RESEARCH PAPER

Green Synthesis of Poly(ethylene oxide)-coated Sulfonated Copper Ferrite Nanoparticles and its Highly Efficient Application in the Synthesis of Dihydropyrimidine Derivatives

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ABSTRACT

In this work, an immobilization of SO_3H groups on the surface of poly(ethylene oxide)-coated copper ferrite nanoparticles was reported. The prepared $CuFe_2O_4$@PEO-SO_3H is an effective, green, magnetically recoverable, bimetallic, eco-friendly, and heterogeneous solid acid catalyst. Using a green solvent in mild reaction conditions and short reaction times can provide several advantages for this work. The prepared nanocatalyst was characterized using conventional instrumental techniques such as Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM) images, energy-dispersive X-ray spectroscopy (EDX), elemental mapping, vibrating sample magnetometer (VSM) data, transmission electron microscopy (TEM), and X-ray diffraction (XRD) studies. The application of the present green nanocatalyst as a heterogeneous magnetic nanocomposite catalyst was investigated and developed for the green synthesis of chemically and biologically important dihydropyrimidines derivatives at room temperature in high-to-excellent yields via a simple and convenient method in a one-pot three component Biginelli condensation reaction. Due to the magnetic property of the catalyst, it can be easily recycled from the reaction mixture by an external magnet and reused without any considerable loss of activity.

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Characterization of the selected products

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Spectral data and Characterization of Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin -5-carboxylate (4j).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm):

1.07–1.123 (3H, t, *J* = 11.5 Hz, CH_3), 3.45 (3H, s, CH_3), 3.95–4.00 (2H, q, *J* = 11.5 Hz, CH_2), 5.05 (1H, s, CH), 6.65–6.69 (2H, d, *J* = 8.5 Hz, H–Ar), 7.55–7. 153 (2H, d, *J* = 8.5 Hz, H–Ar), 9.45 (1H, s, NH), 9.11 (1H, s, NH), 9.13 (1H, s, OH).

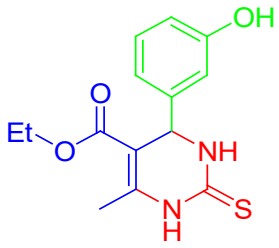


Fig. S1 FT-IR spectrum of compound (**4j**)

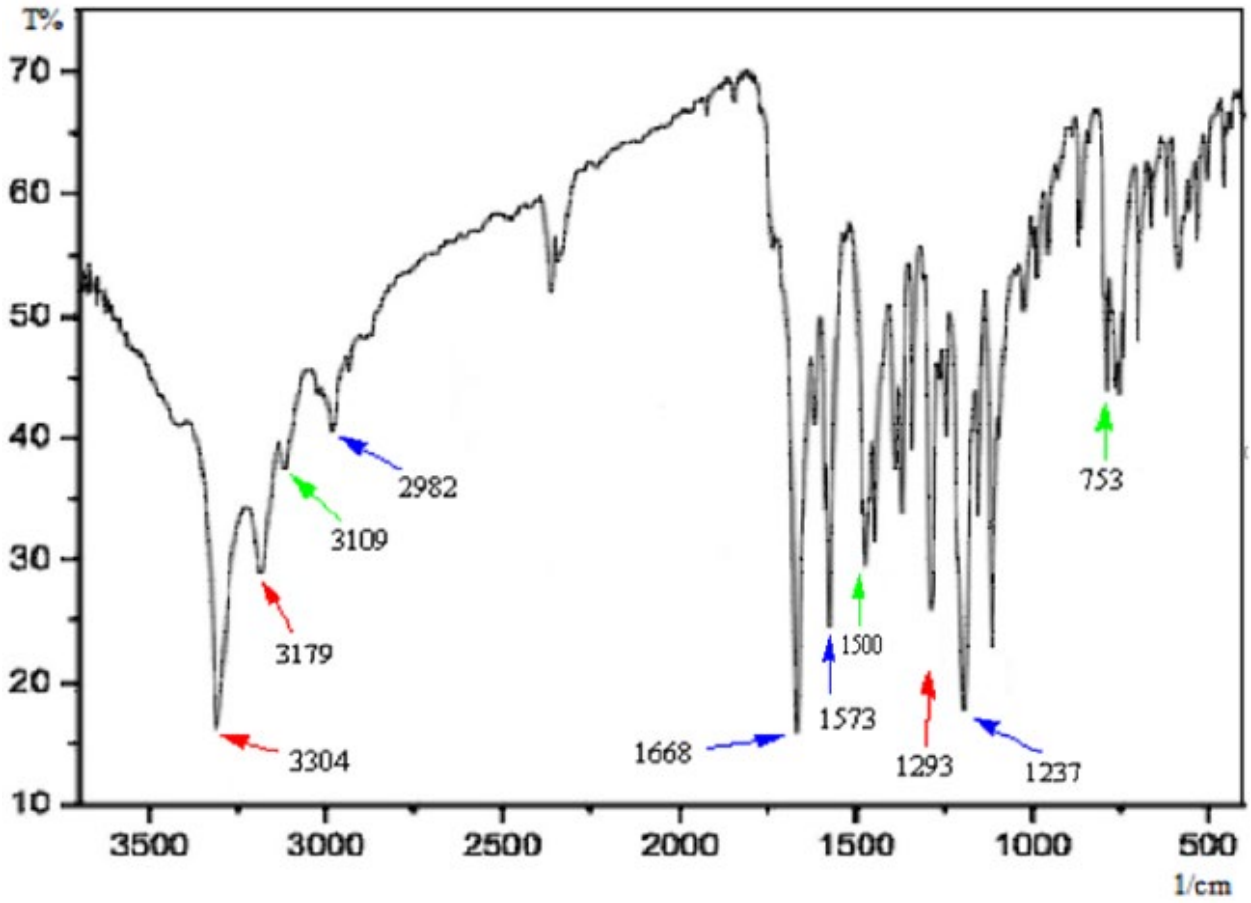
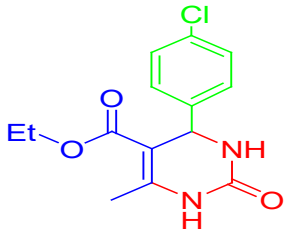


Fig. S2 ^{1}H NMR spectrum of compound (**4j**)

Spectral data and Characterization of Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4a).



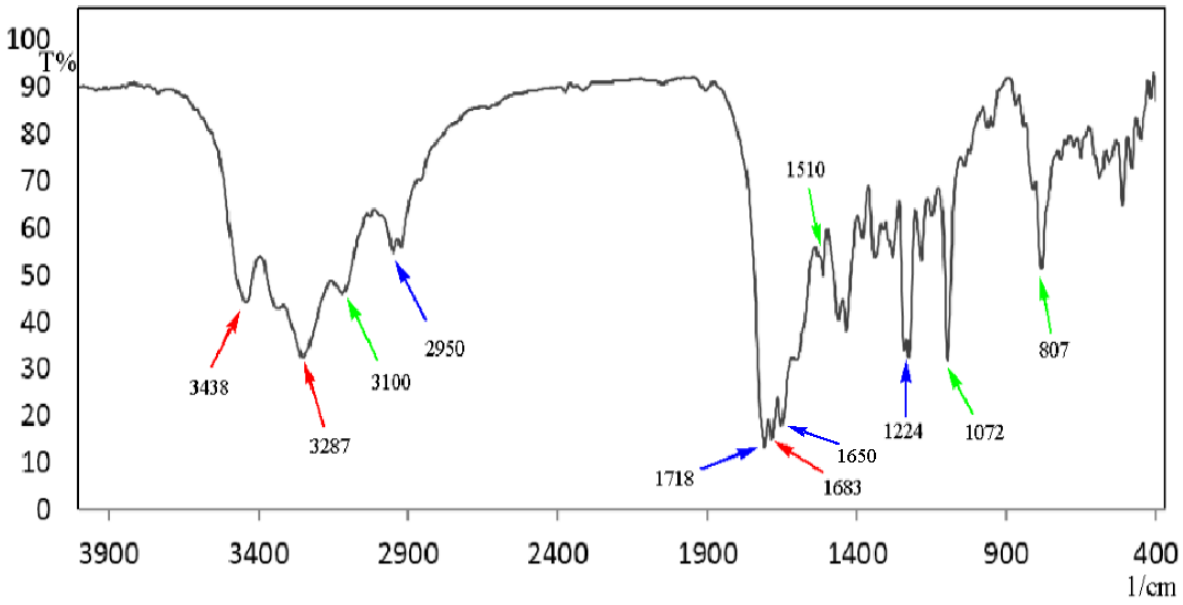
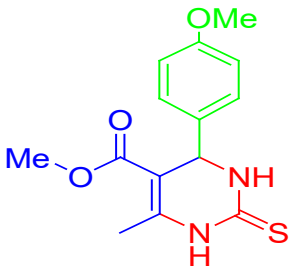


Fig. S3 FT-IR spectrum of compound (**4a**)

Spectral data and Characterization of Methyl 4- (4-methoxyphenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate (4b).



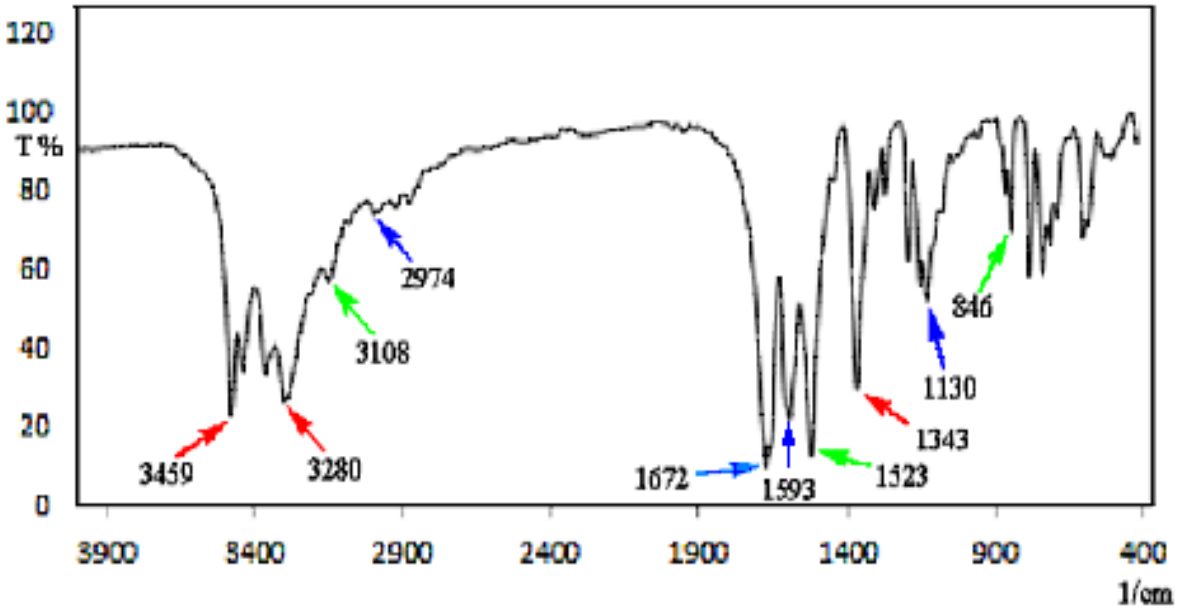


Fig. S4 FT-IR spectrum of compound (**4b**)

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Spectral data of the selected products

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Methyl 4-(3-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine -5-carboxylate (4c).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm):

2.22 (3H, s, CH_3), 3.52 (3H, s, CH_3), 5.04 (1H, s, CH), 6.59–6.65 (3H, m, H–Ar), 7.03 (1H, m, H–Ar), 7.08 (1H, s, OH), 9.22 (1H, s, NH), 9.38 (1H, s, NH).

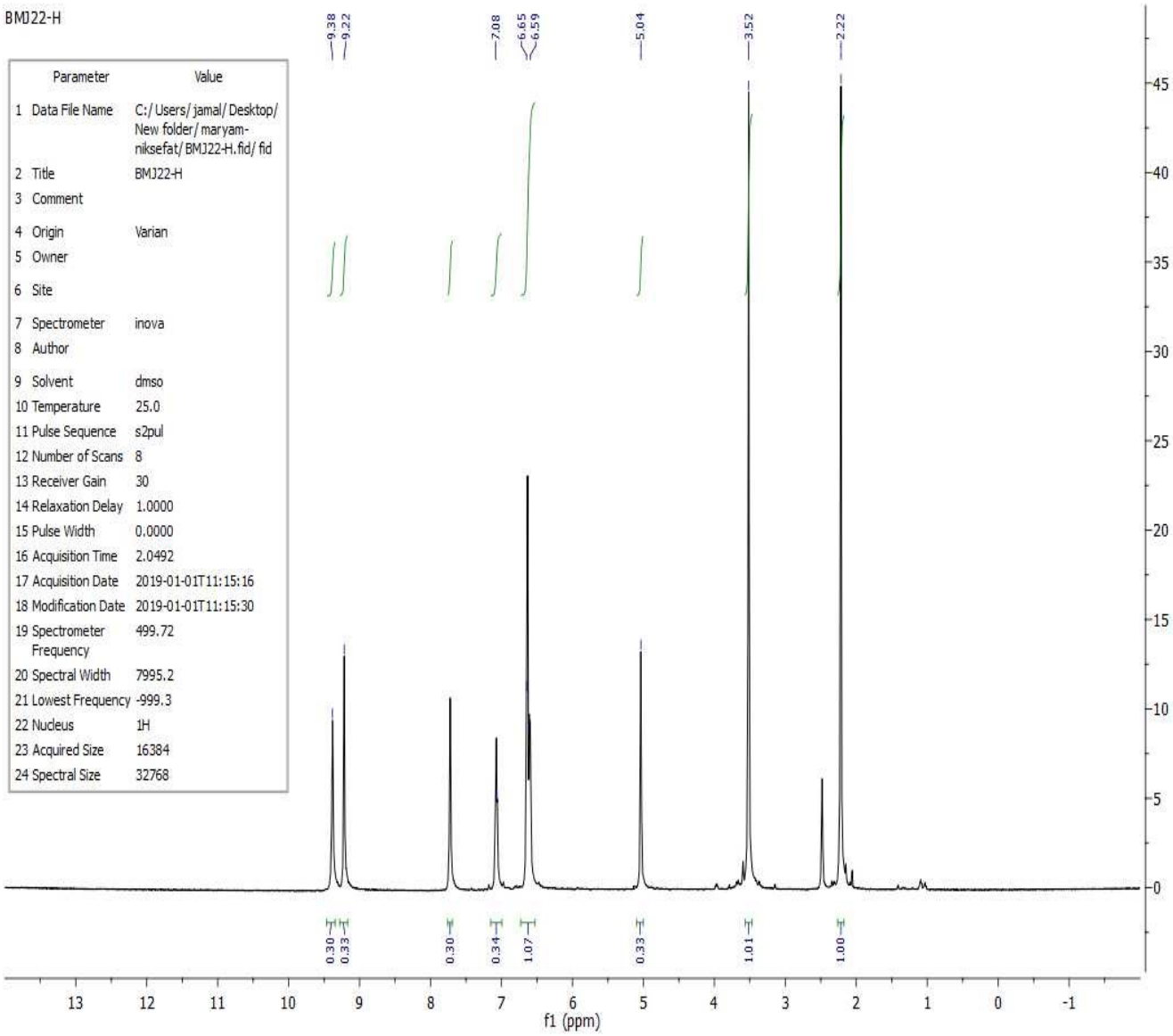

Fig. S1 ^{1}H NMR spectrum of the product **4c**

Methyl 4-(3-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine -5-carboxylate (4c).

^{13}C NMR (125 MHz, $CDCl_3$); δ_C (ppm) :

18.3, 51.3, 54.1, 99.5, 113.4, 114.6, 117.2, 129.8, 146.5, 148.9, 152.8. 157.8, 166.3.

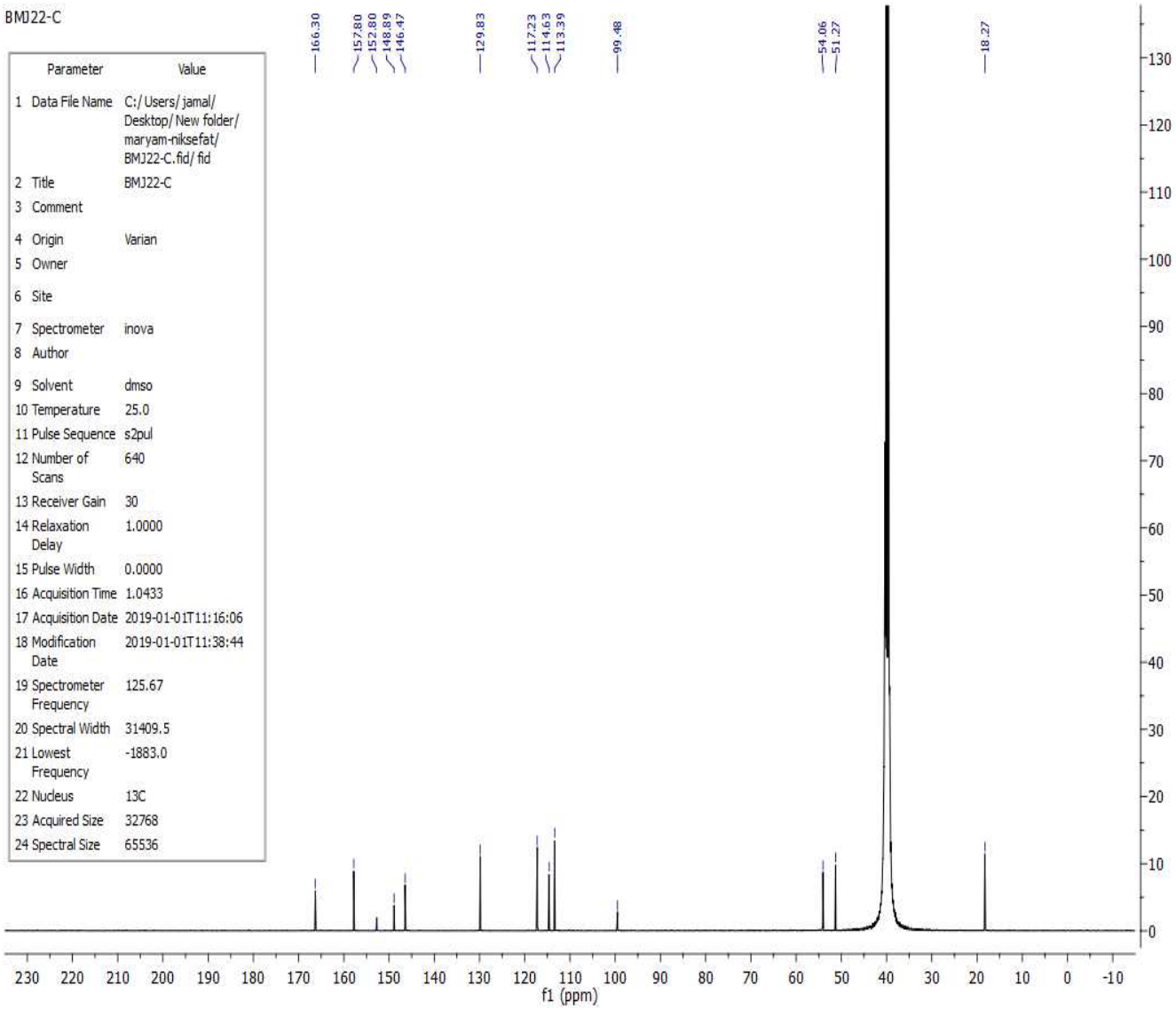

Fig. S2 ^{13}C NMR spectrum of the product **4c**

Ethyl 4-(3-nitrophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4m).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm):

1.08 (3H, t, J = 7.1 Hz, CH_3), 2.17 (3H, s, CH_3), 3.93 (2H, q, J = 7.1 Hz, CH_2), 6.11 (1H, d, J = 3.4 Hz, CH), 7.15–7.33 (5H, m, H–Ar), 7.74 (1H, s, NH), 9.19 (1H, s, NH).

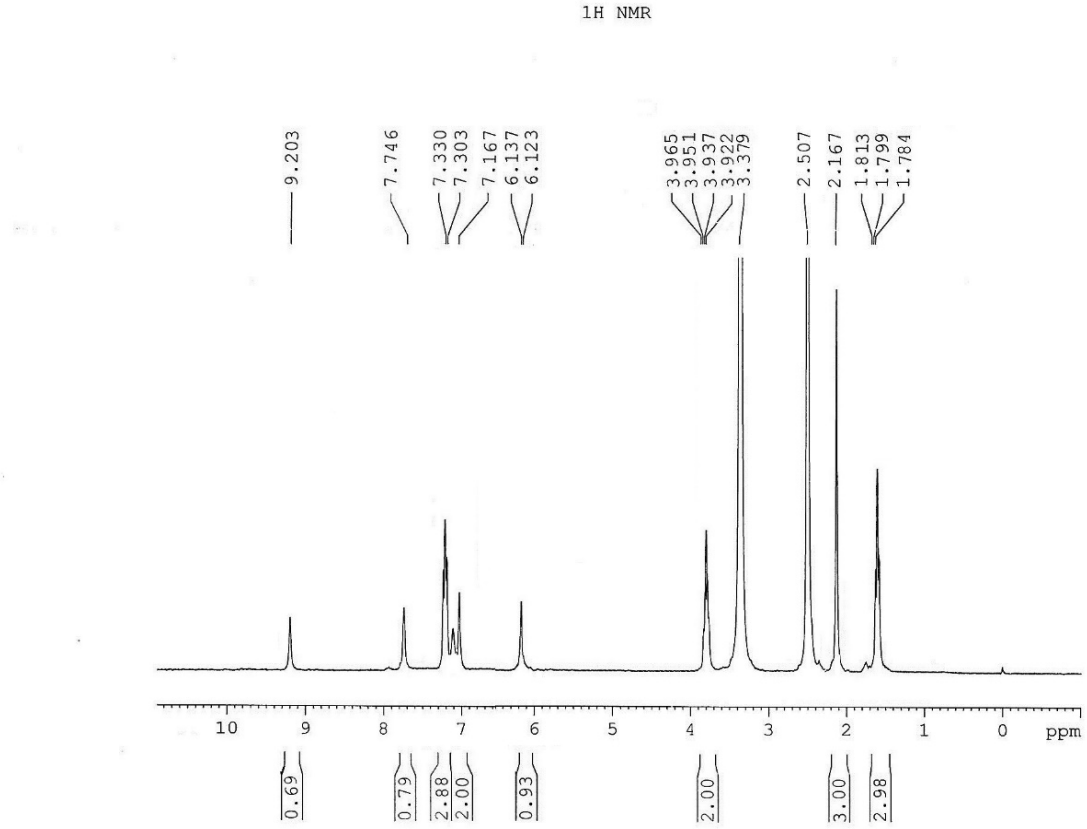

Fig. S3 ^{1}H NMR spectrum of the product **4m**

Ethyl 4-(3-nitrophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4m).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm):

14.0, 15.9, 52.5, 60.7, 105.0, 121.5, 123.6, 127.5, 132.0, 132.5, 135.5, 140.6, 146.6, 160.6.

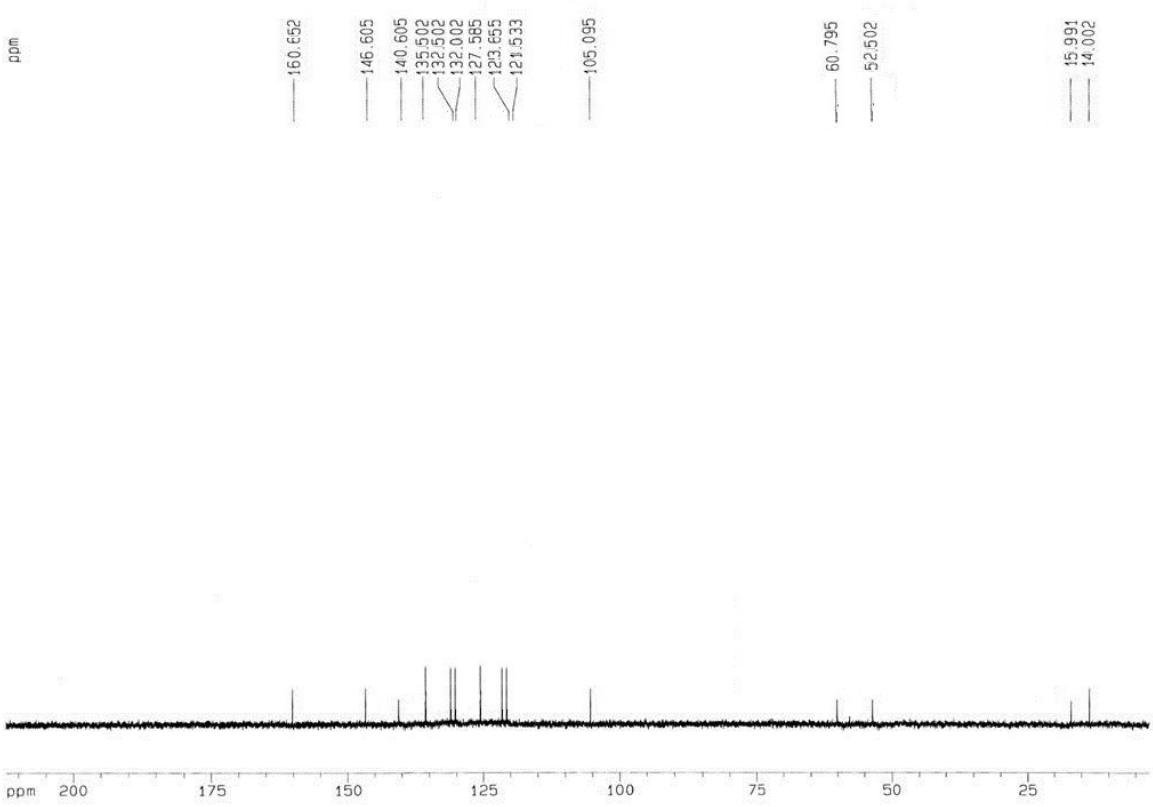

Fig. S4 ^{13}C NMR spectrum of the product **4m**

Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4n).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) :

1.06–1.09 (3H, t, J = 7 Hz, CH_3), 2.21 (3H, s, CH_3), 3.93–3.97 (2H, q, J = 6.5 Hz, CH_2), 5.01 (1H, s, CH), 6.65–6.67 (2H, d, J = 8.5 Hz, H–Ar), 6.99–7.01 (2H, d, J = 8.5 Hz, H–Ar), 7.62 (1H, s, OH), 9.11 (1H, s, NH), 9.13 (1H, s, NH).

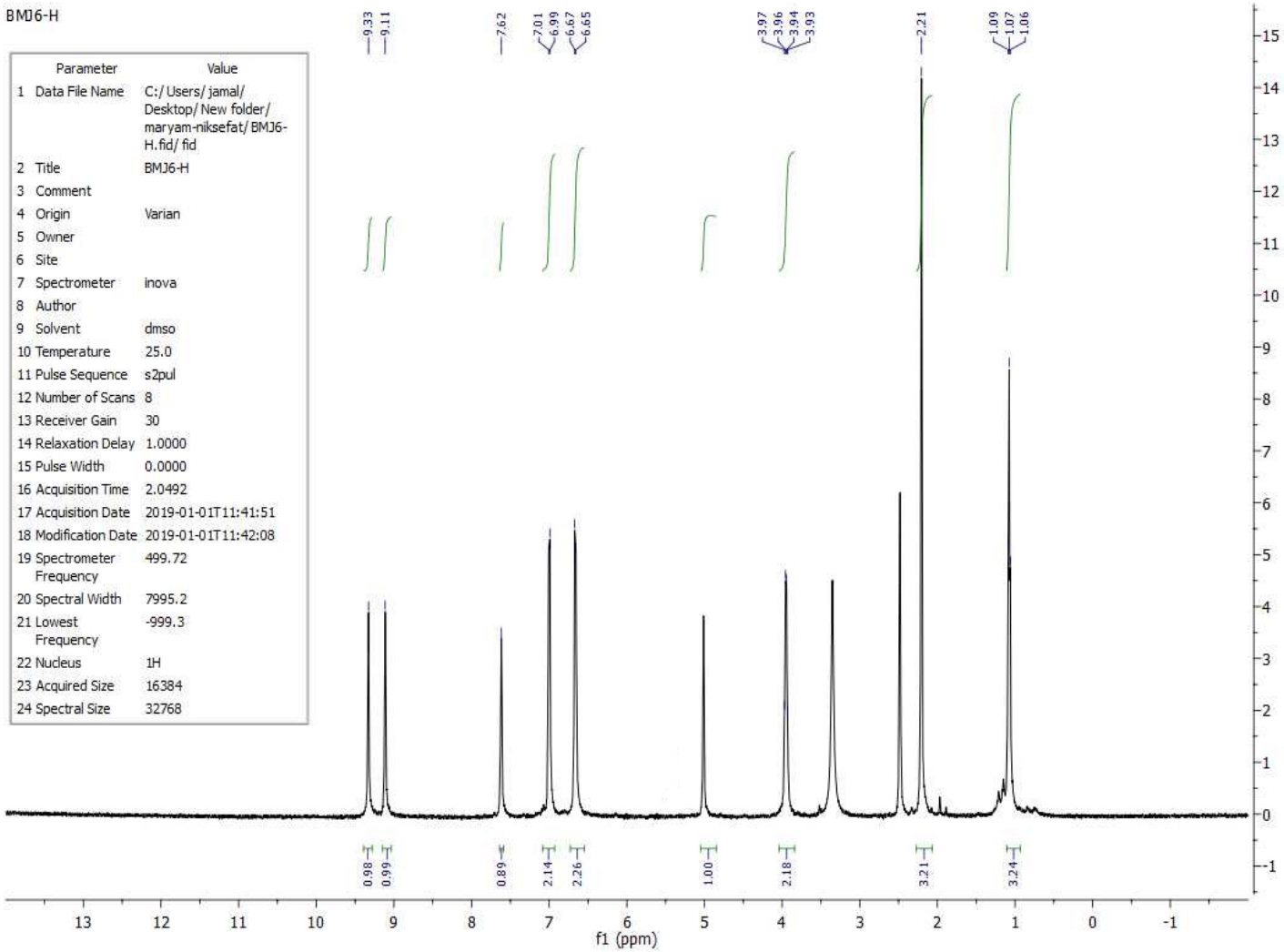

Fig. S5 ^{1}H NMR spectrum of the product **4n**

Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4n):

^{13}C NMR (125 MHz, $CDCl_3$): δ_C(ppm):

14.5, 18.2, 53.8, 59.5, 100.0, 115.4, 127.8, 135.8, 148.2, 152.6, 156.9, 165.8.

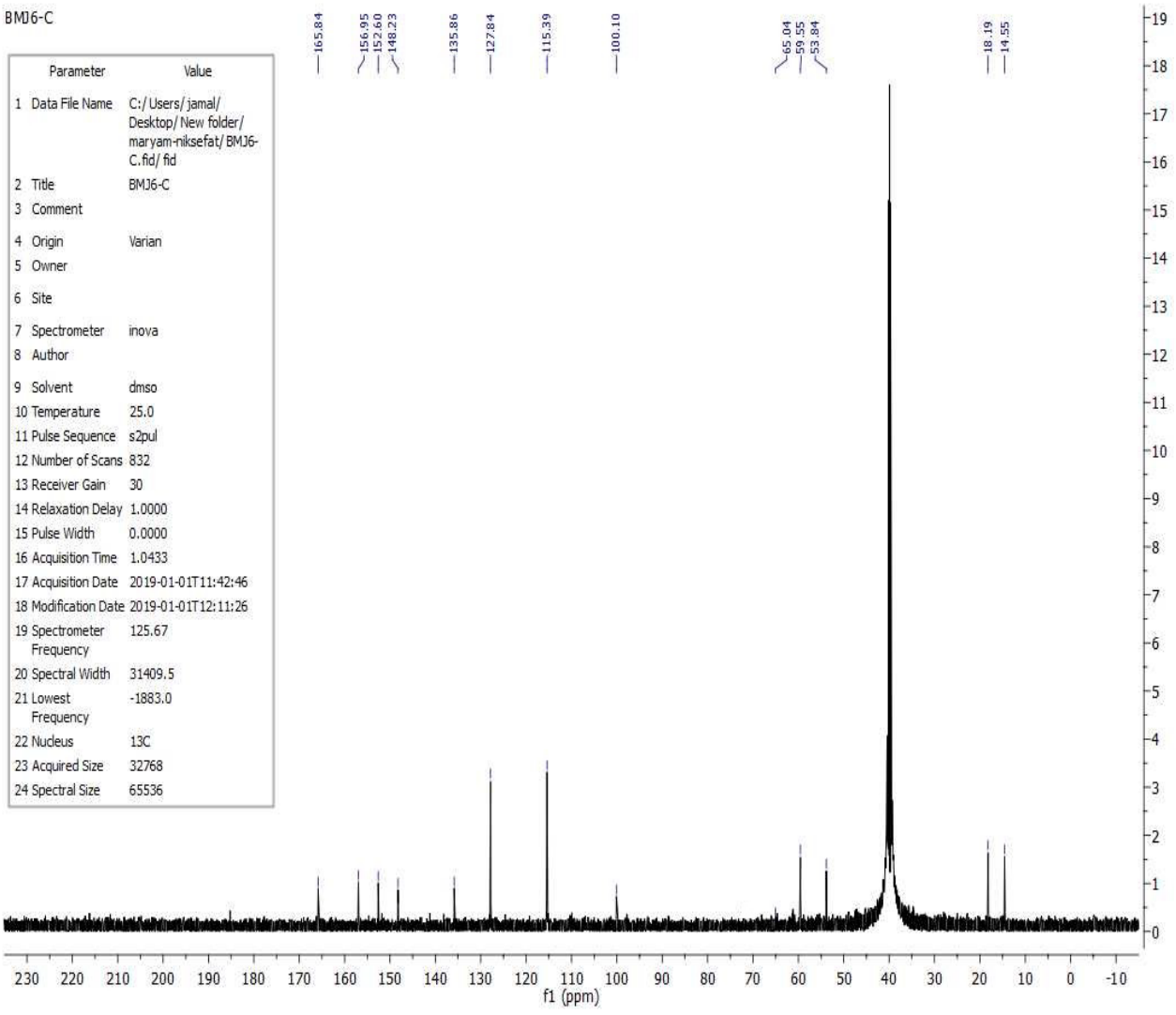

Fig. S6 ^{13}C NMR spectrum of the product **4n**

Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4o).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm) :

1.05 (3H, CH_3), 2.22 (3H, s, CH_3), 3.94 (2H, q, CH_2), 5.12 (1H, s, CH), 7.16 (2H, H–Ar), 7.22 (2H, H–Ar), 7.75 (1H, s, NH), 9.23 (1H, s, NH).

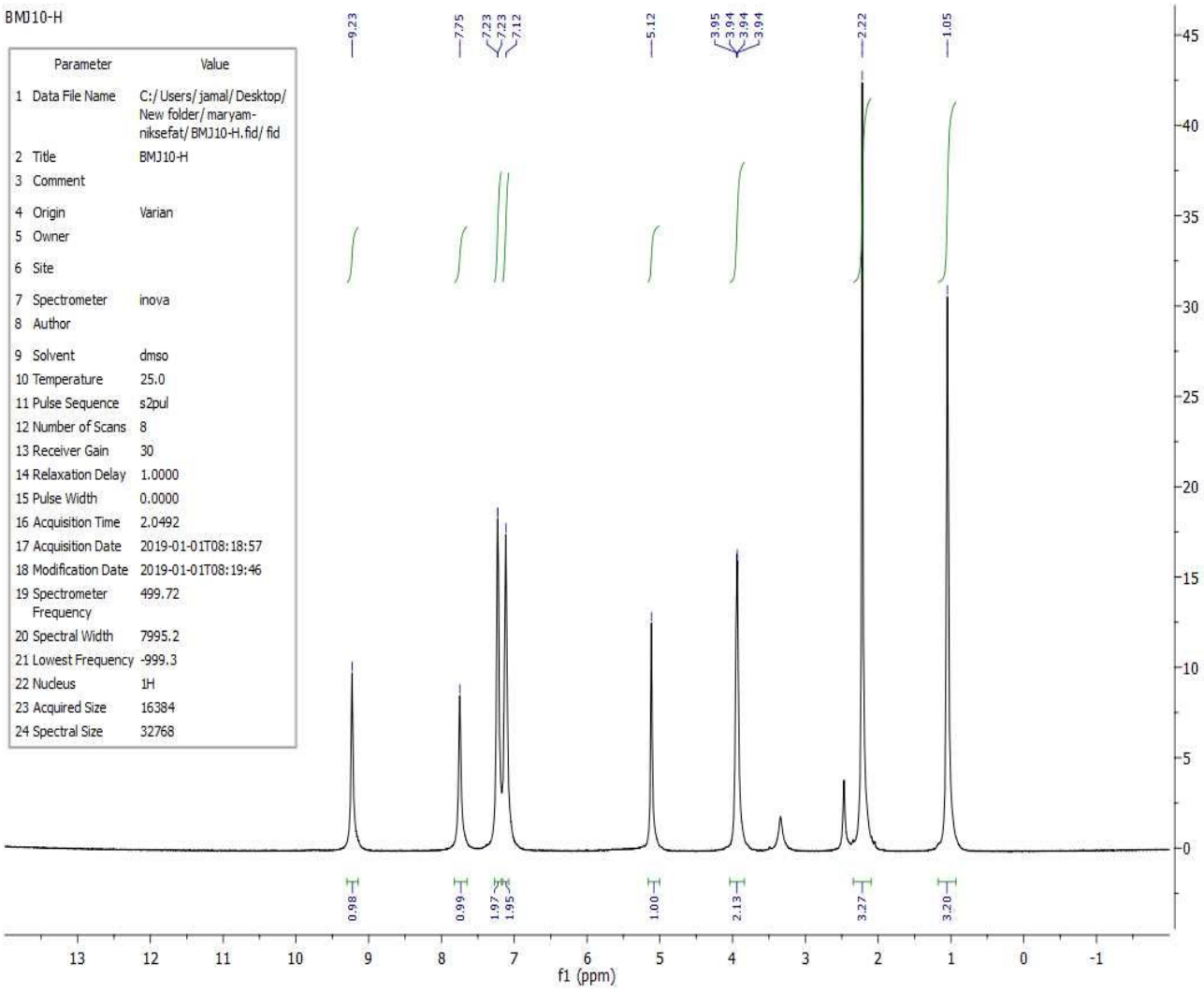

Fig. S7 ^{1}H NMR spectrum of the product **4o**

Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4o).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C (ppm) :

14.5, 18.2, 53.7, 59.6, 99.5, 115.5, 115.6, 128.7, 141.5, 149.0, 152.4, 160.7, 162.7, 165.6.

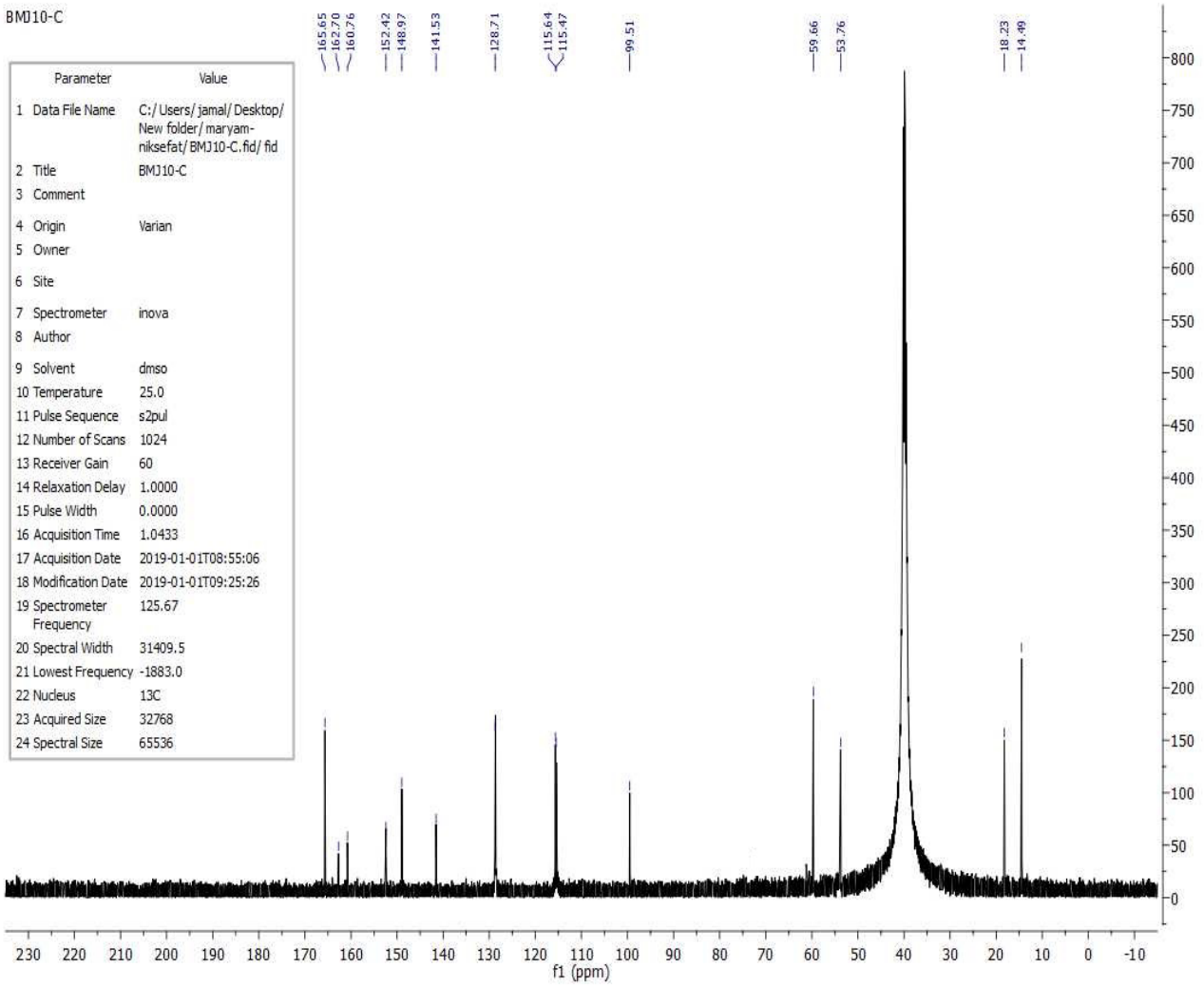

Fig. S8 ^{13}C NMR spectrum of the product **4o**

Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4p).

^{1}H NMR (500 MHz, DMSO): δ_H (ppm) :

2.21 (3H, s, CH_3), 3.49 (3H, s, CH_3), 5.10 (1H, d, J = 3.3 Hz, CH), 7.18–7.29 (5H, m, H–Ar), 7.72 (1H, s, NH), 9.18 (1H, s, NH).

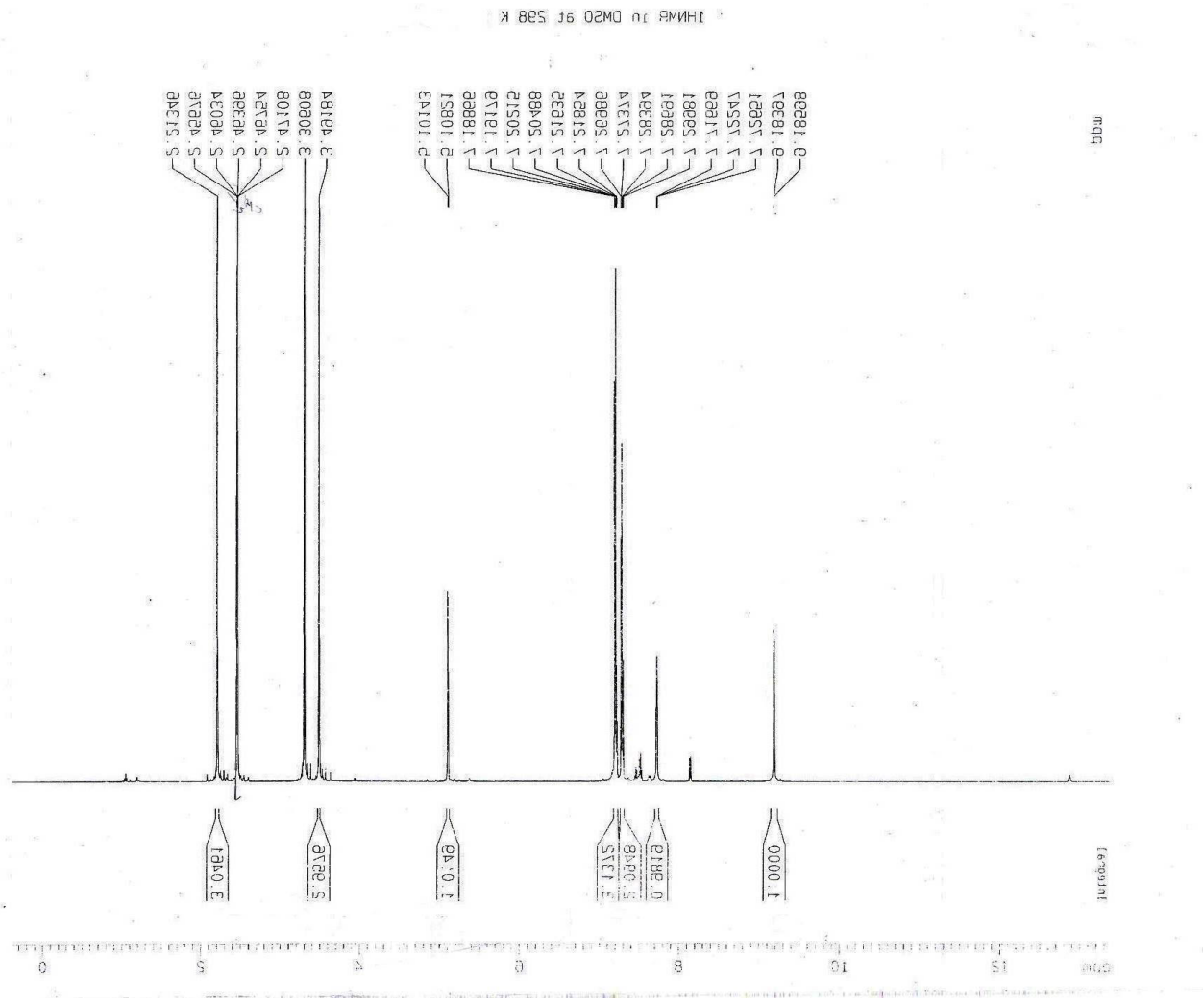

Fig. S9 ^{1}H NMR spectrum of the product **4p**

Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4p).

^{13}C NMR (125 MHz, $CDCl_3$); δ_C(ppm):

18.7, 51.3, 55.6, 101.2, 126.6, 128.1, 128.9, 143.7, 146.9, 153.9, 166.3.

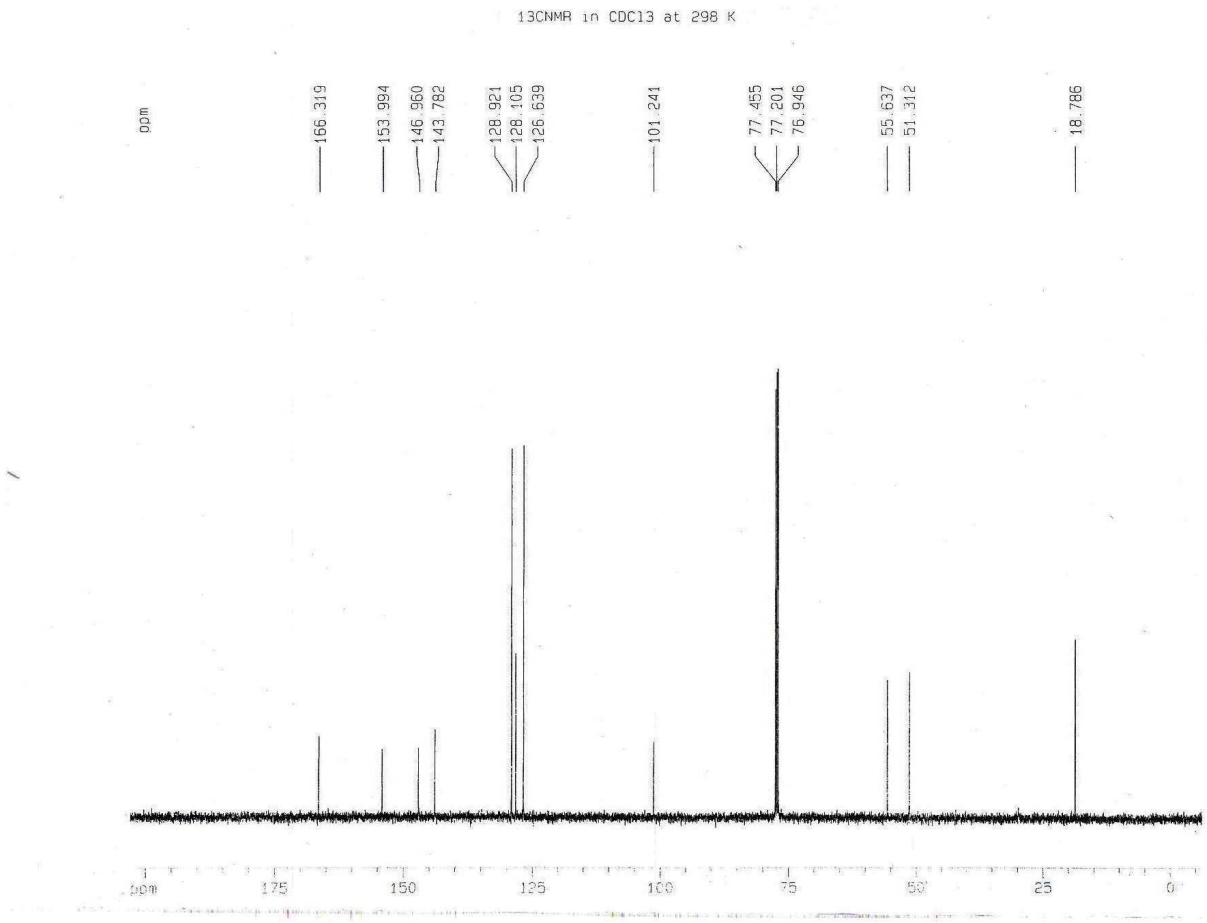

Fig. S10 ^{13}C NMR spectrum of the product **4p**

Methyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4q).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H (ppm):

2.31 (3H, s, CH_3), 3.59 (3H, s, CH_3), 5.26 (1H, d, J = 3.5 Hz, CH), 7.26 (4H, m, H–Ar), 7.51 (1H, s, NH), 9.11 (1H, s, NH).

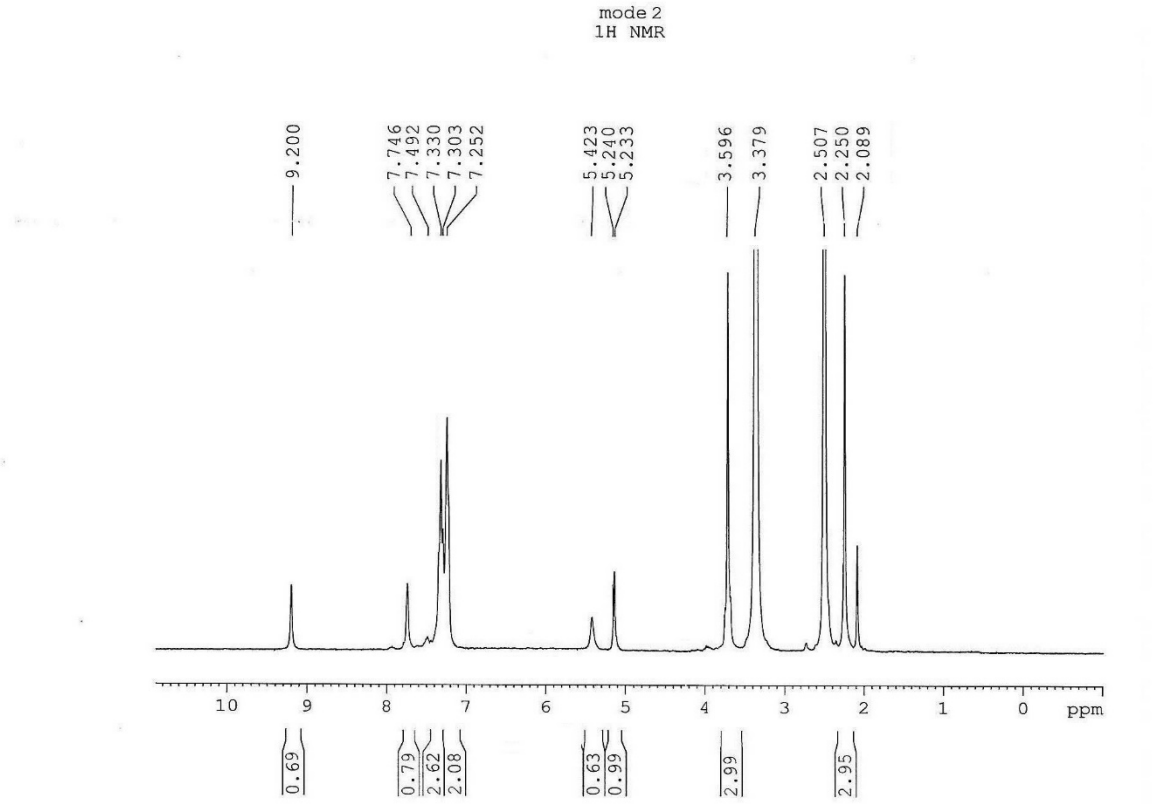

Fig. S11 ^{1}H NMR spectrum of the product **4q**

Methyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4q):

^{13}C NMR (125 MHz, $CDCl_3$); δ_C (ppm):

18.7, 52.6, 57.7, 98.9, 121.2, 123.6, 127.5, 135.0, 142.6, 146.6, 152.6.

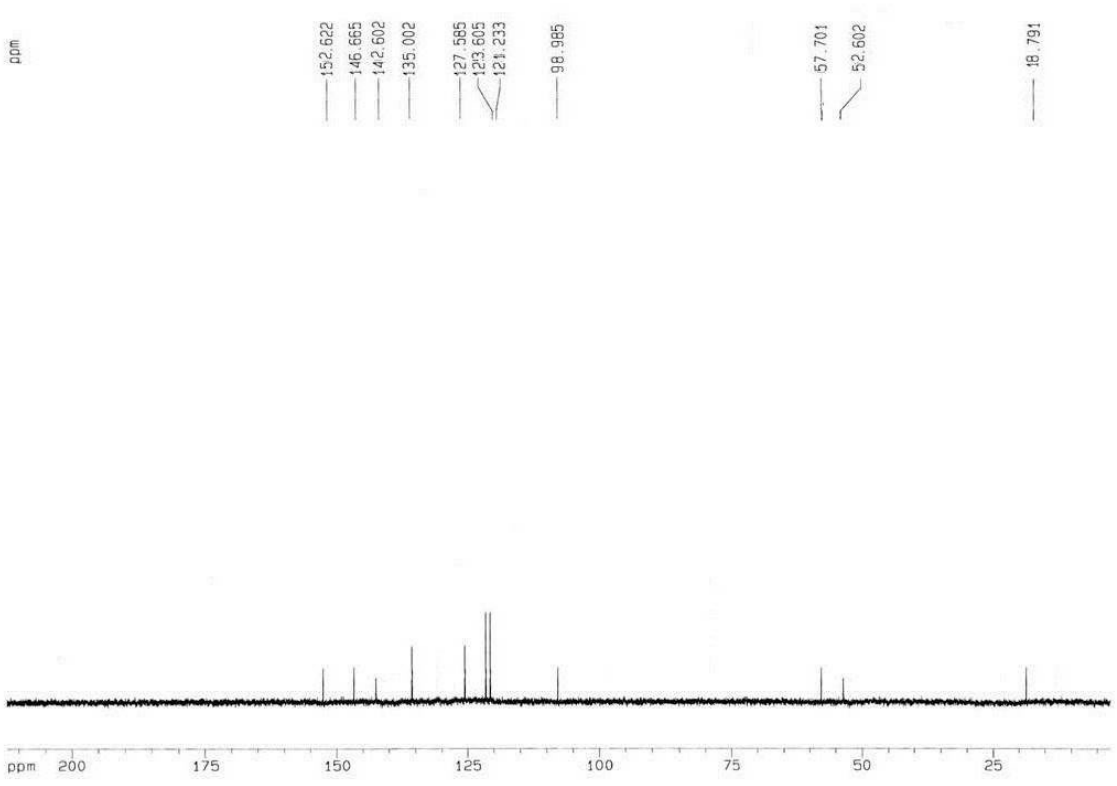

Fig. S12 ^{13}C NMR spectrum of the product **4q**