Supporting Information

Concentrated solar radiation as a renewable heat source for preparative-scale and solvent-free Biginelli reaction

Yatin U.Gadkari,[a] Navnath.T.Hatvate,[a] Balaram.S.Takle,[b] Vikas.N.Telvekar[a]

[a]Department of Pharmaceutical Sciences and Technology, Institute of Chemical Technology, Mumbai, 400 019, India.

[b]Department of Chemistry and Biochemistry, University of California Santa Barbara, California 93106 USA.

Table of Contents

1. General information

All the chemicals and solvents used were purchased from commercial sources Sigma-Aldrich, Avra**,** SD Fine chemical and Spectrochem companies and were used without further 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 target compounds were characterized by their ^{1}H, ^{13}C NMR and Mass spectra. ^{1}H and ^{13}C NMR spectra were obtained on a 400-MR NMR Spectrometer from Agilent Technologies using tetramethylsilane (TMS) as an internal standard and DMSO-d_6 as a solvent. The following abbreviations are used for the multiplicities: s, singlet; d, doublet; dd, doublet of doublet; ddd, doublet of doublet of doublet; t, triplet; q, quadruplet; m, multiplet; dt, doublet of triplet; bs, broad singlet. Mass spectra were recorded on a direct insertion probe on Agilent Technologies 5975 series. Melting points of all the compounds were recorded by AnalabThermoCal melting point apparatus in the open capillary tube. The intensity of solar radiation was measured with the help of Pyranometer (Dynalab Tech. Ltd. India) i.e. solar radiation flux density (W/m2).It also measures solar irradiation over a view of 180°.The accurate electronic balance was also used. All the reactions studies were performed in King circle, Mumbai, India (19°01′18″N 72°51′53″E/19.021632°N) in the month of February and March between 12:30 pm to 1:30 pm which is peak solar intensity timing. All reagents used are analytical pure and employed directly untreated except for special instructions.

2. Experiments conducted at various months in India

Month	Time (min)	Yield (%)
January	5	93
February	3	95
March	3	97
April	3	97
May	3	97
June*	120	49
July*	120	50
August*	120	41
September	5	93
October	3	97
November	3	97
December	5	92

*Cloudy and rainy atmosphere resulted in longer reaction time with poor chemical yields.

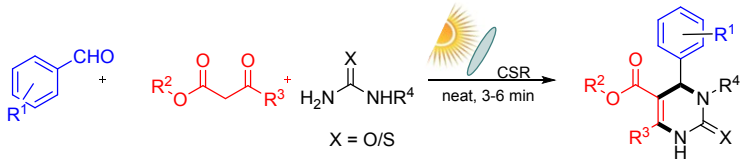
3. Eco-scale calculations

Parameter	**Current work**		**Previous work** (ref 10)	
	Details	Penalty points	Details	Penalty points
Yield	98%	1	88%	6
Cost of reactants to obtain 10 mmol product	Benzaldehyde Urea Ethylacetoacetate Ethanol	0 0 0 0	Benzaldehyde Urea Ethylacetoacetate $FeCl_3$ *i*-PrOH tetraethylorthosilicate	0 0 0 0 0 0
Safety	N/A	0	$FeCl_3$ tetraethylorthosilicate	5 (N) 10 (N, F)
Technical setup	Common setup	0	Ultrasound, pressure tube	2
Temperature/time	rt, <1 h	0	Reflux >1 h	3
Workup and purification	Simple filtration and/or crystallization	1	Simple filtration and/or re-crystallization	1
Eco-scale score=		**98**		**73**

(100 – sum of penalties)	

(N) = Harmful to the environment, (F) = Flammable

4. General procedure for the synthesis of 3,4-dihydropyrimidin-2 (1H)-ones/thiones

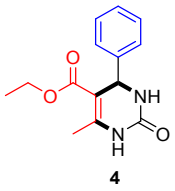


A mixture of aldehyde (10 mmol), (m)ethyl acetoacetate (10 mmol), urea or thiourea (10 mmol) was taken in a round bottom flask (RBF). RBF was kept under the concentrated solar radiation (CSR) setup with continuous stirring on a magnetic stirrer. After 3-6 minute, the precipitate was observed. Progress of the reaction was monitored by TLC. Precipitated product washed with water and recrystallized from hot ethanol to afford pure 3,4-dihydropyrimidin-2(1H)-ones/thiones.

Fig S1. CSR reaction set-up

5. Compound Characterization Data

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



4

Melting point: 202-204 °C (Lit: 202-204°C)

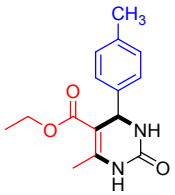
^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) 9.15 (s, 1H), 7.68 (s, 1H), 7.31-7.19 (m, 5H), 5.11 (s, 1H), 3.98 (q, *J*= 8Hz, 2H), 2.21 (s, 3H), 1.08 (t, *J*=8 Hz, 3H)

^{13}C NMR: (400 MHz, DMSO-d_6): δ(ppm) 165.75, 152.52, 148.75, 145.29, 128.79, 127.66, 126.65, 99.79, 59.59, 54.4, 18.2, 14.5;

MS (GCMS) m/z**:** 261.3$(M+H)^+$ (245.1, 231.3, 214.1, 183.2, 155.2, 137.2, 110.2, 77.2, 51.1)

D_2O Exchange ^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) 7.30-7.18 (m, 5H), 5.11 (s, 1H), 3.98 (q, *J*= 6.0 Hz, 2H), 2.21 (s, 3H), 1.08 (t, *J*= 6.0 Hz, 3H).

- **Ethyl4-(4-methylphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5)[1-4]**



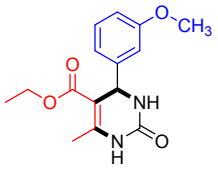
5

Melting point: 216-217°C (Lit: 216-217°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.11 (s, 1H), 7.64 (s, 1H), 7.08 (s, 4H), 5.07 (d, 1H, *J*=3.2Hz), 3.97 (q, 2H, *J*=8 Hz), 2.22 (s, 3H), 2.20 (s, 3H), 1.08 (t, 3H, *J*=8Hz);

MS (GCMS) m/z: 275.4 $(M+H)^+$ (259.3, 245.3, 228.3, 201.3, 183.3, 155.2, 137.2, 91.1, 51.2)

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



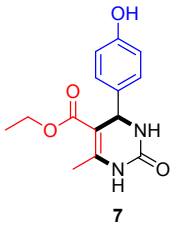
6

Melting point: 206-208°C (Lit: 207-208°C)

^{1}H NMR : (400 MHz, DMSO-d_6): δ (ppm) = 9.14 (s, 1H), 7.68 (s, 1H), 7.23 (t, 1H, *J*=8 Hz), 6.79 (t, 3H, *J*=10 Hz), 5.09 (d, 1H, *J*=4 Hz), 3.99 (q, 2H, *J*=8 Hz), 3.69 (s, 3H), 2.21 (s, 3H), 1.09 (t, 3H, *J*=8 Hz);

MS (GCMS) m/z: 290.1(M+H)$^+$ (261.1, 244.1, 207.5, 183.1, 155.0,137.1)

- **Ethyl4-(4-hydroxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(7)[2]**



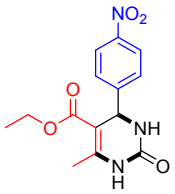
7

Melting point: 245-246°C (Lit: 245-247°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.30(s, 1H), 9.05 (s, 1H), 7.56 (s, 1H), 7.0 (d, 2H, *J*=8.0Hz), 6.66 (d, 2H, *J*=8.0Hz), 5.01 (s, 1H), 3.96 (q, 2H, *J*=8 Hz), 2.20 (s, 3H), 1.08 (t, 3H, *J*=8 Hz);

MS (GCMS) m/z: 276.1(M+H)$^+$ (261.1, 247.2, 230.2, 203.2, 226.2,183.2, 155.2, 137.2)

- **Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8)[1-4]**



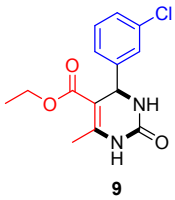
8

Melting point: 208-209°C (Lit: 208-211°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.31 (s, 1H), 8.19 (d, 2H, *J*=8 Hz), 7.85 (s, 1H), 7.48 (d, 2H, *J*=8 Hz), 5.24 (s, 1H), 3.97 (q, 2H, *J*=4 Hz), 2.23 (s, 3H), 1.08 (t, 3H, *J*=8 Hz);

MS (GCMS) m/z: 306.3 $(M+H)^+$ (276.3, 232.3, 183.3, 155.2, 137.2, 110.2, 76.2, 50.2)

- **Ethyl 4-(3-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9)[1]**



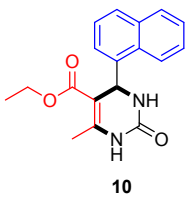
9

Melting point: 200-201°C (Lit: 201-202°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.19 (s, 1H), 7.72 (s, 1H), 7.36 (d, 2H, *J* = 8Hz), 7.22 (d, 2H, *J* = 8Hz), 5.11 (s, 1H,), 3.97 (q, 2H, *J*= 8Hz), 2.21 (s, 3H), 1.07 (t, 3H, *J*= 8Hz);

MS (GCMS) m/z: 295.1 $(M+H)^+$ (265.1, 221.1, 183.2, 155.2, 137.1, 75.1,50.1)

- **Ethyl 6-methyl-4-(naphthalen-1-yl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (10)[1,4]**



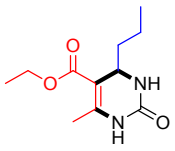
10

Melting point: 253-254°C (Lit: 253-254°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.21 (s, 1H), 8.26 (d,1H, *J*=8.2Hz), 7.91-7.80 (m, 3H), 7.70-7.39 (m, 4H), 6.03 (s, 1H), 3.79 (q, 2H, *J*=8 Hz), 2.32 (s, 3H), 0.79 (t, 3H, *J*=8 Hz);

MS (GCMS) m/z: 310.4$(M+H)^+$ (310.3, 295.3, 281, 264, 246, 237, 183, 155, 137, 128, 110, 77, 55)

- **Ethyl 4-propyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(11)[5]**



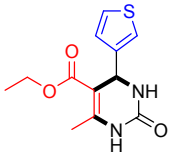
11

Melting point: 168-170°C (Lit: 168-170°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 8.88 (s, 1H), 7.28 (s, 1H), 4.06-3.98 (m, 3H), 2.12 (s, 3H), 1.36-1.13 (m, 7H), 0.83 (t, 6H, *J*=8 Hz).

MS (GCMS) m/z: 226.2 $(M+H)^+$

- **Ethyl 6-methyl-2-oxo-4-(thiophen-3-yl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate(13)[1-4]**



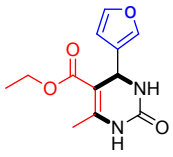
13

Melting point: 231-233°C (Lit: 231-232°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.26 (s, 1H), 7.86 (s, 1H), 7.31 (s, 1H), 6.91 (s, 1H), 6.85 (s, 1H), 5.38 (d, 1H, *J*=4 Hz), 4.06 (q, 2H, *J*=8 Hz), 2.18 (s, 3H), 1.15 (t, 3H, *J*= 8 Hz);

MS (GCMS) m/z: 266.3$(M+H)^+$ (237.2, 220.02, 193.2, 183, 155.2, 137, 110.2, 67.2)

- **Ethyl 6-methyl-2-oxo-4-(Furan-3-yl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate(14)[1-4]**



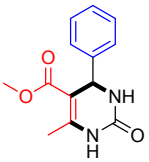
14

Melting point: 198-201°C (Lit: 199-201°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.14 (s, 1H), 8.79 (s, 1H), 7.38 (s, 1H), 7.10 (s, 1H), 6.14 (s, 1H), 4.75 (s, 1H), 4.05 (q, 2H, *J*=8 Hz), 2.20 (s, 3H), 1.16 (t, 3H, *J*= 8 Hz);

MS (GCMS) m/z: 251.2$(M+H)^+$

- **Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate(15)[4]**



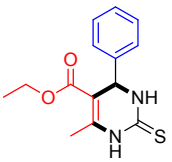
15

Melting point: 210-212°C (Lit: 209-212°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.16 (s, 1H), 7.70 (s, 1H), 7.30-7.19 (m, 5H), 5.11 (s, 1H), 3.5 (s, 3H), 2.21 (s, 3H, *J*=7.1Hz)

MS (GCMS) m/z: 247.2$(M+H)^+$ (231.2, 204.3, 187.2, 169.2, 137.2, 115.2, 102.2, 77.1, 55.1)

- **Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (17)[2-4]**



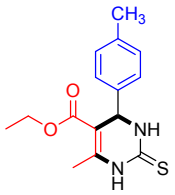
17

Melting point: 208-209°C (Lit: 208-210°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 10.28 (s, 1H), 9.60 (s, 1H), 7.33-7.18 (m, 5H), 5.14 (s, 1H), 4.0 (q, 2H, *J*=8 Hz), 2.26 (s, 3H), 1.08 (t, 3H, *J*=8 Hz)

MS (GCMS) m/z: 277.3$(M+H)^+$ (261.1, 247.0, 231.3, 218.0, 199.2, 171.2, 144.2, 77.2, 51.2)

- **Ethyl 4-(4-methylphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(18)[2-4]**



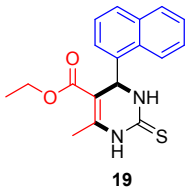
18

Melting point: 191-192°C (Lit: 192-193°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 10.23 (s, 1H), 9.55 (s, 1H), 7.12 (d, 2H, *J*=8 Hz), 7.07 (d, 2H, *J*=8 Hz), 5.09 (s, 1H), 4.0 (q, 2H, *J*=8 Hz), 2.24 (d, 6H, *J*=4 Hz), 1.09 (t, 3H, *J*=8 Hz);

MS (GCMS) m/z: 291.3$(M+H)^+$(275.3, 261.3, 245.2, 232.3, 217.3, 199.1, 186.2, 158.2, 115.2, 65.2)

- **Ethyl 6-methyl-4-(naphthalen-1-yl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (19)[4]**

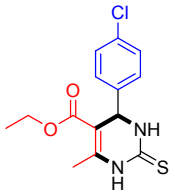


19

Melting point: 199-200°C; (Lit: 199-201°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 10.35 (s, 1H), 9.62 (d, 1H, *J*=8.2Hz), 8.36 (d, 1H, *J*=4 Hz), 7.92 (m, 2H), 7.90 (m,4H), 6.05 (s, 1H, *J*=3.0Hz), 3.82 (q, 2H, *J*=8 Hz), 2.38 (s, 3H), 0.90 (t, 3H, *J*=8 Hz);

- **Ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (20)[2-4]**



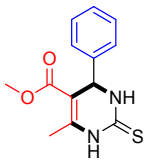
20

Melting point: 191-192°C (Lit: 192-194°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 8.74 (s, 1H), 8.38 (s, 1H), 7.36 (d, 2H, *J*=8 Hz), 7.30 (d, 2H, *J*=8 Hz), 6.09 (s, 1H), 3.91 (q, 2H, *J*=8 Hz), 1.43 (s, 3H), 0.93 (t, 3H, *J*=8 Hz);

MS (GCMS) m/z: 310.$(M+H)^+$ (281.05, 265.05, 237.0, 222.0, 199.0, 171.0, 153.0, 126.0

- **Methyl 6-methyl-2-thioxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate(21)[4]**



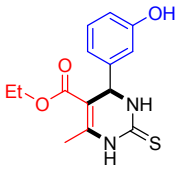
21

Melting point: 228-229°C (Lit : 227-229°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 8.73 (s, 1H), 8.32 (s, 1H), 7.26 (s, 5H), 6.08 (s, 1H), 3.8 (s, 3H), 1.41 (s, 3H)

MS (GCMS) m/z: 262.1$(M+H)^+$ (247.1, 203.0, 185.0, 153.0)

- **Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(27)[4]**

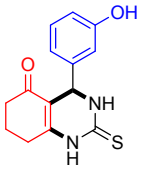


27

Melting point: 184-185°C (Lit: 184 -186°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 9.30(s, 1H), 9.10 (s, 1H), 7.63 (s, 1H), 7.07 (t, 1H, *J*=8.0Hz), 6.64 (m, 3H), 5.02 (s, 1H), 3.99 (q, 2H, *J*=8 Hz), 2.20 (s, 3H), 1.10 (t, 3H, *J*=8 Hz);

- **4-(3-hydroxyphenyl)-2-thioxo-1,2,3,4,7,8-hexahydroquinazolin-5(6H)-one (28)[6,7]**



28

Melting point: 217-219°C (Lit: 217 -221°C)

^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) = 10.52 (s, 1H), 9.59 (s, 1H), 9.38(s, 1H) 7.06 (t, 1H), 6.63(m, 3H), 5.07 (s, 1H), 2.25-2.17 (m, 2H), 1.94-1.77 (m, 2H)

MS (GCMS) m/z: 274.3 $(M+H)^+$

6. Energy calculations

A.1. Energy delivered during the Conventional method

Voltage input in magnetic stirrer (Model RQ1210, Deepali United Mfg.Ltd.India) = 230 V

Current measured using a digital multimeter (KUSAM-MECO Model 2718, Kusam Electrical Industries Ltd.,Mumbai,India) = 37 mA = 37 × 10^{-3}A.

Power input in magnetic stirrer = Voltage input × Current measured = 230 (V) × 37× 10^{-3} (A) = 8.51 W (J/s)

Efficiency of magnetic stirrer taken for the calculation = 80% (estimated independently using calorimetric studies)

Actual power input in overhead stirrer = power input in magnetic stirrer (W) × 80/100 = 8.51 (W) × 80/100 = 6.808 W (J/s)

Time required for completion of reaction = 6 h (21,600 s)

Net energy delivered during conventional method = Power input in magnetic stirrer × time required for completion of reaction = 6.808 (J/s) × 21,600 s = 147.05 kJ

Quantity of material processed = Quantity of (Ethyl acetoacetate + Benzaldehyde + Urea + Copper(II) triflate+acetonitrile) in g. = 1.3+1.1+0.7+0.01 +3.12 = 6.23 g.

Net energy supplied for processing of material using conventional method = Net energy delivered during conventional method / Quantity of material processed = 147.05 (kJ) / 6.23 (g) = **23.60** (kJ)/g.

A.2.Energy calculated by Concentrated Solar Radiation (CSR)

Total energy consumed in the process = Energy delivered by Solar + Energy delivered by Magnetic stirrer for 4 min

Solar energy during irradiation will be = cross sectional area of the lens × solar intensity = 9×10^{-2} m^2 × 950 W/ m^2 = 85.5 W.

The efficiency of irradiations to be taken for calculation = 10% of estimated energy calculations (0.1 × 85.5 W = 8.55 W (J/s)

Energy delivered in 4 min (240 s) = 8.55 × 240 s = 20,52 J = 2.05 kJ

Net energy delivered during 4 min stirring = Power input in magnetic stirrer × Time required for completion of reaction = 6.808 (J/s) × 240 (s) = 1633.92 J = 1.63 kJ

Thus total energy requirement of CSR process = Solar irradiation energy + Net energy delivered during 4 min of stirring = 2.05 kJ+ 1.63 kJ = 3.68 kJ

Quantity of material processed = Quantity of (Ethyl acetoacetate + Benzaldehyde + Urea) in g. = 1.3+1.1+0.7 = 3.1 g.

Net energy supplied for processing of material during 4 min = Net energy delivered during 4 min / Quantity of material processed = 3.68 (kJ) /3.1 (g) = **1.18** kJ/g

The amount of energy saved during process = Net energy supplied for processing of material using conventional method for 6 h – Net energy supplied for processing of material using CSR = (23.60-1.18) kJ/g =**22.42** kJ/g

Percent of energy saved during the process = (the amount of energy saved during process / net energy supplied for processing of material using conventional method) × 100 = (22.42/23.60) × 100 = **95.01** %

7. References

1 K. K. Pasunooti, H. Chai, C. N. Jensen, B. K. Gorityala, S. Wang, X. W. Liu, *Tetrahedron Letters,* 2011, **52**, 80-84.

2 N. M. Thorat, S. R. Thopate, *Letters in Organic Chemistry*, 2015, **12**, 210-216.

3 R. B. Carvalho, S. V Joshi, *Green chemistry*, 2019, **21**, 1921-1924.

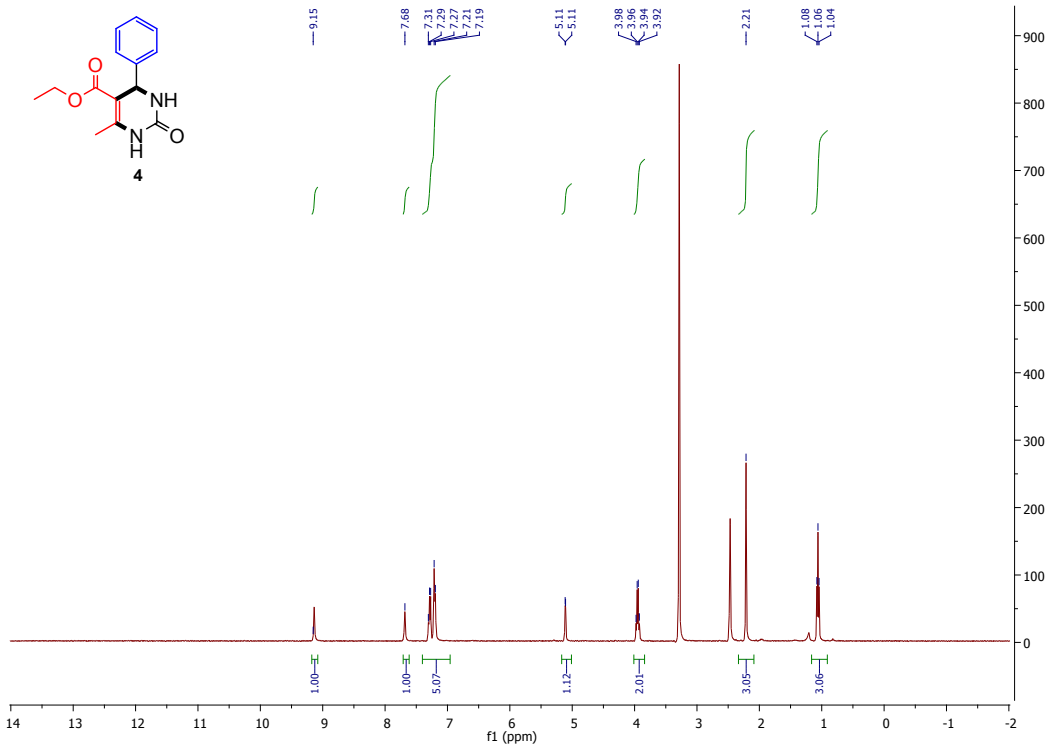
4 K. A. Dilmaghani, B. Zeynizadeh, H. Parasajam, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 2012, **187**, 544-553.

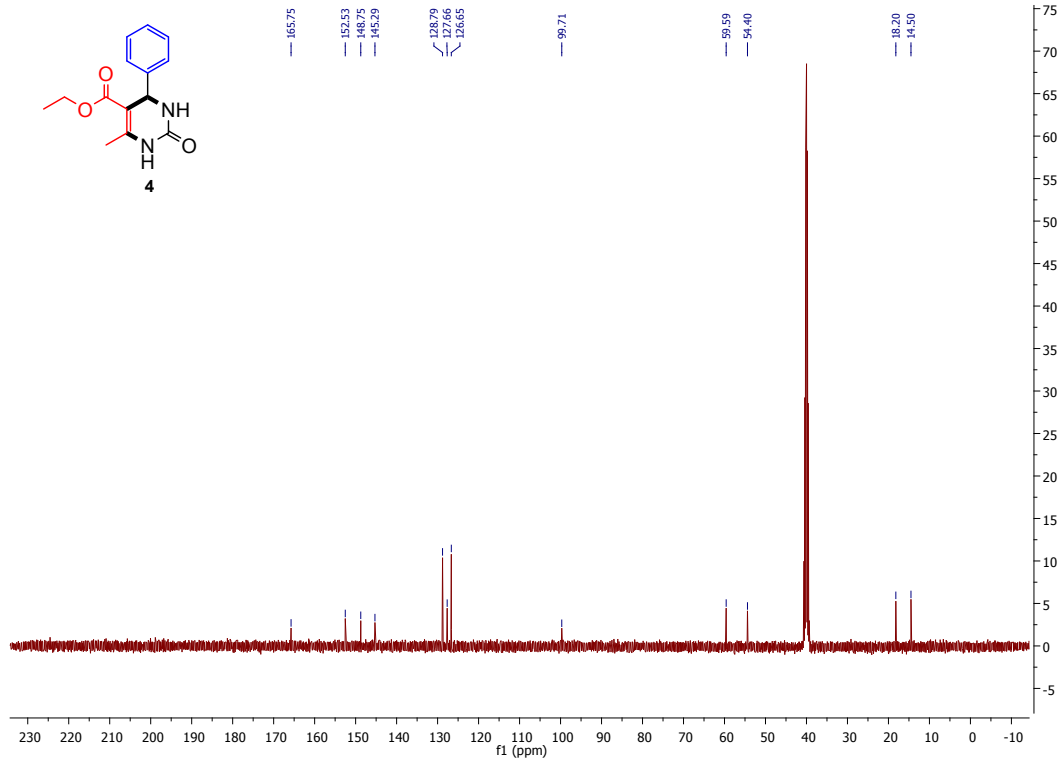
5 D. L. Da Silva, S. A. Fernandes, A. A. Sabino, Â. de Fátima, *Tetrahedron letters*, 2011, **52**, 6328-6330.

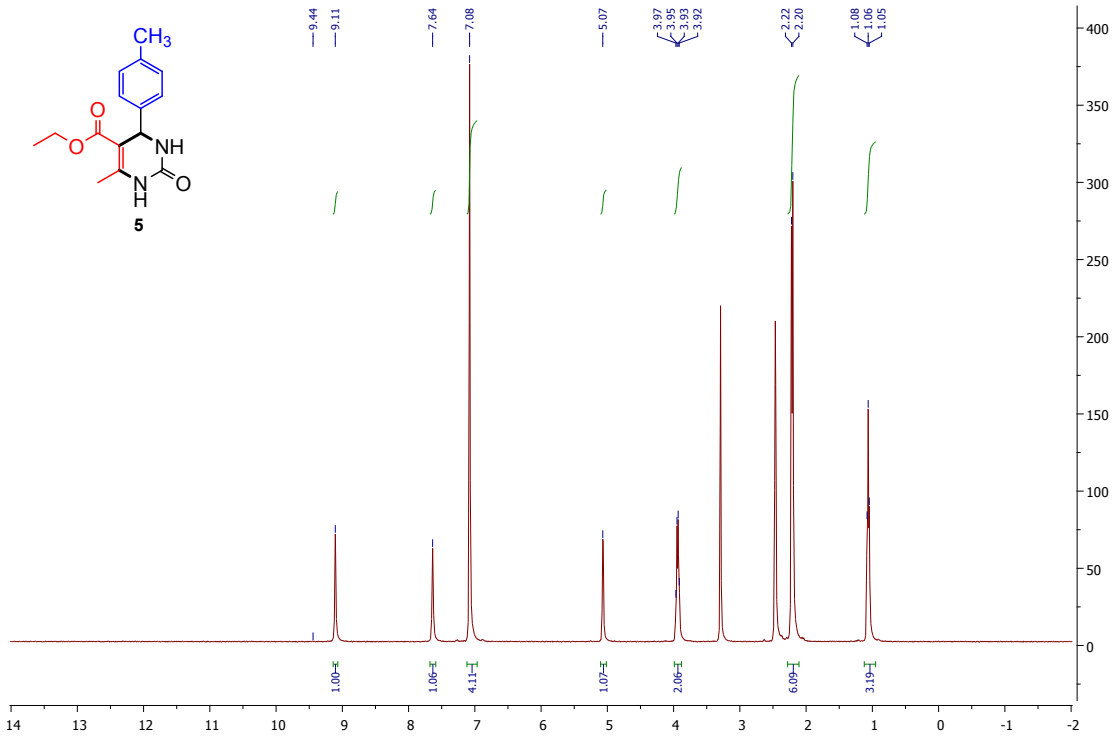
6 H. G. Alvim, T. B. de Lima, H. C. de Oliveira, F. C. Gozzo, J. L. de Macedo, P. V. Abdelnur, B. A. Neto, *Acs Catalysis*, 2013, **3**, 1420-1430

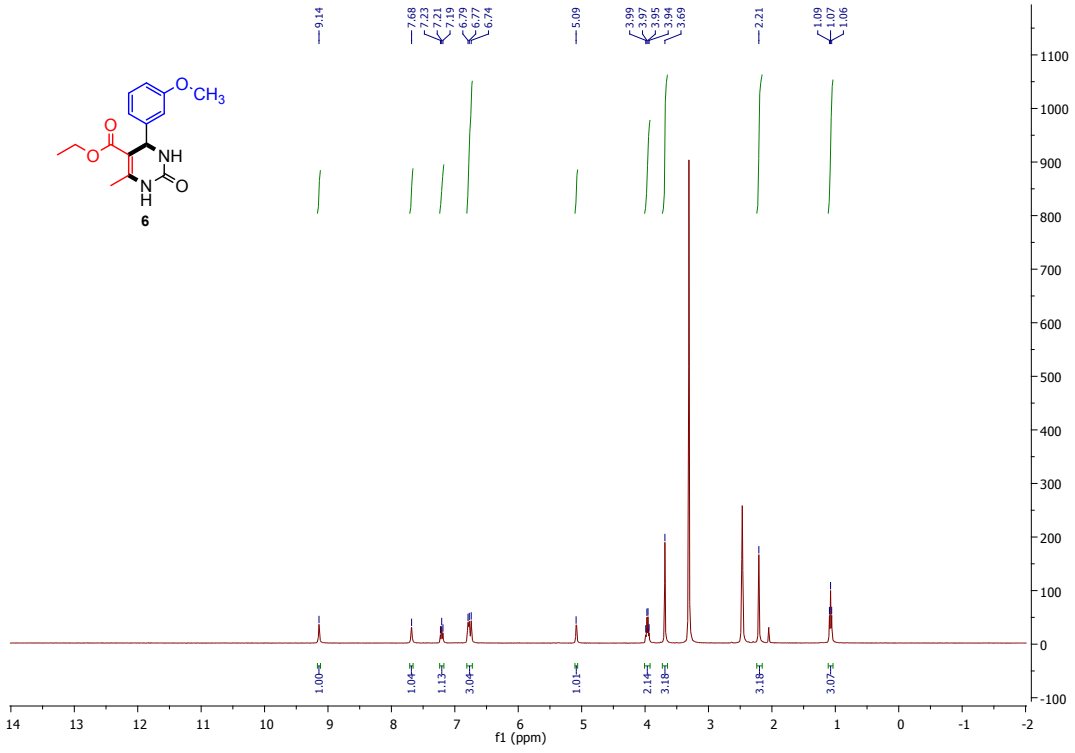
7 G. C. Silva, J. R. Correa, M. O. Rodrigues, H. G. Alvim, B. C. Guido, C. C. Gatto, B. A. Neto, *RSC Advances,* 2015, **5**, 48506-48515.

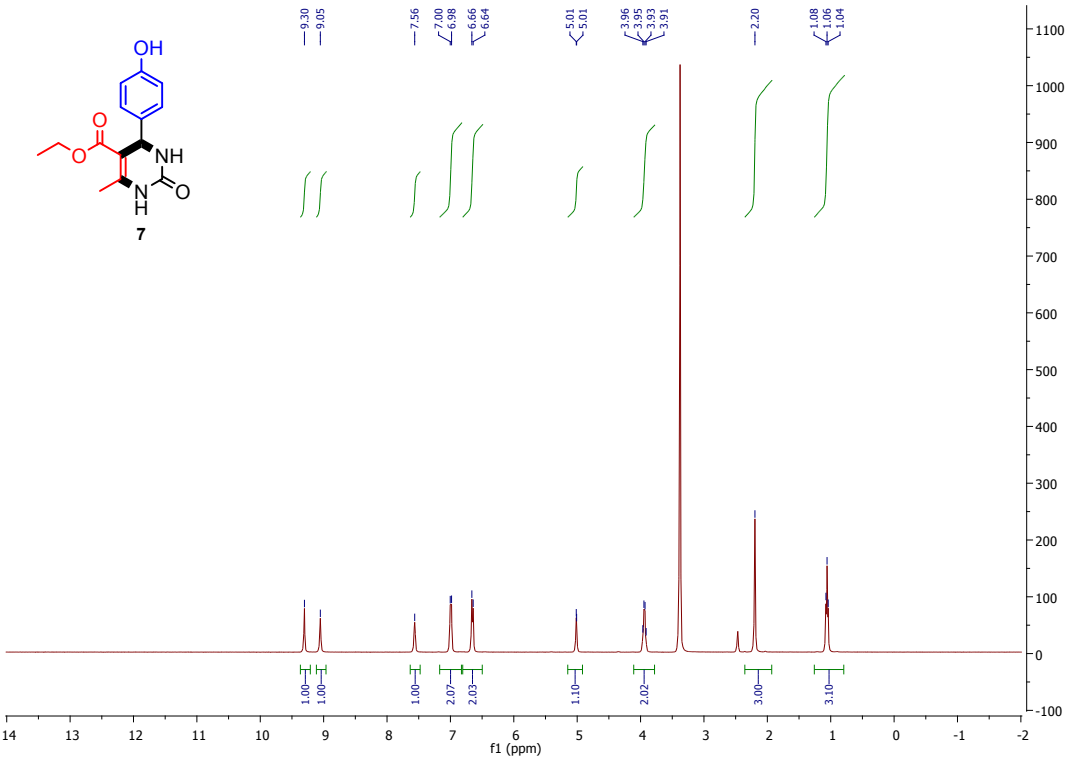
8. NMR spectra

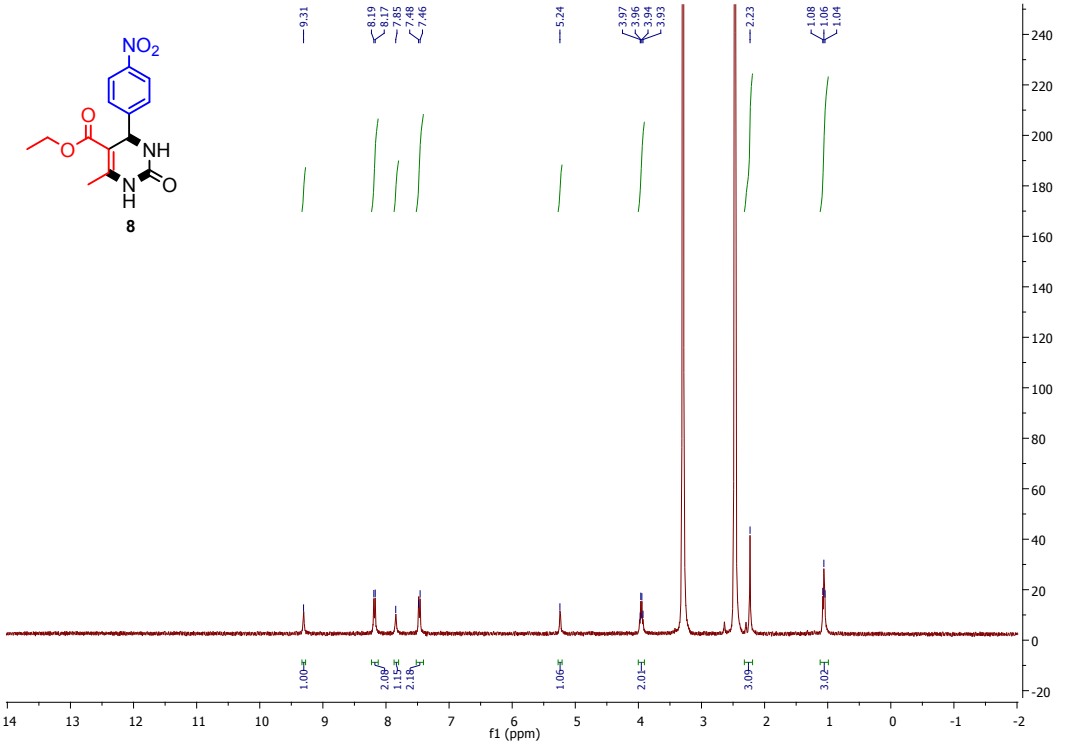


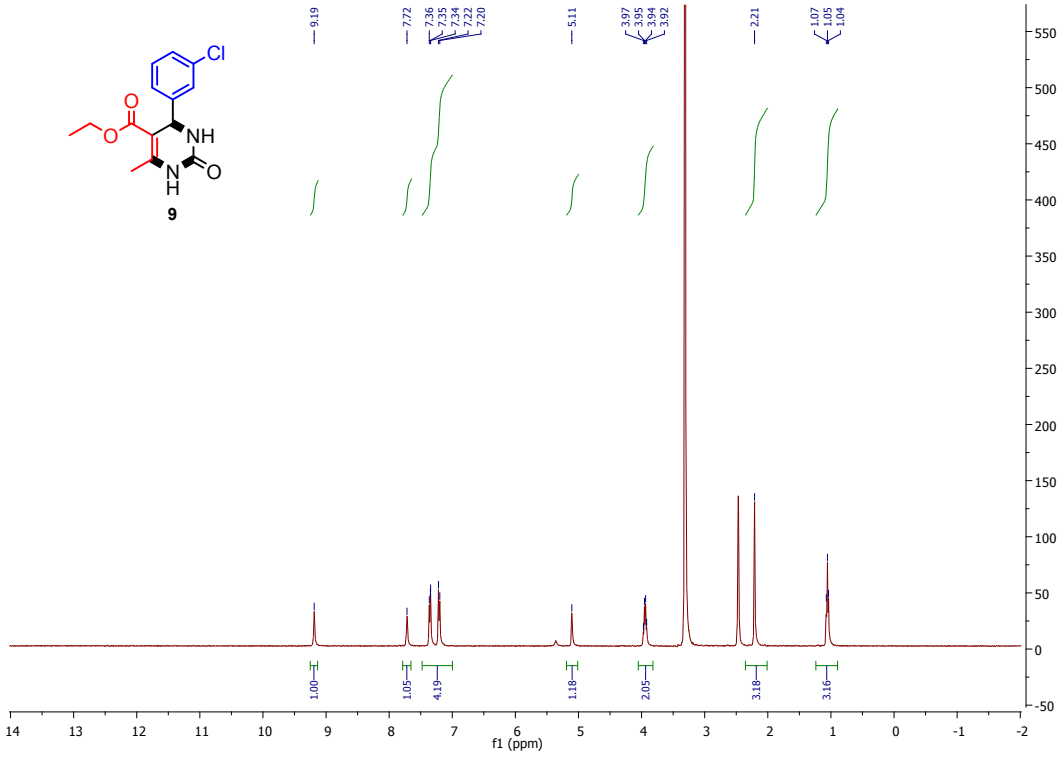


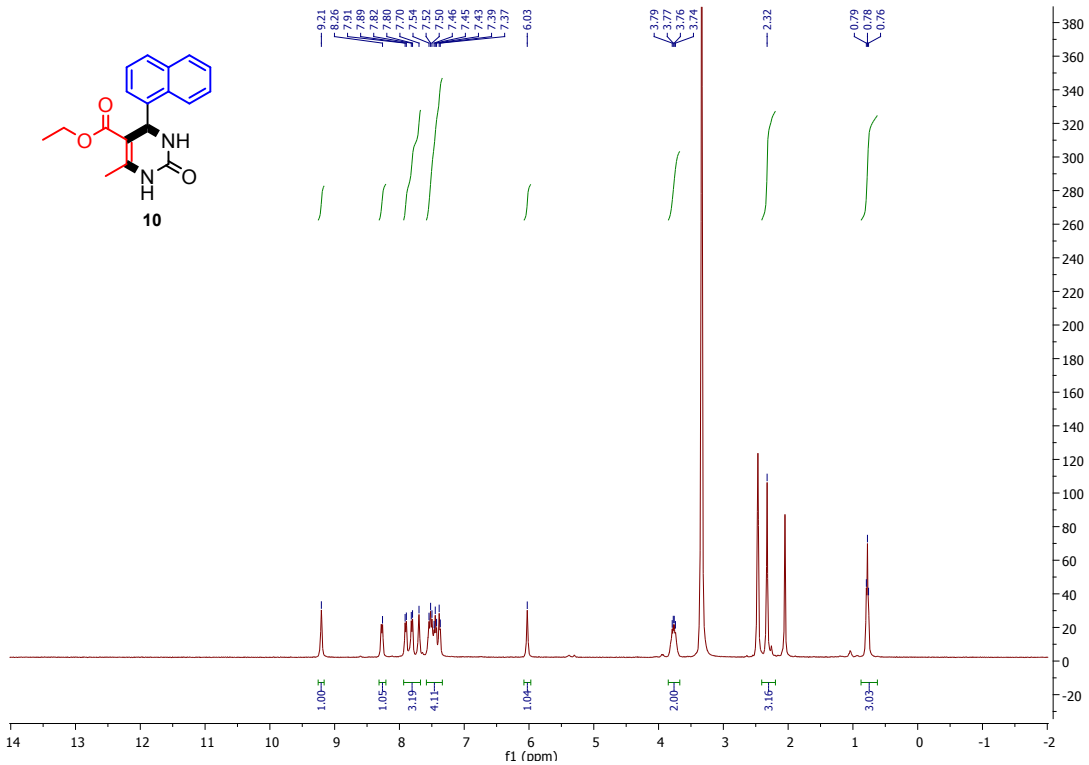

CH3
O
O
NH
N
H
O
5
9.44
9.11
7.64
7.08
5.07
3.97
3.95
3.93
3.92
2.22
2.20
1.08
1.06
1.05
1.00
1.06
4.11
1.07
2.06
6.09
3.19

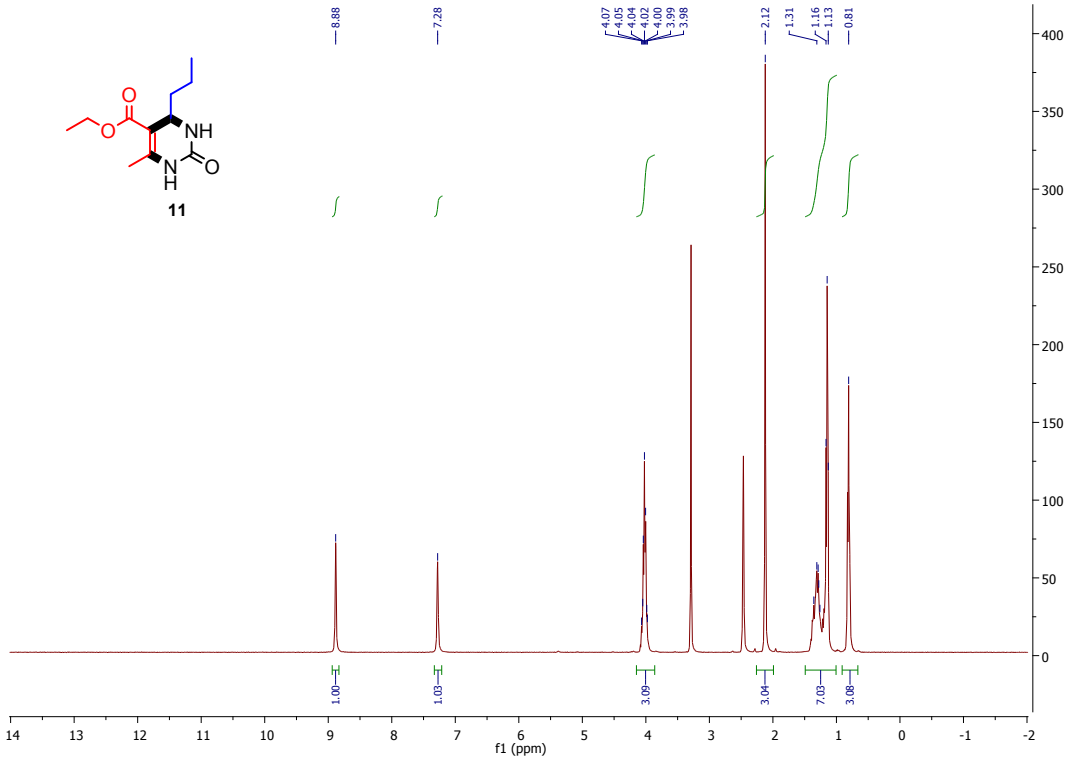

O
CH3
O
O
NH
N
H
O
6
9.14
7.68
7.23
7.21
7.19
6.79
6.77
6.74
5.09
3.99
3.97
3.95
3.94
3.69
2.21
1.09
1.07
1.06
1.00
1.04
1.13
3.04
1.01
2.14
3.19
3.18
3.07
f1 (ppm)

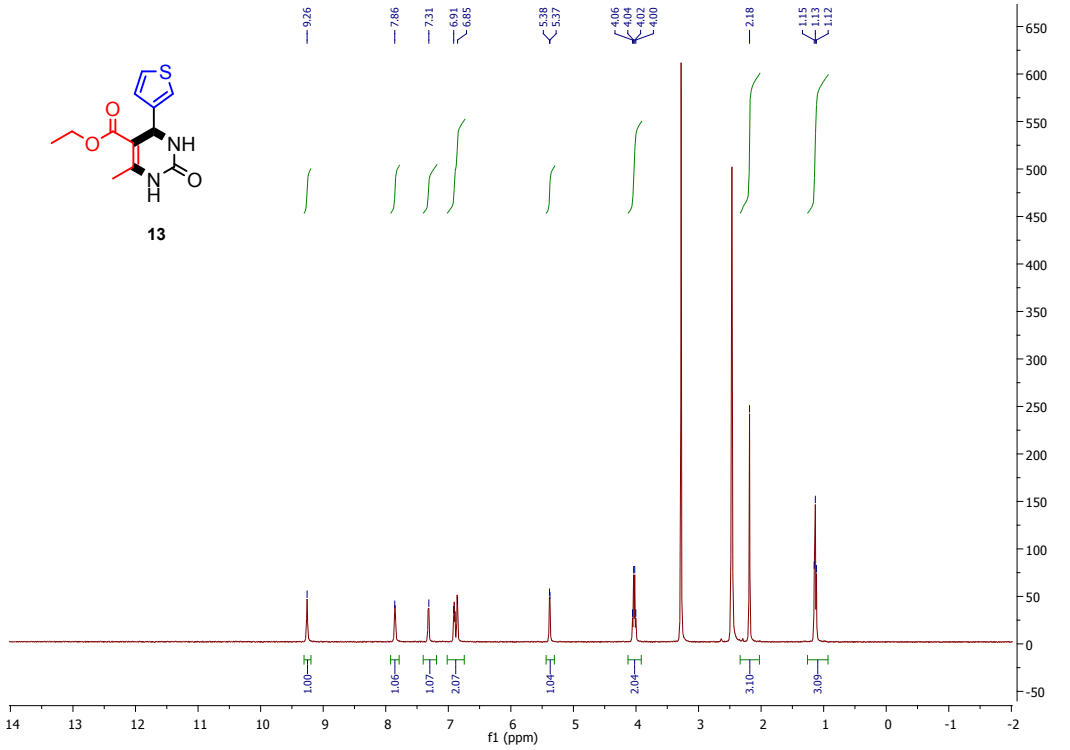

OH
O
O
NH
N
H
O
7
9.30
9.05
7.56
7.00
6.98
6.66
6.64
5.01
5.01
3.96
3.95
3.93
3.91
2.20
1.08
1.06
1.04
1.00
1.00
1.00
2.07
2.03
1.10
2.02
3.00
3.10
f1 (ppm)

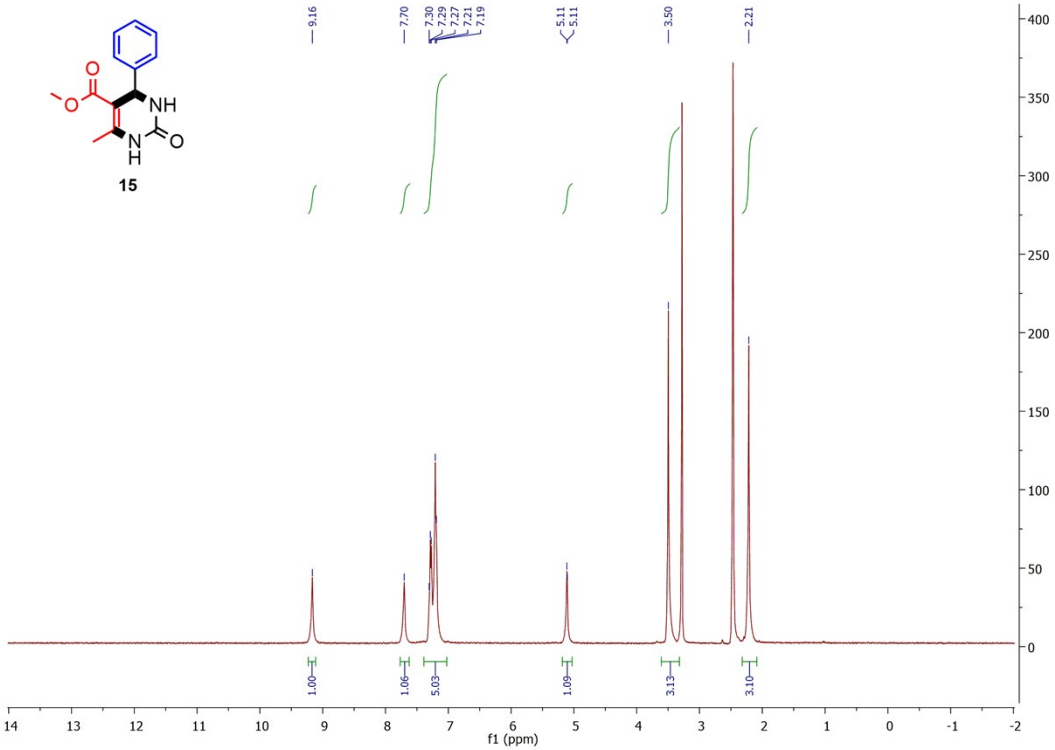

NO2
O
O
NH
N
H
O
8
9.31
8.19
8.17
7.85
7.48
7.46
5.24
3.97
3.96
3.94
3.93
2.23
1.08
1.06
1.04
1.00
2.09
1.15
2.18
1.06
2.01
3.09
3.02
f1 (ppm)

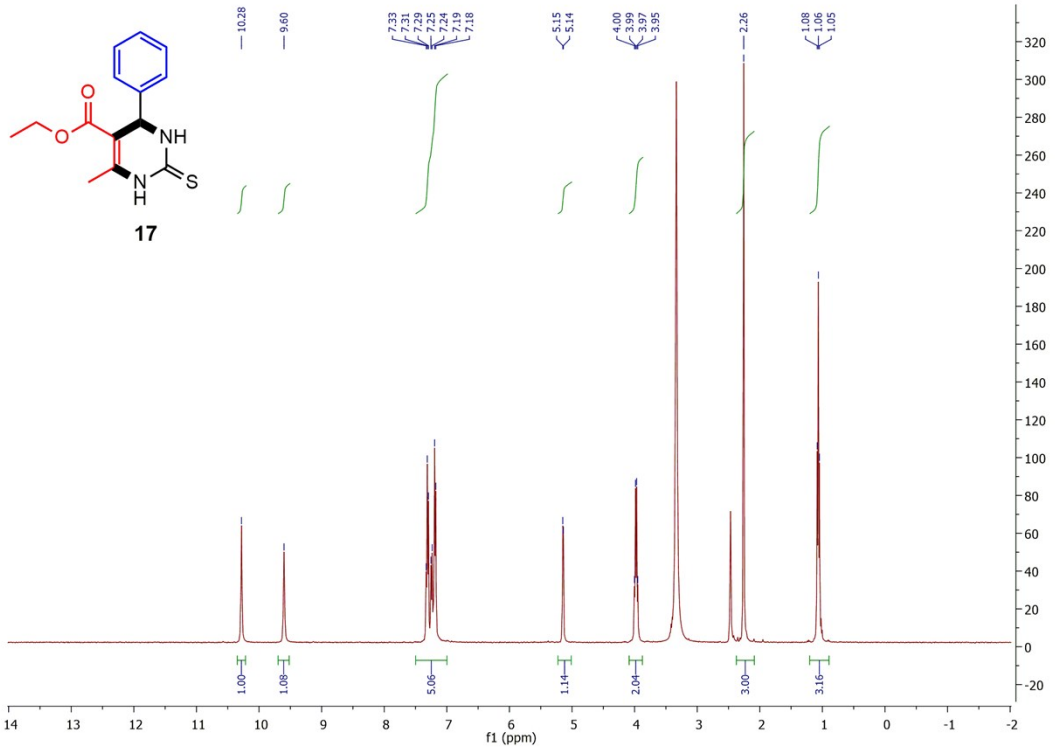

Cl
O
O
NH
N
H
O
9
9.19
7.72
7.36
7.35
7.34
7.23
7.20
5.11
3.97
3.95
3.94
3.92
2.21
1.07
1.05
1.04
1.00
1.05
4.19
1.18
2.05
3.18
3.16
f1 (ppm)

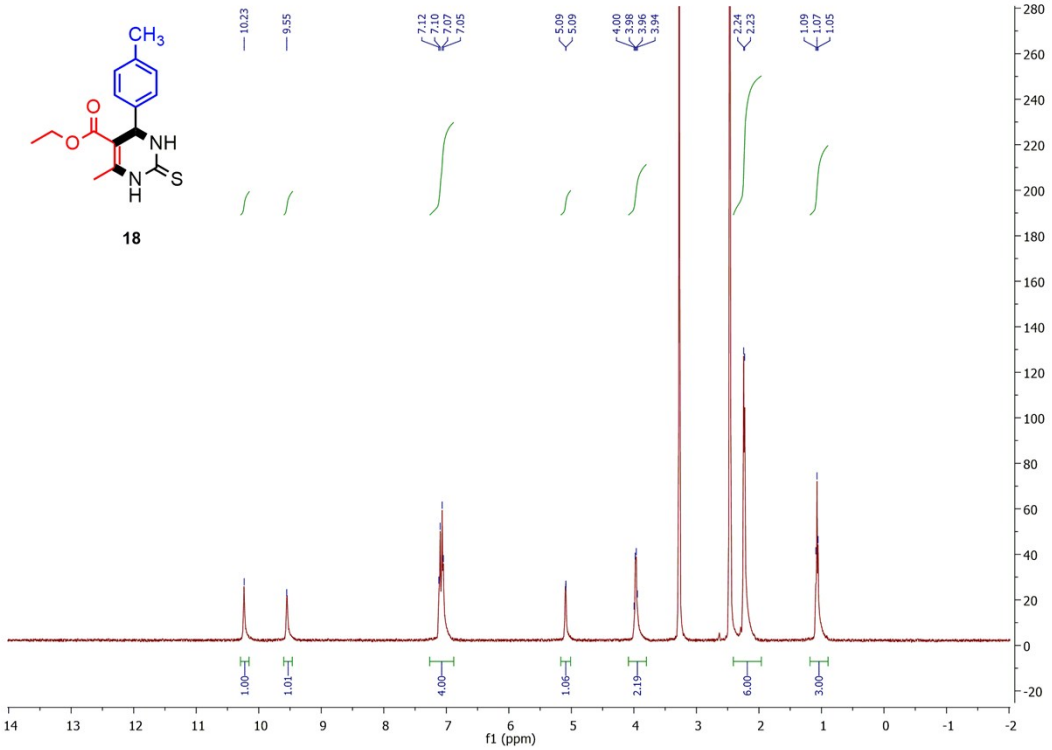

O
O
NH
N
H
O
10
9.21
8.26
7.91
7.89
7.82
7.80
7.70
7.54
7.52
7.50
7.46
7.45
7.43
7.39
7.37
6.03
3.79
3.77
3.76
3.74
2.32
0.79
0.78
0.76
1.00
1.05
3.19
4.11
1.04
2.00
3.16
3.03
f1 (ppm)

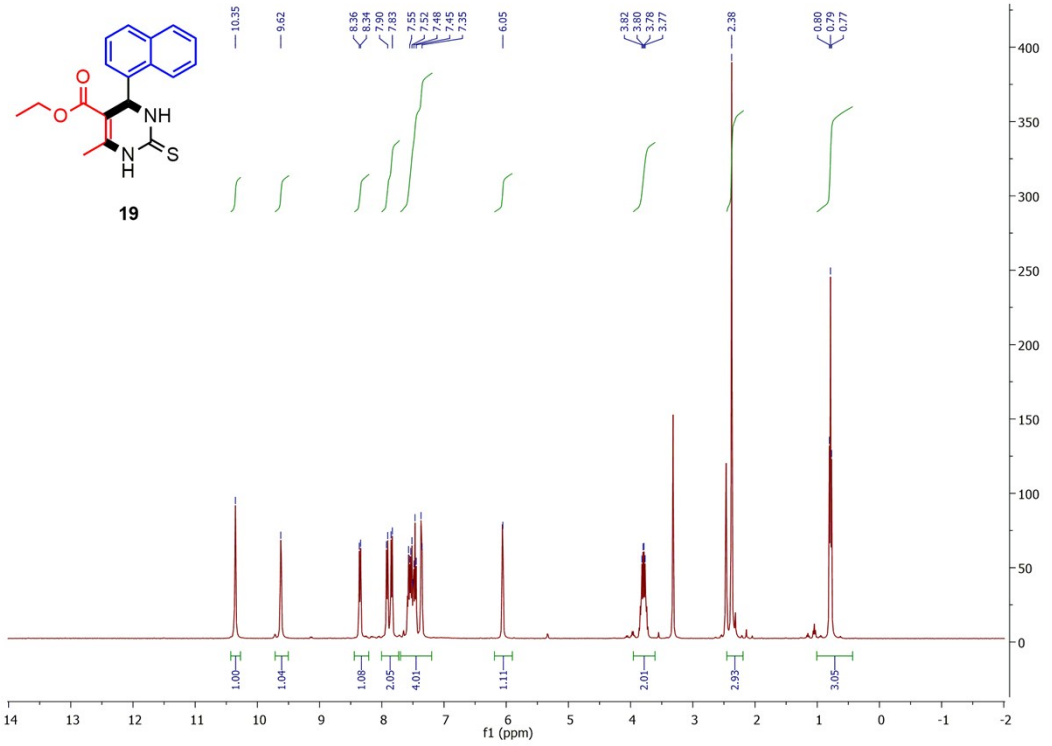

11
8.88
7.28
4.07
4.05
4.04
4.02
4.00
3.99
3.98
2.12
1.31
1.16
1.13
0.81
1.00
1.03
3.09
3.04
7.03
3.08
f1 (ppm)

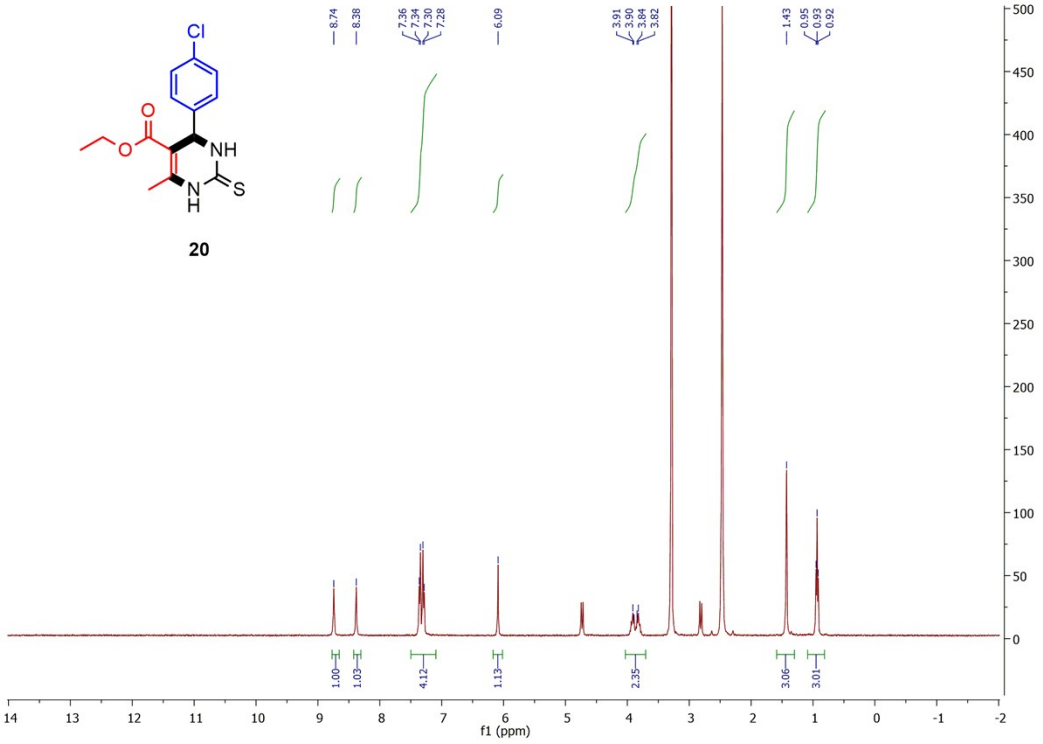

13
9.26
7.86
7.31
6.91
6.85
5.38
5.37
4.06
4.04
4.02
4.00
2.18
1.15
1.13
1.12
1.00
1.06
1.07
2.07
1.04
2.04
3.10
3.09
f1 (ppm)


15
9.16
7.70
7.30
7.29
7.27
7.21
7.19
5.11
5.11
3.50
2.21
1.00
1.06
5.03
1.09
3.13
3.10
f1 (ppm)

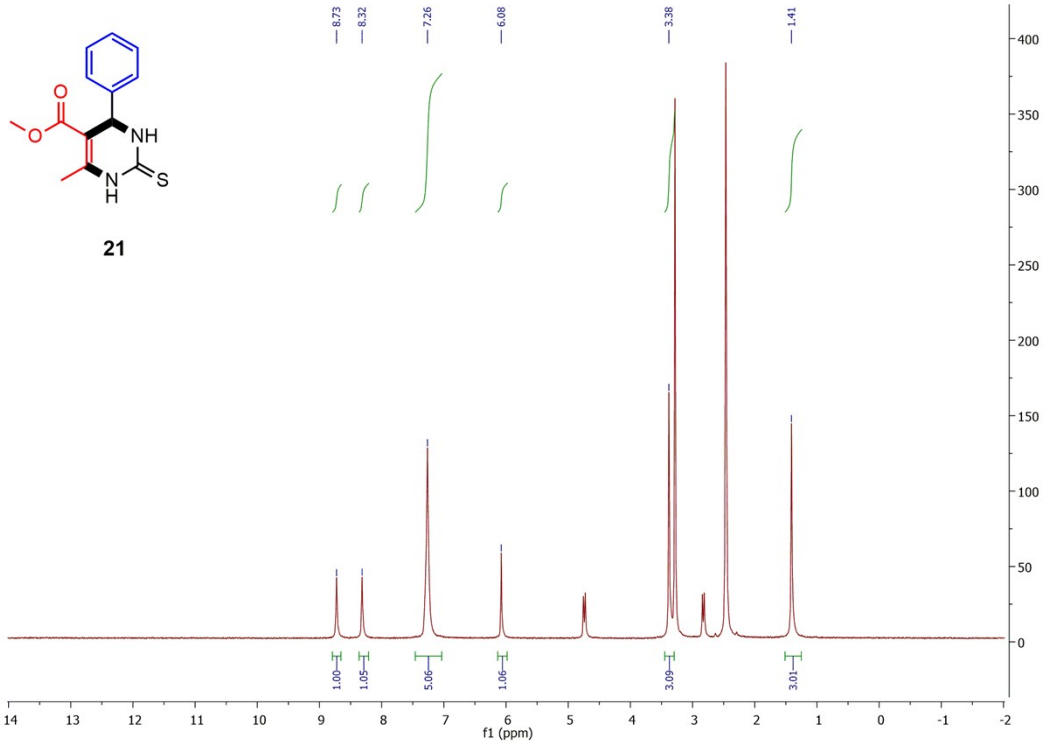

17
10.28
9.60
7.33
7.31
7.29
7.25
7.24
7.19
7.18
5.15
5.14
4.00
3.99
3.97
3.95
2.26
1.08
1.06
1.05
1.00
1.08
5.06
1.14
2.04
3.00
3.16
f1 (ppm)


CH3
O
O
NH
N
H
S
18
10.23
9.55
7.12
7.10
7.07
7.05
5.09
5.09
4.00
3.98
3.96
3.94
2.24
2.23
1.09
1.07
1.05
1.00
1.01
4.00
1.06
2.19
6.00
3.00
f1 (ppm)

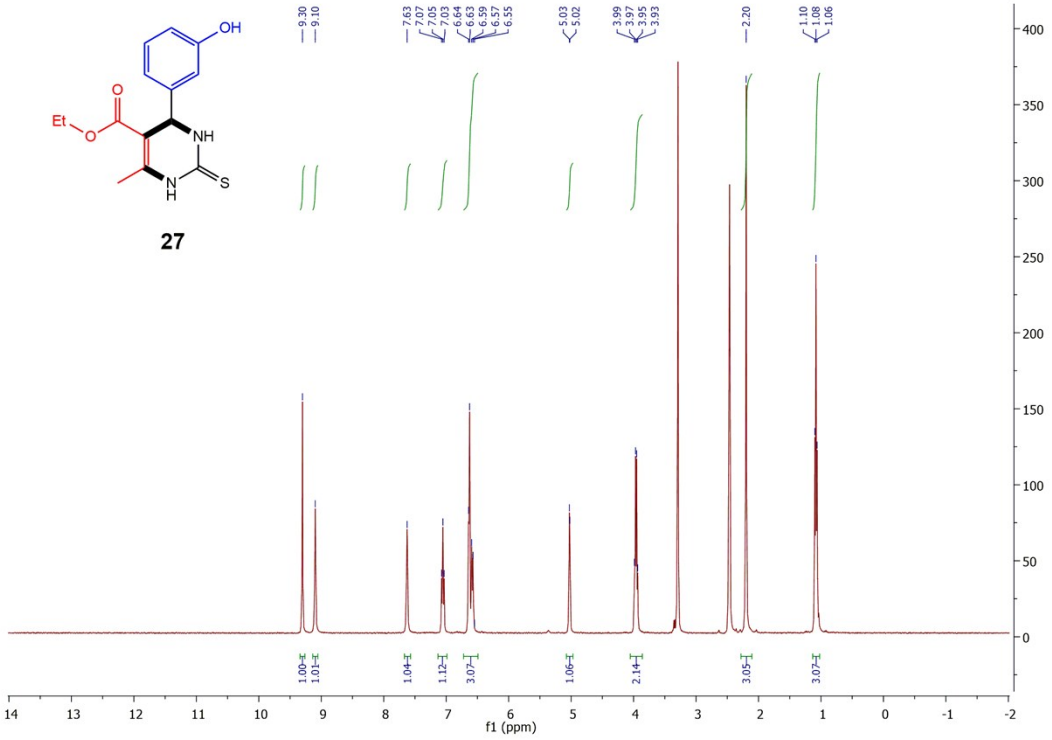

O
O
NH
N
H
S
19
10.35
9.62
8.36
8.34
7.90
7.83
7.55
7.52
7.48
7.45
7.35
6.05
3.82
3.80
3.78
3.77
2.38
0.80
0.79
0.77
1.00
1.04
1.08
2.05
4.01
1.11
2.01
2.93
3.05
f1 (ppm)


Cl
O
O
NH
N
H
S
8.74
8.38
7.36
7.34
7.30
7.28
6.09
3.91
3.90
3.84
3.82
1.43
0.95
0.93
0.92
1.00
1.03
4.12
1.13
2.35
3.06
3.01
f1 (ppm)

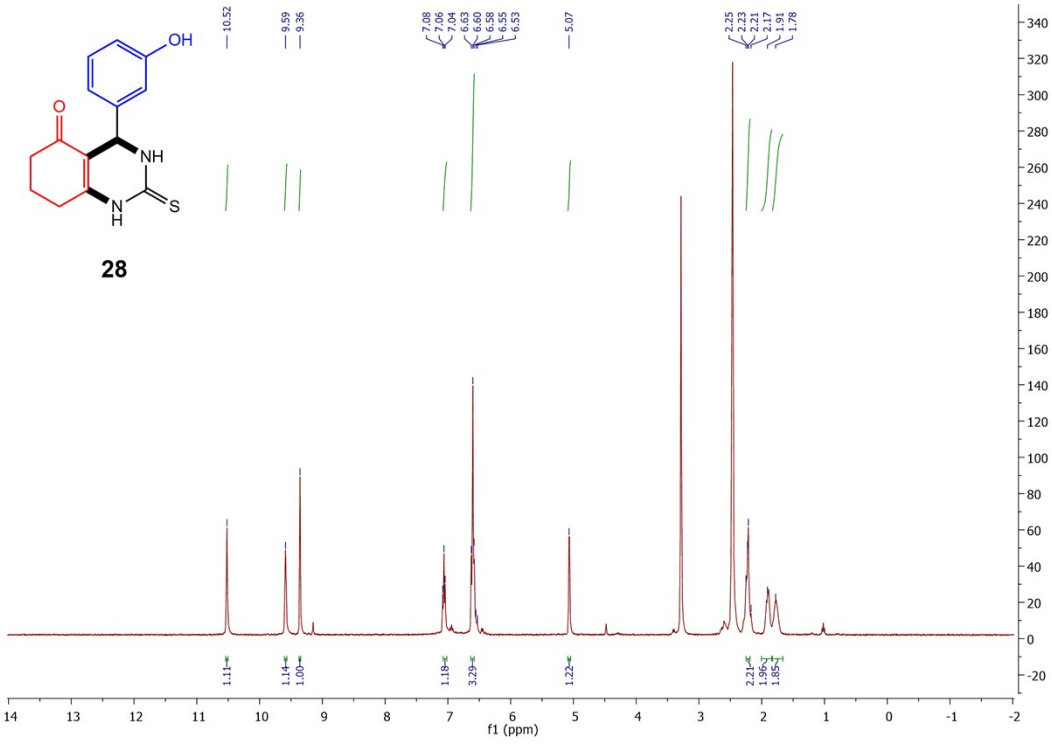
20


O
O
NH
N
H
S
8.73
8.32
7.26
6.08
3.38
1.41
1.00
1.05
5.06
1.06
3.09
3.01
f1 (ppm)

21


OH
O
Et
O
NH
N
H
S
9.30
9.10
7.63
7.07
7.05
7.03
6.64
6.63
6.59
6.57
6.55
5.03
5.02
3.99
3.97
3.95
3.93
2.20
1.10
1.08
1.06
1.00
1.01
1.04
1.12
3.07
1.06
2.14
3.05
3.07
f1 (ppm)

27


OH
O
NH
N
H
S
10.52
9.59
9.36
7.08
7.06
7.04
6.63
6.60
6.58
6.55
6.53
5.07
2.25
2.23
2.21
2.17
1.91
1.78
1.11
1.14
1.00
1.18
3.29
1.22
2.21
1.96
1.85
f1 (ppm)

28