Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Sulfated polyborate: a new and eco-friendly catalyst for one-pot multi-component synthesis of 3,4-dihydropyrimidones via Biginelli reaction

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1. Experimental:

1.1. Materials and methods:

Melting points of all the compounds were recorded by AnalabThermoCal melting point apparatus in the open capillary tube and are uncorrected. The FTIR spectra (KBr) were recorded on Shimadzu FTIRAffinity-1 Fourier Transform Infrared spectrophotometer. ^{1}H NMR spectra were recorded on MR400 Agilent Technology NMR spectrometer using tetramethylsilane (TMS) as an internal standard and DMSO-d_6/$CDCl_3$ as solvent. X-ray diffractograms (XRD) were recorded on Rigakuminiflex X-ray Diffractometer. The SEM-EDAX characterization was performed on a JEOL JSM-638DLA scanning electron microscope equipped with energy dispersive X-ray spectrometer. The potentiometric analysis was performed on Elico LI 120 pH meter. The chirality has been ascertained on JASCO P-2000 polarimeter. Chemicals and solvents used were of LR grade and purchased from SD fine, Avra Synthesis and Spectrochem and used without purification. The purity determination of the starting materials and reaction monitoring was accomplished by thin-layer chromatography (TLC) on Merck silica gel G F_{254} plates. All the products are known compounds and were characterized by ^{1}H NMR spectroscopy for structural identification.

1.2. Preparation and characterization of sulfated polyborate catalyst:

Boric acid was heated in a petri dish at 200 °C for 4h to convert it to the polyboric acid; resultant glassy solid was ground into fine powder. Polyboric acid powder (5 g) was suspended in chloroform (20 ml) in 250 ml round bottom flask, chlorosulfonic acid (4.23 ml) was added drop wise over 30 minutes at room temperature. The mixture was stirred for 120 minutes at the same temperature. The reaction was quenched by adding ethanol (10 ml). Residual HCl gas was eliminated by nitrogen flush, the solid was filtered and washed several times with chloroform. Finally solid sulfated polyborate was dried at 100 °C in hot air oven till constant weight.

The catalyst was characterized by various analytical techniques such as potentiometric analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) energy dispersive X-ray spectroscopy (EDAX).

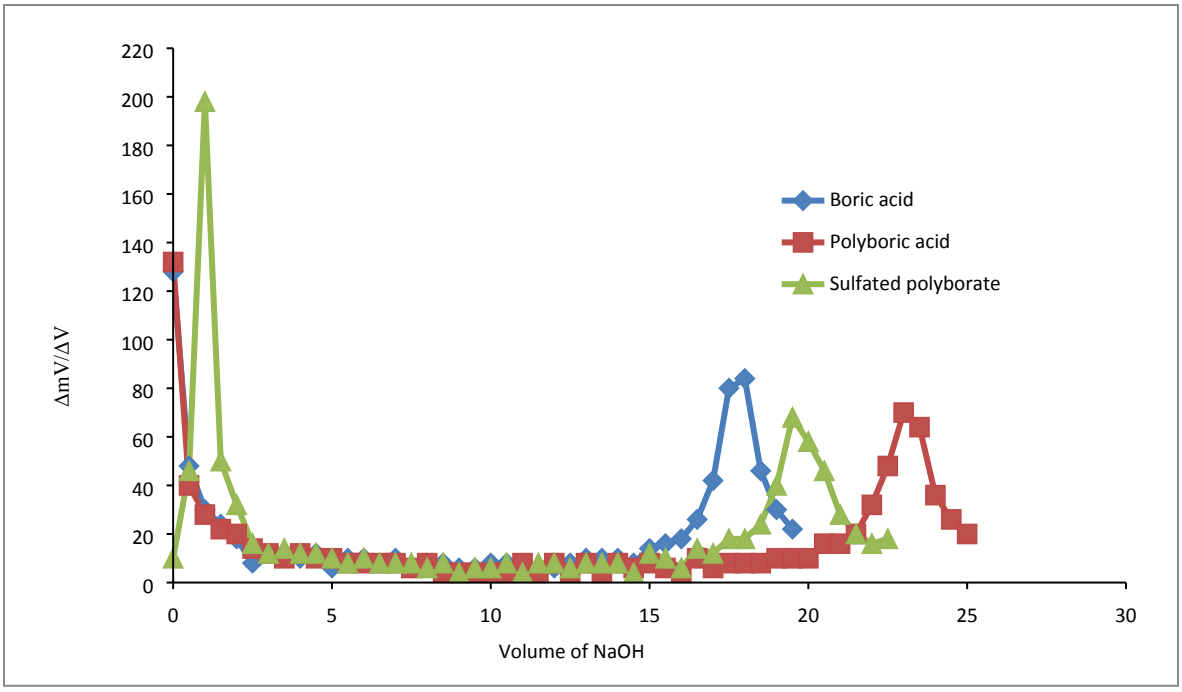


Figure 1. Potentiometric titration of Boric acid, Polyboric acid and Sulfated polyborate catalyst.

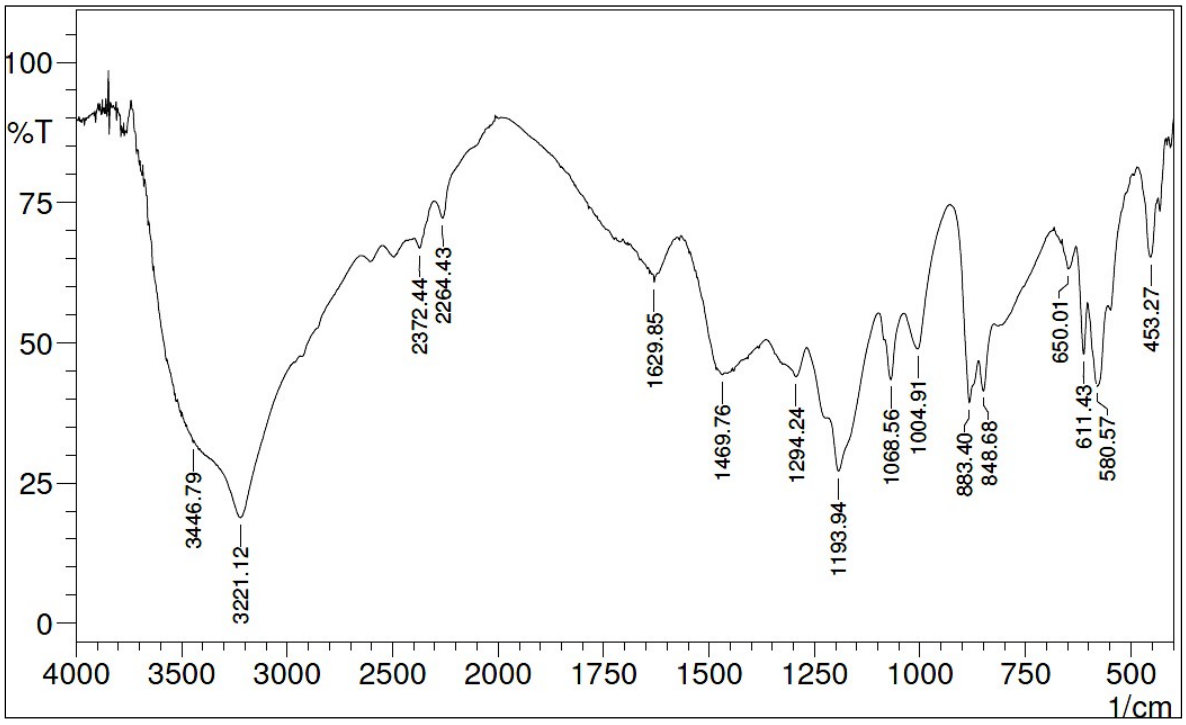


Figure 2. FTIR spectrum of the catalyst.

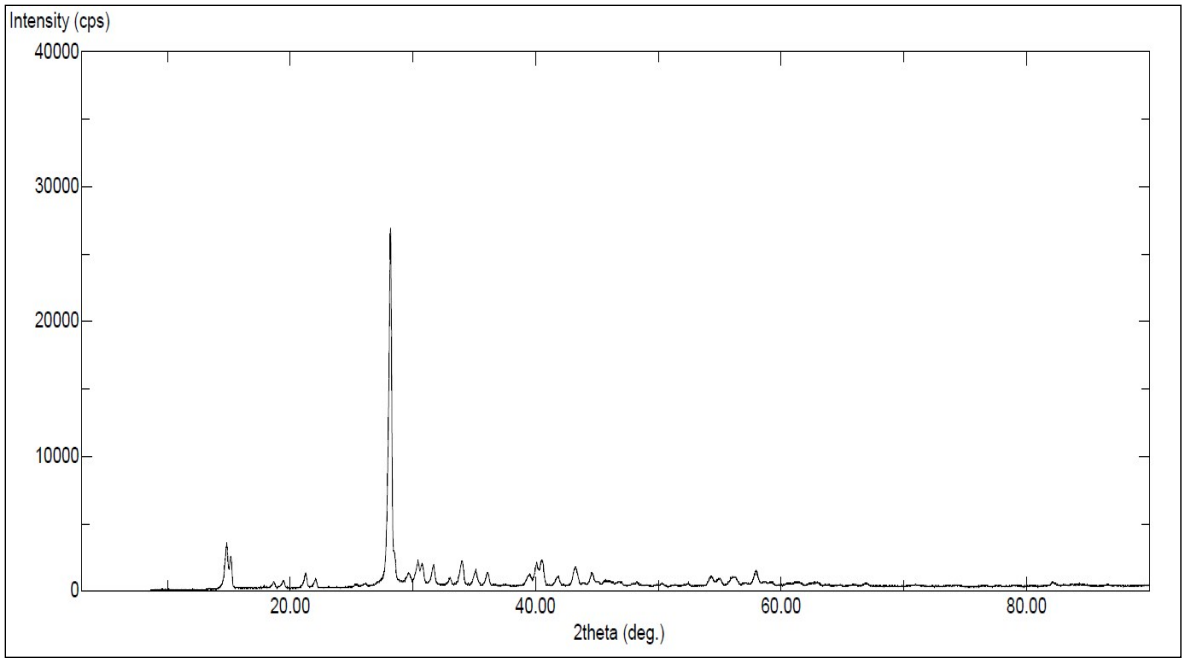


Figure 3. X-ray diffraction pattern of the catalyst.

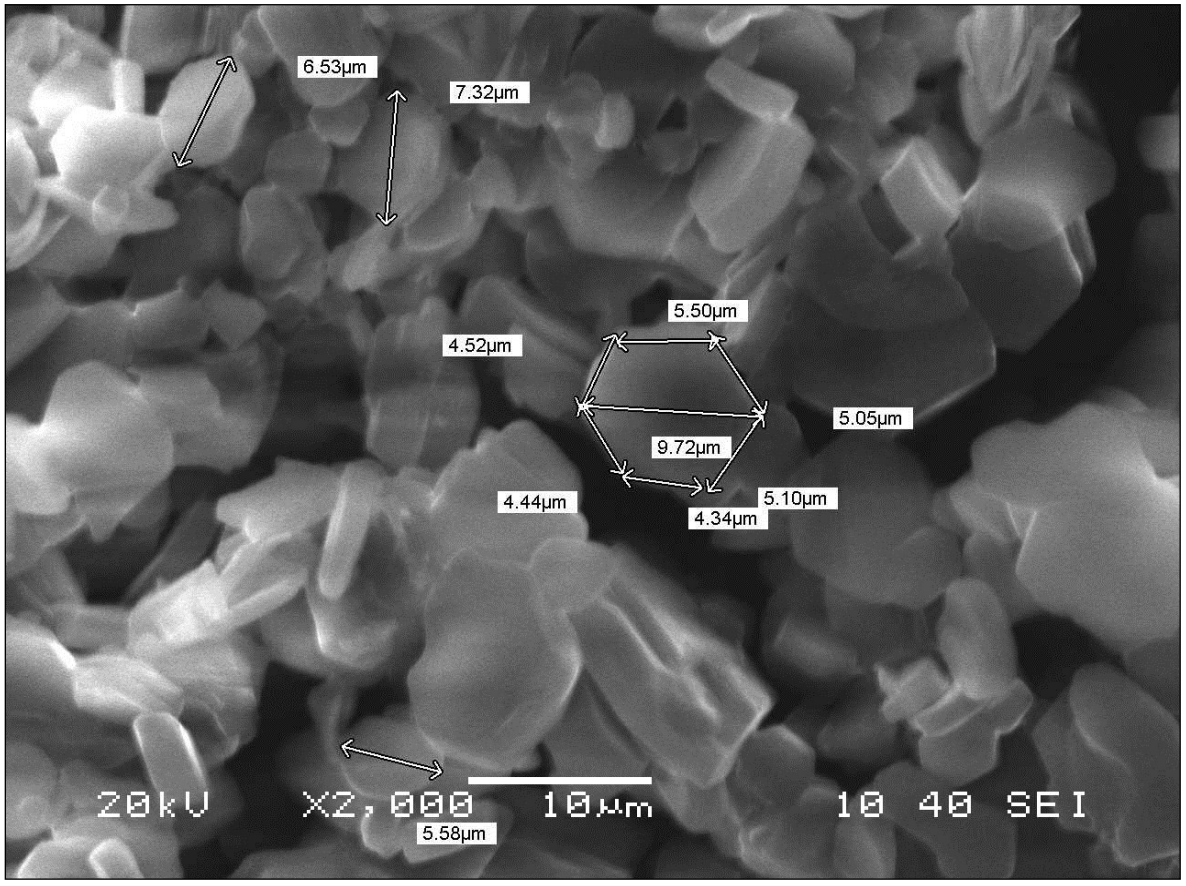


Figure 4. SEM image of the catalyst.

1.3. General procedure for Biginelli reaction catalyzed by sulfated polyborate:

A mixture of β-ketoester/β-diketone (2 mmol), aldehyde (2 mmol), urea or thiourea (2.4mmol) and sulfated polyborate (5% by wt.) was heated at 100 °C. The reaction was monitored by thin layer chromatography. After completion of the reaction, reaction mixture was cooled to room temperature and quenched by water; solid precipitated was filtered at vacuum pump, washed with water (3 X 5 mL), dried under vacuum and recrystallized from ethanol to afford the pure product.

2. ^{1}H NMR Spectral data of synthesized compounds for Table 4

a) Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 1)[1]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 1H), 7.74 (s, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 5.10 (s, 1H), 3.95 (q, J = 7.1 Hz, 2H), 2.22 (s, 3H), 1.07 (t, J = 7.0 Hz, 3H).

b) Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 2)[1]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.62 (s, 1H), 7.10 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 18.7 Hz, 2H), 5.05 (s, 1H), 3.93 (q, J = 7.0 Hz, 2H), 3.70 (s, 3H), 2.22 (s, 3H), 1.10 – 1.04 (t, 3H).

c) Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 3)[2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 9.07 (s, 1H), 7.57 (s, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 4.99 (s, 1H), 3.97 – 3.90 (q, 2H), 2.18 (s, 3H), 1.05 (t, J = 7.0 Hz, 3H).

d) Ethyl 4-(4-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 4)[3]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 1H), 7.74 (s, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 5.10 (s, 1H), 3.95 (q, J = 7.1 Hz, 2H), 2.22 (s, 3H), 1.07 (t, J = 7.0 Hz, 3H).

e) Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 5)[1]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21 (s, 1H), 7.73 (s, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 5.10 (s, 1H), 3.99 – 3.91 (q, 2H), 2.20 (s, 3H), 1.05 (t, J = 7.0 Hz, 3H).

f) Ethyl 4-(4-methylphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 6)[2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.13 (s, 1H), 7.66 (s, 1H), 7.09 (s, 4H), 5.07 (s, 1H), 3.95 (q, *J* = 7.0 Hz, 2H), 2.22 (d, *J* = 9.3 Hz, 6H), 1.07 (t, *J* = 7.0 Hz, 3H).

g) Ethyl 4-(4-nitrophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 7)[1]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 1H), 7.74 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 5.10 (s, 1H), 3.95 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.07 (t, *J* = 7.0 Hz, 3H).

h) Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 8)[2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 7.71 (s, 1H), 7.23 (d, *J* = 5.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 5.10 (s, 1H), 3.97 – 3.91 (q, 2H), 2.21 (s, 3H), 1.06 – 1.03 (t, 3H).

i) Ethyl 4-(4-(dimethylamino)phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 9)[3]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (s, 1H), 7.54 (s, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 8.2 Hz, 2H), 4.99 (s, 1H), 3.97 – 3.91 (q, 2H), 2.81 (s, 6H), 2.18 (s, 3H), 1.07 (t, *J* = 6.6 Hz, 3H).

j) Ethyl 4-(2-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 10)[4]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 1H), 7.20 (d, *J* = 25.0 Hz, 2H), 7.00 - 6.83 (m, 3H), 5.45 (s, 1H), 3.90 – 3.85 (q, 2H), 3.75 (s, 3H), 2.23 (s, 3H), 0.98 (t, *J* = 6.8 Hz, 3H).

k) Ethyl 4-(2-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 11)[1]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 1H), 7.66 (s, 1H), 7.34 - 7.23 (m, 4H), 5.58 (s, 1H), 3.89 – 3.81 (q, 2H), 2.25 (s, 3H), 0.94 (t, *J* = 7.0 Hz, 3H).

l) Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 12)[1]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.34 (s, 1H), 9.66 (s, 1H), 7.35 – 7.21 (m, 5H), 5.17 (s, 1H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

m) Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 13)[1]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.25 (s, 1H), 9.57 (s, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.07 (s, 1H), 3.96 (q, *J* = 7.0 Hz, 2H), 3.68 (s, 3H), 2.24 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).

n) Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 14)[1]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.35 (s, 1H), 9.63 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 5.12 (s, 1H), 3.97 (q, *J* = 10.6 Hz, 2H), 2.25 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

o) Ethyl 4-(2-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 15)[5]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.19 (s, 1H), 9.21 (s, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.08 - 6.96 (m, 2H), 6.85 (t, *J* = 8.9 Hz, 1H), 5.45 (s, 1H), 3.93 – 3.87 (q, 2H), 3.75 (s, 3H), 2.25 (s, 3H), 0.99 (t, *J* = 9.9 Hz, 3H).

p) Ethyl 4-(2-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 16)[6]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.33 (s, 1H), 9.57 (s, 1H), 7.39 – 7.24 (m, 4H), 5.60 (s, 1H), 3.88 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 0.97 (t, *J* = 7.1 Hz, 3H).

q) Ethyl 6-methyl-2-oxo-4-propyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 17)[3]:
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 7.28 (s, 1H), 4.03 (dd, J = 14.4, 7.1 Hz, 3H), 2.12 (s, 3H), 1.53 – 1.03 (m, 7H), 0.80 (t, J = 6.6 Hz, 3H).

r) Ethyl 4-cyclopropyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 18): ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.95 (s, 1H), 7.27 (s, 1H), 4.03 (qd, J = 10.8, 3.8 Hz, 2H), 3.68 – 3.57 (m, 1H), 2.13 (s, 3H), 1.15 (t, J = 7.0 Hz, 3H), 0.89 (d, J = 6.1 Hz, 1H), 0.38 – 0.21 (m, 3H), 0.14 (d, J = 5.3 Hz, 1H).

s) Ethyl 4-cyclohexyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 19)[7]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 1H), 7.24 (s, 1H), 4.11 – 3.94 (m, 2H), 3.88 (s, 1H), 2.12 (s, 3H), 1.60 (d, J = 41.2 Hz, 4H), 1.30 (d, J = 26.6 Hz, 2H), 1.19 – 0.91 (m, 7H), 0.82 (dd, J = 23.9, 12.6 Hz, 1H).

t) Ethyl 6-methyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 20)[3]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.11 (s, 1H), 7.51 (s, 1H), 7.36 (d, J = 7.6 Hz, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.32 (d, J = 15.8 Hz, 1H), 6.15 (dd, J = 15.9, 5.9 Hz, 1H), 4.68 (s, 1H), 4.04 (dt, J = 18.1, 10.8 Hz, 2H), 2.16 (s, 3H), 1.16 (t, J = 7.0 Hz, 3H).

u) Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (entry 21)[2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 7.72 (s, 1H), 7.28 (t, J = 7.3 Hz, 2H), 7.19 (d, J = 7.6 Hz, 3H), 5.10 (s, 1H), 3.49 (s, 3H), 2.21 (s, 3H).

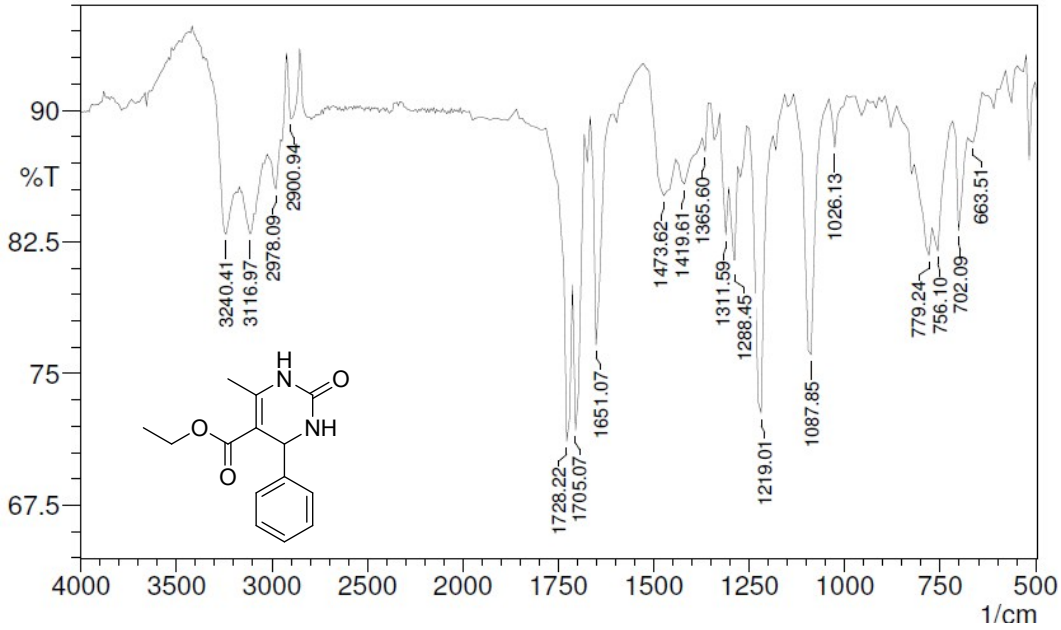
v) 7,7-Dimethyl-4-phenyl-3,4,7,8-tetrahydroquinazoline-2,5(1*H*,6*H*)-dione (entry 22)[8,9]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.42 (s, 1H), 7.72 (s, 1H), 7.31 – 7.07 (m, 5H), 5.11 (s, 1H), 2.41 – 1.91 (m, 4H), 0.97 (s, 3H), 0.85 (s, 3H).

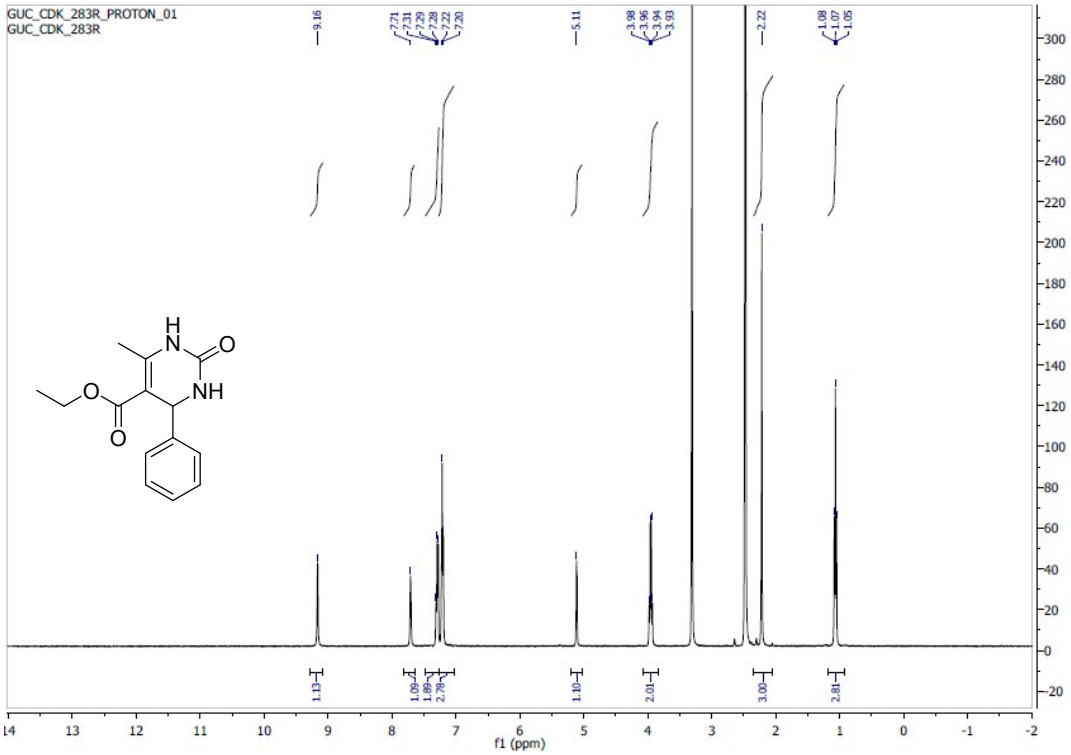
3. Copies of FTIR and ^{1}H NMR spectra of synthesized compounds

Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 1)

FTIR :



^{1}H NMR (DMSO-d_6, 400 MHz):



Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 2)

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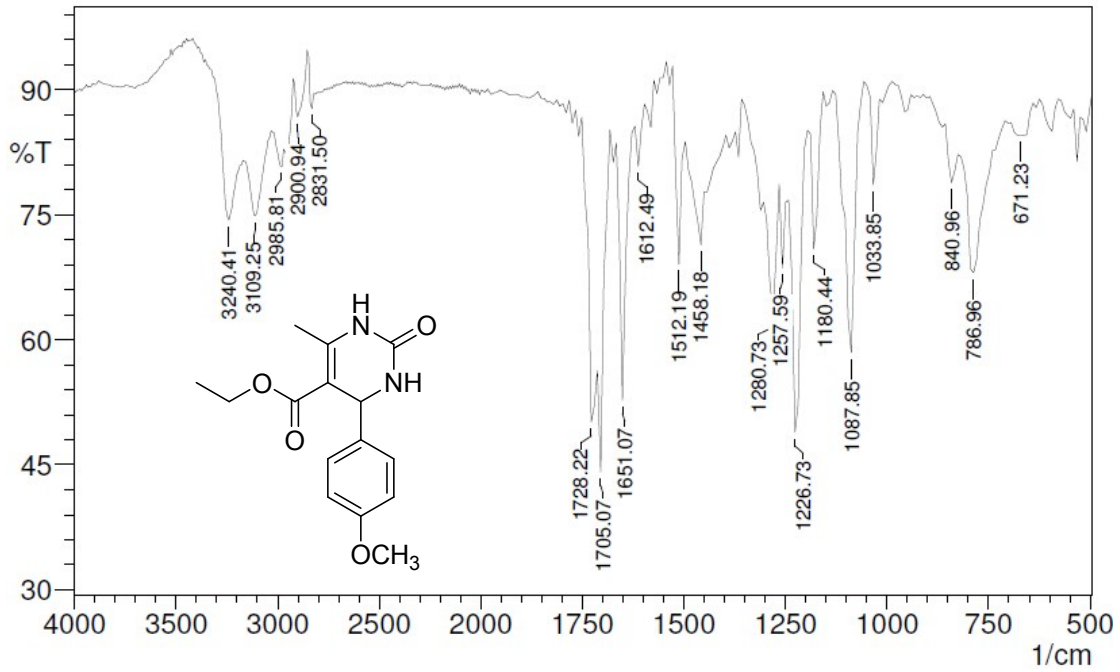
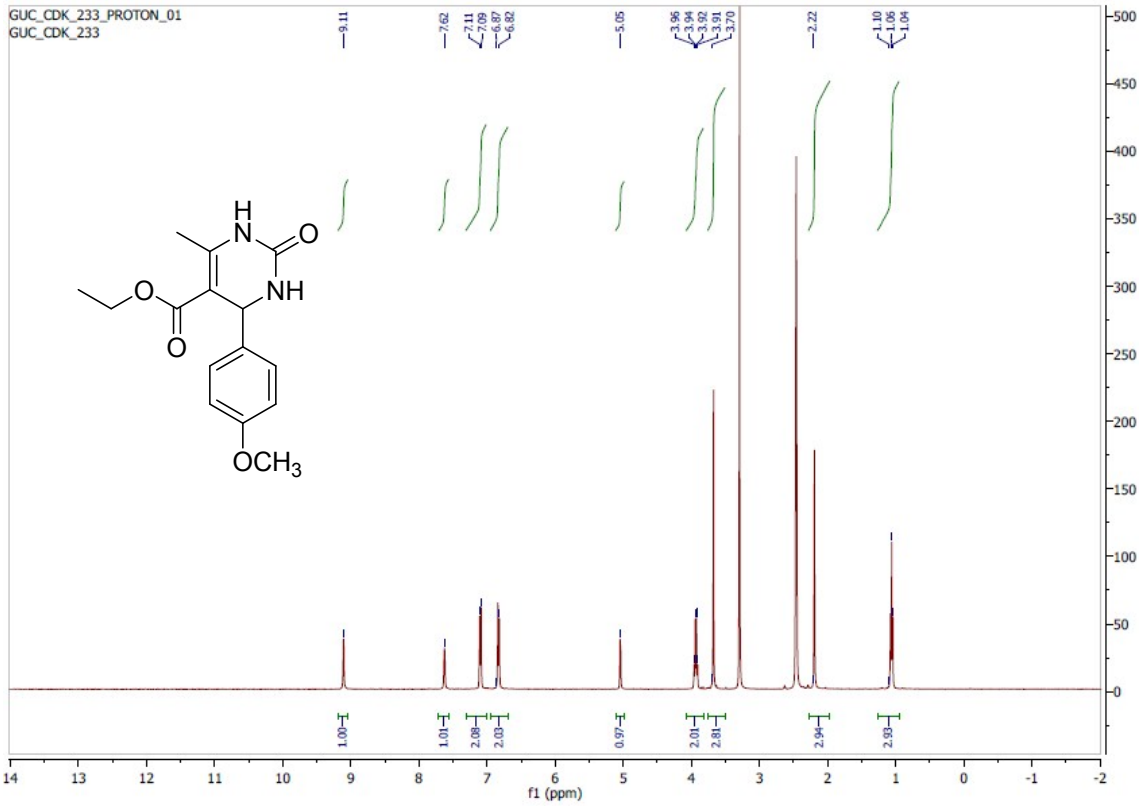
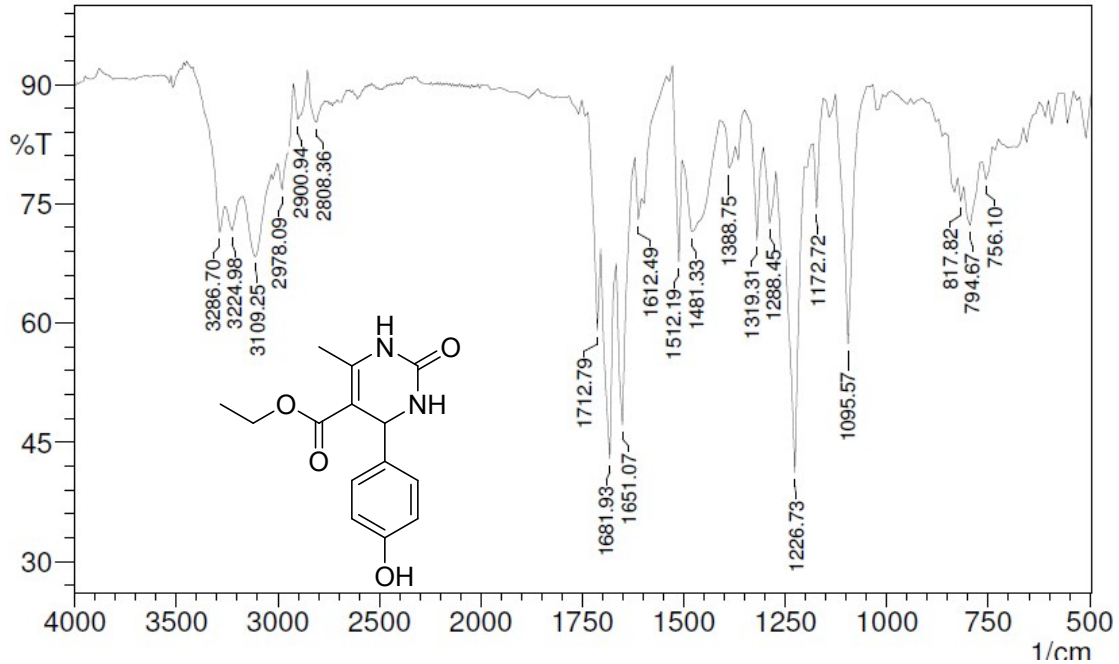


^{1}H NMR (DMSO-d_6, 400 MHz):

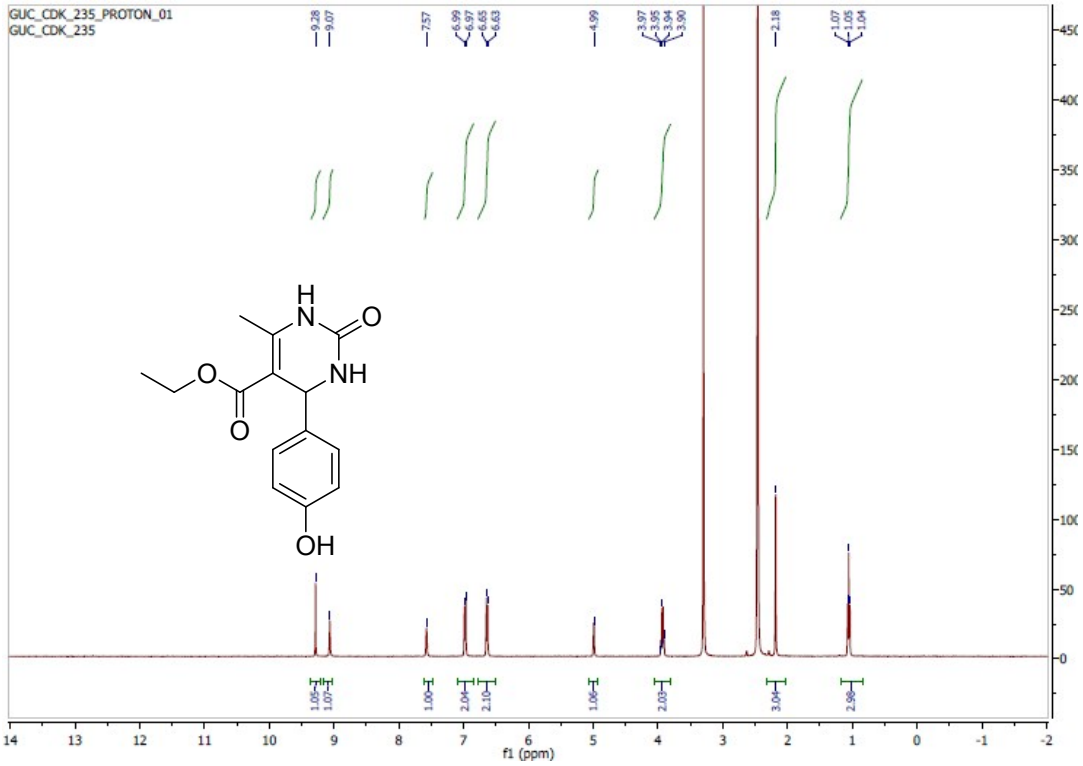


Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 3)

FTIR:



^{1}H NMR (DMSO-d_6, 400 MHz):



Ethyl 4-(4-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 4)

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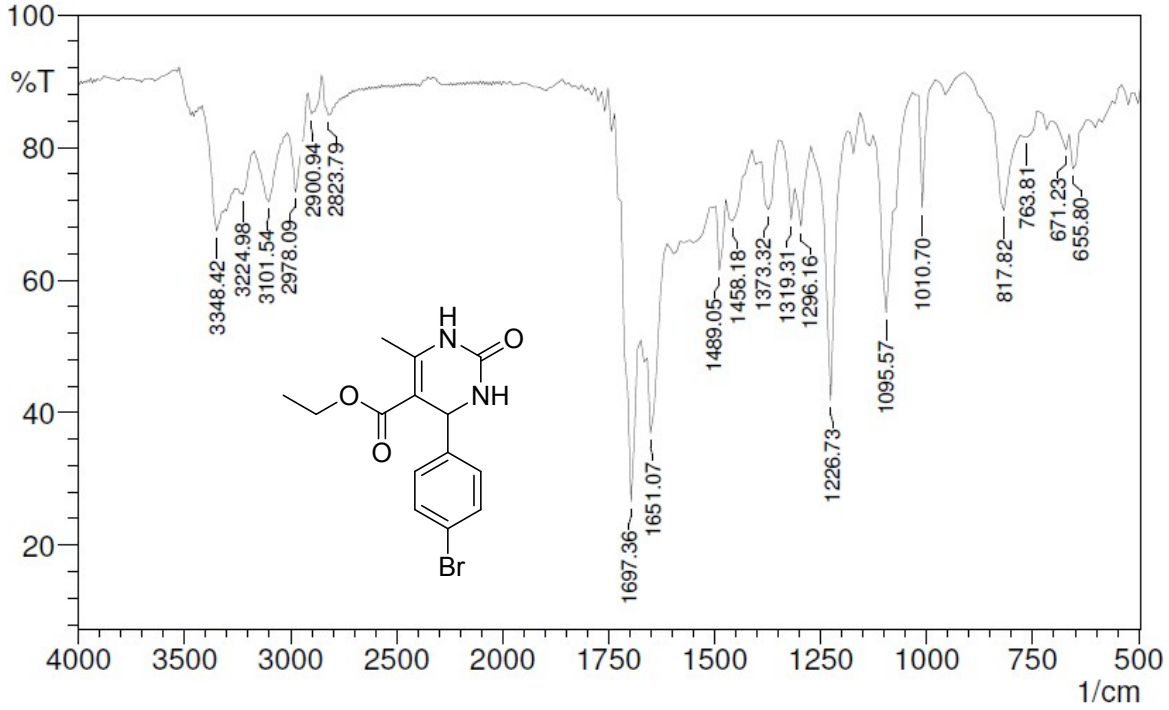
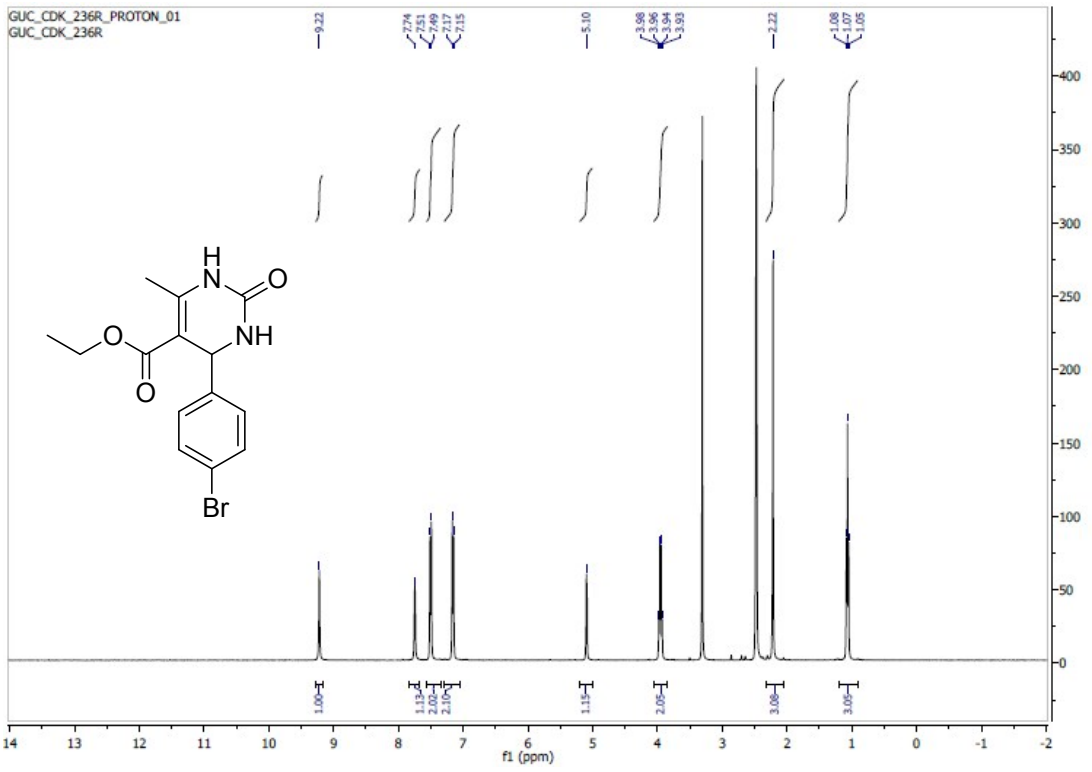
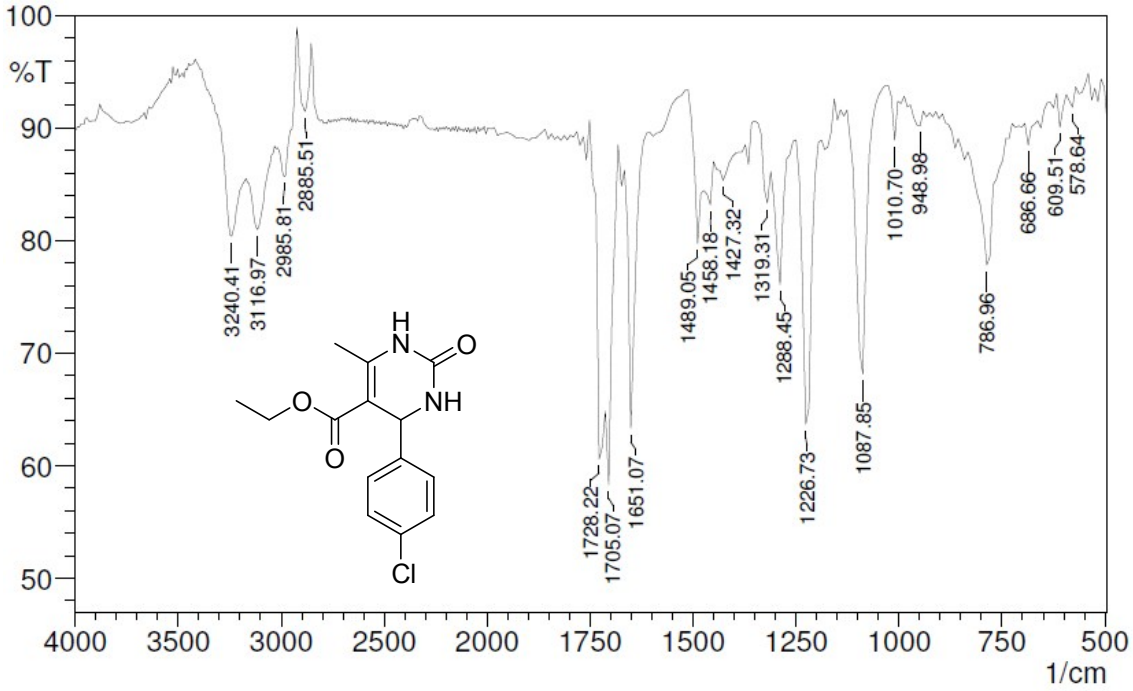


^{1}H NMR (DMSO-d_6, 400 MHz):

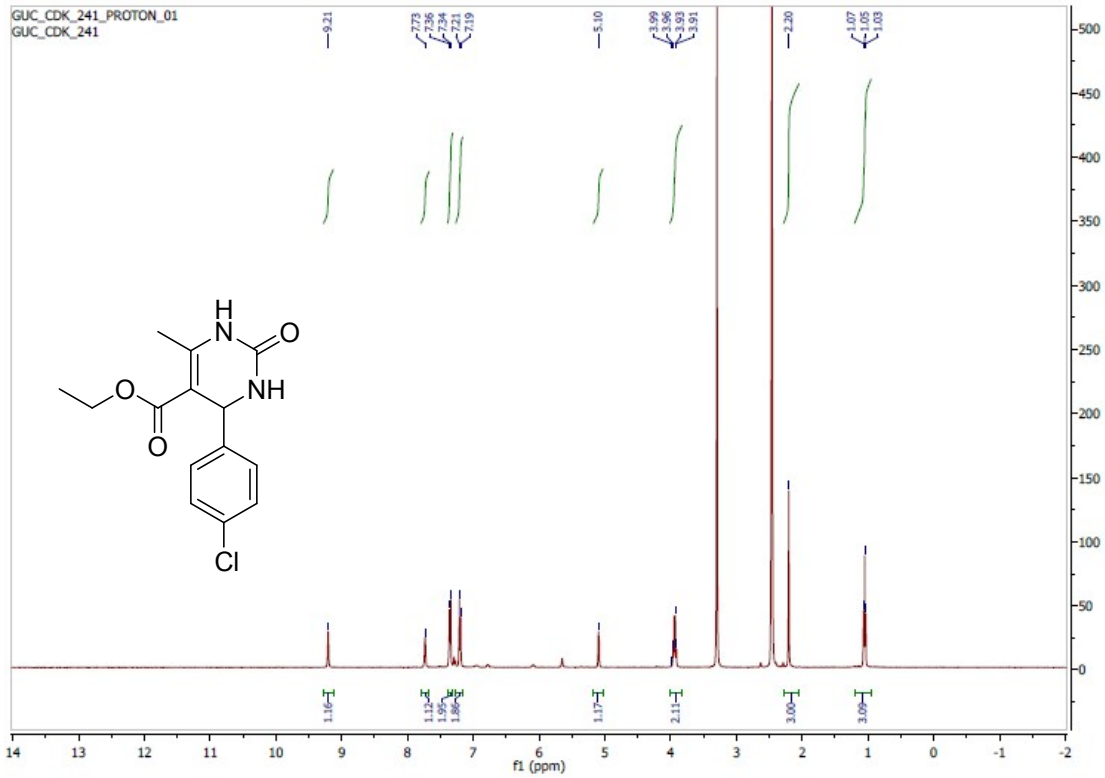


Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 5)

FTIR:

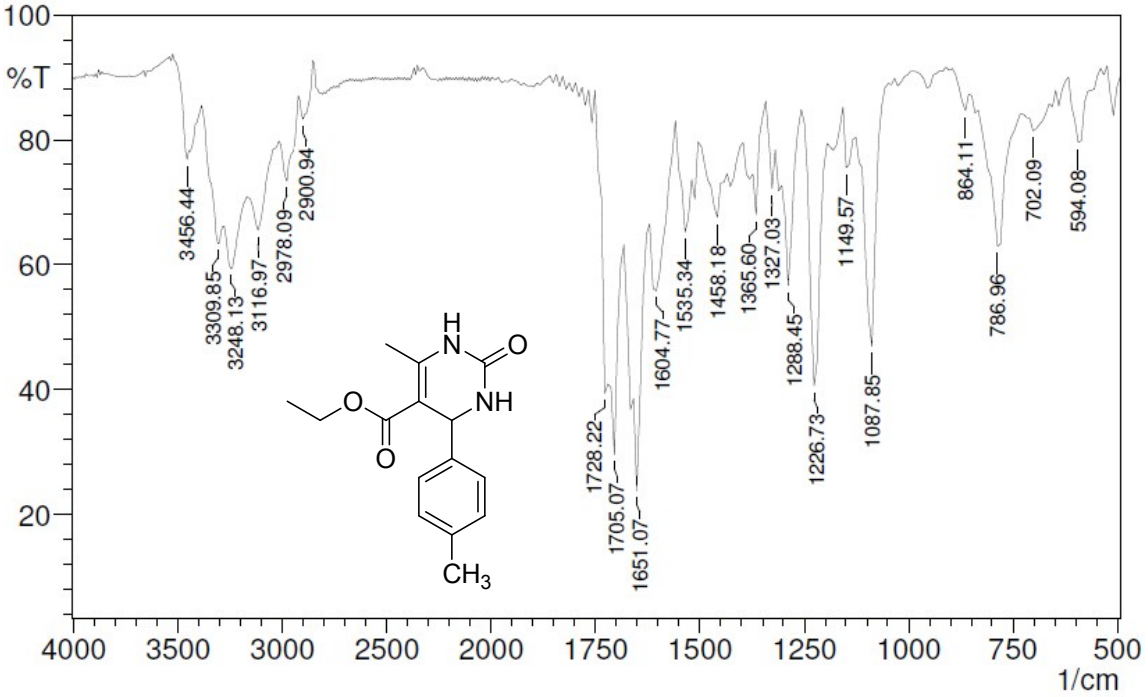


^{1}H NMR (DMSO-d_6, 400 MHz):

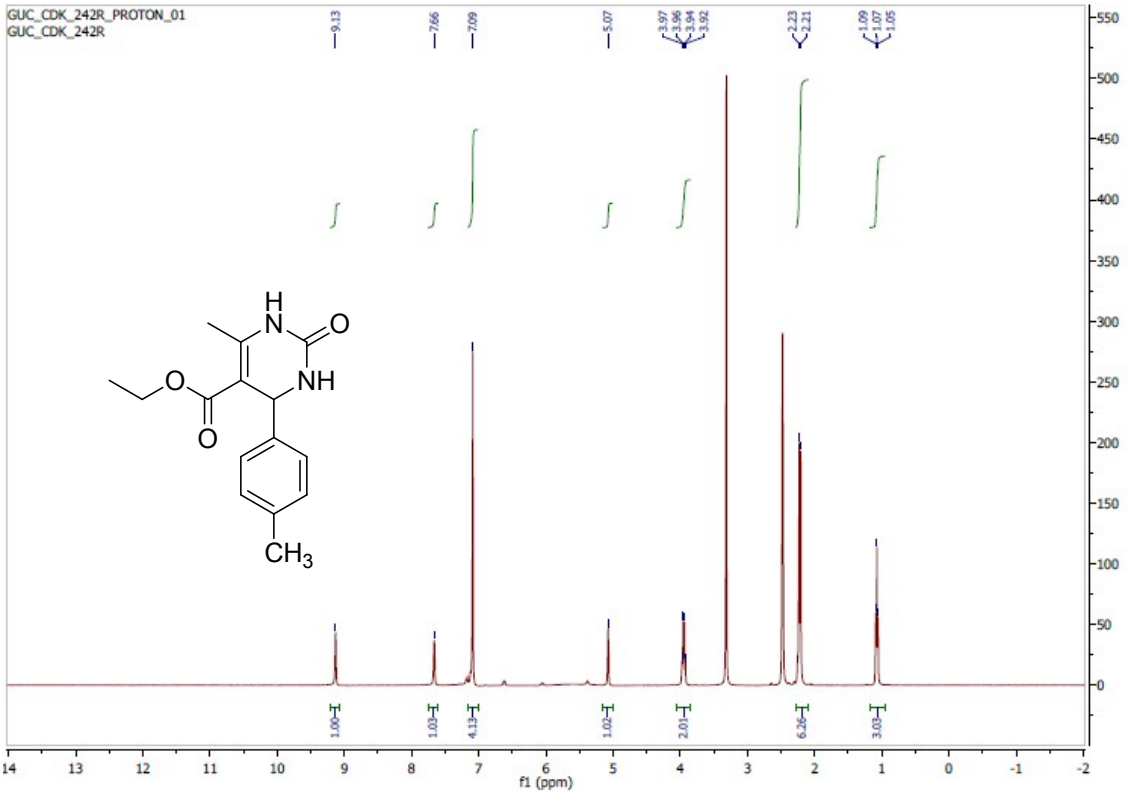


Ethyl 4-(4-methylphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 6)

FTIR:

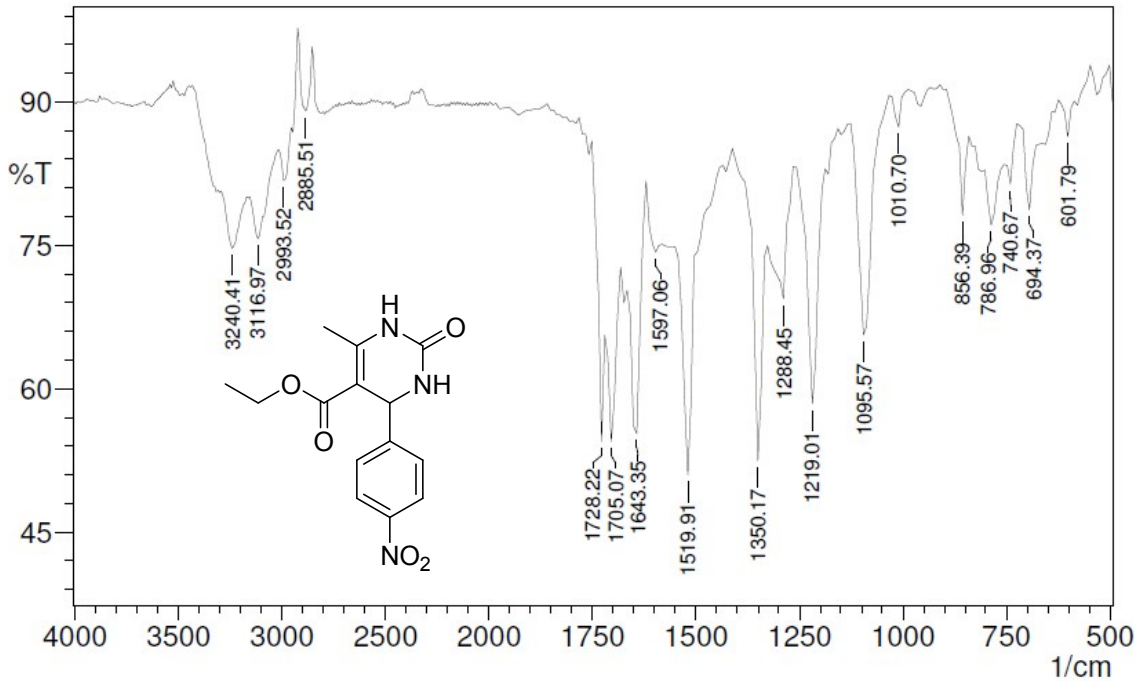


^{1}H NMR (DMSO-d_6, 400 MHz):

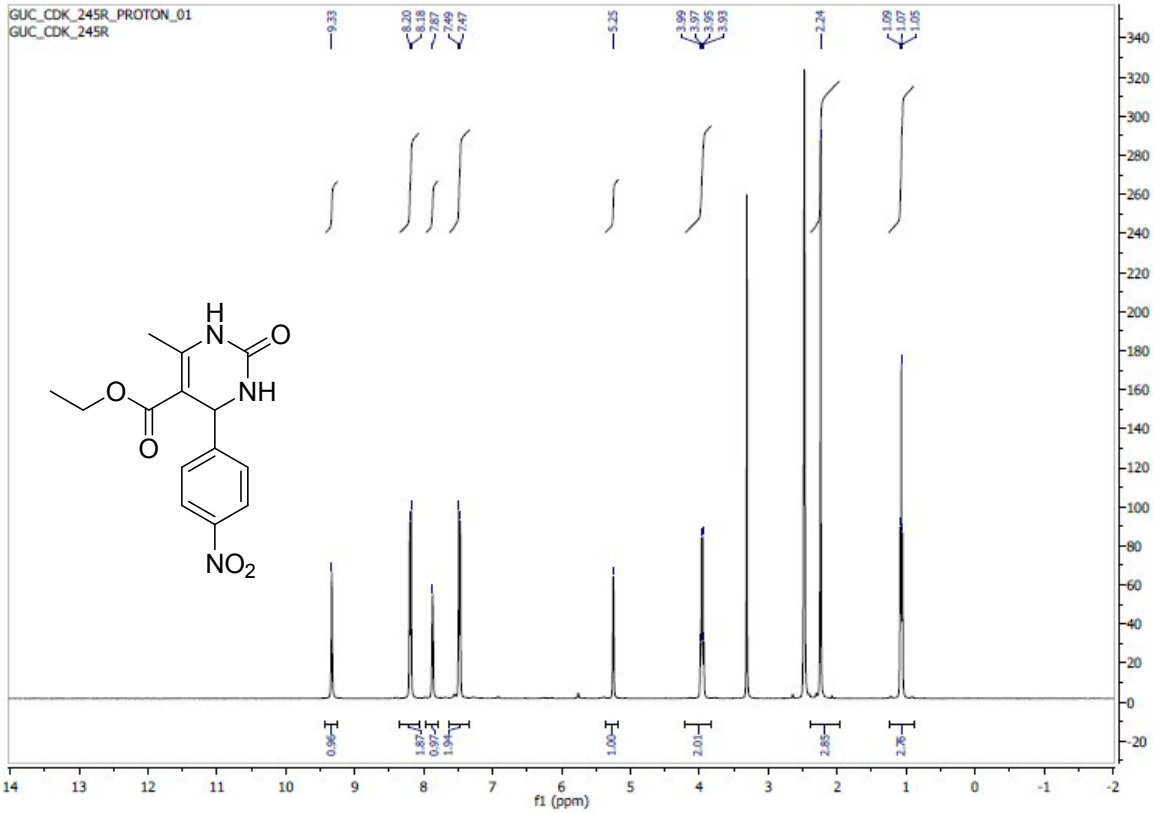


Ethyl 4-(4-nitrophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 7)

FTIR:

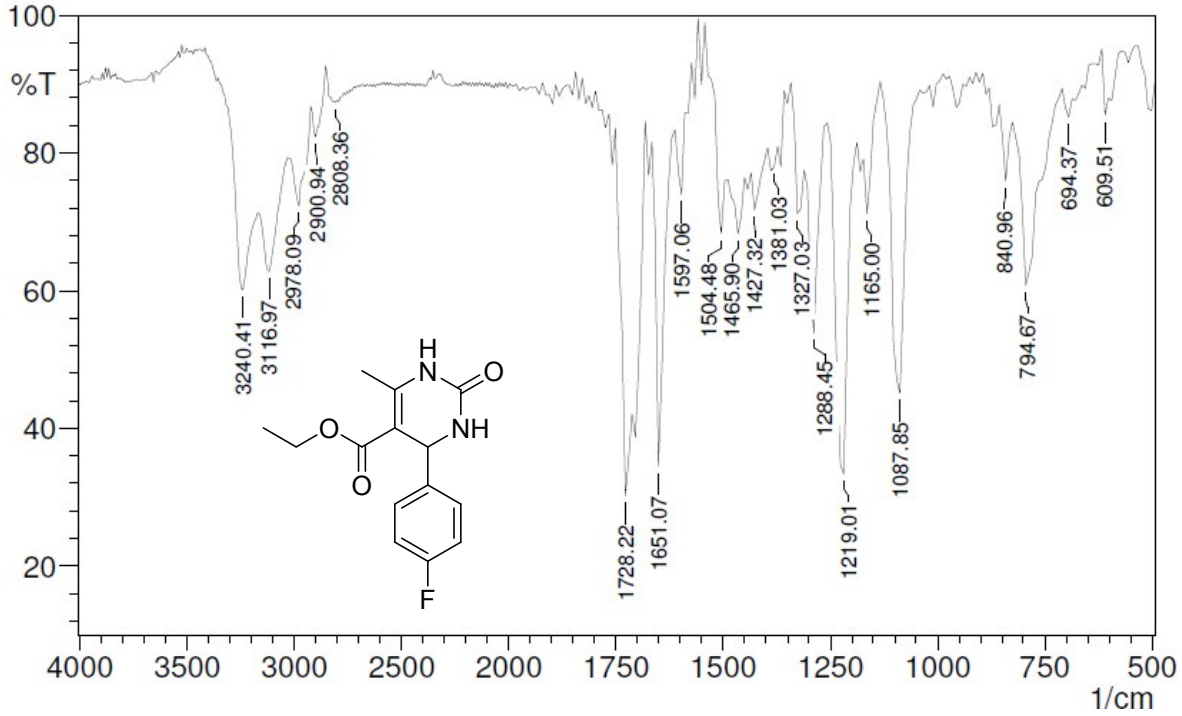


^{1}H NMR (DMSO-d_6, 400 MHz):

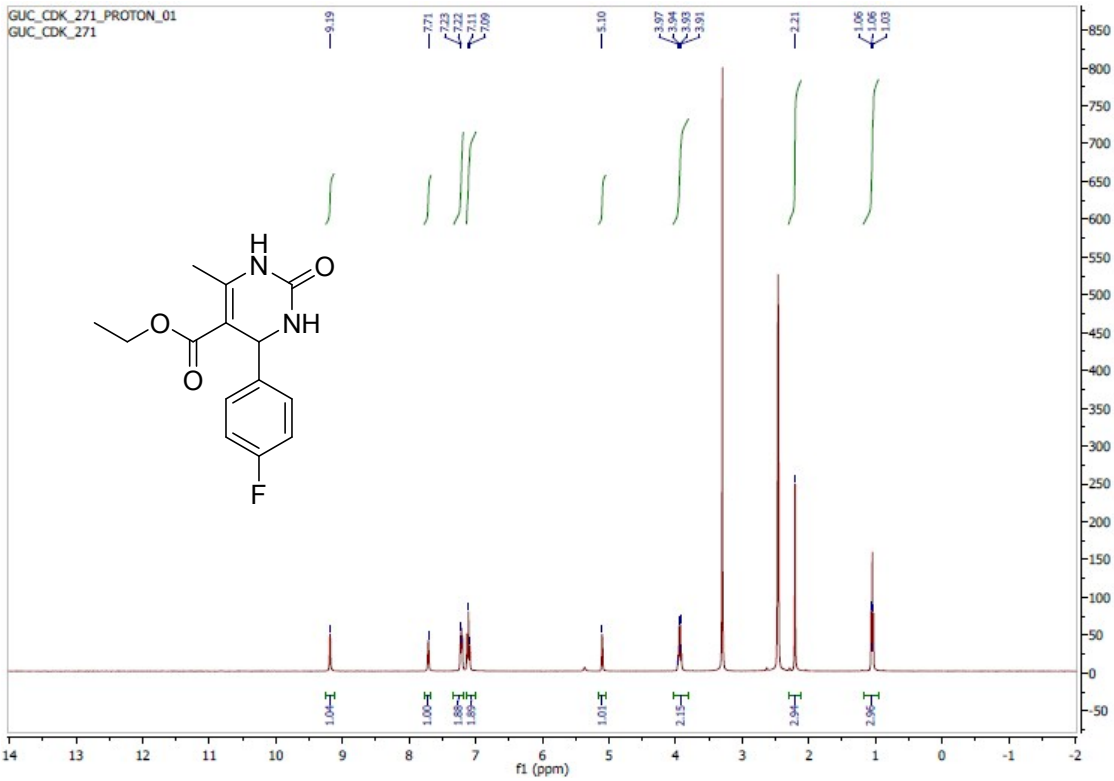


Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 8)

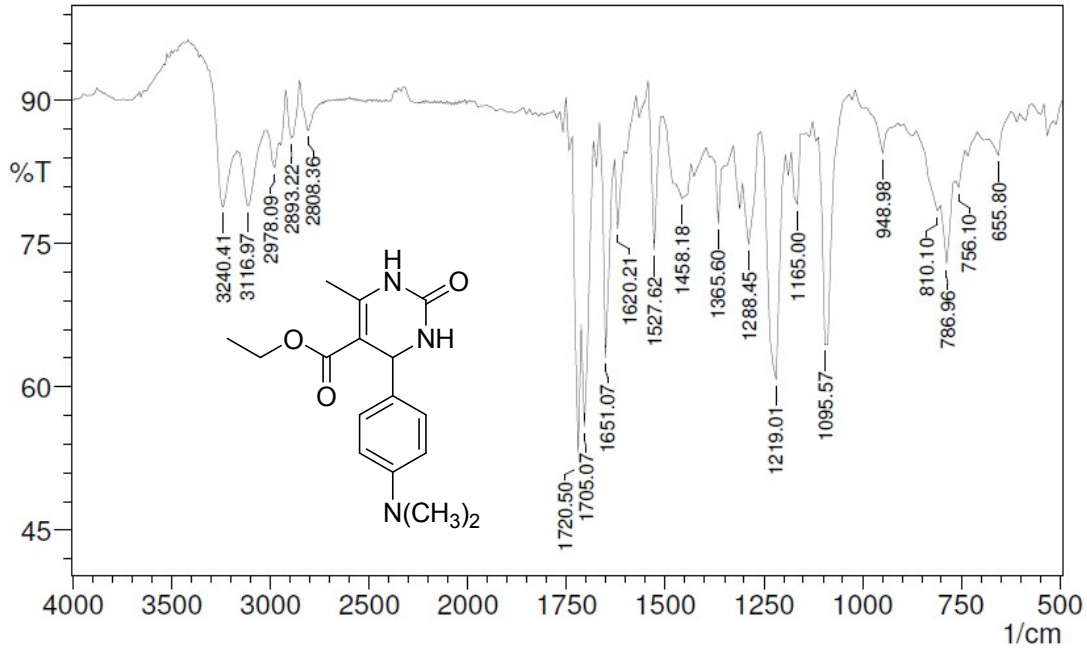
FTIR:



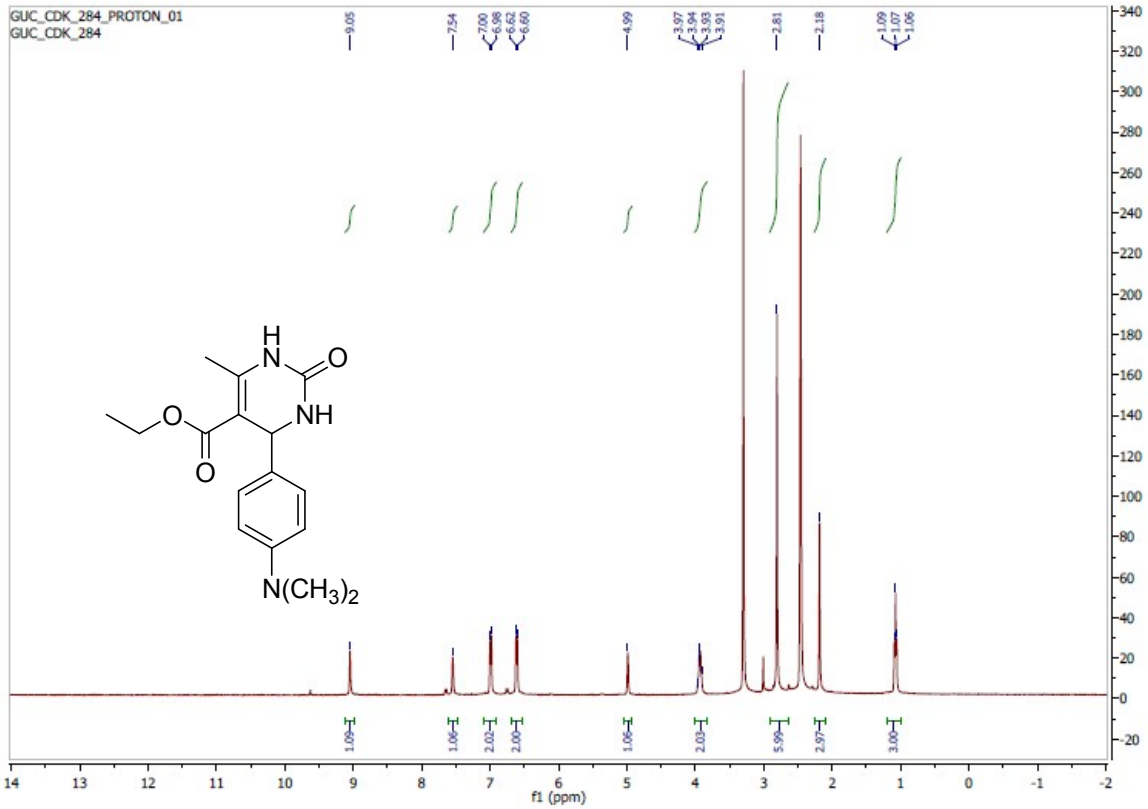
^{1}H NMR (DMSO-d_6, 400 MHz):



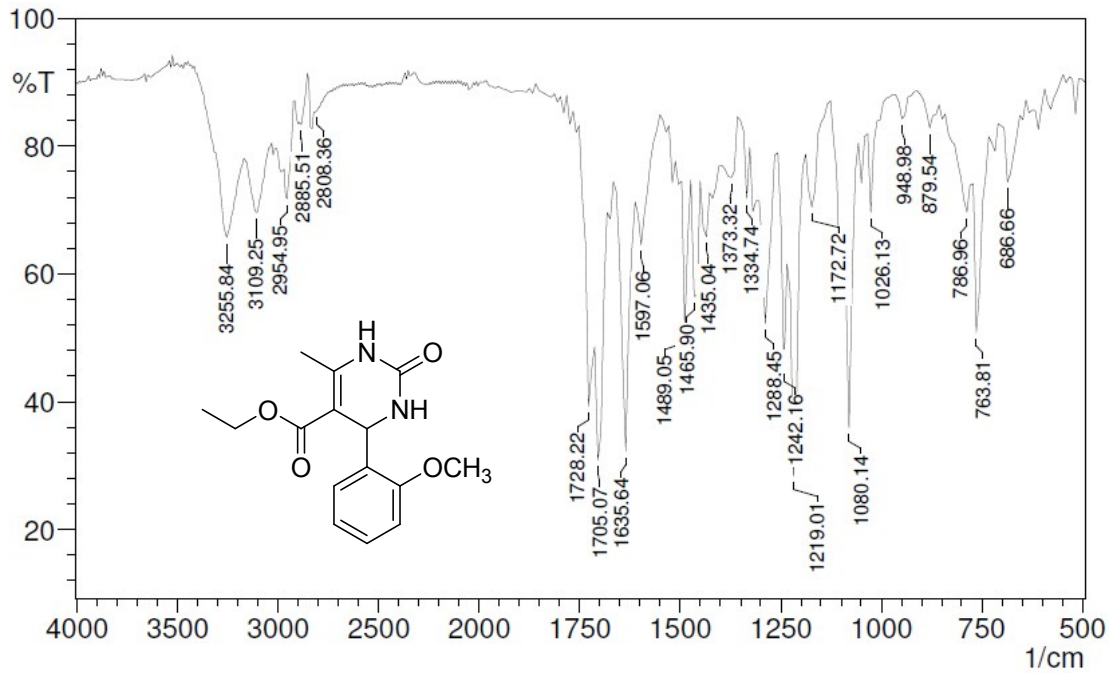
Ethyl 4-(4-(dimethylamino)phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 9) FTIR:



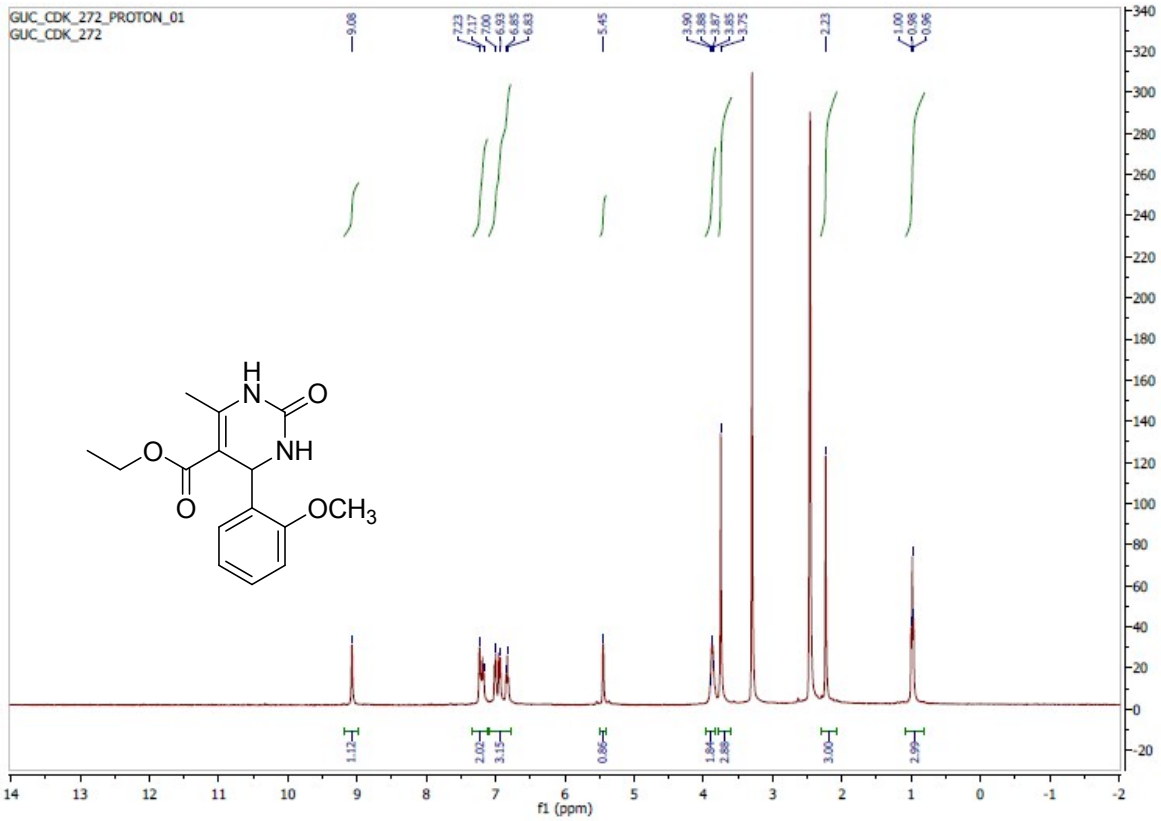
^{1}H NMR (DMSO-d_6, 400 MHz):



Ethyl 4-(2-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 10) FTIR:

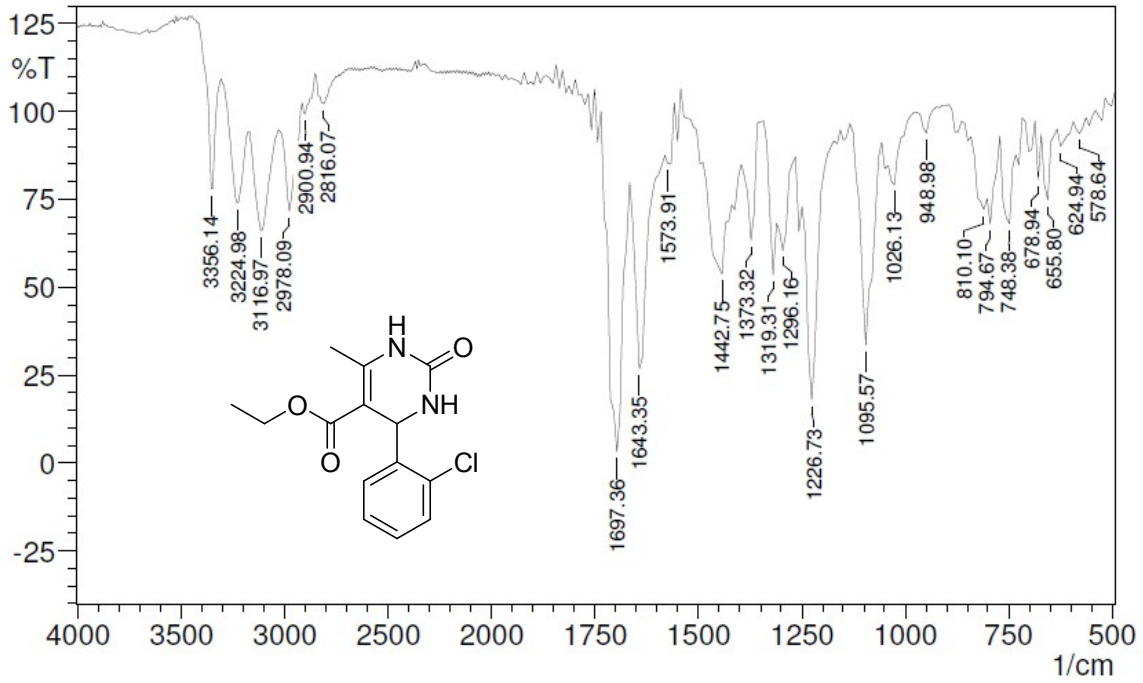


^{1}H NMR (DMSO-d_6, 400 MHz):

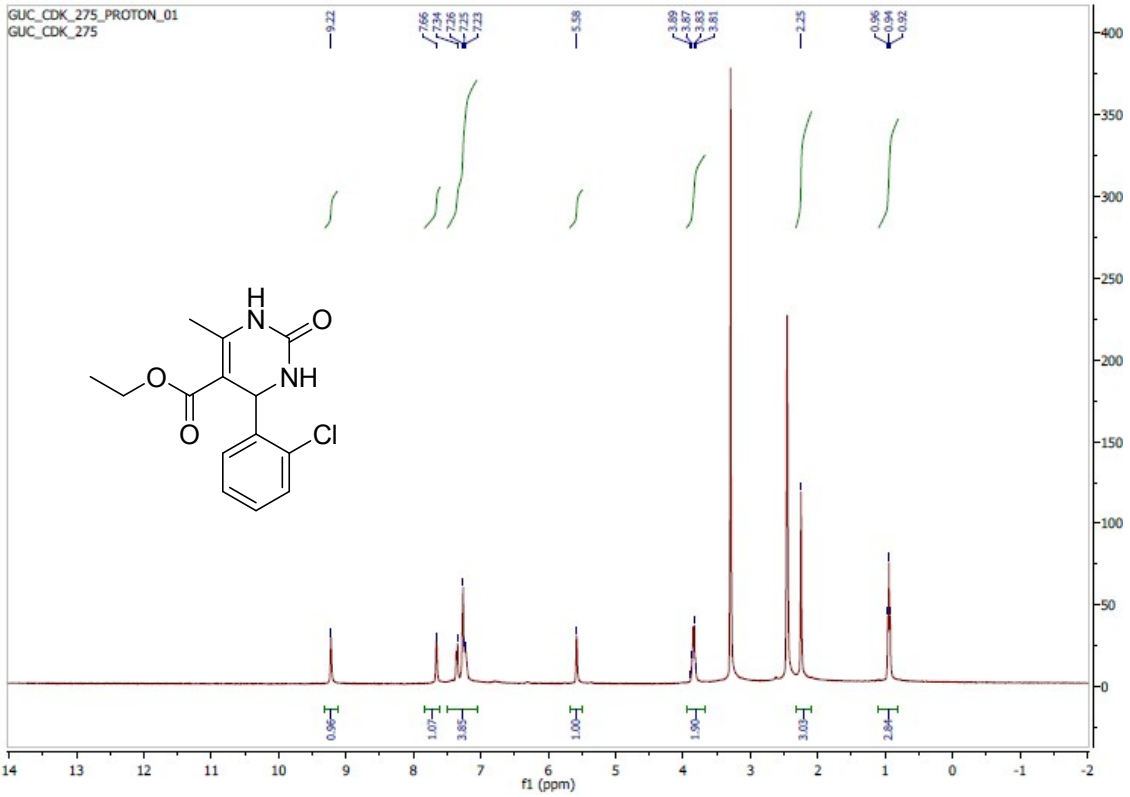


Ethyl 4-(2-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 11)

FTIR:

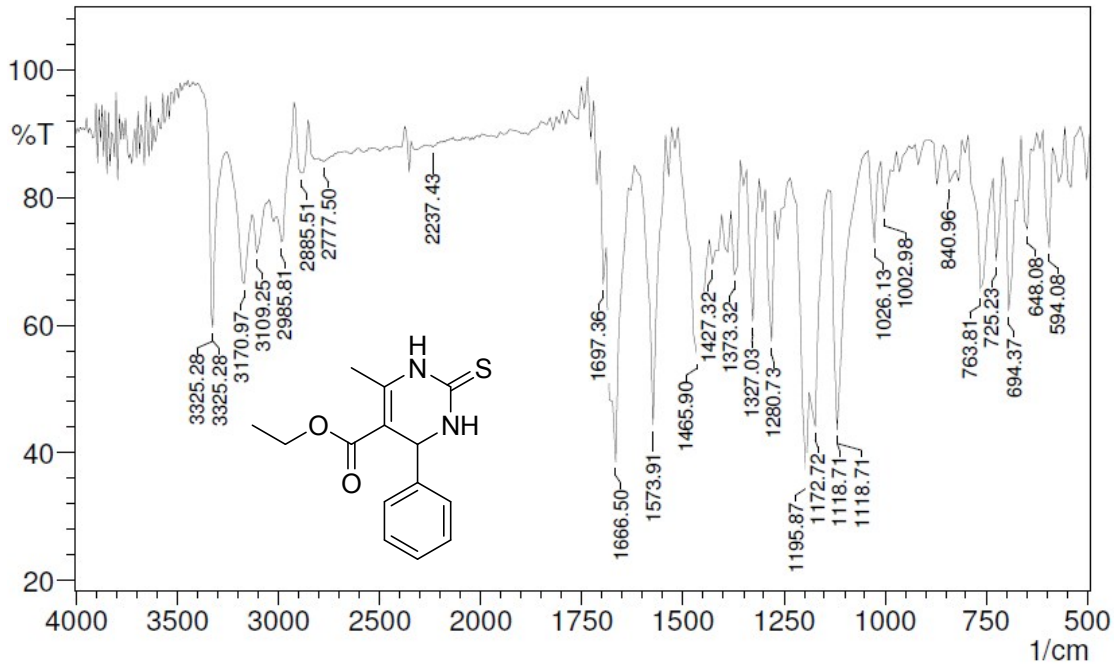


^{1}H NMR (DMSO-d_6, 400 MHz):

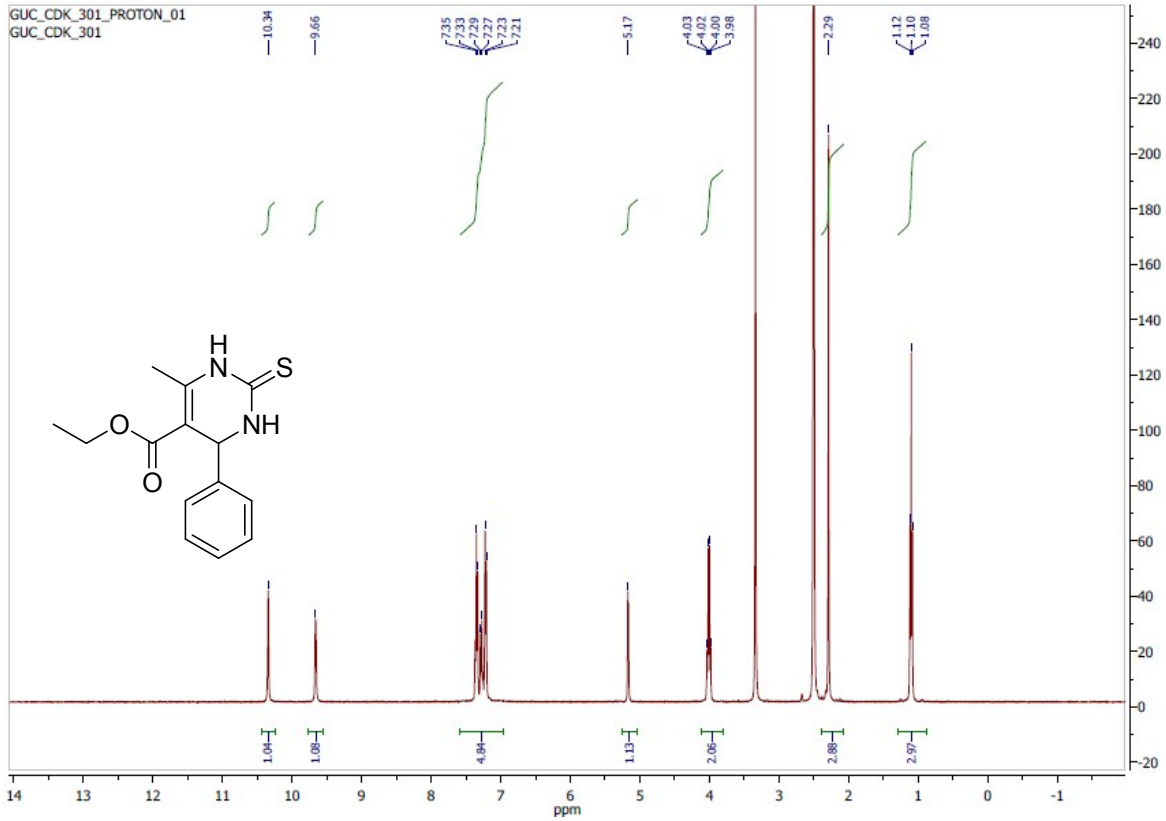


Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 12)

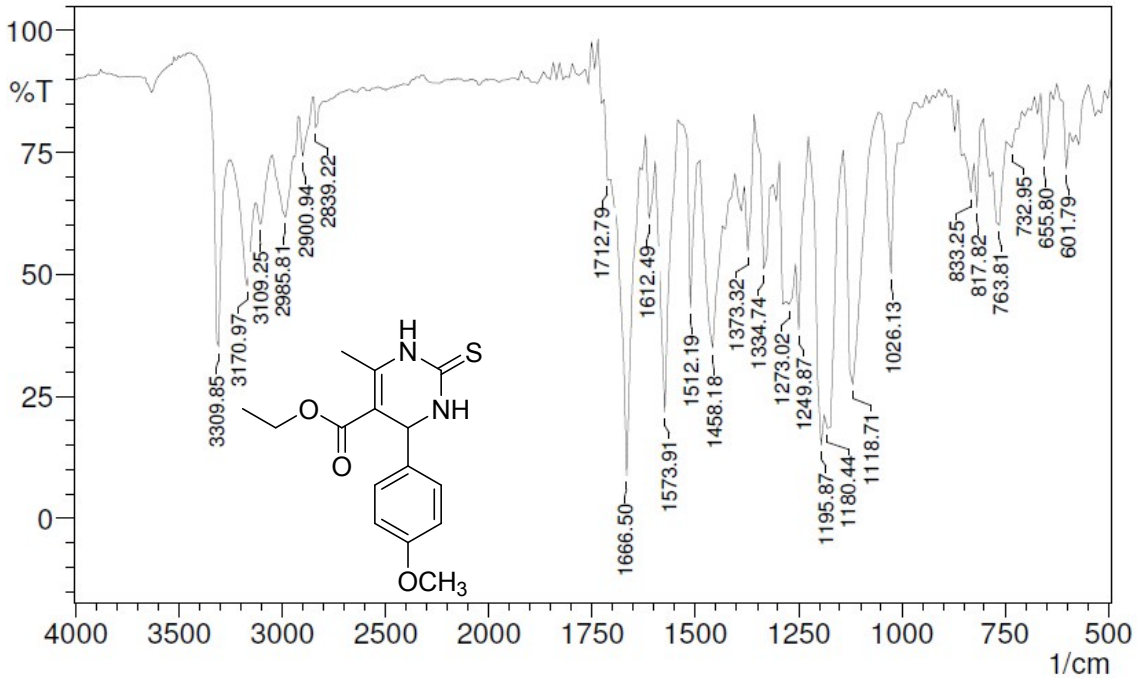
FTIR:



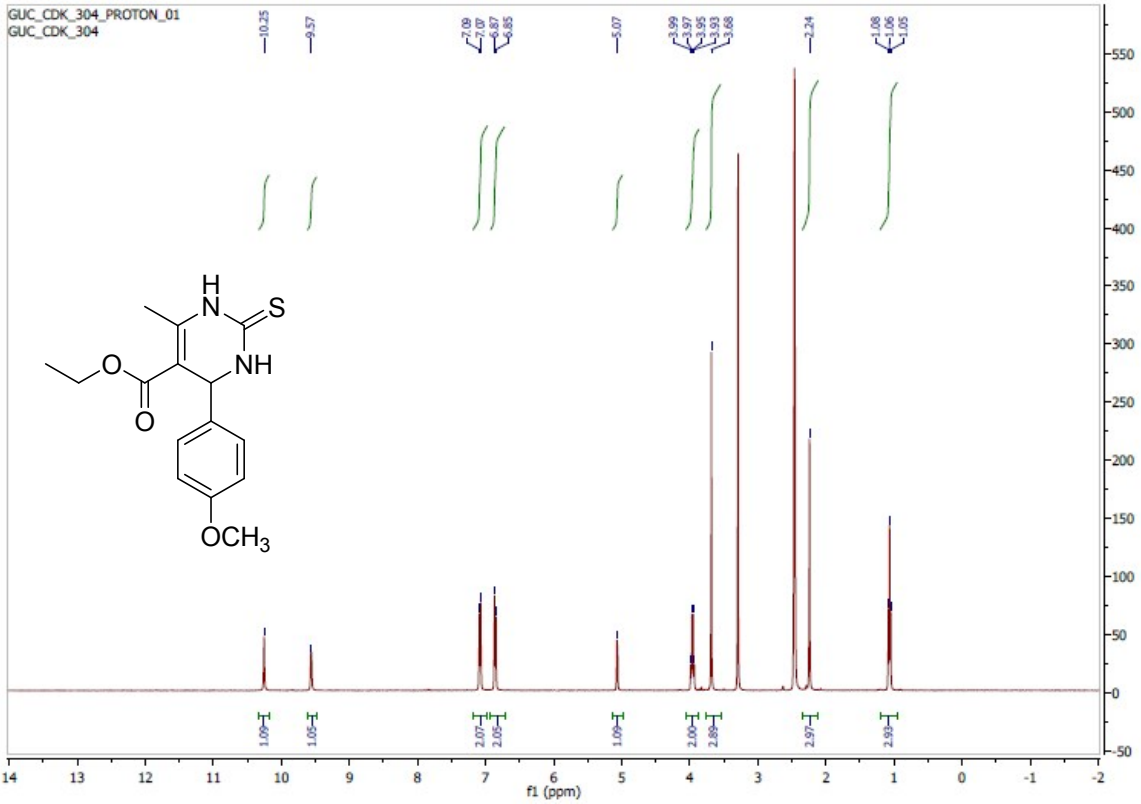
^{1}H NMR (DMSO-d_6, 400 MHz):



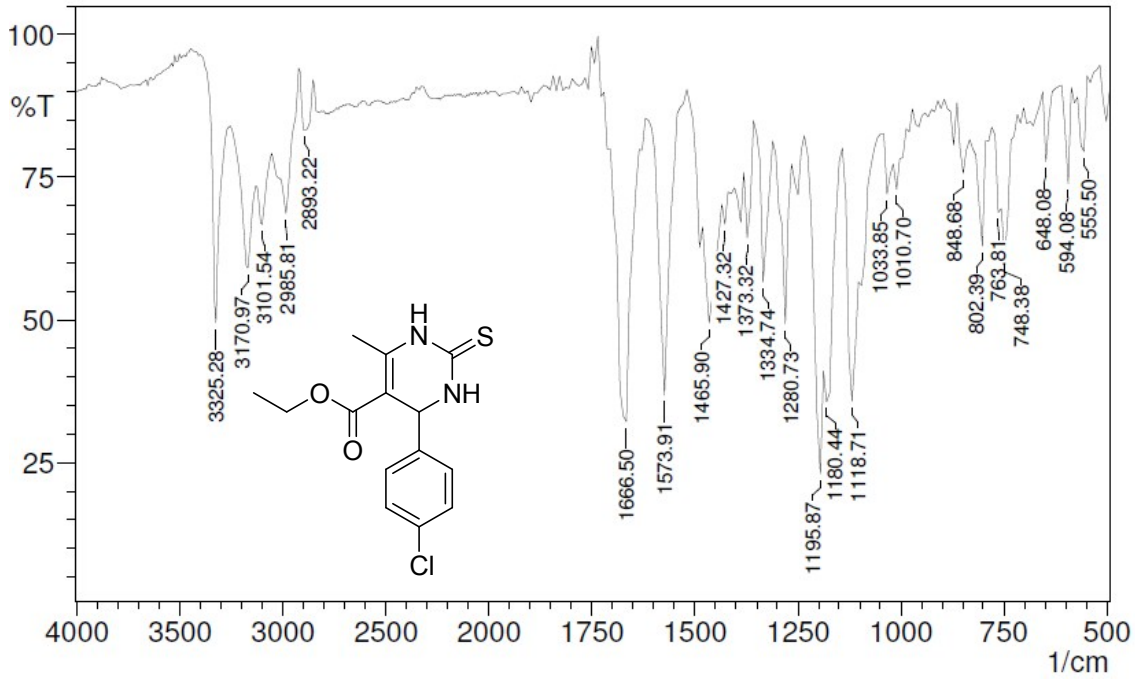
Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 13) FTIR:



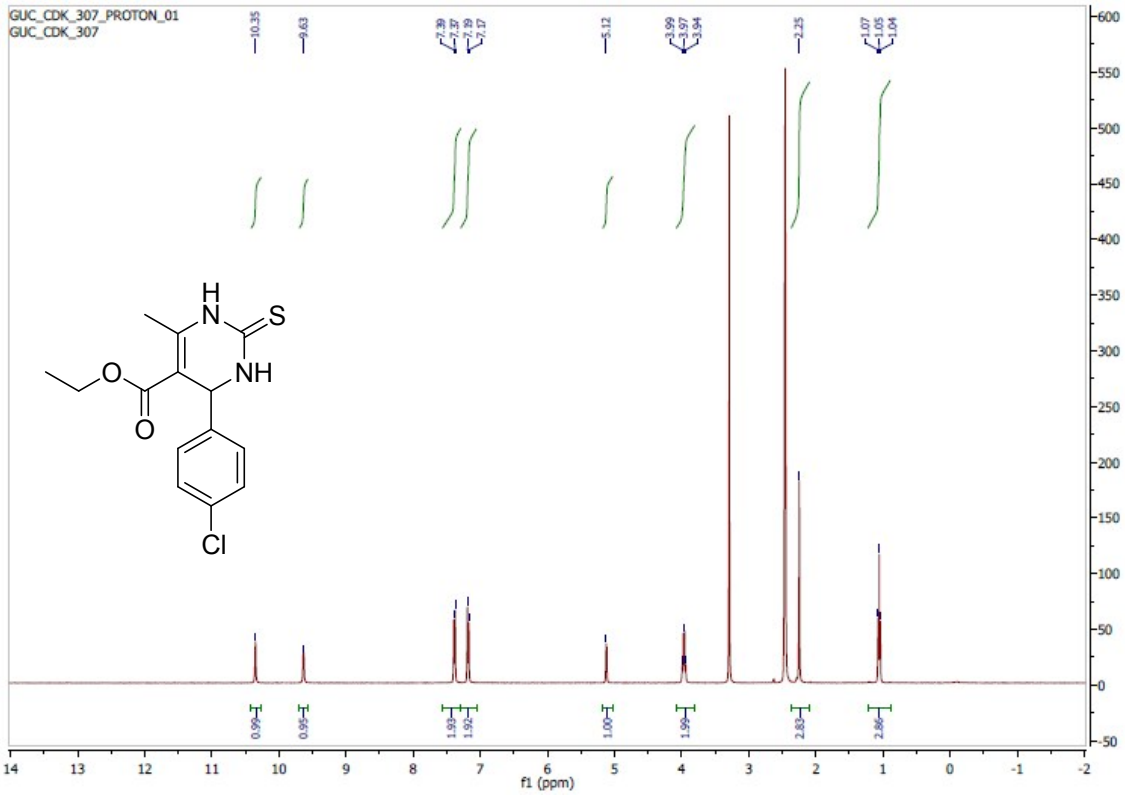
^{1}H NMR (DMSO-d_6, 400 MHz):



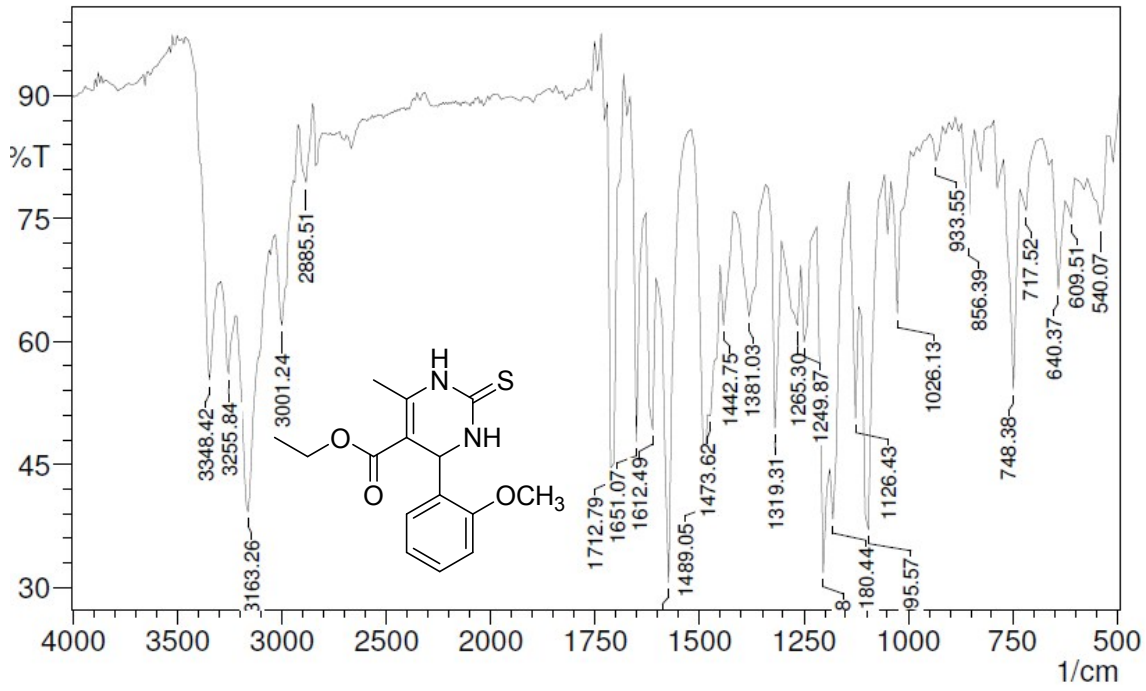
Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 14) FTIR:



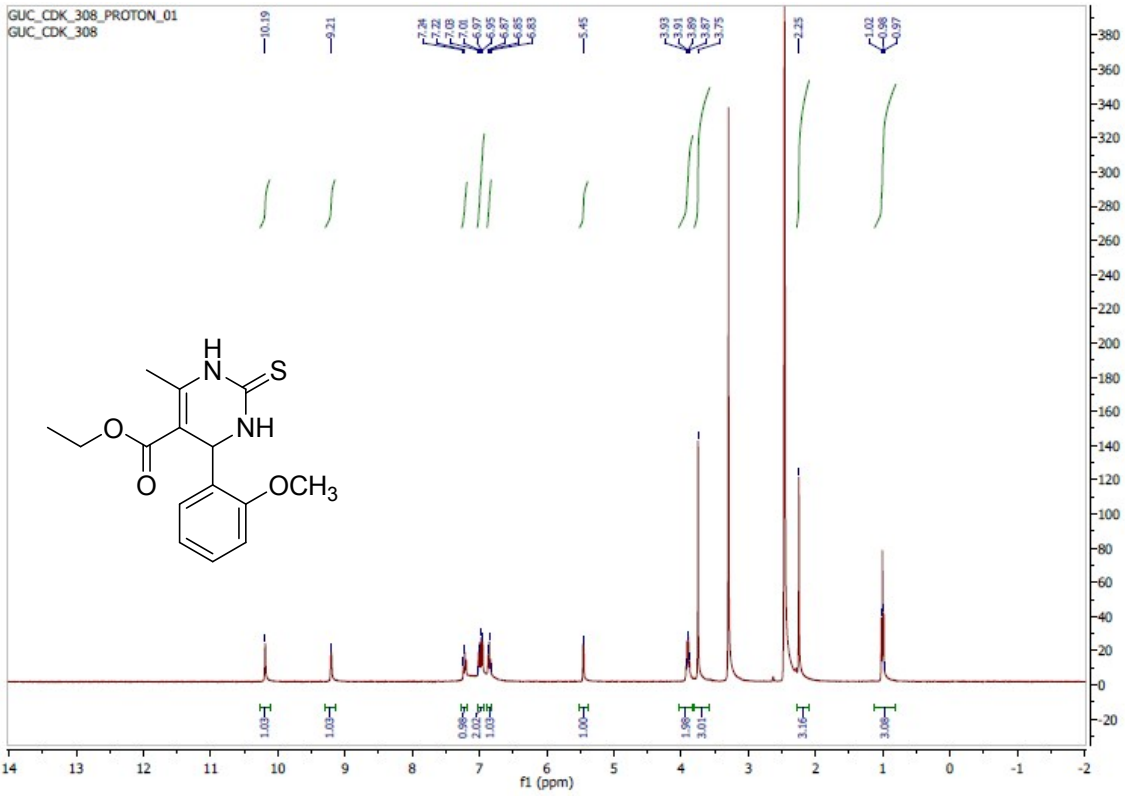
^{1}H NMR (DMSO-d_6, 400 MHz):



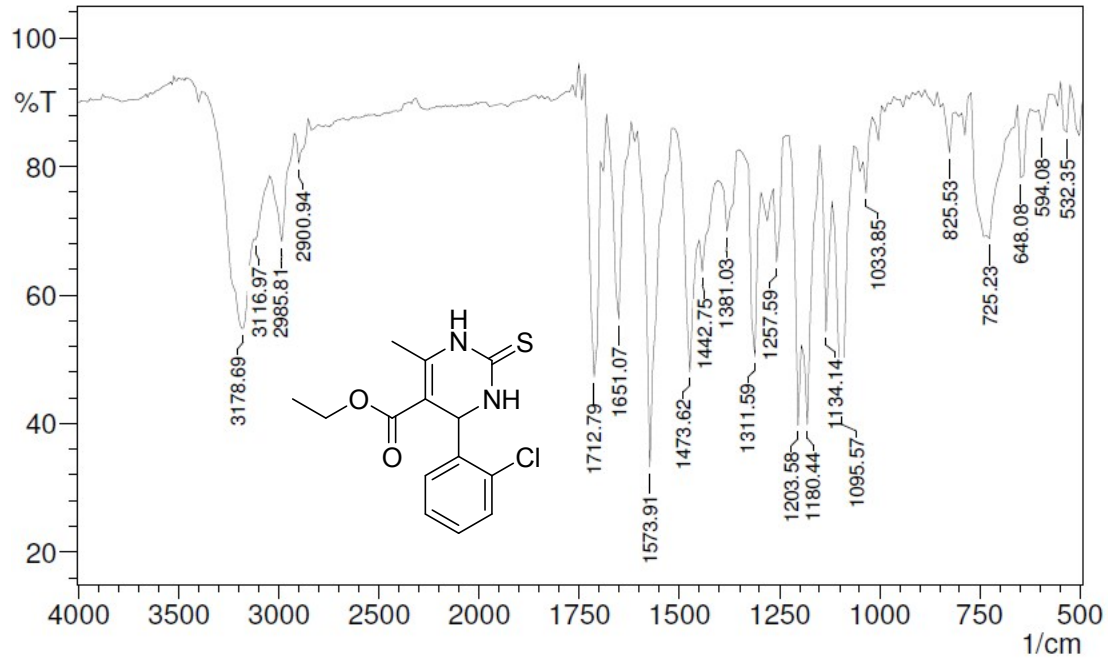
Ethyl 4-(2-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 15) FTIR:



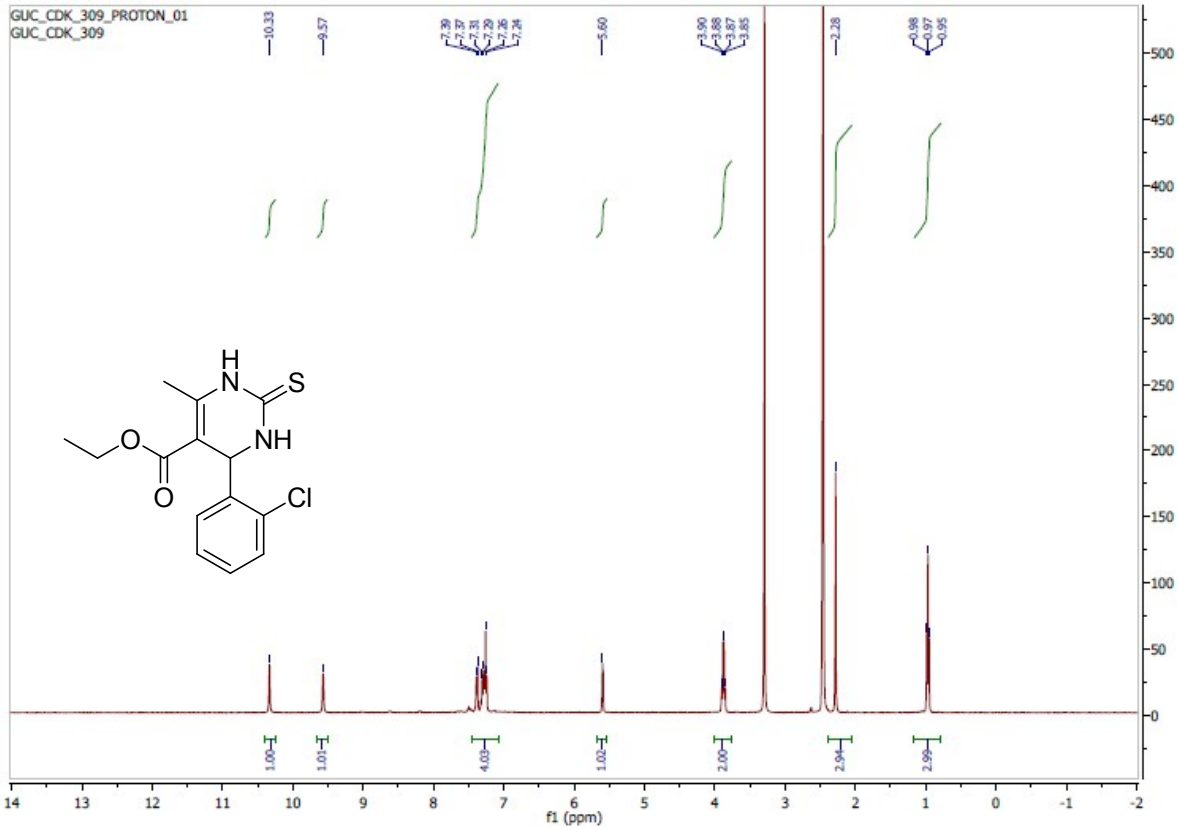
^{1}H NMR (DMSO-d_6, 400 MHz):



Ethyl 4-(2-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 16) FTIR:

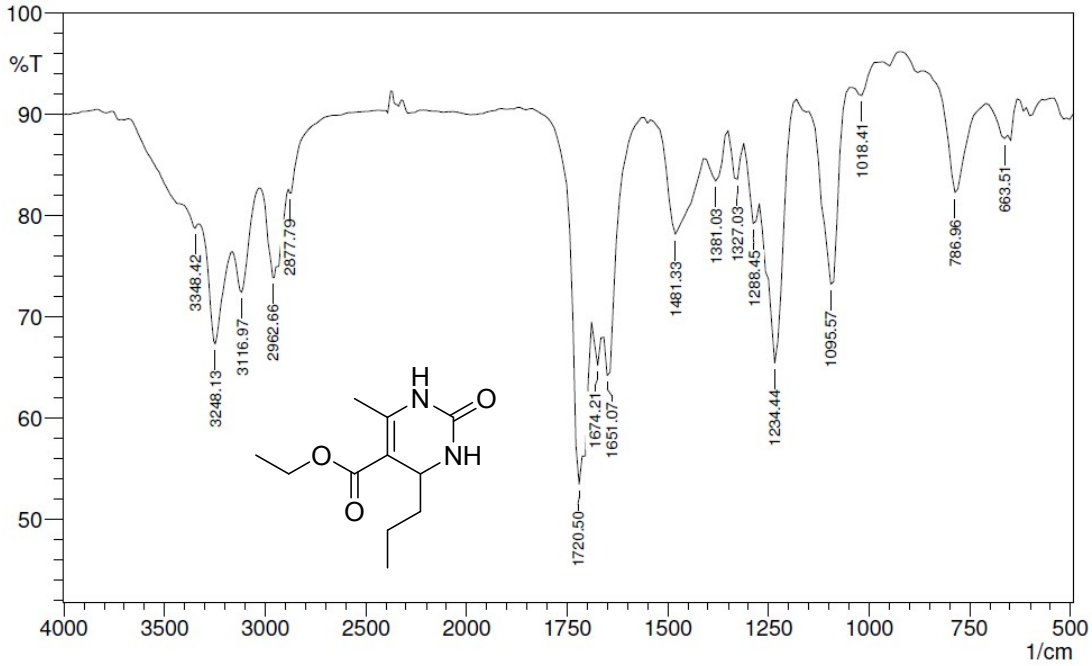


^{1}H NMR (DMSO-d_6, 400 MHz):

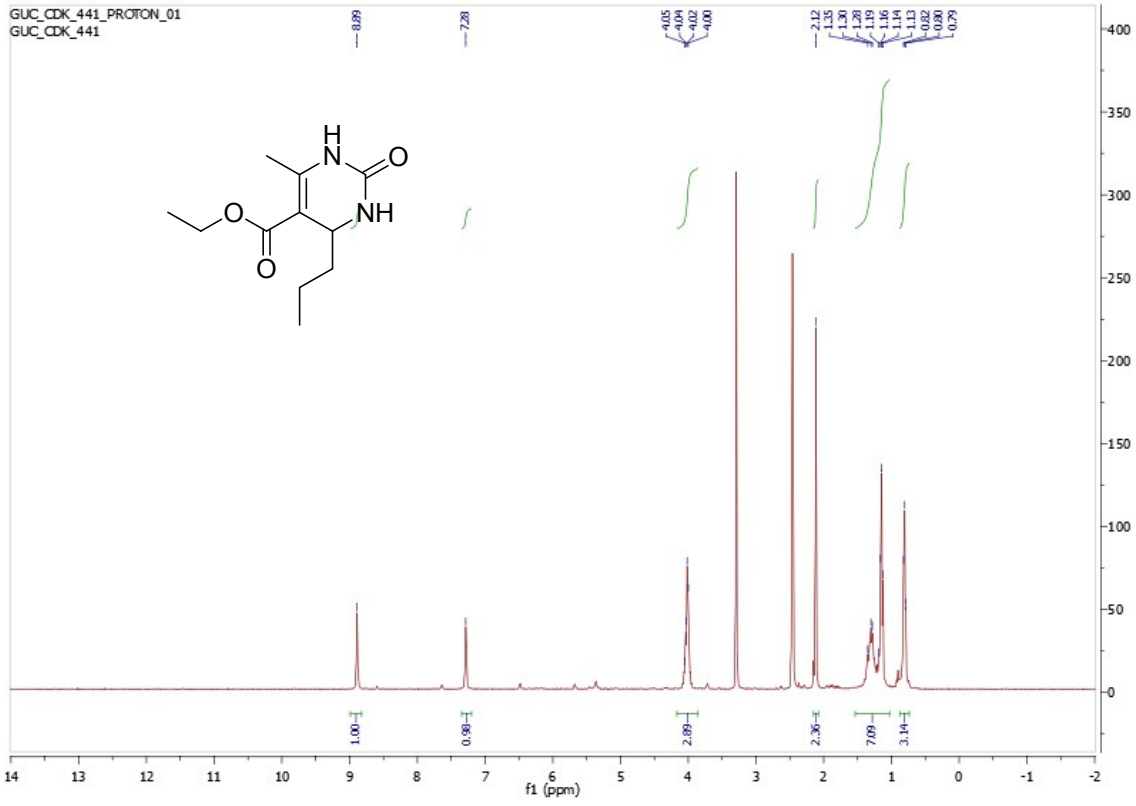


Ethyl 6-methyl-2-oxo-4-propyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 17):

FTIR:

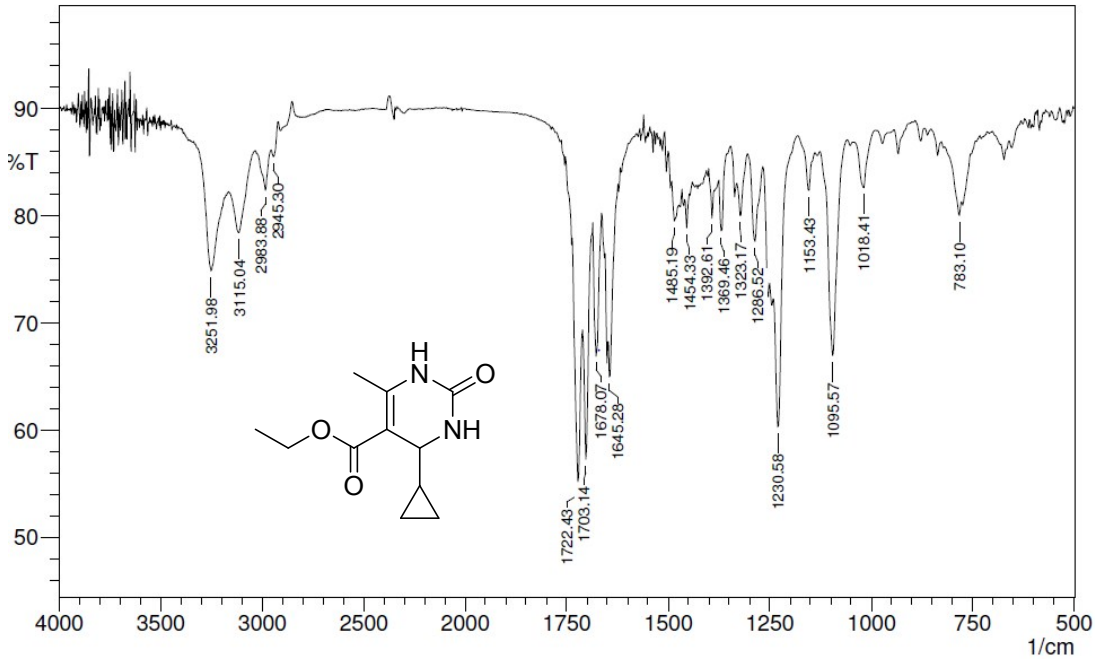


^{1}H NMR (DMSO-d_6, 400 MHz):

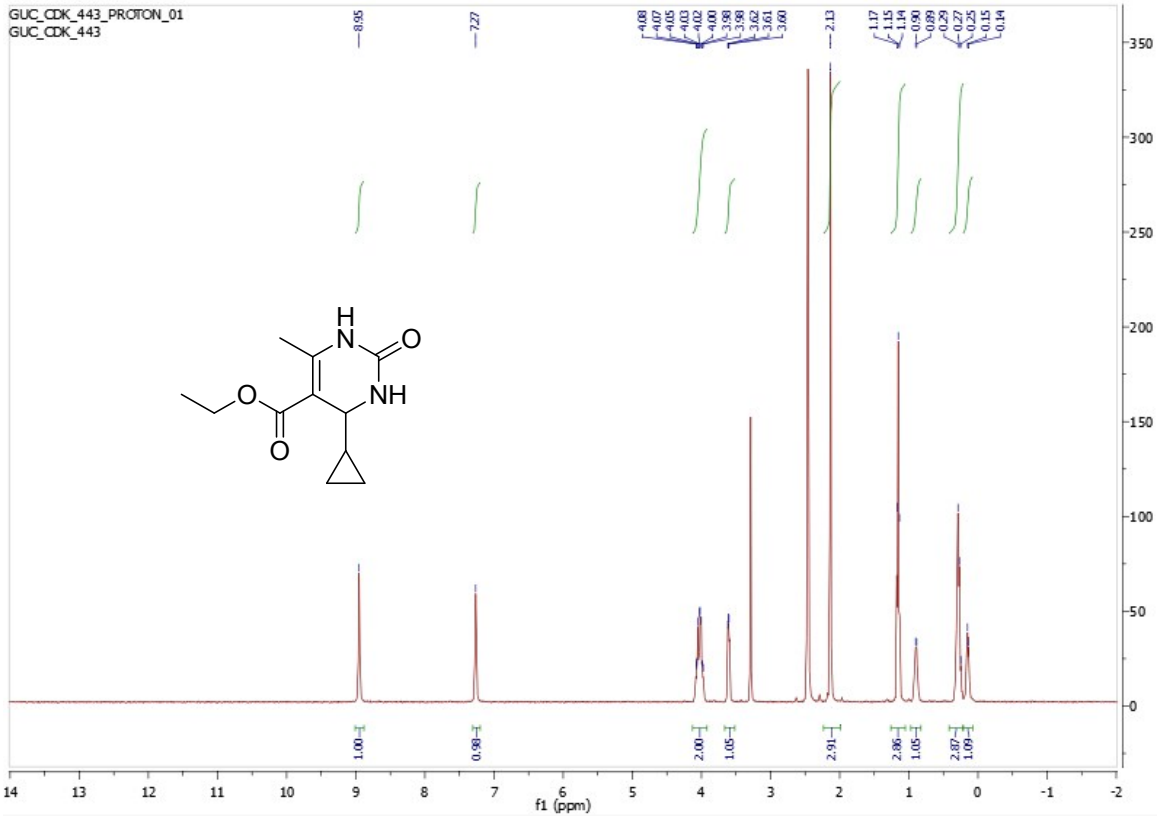


Ethyl 6-cyclopropyl-4-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 18):

FTIR:

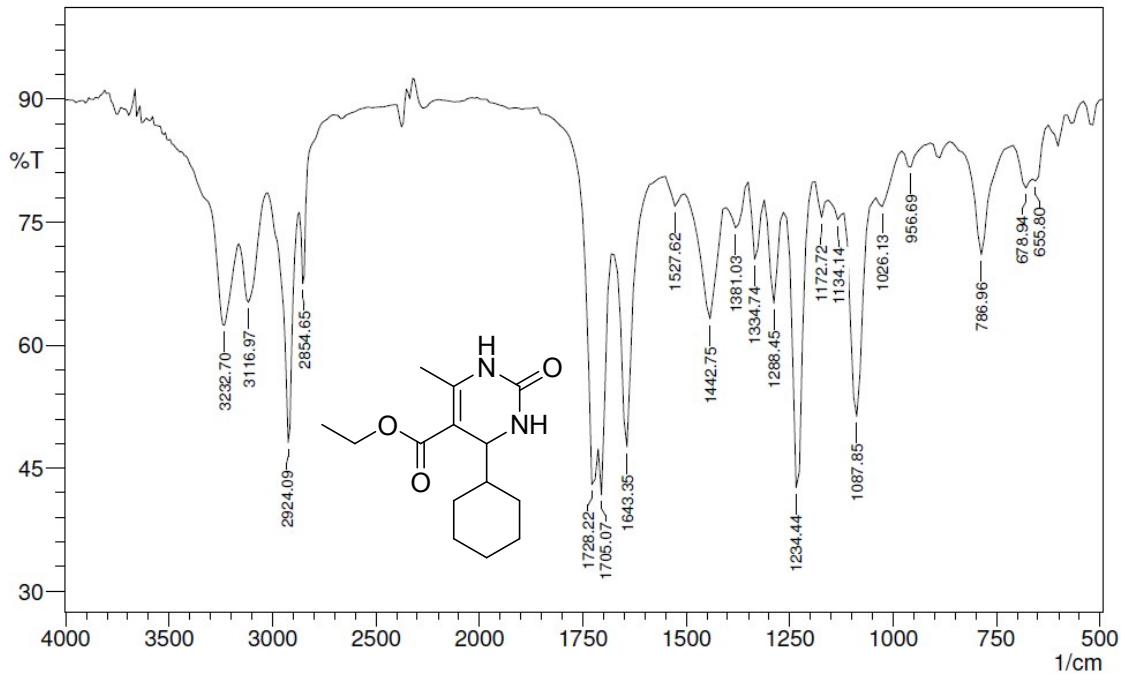


^{1}H NMR (DMSO-d_6, 400 MHz):

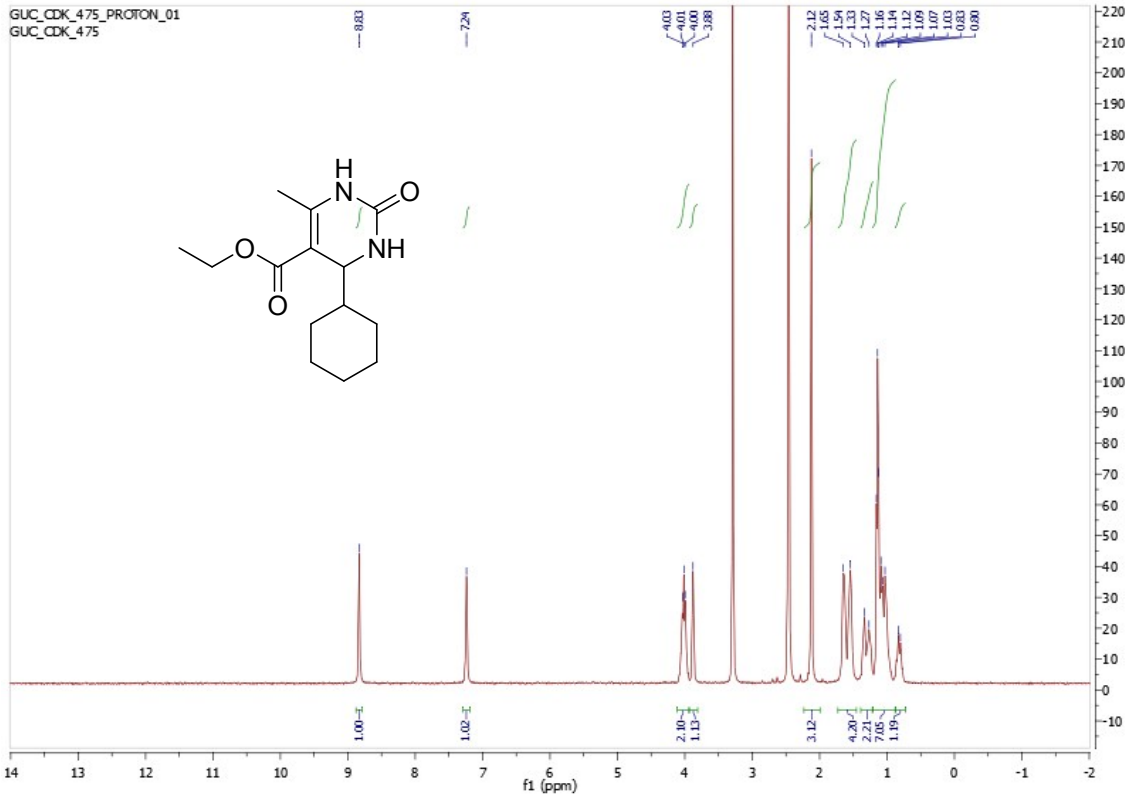


Ethyl 4-cyclohexyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 19):

FTIR:

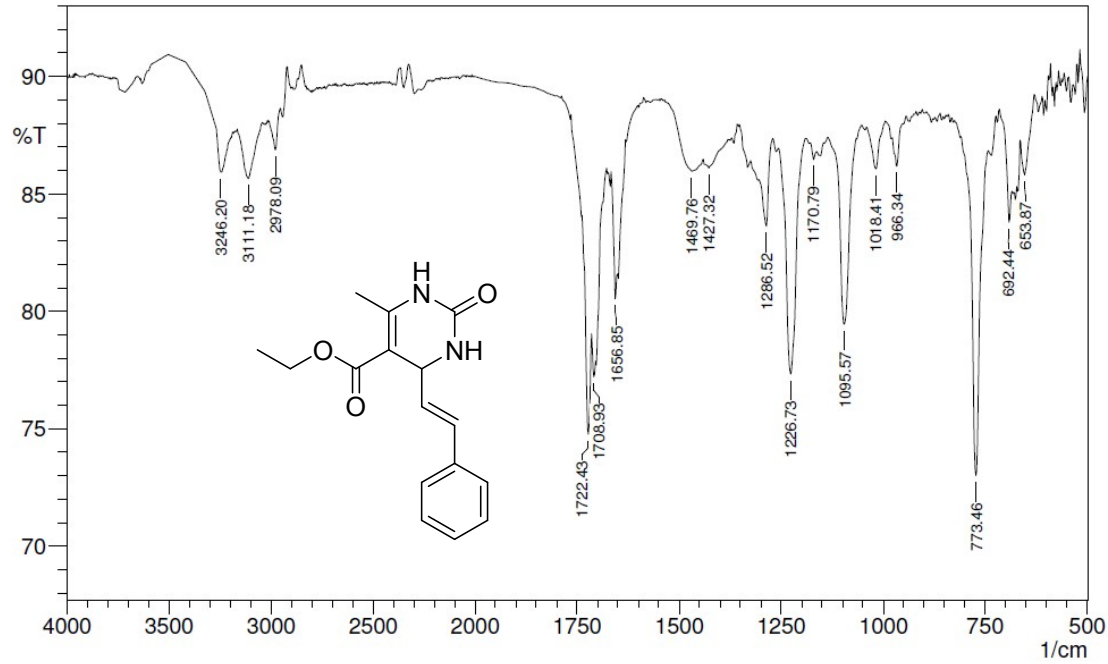


^{1}H NMR (DMSO-d_6, 400 MHz):

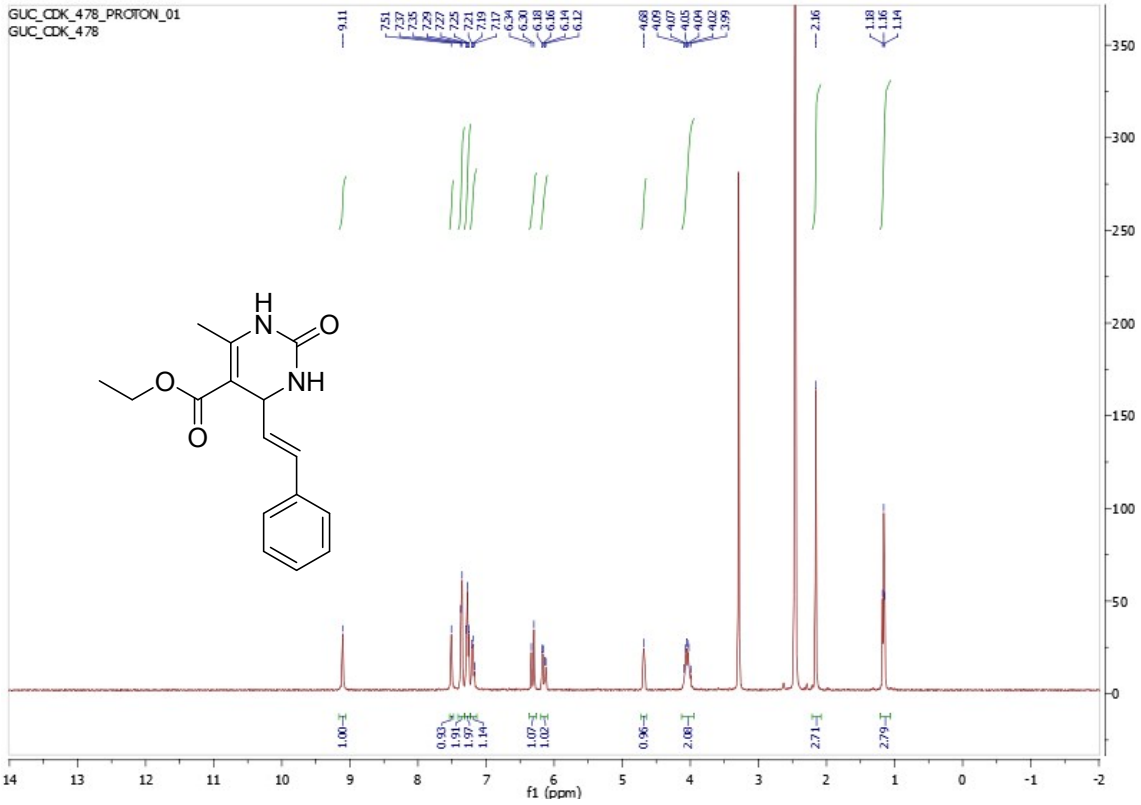


Ethyl 6-methyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 20):

FTIR:

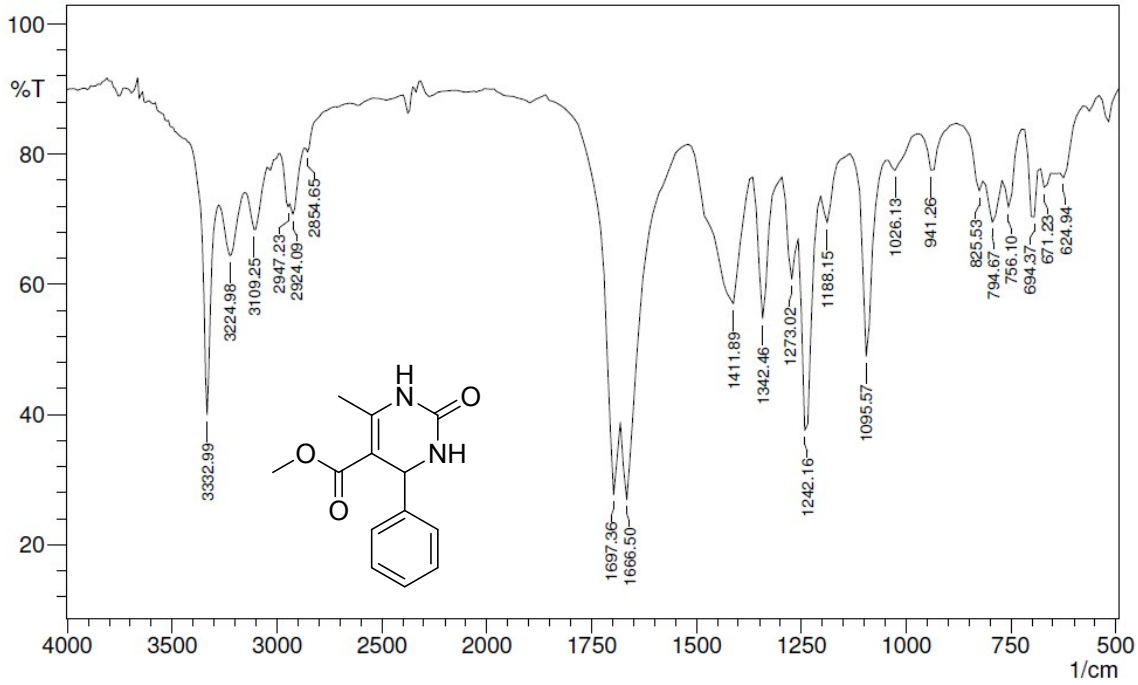


^{1}H NMR (DMSO-d_6, 400 MHz):

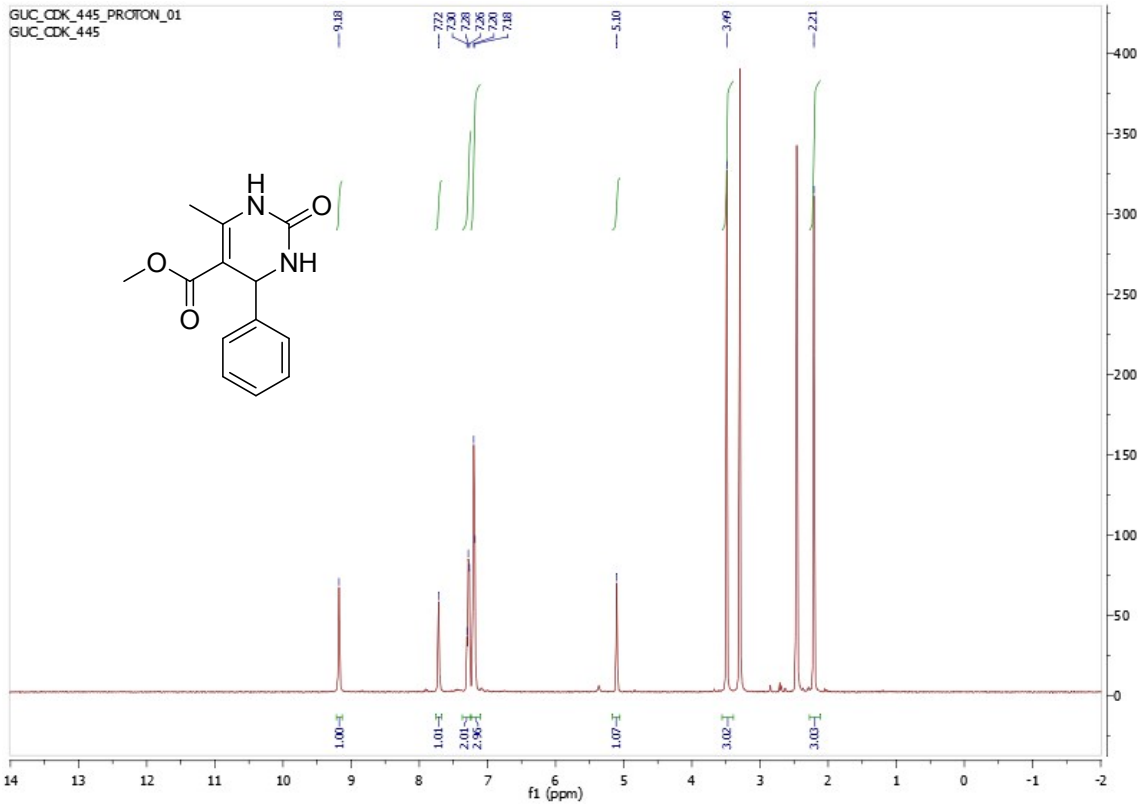


Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (Table 4, entry 21):

FTIR:

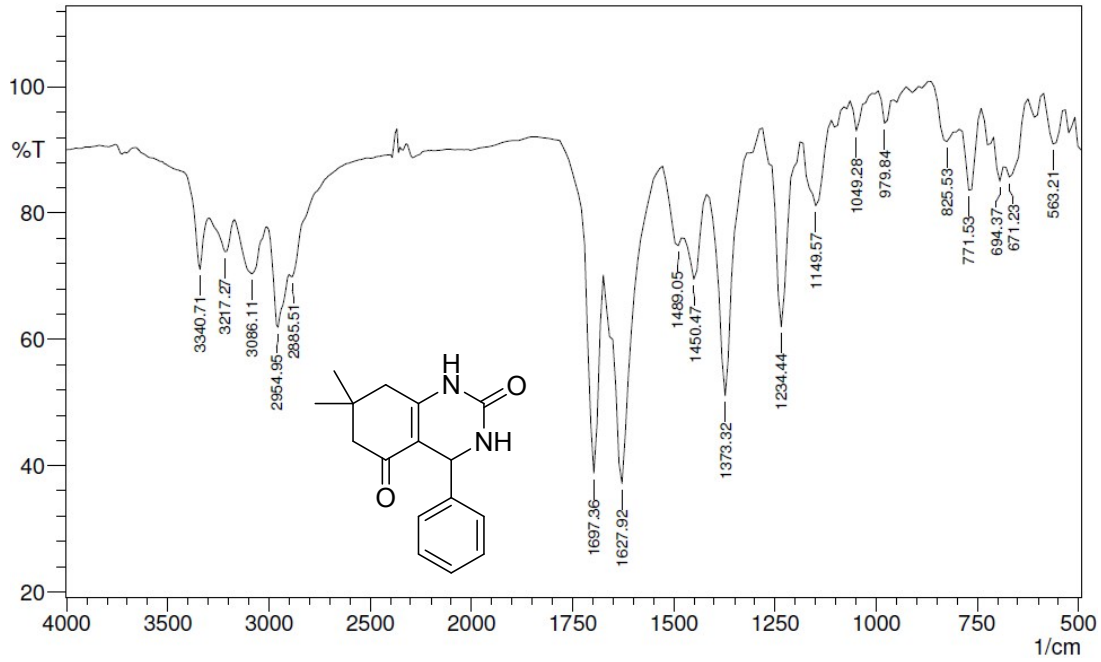


^{1}H NMR (DMSO-d_6, 400 MHz):

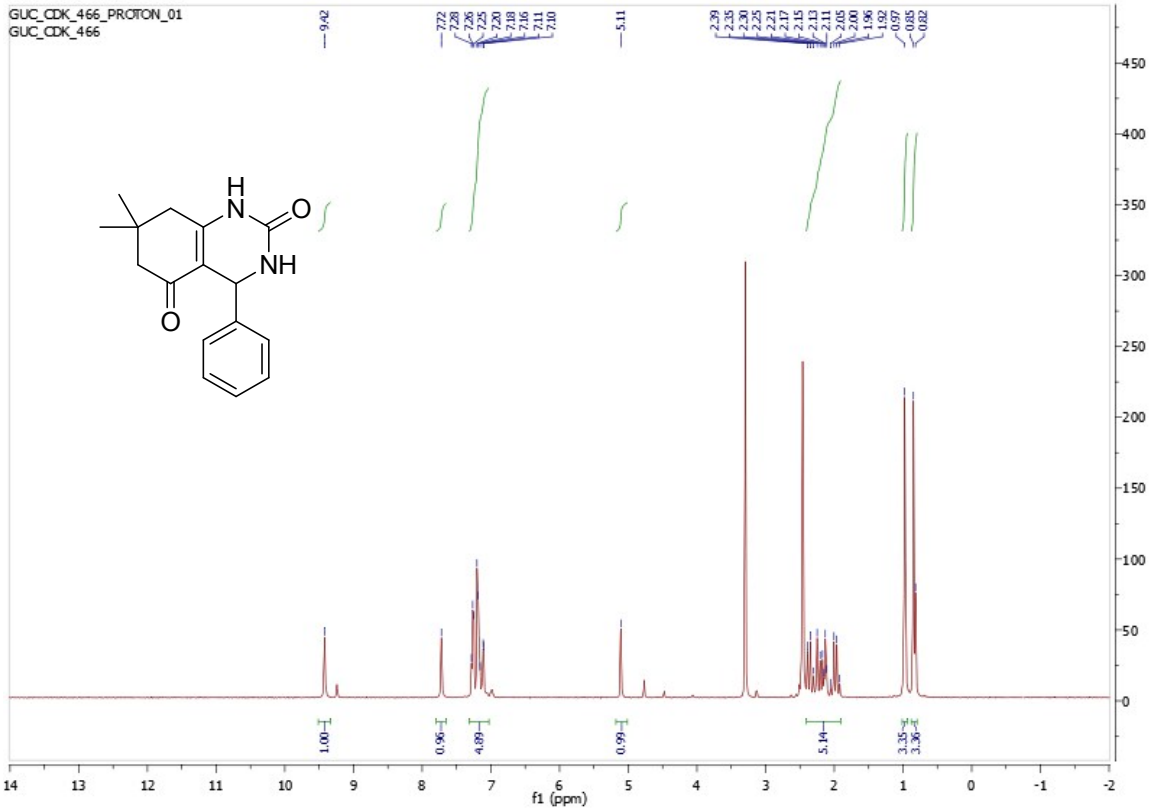


7,7-Dimethyl-4-phenyl-3,4,7,8-tetrahydroquinazoline-2,5(1*H*,6*H*)-dione (Table 4, entry 22):

FTIR:



^{1}H NMR (DMSO-d_6, 400 MHz):



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