

## Supplementary Information

### Copper (II) nanodots stabilized on *Cassia fistula* galactomannan: preparation and catalytic application towards fast solvent-free Biginelli reaction

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## 1. General and Instrumental Information

Commercially available chemicals purchased from Merck, Avra and SRL were used without further purification. The galactomannan from *Cassia fistula* seeds were separated as follows: The seeds were separated from *Cassia fistula* pods and washed, dried and grinded to fine powder. The 10 gm of fine powder of *Cassia fistula* seeds was soaked for 12 h in 100 mL of 2% v/v acetic acid. After 12 h gel was extracted by diluting with lukewarm water (100 mL) and filtered to obtain gum mucilage, in which ethanol (100 mL) was added. The galactomannan was precipitated out, which dried in oven and grinded to get powdered gum.

TLC (thin layer chromatography) was carried out on precoated plates (Merck silica gel 60,  $f_{254}$ ), and the spots were visualized with UV light.  $^1\text{H}$  NMR for compounds were recorded at 400 MHz instrument, respectively, using  $\text{DMSO-d}_6$  and  $\text{CDCl}_3$  as the solvent. Chemical shifts were recorded in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\delta$  0.00) or chloroform ( $\delta$  7.26, singlet).  $^1\text{H}$  NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. The melting points were recorded on a Buchi M-560 melting point apparatus and are reported as uncorrected.

Infrared spectrums were recorded by using KBr pellet on a Perkin Elmer Spectrum Two spectrometer and reported in wavenumbers ( $\text{cm}^{-1}$ ).

The morphological studies of CFG and  $\text{Cu(II)NDs@CFG}$  catalyst were studied using field emission scanning electron microscopy (FESEM) after being dispersed in ethanol, drop cast onto a cover slip, supported on a metal stub and platinum sputter coated to reduce charge. Field emission scanning electron microscope (FESEM) operated at a 5 kV accelerating voltage, manufactured by *Carl Zeiss* in England, was used to capture the pictures of the materials. The elemental compositions of catalyst  $\text{Cu(II)NDs@CFG}$  were measured from the energy-dispersive X-ray (EDX) by Scanning Electron Microscope of *Carl Zeiss*.

The ICP-MS analysis of catalyst was conducted after their acid digestions on Thermo Scientific, iCAP-Q ICP-MS machine.

XRD of powder samples (CFG and  $\text{Cu(II)NDs@CFG}$ ) were taken by Bruker D8-Advance with X-ray source of 2.2kW Cu anode, 40 kV/40 mA.

The HRTEM studies of  $\text{Cu(II)NDs@CFG}$  catalyst were studied using Tecnai G2 20 TWIN after being dispersed in ethanol, drop cast onto a copper grid, and used to capture the pictures of the materials.

The elemental chemical state on the  $\text{Cu(II)NDs@CFG}$  catalysts surface was analyzed by XPS (K-Alpha, Thermo Fisher Scientific). Using Zetasizer (Malvern Instrument Ltd., UK).

TGA of CFG and  $\text{Cu(II)NDs@CFG}$  catalyst was carried out at instrument EXSTAR TG/DTA 6300 (model: SII 6300 EXSTAR) in air (20 ml/minute).

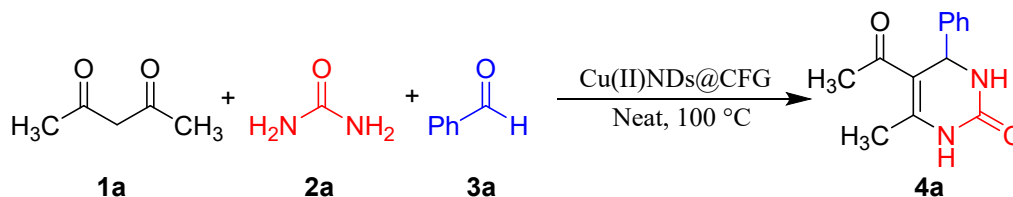
The high precision gas/vapour adsorption surface area analyzer (BELSORP-mini II) was used to record the surface physical parameters (N<sub>2</sub> isotherm, specific surface area and average pore diameter) of CFG and Cu(II)NDs@CFG catalyst. All the data were reported from BELMaster Version 2.3.1 software.

Degassing was performed by using the following points:

- Initially the samples were heated at 100 °C for 2 hours.
  - Again, the samples were heated at 100 °C for 2 hours by passing N<sub>2</sub> through the samples.
- After the above procedure, the BET experiment was performed.

## 2. Gram scale Cu(II)NDs@CFG catalyzed Biginelli reaction

In a 50 mL round bottomed flask equipped with magnetic stirrer a mixture of an benzaldehyde (10.0 mmol), acetylacetone (10.0 mmol), urea (12.0 mmol) and Cu(II)NDs@CFG (250 mg) under solvent free condition was heated for 30 minutes at 100 °C (scheme 3). After completion of reaction (monitored by TLC, ethyl acetate/n-hexane = 1/4), cooled the reaction mixture at room temperature. Added 30 ml ethanol into reaction mixture and stirred for 10 minutes. Separated the catalyst by simple filtration and removed the solvent under reduced pressure. Later, the product was washed with water and ether. Further the product was recrystallized by ethanol. Yield of product **4a** was 78% (1.749 grams).

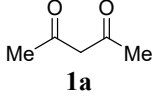
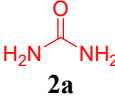
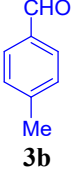
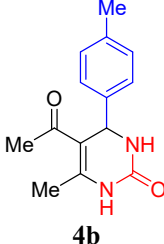
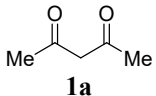
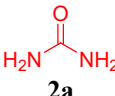
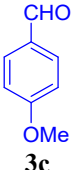
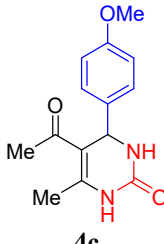
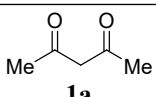
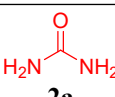
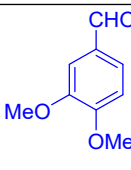
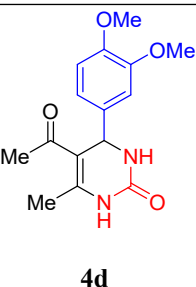
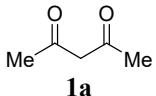
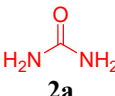
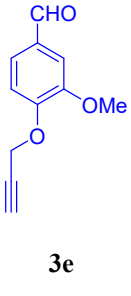
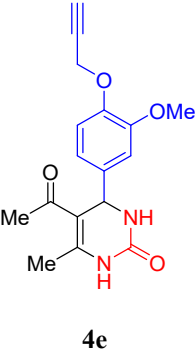
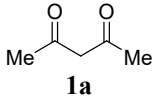
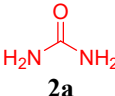
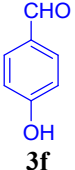
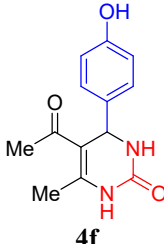
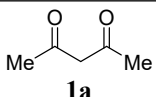
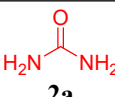
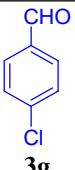
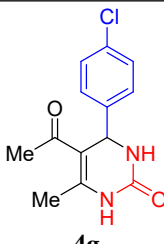


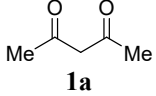
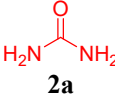
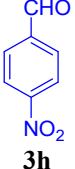
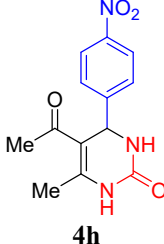
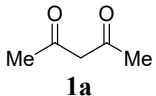
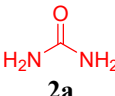
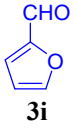
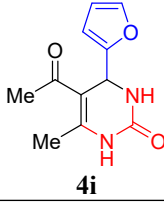
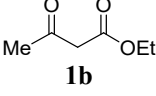
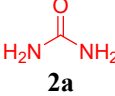
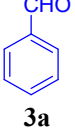
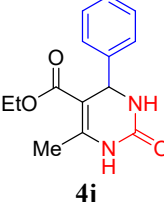
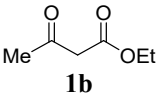
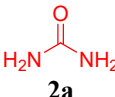
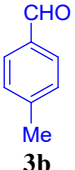
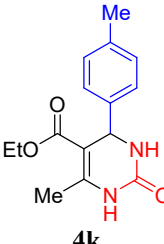
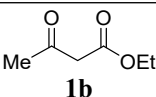
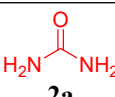
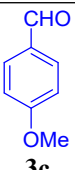
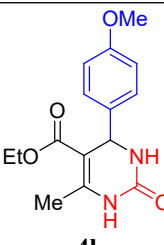
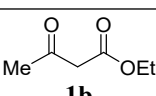
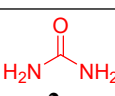
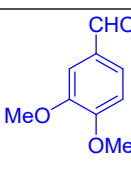
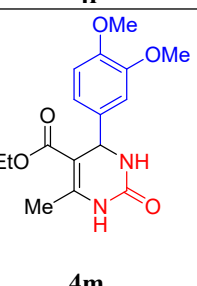
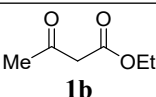
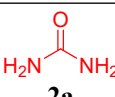
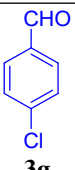
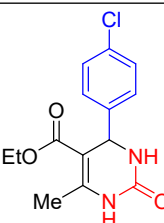
**Scheme 3.** Cu(II)NDs@CFG catalyzed gram-scale synthesis of 5-acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (**3a**).

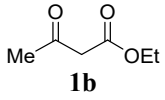

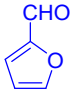
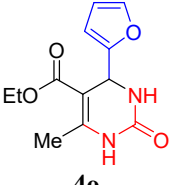
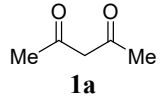

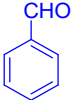
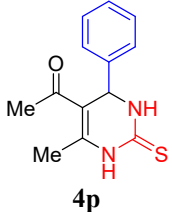
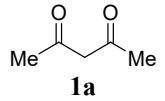

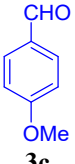
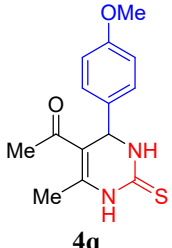
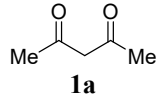

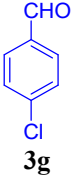
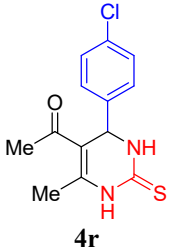
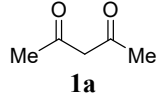

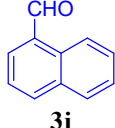
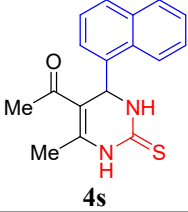
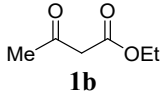

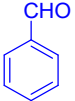
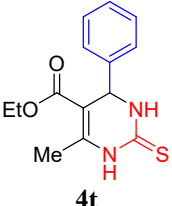
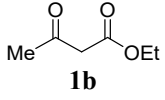

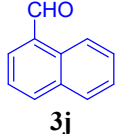
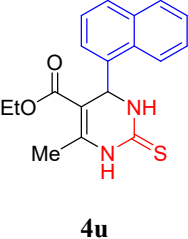
## 3. Substrate scope of products:

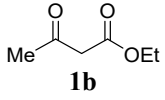

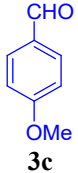
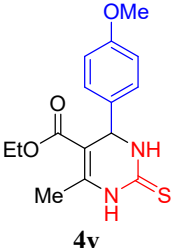
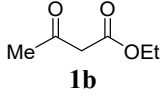

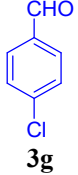
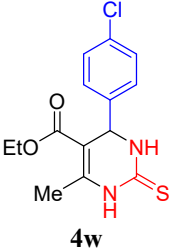
**Table 1.** Substrate scope

S. No.	Diketone	Urea/Thiourea	Aldehydes	DHPM	Reaction time (min.)	% Yield	Melting point (°C) reported	Melting point (°C) found	TON <sup>a</sup>	TOF (h <sup>-1</sup> ) <sup>b</sup>
1					10	86 %	238-240	236-238	122.85	740

2	 <b>1a</b>	 <b>2a</b>	 <b>3b</b>	 <b>4b</b>	10	70 %	204-206	205-207	100	602
3	 <b>1a</b>	 <b>2a</b>	 <b>3c</b>	 <b>4c</b>	10	80 %	169-171	170-172	114.28	688
4	 <b>1a</b>	 <b>2a</b>	 <b>3d</b>	 <b>4d</b>	15	89 %	186-188	185-186	127.14	508.56
5	 <b>1a</b>	 <b>2a</b>	 <b>3e</b>	 <b>4e</b>	15	64 %	183	176-179	91.72	366.88
6	 <b>1a</b>	 <b>2a</b>	 <b>3f</b>	 <b>4f</b>	15	78 %	260-262	260-261	111.42	445.71
7	 <b>1a</b>	 <b>2a</b>	 <b>3g</b>	 <b>4g</b>	15	65 %	215-218	215-216	92.85	371.43

8	 <b>1a</b>	 <b>2a</b>	 <b>3h</b>	 <b>4h</b>	15	78 %	236-238	236-238	111.42	445.71
9	 <b>1a</b>	 <b>2a</b>	 <b>3i</b>	 <b>4i</b>	10	75 %	231-233	230-232	107.14	645.43
10	 <b>1b</b>	 <b>2a</b>	 <b>3a</b>	 <b>4j</b>	20	76 %	202-204	201-203	108.57	326.03
11	 <b>1b</b>	 <b>2a</b>	 <b>3b</b>	 <b>4k</b>	20	91 %	201-203	200-201	130	390.39
12	 <b>1b</b>	 <b>2a</b>	 <b>3c</b>	 <b>4l</b>	25	78 %	201-203	200-201	111.43	267.85
13	 <b>1b</b>	 <b>2a</b>	 <b>3d</b>	 <b>4m</b>	25	80 %	176-178	174-175	114.28	274.72
14	 <b>1b</b>	 <b>2a</b>	 <b>3g</b>	 <b>4n</b>	120	82 %	212-214	210-211	117.14	58.57

15	 <b>1b</b>	 <b>2a</b>	 <b>3i</b>	 <b>4n</b>	70	74 %	207-209	202-204	105.71	91.13
16	 <b>1a</b>	 <b>2b</b>	 <b>3a</b>	 <b>4p</b>	70	77 %	183	183-184	110	94.82
17	 <b>1a</b>	 <b>2b</b>	 <b>3c</b>	 <b>4q</b>	120	74 %	156-158	155-157	105.71	52.85
18	 <b>1a</b>	 <b>2b</b>	 <b>3g</b>	 <b>4r</b>	120	67 %	193-194	190-192	95.71	47.85
19	 <b>1a</b>	 <b>2b</b>	 <b>3j</b>	 <b>4s</b>	120	77 %	210-212	210-211	110	55
20	 <b>1b</b>	 <b>2b</b>	 <b>3a</b>	 <b>4t</b>	120	68 %	209-211	208-209	97.14	48.57
21	 <b>1b</b>	 <b>2b</b>	 <b>3j</b>	 <b>4u</b>	120	65 %	218-220	220-222	92.85	46.42

22					120	71 %	149-151	155-151	101.42	50.71
23					120	65 %	182-184	184-186	92.85	46.42

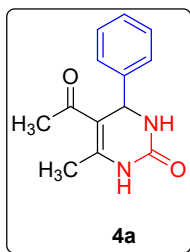
*Number of moles of product*

$${}^a\text{TON}^1 (\text{turnover number}) = \frac{\text{Number of moles of product}}{\text{Number of moles of Cu (used in 25 mg of catalyst)}}$$

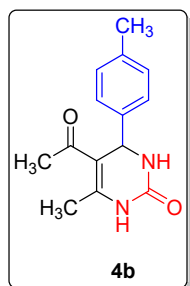
*TON*

$${}^b\text{TOF}^1 (\text{turnover frequency}) = \frac{\text{TON}}{\text{Time of reaction}}$$

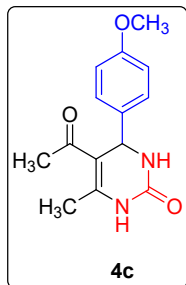
#### 4. Characterization of Products:



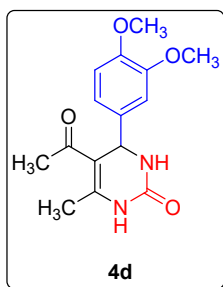
**5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (4a)<sup>2</sup>:** The compound **4a** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 86% yield; mp 236-238 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.10 (s, 1H), 7.75 (s, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 6.3 Hz, 3H), 5.20 (d, *J* = 3.7 Hz, 1H), 2.23 (s, 3H), 2.04 (s, 3H).



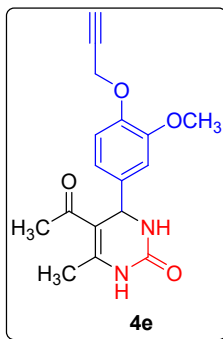
**5-Acetyl-6-methyl-4-(p-tolyl)-3,4-dihydropyrimidin-2(1H)-one (4b)**<sup>3</sup>: The compound **4b** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 70% yield; mp 205-207 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (s, 1H), 7.22 – 7.10 (m, 4H), 5.64 (s, 1H), 5.41 (s, 1H), 2.34 (d, *J* = 7.58 Hz, 6H), 2.11 (s, 3H).



**5-Acetyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4c)**<sup>4</sup>: The compound **4c** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. Yellow solid 80% yield; mp 170-172 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.84 (s, 1H), 7.20 (s, 2H), 6.82 (s, 2H), 6.48 (s, 1H), 5.36 (s, 1H), 3.75 (s, 3H), 2.30 (s, 3H), 2.08 (s, 3H).



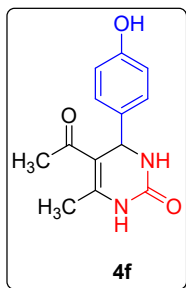
**5-Acetyl-4-(3,4-dimethoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4d)**<sup>5</sup>: The compound **4d** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. Yellow solid 89% yield; mp 185-186 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.71 (s, 1H), 6.89 – 6.73 (m, 3H), 6.38 (s, 1H), 5.38 (s, 1H), 3.82 (d, *J* = 5.62 Hz, 6H), 2.31 (s, 3H), 2.10 (s, 3H).



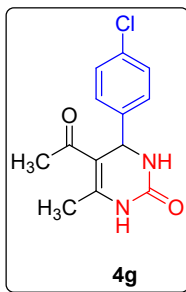
**5-Acetyl-4-(3-methoxy-4-(prop-2-yn-1-yloxy)phenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4e)**<sup>6</sup>: The compound **4e** was prepared by optimized reaction condition and purified



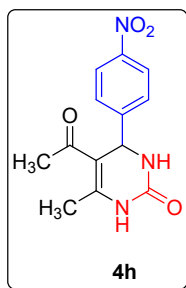
by recrystallisation in ethanol. Yellow solid 64% yield; mp 176-179 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.14 (s, 1H), 7.77 (s, 1H), 6.98 – 6.89 (m, 2H), 6.70 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.22 (d, *J* = 3.5 Hz, 1H), 4.72 (s, 2H), 3.73 (s, 3H), 3.42 (s, 1H), 2.28 (s, 3H), 2.10 (s, 3H).



**5-Acetyl-4-(4-hydroxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4f)<sup>7</sup>:** The compound **4f** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. Yellow solid 78% yield; mp 260-261 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.36 (s, 1H), 9.11 (s, 1H), 7.71 (s, 1H), 7.04 (d, *J* = 8.56 Hz, 2H), 6.70 (d, *J* = 8.56 Hz, 2H), 5.14 (d, *J* = 3.42 Hz, 1H), 2.26 (s, 3H), 2.05 (s, 3H).

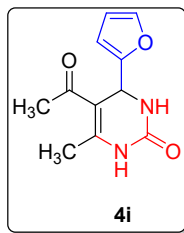


**5-Acetyl-4-(4-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4g)<sup>2</sup>:** The compound **4g** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. Yellow solid 65% yield; mp 215-216 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (s, 1H), 7.30 (d, *J* = 8.56 Hz, 2H), 7.24 (d, *J* = 8.56 Hz, 2H), 5.94 (s, 1H), 5.45 (d, *J* = 3.18 Hz, 1H), 2.35 (s, 3H), 2.17 (s, 3H).

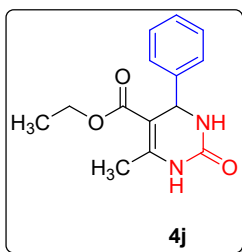


**5-Acetyl-6-methyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (4h)<sup>4</sup>:** The compound **4h** was prepared by optimized reaction condition and purified by recrystallisation in ethanol.

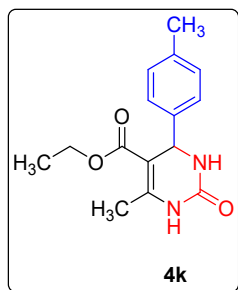
Yellow solid 78% yield; mp 236-238 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.35 (s, 1H), 8.21 (d, *J* = 8.80 Hz, 2H), 8.00 (s, 1H), 7.51 (d, *J* = 8.80 Hz, 2H), 5.39 (s, 1H), 2.32 (s, 3H), 2.19 (s, 3H).



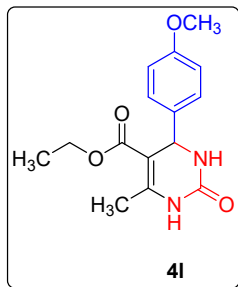
**5-Acetyl-4-(furan-2-yl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4i)**<sup>8</sup>: The compound **4i** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 75% yield; mp 230-232 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.21 (s, 1H), 7.83 (s, 1H), 7.51 (s, 1H), 6.35 (dd, *J* = 3.2, 2.1 Hz, 1H), 6.13 (d, *J* = 3.2 Hz, 1H), 5.33 (d, *J* = 3.7 Hz, 1H), 2.23 (s, 3H), 2.16 (s, 3H).



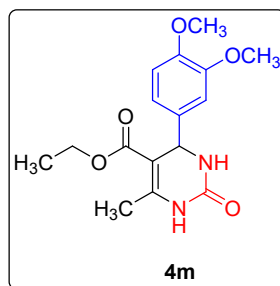
**Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4j)**<sup>4</sup>: The compound **4j** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 76% yield; mp 201-203 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.12 (s, 1H), 7.72 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.46 Hz, 3H), 5.56 (s, 3H), 5.16 (d, *J* = 3.55 Hz, 1H), 2.23 (s, 3H), 1.06 (t, *J* = 7.09 Hz, 3H).



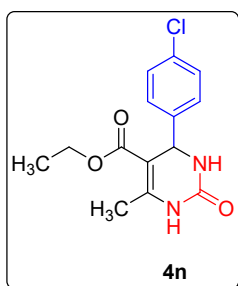
**Ethyl 6-methyl-2-oxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4k)**<sup>4</sup>: The compound **4k** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 91% yield; mp 200-201 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.09 (s, 1H), 7.66 (s, 1H), 7.10 (s, 4H), 5.56 (s, 2H), 5.12 (s, 1H), 2.23 (s, 6H), 1.07 (t, *J* = 7.15 Hz, 3H).



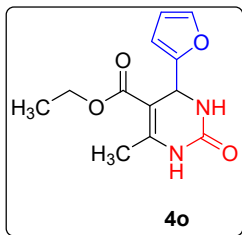
**Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4l)<sup>4</sup>:** The compound **4l** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 78% yield; mp 200-201 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.10 (s, 1H), 7.66 (s, 1H), 7.14 (d, *J* = 8.56 Hz, 2H), 6.85 (d, *J* = 8.56 Hz, 2H), 5.59 (s, 3H), 5.11 (s, 1H), 3.68 (s, 2H), 2.23 (s, 3H), 1.07 (t, *J* = 7.09 Hz, 3H).



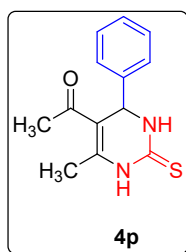
**Ethyl 4-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4m)<sup>9</sup>:** The compound **4m** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 80% yield; mp 174-175 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.09 (s, 1H), 7.67 (s, 1H), 6.87 (d, *J* = 8.31 Hz, 2H), 6.73 (d, *J* = 8.19 Hz, 1H), 5.57 (s, 2H), 5.11 (s, 1H), 3.69 (d, *J* = 2.93 Hz, 6H), 2.23 (s, 3H), 1.08 (t, *J* = 7.09 Hz, 3H).



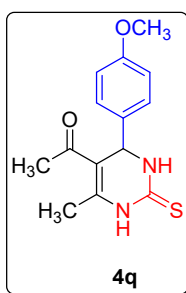
**Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4n)<sup>4</sup>:** The compound **4n** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 82% yield; mp 210-211 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.26 (s, 1H), 7.78 (s, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 5.14 (d, *J* = 3.4 Hz, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H).



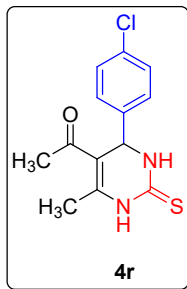
**Ethyl 4-(furan-2-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4o)<sup>2</sup>:** The compound **4o** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 74% yield; mp 202-204 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 9.17 (s, 1H), 7.72 (s, 1H), 7.48 (d, *J* = 2.20 Hz, 1H), 6.34 (dd, *J* = 3.24, 2.02 Hz, 1H), 6.09 (d, *J* = 3.18 Hz, 1H), 5.22 (d, *J* = 3.55 Hz, 1H), 4.00 (q, *J* = 7.09, 3.18 Hz, 2H), 2.20 (s, 3H), 1.10 (t, *J* = 7.09 Hz, 3H).



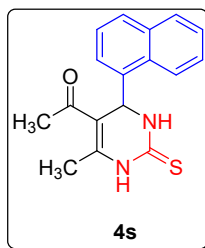
**1-(6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethan-1-one (4p)<sup>4</sup>:** The compound **4p** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 77% yield; mp 183-184 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (s, 1H), 7.43 – 7.27 (m, 6H), 5.46 (s, 1H), 2.36 (s, 3H), 2.15 (s, 3H).



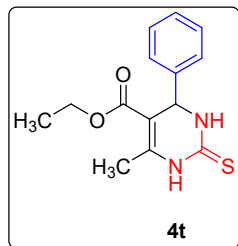
**1-(4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethan-1-one (4q)<sup>2</sup>:** The compound **4q** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 74% yield; mp 155-157 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (s, 1H), 7.90 (s, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 6.83 (s, 2H), 5.37 (s, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 2.10 (s, 3H).



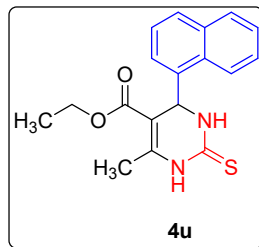
**1-(4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethan-1-one (4r)<sup>2</sup>:** The compound **4r** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 67% yield; mp 190-192 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (s, 1H), 7.54 (s, 1H), 7.31 (d, *J* = 8.56 Hz, 2H), 7.22 (d, *J* = 8.44 Hz, 2H), 5.46 (s, 1H), 2.36 (s, 3H), 2.19 (s, 3H).



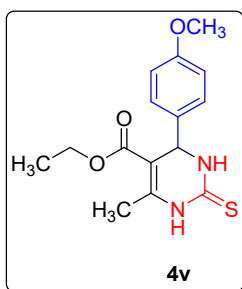
**1-(6-methyl-4-(naphthalen-1-yl)-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethan-1-one (4s)<sup>10</sup>:** The compound **4s** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 77% yield; mp 210-211 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.35 (s, 1H), 9.79 – 9.73 (m, 1H), 8.49 (d, *J* = 8.56 Hz, 1H), 7.98 (d, *J* = 9.41 Hz, 1H), 7.90 (d, *J* = 8.19 Hz, 1H), 7.68 – 7.54 (m, 2H), 7.50 (t, *J* = 7.70 Hz, 1H), 7.33 (d, *J* = 6.85 Hz, 1H), 6.19 (d, *J* = 4.16 Hz, 1H), 2.45 (s, 3H), 2.05 (s, 3H).



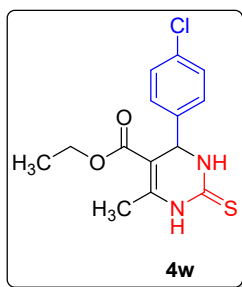
**Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4t)<sup>4</sup>:** The compound **4t** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 68% yield; mp 208-209 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.22 (s, 1H), 9.56 (s, 1H), 7.36 – 7.17 (m, 5H), 5.19 (s, 1H), 3.99 (s, 2H), 2.27 (s, 3H), 1.06 (t, *J* = 8 Hz, 3H).



**Ethyl 6-methyl-4-(naphthalen-1-yl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4u)**<sup>11</sup>: The compound **4u** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 65% yield; mp 220-222 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.72 (s, 1H), 8.07 (d, *J* = 8.31 Hz, 1H), 7.96 – 7.81 (m, 2H), 7.77 (d, *J* = 9.66 Hz, 1H), 7.52 (p, *J* = 6.66 Hz, 2H), 7.41 (d, *J* = 6.60 Hz, 2H), 6.10 (s, 1H), 3.96 – 3.79 (m, 2H), 2.34 (s, 3H), 0.83 (t, *J* = 7.15 Hz, 3H).



**Ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4v)**<sup>12</sup>: The compound **4v** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 71% yield; mp 150-151 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 1H), 7.73 (s, 1H), 7.19 (d, *J* = 8.41 Hz, 2H), 6.82 (d, *J* = 8.62 Hz, 2H), 5.32 (d, *J* = 3.13 Hz, 1H), 4.07 (qq, *J* = 7.48, 3.84 Hz, 2H), 3.77 (s, 3H), 2.34 (s, 3H), 1.16 (t, *J* = 7.11 Hz, 3H).



**Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4w)**<sup>12</sup>: The compound **4w** was prepared by optimized reaction condition and purified by recrystallisation in ethanol. White solid 65% yield; mp 184-186 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 1H), 7.82 (s, 1H), 7.35 – 7.17 (m, 4H), 5.36 (s, 1H), 4.10 (qt, *J* = 6.97, 3.36 Hz, 2H), 2.35 (s, 3H), 1.17 (t, *J* = 7.01 Hz, 3H).

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## 6. EDS spectra of Cu(II)NDs@CFG

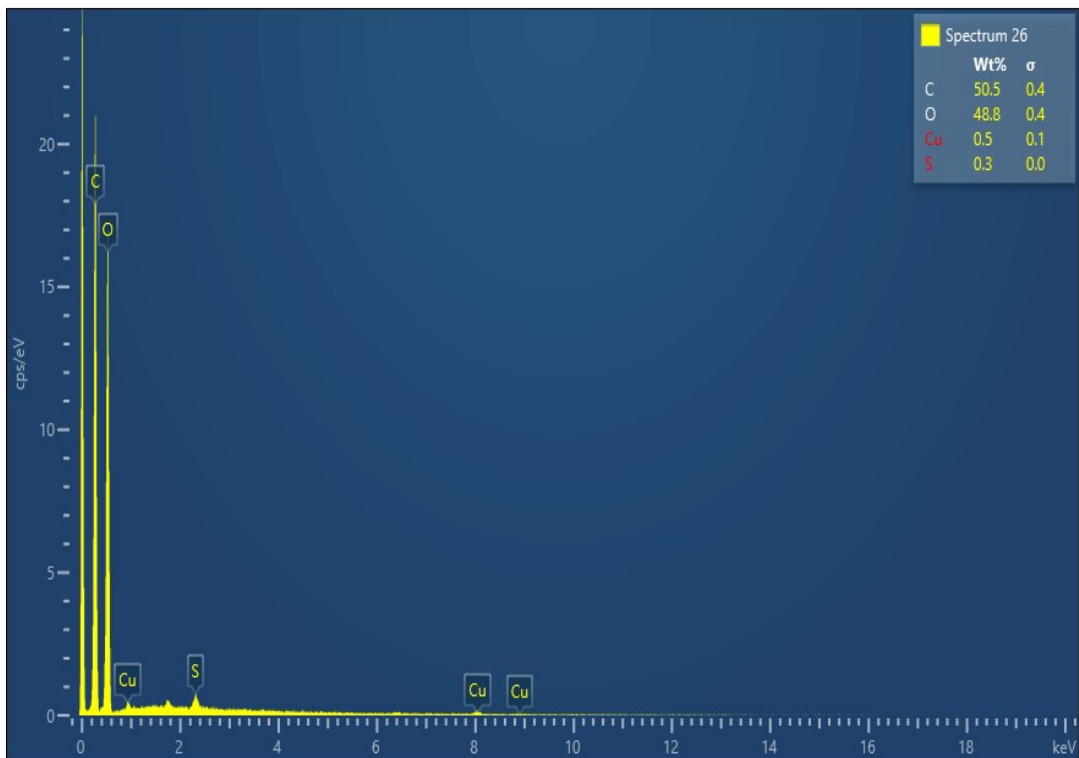


Fig. 1 EDS spectra of Cu(II)NDs@CFG

## 7. BJH plot of CFG and Cu(II)NDs@CFG

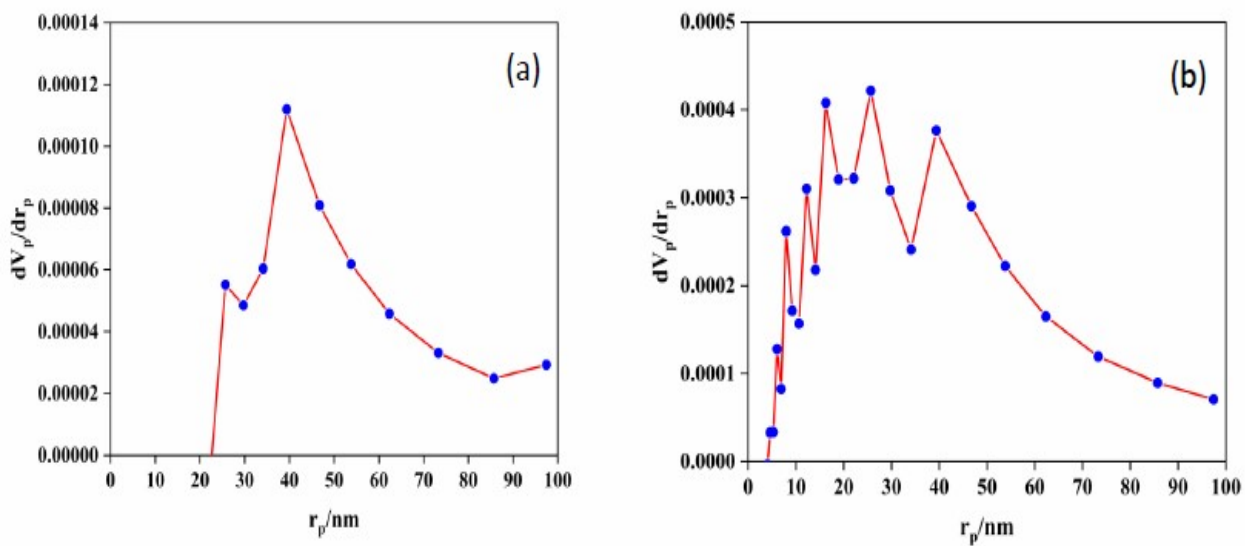
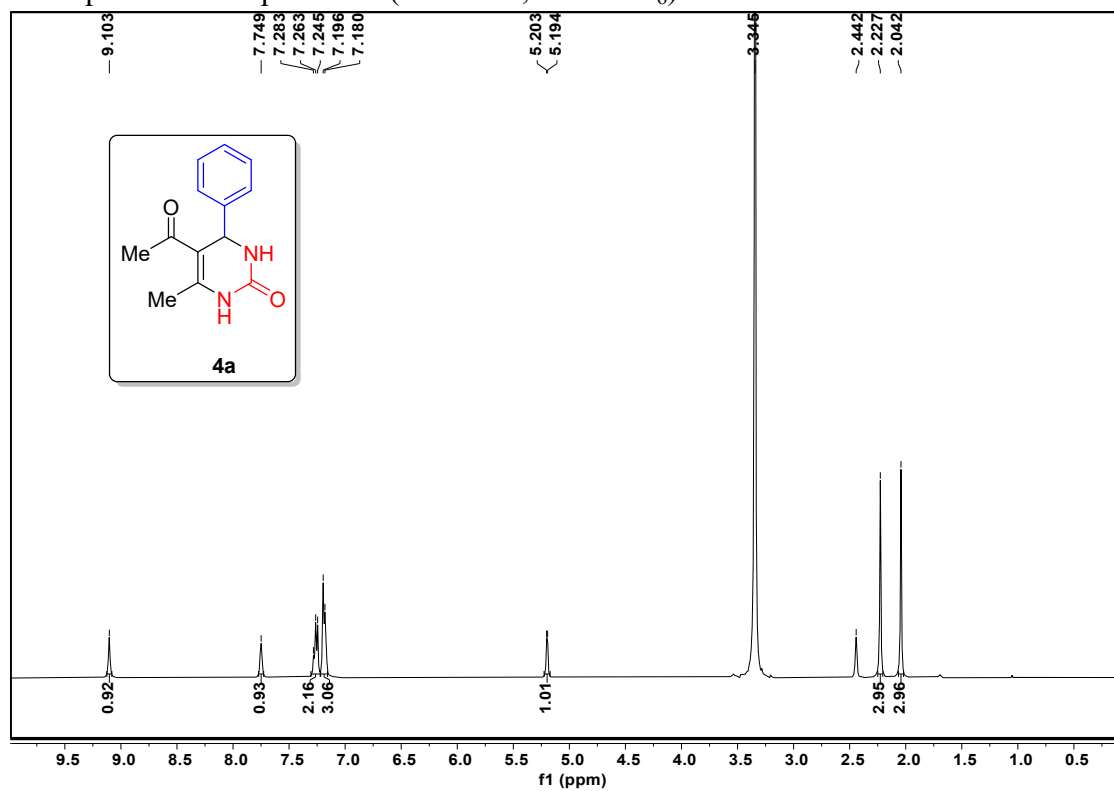


Fig. 2 BJH plot of (a) CFG and (b) Cu(II)NDs@CFG.

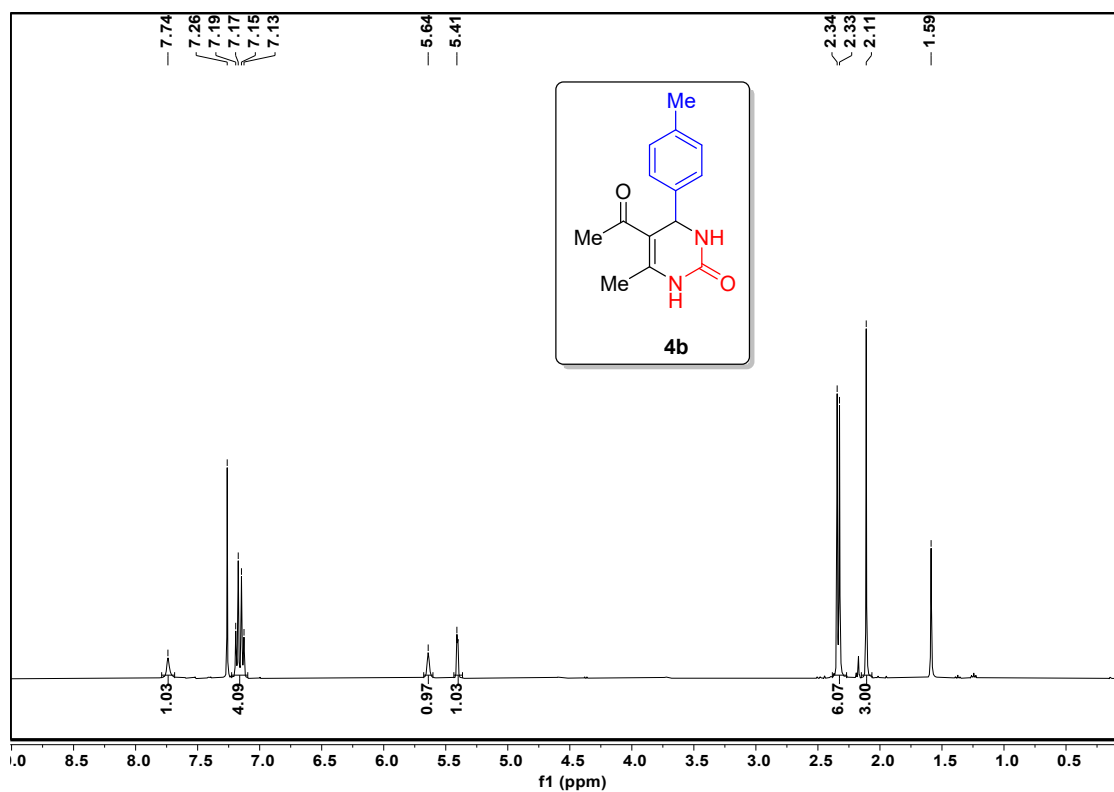


## 8. <sup>1</sup>H NMR Spectra of compounds

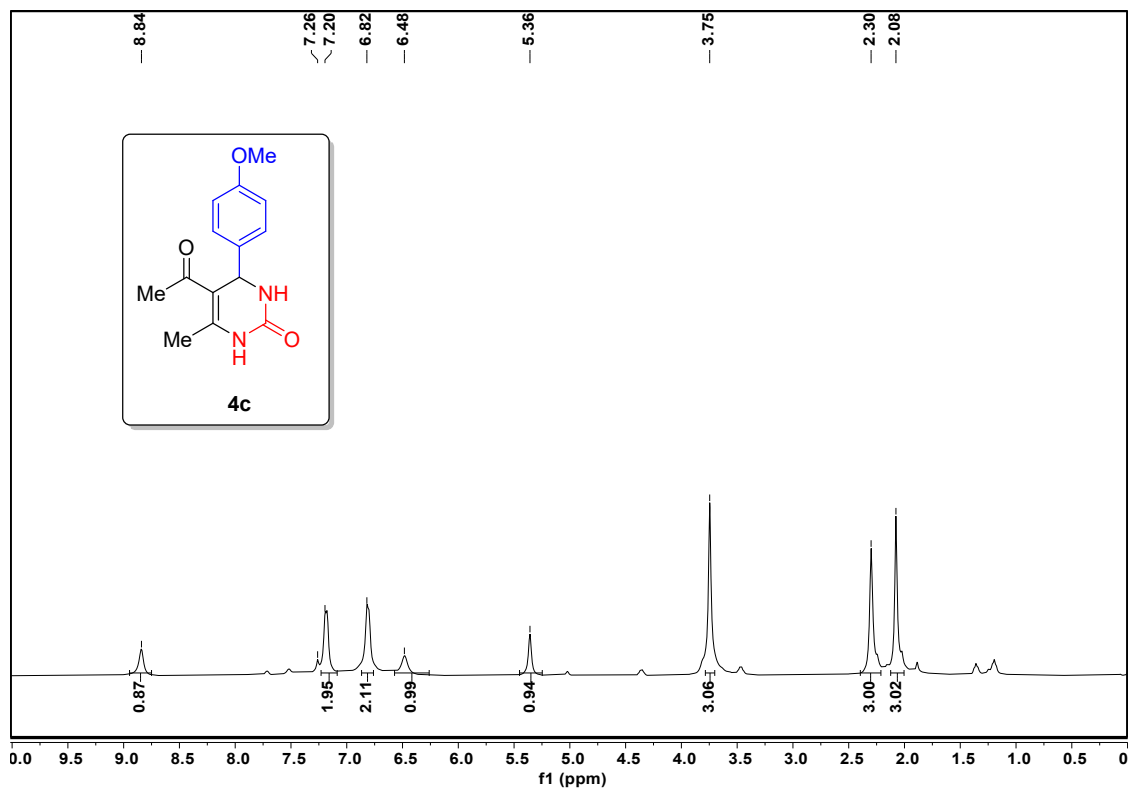
<sup>1</sup>H NMR Spectra of compound **4a** (400 MHz, DMSO-d<sub>6</sub>)



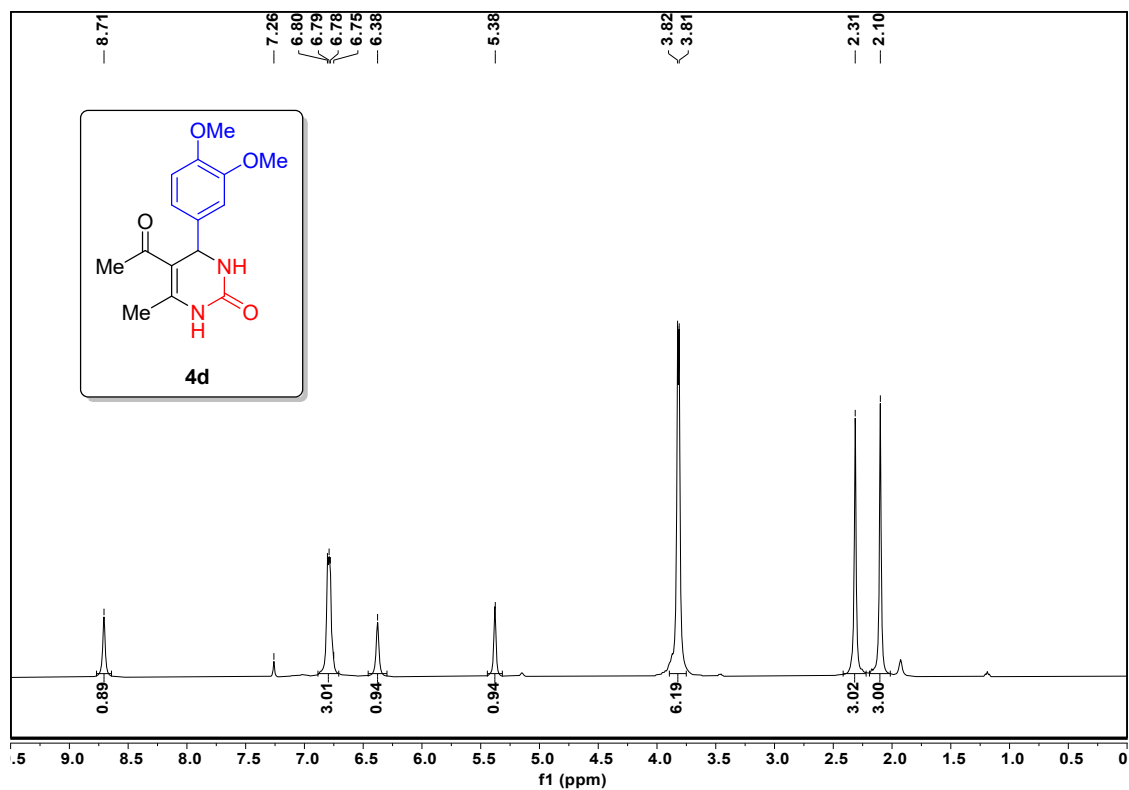
<sup>1</sup>H NMR Spectra of compound **4b** (400 MHz, CDCl<sub>3</sub>)



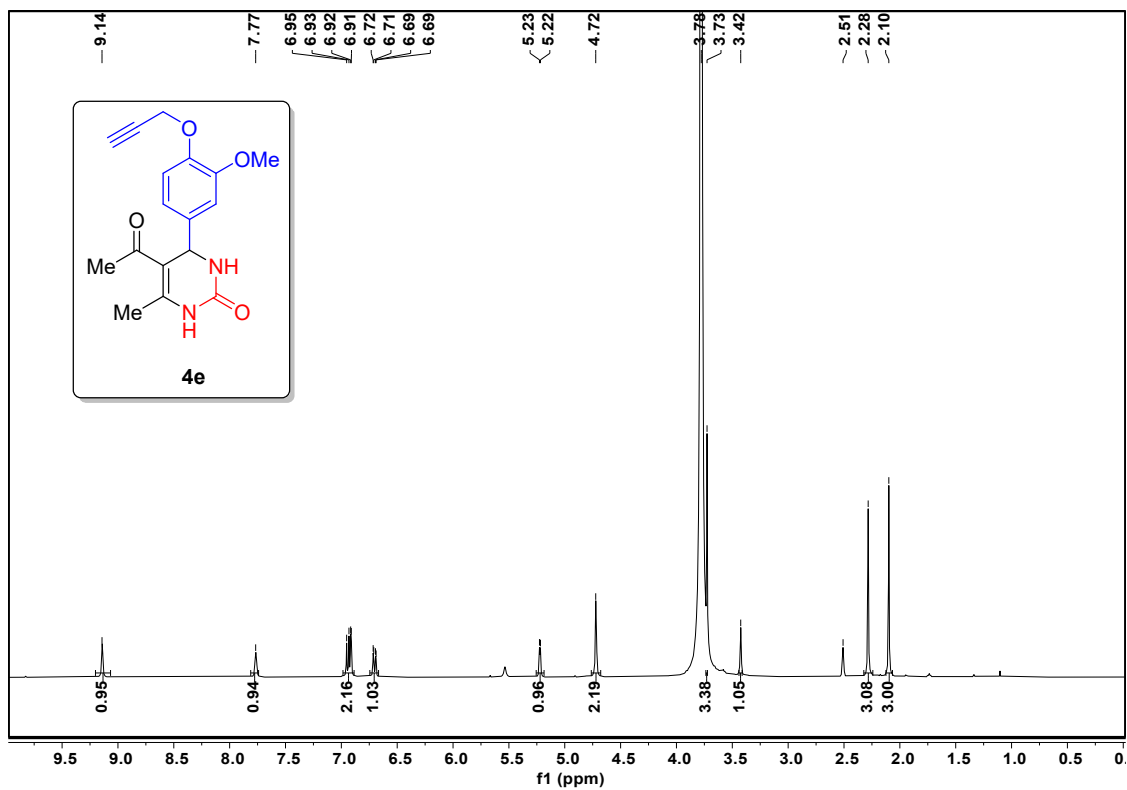
$^1\text{H}$  NMR Spectra of compound **4c** (400 MHz,  $\text{CDCl}_3$ )



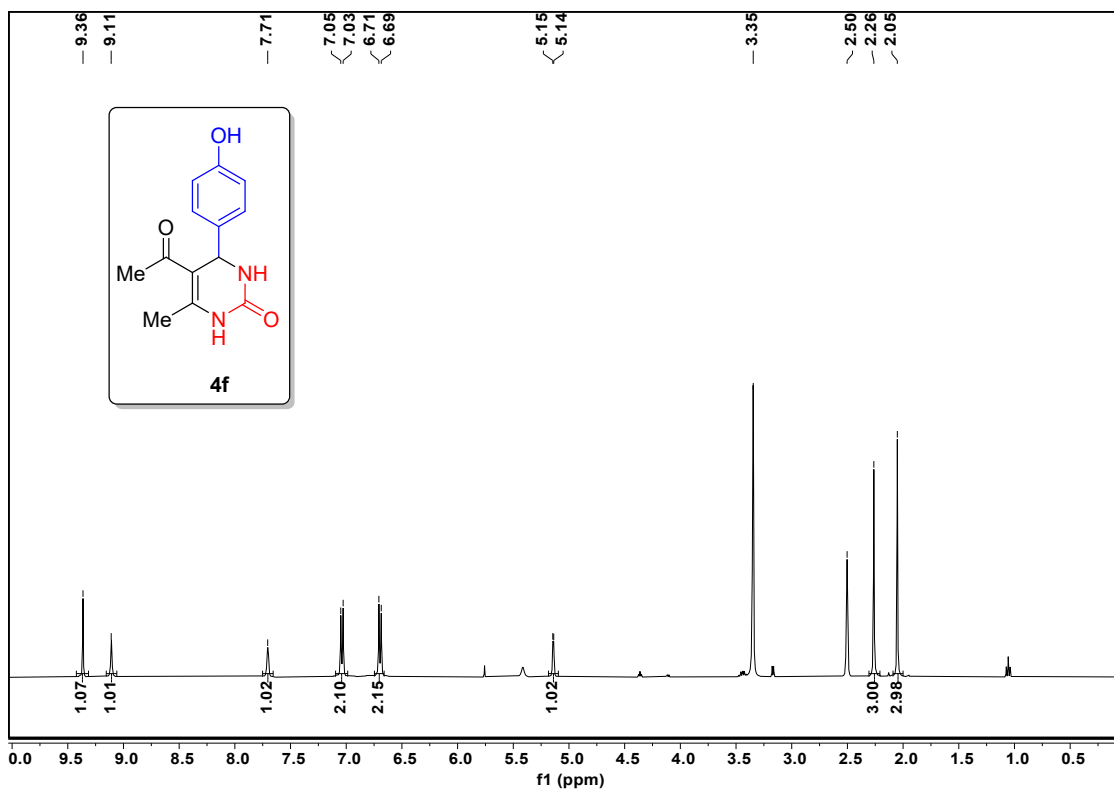
$^1\text{H}$  NMR Spectra of compound **4d** (400 MHz,  $\text{CDCl}_3$ )



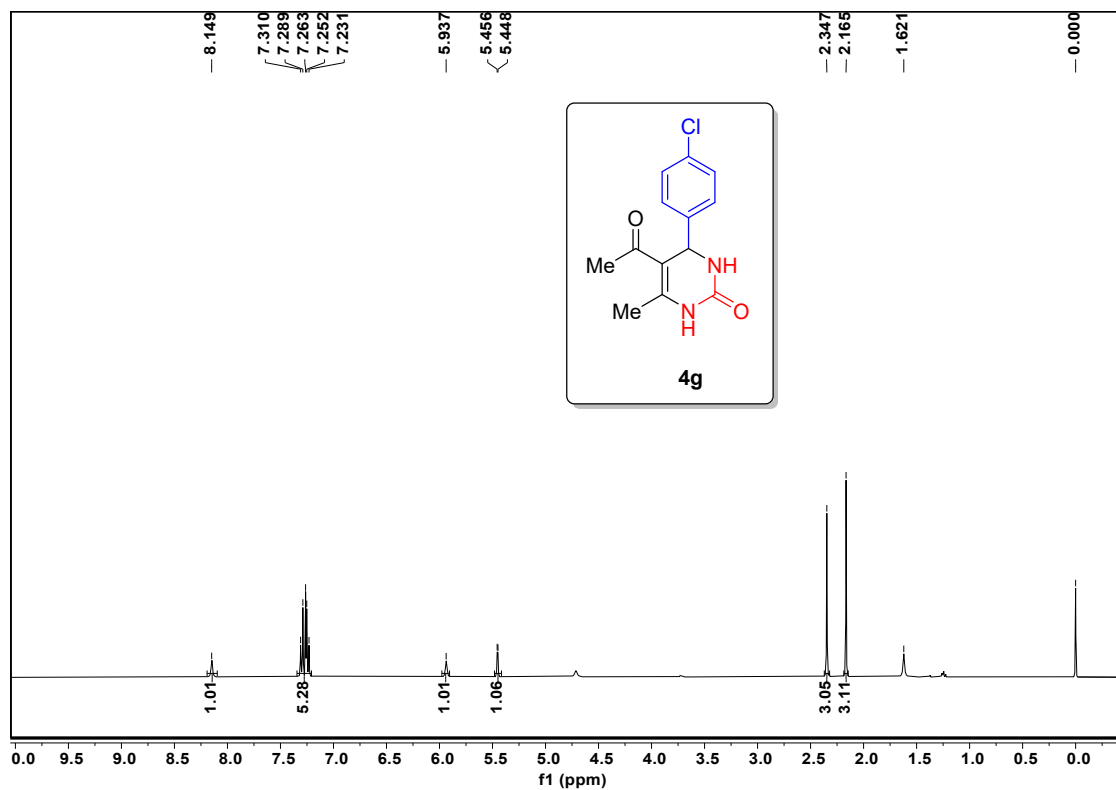
<sup>1</sup>H NMR Spectra of compound **4e** (400 MHz, DMSO-d<sub>6</sub>)



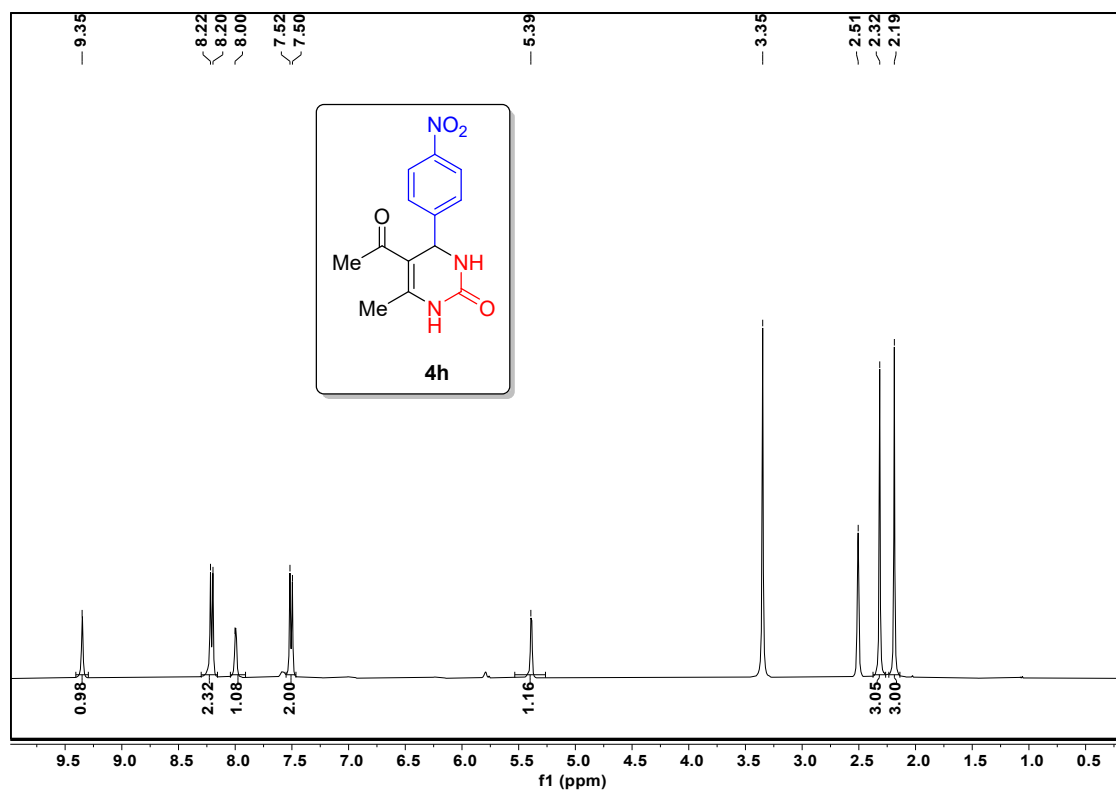
<sup>1</sup>H NMR Spectra of compound **4f** (400 MHz, DMSO-d<sub>6</sub>)



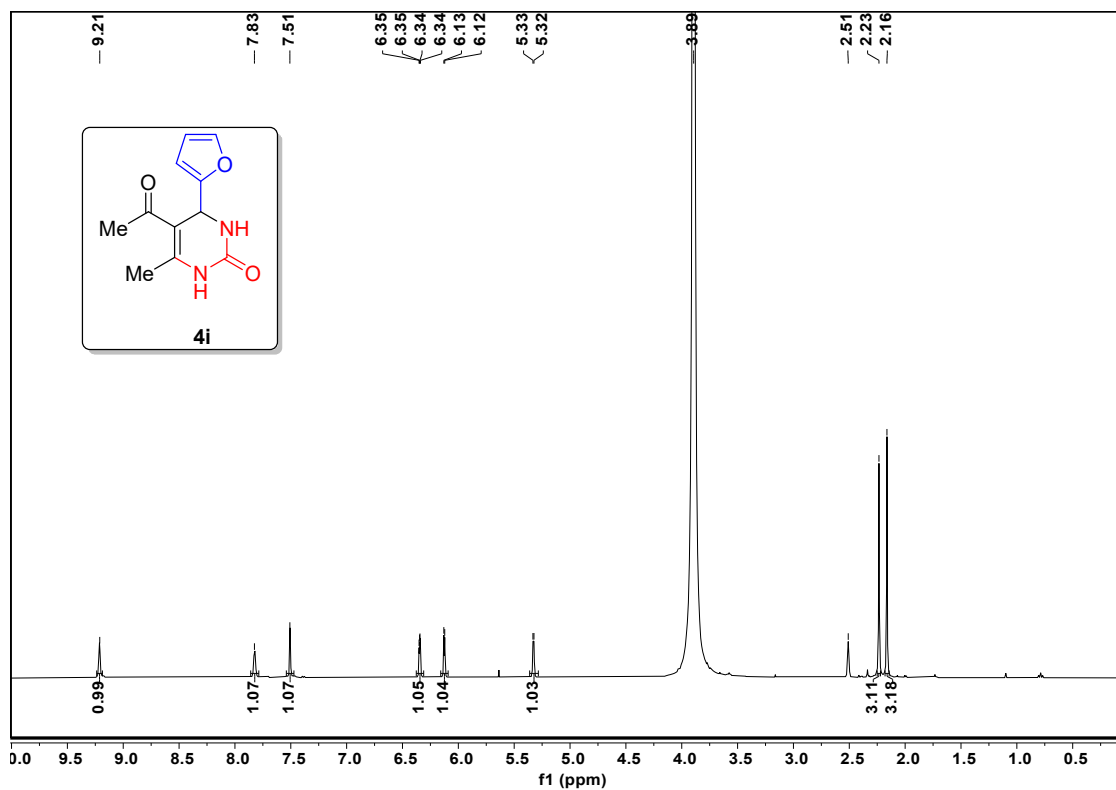
<sup>1</sup>H NMR Spectra of compound **4g** (400 MHz, CDCl<sub>3</sub>)



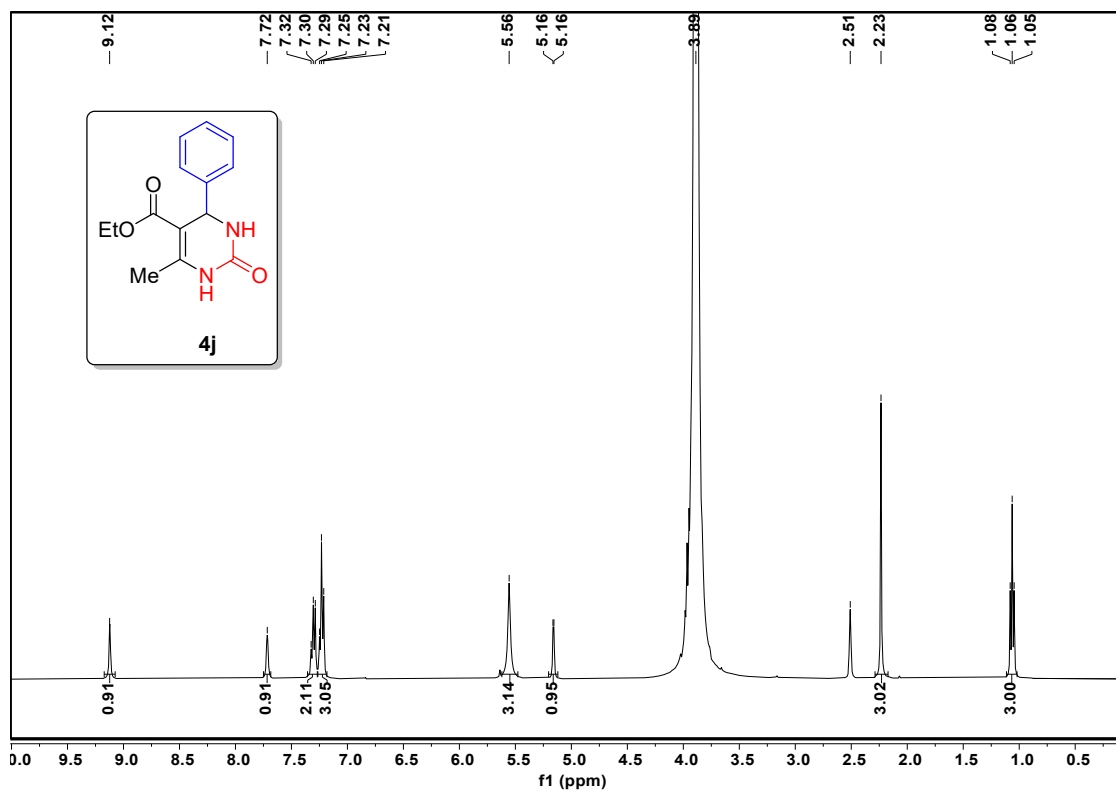
<sup>1</sup>H NMR Spectra of compound **4h** (400 MHz, DMSO-d<sub>6</sub>)



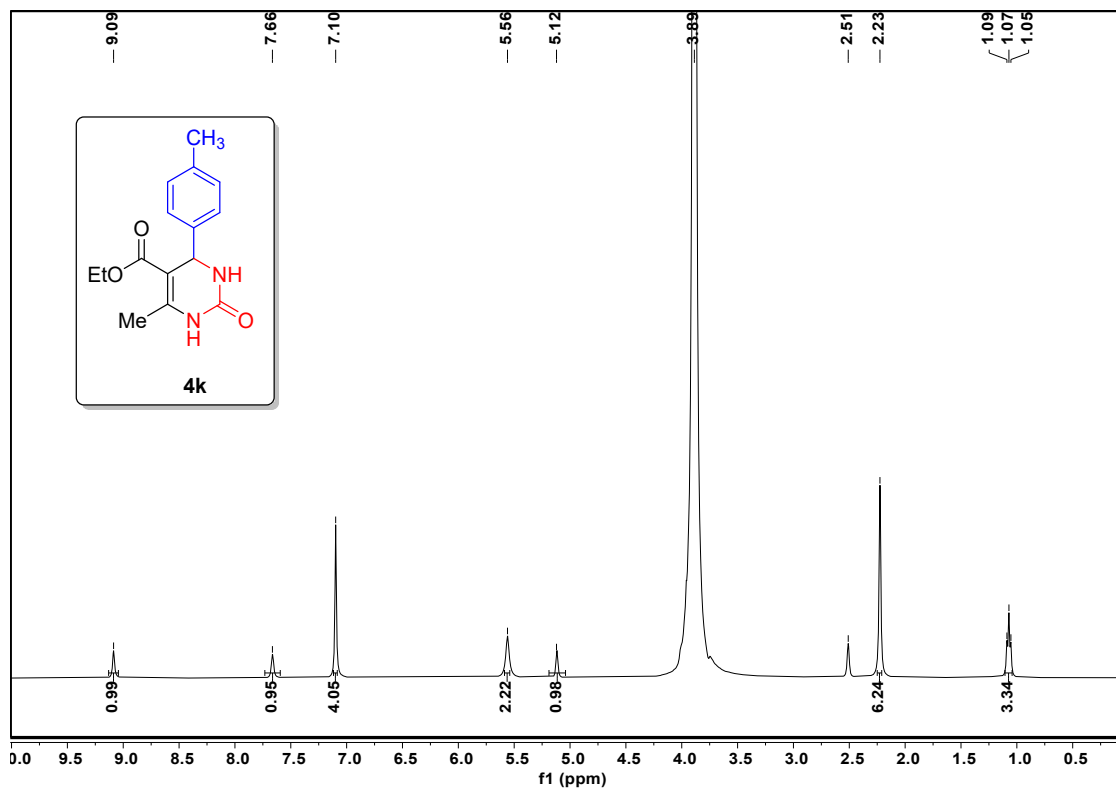
<sup>1</sup>H NMR Spectra of compound **4i** (400 MHz, DMSO-d<sub>6</sub>)



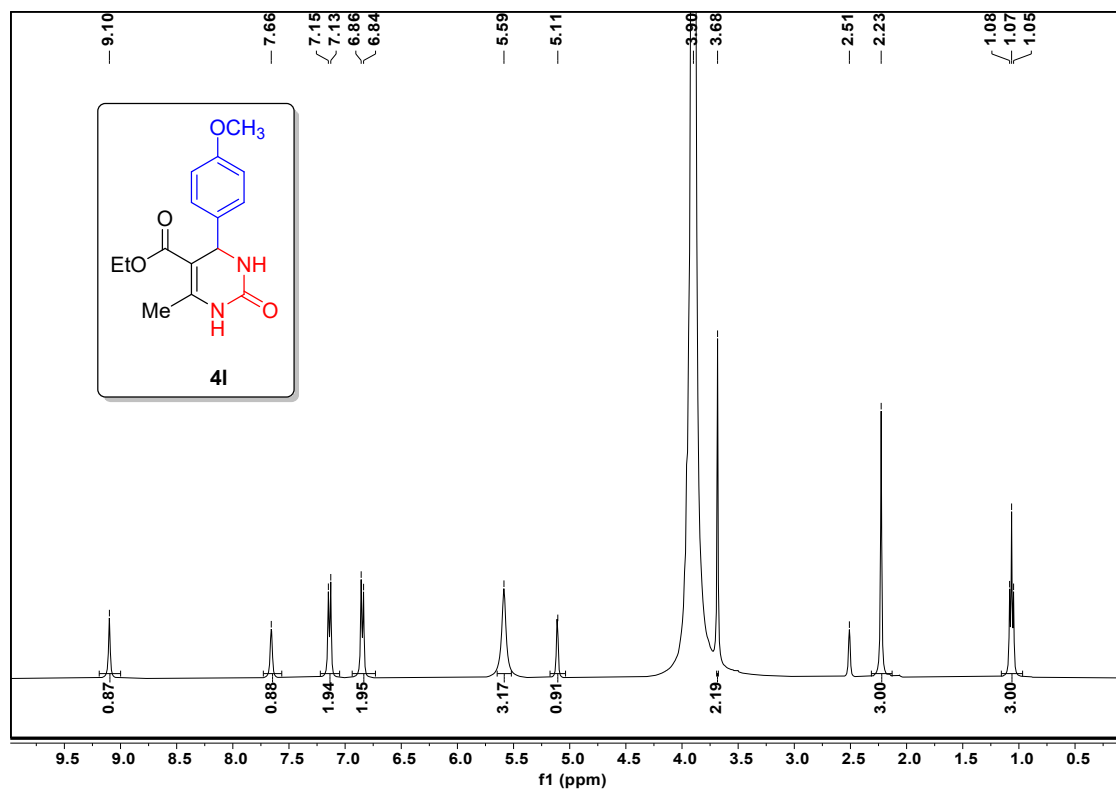
<sup>1</sup>H NMR Spectra of compound **4j** (400 MHz, DMSO-d<sub>6</sub>)



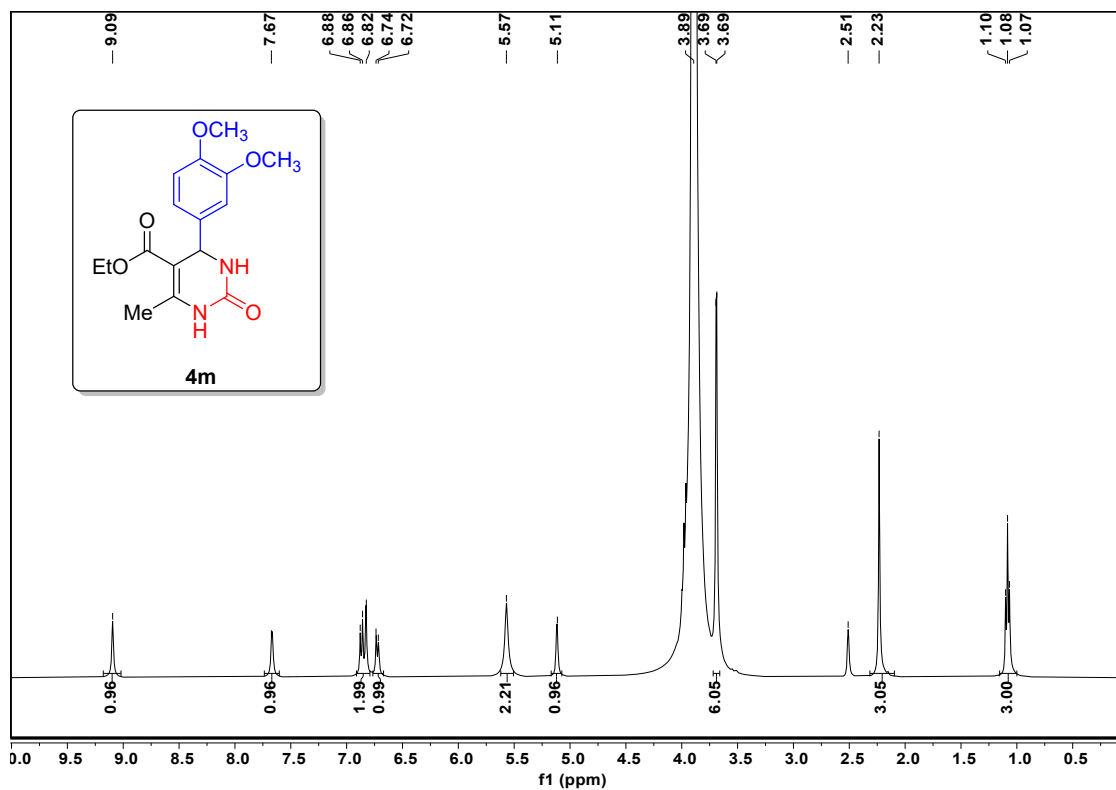
<sup>1</sup>H NMR Spectra of compound **4k** (400 MHz, DMSO-d<sub>6</sub>)



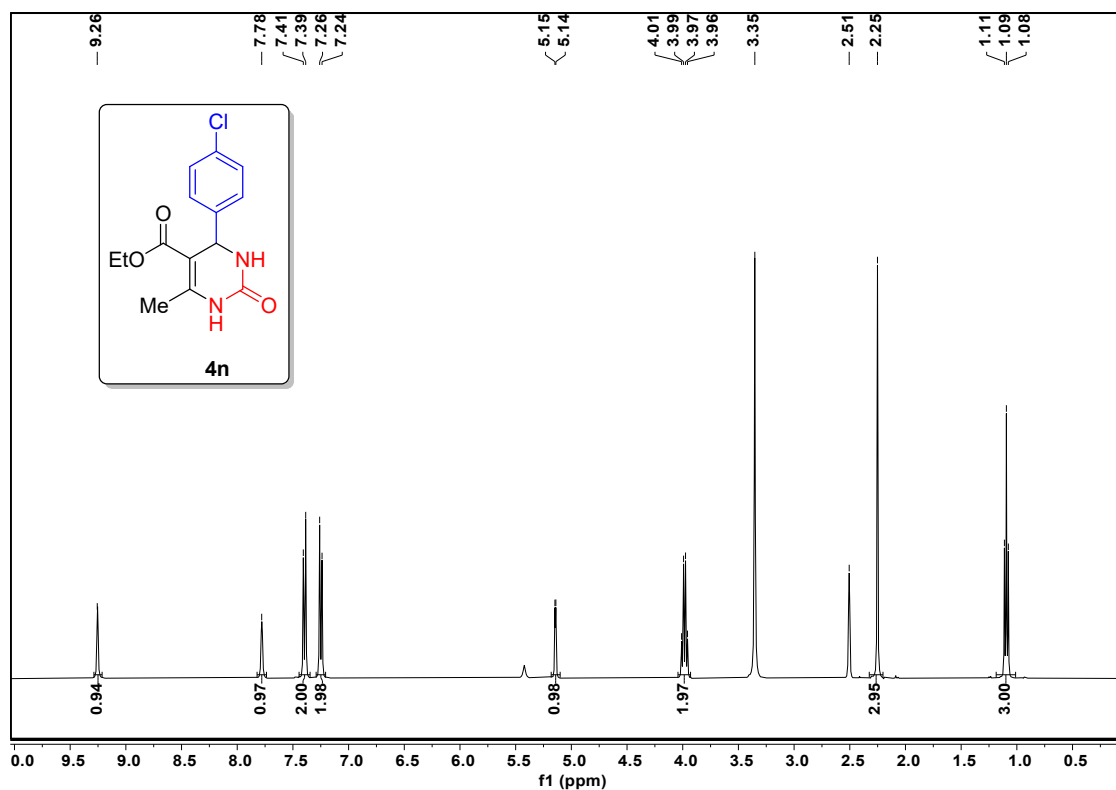
<sup>1</sup>H NMR Spectra of compound **4l** (400 MHz, DMSO-d<sub>6</sub>)



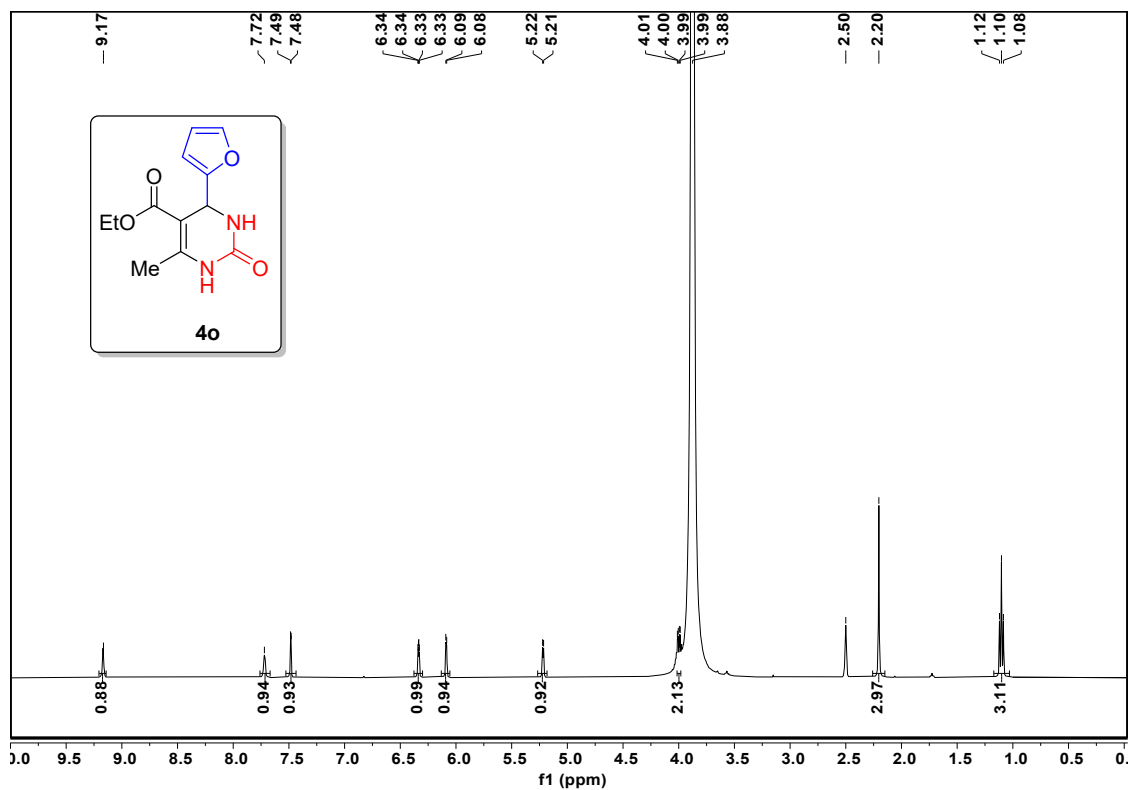
<sup>1</sup>H NMR Spectra of compound **4m** (400 MHz, DMSO-d<sub>6</sub>)



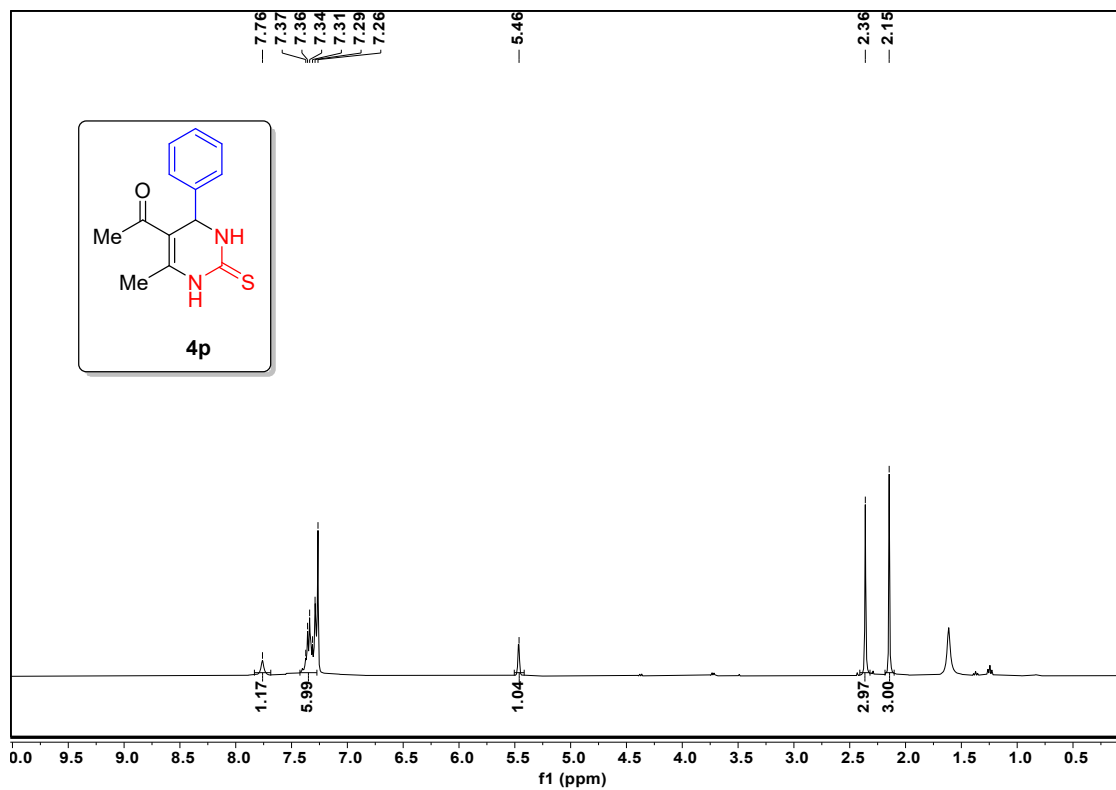
<sup>1</sup>H NMR Spectra of compound **4n** (400 MHz, DMSO-d<sub>6</sub>)



<sup>1</sup>H NMR Spectra of compound **4o** (400 MHz, DMSO-d<sub>6</sub>)

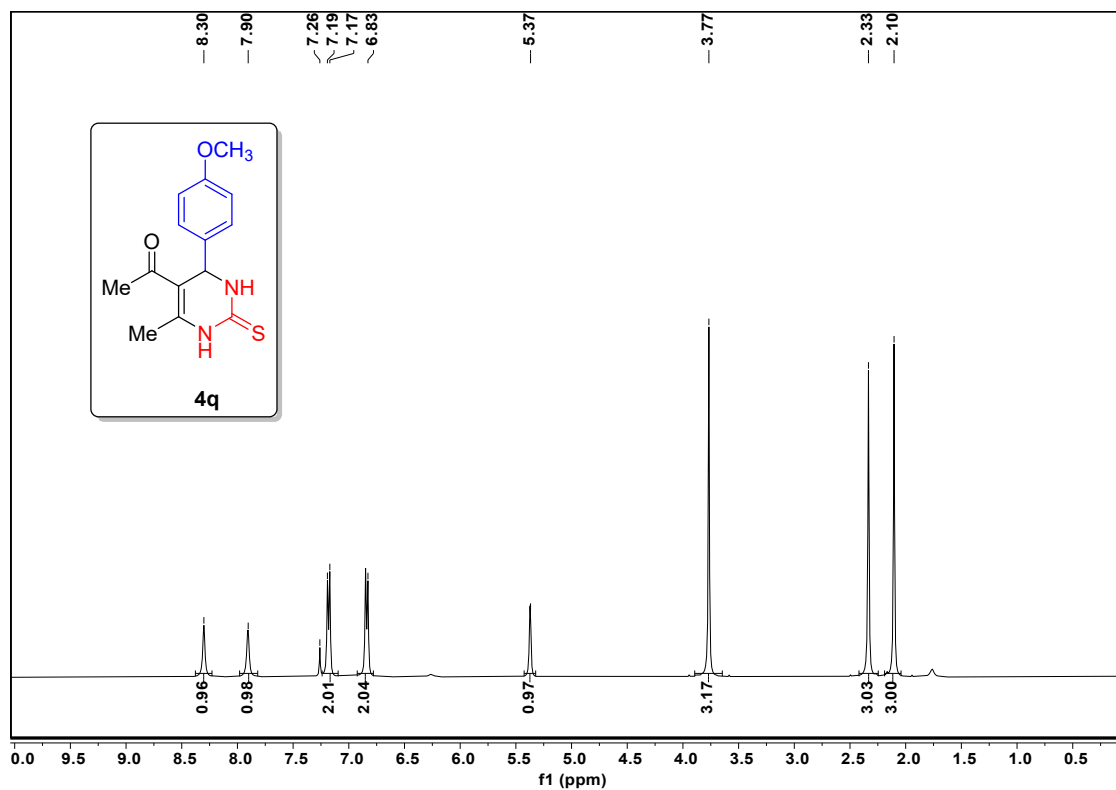


<sup>1</sup>H NMR Spectra of compound **4p** (400 MHz, CDCl<sub>3</sub>)

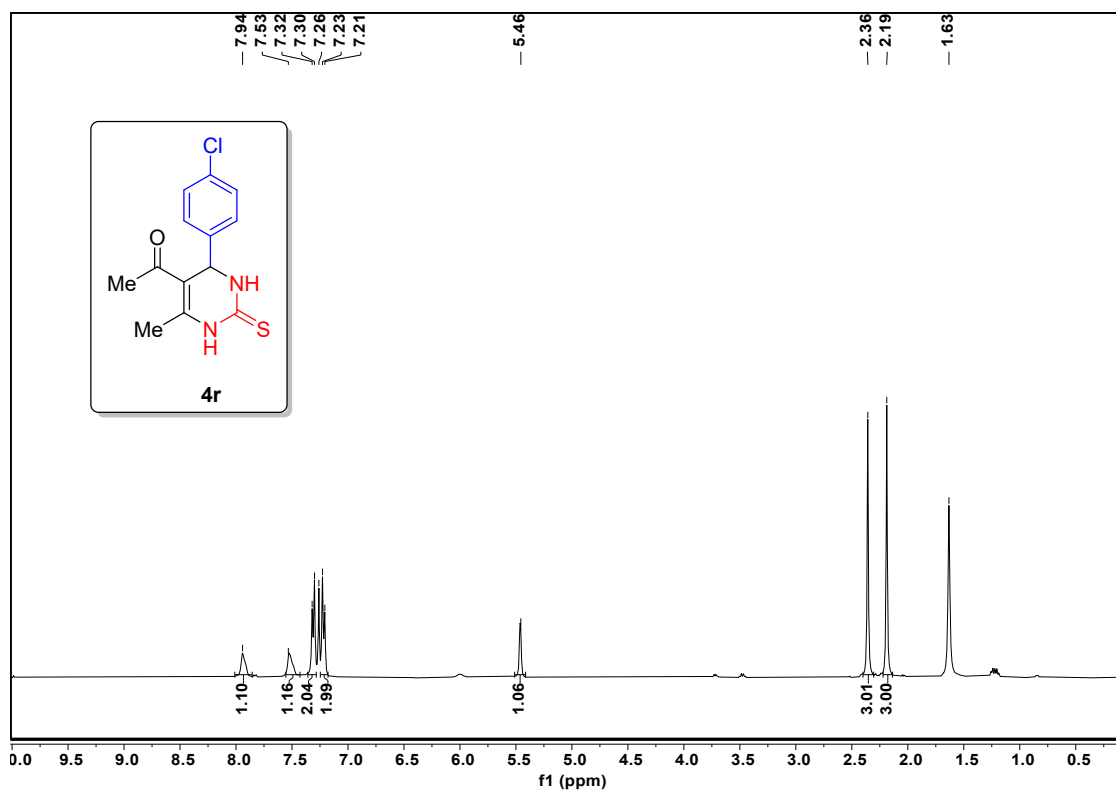




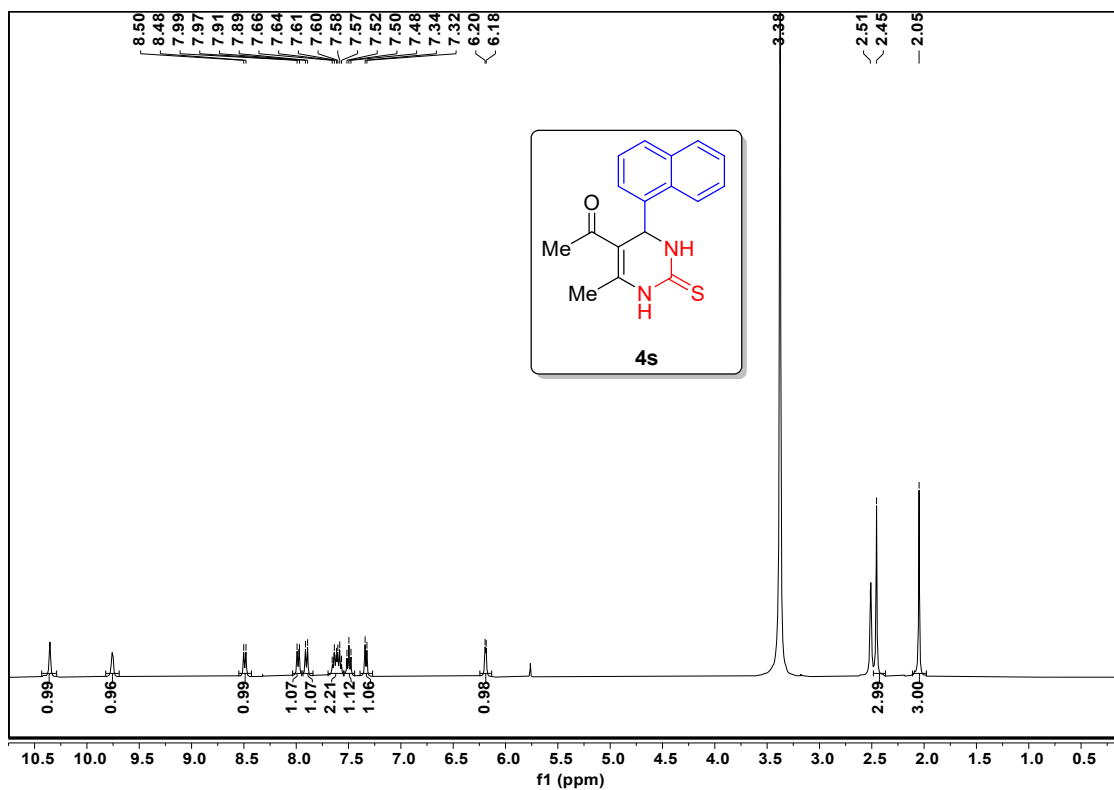
<sup>1</sup>H NMR Spectra of compound **4q** (400 MHz, CDCl<sub>3</sub>)



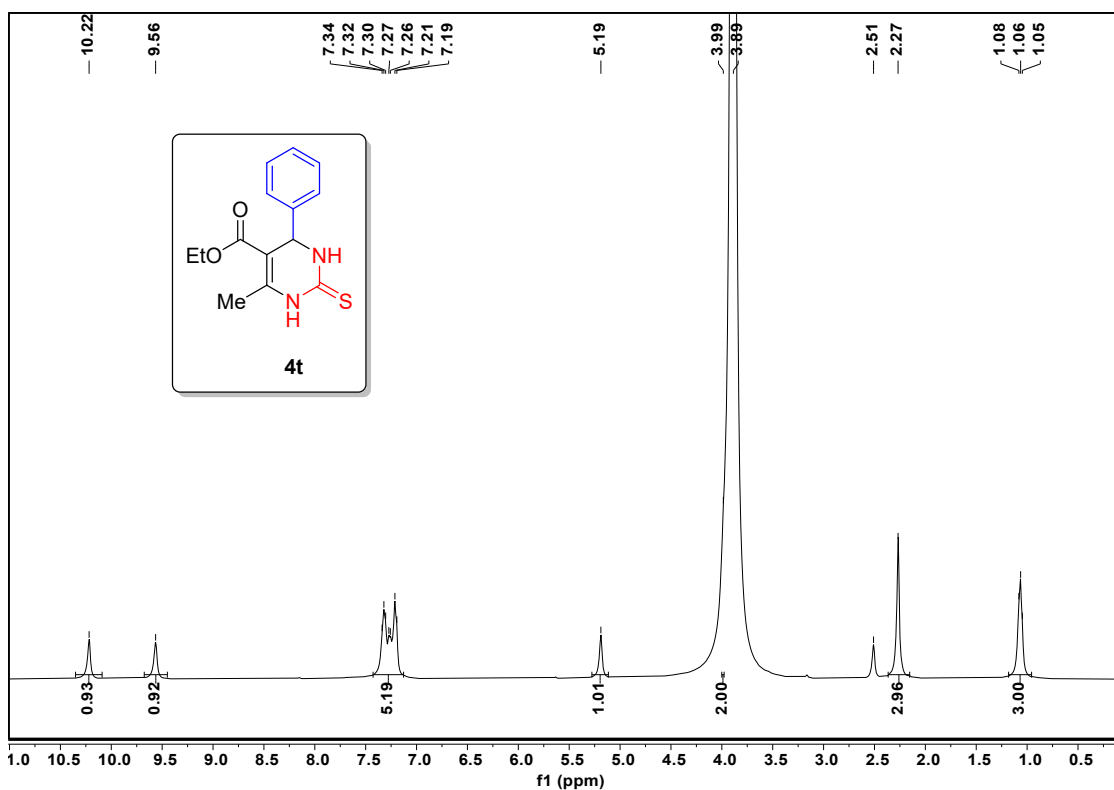
<sup>1</sup>H NMR Spectra of compound **4r** (400 MHz, CDCl<sub>3</sub>)



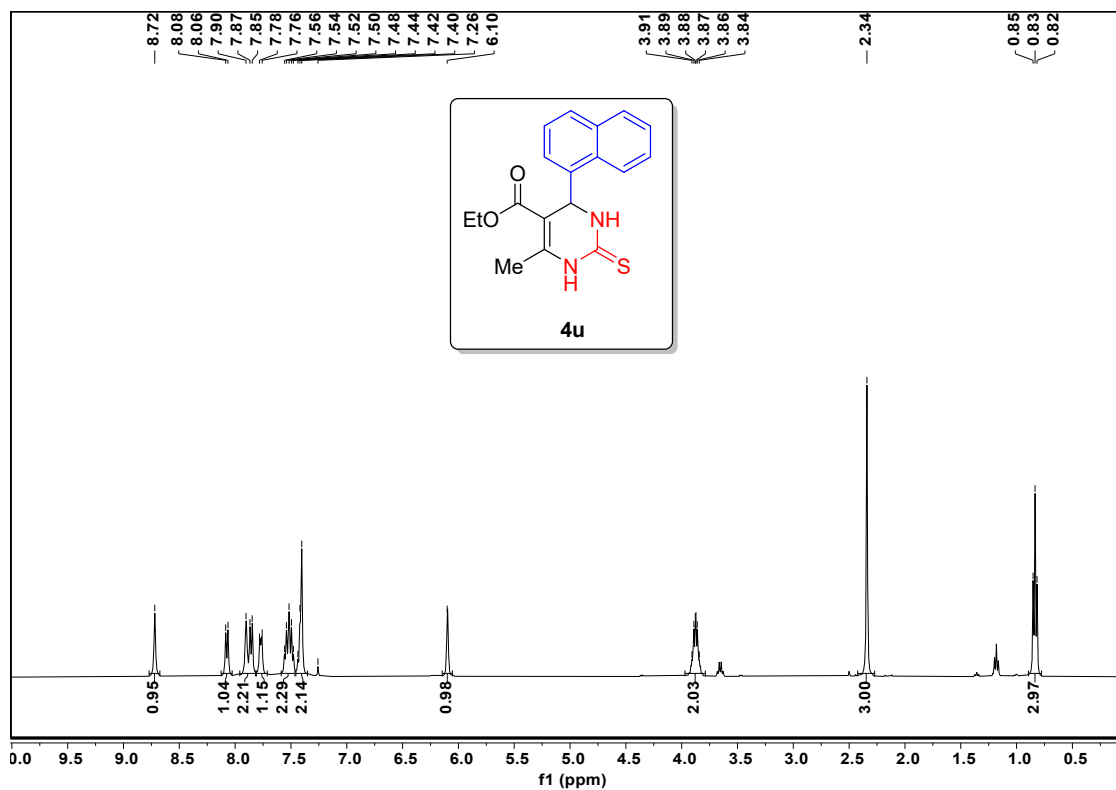
<sup>1</sup>H NMR Spectra of compound **4s** (400 MHz, DMSO-d<sub>6</sub>)



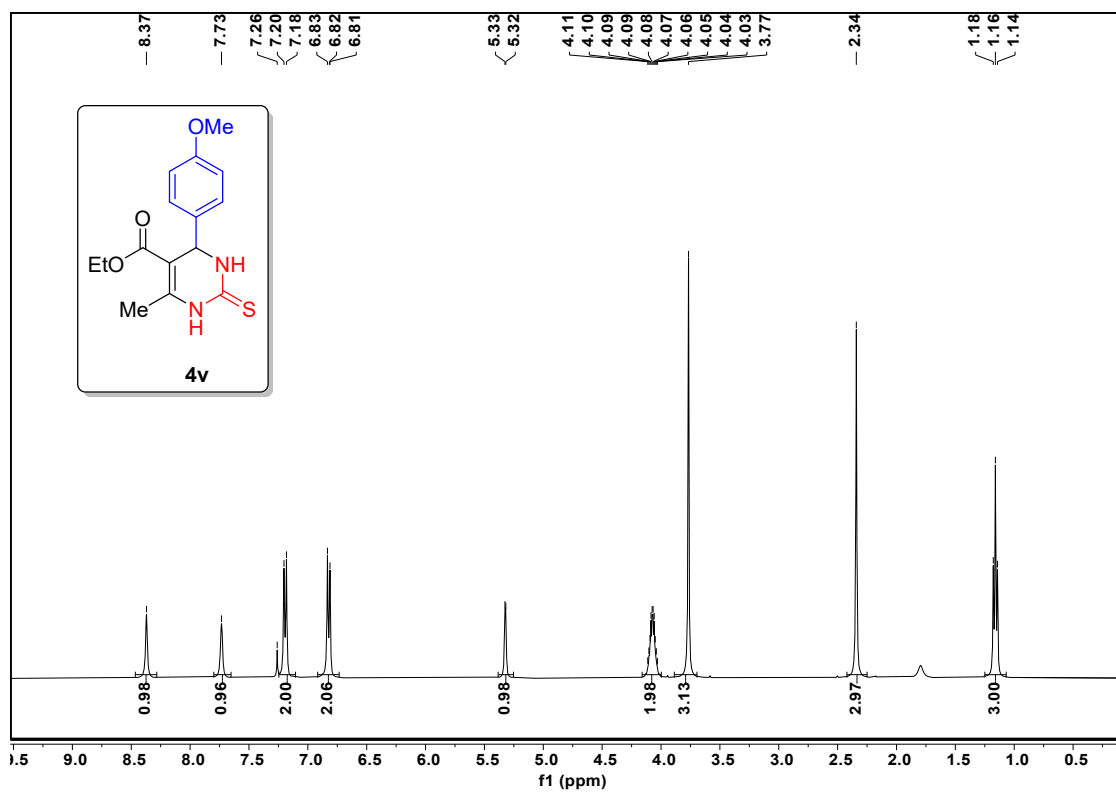
<sup>1</sup>H NMR Spectra of compound **4t** (400 MHz, DMSO-d<sub>6</sub>)



<sup>1</sup>H NMR Spectra of compound **4u** (400 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR Spectra of compound **4v** (400 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR Spectra of compound **4w** (400 MHz, CDCl<sub>3</sub>)

