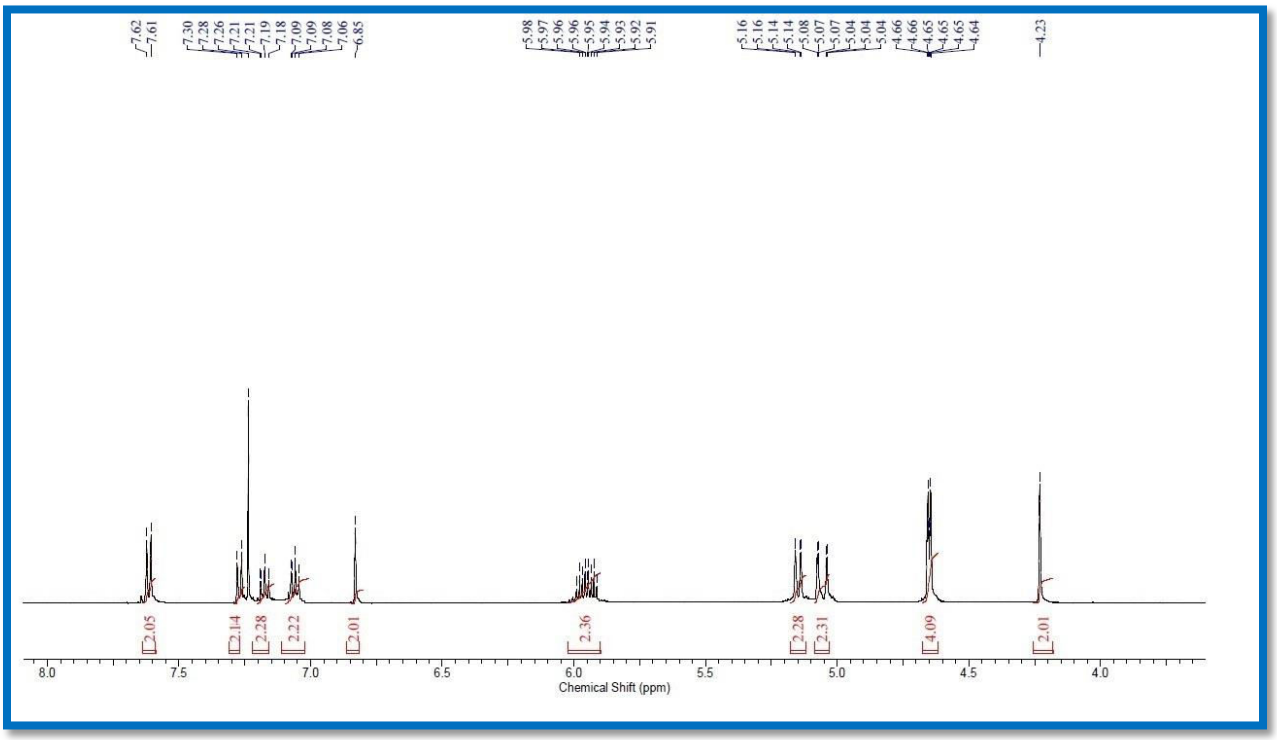


^{1}H-NMR of compound 2m



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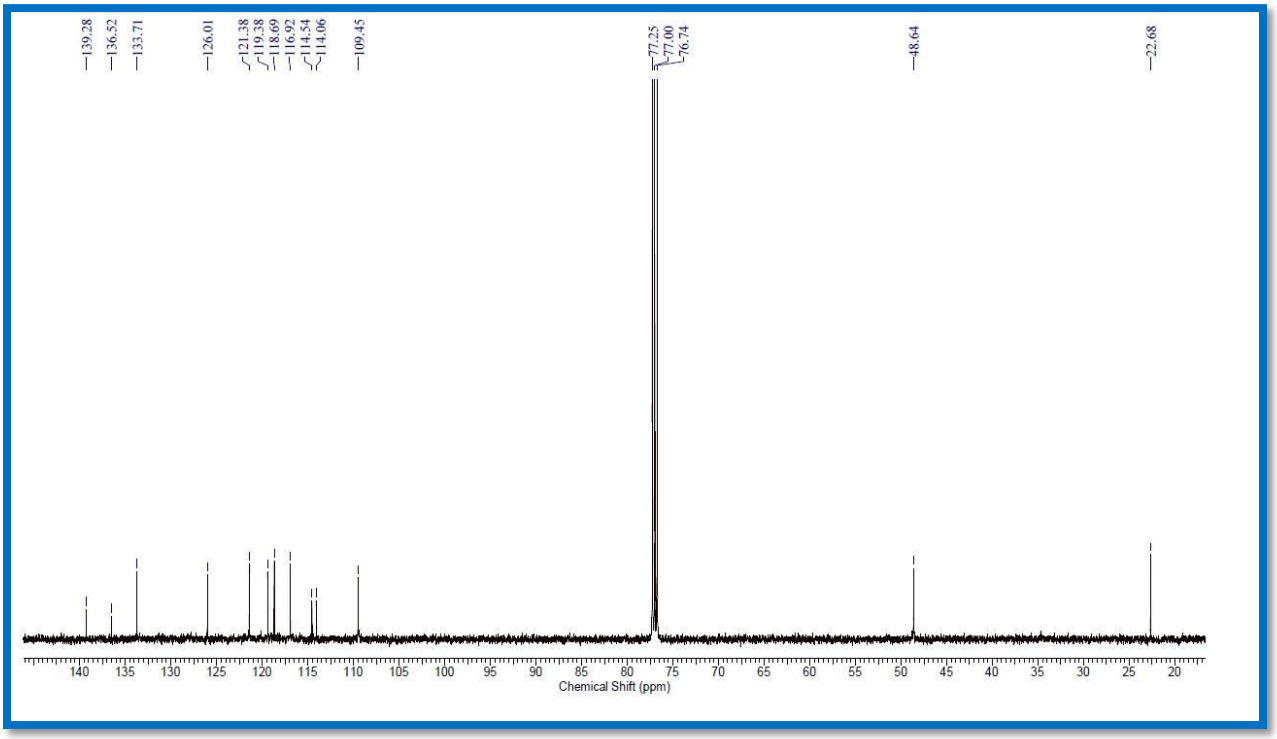

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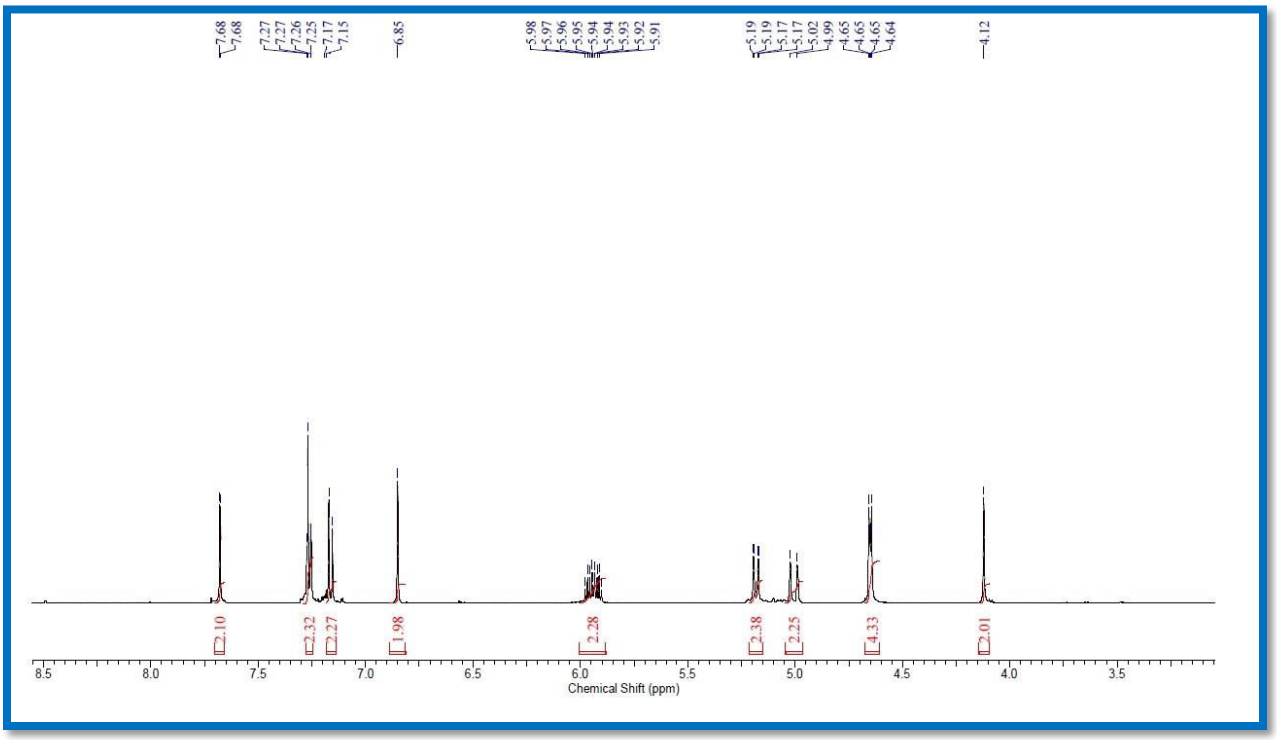
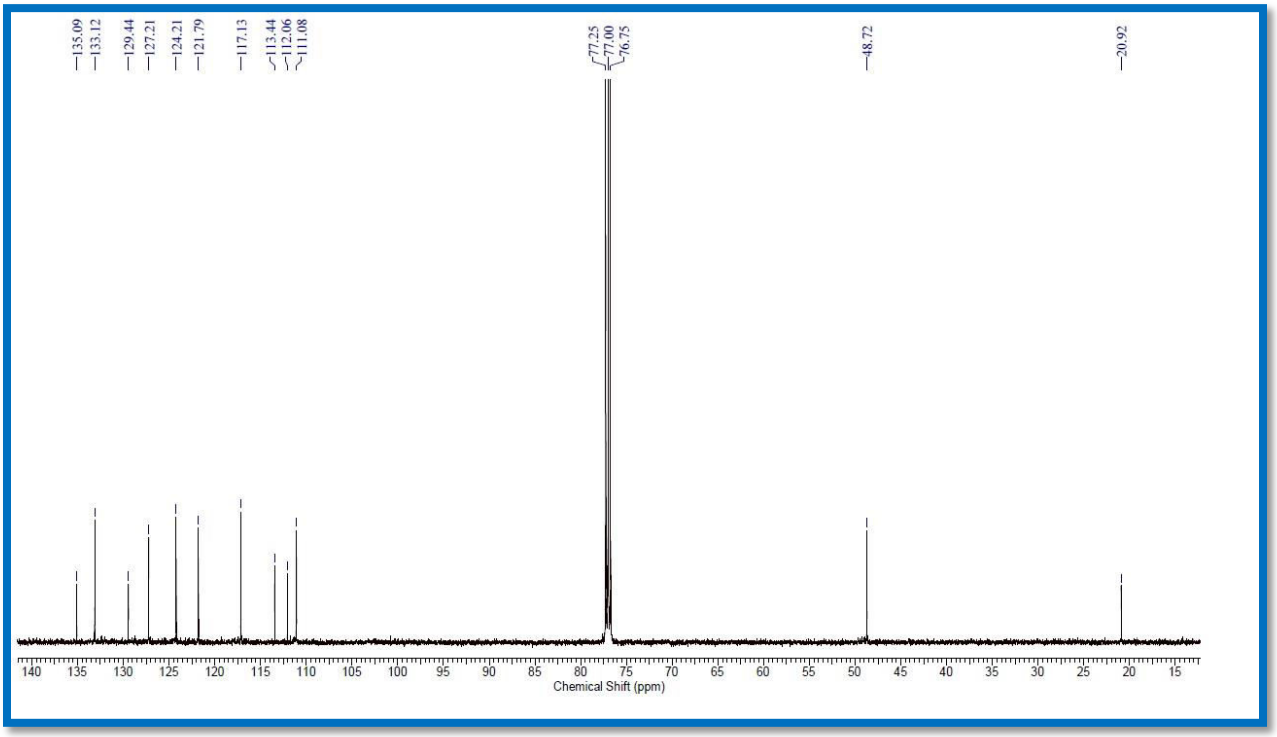
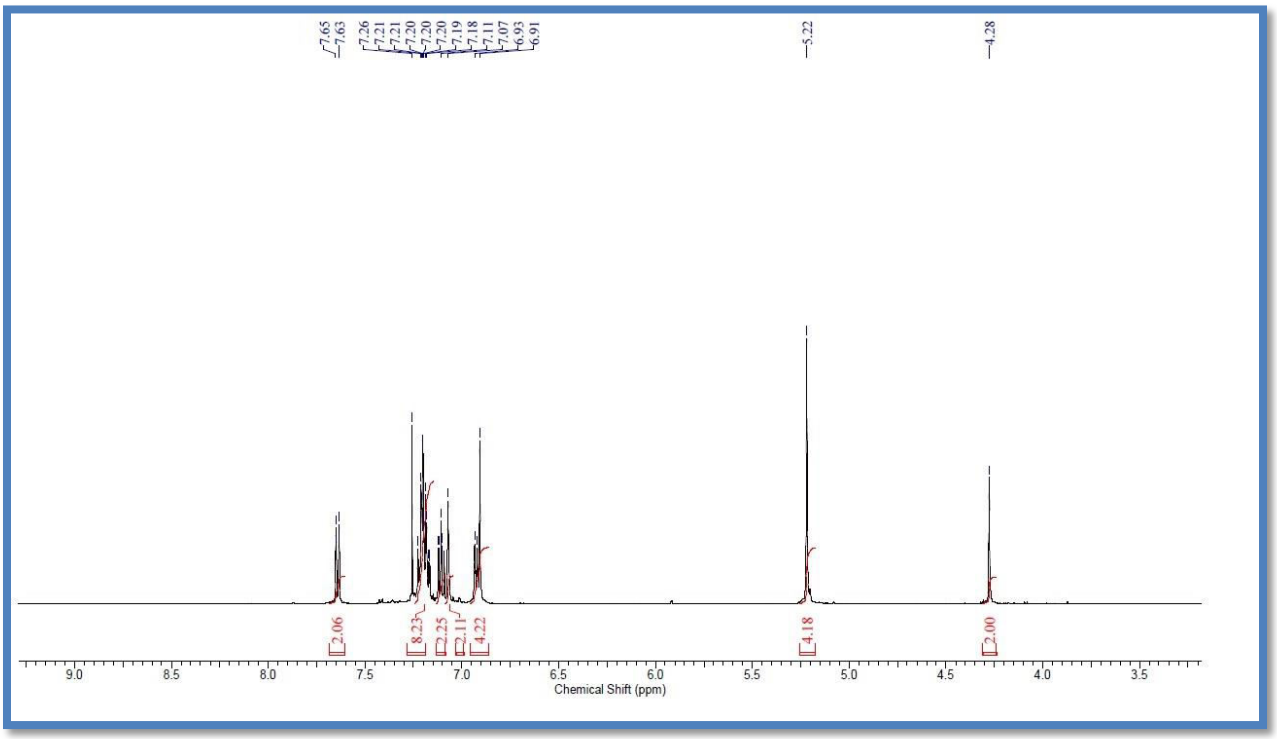


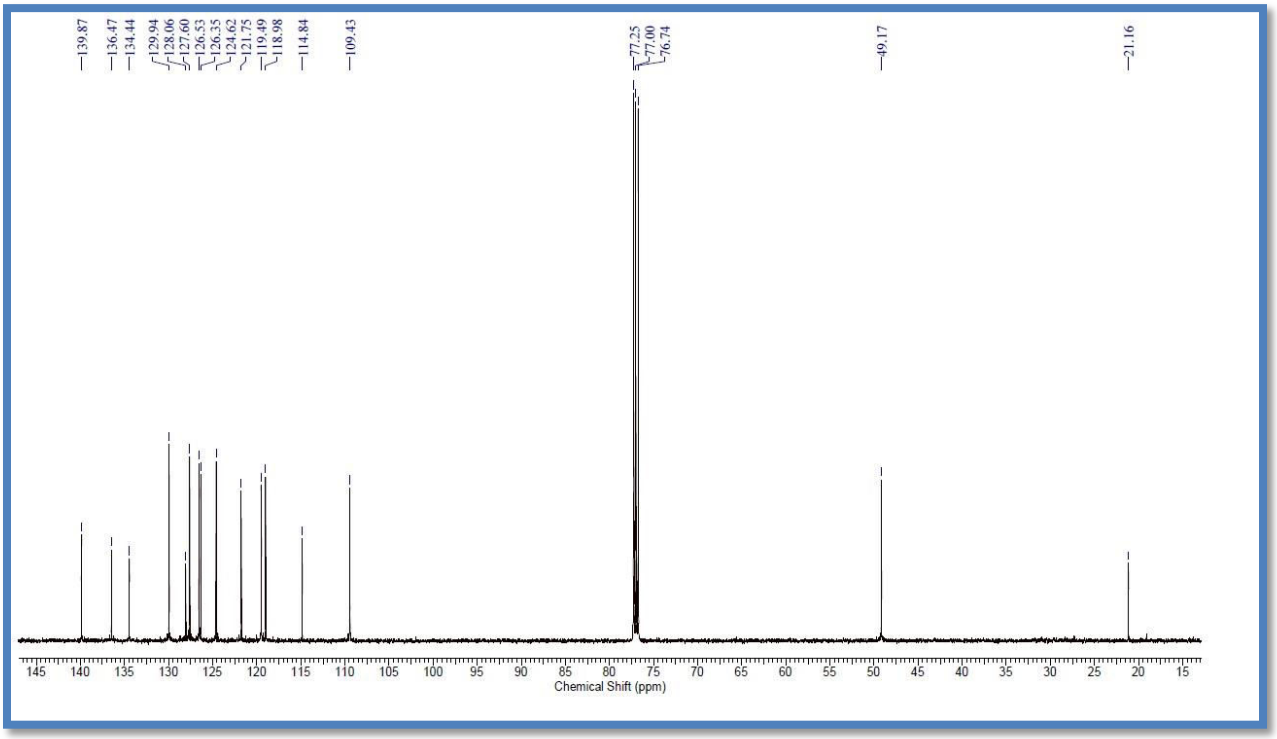
^{13}C-NMR of compound 2n



^{1}H-NMR of compound 2o



^{13}C-NMR of compound 2o



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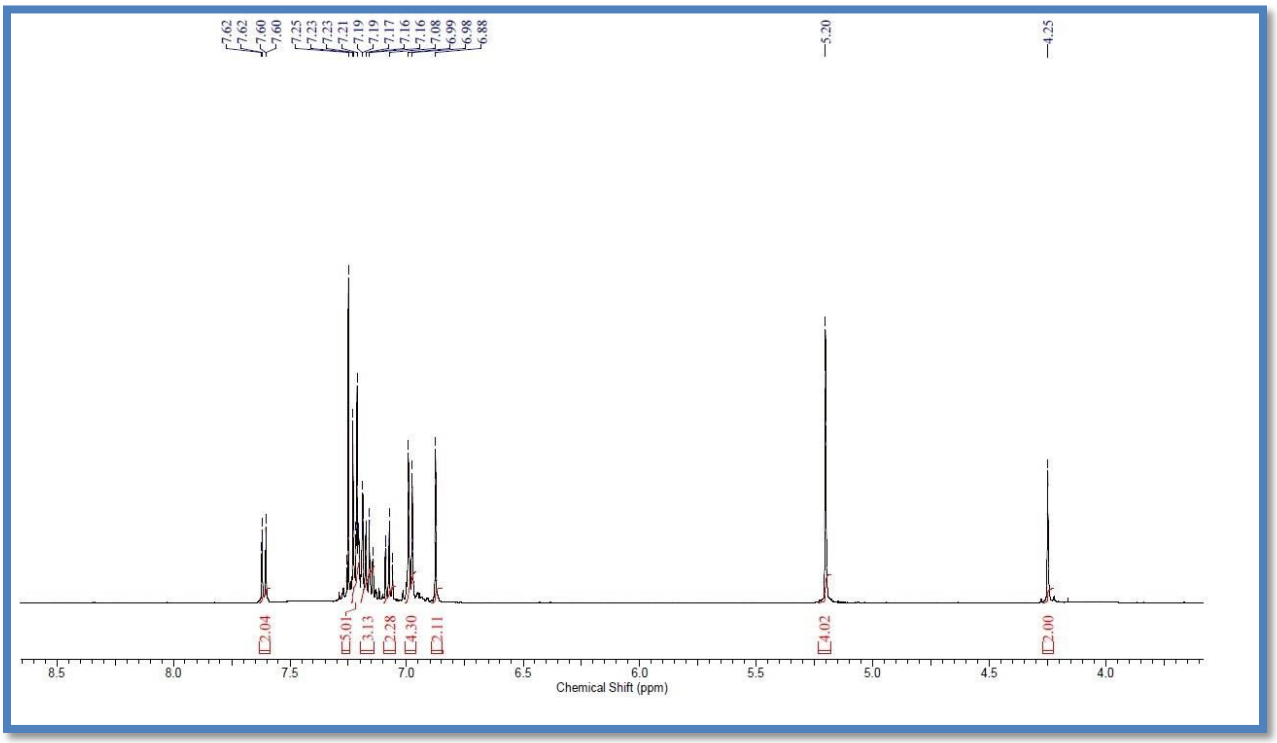
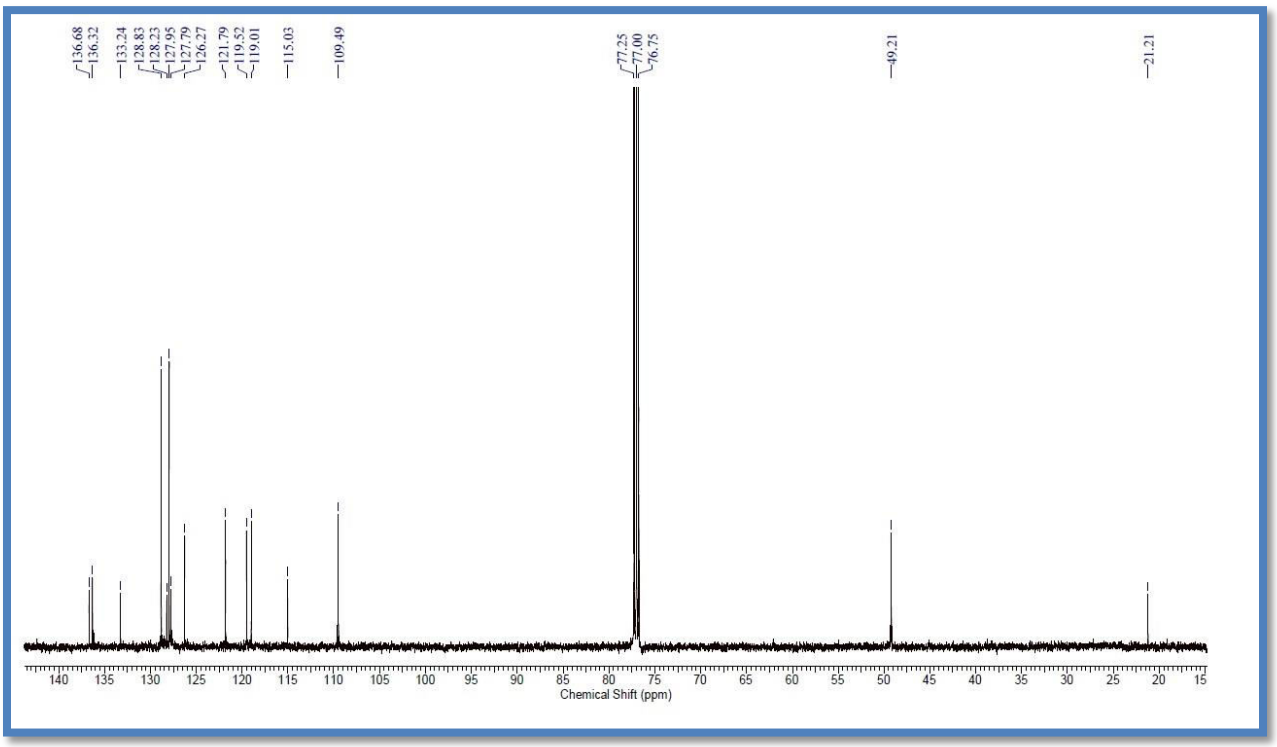
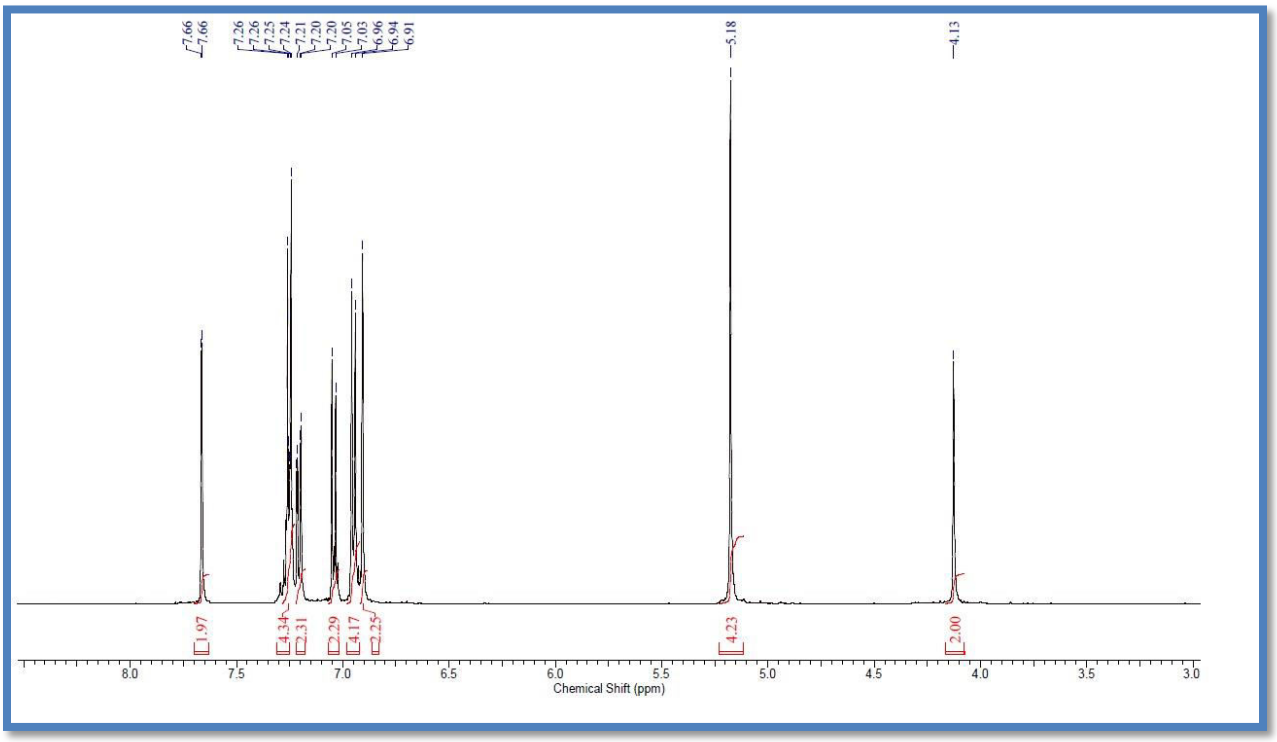


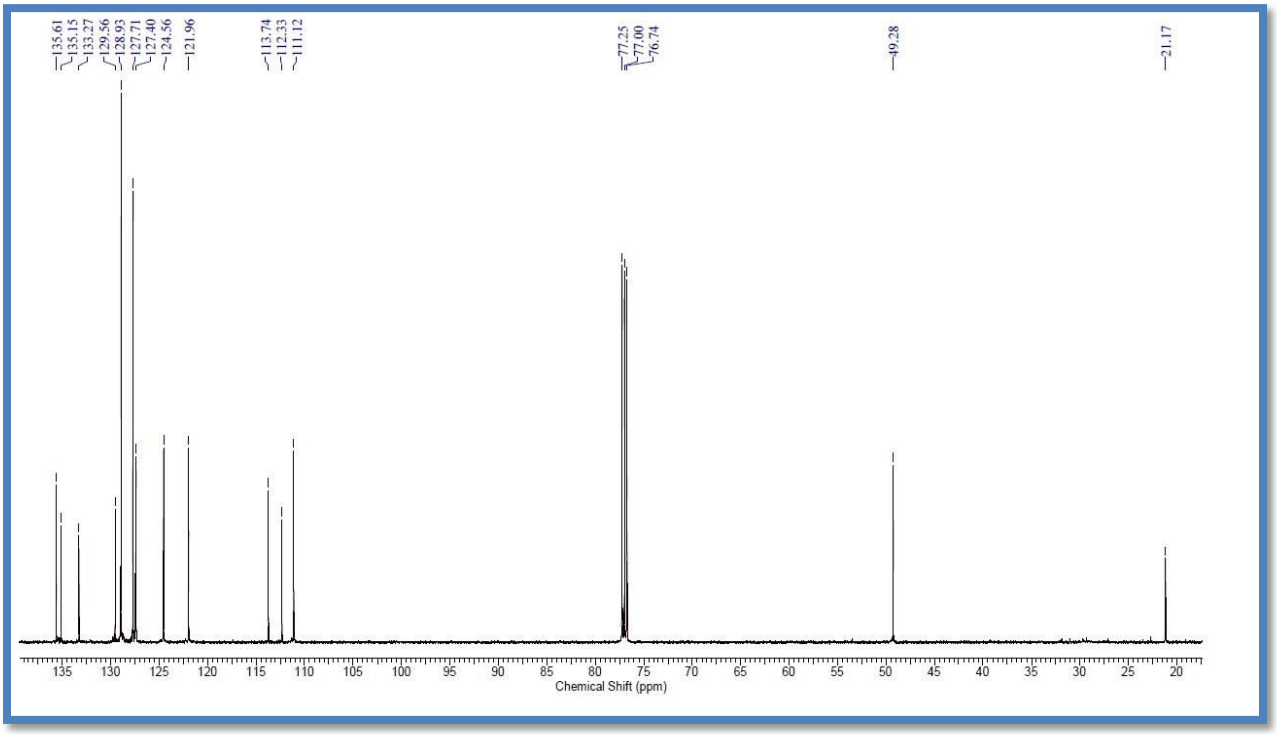
^{13}C-NMR of compound 2p



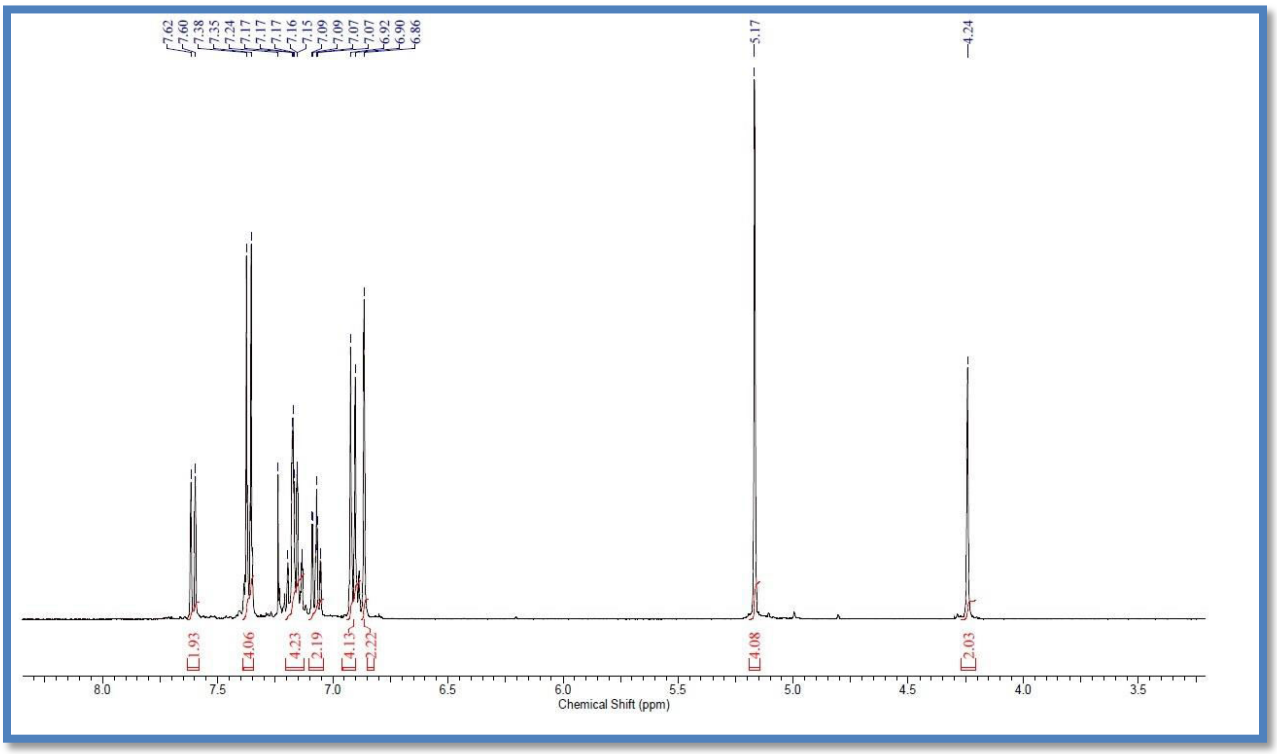
^{1}H-NMR of compound 2q



^{13}C-NMR of compound 2q



^{1}H-NMR of compound 2r



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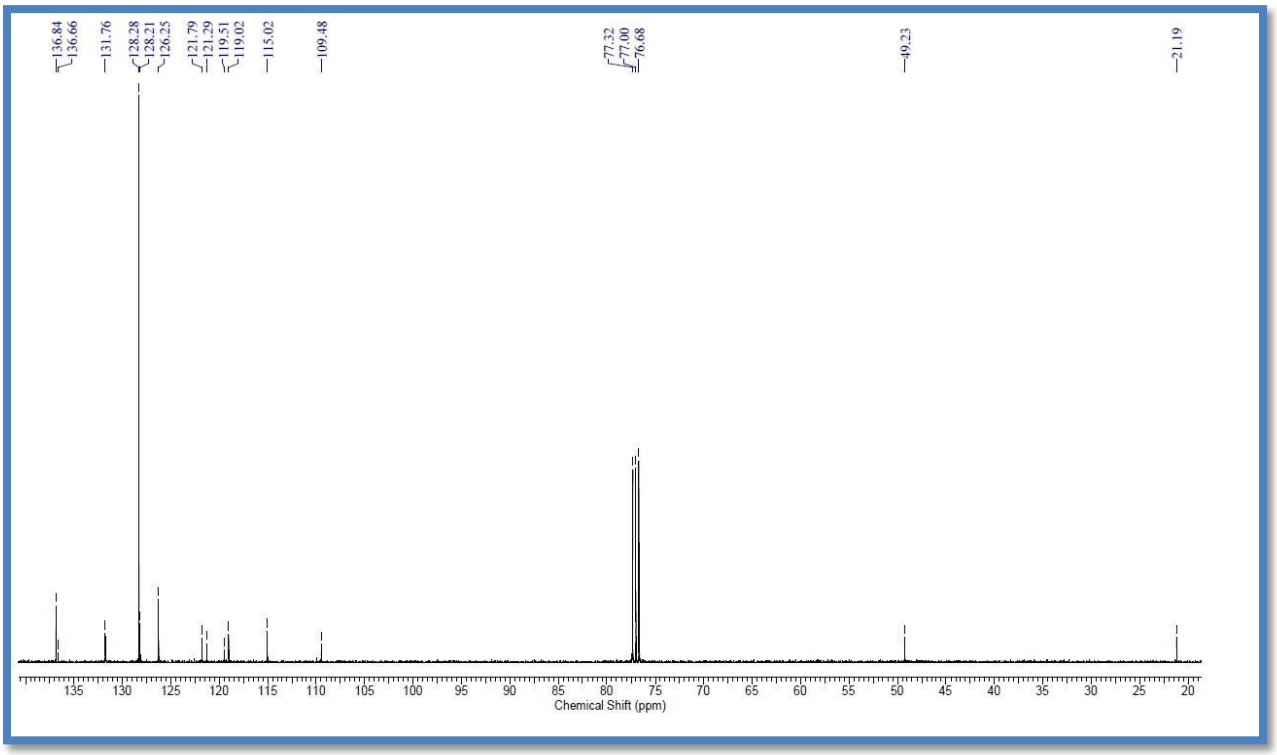

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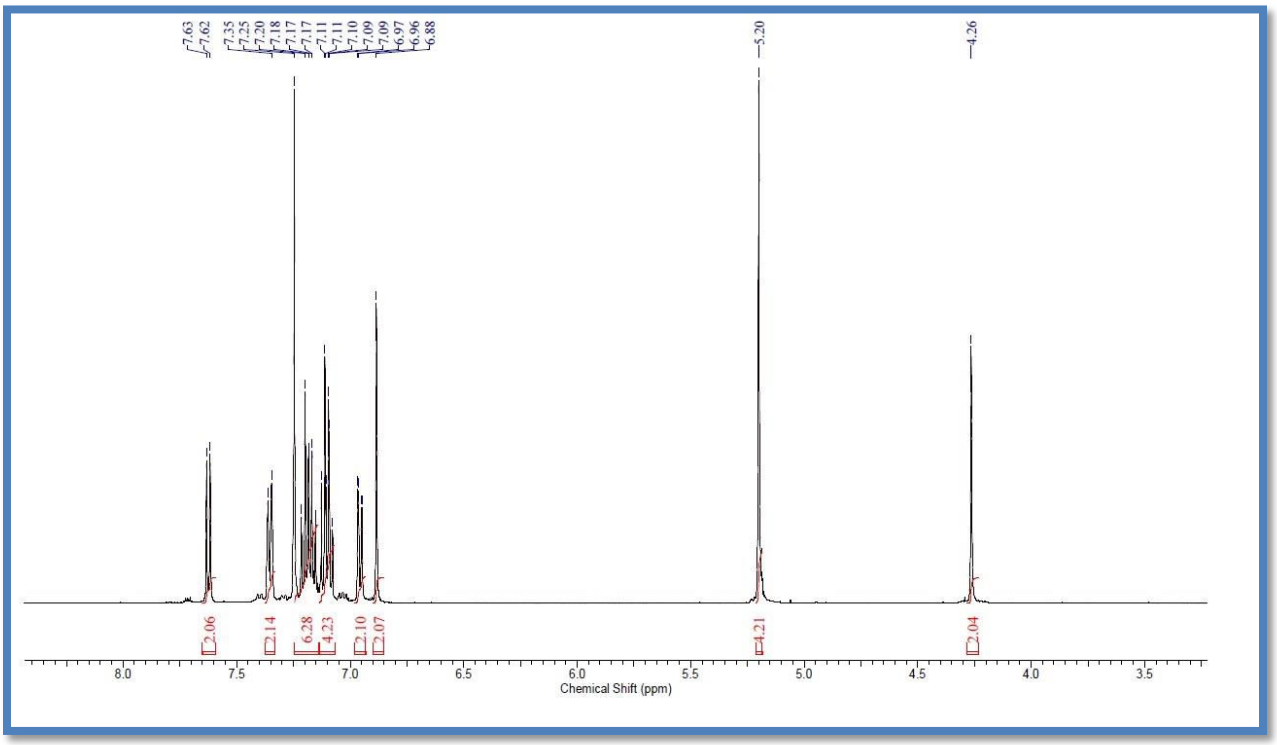

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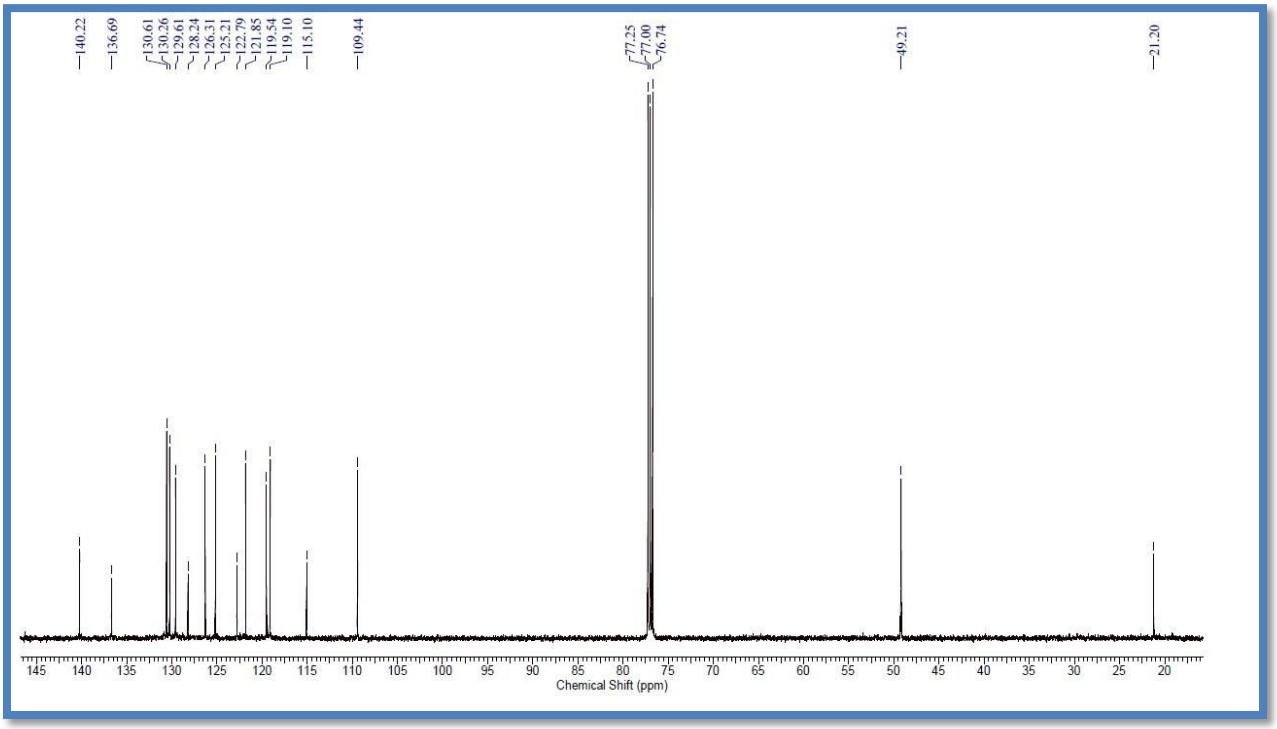
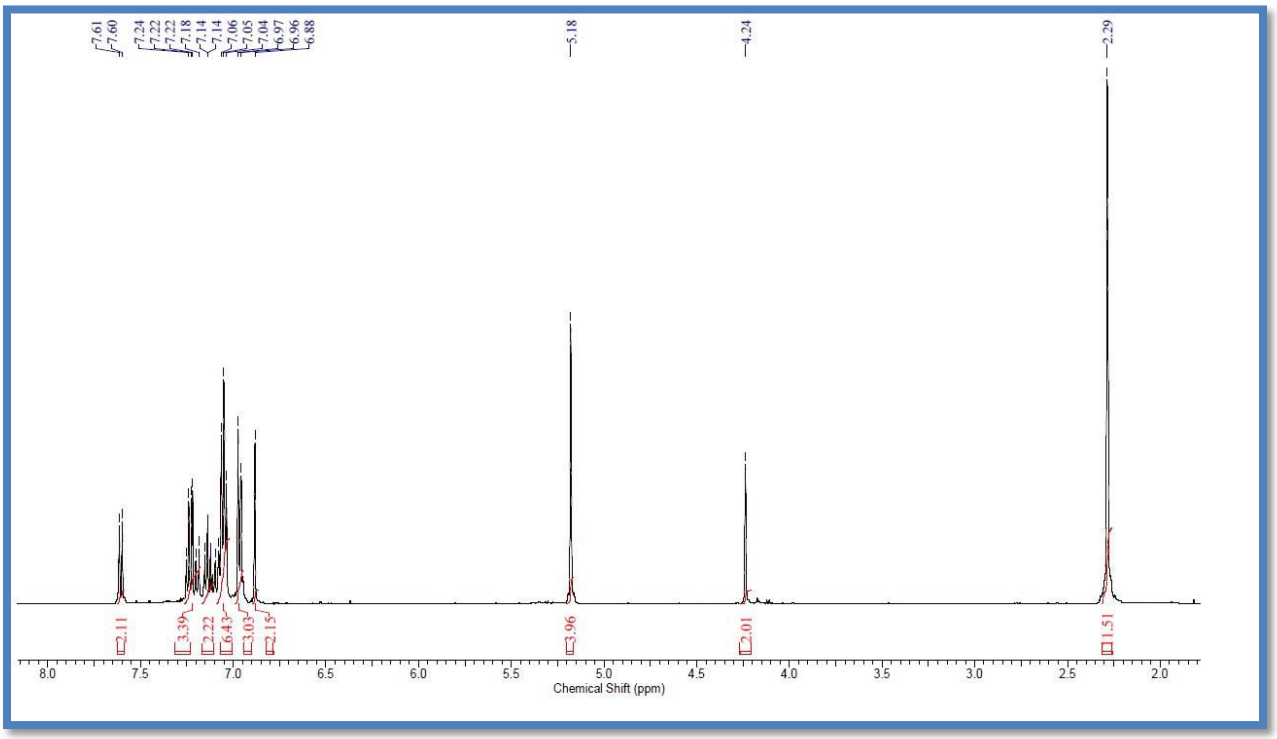


^{1}H-NMR of compound 2t



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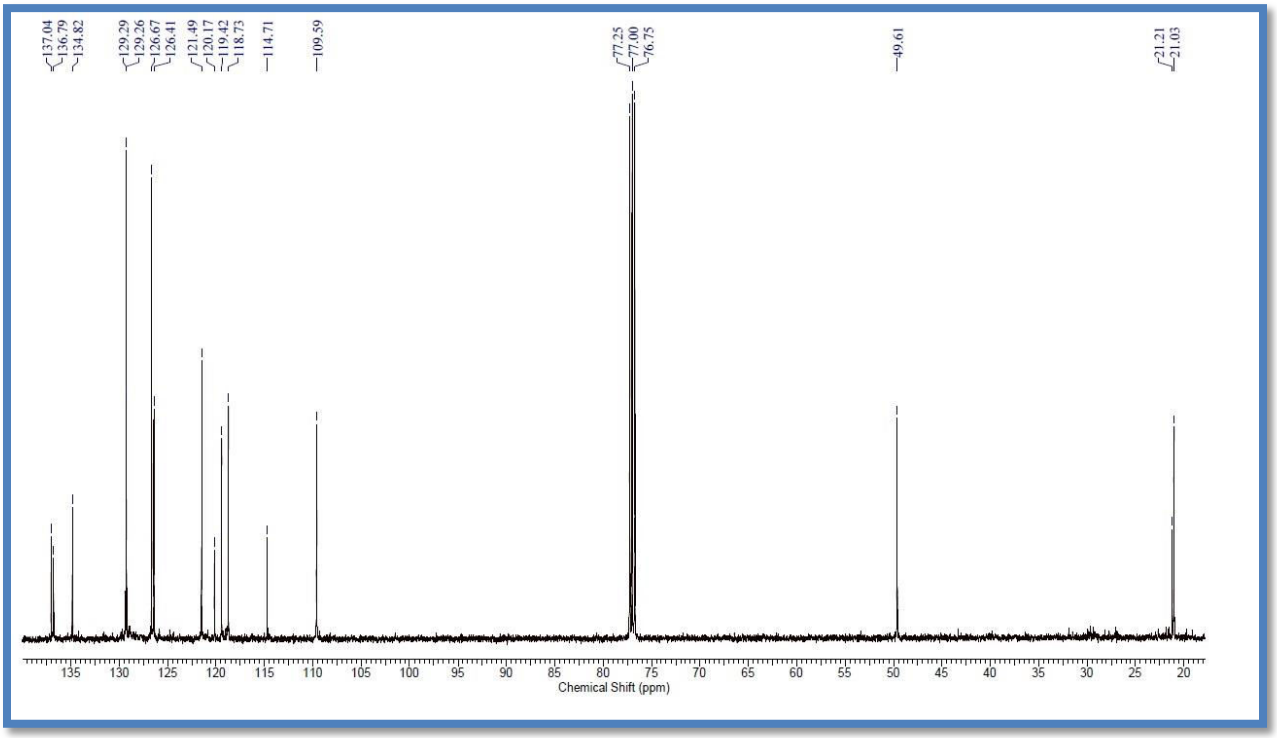
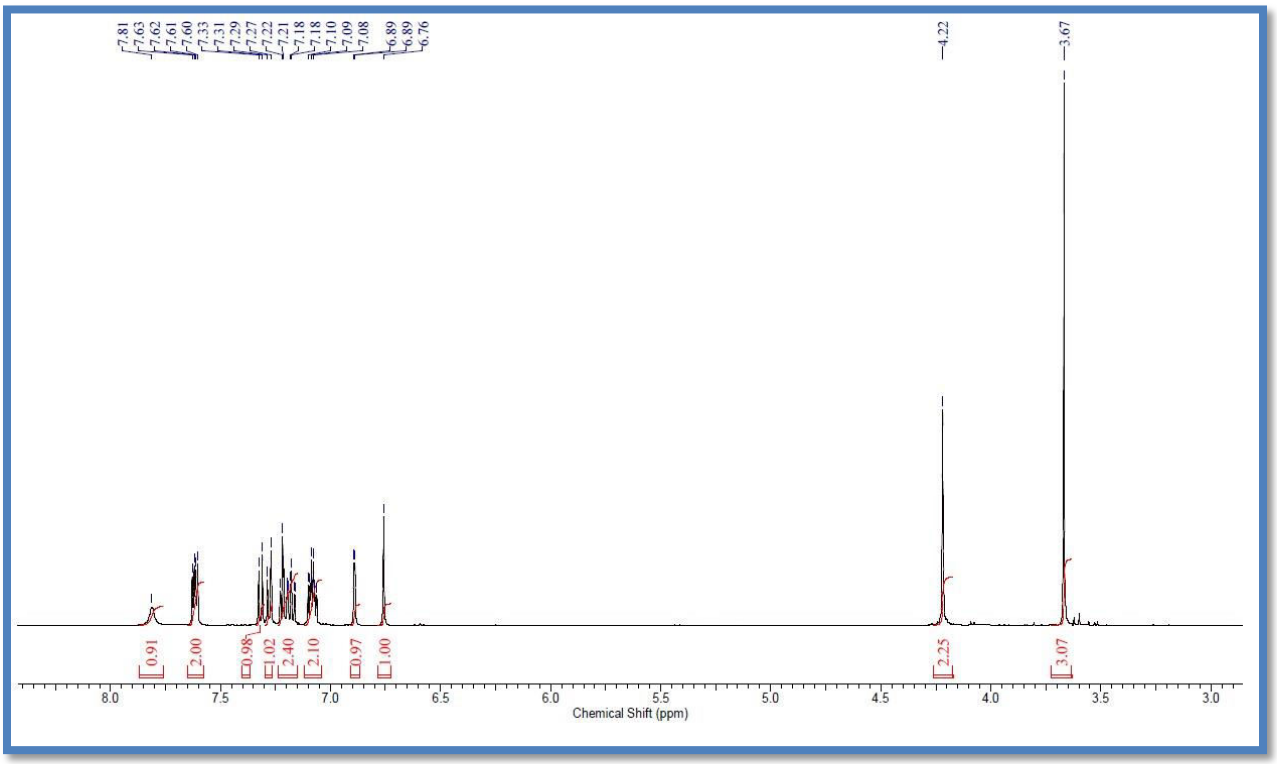
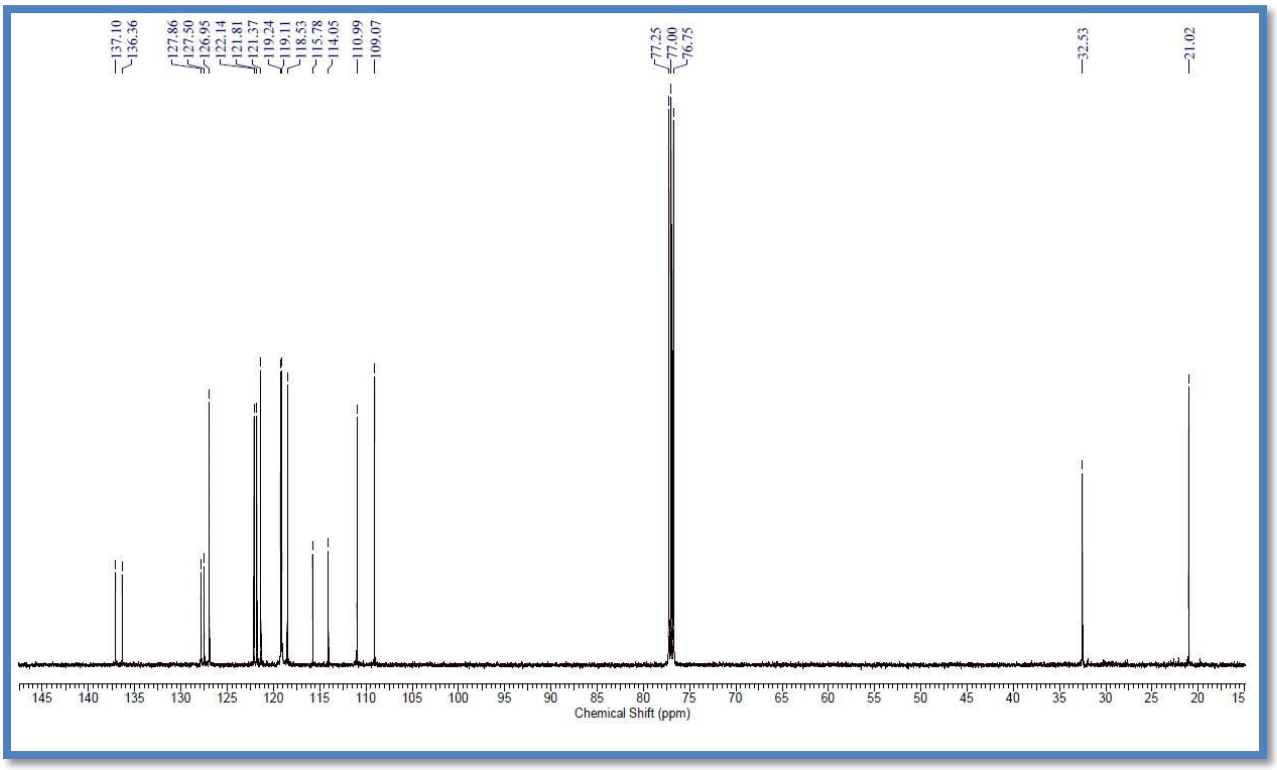


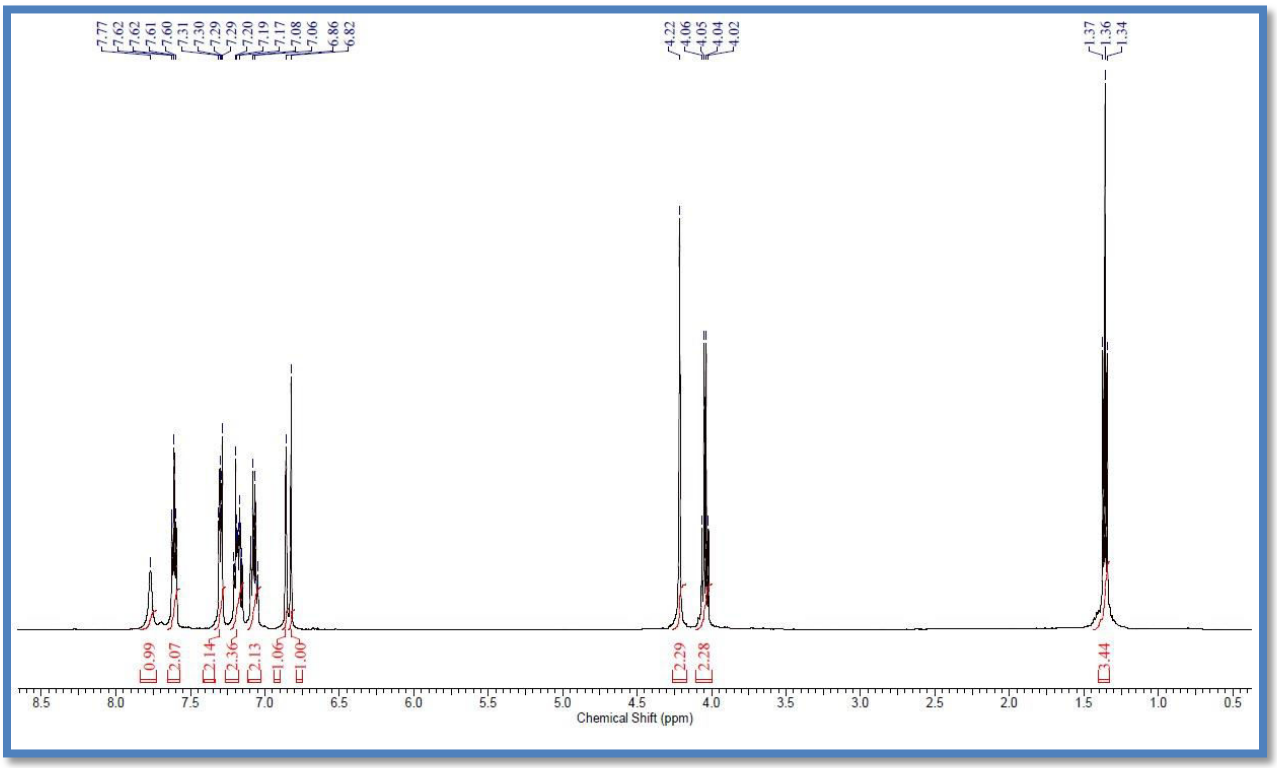
^{1}H-NMR of compound 2'a



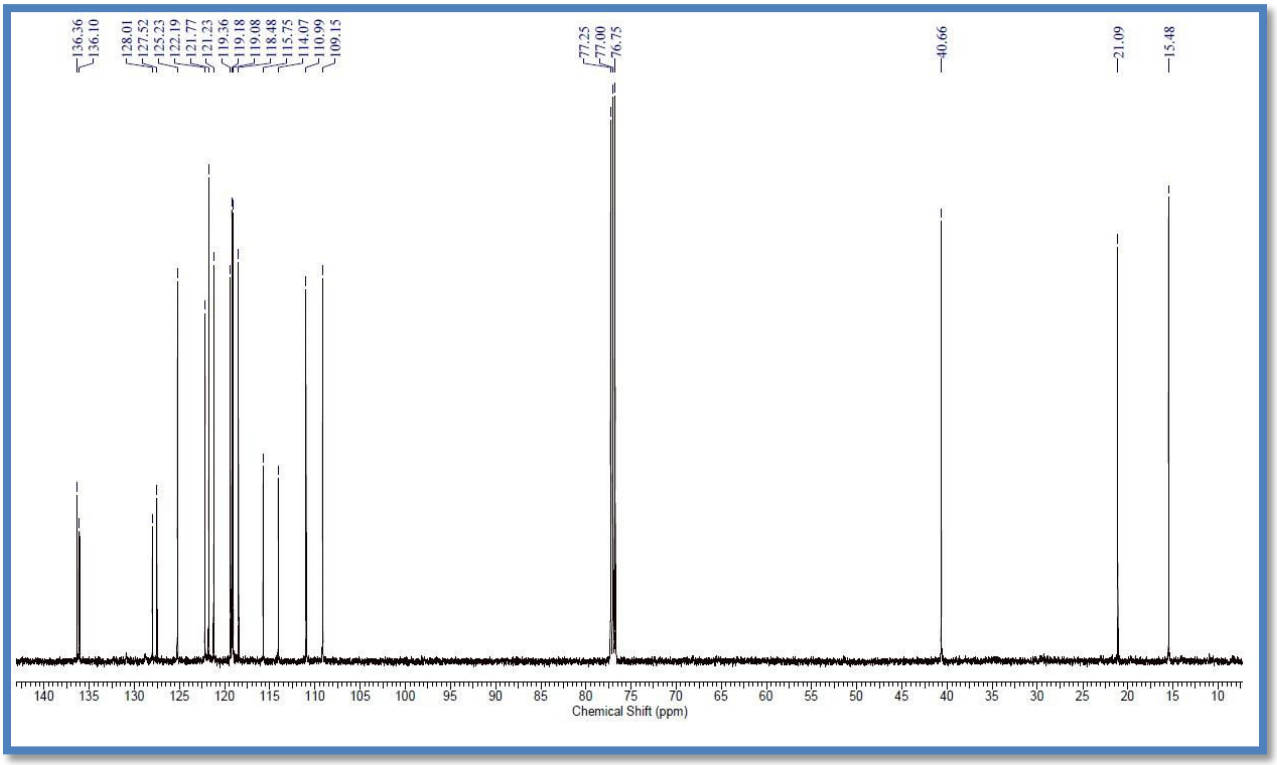
^{13}C-NMR of compound 2'a



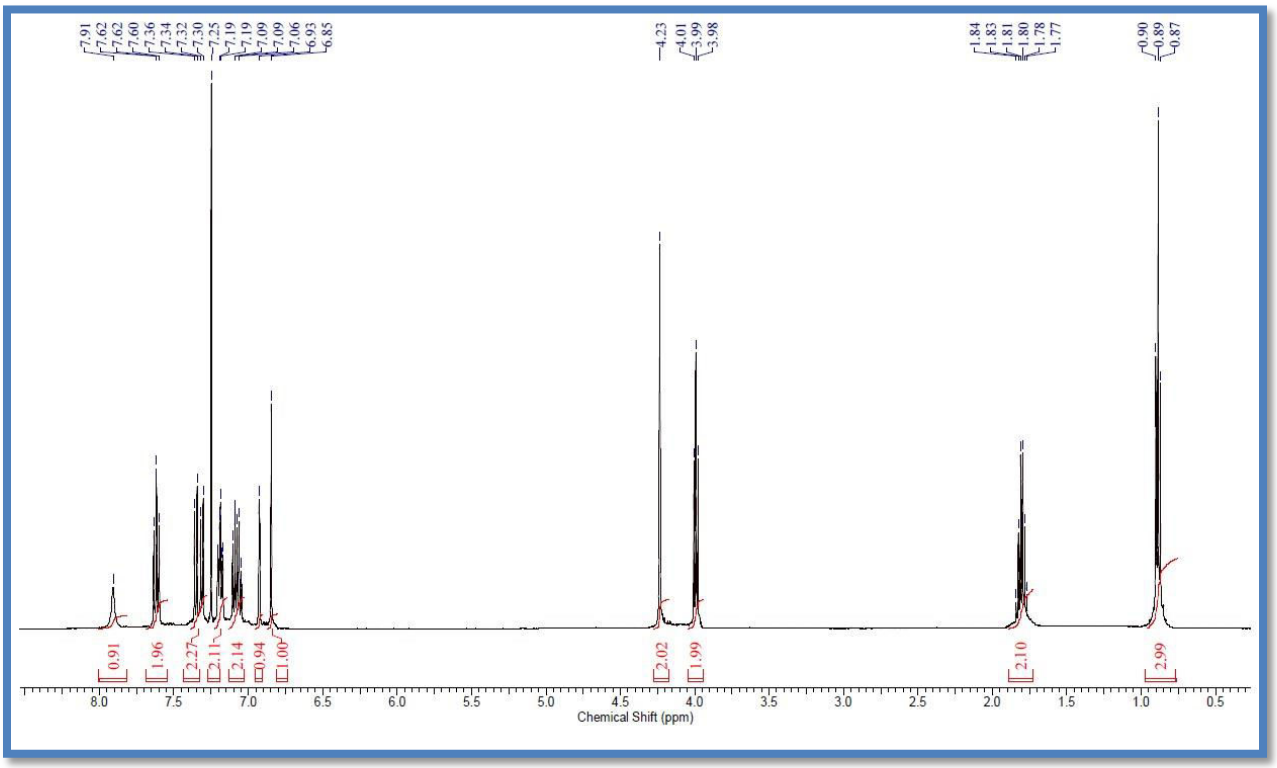
^{1}H-NMR of compound 2'b



^{13}C-NMR of compound 2'b



^{1}H-NMR of compound 2'c



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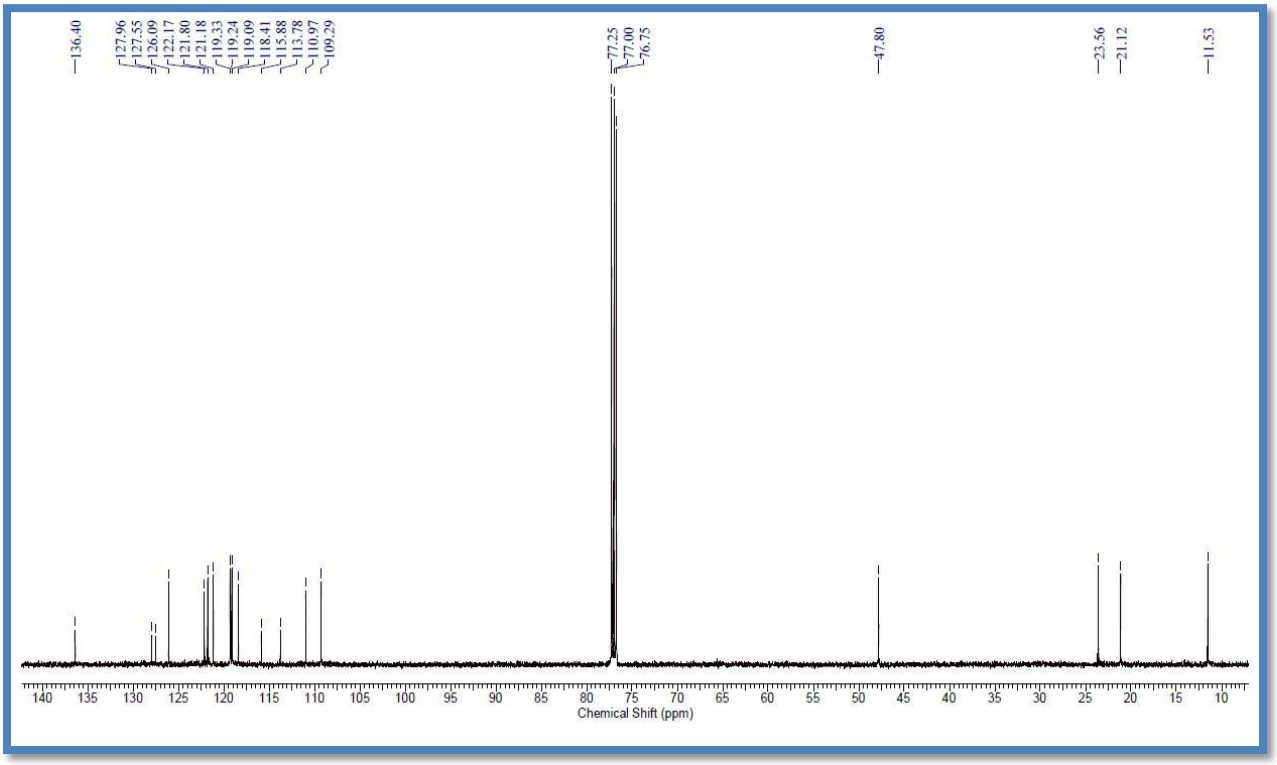
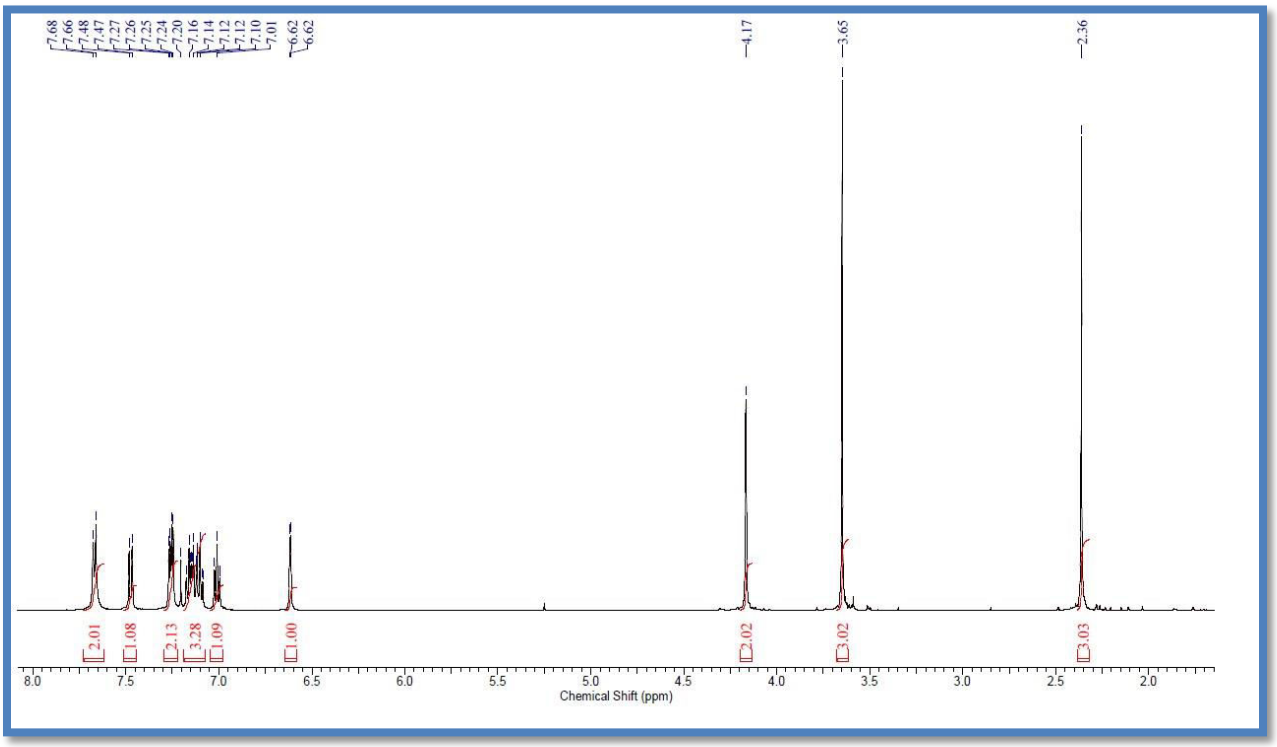


^{1}H-NMR of compound 2'd



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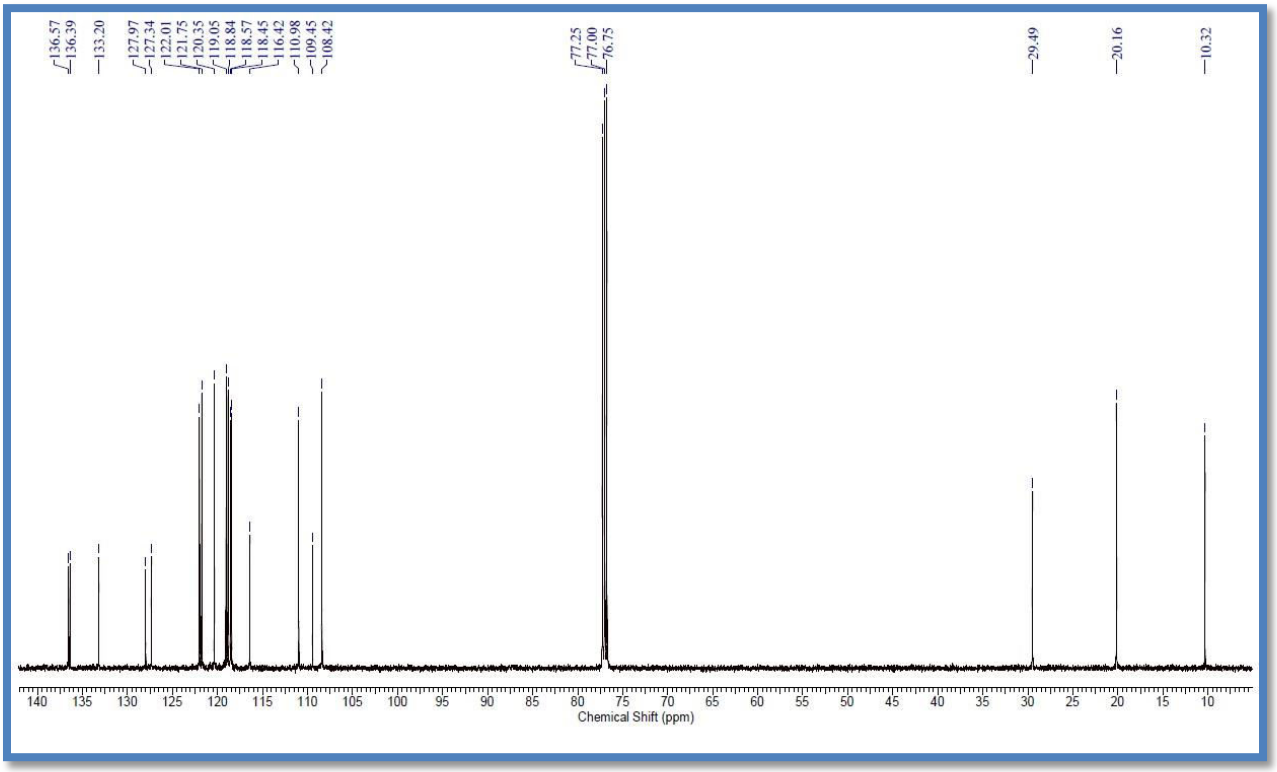
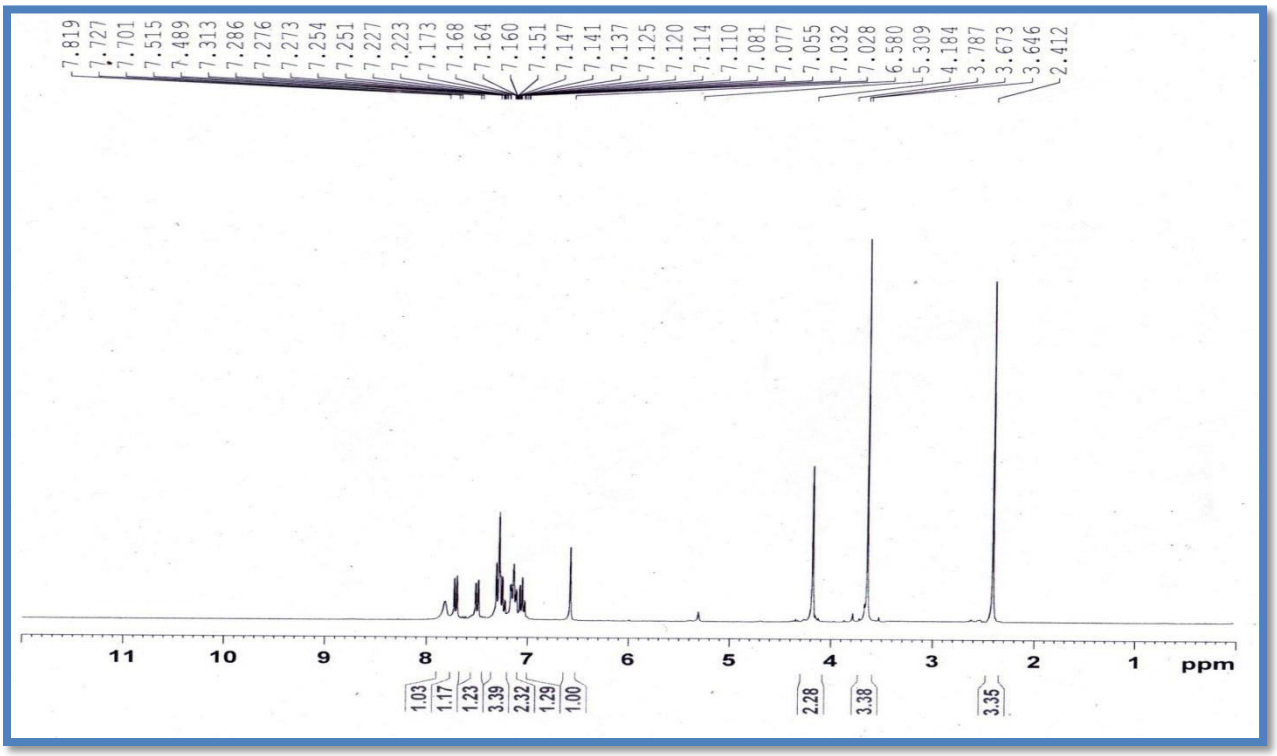
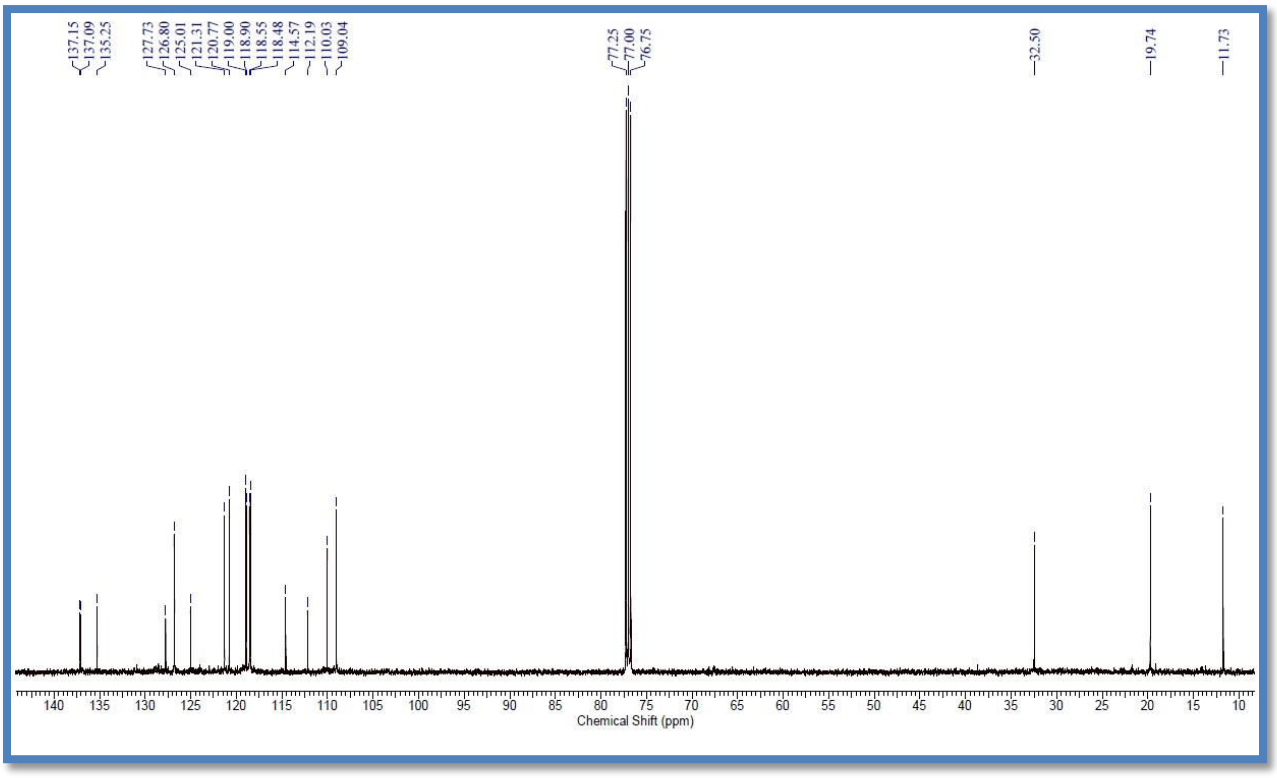


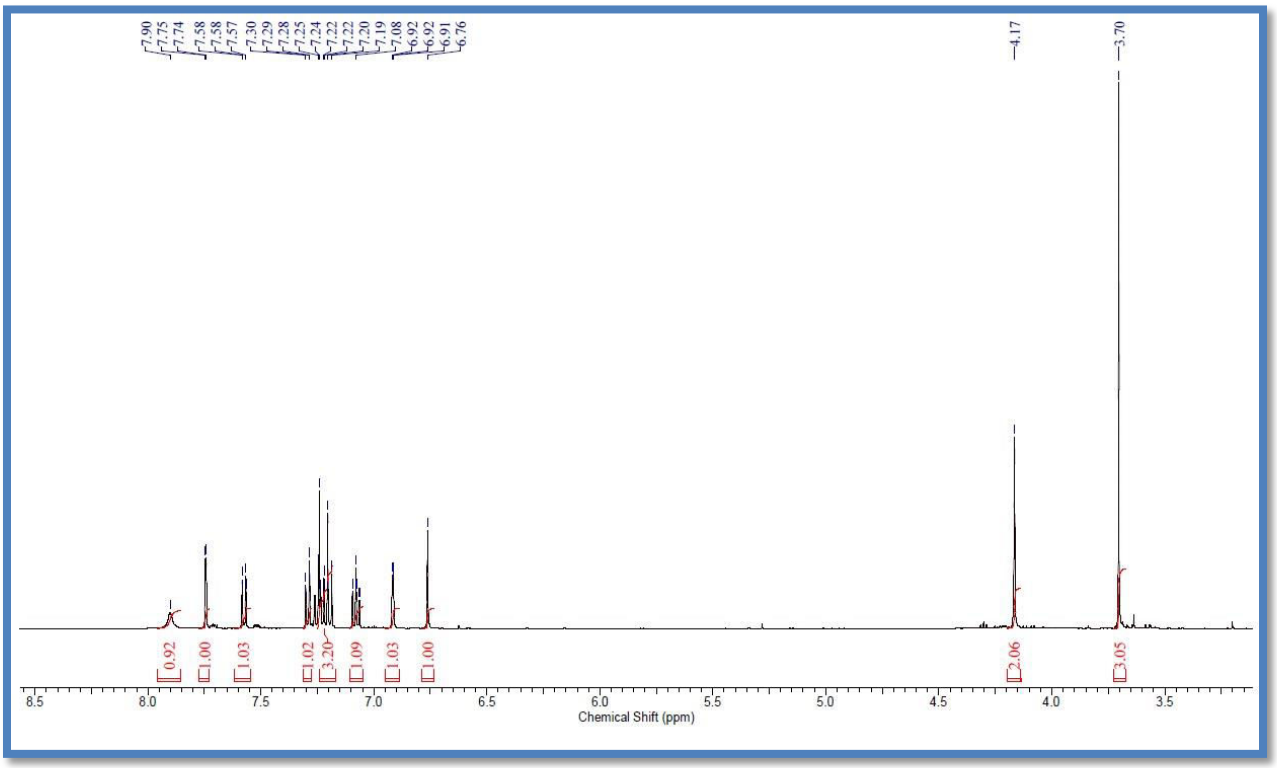
^{1}H-NMR of compound 2'e



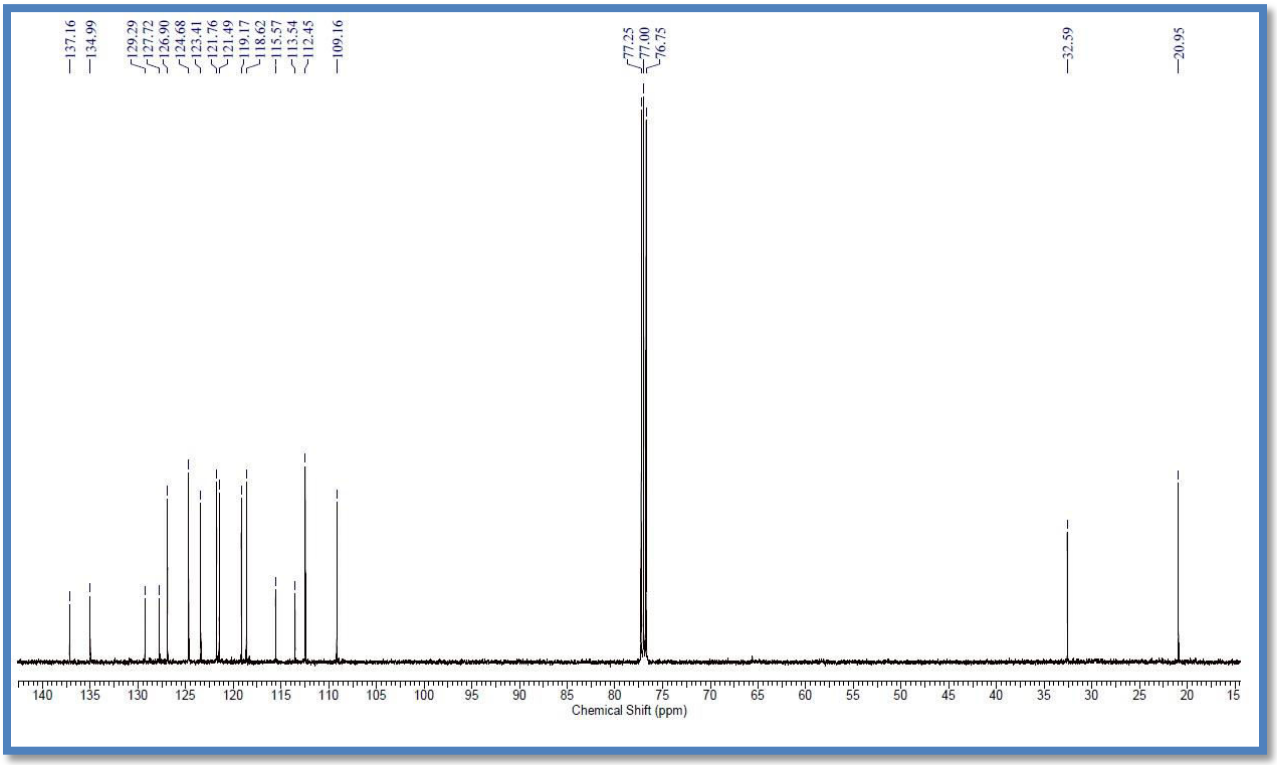
^{13}C-NMR of compound 2'e



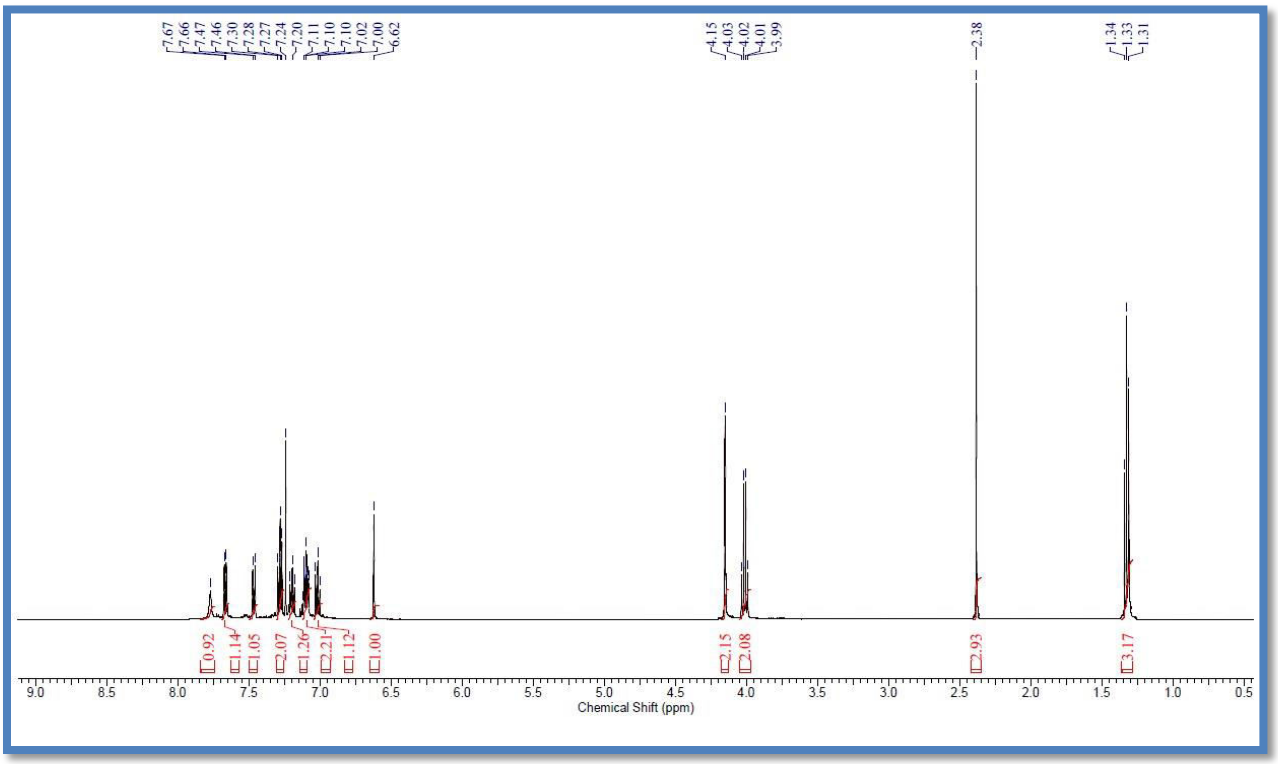
^{1}H-NMR of compound 2'f



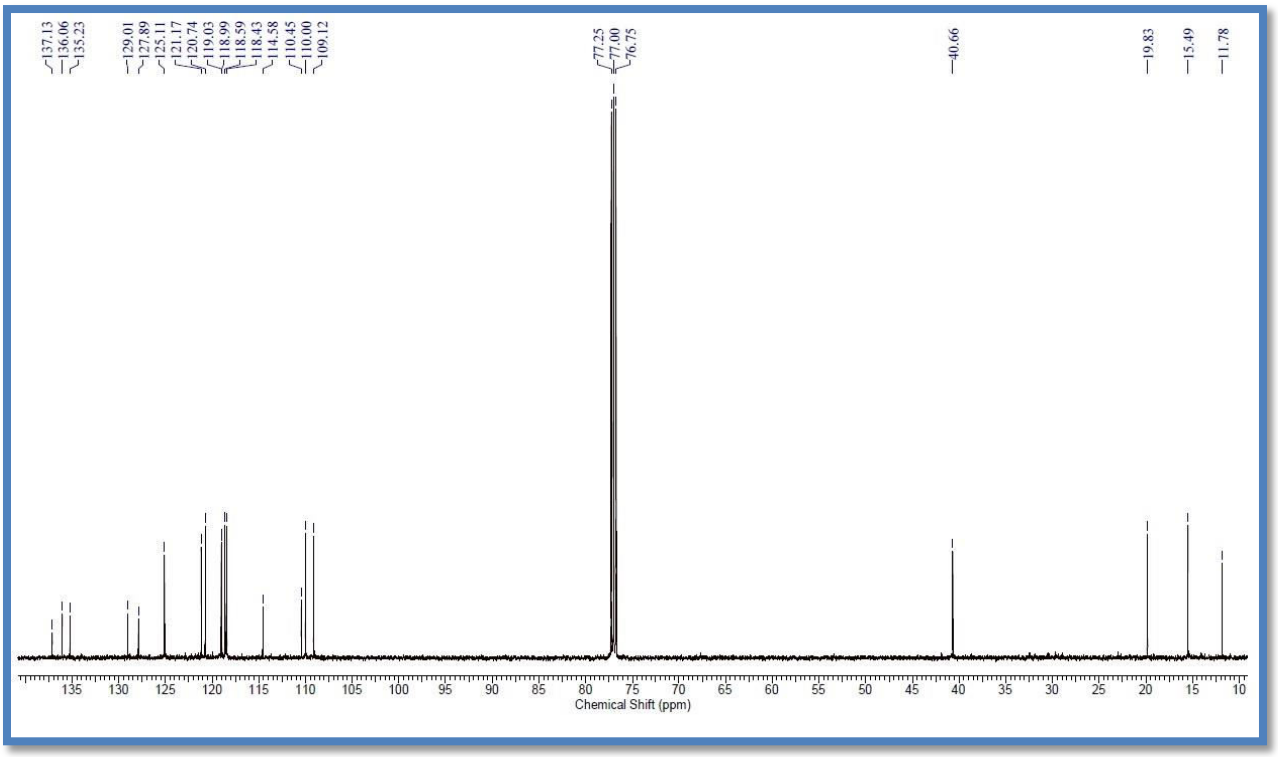
^{13}C-NMR of compound 2'f



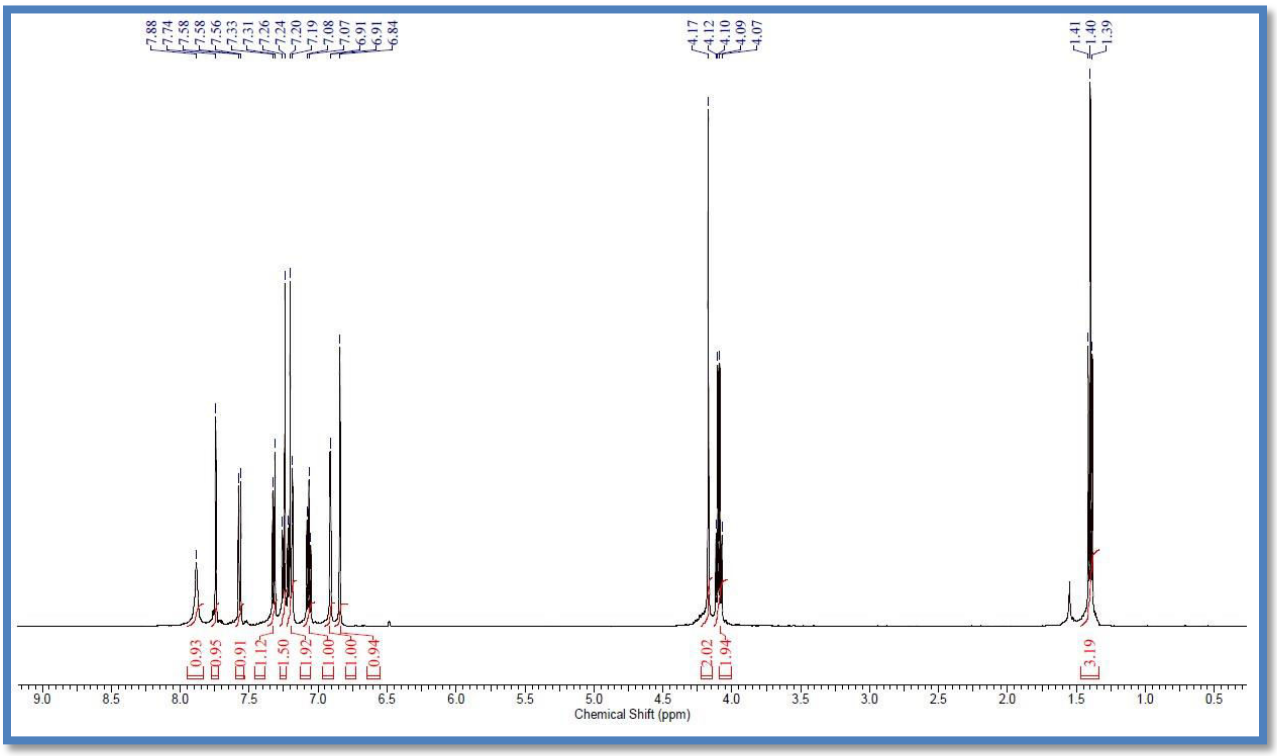
^{1}H-NMR of compound 2'g



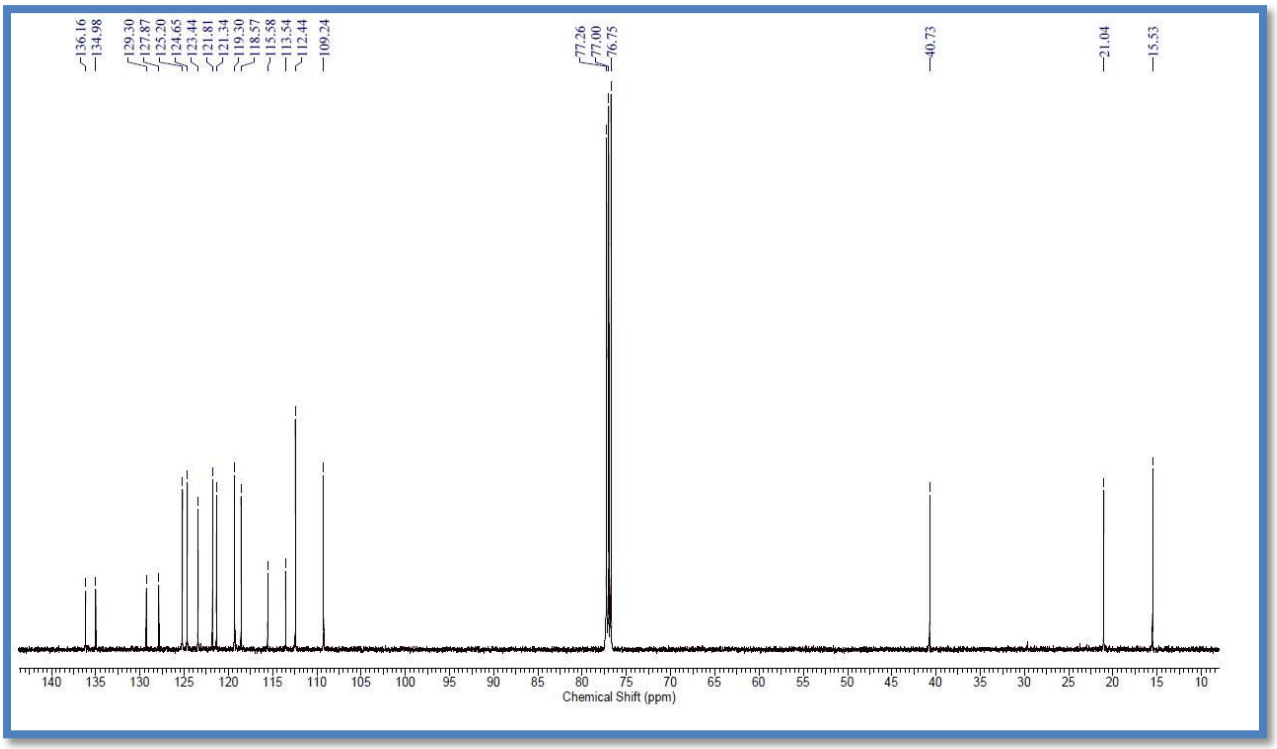
^{13}C-NMR of compound 2'g



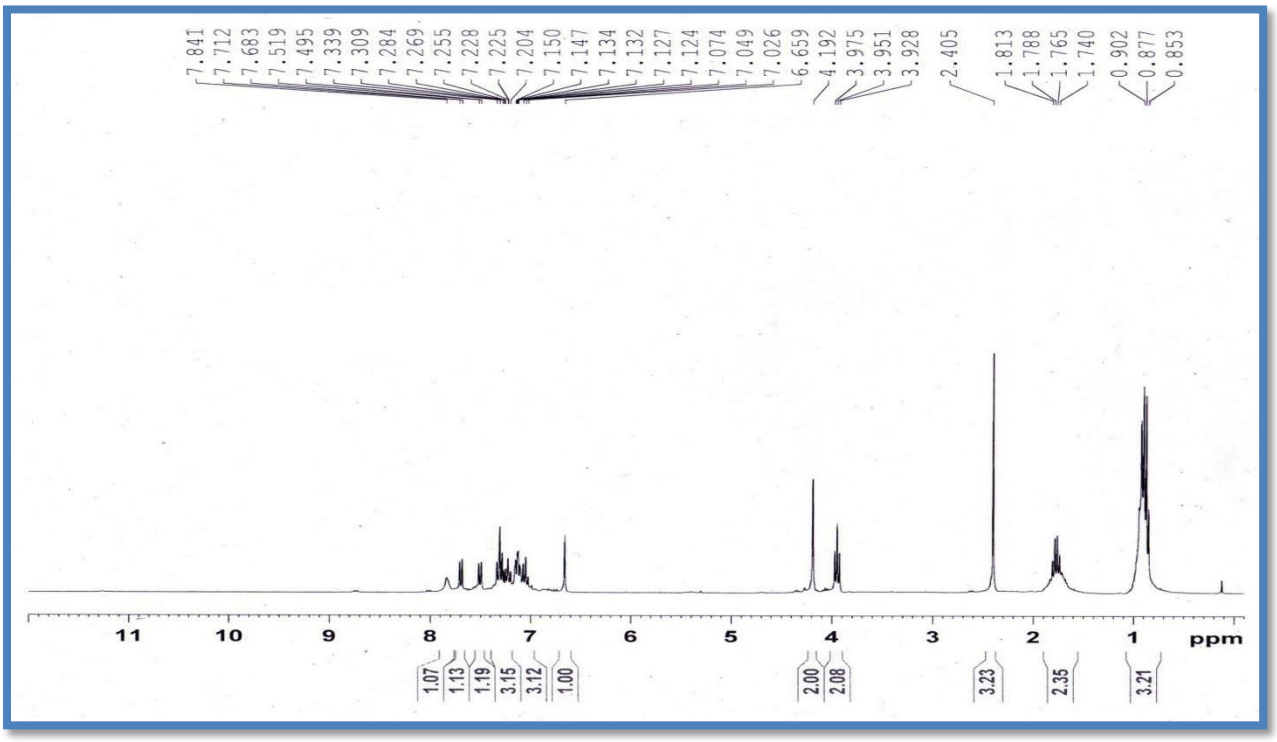
^{1}H-NMR of compound 2'h



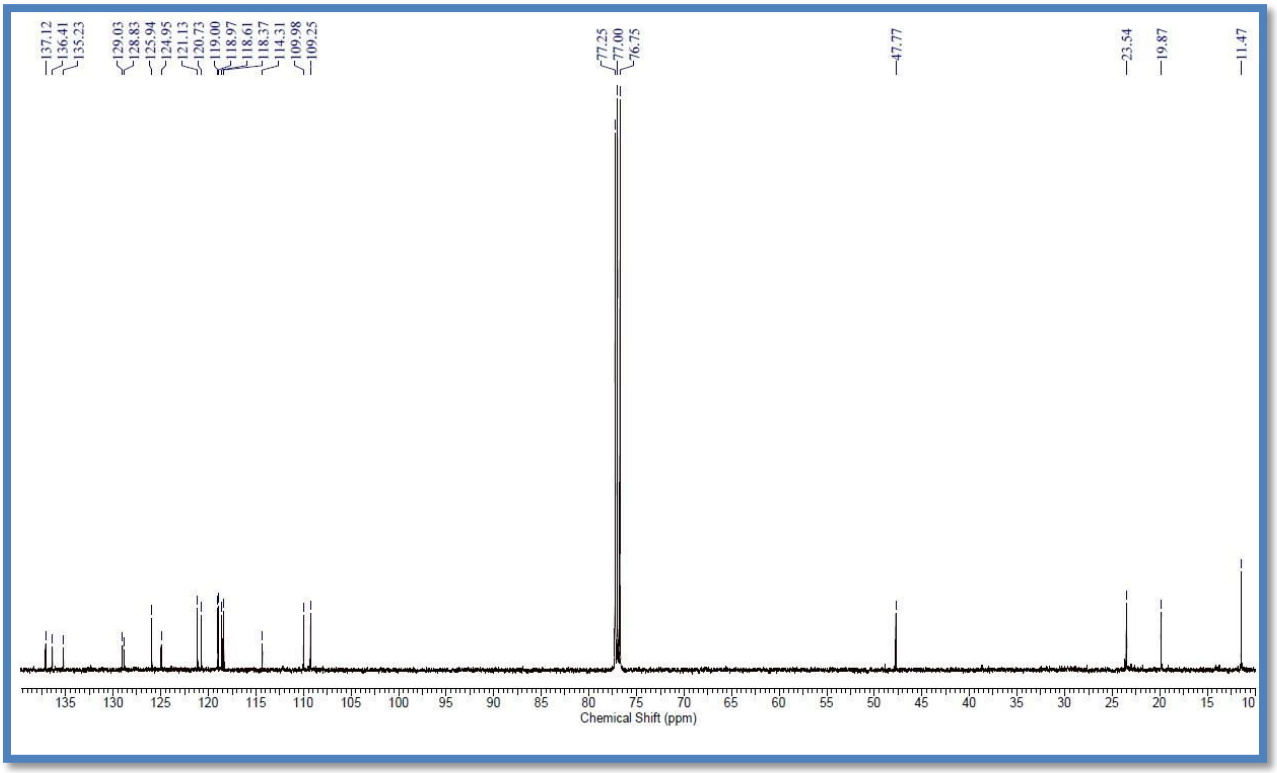
^{13}C-NMR of compound 2'h



^{1}H-NMR of compound 2'i



^{13}C-NMR of compound 2'i



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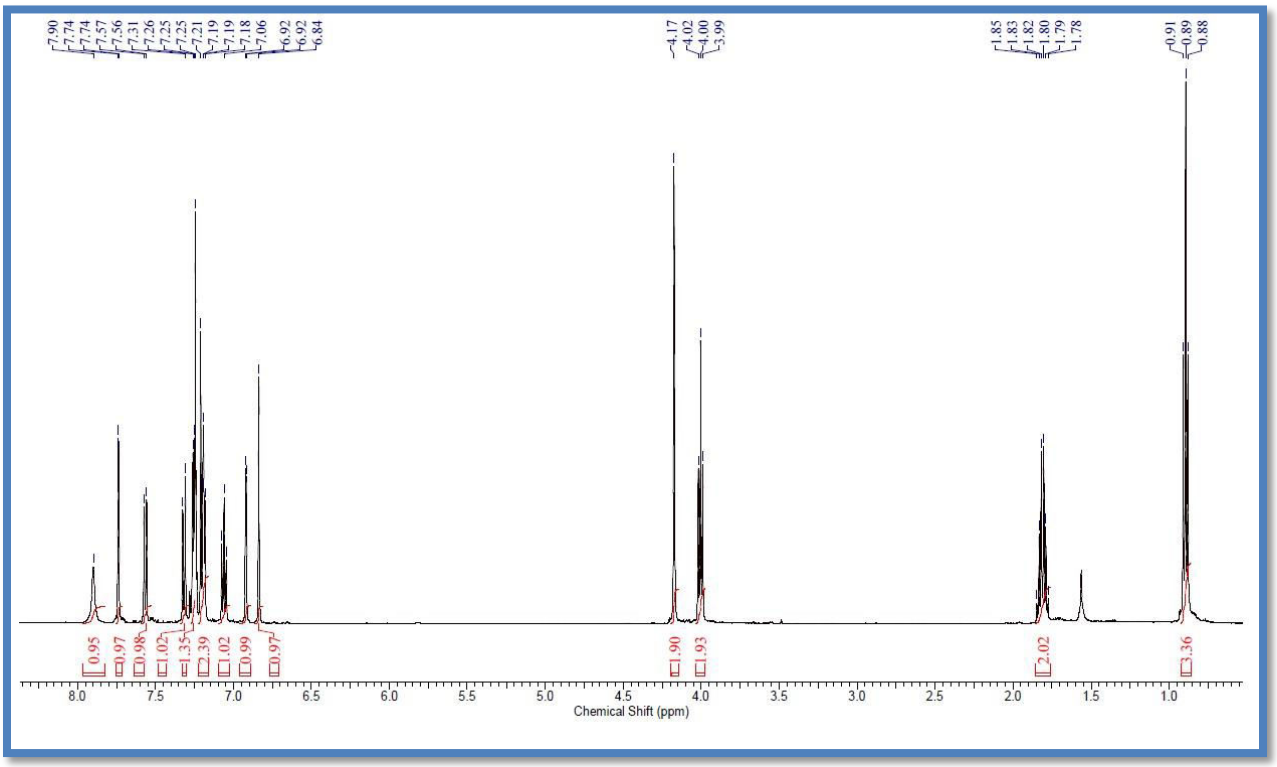
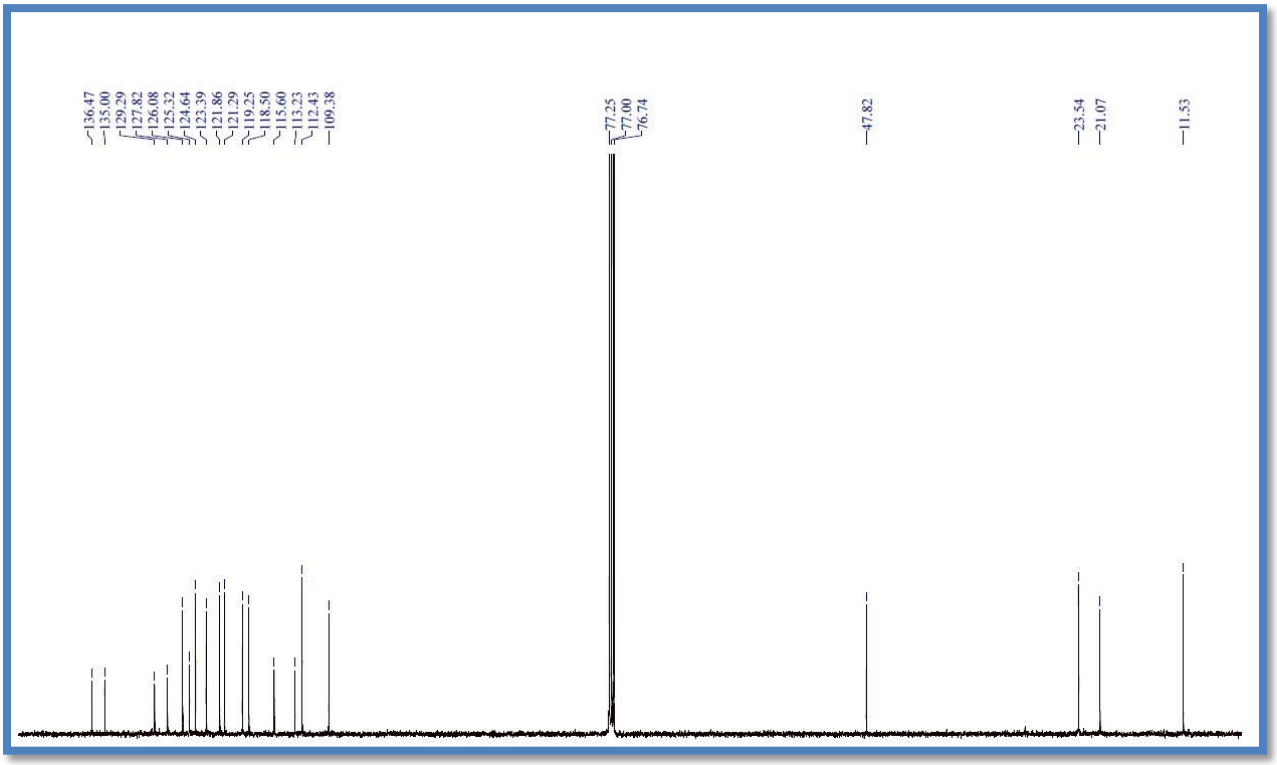
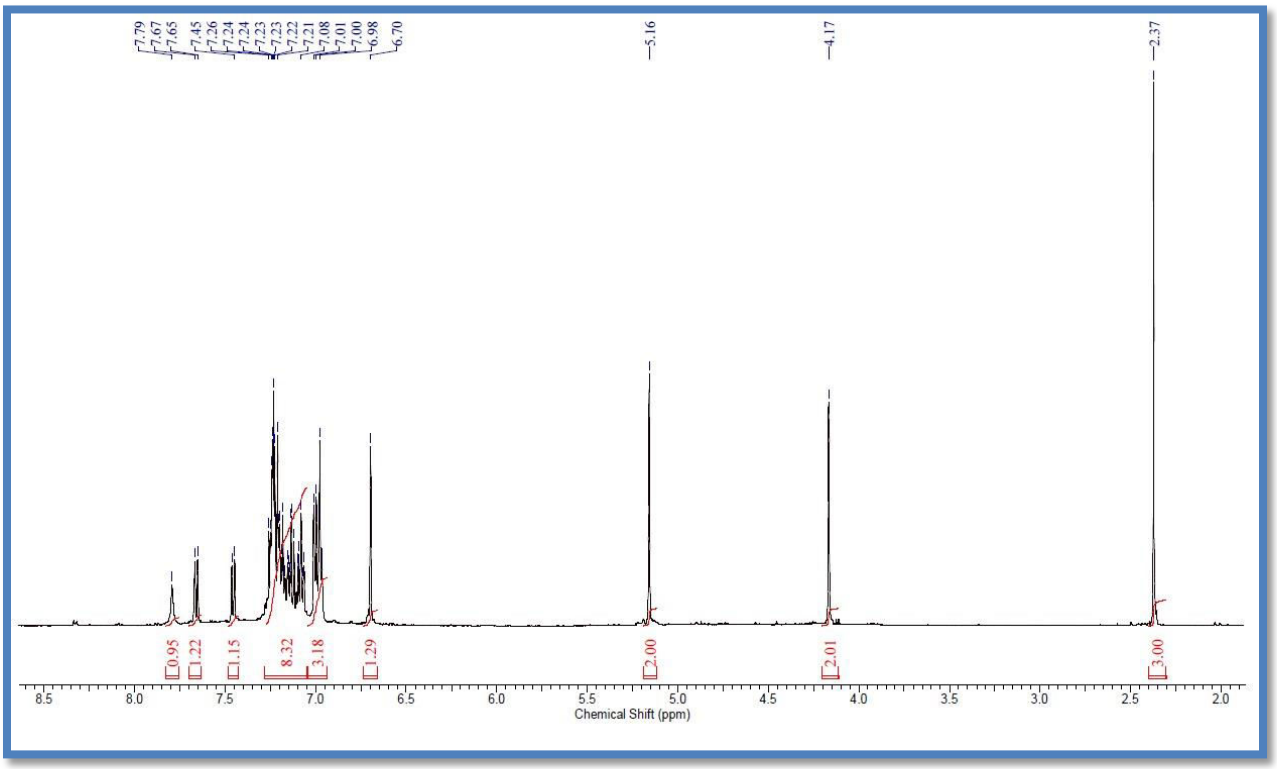


^{13}C-NMR of compound 2'j



^{1}H-NMR of compound 2'k



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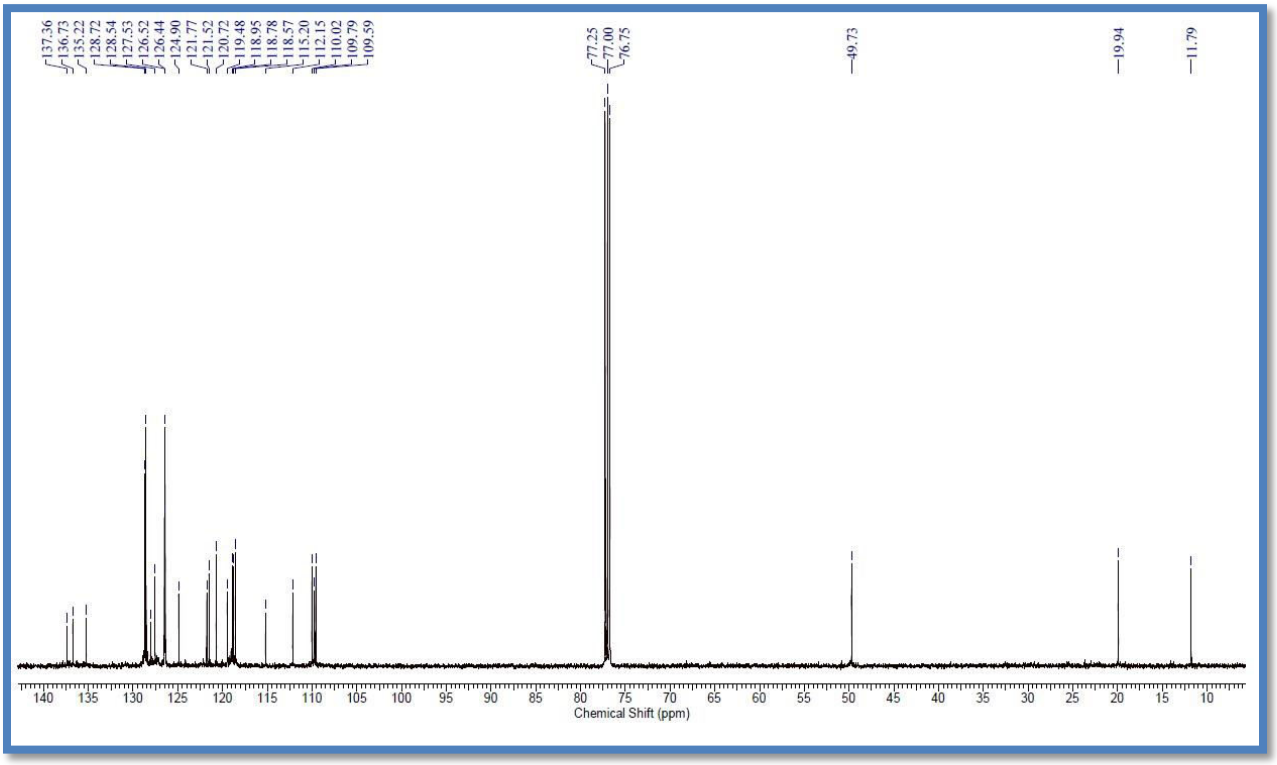
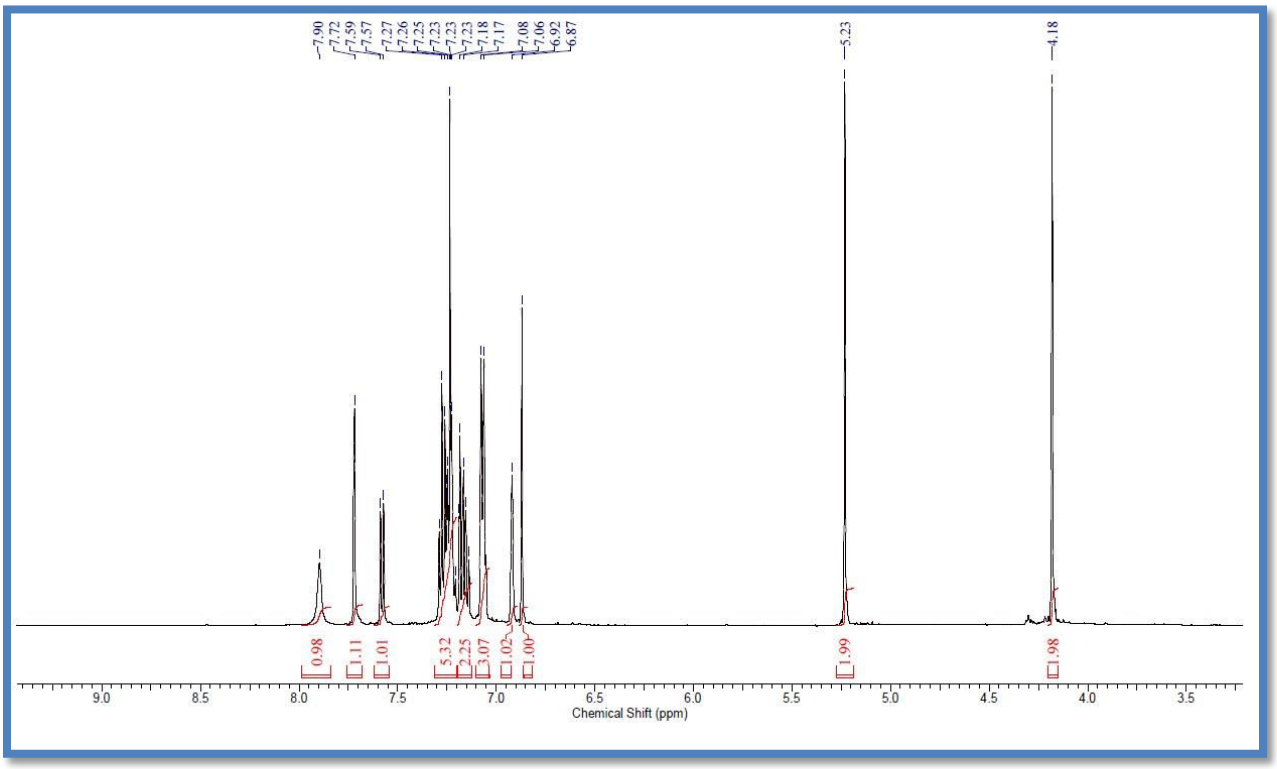


^{1}H-NMR of compound 2'l



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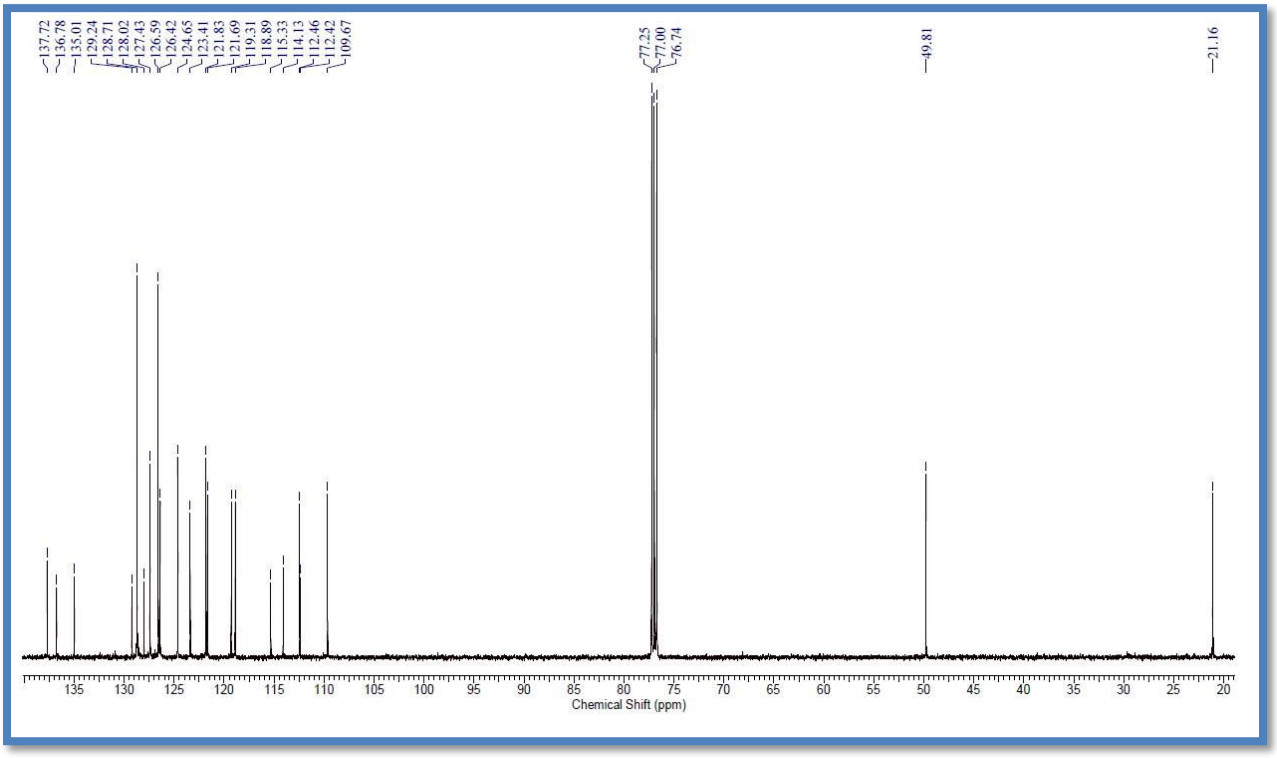
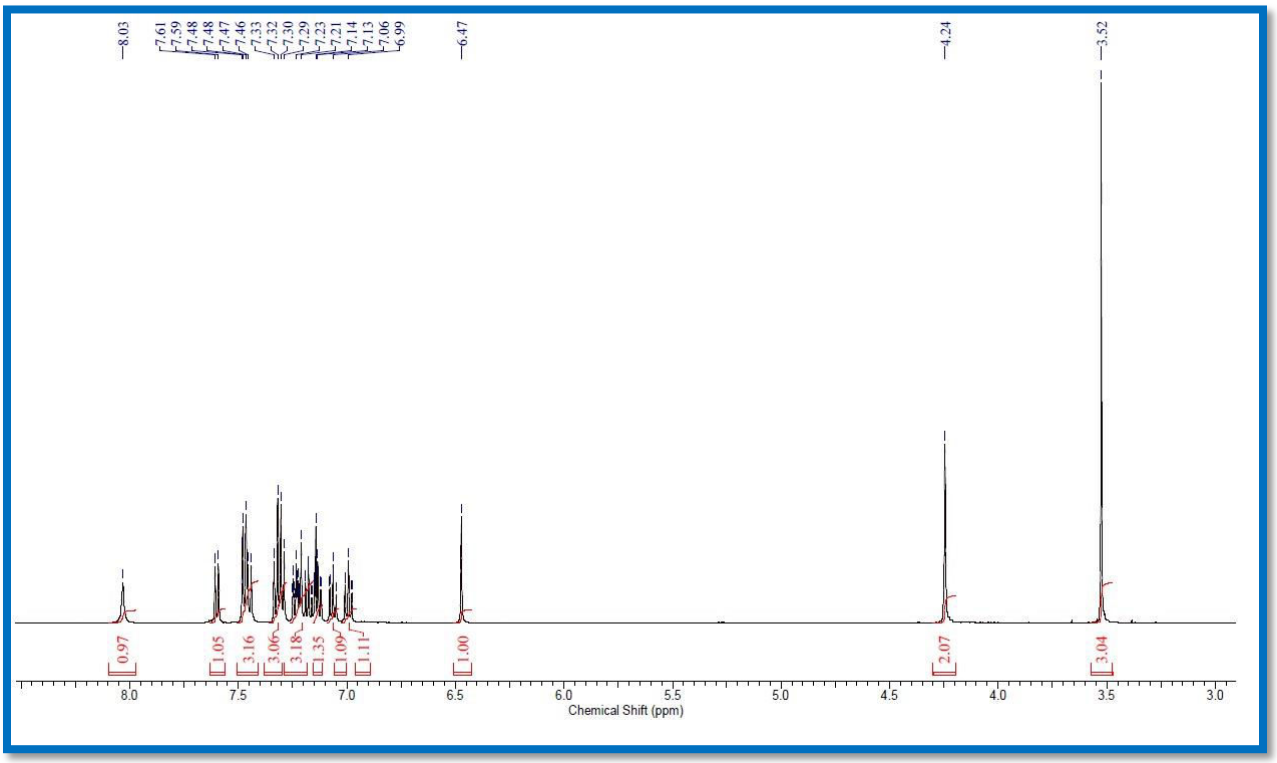


^{1}H-NMR of compound 2'm



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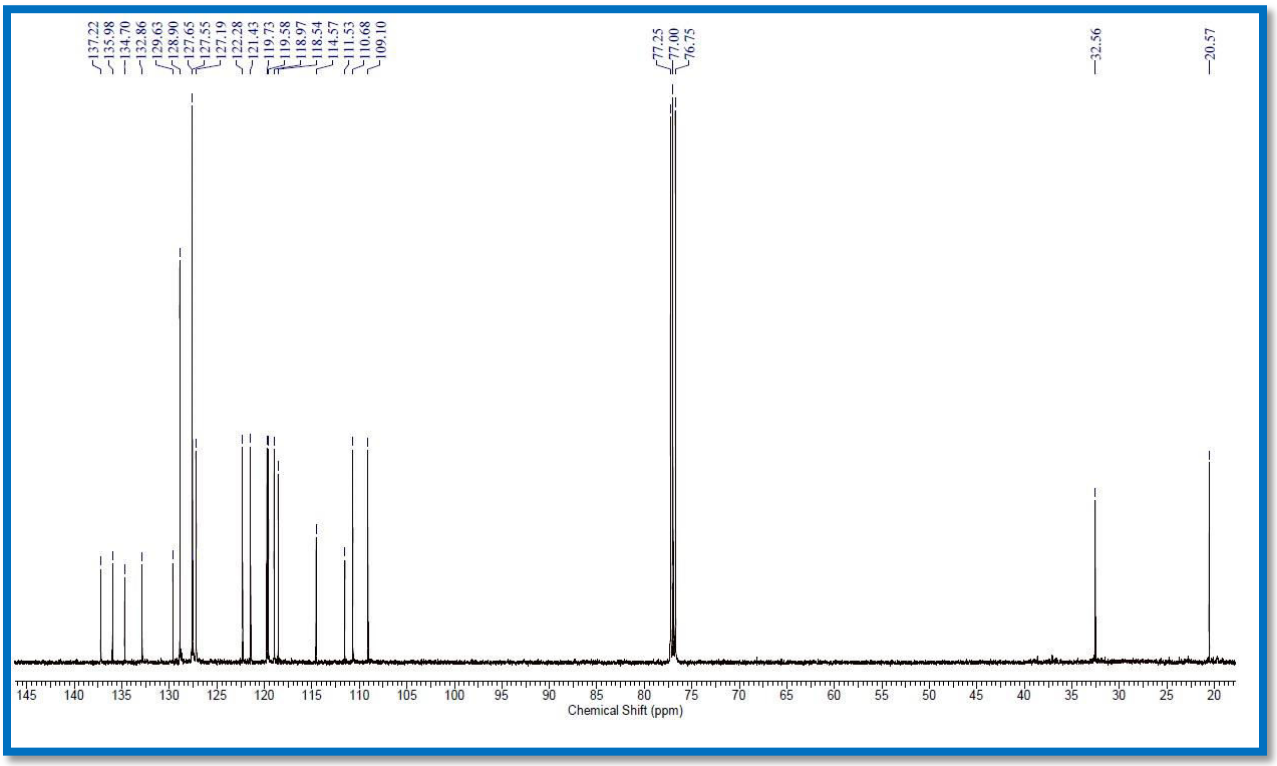

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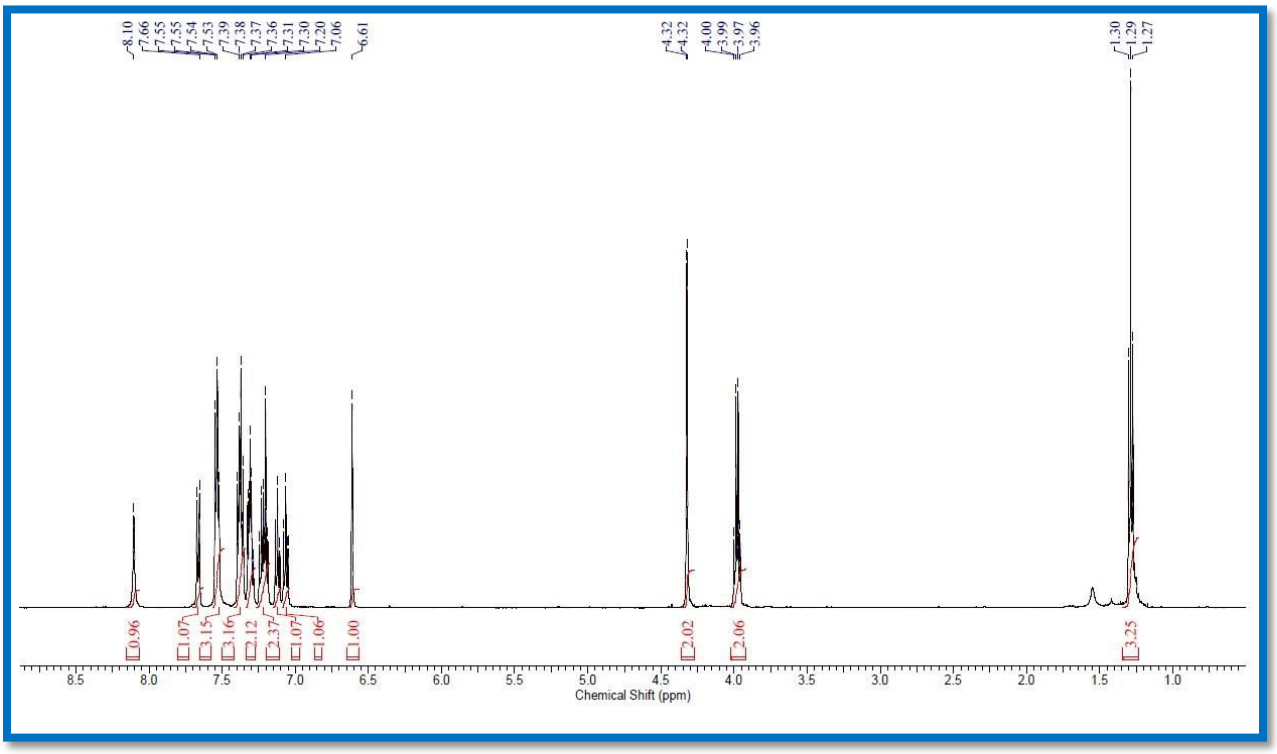

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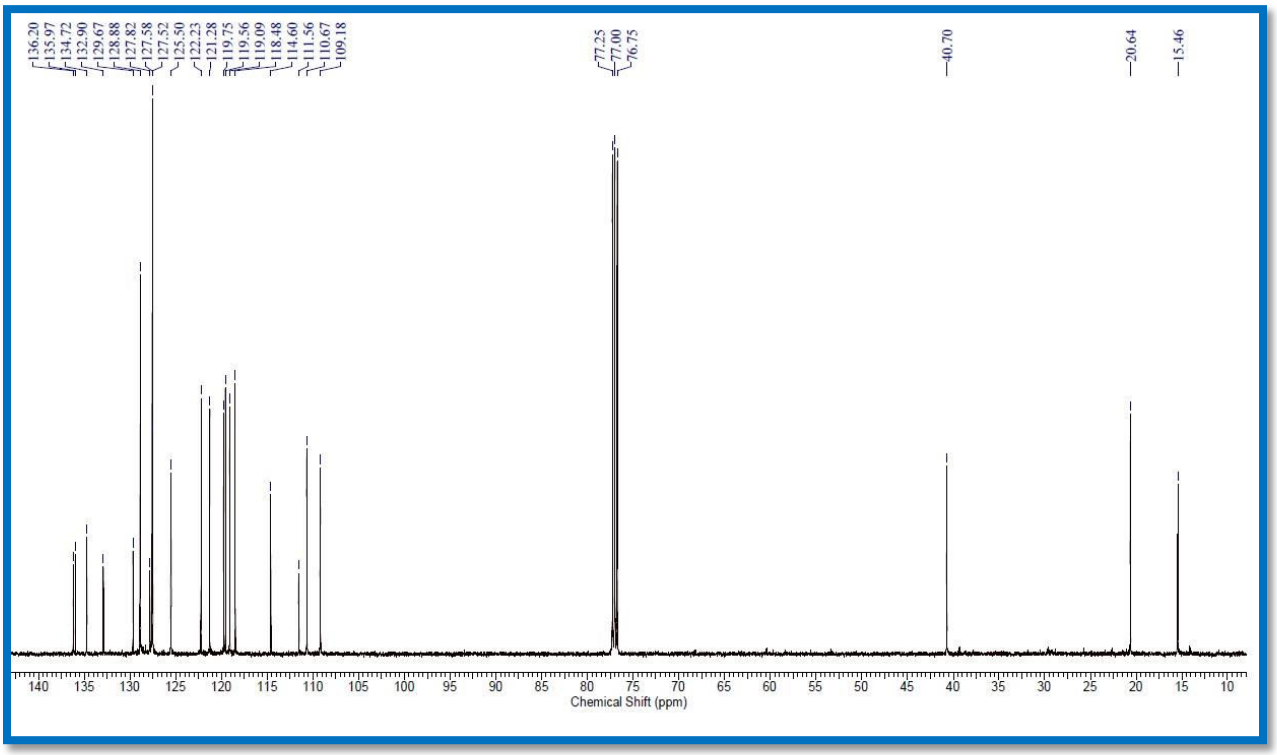
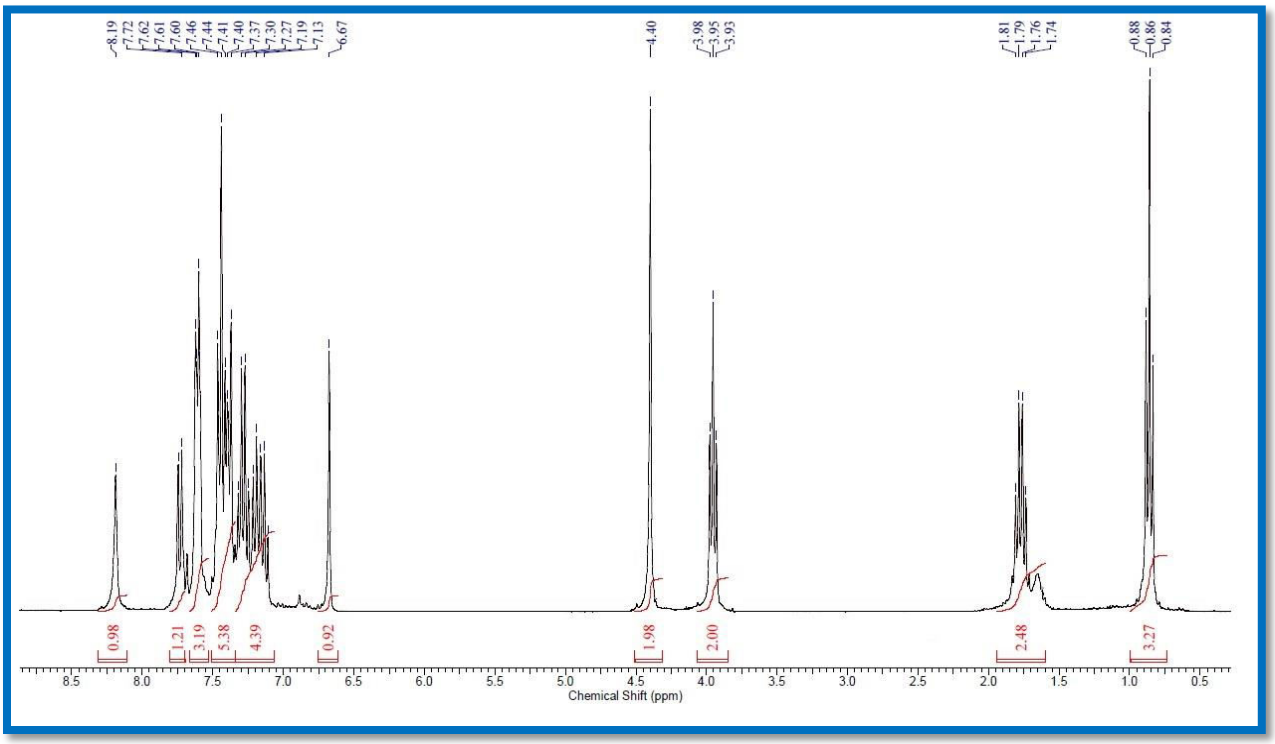


^{1}H-NMR of compound 2'o



^{13}C-NMR of compound 2'o