Supporting Information

Application of magnetic materials bearing Brønsted acid sites - based on the modification of amorphous carbon with ionic liquids as catalysts for synthesis of dihydropyrimidinone derivatives *via* the Biginelli reaction

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Section S1. Chemicals, supplies and instruments

S1.1. Chemicals and supplies

Rice husk (Long An Province, Viet Nam), 3-glycidyloxypropyltrimethoxysilane (98%), acid *p*-phenolsulfonic (85%), paraformaldehyde (95%), benzaldehyde (99.0%), 2-chlorobenzaldehyde (99.0%), 4-chlorobenzaldehyde (97%), 4-bromobenzaldehyde (99.0%), 4-fluorobenzaldehyde (98.5%), 4-methylbenzaldehyde (97%), 4-methoxybenzaldeyde (98.5%), 4-hydroxybenzaldehyde (98%), 4-hydroxy-3-methoxybenzaldehyde (99%), 4-(dimethylamino)benzaldehyde (98%), cinnamaldehyde (99%), cyclohexanecarbaldehyde (97%), ethyl acetoacetate (99%), urea (99%) were obtained from Sigma-Aldrich, ethanol (99.5%), cyclohexane (99.7%), ethyl acetate (99.5%), *n*-hexane (99.5%) were obtained from Chemsol, iron (III) chloride were obtained from China, Xilong 99%, thiourea (99.0%), TLC (silica gel 60 F254) were obtained from Merck.

S1.2. Analytical techniques

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500 instruments using DMSO-d_6 as solvent and solvent peaks or TMS as internal standards. Fourier-transform infrared spectroscopy (FT-IR) analysis on a JASCO FT/IR-6600 spectrometer in the range of 600-4000 cm^{-1}, scanning electron microscopy (SEM) on a JSM-IT200, JEOL, Japan, elemental analysis (EDX) equipped with SEM on a JSM-IT200, JEOL, Japan, thermogravimetric analysis (TGA) using a TA Q500 system, vibrating sample magnetometer (VSM) on a PPMS600 system from Quantum Design, and inductively coupled plasma-mass spectrometry (ICP-MS).

Table S1. Elemental density of Fe by ICP–OES of BMSA, KH-Si, and KS71.

Material	Fe (mg/kg)
BMSA	76210.55
KH-Si	76766.14
KS71	76512.09

Calculate the pH acidity of KS71:

The mass of catalysts weighed for the experiment:

+ Total titration: KS71 = 50.4 mg, KH-Si = 47.9 mg, BMSA = 51.8 mg

+ Titration -SO_3H group: KS71 = 50.3 mg

Calculate total acid concentration (-OH, -COOH, -SO_3H…):

- Titration results with HCl 0.1 N using phenolphthalein indicator with three repetitions of three catalyst stages KS71, KH-Si, BMSA:

	V_1 (mL)	V_2 (mL)	V_3 (mL)
KS71	11.500	11.550	11.550
KH-Si	12.400	12.400	12.500
BMSA	9.500	9.550	9.500

- Re-titration results of NaOH concentration used to conduct the experiment. 10 mL NaOH was titrated with HCl 1N using phenolphthalein indicator (three repetitions):

V_1 = 15.200 mL, V_2 = 15.200 mL, V_3 = 15.200 mL

➔ $V_{avg} = \frac{V1 + V2 + V3}{3} = \frac{15.200 + 15.200 + 15.200}{3} = 15.200\ mL$

➔ $C_{NaOH} = \frac{CHCl\ .\ Vavg}{VNaOH} = \frac{1\ .\ 15.200}{10} = 1.520\ (N)$

- Calculate KS71stage:

$V_{avg\ KS71} = \frac{11.500 + 11.550 + 11.550}{3} = 11.530\ mL$

➔ $C_{NaOH\ KS71\ titration} = \frac{CHCl\ .\ VHCl}{VKS71} = \frac{0.1\ .\ 11.530\ .\ 10}{10} = 1.153$ (N) (with dilute factor = 10)

➔ $C_{NaOH\ KS71\ reaction} = C_{NaOH} - C_{NaOH\ KS71\ titration} = 1.520 - 1.153 = 0.370$ (N)

➔ $C_{acid\ KS71} = \frac{CNaOH\ KS71\ reaction\ .\ VNaOH}{mKS71} = \frac{0.370\ .\ 20}{50.4} = 0.15$ (mmol/mg)

- Calculate KH-Si stage:

$V_{avg\ KH\text{-}Si} = \frac{12.400 + 12.400 + 12.500}{3} = 12.430\ mL$

➔ $C_{NaOH\ KH\text{-}Si\ titration} = \frac{CHCl\ .\ VHCl}{VKH - Si} = \frac{0.1\ .\ 12.430\ .\ 10}{10} = 1.243$ (N) (with dilute factor = 10)

➔ $C_{NaOH\ KH\text{-}Si\ reaction} = C_{NaOH} - C_{NaOH\ KH\text{-}Si\ titration} = 1.520 - 1.243 = 0.280$ (N)

➔ $C_{acid\ KH\text{-}Si}$ =

$$\frac{CNaOH\ KH-Si\ reaction\ .\ VNaOH}{mKH-Si} = \frac{0.280\ .\ 20}{47.9} = 0.120 \text{ (mmol/mg)}$$

- Calculate BMSA stage:

$$V_{avg\ BMSA} = \frac{9.500 + 9.550 + 9.500}{3} = 9.520\ mL$$

➔ $C_{NaOH\ BMSA\ titration}$ = $\frac{CHCl\ x\ VHCl}{VBMSA} = \frac{0.1\ x\ 9.520\ .\ 10}{10} = 0.952$ (N) (with dilute factor = 10)

➔ $C_{NaOH\ BMSA\ reaction} = C_{NaOH} - C_{NaOH\ BMSA\ titration}$ = 1.520 – 0.952 = 0.568 (N)

➔ $C_{acid\ BMSA}$ =

$$\frac{CNaOH\ BMSA\ reaction\ .\ VNaOH}{mBMSA} = \frac{0.568\ .\ 20}{51.8} = 0.220 \text{ (mmol/mg)}$$

+) Calculate acid concentration of -SO_3H group:

- Titration results using NaOH 0.01 N with phenolphthalein as indicator (repeat 3 times):

V_1 = 0.350 mL, V_2 = 0.350 mL, V_3 = 0.350 mL

➔ V_{avg} = $\frac{0.350 + 0.350 + 0.350}{3} = 0.350$ mL

➔ $C_{acid\ of\ -SO3H}$ = $\frac{CNaOH\ .\ Vavg}{m\ KS71} = \frac{0.350\ .\ 0.01}{50.3\ .\ 10\text{^}3} = 0.0700$ (mmol/g)

S1.3. Catalyst KS71-SiO_2

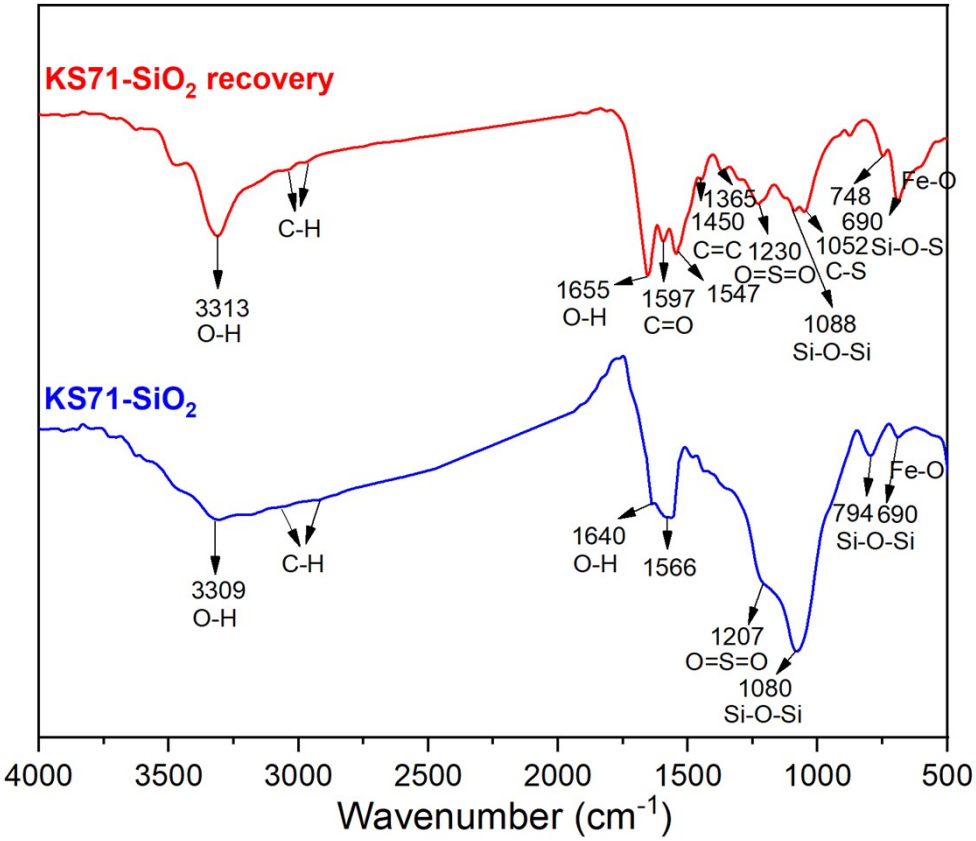


Fig. S1.1. FT-IR spectra of KS71-SiO_2 catalyst.

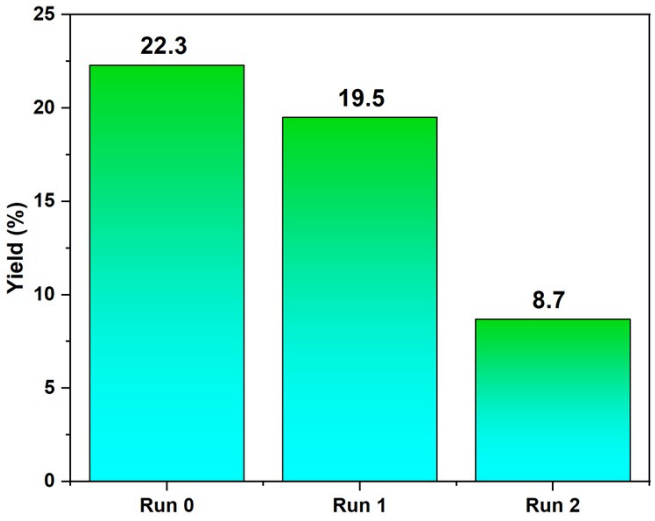


Fig. S1.2. Reusability of the KS71-SiO_2.

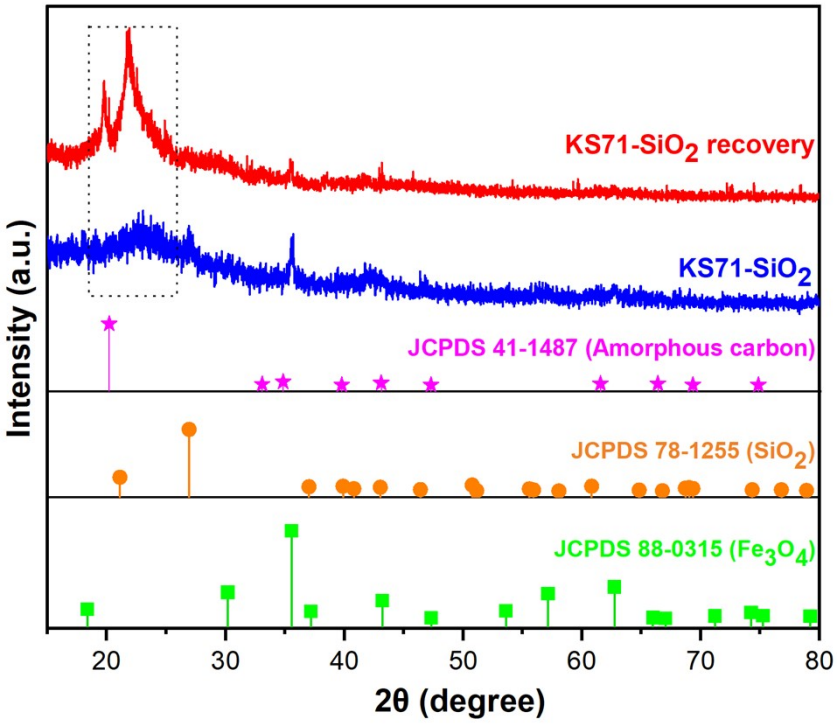


Fig. S1.3. XRD pattern of KS71-SiO_2 (blue) and KS71-SiO_2 recovery (red).

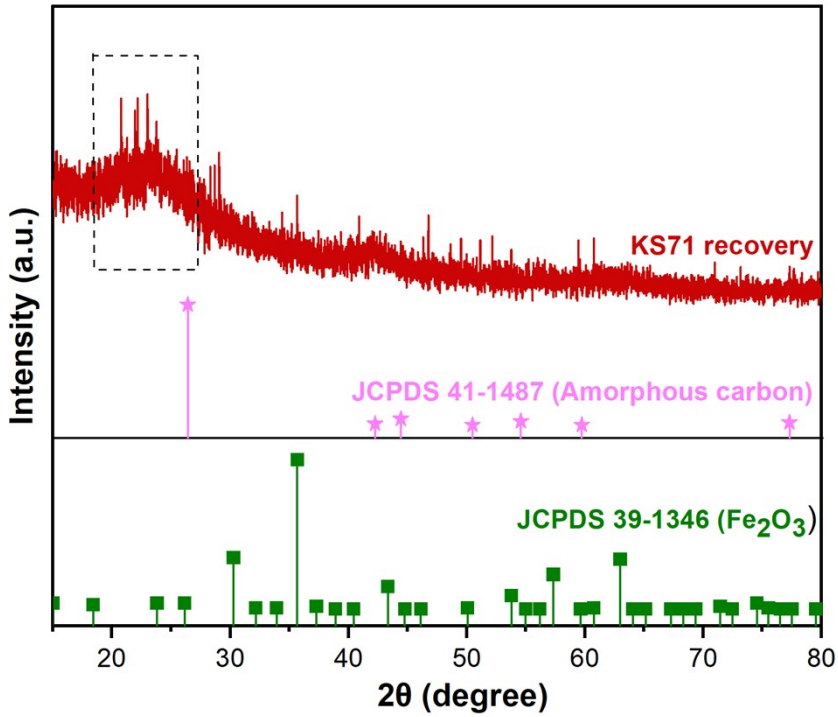
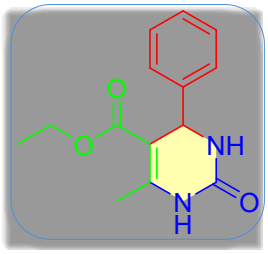


Fig. S1.4. XRD pattern of KS71 recovery.

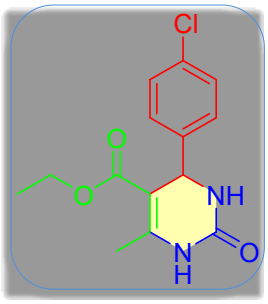
Section S2. Spectra data

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



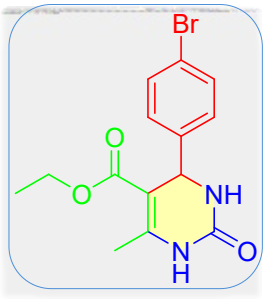
Benzaldehyde (106.1 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 133.9 mg, yield: 52%. R_f = 0.37 (*n*-hexane:ethyl acetate = 5:5); m.p. = 206-209 °C [Lit. = 205-209 °C] [1, 2]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.09 (t, J = 15.0 Hz, 5.0 Hz, 3H), 2.24 (s, 3H), 3.98 (q, J = 15.0 Hz, 5.0 Hz, 2H), 5.14 (d, J = 5.0 Hz, 1H), 7.25 – 7.22 (m, 3H), 7.33 – 7.30 (m, 2H), 7.72 (s, 1H), 9.18 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ =14.5, 18.2, 54.4, 59.7, 99.7, 126.7, 127.7, 128.9, 145.3, 148.8, 152.6, 165.8 ppm.

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



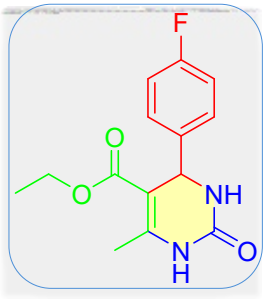
4-Chlorobenzaldehyde (140.5 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 110.1 mg, yield: 37%. R_f = 0.37 (*n*-hexane:ethyl acetate = 5:5); m.p. = 223-224 °C [Lit. = 217-218 °C] [3]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.09 (t, J = 15.0 Hz, 10.0 Hz, 3H), 2.25 (s, 3H), 3.98 (q, J = 10.0 Hz, 5.0 Hz, 2H), 5.14 (d, J = 5.0 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.76 (s, 1H), 9.24 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ =14.6, 18.3, 53.9, 59.7, 99.3, 128.7, 128.8, 132.3, 144.3, 149.2, 152.4, 165.7 ppm.

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



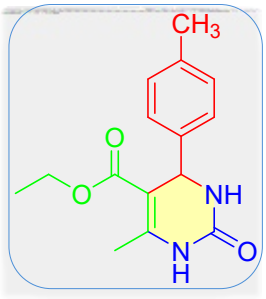
4-Bromobenzaldehyde (185.0 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 105.6 mg, yield: 31%. R_f = 0.33 (*n*-hexane:ethyl acetate = 5:5); m.p. = 228-230 °C [Lit. = 228-230 °C] [4]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.10 (t, J = 15.0 Hz, 5.0 Hz, 3H), 2.25 (s, 3H), 3.98 (q, J = 10.0 Hz, 5.0 Hz, 2H), 5.12 (d, J = 5.0 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.78 (s, 1H), 9.26 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ =14.6, 18.3, 53.9, 59.7, 99.2, 120.8, 129.0, 131.8, 144.7, 149.2, 152.4, 165.7 ppm.

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



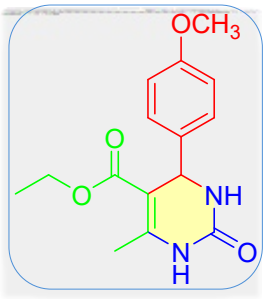
4-Fluorobenzaldehyde (124.1 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 98.5 mg, yield: 35%. R_f = 0.19 (*n*-hexane:ethyl acetate = 5:5); m.p. =188-191 °C [Lit. = Not found] [2]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.09 (t, J = 15.0 Hz, 5.0 Hz, 3H), 2.25 (s, 3H), 4.00 – 3.96 (m, 2H), 5.15 (d, J = 5.0 Hz, 1H), 7.15 (t, J = 9.0 Hz, 18.0 Hz, 2H), 7.26 (m, 2H), 7.74 (s, 1H), 9.22 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ =14.5, 18.3, 53.8, 59.7, 99.6, 115.6 (J = 21.3 Hz), 128.7 (J = 8.8 Hz), 141.6 (J = 3.8 Hz), 141.6, 149.0, 152.4, 161.8 (J = 241.3 Hz), 165.7 ppm.

Ethyl 6-methyl-2-oxo-4-(*p*-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5a)



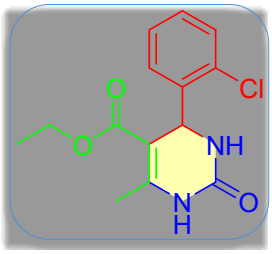
4-Methylbenzaldehyde (120.1 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 103.4 mg, yield: 38%. R_f = 0.35 (*n*-hexane:ethyl acetate = 5:5); m.p. = 216-218 °C [Lit. = 216-217 °C] [3]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.10 (t, J = 10.0 Hz, 5.0 Hz, 3H), 2.24 (s, 3H), 2.26 (s, 3H), 3.98 (q, J = 15.0 Hz, 10.0 Hz, 2H), 5.10 (d, J = 5.0 Hz, 1H), 7.12 (s, 4H), 7.68 (s, 1H), 9.15 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ =14.6, 18.2, 21.1, 54.1, 59.6, 99.9, 126.6, 129.4, 136.8, 142.4, 148.6, 152.6, 165.8 ppm.

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



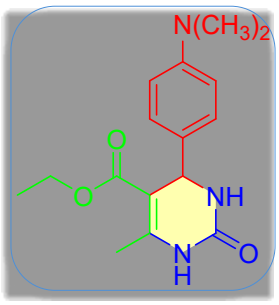
4-Methoxybenzaldehyde (136.2 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 109.5 mg, yield: 37%. R_f = 0.24 (*n*-hexane:ethyl acetate = 5:5); m.p. = 204-206 °C [Lit. = 200-202 °C] [4]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.10 (t, J = 15.0 Hz, 10.0 Hz, 3H), 2.24 (s, 3H), 3.72 (s, 3H), 3.98 (q, J = 15.0 Hz, 10.0 Hz, 2H), 5.09 (d, J = 5.0 Hz, 1H), 6.87 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 7.66 (s, 1H), 9.15 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ =14.6, 18.2, 53.8, 55.5, 59.6, 100.0, 114.2, 127.9, 137.5, 148.5, 152.6, 158.9, 165.9 ppm.

Ethyl 4-(2-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (7a)



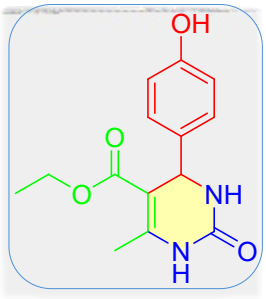
2-Chlorobenzaldehyde (140.5 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 103.4 mg, yield: 35%. R_f = 0.37 (*n*-hexane:ethyl acetate = 5:5); m.p. = 223- 224 °C [Lit. = 220-222 °C] [4]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 0.99 (t, J = 15.0 Hz, 10.0 Hz, 3H), 2.30 (s, 3H), 3.89 (q, J = 15.0 Hz, 5.0 Hz, 2H), 5.63 (d, J = 5.0 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.34 – 7.29 (m, 2H), 7.40 (d, J = 7.5 Hz, 1H), 7.69 (s, 1H), 9.26 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ =14.4, 18.1, 52.0, 59.5, 98.4, 128.2, 129.3, 129.5, 129.8, 132.2, 142.2, 149.8, 151.8, 165.4 ppm.

Ethyl 4-(4-(dimethylamino)phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8a)



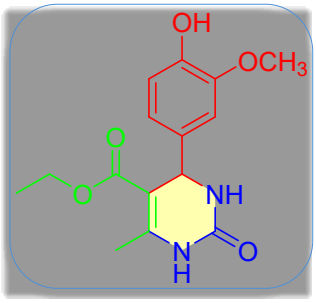
4-(Dimethylamino)benzaldehyde (149.1 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 106.2 mg, yield: 35%. R_f = 0.19 (*n*-hexane:ethyl acetate=5:5); m.p. = 226-228 °C [Lit. = 258-261 °C] [1]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.11 (t, J = 15.0 Hz, 10.0 Hz, 3H), 2.23 (s, 3H), 2.85 (s, 6H), 4.01 – 3.94 (m, 2H), 5.03 (d, J = 5.0 Hz, 1H), 6.65 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 7.60 (s, 1H), 9.10 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 14.6, 18.2, 40.7, 53.8, 59.6, 100.3, 112.7, 127.4, 133.1, 148.0, 150.2, 152.8, 166.0 ppm.

Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9a)



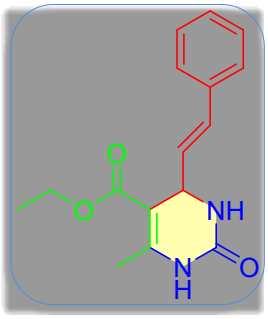
4-Hydroxybenzaldehyde (122.1 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 117.7 mg, yield: 42%. R_f = 0.13 (*n*-hexane:ethyl acetate = 5:5); m.p. = 225-226 °C [Lit. = 225-226 °C] [3]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.10 (t, J = 15.0 Hz, 5.0 Hz, 3H), 2.23 (s, 3H), 3.97 (q, J = 10.0 Hz, 5.0 Hz, 2H), 5.04 (d, J = 5.0 Hz, 1H), 6.68 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 7.62 (s, 1H), 9.12 (s, 1H), 9.34 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ =14.6, 18.2, 53.9, 59.6, 100.2, 115.4, 127.9, 135.9, 148.2, 152.6, 157.0, 165.9 ppm.

Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (10a)



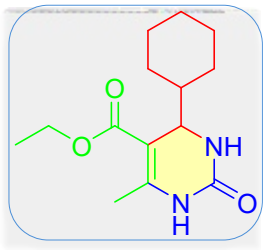
4-Hydroxy-3-methoxybenzaldehyde (152.1 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 101.1 mg, yield: 33%. R_f = 0.08 (*n*-hexane:ethyl acetate = 5:5); m.p. = 215-217 °C [Lit. = 236-237 °C] [5]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.11 (t, J = 15.0 Hz, 10.0 Hz, 3H), 2.23 (s, 3H), 3.72 (s, 3H), 3.99 (q, J = 10.0 Hz, 5.0 Hz, 2H), 5.06 (d, J = 5.0 Hz, 1H), 6.61 (dd, J = 8.0 Hz, 1.5 Hz 2H), 6.70 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 1.5 Hz, 1H), 7.64 (s, 1H), 8.92 (s, 1H), 9.13 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 14.6, 18.2, 54.0, 56.0, 59.6, 100.0, 111.3, 115.7, 118.7, 136.4, 146.2, 147.7, 148.4, 152.7, 165.9 ppm.

Ethyl (*E*)-6-methyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (11a)



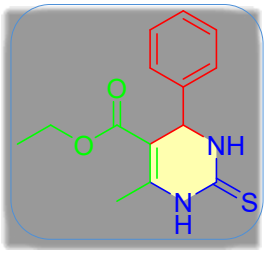
Cinnamaldehyde (132.1 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, m = 100.2 mg, yield: 35%. R_f = 0.26 (*n*-hexane:ethyl acetate = 5:5); m.p. = 254-256 °C [Lit. = 228-230 °C] [6]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.20 (t, J = 15.0 Hz, 10.0 Hz, 3H), 2.20 (s, 3H), 4.15 – 4.03 (m, 2H), 4.73 (t, J = 9.0 Hz, 3.5 Hz, 1H), 6.20 (dd, J = 16.0 Hz, 6.5 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 7.24 (t, J = 7.0 Hz, 14.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 15.0 Hz, 2H), 7.40 (d, J = 7.5 Hz, 2H), 7.57 (s, 1H), 9.17 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 14.7, 18.2, 52.4, 59.7, 98.2, 126.8, 128.1, 128.6, 129.2, 130.4, 136.7, 149.0, 153.1, 165.7 ppm.

Ethyl 4-cyclohexyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (12a)



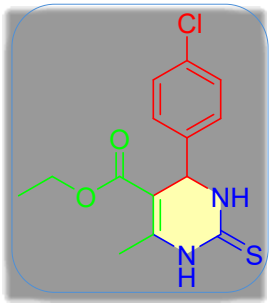
Cylohexanecarbaldehyde (112.2 mg), ethyl acetoacetate (130.1 mg), urea (60.0 mg), KS71 (5 mg). White solid, mg = 28.9 mg, yield 11%. R_f = 0.36 (*n*-hexane:ethyl acetate = 5:5); m.p. = 209-210 °C [Lit. = 233-234 °C] [3]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 0.89 – 0.81 (m, 1H), 1.13 – 1.01 (m, 4H), 1.18 (t, J = 15.0 Hz, 5.0 Hz, 3H), 1.39 – 1.28 (m, 2H), 1.69 – 1.58 (m, 4H), 2.16 (s, 3H), 3.92 (t, J = 10.0 Hz, 5.0 Hz, 1H), 4.11 – 4.00 (m, 2H), 7.27 (s, 1H), 8.87 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 14.7, 18.2, 26.1, 26.3, 26.5, 26.7, 29.0, 45.3, 55.4, 59.5, 98.5, 148.9, 153.7, 160.1, 166.3 ppm.

Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (13a)



Benzaldehyde (106.1 mg), ethyl acetoacetate (130.1 mg), thiourea (76.1 mg), KS71 (5 mg). White solid, m = 42 mg, yield 8%. R_f = 0.82 (*n*-hexane:ethyl acetate = 5:5); m.p. = 209-211 °C [Lit. = 209-210 °C] [3]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.10 (t, J = 15.0 Hz, 10.0 Hz, 3H), 2.29 (s, 3H), 4.01 (q, J = 15.0 Hz, 5.0 Hz, 2H), 5.18 (d, J = 5.0 Hz, 1H), 7.22 (d, J = 7.5 Hz, 2H), 7.27 (t, J =7.5 Hz, 14.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 14.5 Hz, 2H), 9.65 (s, 1H), 10.34 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 14.5, 17.6, 54.5, 60.1, 101.2, 126.8, 128.2, 129.0, 143.9, 145.5, 165.6, 174.7 ppm.

Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (14a)



4-Chlorobenzaldehyde (140.5 mg), ethyl acetoacetate (130.1 mg), thiourea (76.1 mg), KS71 (5 mg). White solid, m = 141.2 mg, yield 23%. R_f = 0.45 (*n*-hexane:ethyl acetate = 5:5); m.p. = 220-221 °C [Lit. = 192-193 °C] [3]. ^{1}H-NMR (500 MHz, DMSO-d_6): δ = 1.10 (t, J = 15.0 Hz, 10.0 Hz, 3H), 2.26 (s, 3H), 3.99 (q, J = 6.5 Hz, 13.5 Hz, 2H), 5.15 (d, J = 5.0 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 7.77 (s, 1H), 9.25 (s, 1H) ppm. ^{13}C-NMR (125 MHz, DMSO-d_6): δ = 14.5, 18.3, 53.9, 59.7, 99.3, 128.7, 128.9, 132.3, 144.3, 149.2, 152.4, 165.7 ppm.

Section S3. ^{1}H, and ^{13}C NMR spectroscopy

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

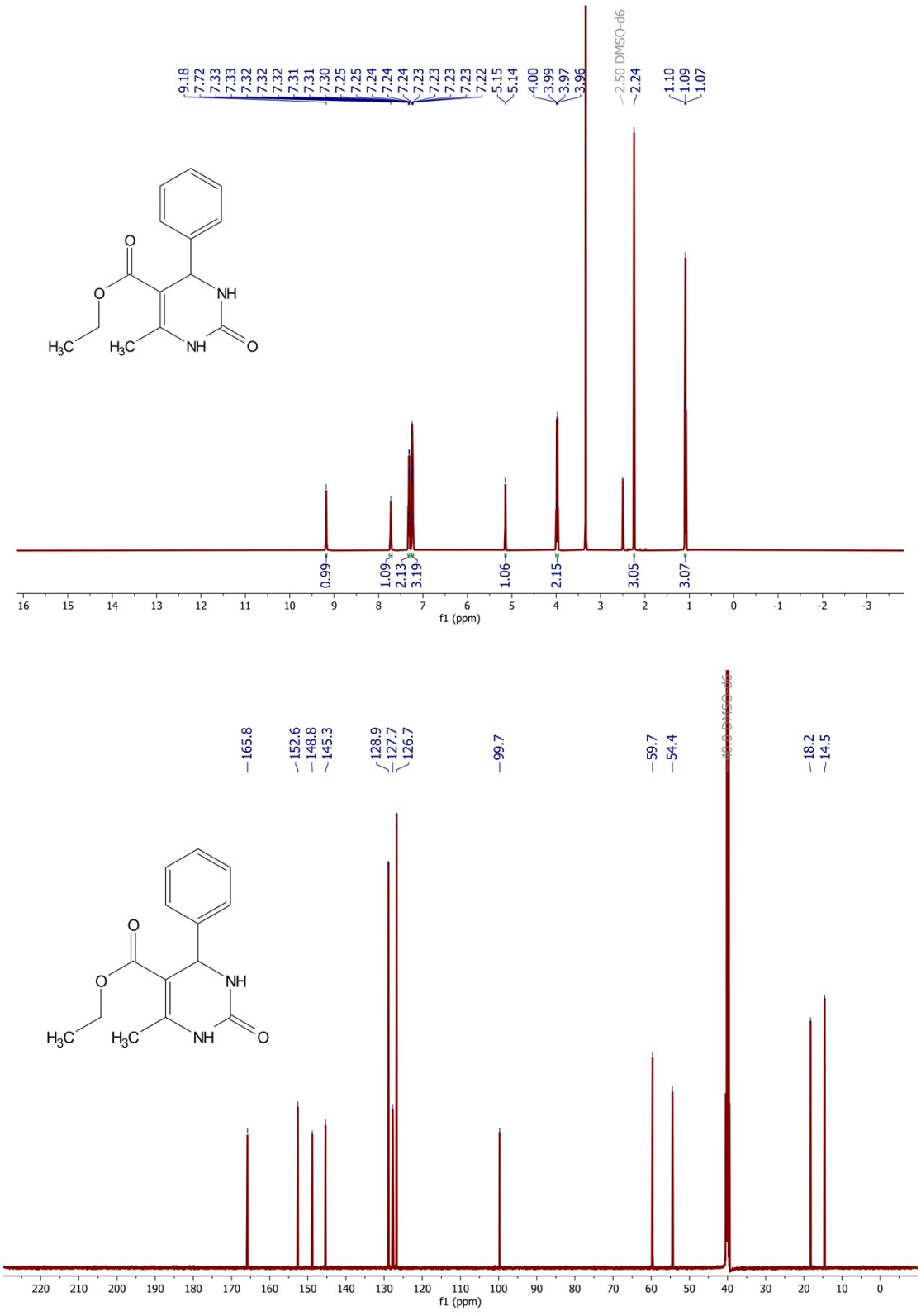


Figure S1. ^{1}H and ^{13}C NMR spectra of Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (**1a**)

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

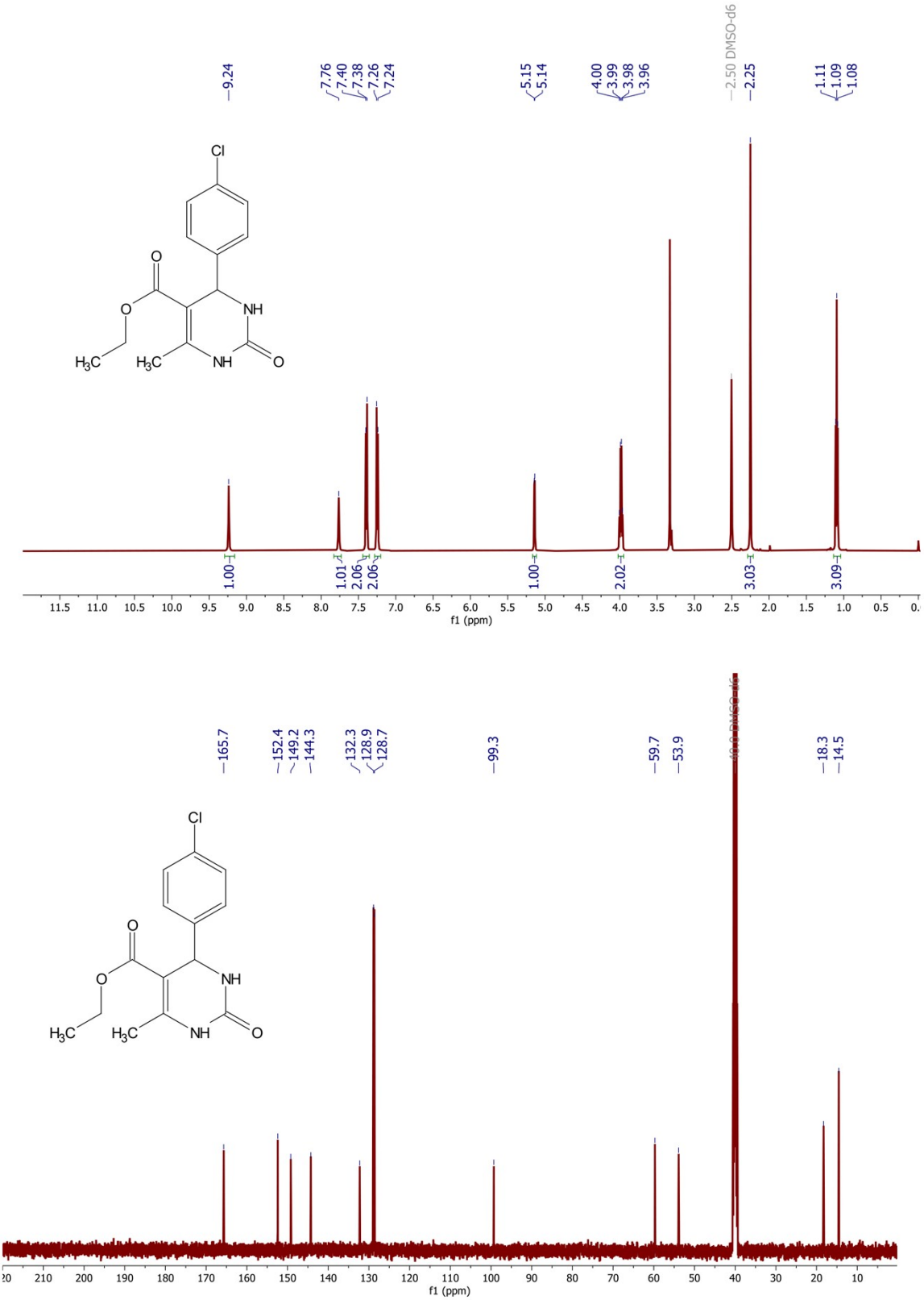


Figure S2. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(2a)**

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

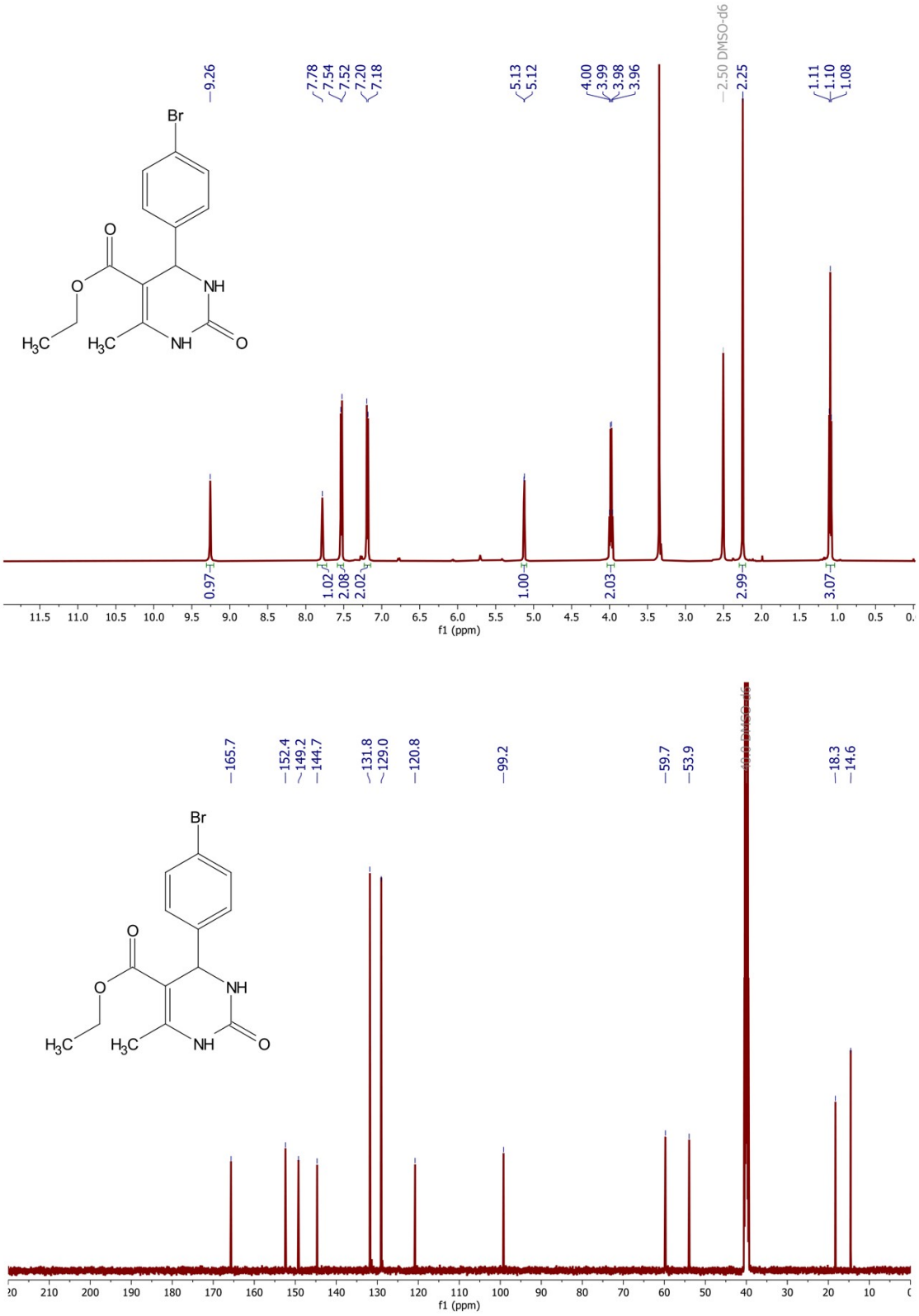


Figure S3. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(4-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(3a)**

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

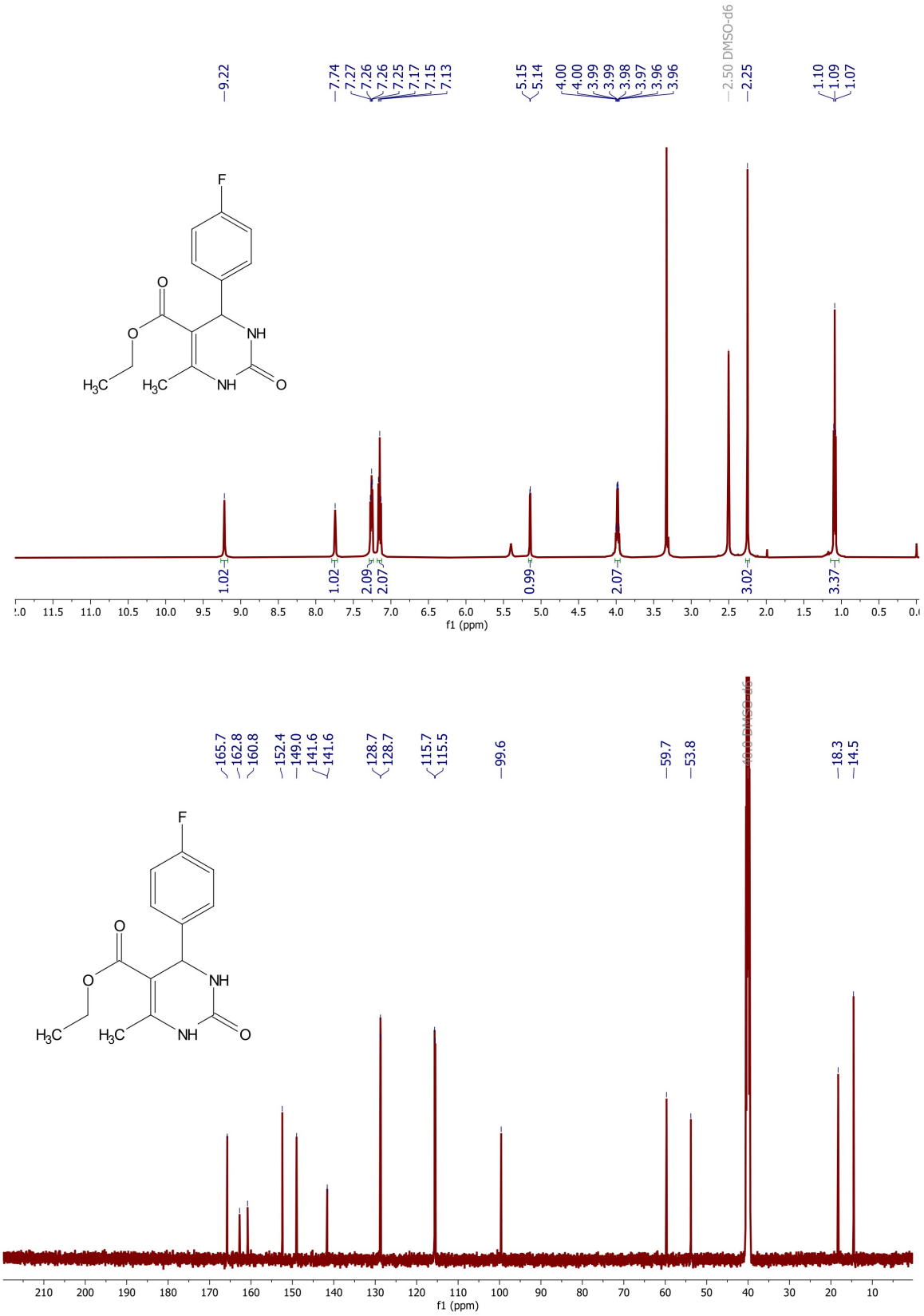


Figure S4. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(4a)**

Ethyl 6-methyl-2-oxo-4-(*p*-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5a)

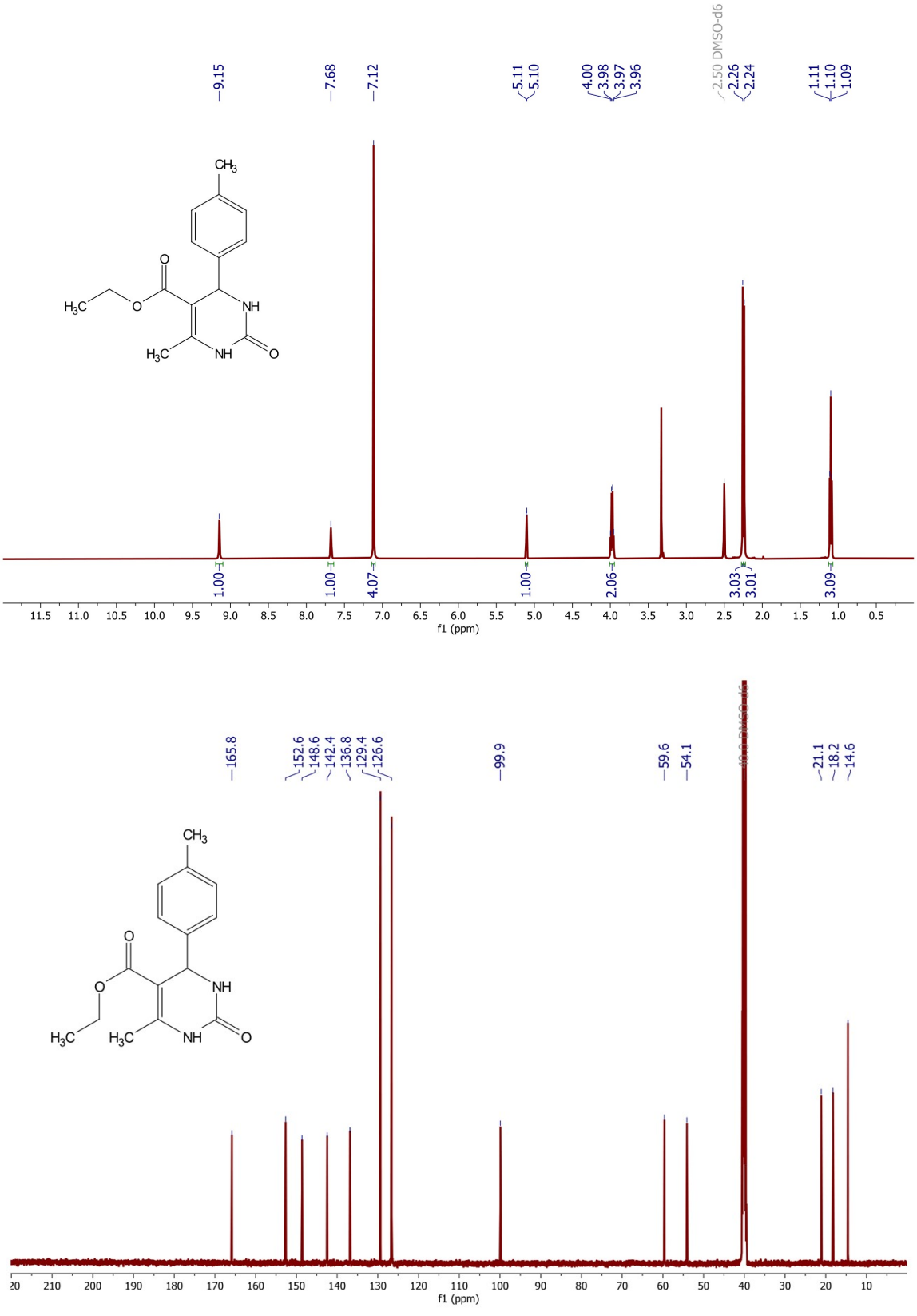


Figure S5. ^{1}H and ^{13}C NMR spectra of Ethyl 6-methyl-2-oxo-4-(*p*-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(5a)**

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

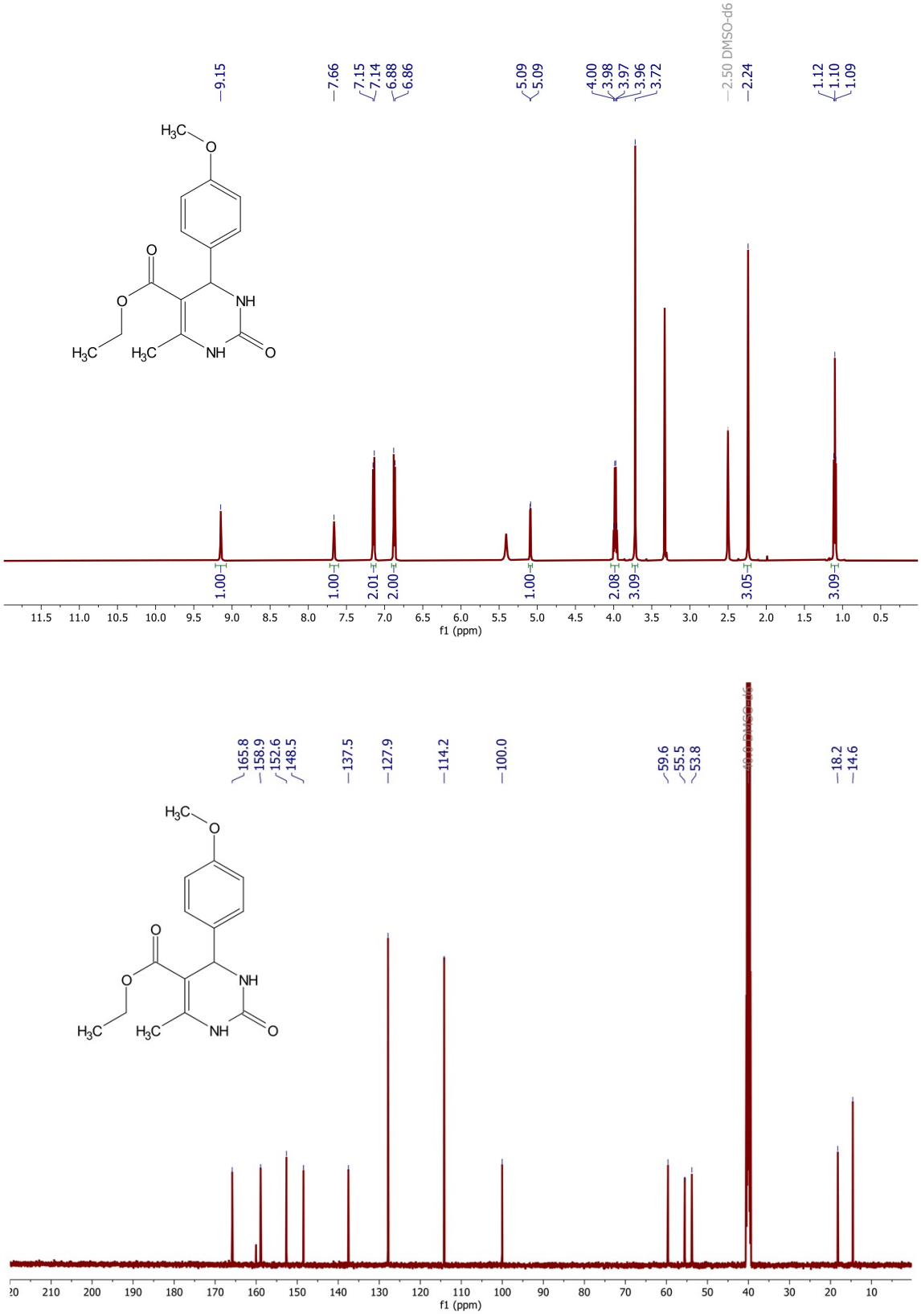


Figure S6. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5- carboxylate **(6a)**

Ethyl 4-(2-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (7a)

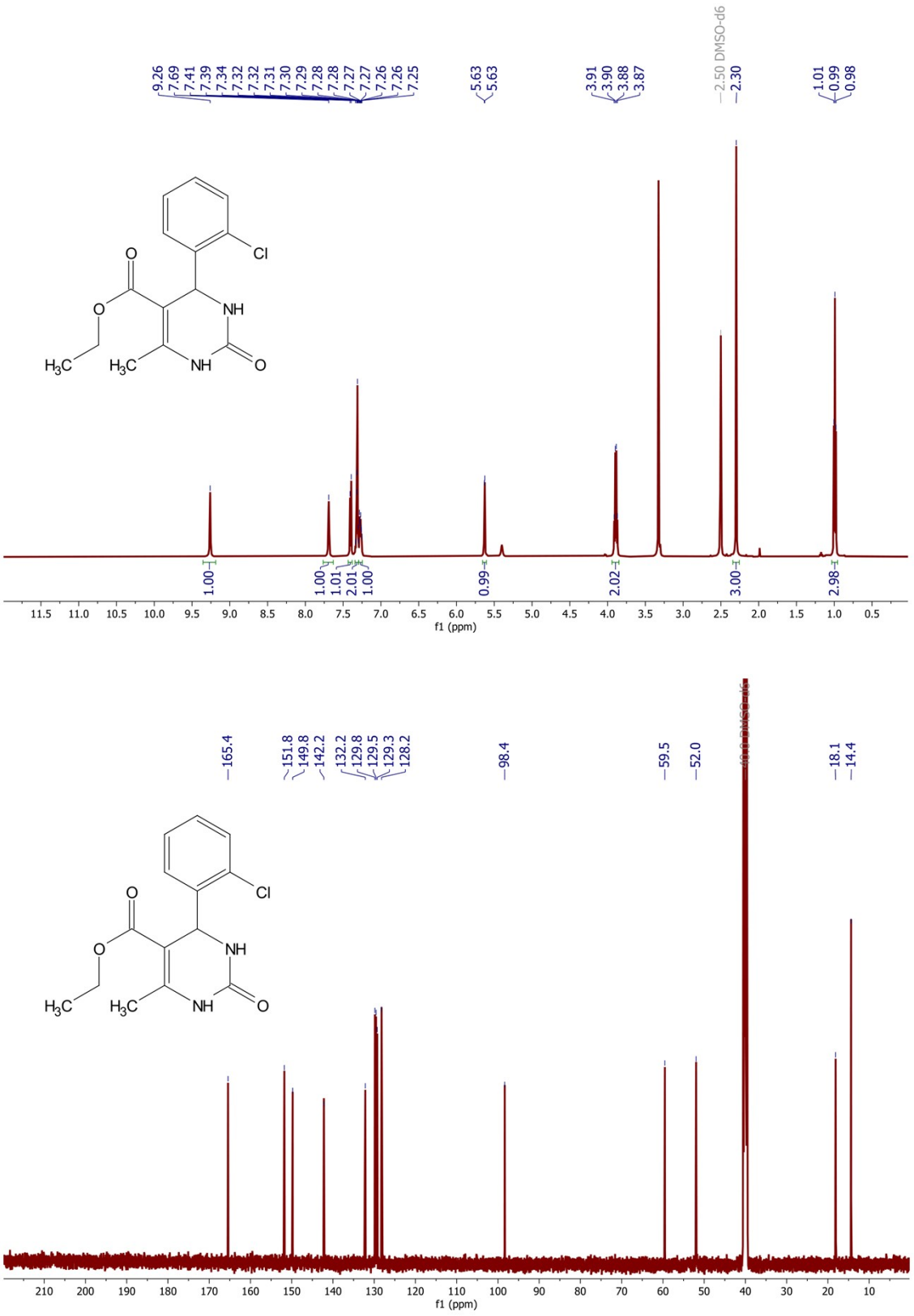


Figure S7. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(2-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(7a)**

Ethyl 4-(4-(dimethylamino)phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8a)

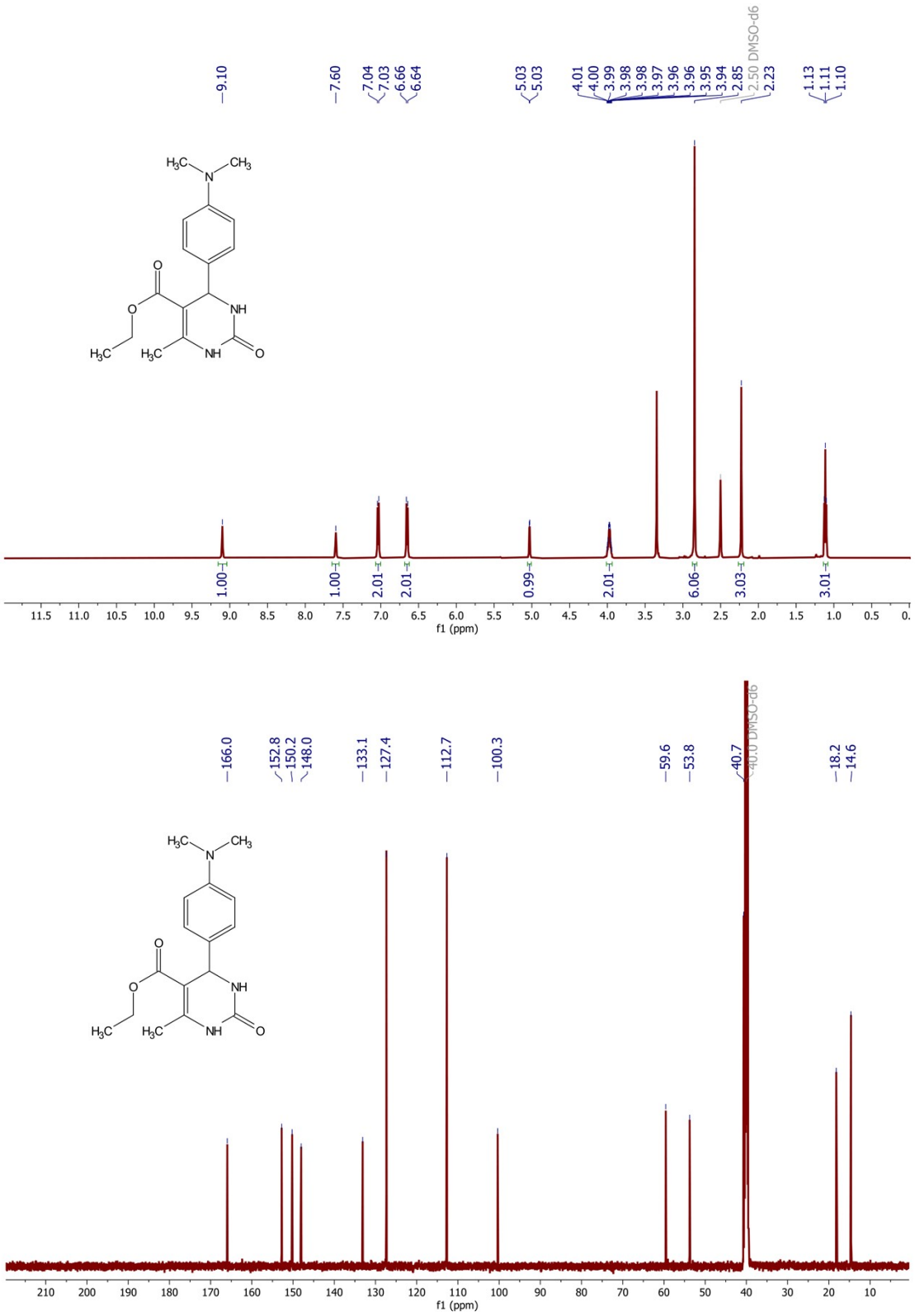


Figure S8. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(4-(dimethylamino)phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(8a)**

Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9a)

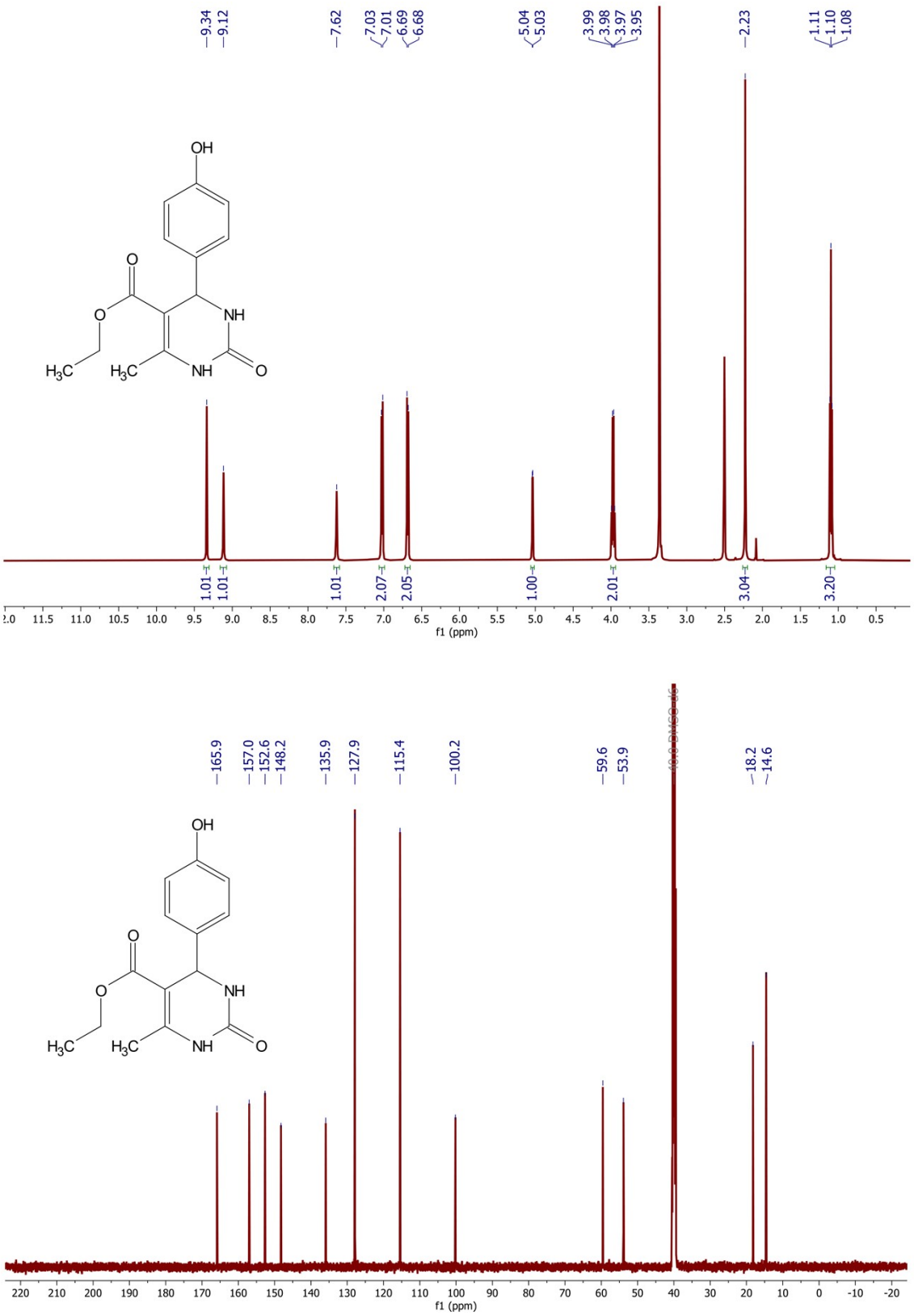


Figure S9. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(9a)**

Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (10a)

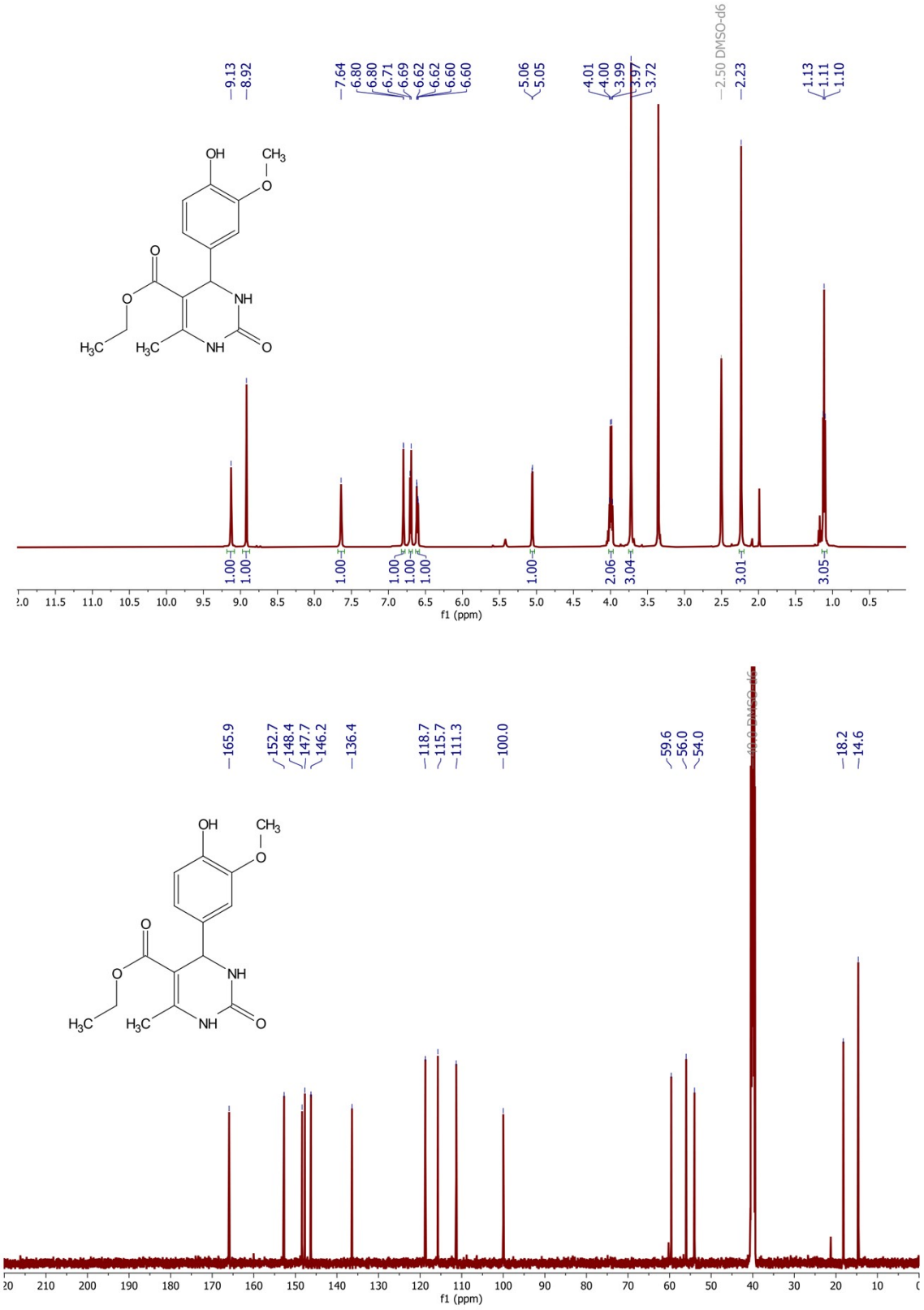


Figure S10. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(4-hydroxy-3-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(10a)**

Ethyl (*E*)-6-methyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (11a)

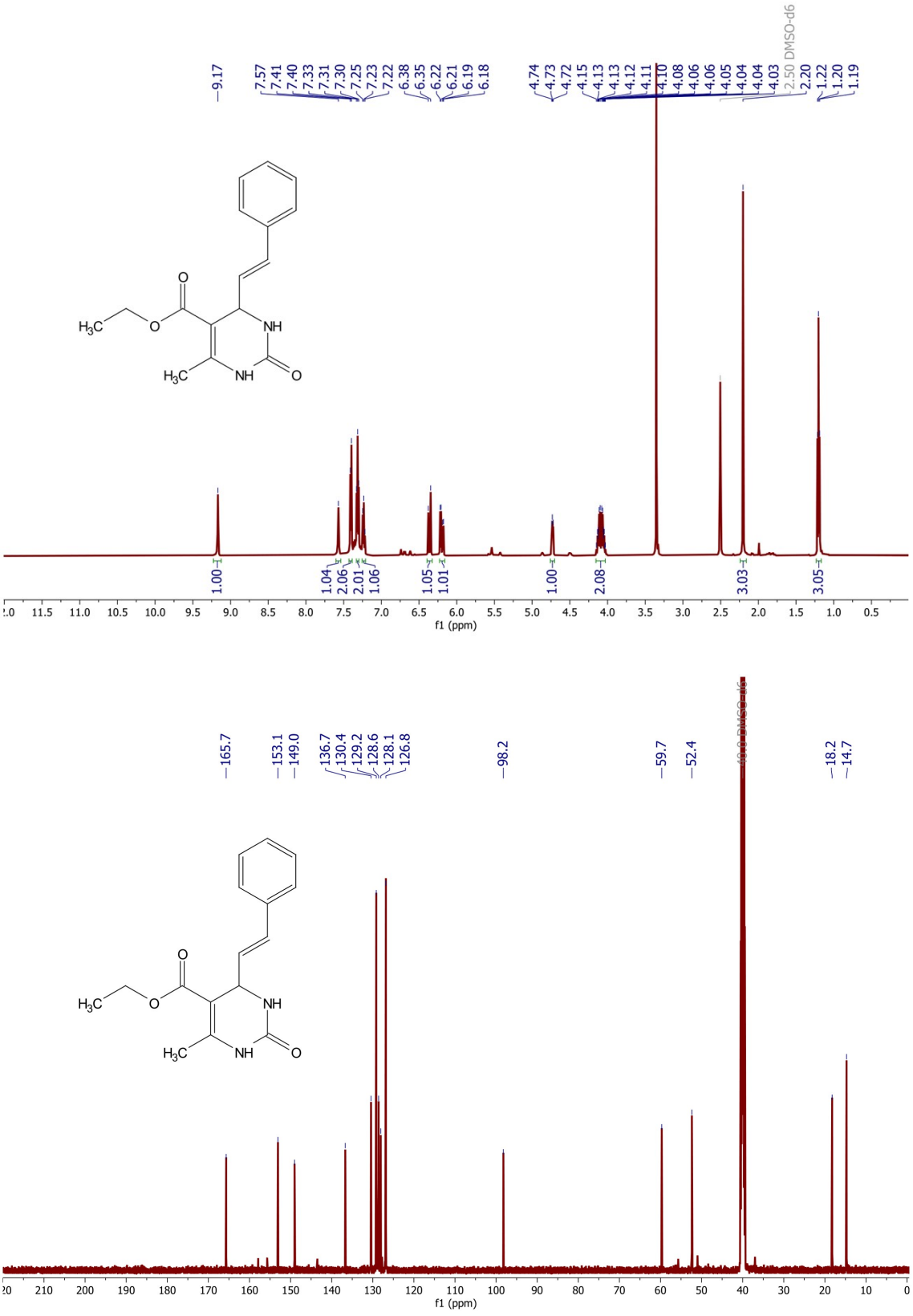


Figure S11. ^{1}H and ^{13}C NMR spectra of Ethyl (*E*)-6-methyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(11a)**

Ethyl 4-cyclohexyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (12a)

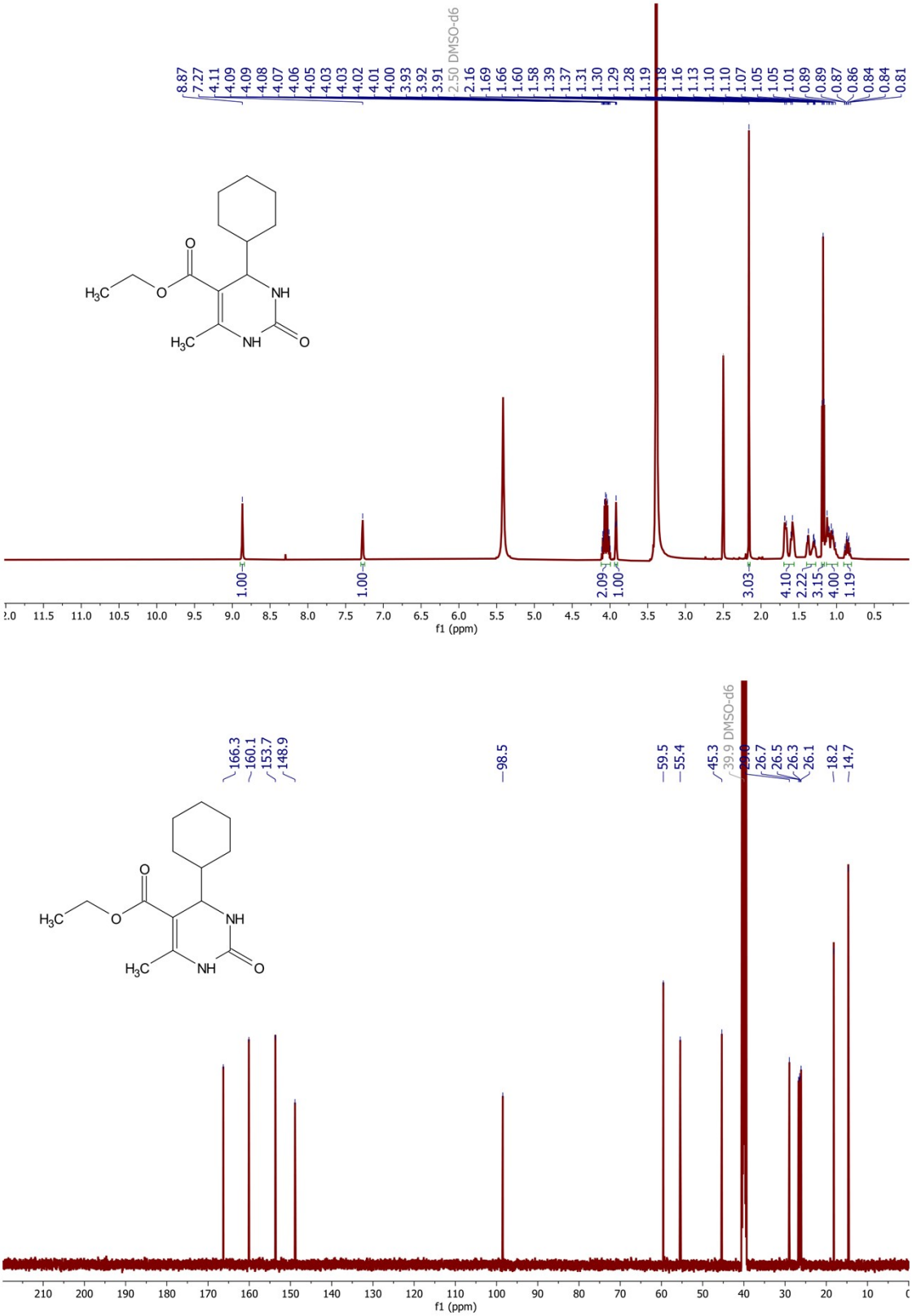


Figure S12. ^{1}H and ^{13}C NMR spectra of Ethyl 4-cyclohexyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(12a)**

Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (13a)

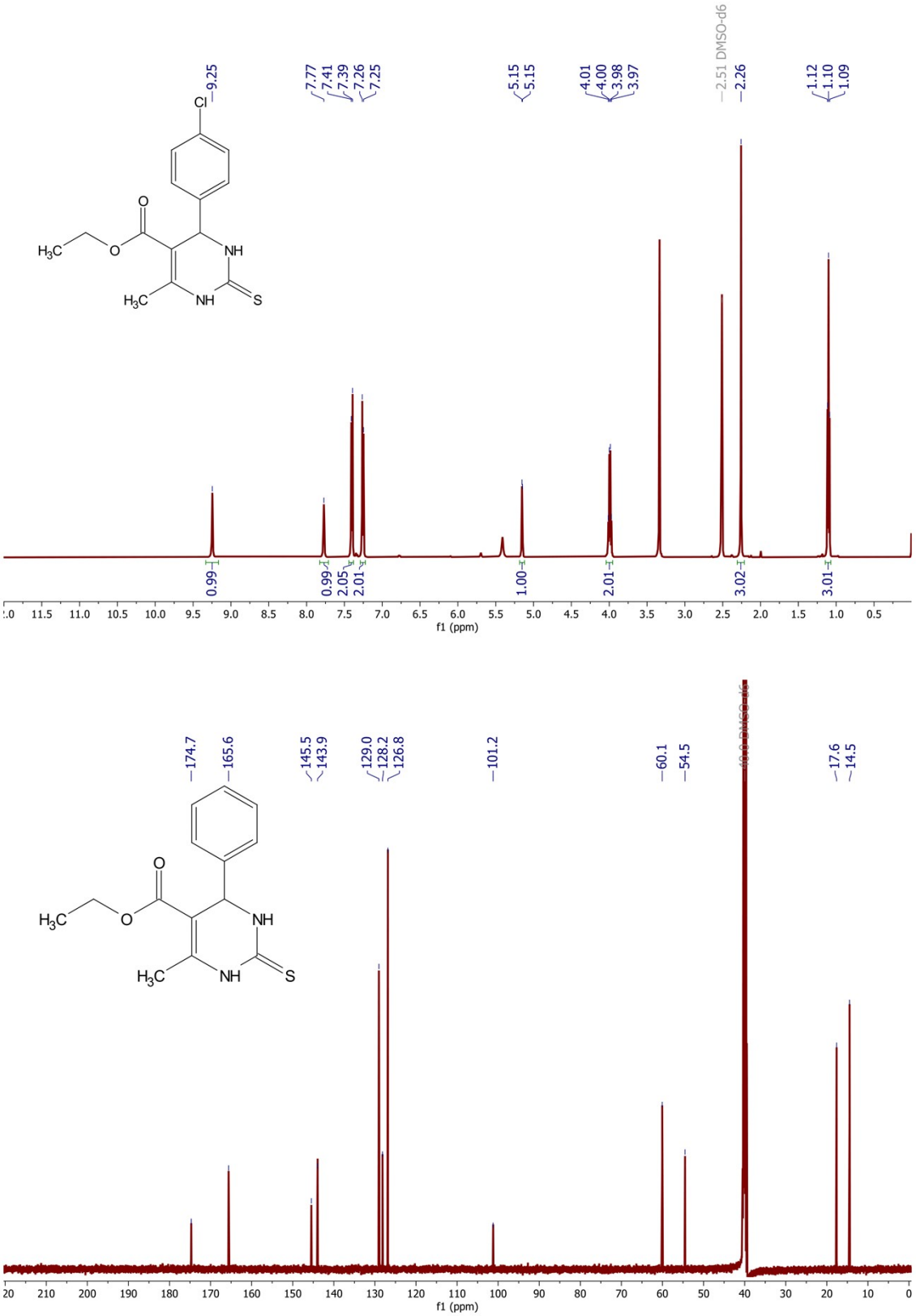


Figure S13. ^{1}H and ^{13}C NMR spectra of Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(13a)**

Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (14a)

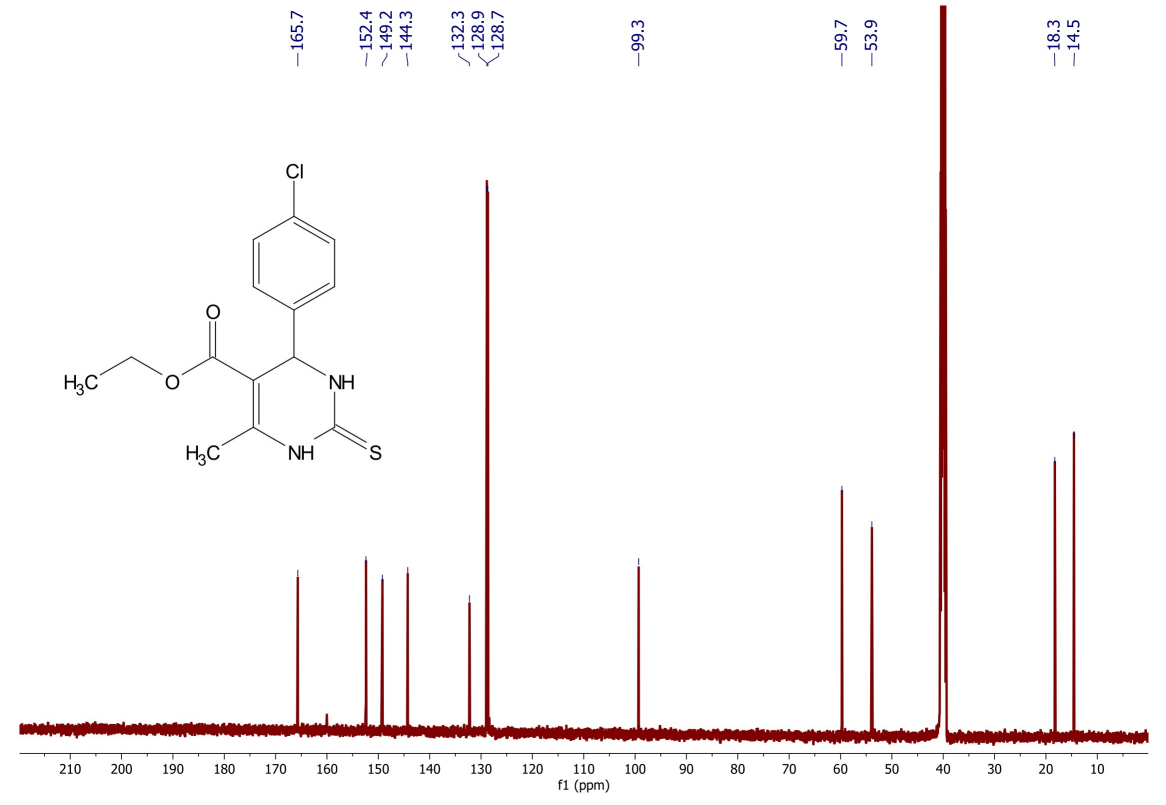


Figure S14. ^{1}H and ^{13}C NMR spectra of Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate **(14a)**

Section S4. References

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