Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Grindstone chemistry: A highly efficient and green method for synthesis of 3,4-dihydropyrimidin-2(1H)-ones by L-tyrosine as catalyst. A Combined Experimental and DFT Study

Anamika Khaskel,[a] Prasanta Gogoi,[a] Pranjit Barman,[a] and Biman Bandyopadhyay[b]*

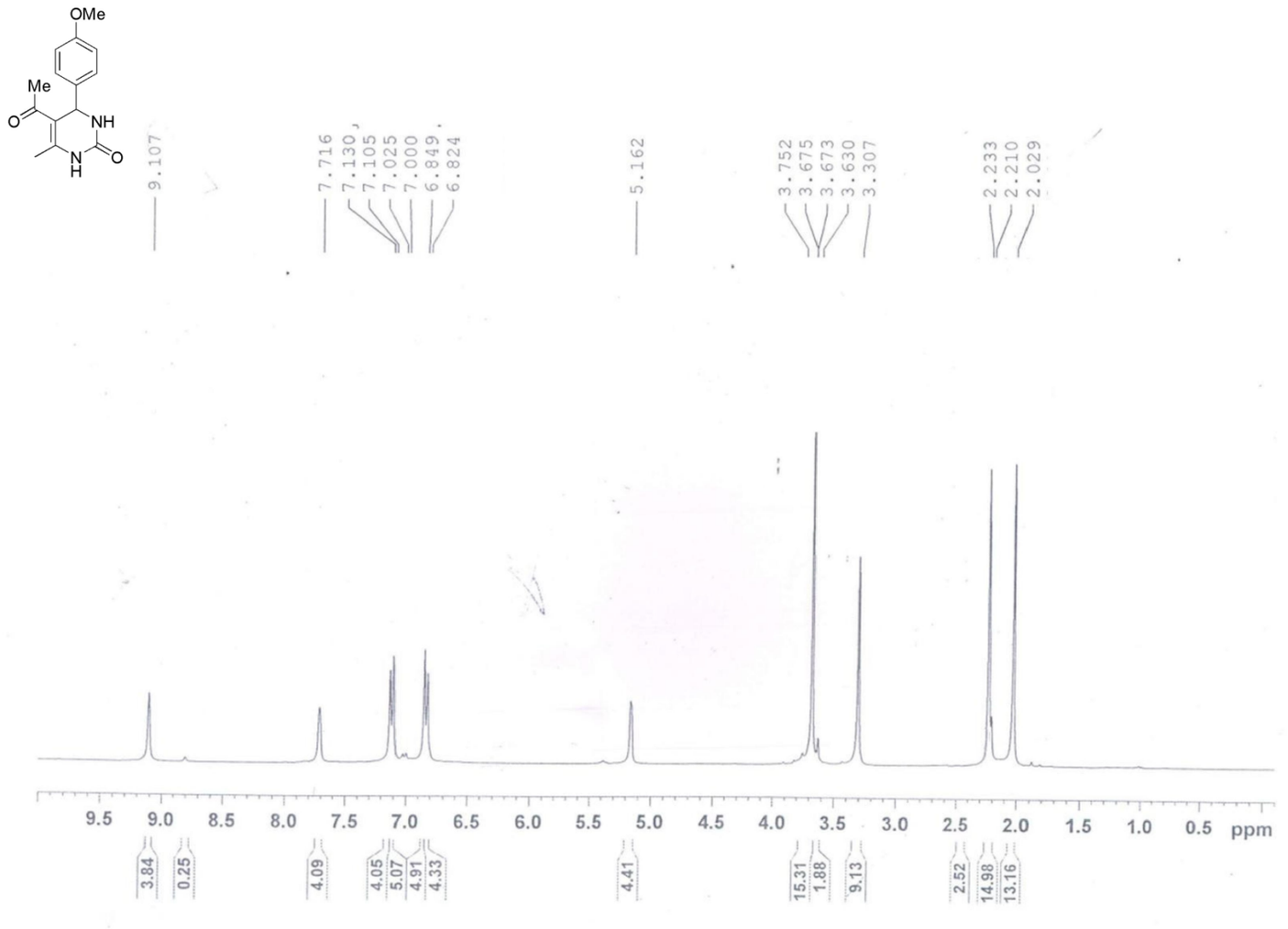
[a]Department of Chemistry, National Institute of Technology, Silchar 788010, Assam, India
Fax +91(3842)224797; Email: barmanpranjit@yahoo.co.in

[b]Institute of Engineering and Management, Salt Lake Electronics Complex, Sector-5, Kolkata700091

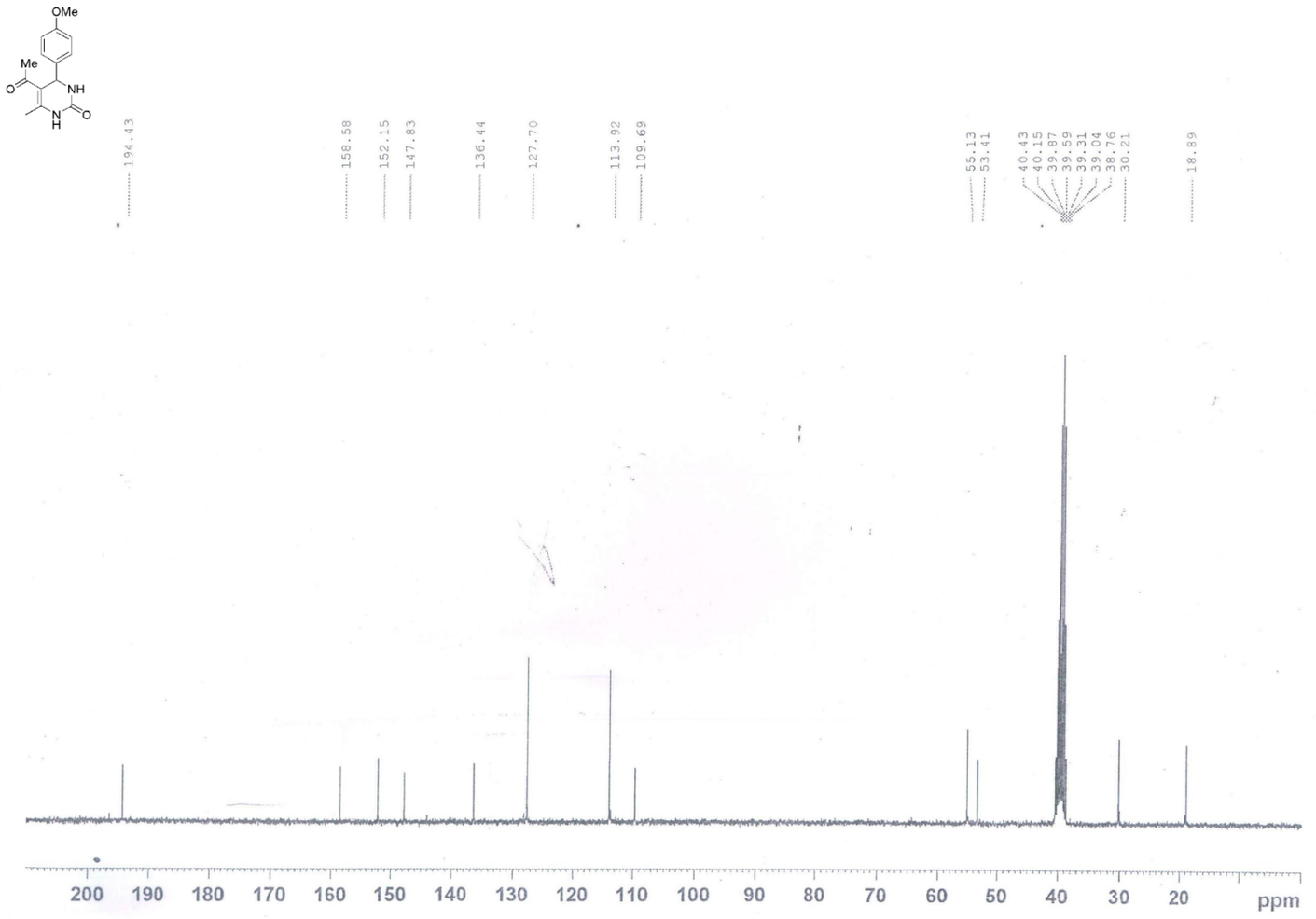
4b. 5-Aceto-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one

M.P. 170ºC; yellow colour, ^{1}H NMR (DMSO, 300 MHz): 2.03 (s, 3H), 2.23 (s, 3H), 3.67 (s, 3H), 5.16 (s, 1H), 6.74 (d, 2H, J = 7.5Hz), 7.13 (d, 2H, J = 7.5 Hz), 7.72 (s, 1H), 9.107 (s, 1H); ^{13}C NMR (DMSO, 75 MHz): 18.89, 30.21, 53.41, 55.13, 109.69, 113.92, 127.70, 136.44, 147.83, 152.15, 158.58, 194.43; Anal. Calcld for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.46; H, 6.26; N, 10.73.

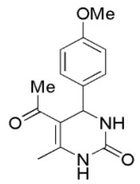
^{1}H NMR of compound 4b

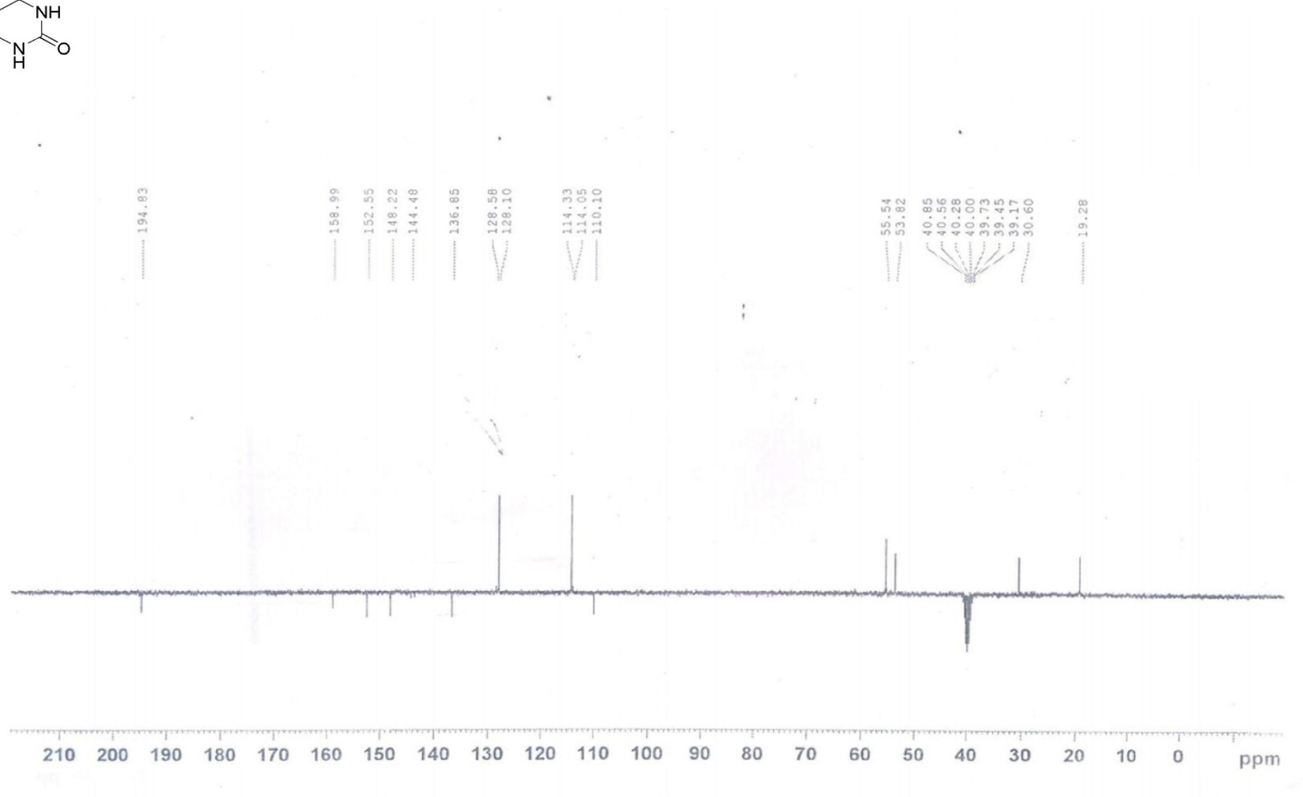


^{13}C NMR of compound 4b



DEPT NMR of compound 4b

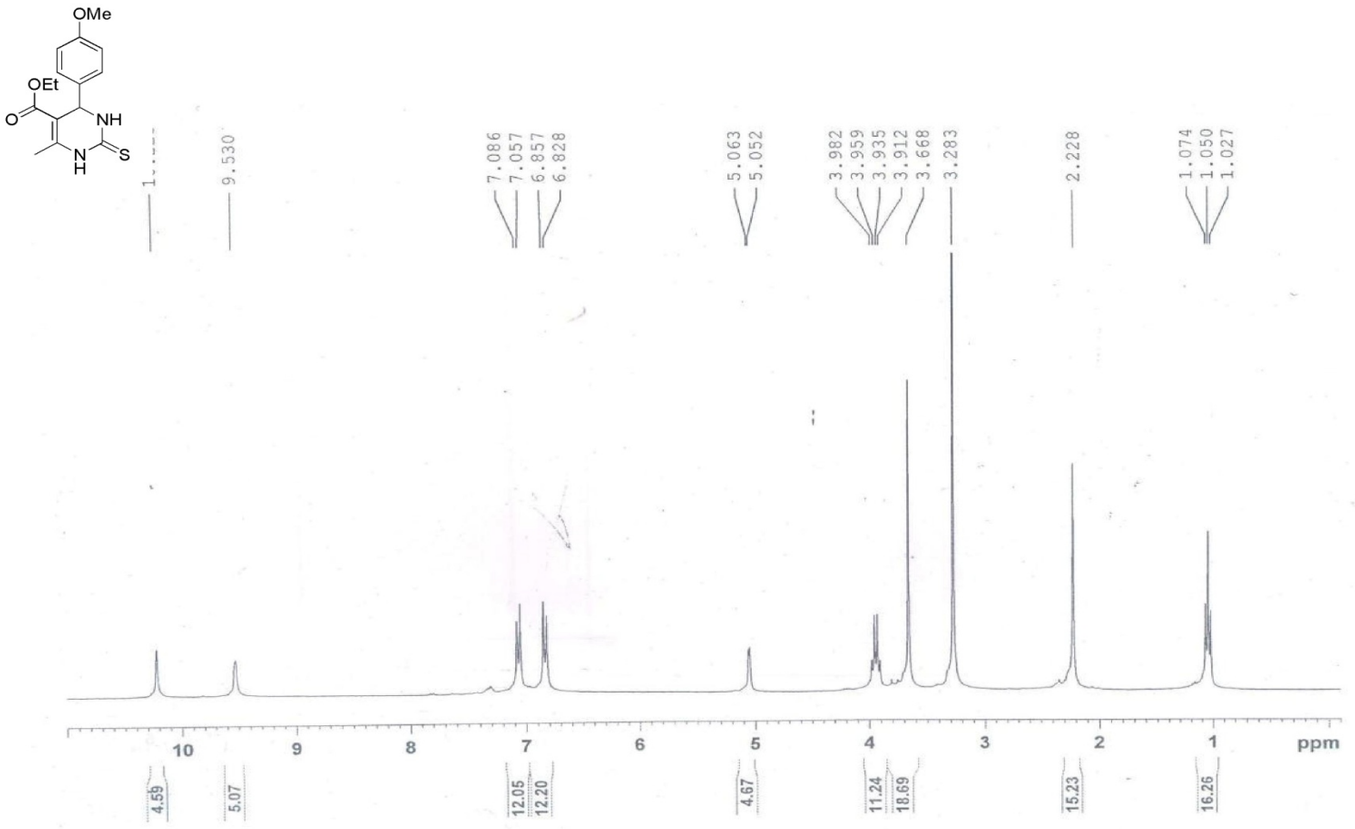




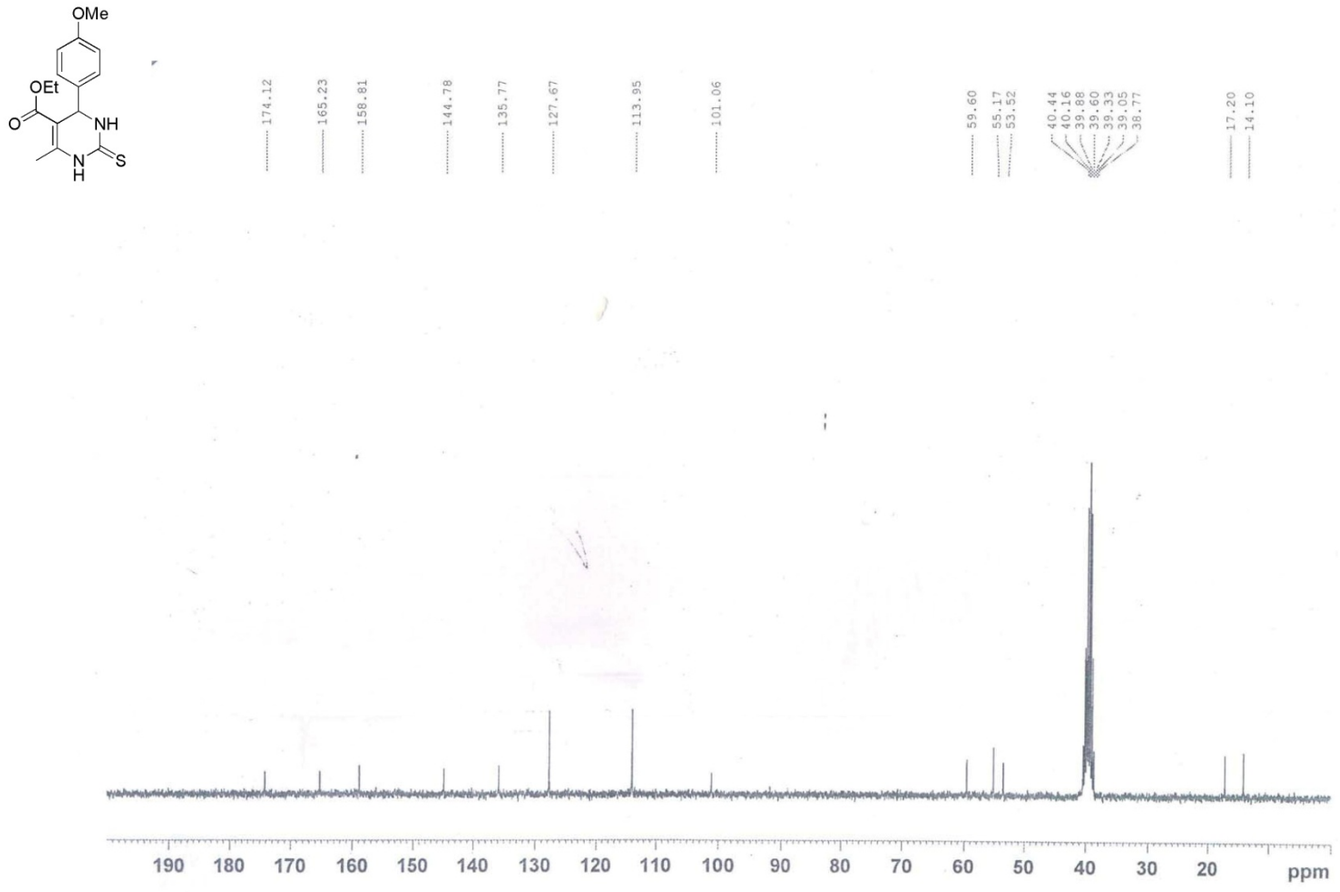
4c. 5-(Ethoxycarbonyl)-6methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione

M.P. 153ºC; yellow colour, ^{1}H NMR (DMSO, 300 MHz): 1.09 (t, 3H, J = 7.2 Hz), 2.28 (s, 3H), 3.67 (s, 3H), 3.93 (q, 2H, J = 7.2 Hz), 6.85 (d, 2H, J = 8.7 Hz), 7.08 (d, 2H, J = 8.7 Hz), 9.53 (s, 1H), 10.22 (s, 1H); ^{13}C NMR (DMSO, 75 MHz): 14.10, 17.20, 53.52, 55.17, 59.60, 101.06, 113.95, 127.67, 135.77, 144.78, 158.81, 174.12; FT-IR (KBr, cm $^{-1}$): 3250, 1652, 1599, 1561 Anal. Calcld for $C_{15}H_{18}N_2O_3S$: C, 58.80; H, 5.92; N, 9.14. Found: C, 58.73; H, 5.96; N, 9.12.

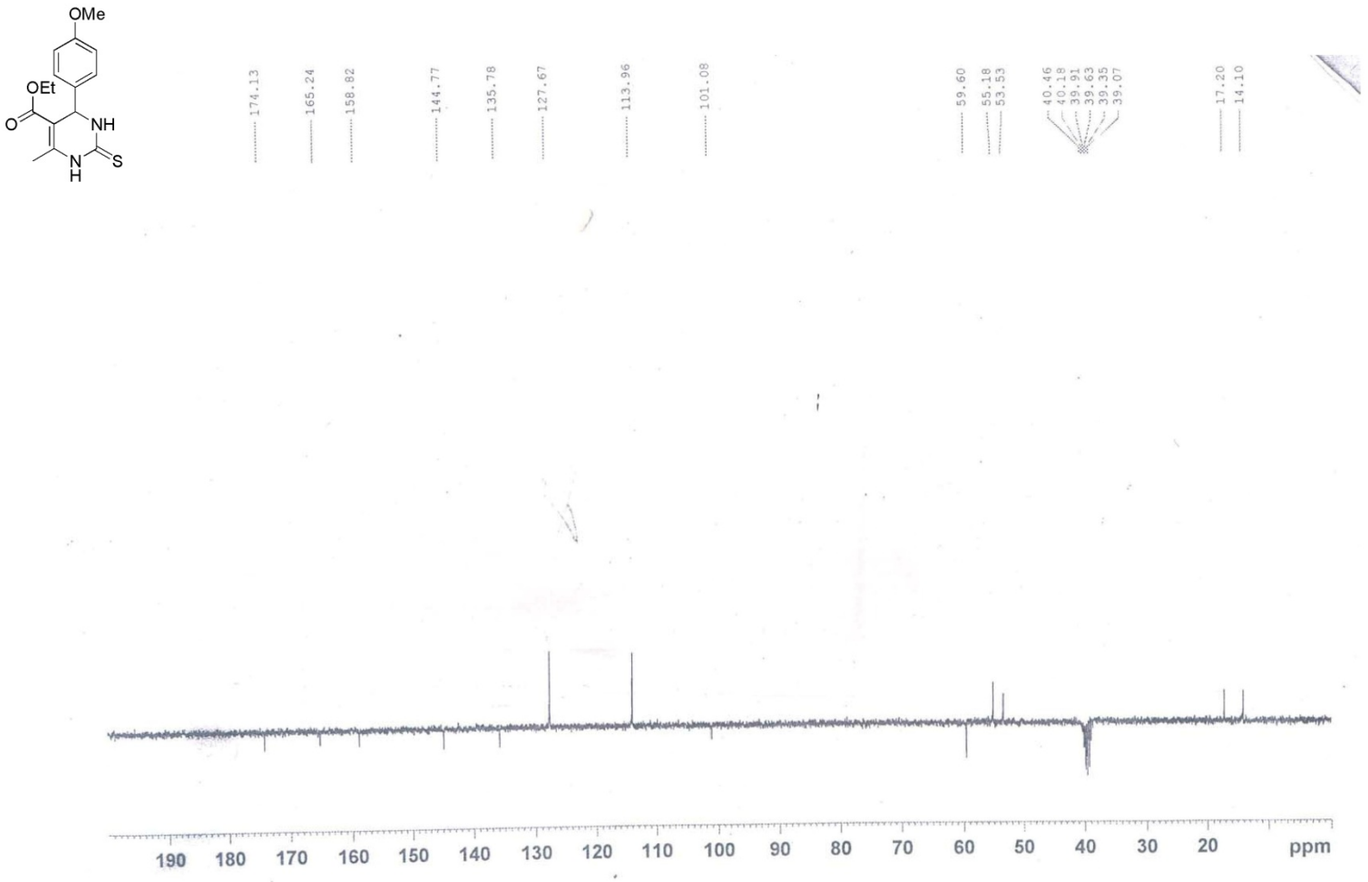
^{1}H NMR of compound 4c



^{13}C NMR of compound 4c



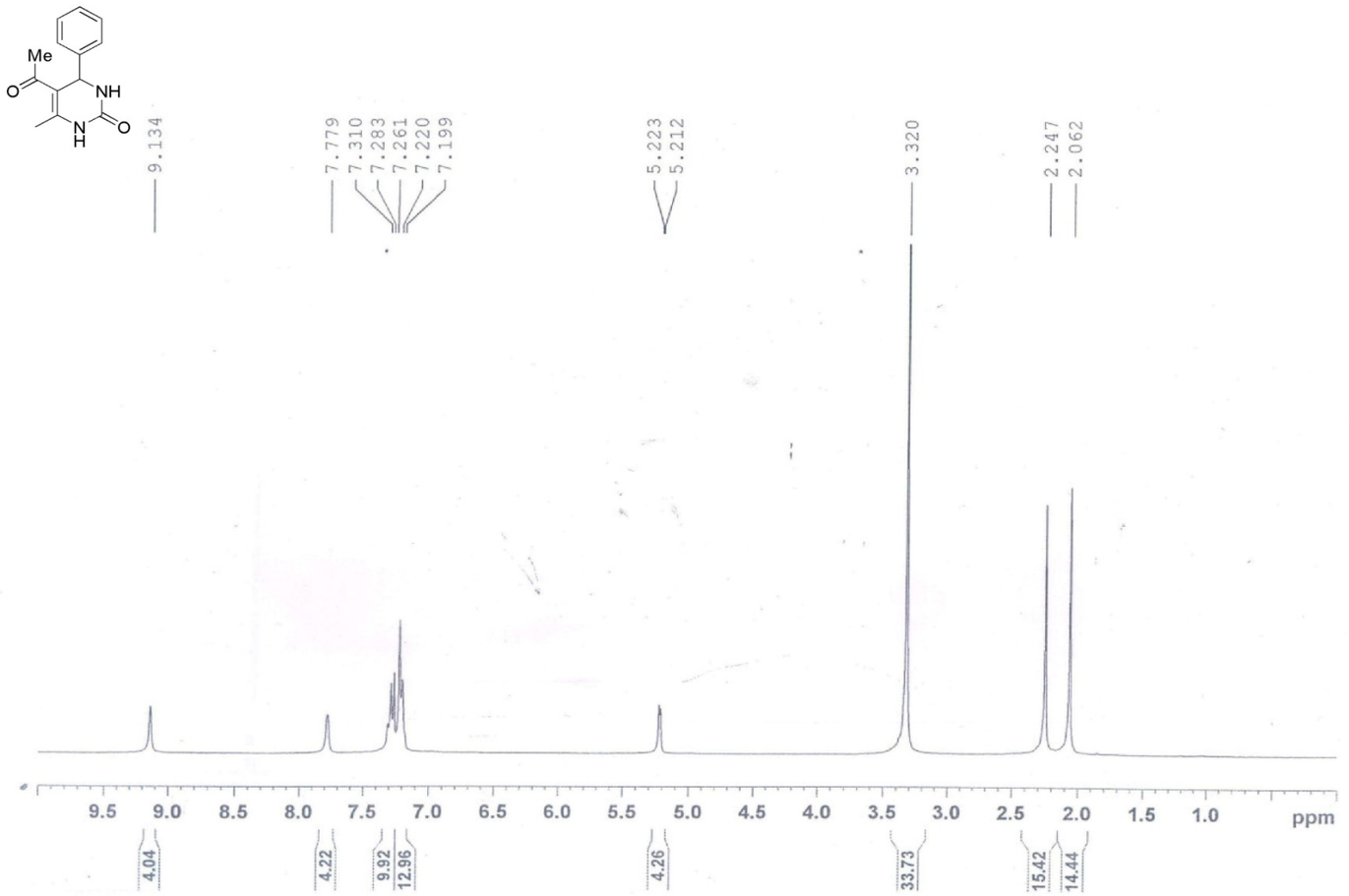
DEPT NMR of compound 4c



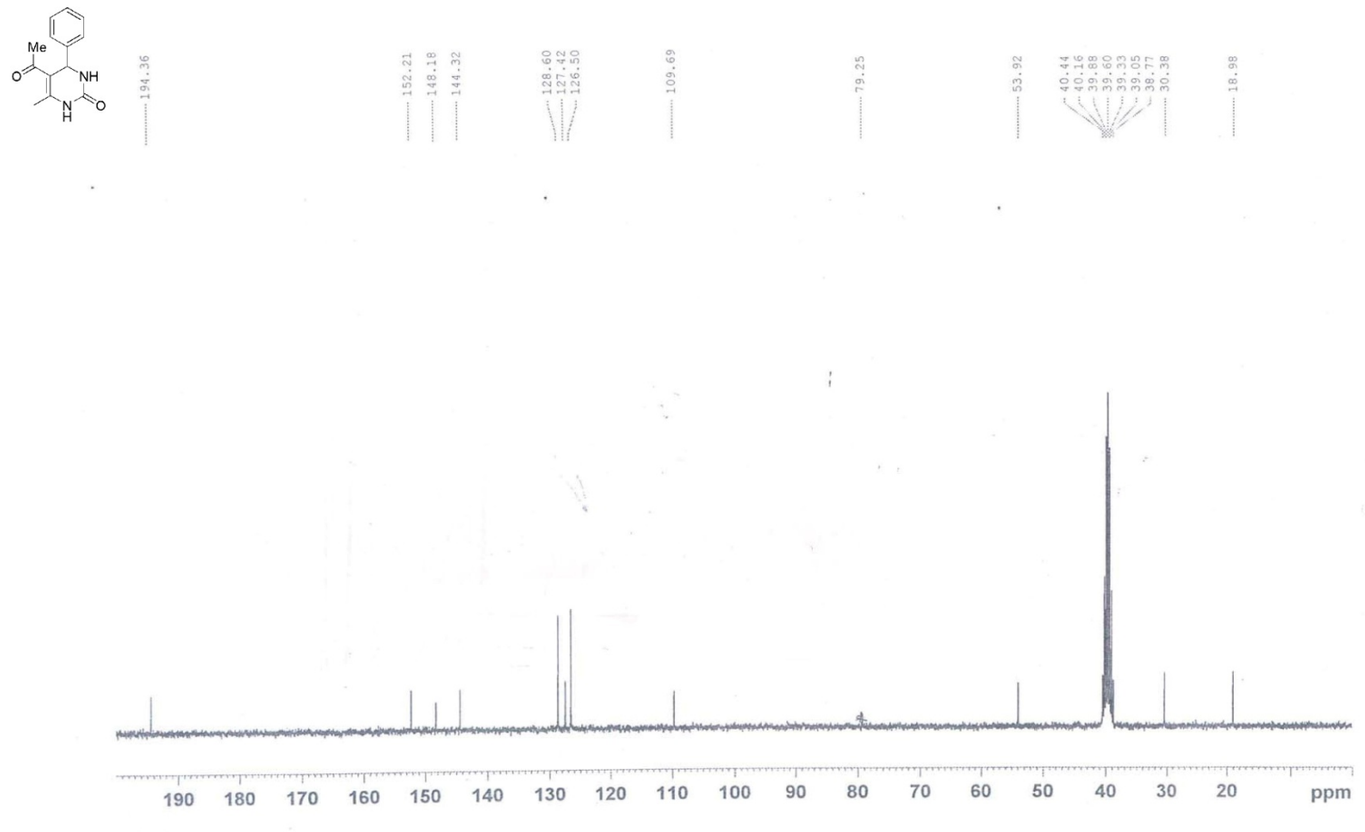
4d. 5-Aceto-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one

M.P. 234ºC; white colour, ^{1}H NMR (DMSO, 300MHz): 2.06 (s, 3H), 2.24(s, 3H), 5.22 (d, 1H), 7.19-7.31(m, 5H), 7.77(s, 1H), 9.13(s, 1H); ^{13}C NMR (DMSO, 75 MHz): 18.98, 30.38, 53.92, 109.69, 126.50, 127.42, 128.60, 144.32, 148.18, 152.21, 194.36; FT-IR (KBr, cm^{-1}): 3259.5, 1714, 1640.5 Anal. Calcld For $C_{13}H_{14}O_2N_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.78; H, 6.18; N, 12.13

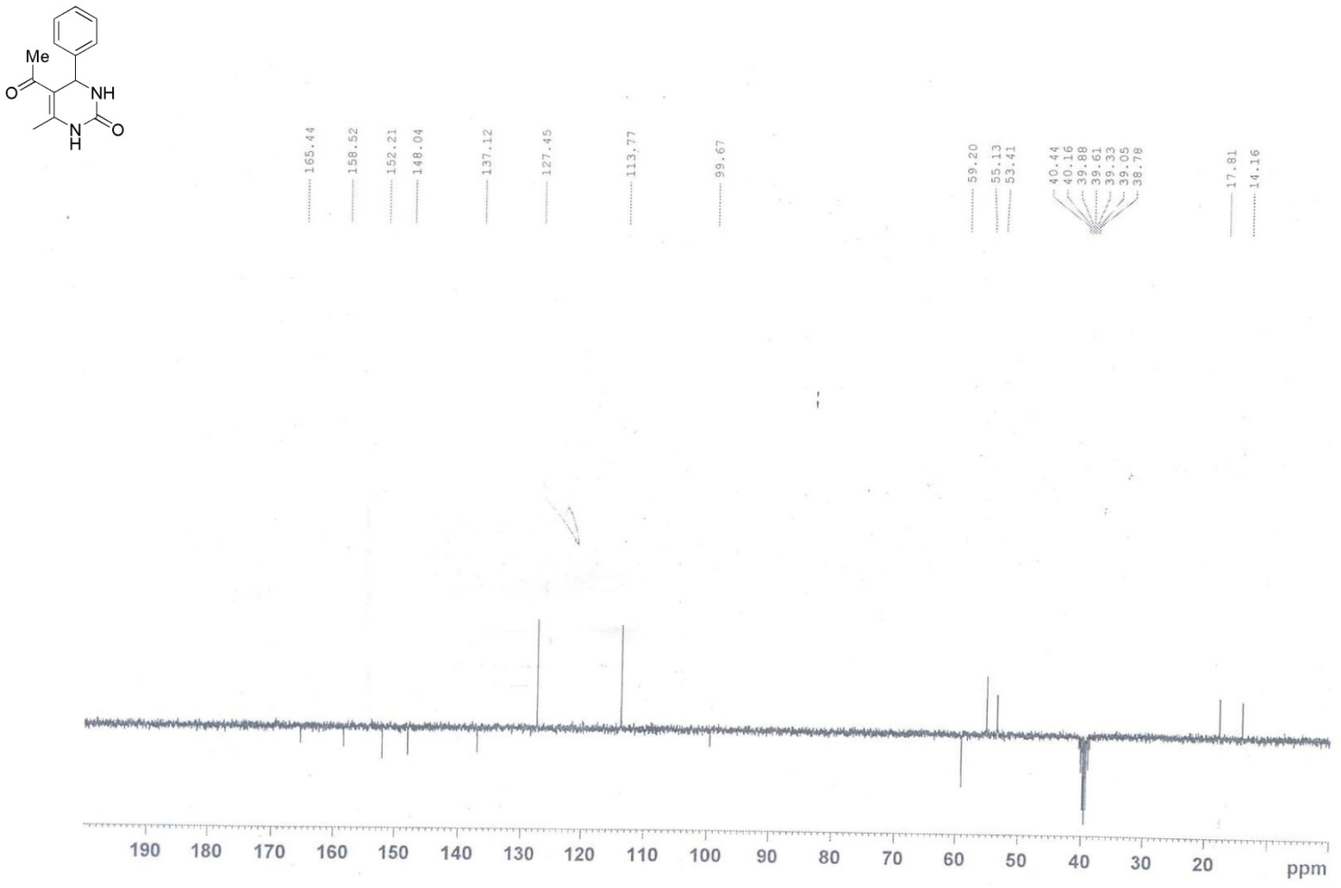
^{1}H NMR of compound 4d



^{13}C NMR of compound 4d



DEPT NMR of compound 4d



4e. **5-(Methoxycarbonyl)-6-methyl-4-phenyl-3,4- dihydropyrimidin-2(1H)-one**

M.P. 210ºC; white colour, ^{1}H NMR (DMSO, 300MHz): 2.21(s, 3H), 3.57 (s, 3H), 5.18 (d, 1H), 7.26-7.33 (m, 5H), 7.79 (s, 1H), 9.23 (s, 1H). FT-IR (KBr, cm^{-1}): 3231.7, 1702, 1642 Anal. Calcld. For $C_{13}H_{14}O_3N_2$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.32; H, 5.80; N, 11.33

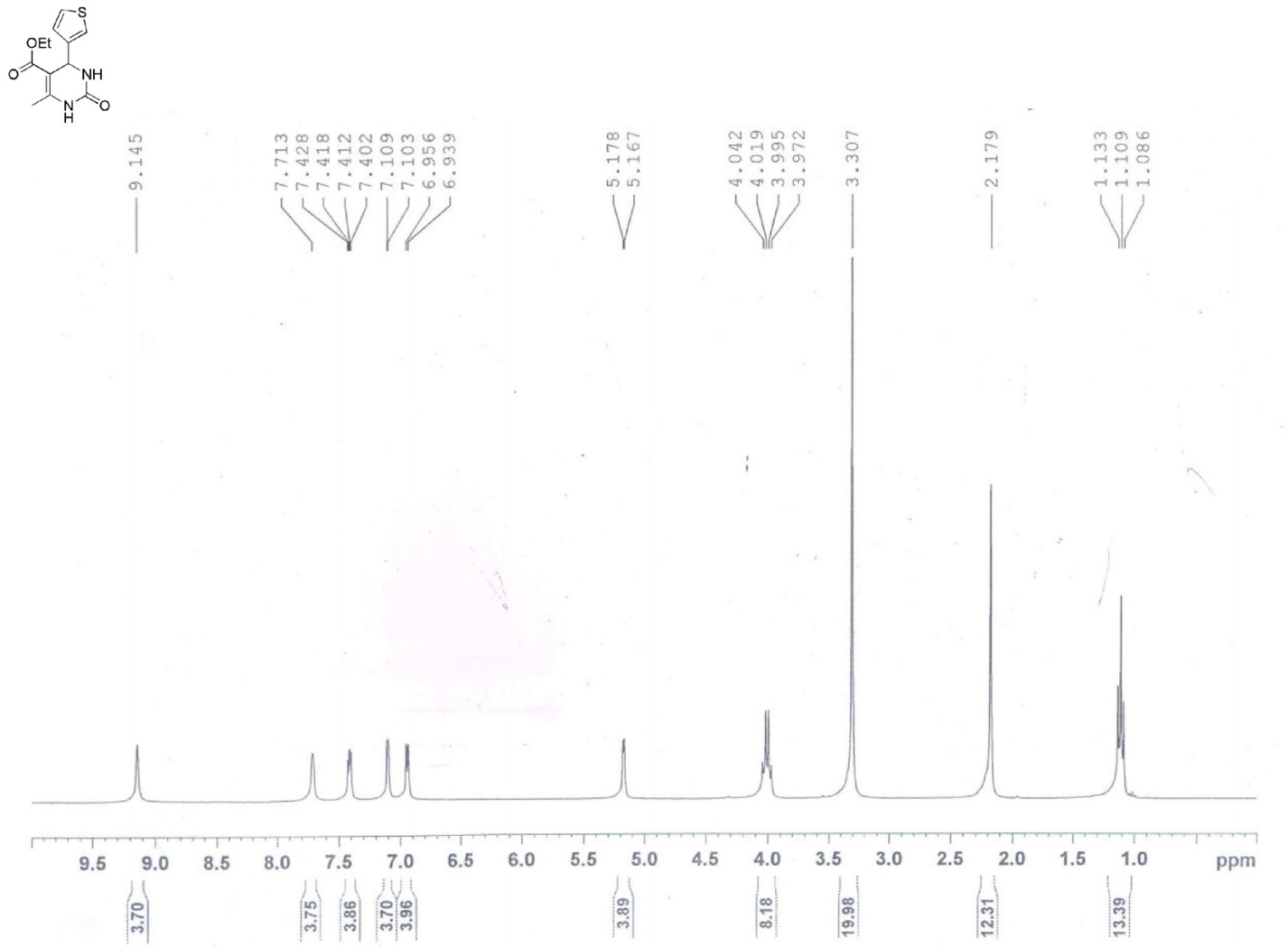
4f. 5-Aceto-6-methyl-4-(3-thienyl)-3,4-dihydropyrimidin-2(1H)-one

M.P 200ºC, Yellow colour, ^{1}H NMR (DMSO, 300 MHz): 2.14 (s, 3H), 2.21 (s, 3H), 5.47 (d,1H), 6.87-6.91(m, 2H), 7.35(d, 2H, J = 4.5 Hz), 7.89 (s, 1H), 9.24 (s, 1H); ^{13}C NMR: 18.85, 30.15, 49.32, 110.51, 123.94, 124.87, 126.73, 148.20, 148.68, 152.23, 193.80. Anal. Calcld for $C_{11}H_{12}N_2O_2S$: C, 55.91; H, 5.12; N, 11.86. Found: C, 55.87; H, 5.16; N, 11.90.

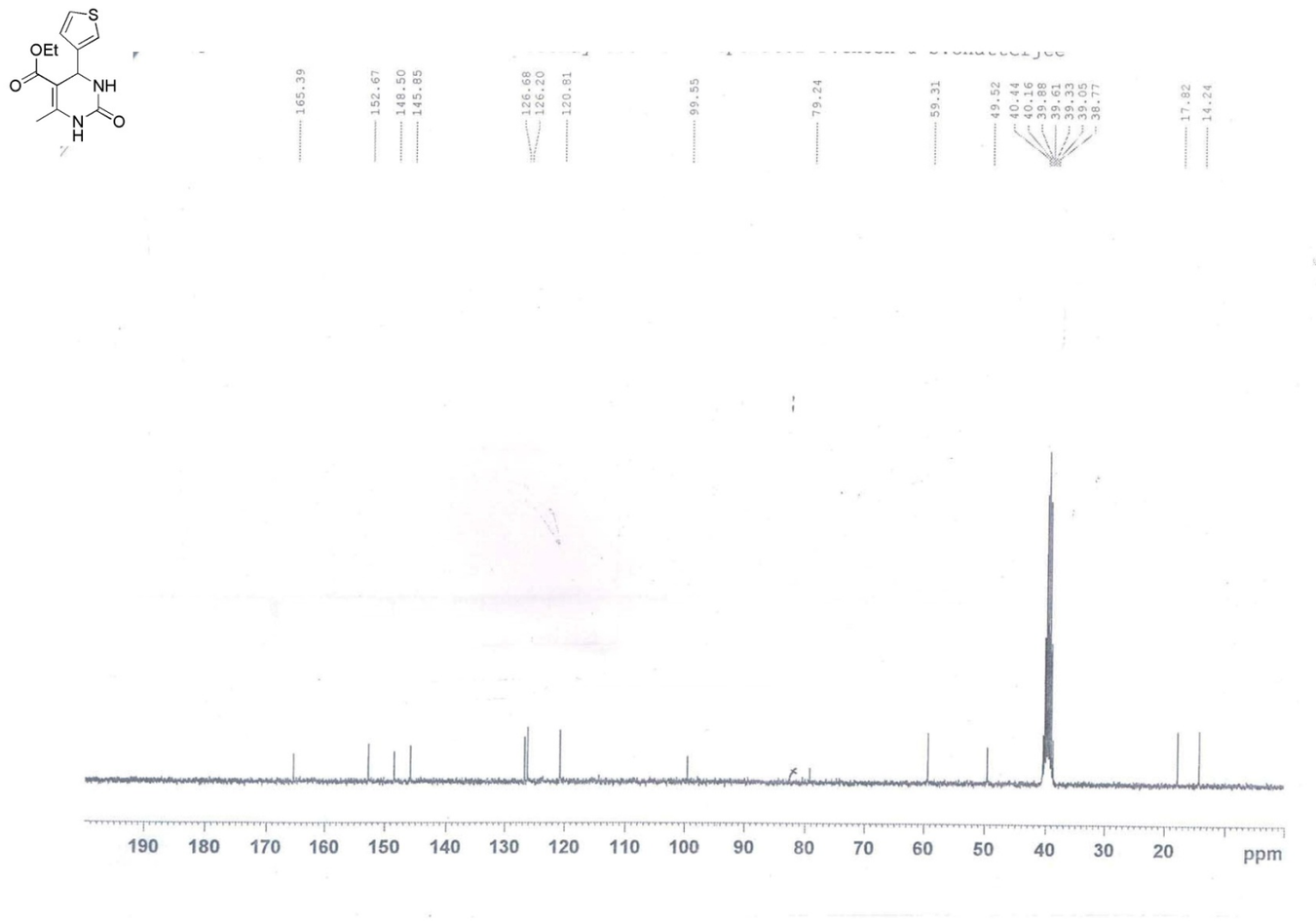
4g. 5-(Ethoxycarbonyl)-4-(3-thienyl)-3,4-dihydropyrimidin-2(1H)-one

M.P 195°C, Yellow colour, ^{1}H NMR (DMSO, 300 MHz): 1.11 (t, 3H, J = 6.9 Hz), 2.18 (s, 3H), 3.99 (q, 2H, J = 6.9 Hz), 5.17 (d, 1H), 6.94 (d, 2H, J = 5.1 Hz), 7.10 (d, 1H), 7.41 (m, 2H, J = 3Hz), 7.71 (s, 1H), 9.15 (s, 1H); ^{13}C NMR (DMSO, 75 MHz): 14.24, 17.82, 49.52, 59.31, 99.55, 120.81, 126.20, 126.68, 145.85, 148.50, 152.67, 165.39. Anal. Calcld. For $C_{12}H_{14}O_3N_2S$: C, 54.12; H, 5.30; N, 10.52. Found: C, 54.08; H, 5.35; N, 10.48.

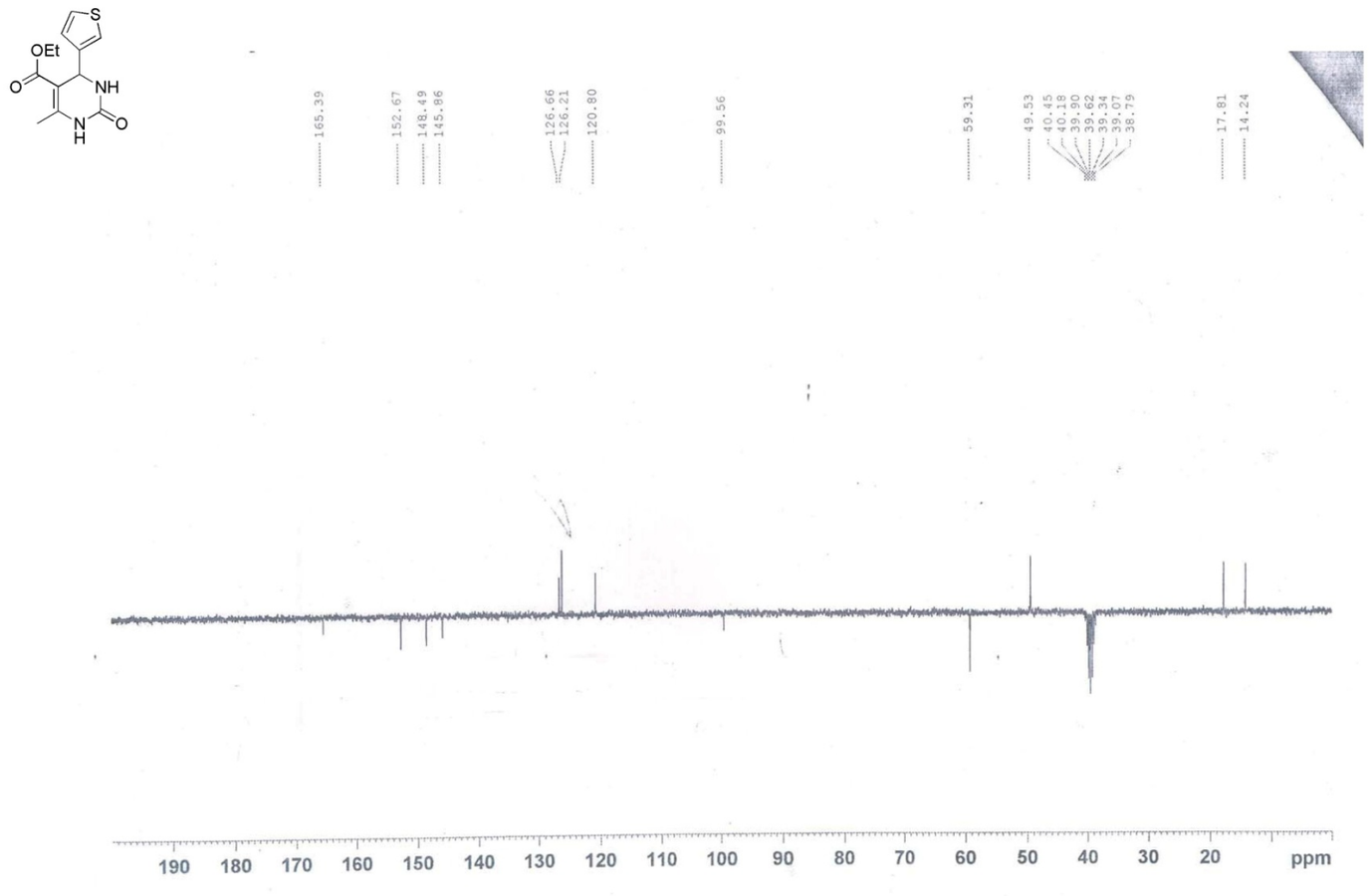
[1]H NMR of compound 4g



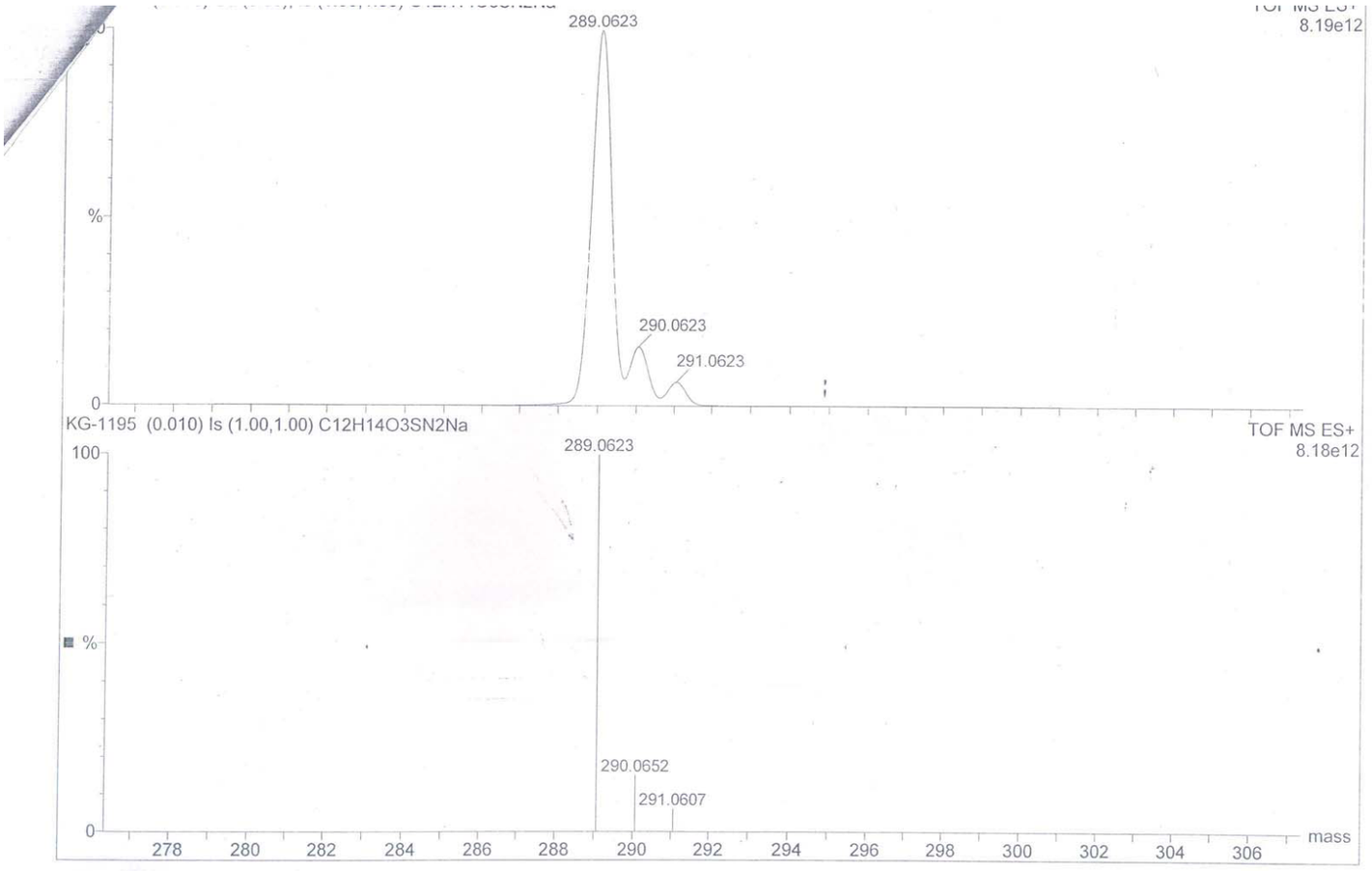
^{13}C NMR of compound 4g

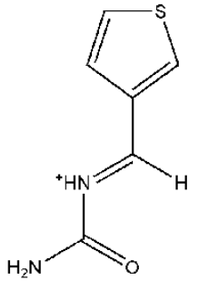


DEPT NMR of compound 4g

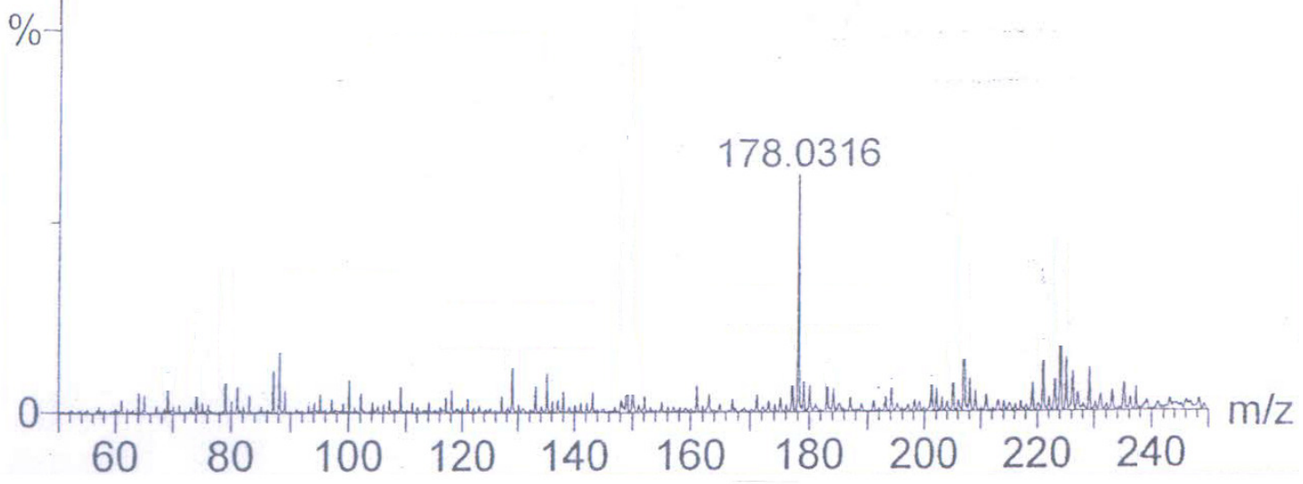


HRMS of compound 4g



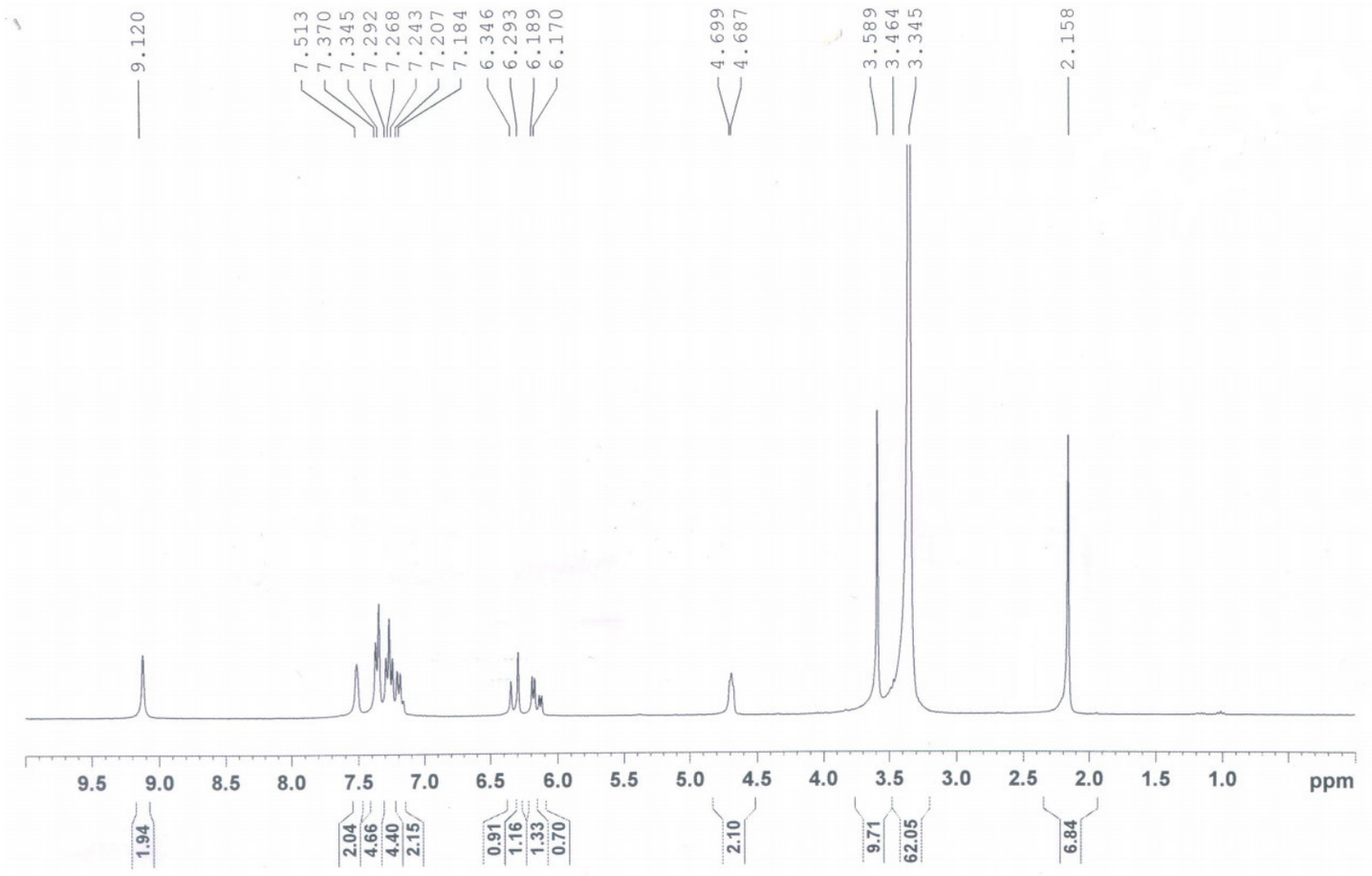


Iminium ion of 4g

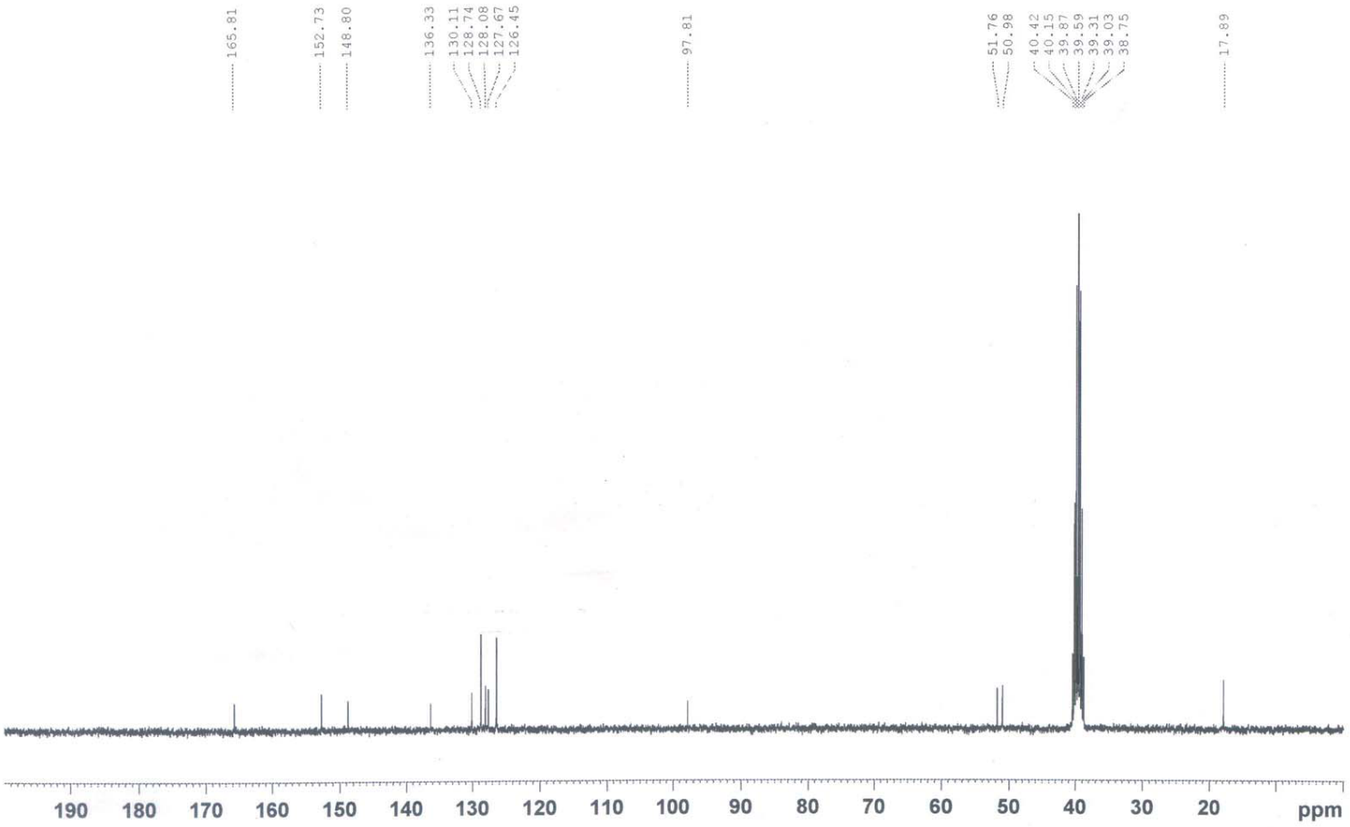


4h. 6-methyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate

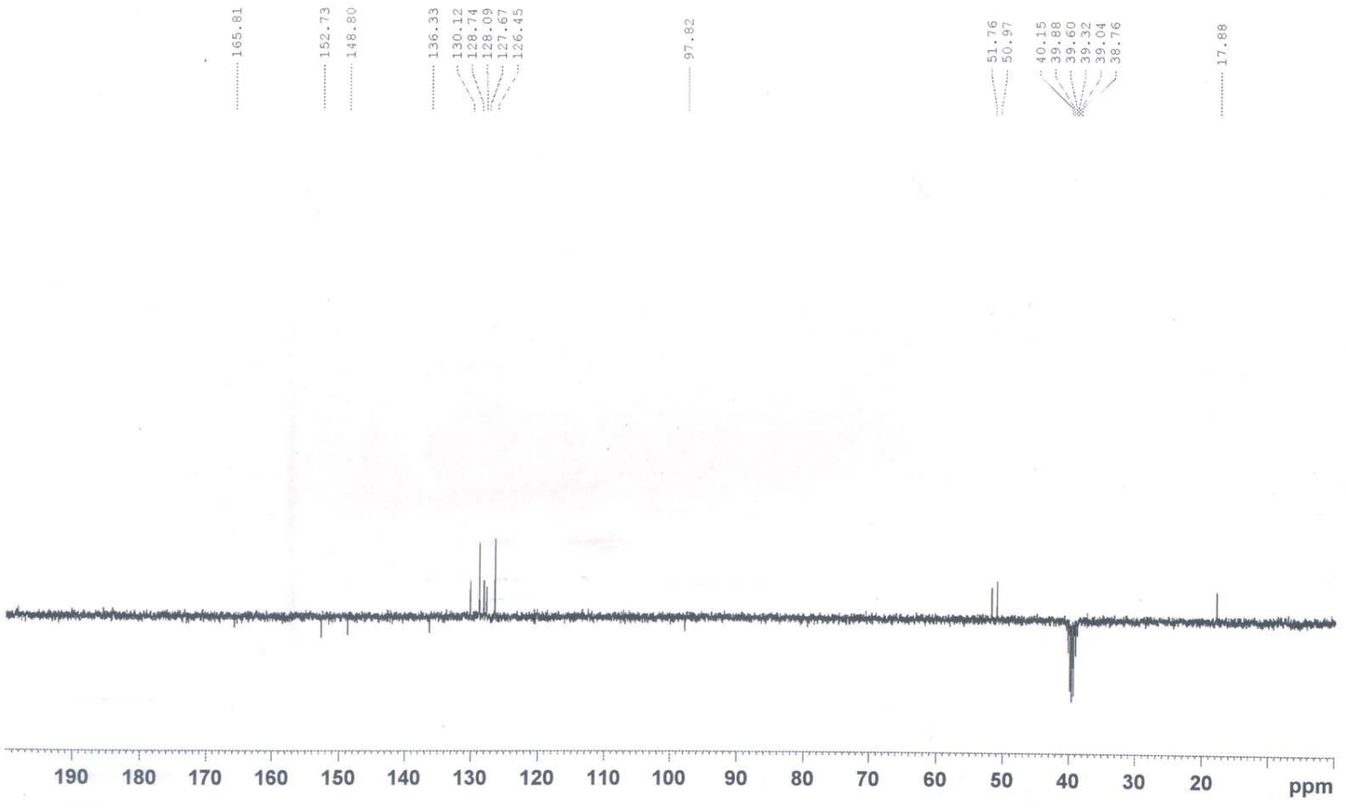
^{1}H NMR of compound 4h



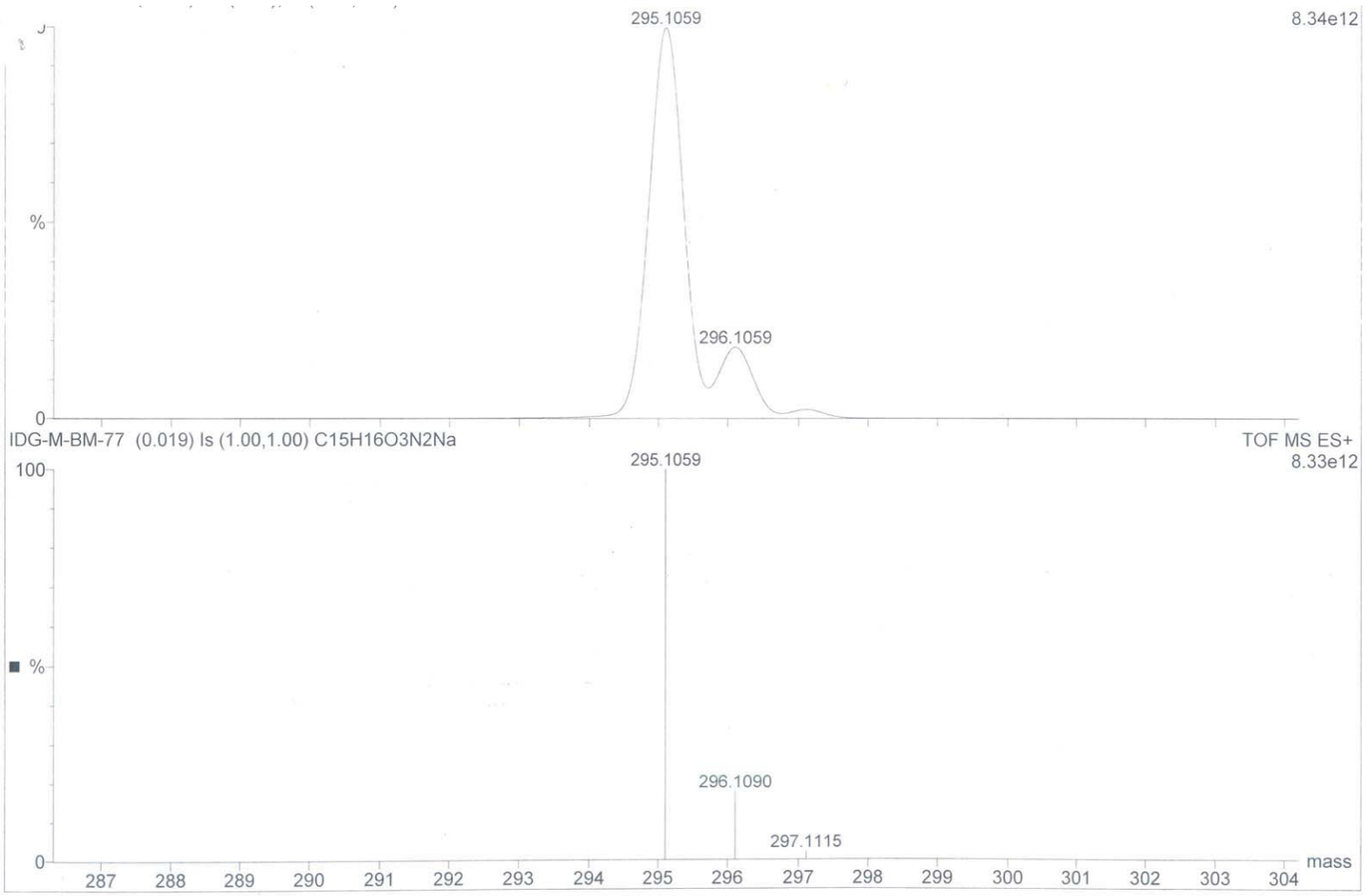
^{13}CNMR of compound 4h

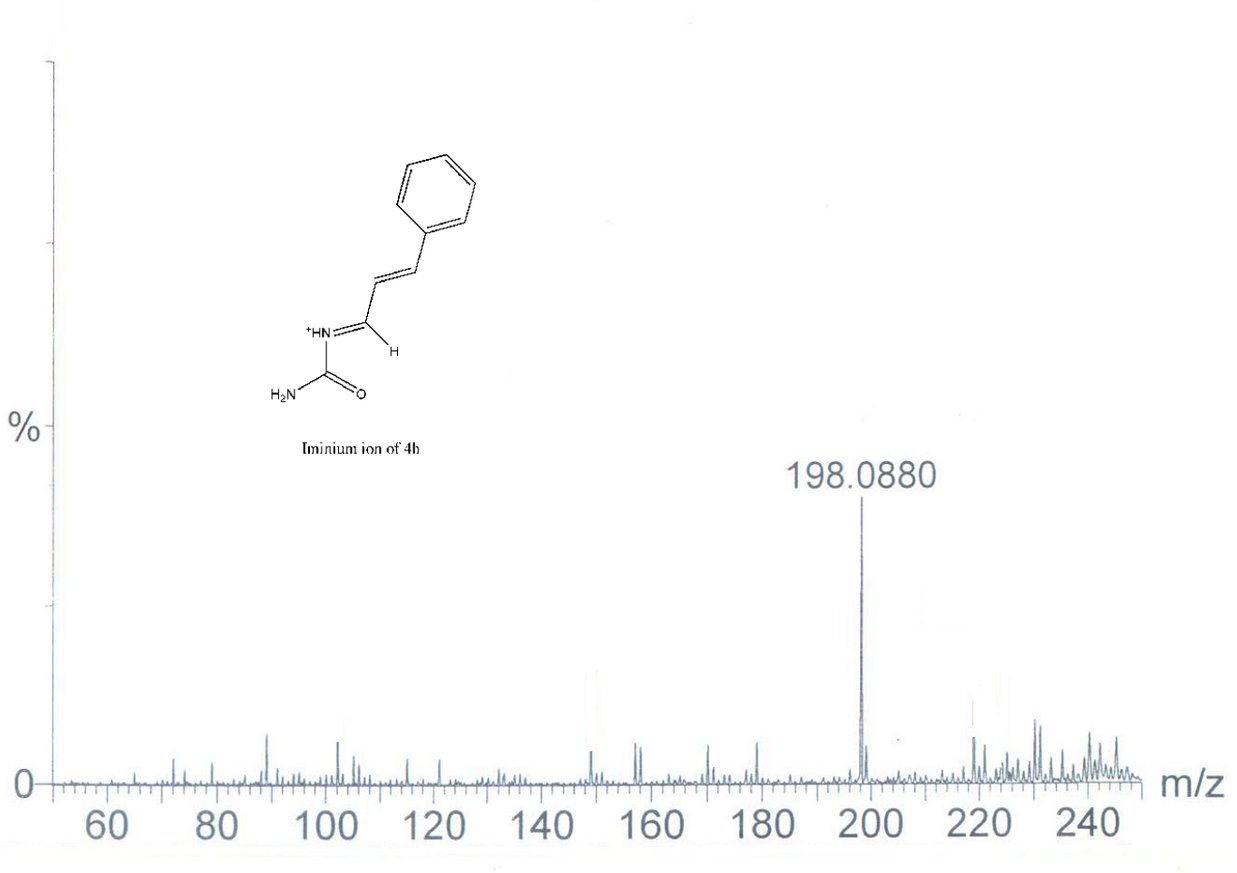


DEPT NMR of compound 4h



HRMS of compound 4h





4i. 5-(Ethoxycarbonyl)-4-(3-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-thione

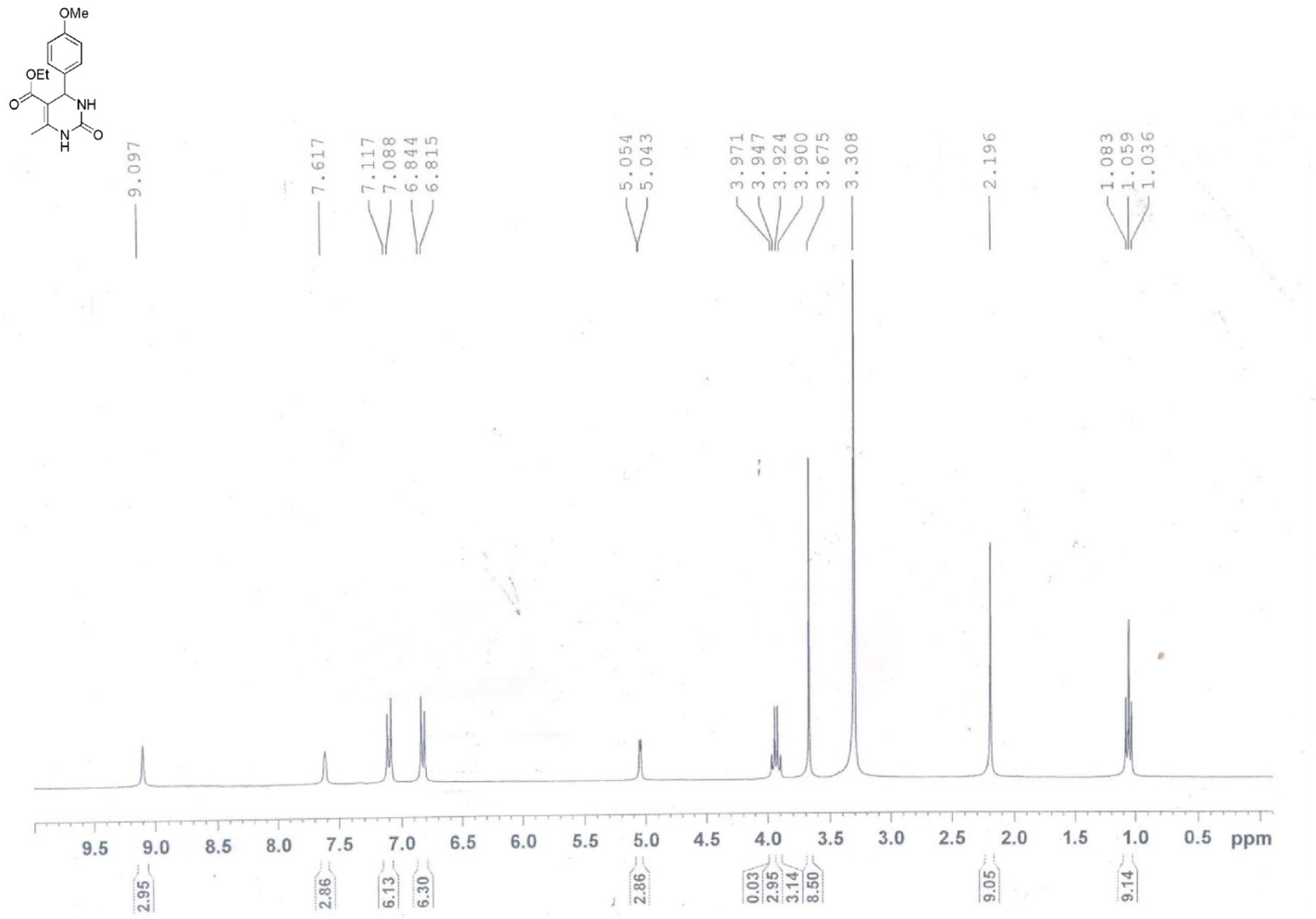
M.P. 185ºC; colourless, ^{1}H NMR (DMSO, 300 MHz): 1.14 (t, 3H), 2.33 (s, 3H), 4.03(q, 2H), 5.13 (d, 1H), 6.75-7.12 (m, 4H), 9.45 (s, 1H), 9.67 (s, 1H). FT-IR (KBr, cm $^{-1}$): 3300, 3180, 1671.5, 1654.9, 1620, 1575. Anal. Calcld. For $C_{14}H_{16}O_3N_2S$: C, 57.52; H, 5.52; N, 9.58. Found: C, 57.58; H, 5.48; N, 9.51.

4k.5-(Ethoxycarbonyl)-6-methyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one

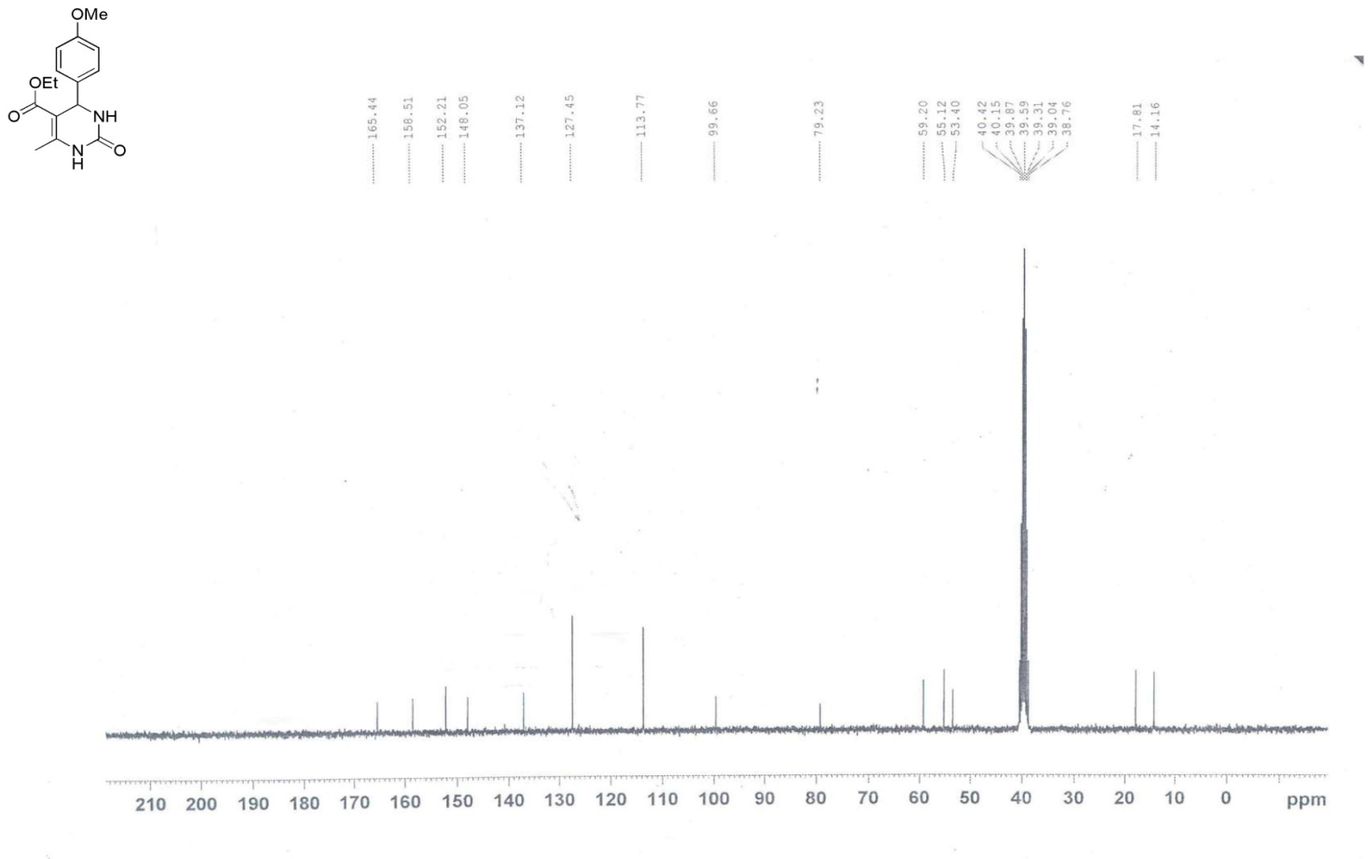
M.P. 201ºC; colourless, ^{1}H NMR (DMSO, 300 MHz): 1.06 (t, 3H, J = 7.2Hz), 2.20 (s, 3H), 3.67 (s, 3H), 3.92 (q, 2H, J = 7.2 Hz), 5.05 (d, 1H), 6.83 (d, 2H, J = 8.7 Hz), 7.10 (d, 2H, J = 8.7Hz), 7.62 (s, 1H), 9.09 (s, 1H); ^{13}C NMR: 14.16, 17.81, 53.40, 55.12, 59.20, 79.23, 99.66, 113.77, 127.45, 137.12, 148.05, 152.21, 158.51, 165.44. FT-IR (KBr, cm $^{-1}$): 3241,

1711.1, 1649.2 Anal. Calcld for $C_{15}H_{18}O_4N_2$: C, 62.06; H, 6.25; N, 9.65. Found: C, 62.10; H, 6.18; N, 9.72.

[1]H NMR of compound 4k



^{13}C NMR of compound 4k



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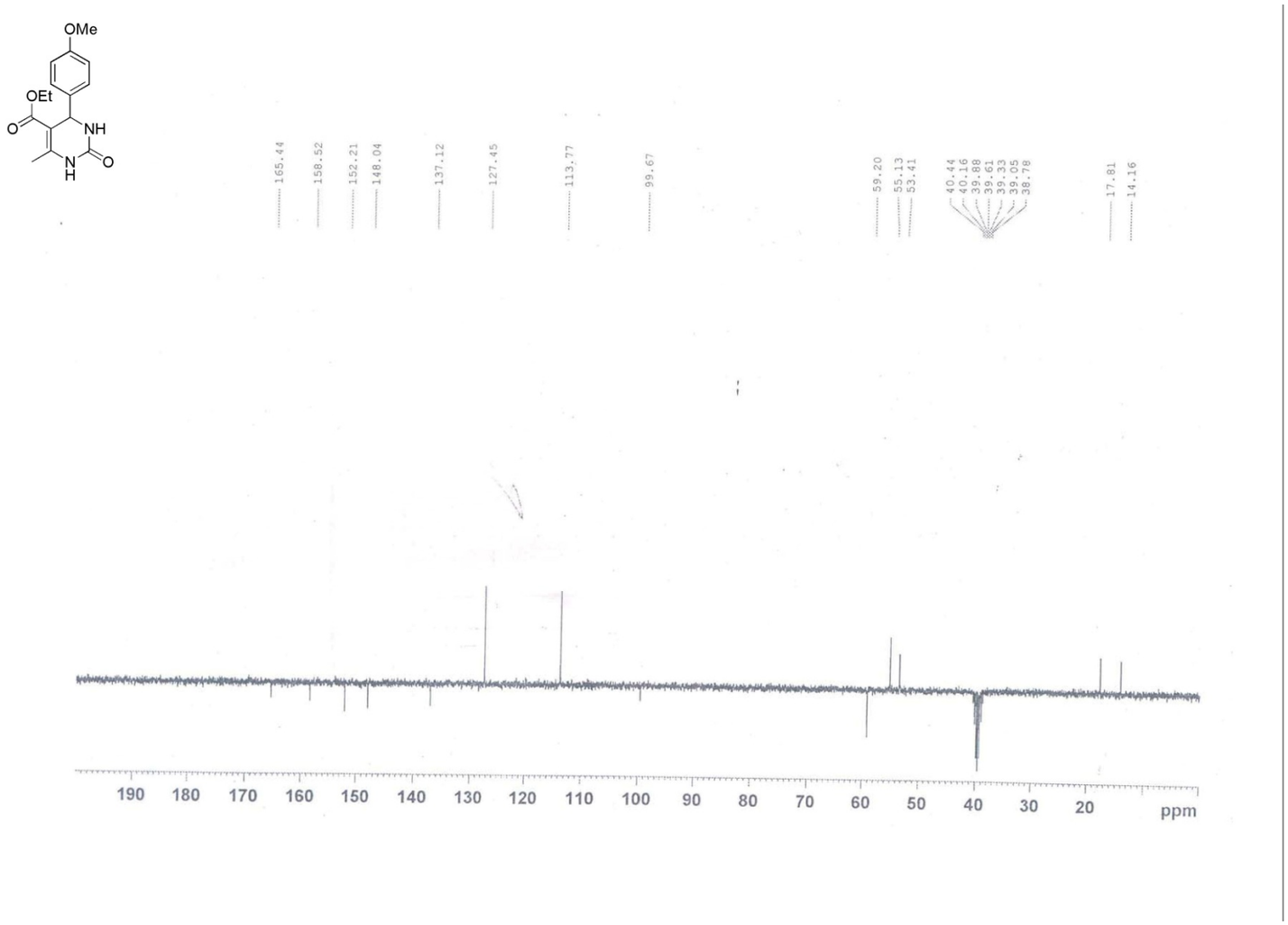
DEPT NMR of compound 4k



4o. 5-(Ethoxycarbonyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one

M.P.258°- 260°C; colourless, ^{1}H NMR (DMSO, 300 MHz): 1.16 (t, 3H, *J* = 7.2 Hz), 2.10 (s, 3H,), 3.87 (s, 2H), 4.02 (q, 2H, *J* = 7.2 Hz), 6.98 (br, 1H, D2O exchangeable, NH), 8.82 (br, 1H, D2O exchangeable, NH).

Relative energies (in kcal/mol) of reactant, product and transition complexes involving glycine (in red) and L-tyrosine (in black) catalysts calculated at B3LYP/6-311++G(d,p) level.