

Supporting Information

Polymer-Supported Dioxidovanadium(V) Complex-Based Heterogeneous Catalyst for Multicomponent Biginelli Reaction Producing Biologically Active 3,4-Dihydropyrimidin-2-(1H)-ones

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Spectral study of Hsal-aebmz (**I**) and complex [V^VO₂(sal-aebmz)] (**1**)

The ¹H NMR spectra (figure) of ligand and complex further confirm the coordination environment of the complex. The ligand shows two broad signals due -OH (12.3 ppm) and -NH (13.3 ppm). The disappearance of the signal due to -OH in the complex confirms the coordination from phenolic oxygen to vanadium. In addition, a significant increase in the chemical shift of azomethine proton (-CH=N-) is observed on moving from ligand (8.6 ppm) to complex (8.9 ppm), which confirms the coordination of azomethine nitrogen atom. The signal of the NH proton could still be seen in the complex at the same position. Methylene protons appear as two triplets at 3.41 and 4.18 ppm. Aromatic protons appear at usual places except for the one that appears very close to the azomethine proton. ⁵¹V NMR spectra of complex **1** were also recorded in DMSO-D₆, which shows only one signal at -541.89 ppm (lit. -540 ppm), which further confirms the identity of the complex formed.

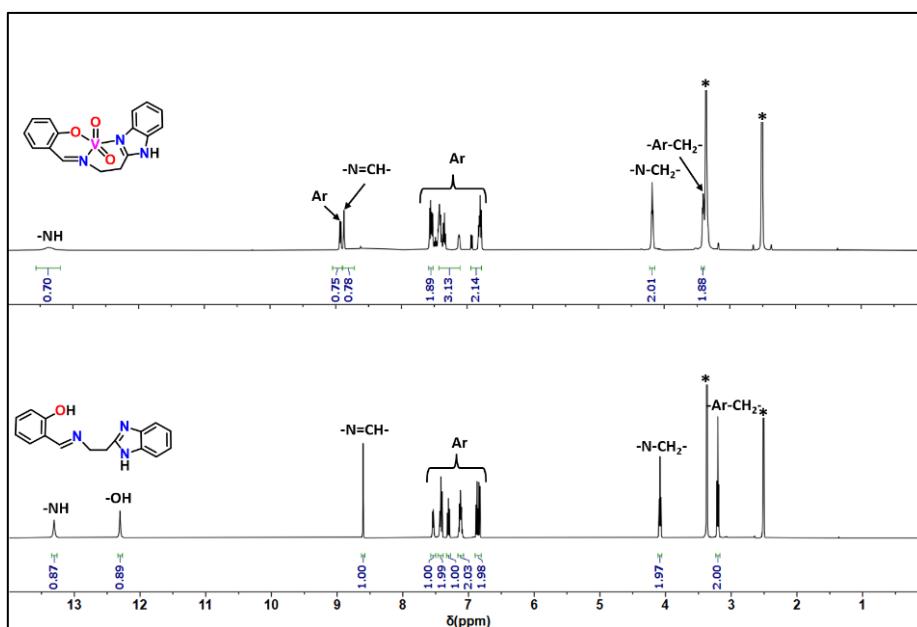


Figure S1. ¹H NMR spectra of Hsal-aebmz (**I**) and complex [V^VO₂(sal-aebmz)] (**1**).

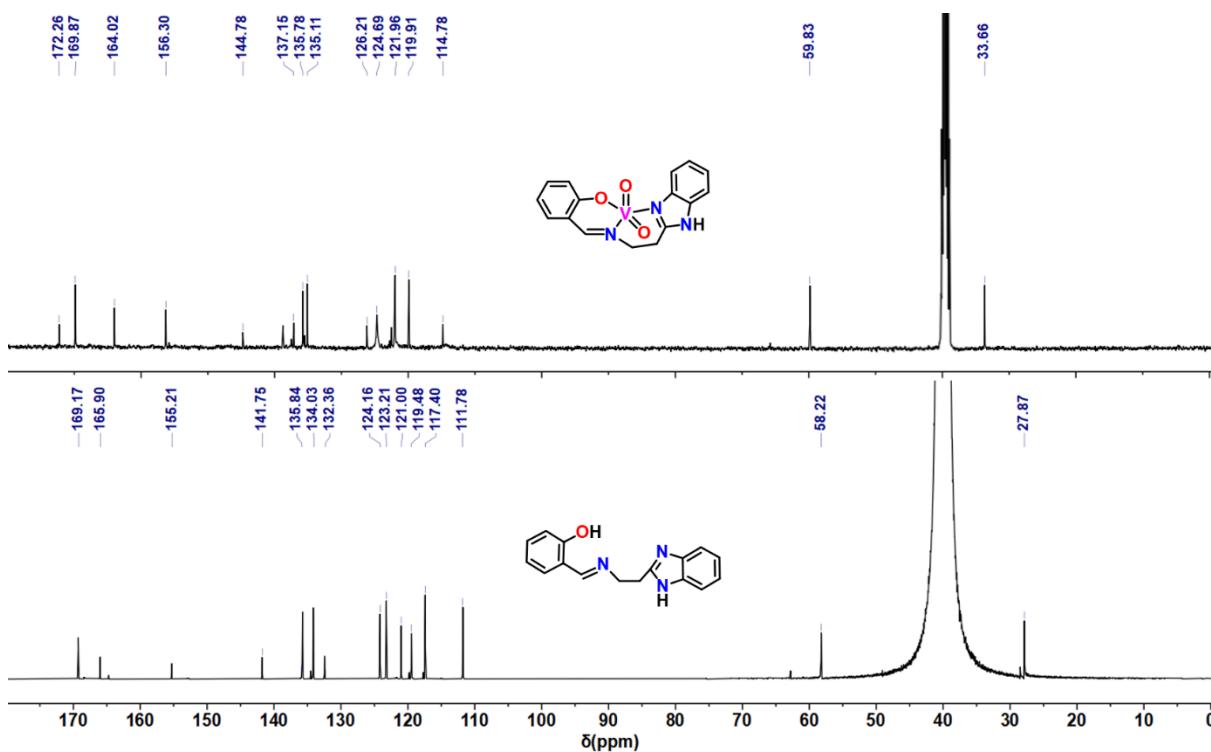


Figure S2. ^{13}C NMR spectra of Hsal-aebmz (**1**) and complex $[\text{V}^{\text{V}}\text{O}_2(\text{sal-aebmz})]$ (**1**).

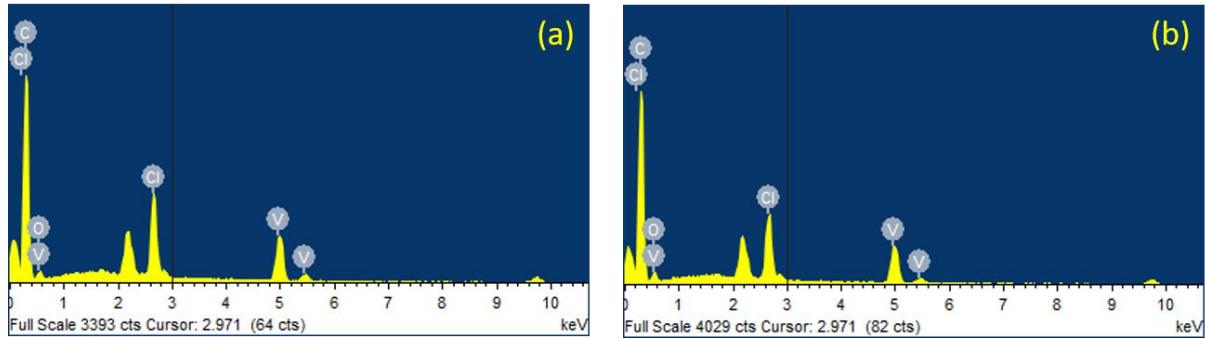
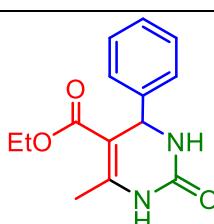


Figure S3. EDS analysis of fresh catalyst **2** (a) and after first catalytic cycle of **2** (b).

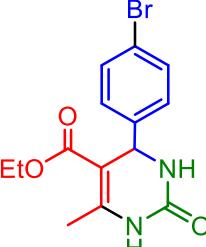
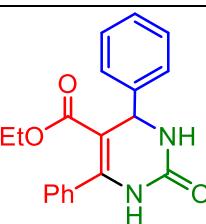
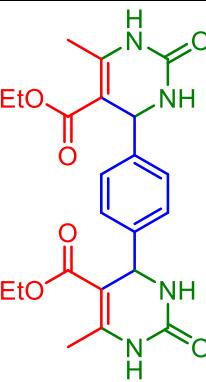
Table S1. Elemental mapping data from EDS analysis for fresh and recycled catalyst.

Element	Weight% (Fresh catalyst)	Weight% (Recycled catalyst)
C	77.91	79.36
O	7.86	7.41
Cl	6.16	5.76
V	8.05	7.47
Total	100.00	100.00

Table S2. ^1H and ^{13}C NMR of synthesized 3,4-dihydropyrimidin-2 (1H)-ones.

Sr. No.	Compound	Melting Point (°C) [Literature Value]	NMR spectra (δ value in ppm).
1.		203-204 [202-204] ^a	^1H NMR (500 MHz, DMSO-d ₆) δ 9.16 (s, 1H), 7.71 (s, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (m, 3H), 5.14 (d, J = 3.3 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H). ^{13}C NMR (500 MHz, DMSO-d ₆): δ 165.30, 152.07, 148.29, 144.83, 128.33, 127.20, 126.20, 99.25, 59.12, 53.93, 17.72, 14.03.

2.		214-216 [215-216] ^a	¹ H NMR (500 MHz, DMSO-d ₆) δ 9.12 (s, 1H), 7.66 (s, 1H), 7.12 (s, 4H), 5.10 (d, <i>J</i> = 3.4 Hz, 1H), 3.98 (q, <i>J</i> = 7.1 Hz, 2H), 2.26 (s, 3H), 2.24 (s, 3H), 1.10 (t, <i>J</i> = 7.1 Hz, 3H). ¹³ C NMR (500 MHz, DMSO-d ₆): δ 165.83, 152.63, 148.58, 142.43, 136.81, 129.34, 126.61, 99.93, 59.60, 54.11, 21.10, 18.21, 14.56.
3.		208-210 [208-211] ^a	¹ H NMR (500 MHz, DMSO-d ₆) δ 9.33 (s, 1H), 8.21 (d, <i>J</i> = 8.8 Hz, 2H), 7.86 (s, 1H), 7.51 (d, <i>J</i> = 8.8 Hz, 2H), 5.28 (d, <i>J</i> = 3.5 Hz, 1H), 3.99 (q, <i>J</i> = 7.1 Hz, 2H), 2.27 (s, 3H), 1.10 (t, <i>J</i> = 7.1 Hz, 3H) ¹³ C NMR (500 MHz, DMSO-d ₆): δ 165.53, 152.47, 152.20, 149.84, 147.22, 128.12, 124.28, 115.00, 98.69, 59.84, 54.17, 18.33, 14.51.
4.		201-203 [201-203] ^a	¹ H NMR (500 MHz, DMSO-d ₆) δ 9.12 (s, 1H), 7.64 (s, 1H), 7.14 (d, <i>J</i> = 8.7 Hz, 2H), 6.87 (d, <i>J</i> = 8.8 Hz, 2H), 5.09 (d, <i>J</i> = 3.4 Hz, 1H), 3.98 (q, <i>J</i> = 7.1 Hz, 2H), 3.72 (s, 3H), 2.24 (s, 3H), 1.10 (t, <i>J</i> = 7.1 Hz, 3H). ¹³ C NMR (500 MHz, DMSO-d ₆): δ 165.85, 158.93, 152.60, 148.44, 137.54, 127.85, 114.18, 100.08, 59.59, 55.45, 53.82, 18.21, 14.57.
5.		212-214 [213-215] ^a	¹ H NMR (500 MHz, DMSO-d ₆) δ 9.22 (s, 1H), 7.76 (s, 1H), 7.39 (d, <i>J</i> = 8.5 Hz, 2H), 7.25 (d, <i>J</i> = 8.4 Hz, 2H), 5.14 (d, <i>J</i> = 3.2 Hz, 1H), 3.98 (q, <i>J</i> = 7.1 Hz, 2H), 2.25 (s, 3H), 1.09 (t, <i>J</i> = 7.0 Hz, 3H).

			¹³ C NMR (500 MHz, DMSO-d ₆): δ 165.16, 151.87, 148.67, 143.76, 131.73, 128.34, 128.14, 98.81, 59.20, 53.38, 17.75, 14.03.
6.		223-225 [223-225] ^a	¹ H NMR (500 MHz, DMSO-d ₆) δ 9.22 (s, 1H), 7.75 (s, 1H), 7.53 (d, <i>J</i> = 8.4 Hz, 2H), 7.19 (d, <i>J</i> = 8.5 Hz, 2H), 5.13 (d, <i>J</i> = 3.3 Hz, 1H), 3.99 (q, <i>J</i> = 7.1 Hz, 2H), 2.25 (s, 3H), 1.11 (t, <i>J</i> = 7.1 Hz, 3H). ¹³ C NMR (500 MHz, DMSO-d ₆): δ 165.67, 152.37, 149.18, 144.68, 131.78, 129.01, 120.75, 99.27, 59.71, 53.97, 18.26, 14.54.
7.		158-160 [160-162] ^b	¹ H NMR (500 MHz, DMSO-d ₆) δ 10.58 (s, 2H), 7.62 (t, <i>J</i> = 7.3 Hz, 4H), 7.51 (m, 3H), 7.44 (m, 3H), 4.20 (s, 1H), 4.12 (q, <i>J</i> = 7.1 Hz, 2H), 1.18 (t, <i>J</i> = 7.1 Hz, 3H). ¹³ C NMR (500 MHz, DMSO-d ₆): δ 168.59, 154.48, 136.20, 134.19, 133.17, 133.14, 129.30, 128.93, 128.88, 128.59, 61.23, 45.91, 14.40.
8.		>300 [300] ^c	¹ H NMR (500 MHz, DMSO-d ₆) δ 9.15 (s, 2H), 7.67 (s, 2H), 7.19 (s, 4H), 5.12 (d, <i>J</i> = 3.3 Hz, 2H), 3.99 (q, <i>J</i> = 7.0 Hz, 4H), 2.24 (s, 6H), 1.10 (t, <i>J</i> = 7.1 Hz, 6H). ¹³ C NMR (500 MHz, DMSO-d ₆): δ 165.80, 152.57, 148.78, 144.38, 126.75, 99.71, 59.65, 54.16, 18.24, 14.54.

9.		>300 [300] ^d	¹ H NMR (500 MHz, CDCl ₃) δ 8.08 (s, 1H), 7.97 (d, J = 8.6 Hz, 4H), 7.80 (d, J = 8.6 Hz, 1H), 7.62 (t, J = 7.4 Hz, 2H), 7.51 (t, J = 7.8 Hz, 4H), 7.45 (q, J = 7.9, 7.0 Hz, 2H), 4.24 (q, J = 7.1 Hz, 4H), 4.02 (s, 4H), 1.36 (t, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 6H). ¹³ C NMR (500 MHz, DMSO-d ₆): δ 193.91, 158.02, 134.28, 129.93, 126.69, 129.31, 128.88, 127.07, 85.43, 61.19, 46.02, 14.46.
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^a Javidi J.; Esmaeilpour M.; Dodeji F. N. Immobilization of phosphomolybdic acid nanoparticles on imidazole functionalized Fe₃O₄@SiO₂: A novel and reusable nanocatalyst for one-pot synthesis of Biginelli-type 3,4-dihydro-pyrimidine-2-(1*H*)-ones/thiones under solvent-free conditions, *Rsc Adv.* **2015**, *5*, 308–315.

^b Meng. F.; Shi L.; Feng G.; Sun L.; Zhou Y. Enantioselective synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones through organocatalytic transfer hydrogenation of 2-hydroxypyrimidines *J. Org. Chem.* **2019**, *84*, 4435–4442.

^c Fu N.; Yuan Y.; Cao Z.; Wang S.; Wang J.; Peppe C. Indium(III) bromide-catalyzed preparation of dihydropyrimidinones: Improved protocol conditions for the Biginelli reaction *Tetrahedron* **2002**, *58*, 4801-4807.

^d Shaker R. M.; Mahmoud A. F.; Abdel-Latif F. F. Synthesis of 2-thioxopyrido[2,3-d]pyrimidine-4-ones and 1,4-bridged bis-2-thioxo-1,2,3,4-tetrahydro-5-pyrimidine carboxylic acid ethyl ester derivatives *Phosphorus Sulfur Silicon* **2000**, *160*, 207–222.

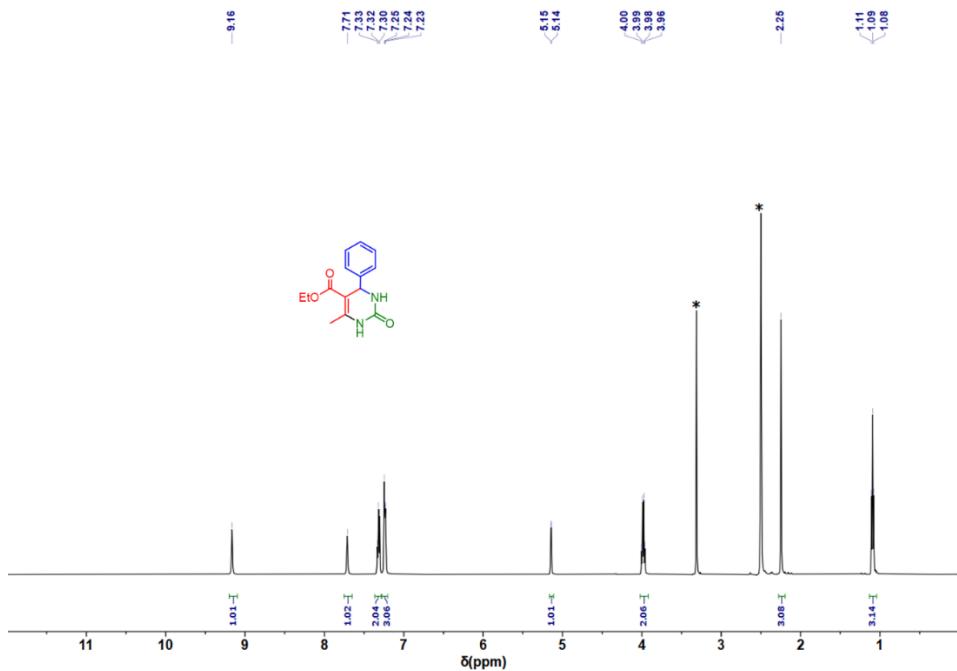


Figure S4. ^1H NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-6-methyl-2-oxo-4-phenyl-, ethyl ester.

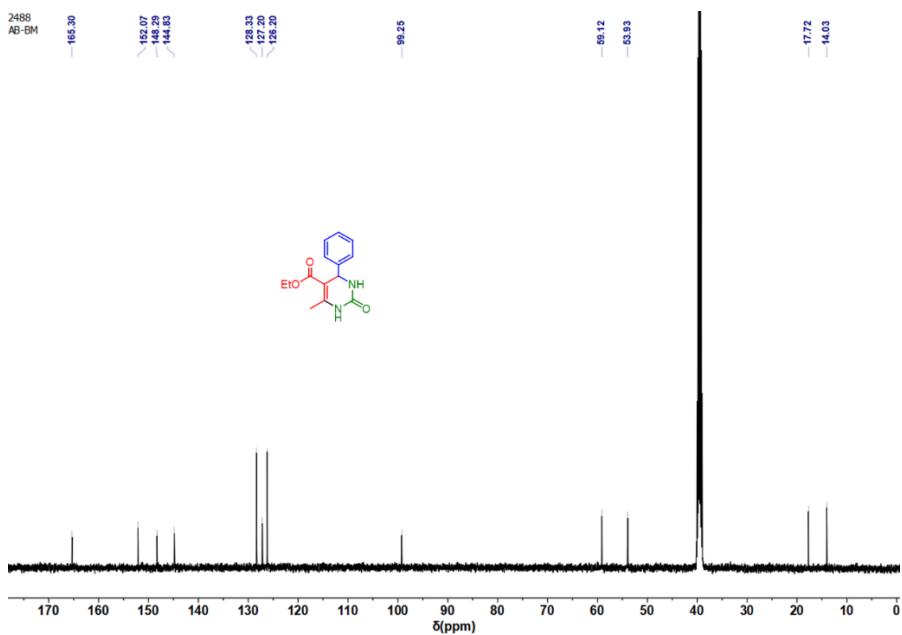


Figure S5. ^{13}C NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-6-methyl-2-oxo-4-phenyl-, ethyl ester.

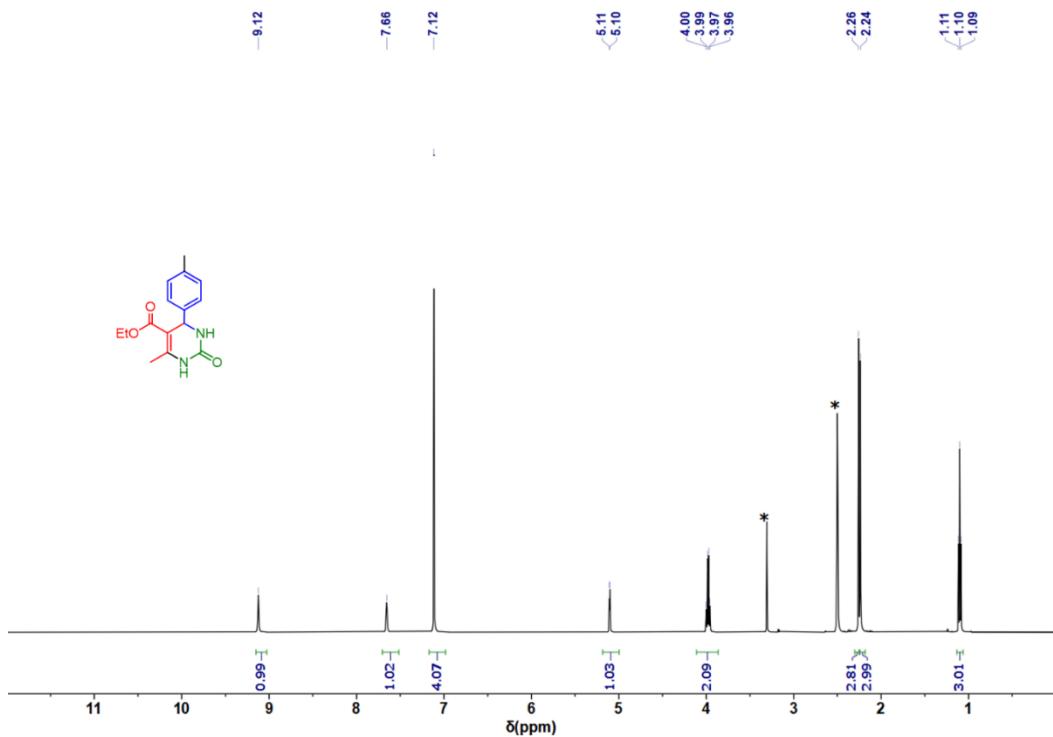


Figure S6. ^1H NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-methylphenyl)-2-oxo-, ethyl ester.

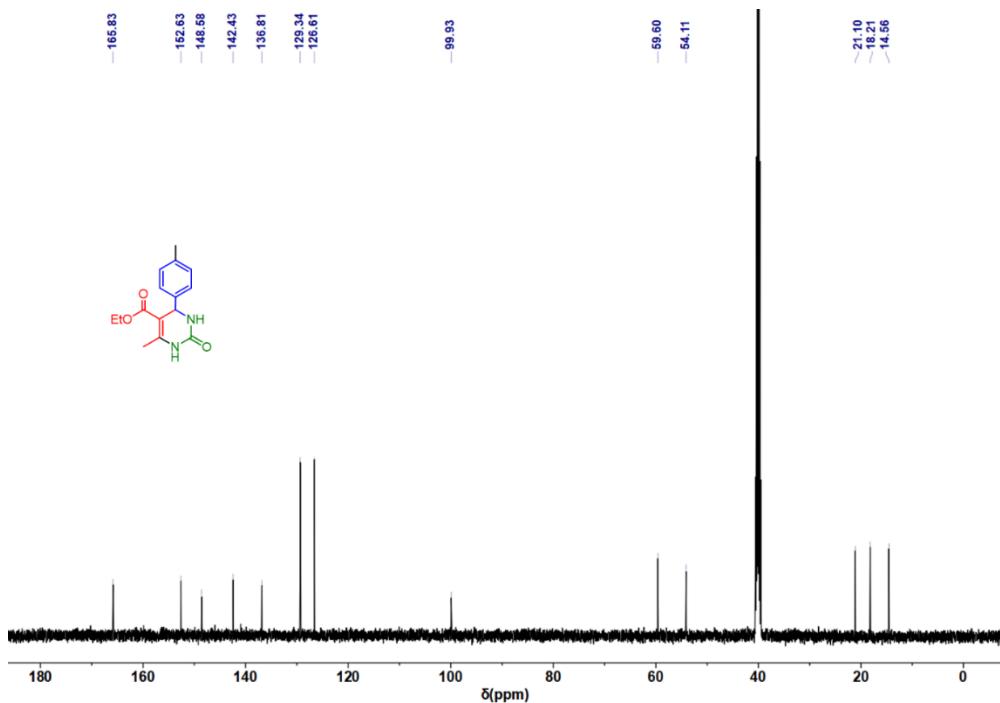


Figure S7. ^{13}C NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-methylphenyl)-2-oxo-, ethyl ester.

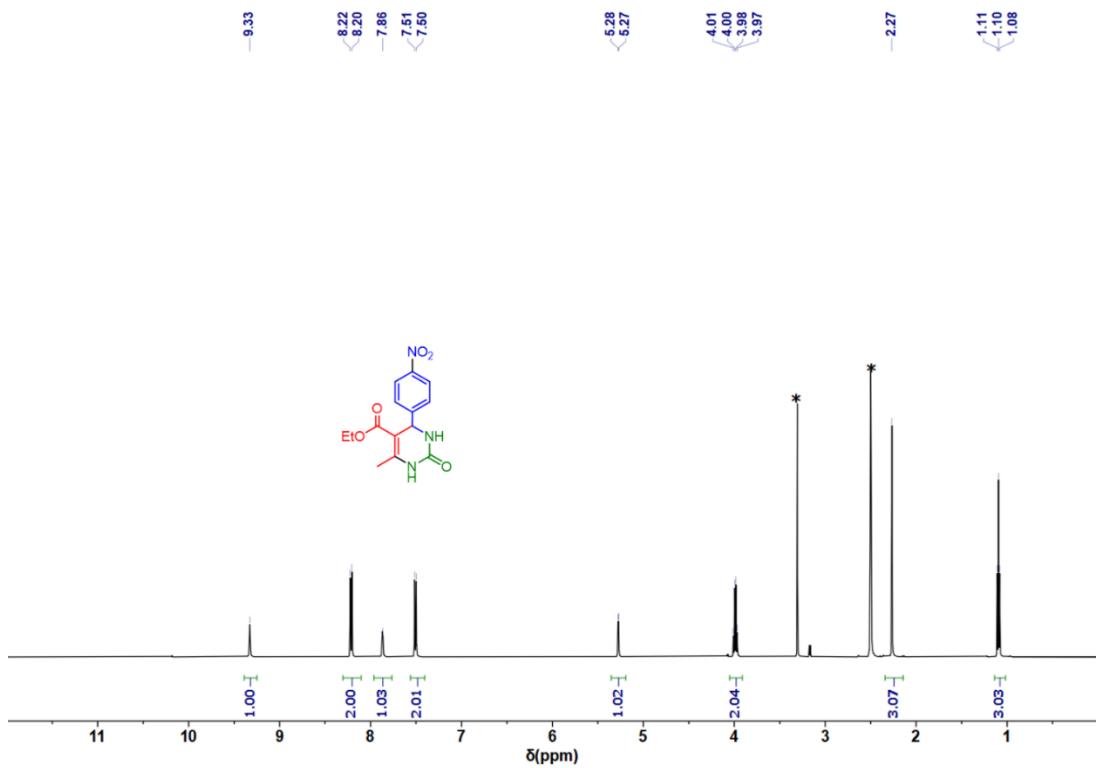


Figure S8. ^1H NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-nitrophenyl)-2-oxo-, ethyl ester.

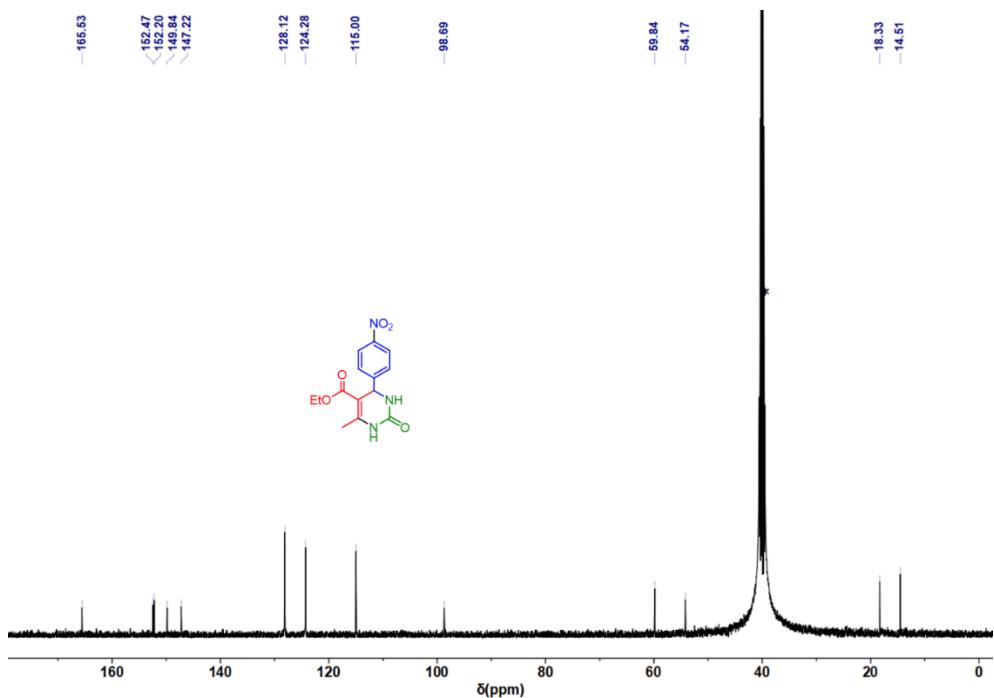


Figure S9. ^{13}C NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-nitrophenyl)-2-oxo-, ethyl ester.

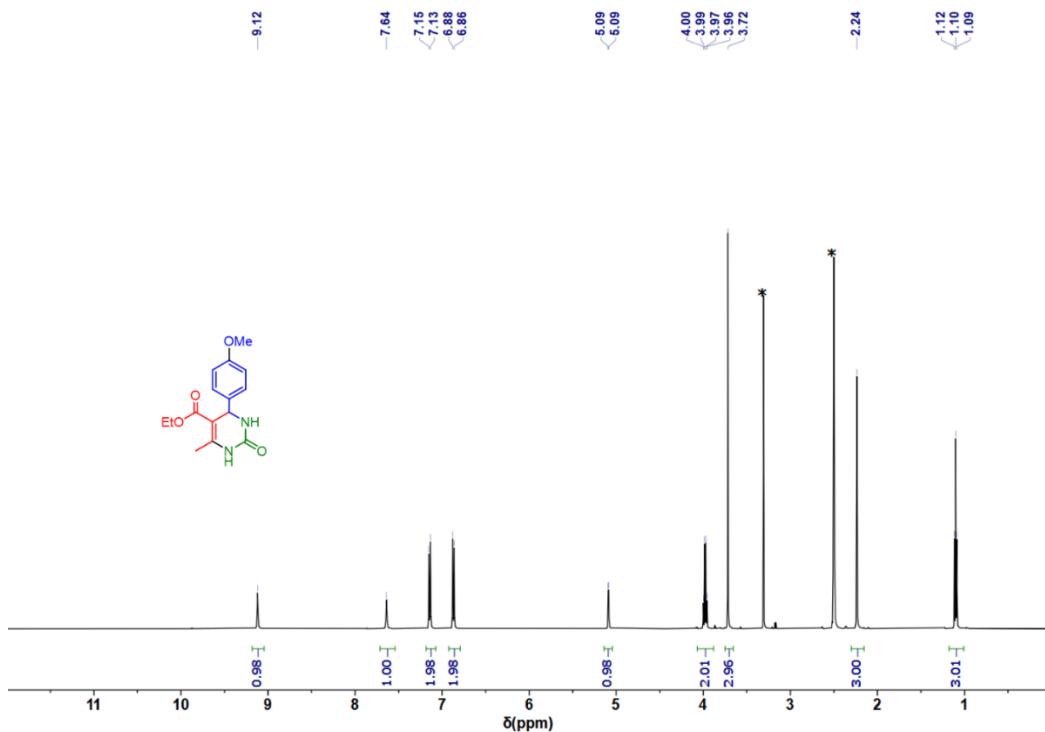


Figure S10. ^1H NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-methoxyphenyl)-2-oxo-, ethyl ester.

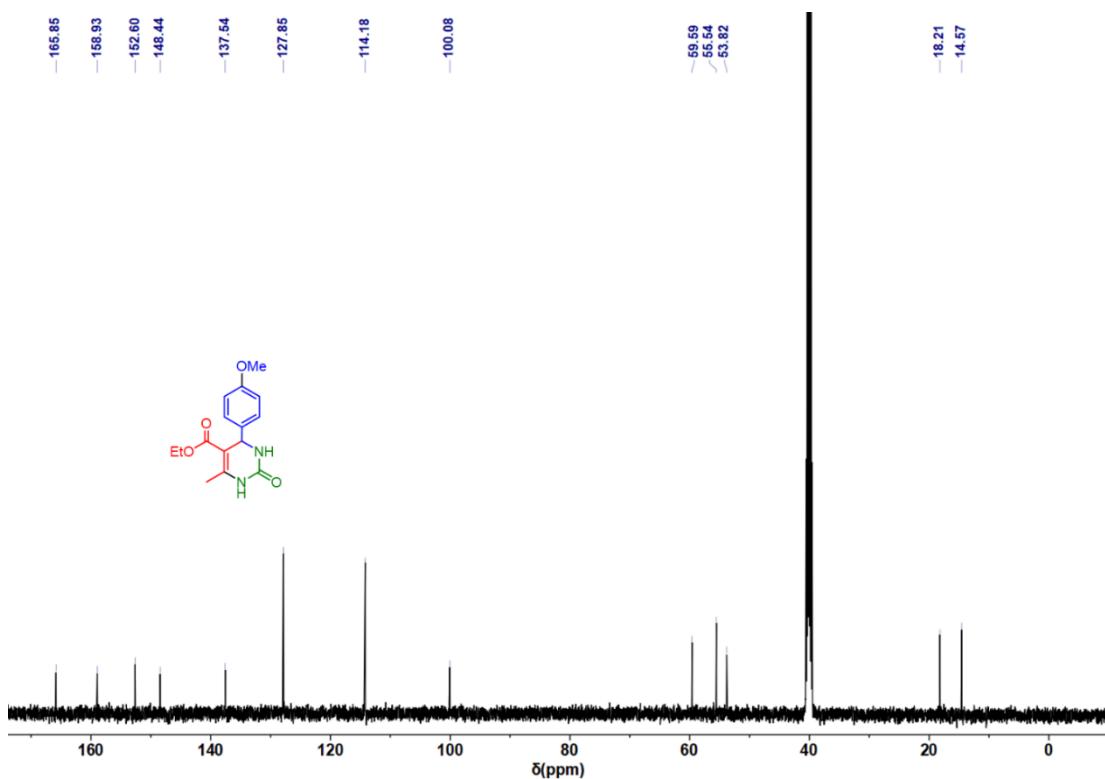


Figure S11. ^{13}C NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-methoxyphenyl)-2-oxo-, ethyl ester.

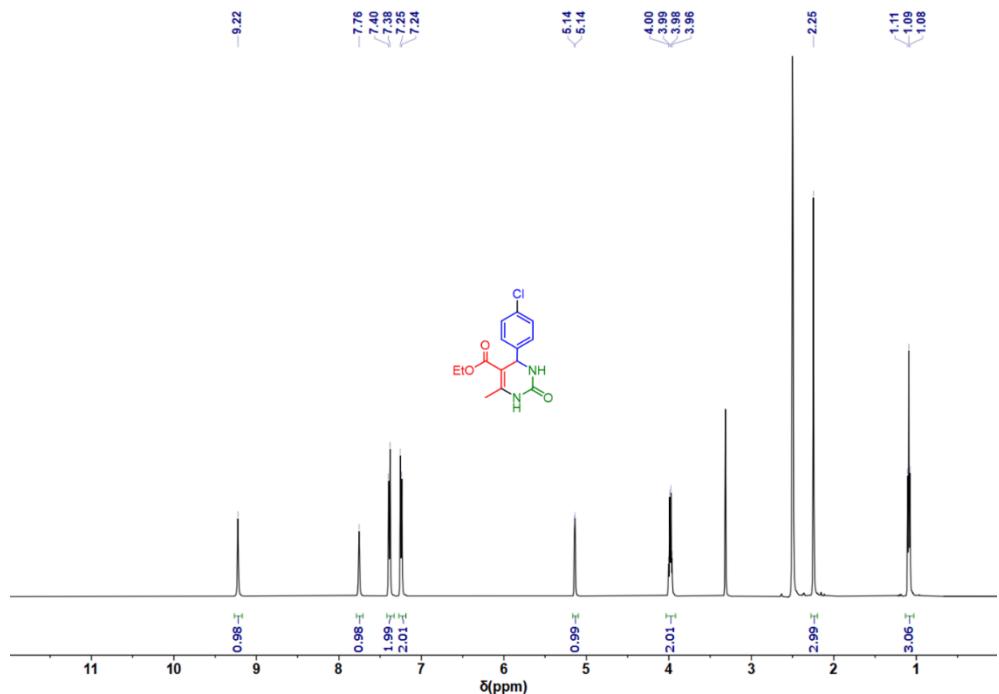


Figure S12. ^1H NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-chlorophenyl)-2-oxo-, ethyl ester.

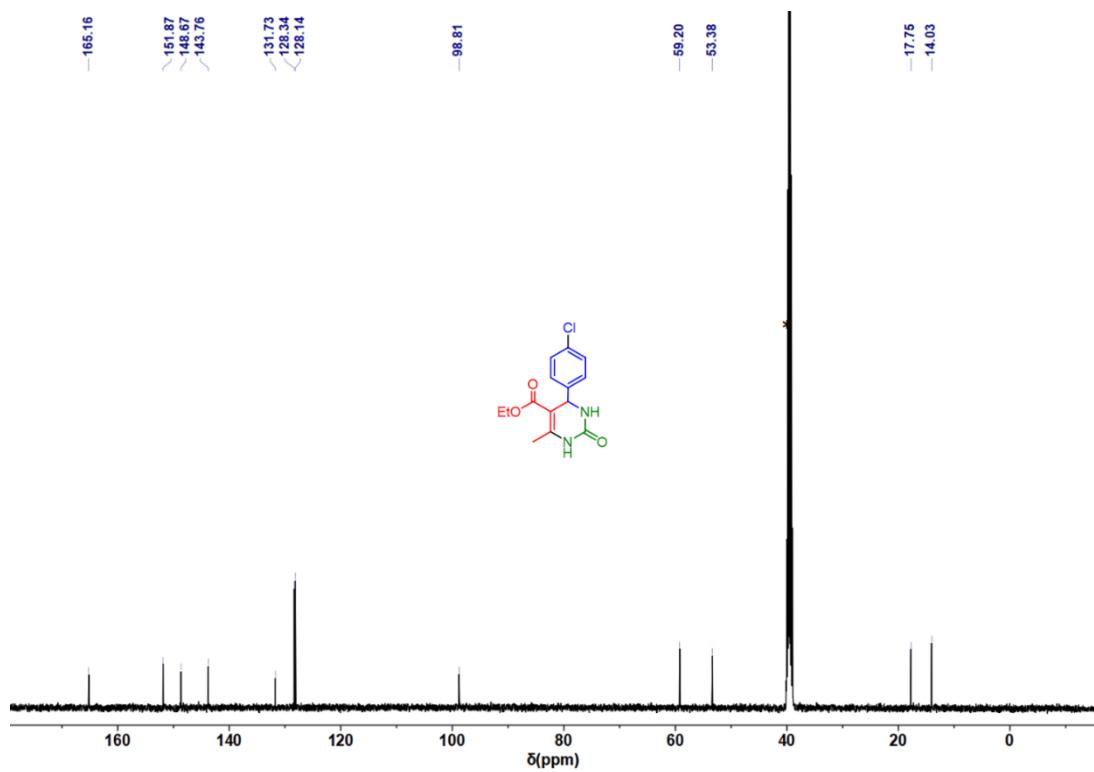


Figure S13. ^{13}C NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-chlorophenyl)-2-oxo-, ethyl ester.

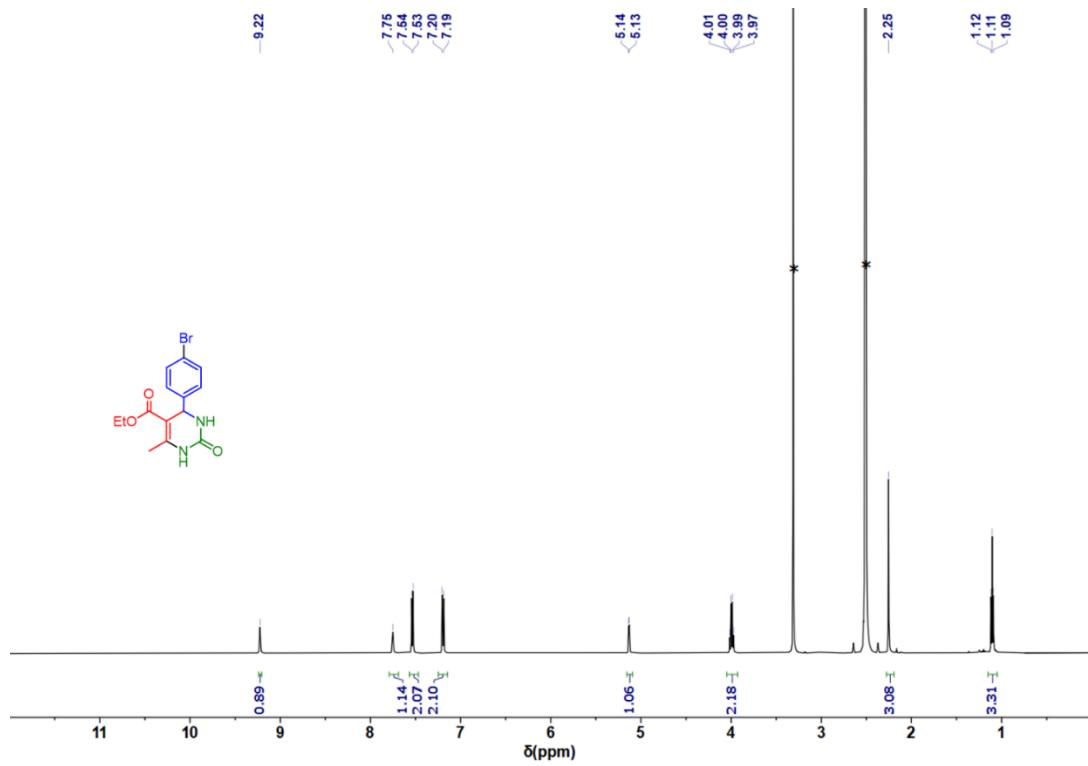


Figure S14. ^1H NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-bromophenyl)-2-oxo-, ethyl ester.

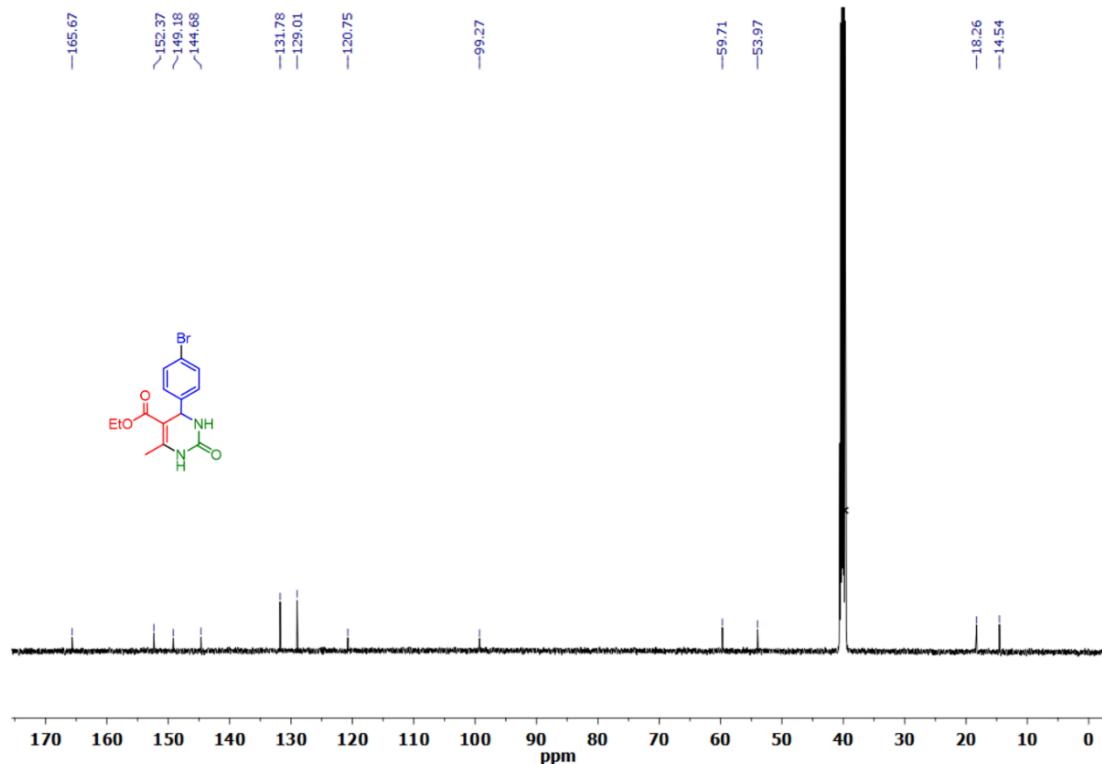


Figure S15. ^{13}C NMR spectrum of 5-pyrimidinecarboxylic acid, 1,2,3,4-tetrahydro-4-(4-bromophenyl)-2-oxo-, ethyl ester.

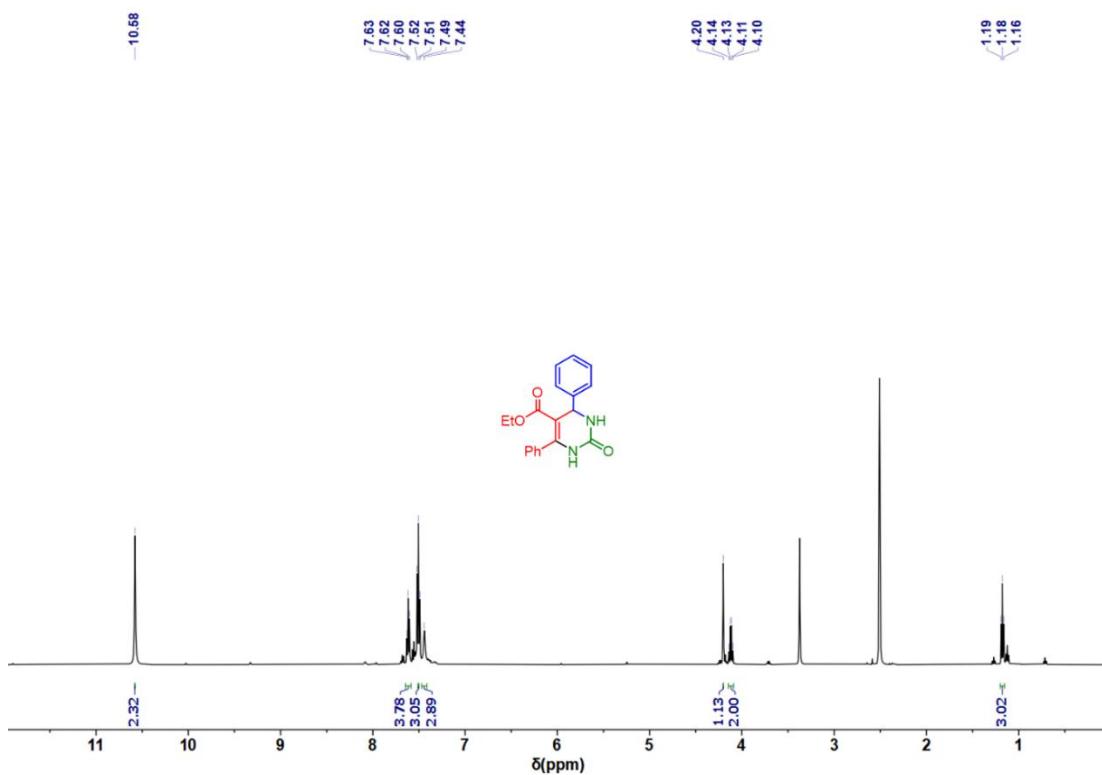


Figure S16. ^1H NMR spectrum of ethyl 2-oxo-4,6-diphenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

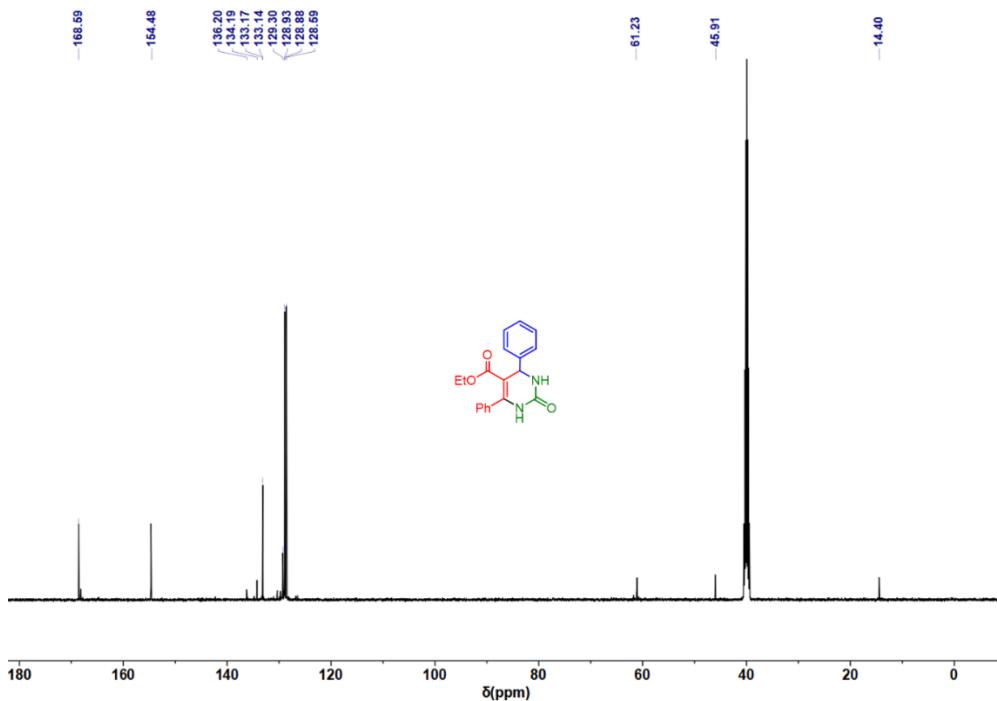


Figure S17. ^{13}C NMR spectrum of ethyl 2-oxo-4,6-diphenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

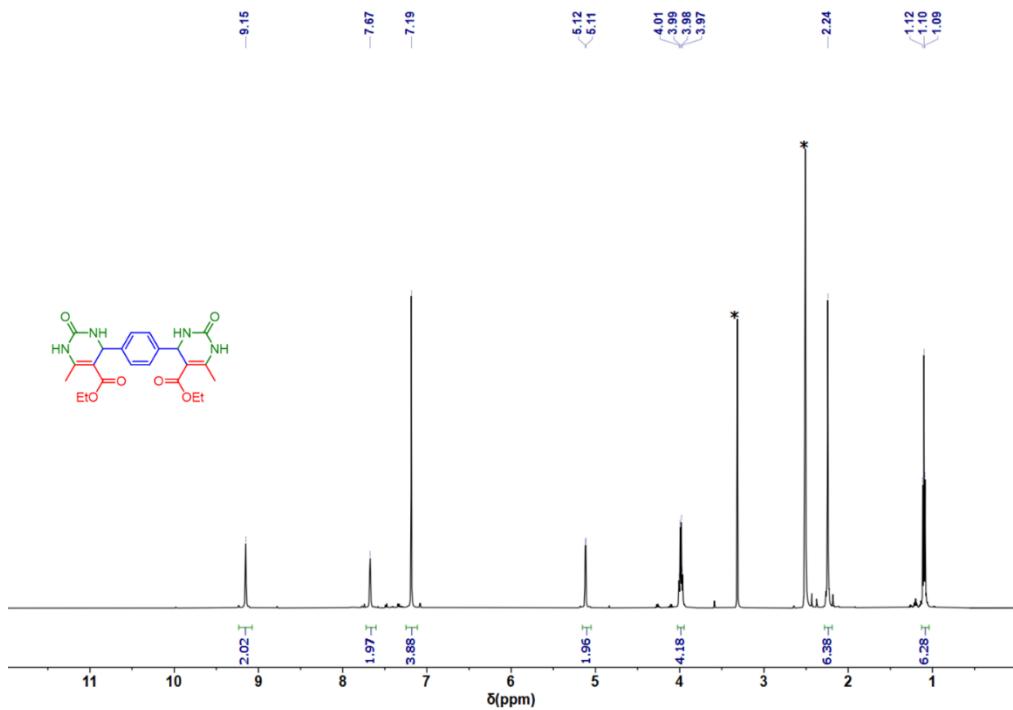


Figure S18. ^1H NMR spectrum of 5-pyrimidinecarboxylic acid, 4,4'-(1,4-phenylene)bis[1,2,3,4-tetrahydro-6-methyl-2-oxo-, 5,5'-diethyl ester].

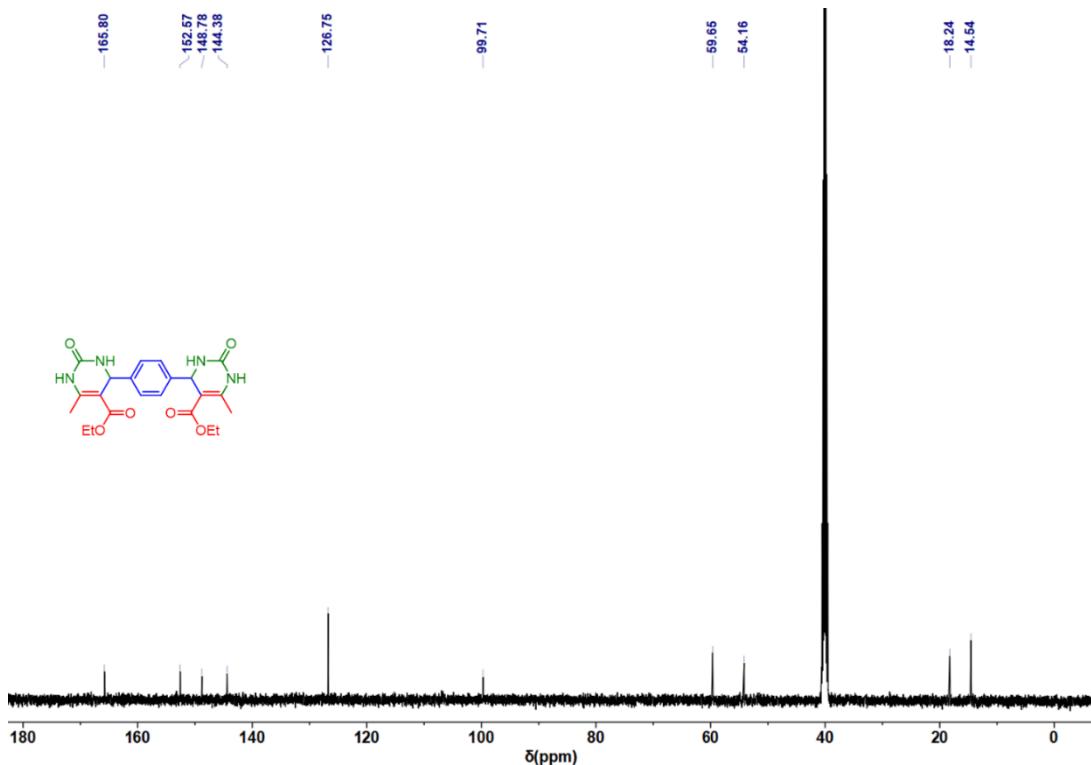


Figure S19. ^{13}C spectrum of 5-pyrimidinecarboxylic acid, 4,4'-(1,4-phenylene)bis[1,2,3,4-tetrahydro-6-methyl-2-oxo-, 5,5'-diethyl ester].

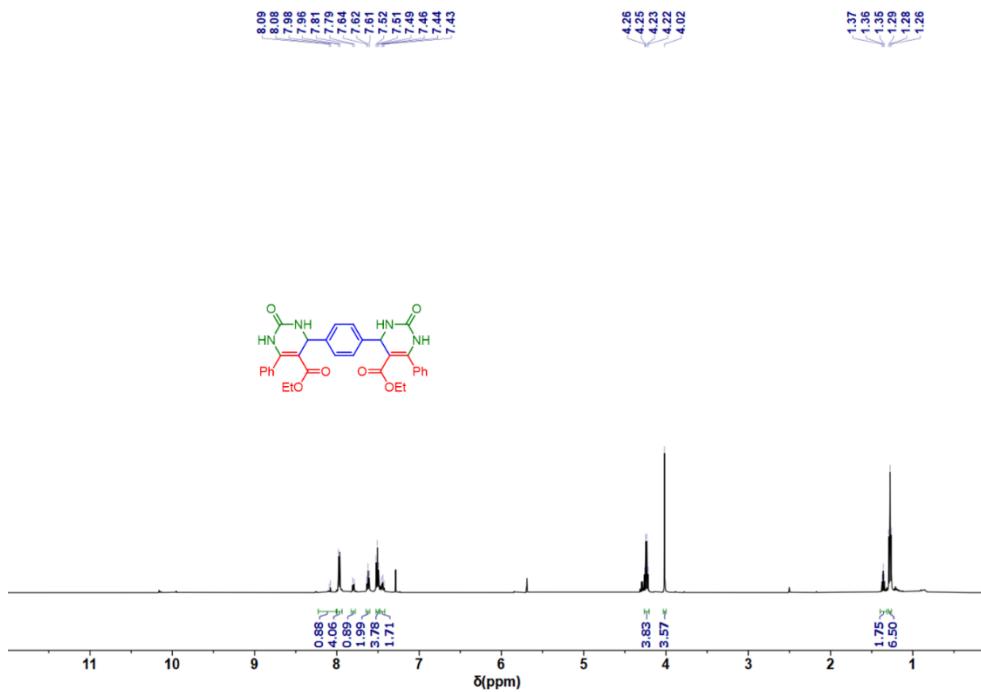


Figure S20. ^1H NMR spectrum of 5-pyrimidinecarboxylic acid, 4,4'-(1,4-phenylene)bis[1,2,3,4-tetrahydro-6-phenyl-2-oxo-, 5,5'-diethyl ester].

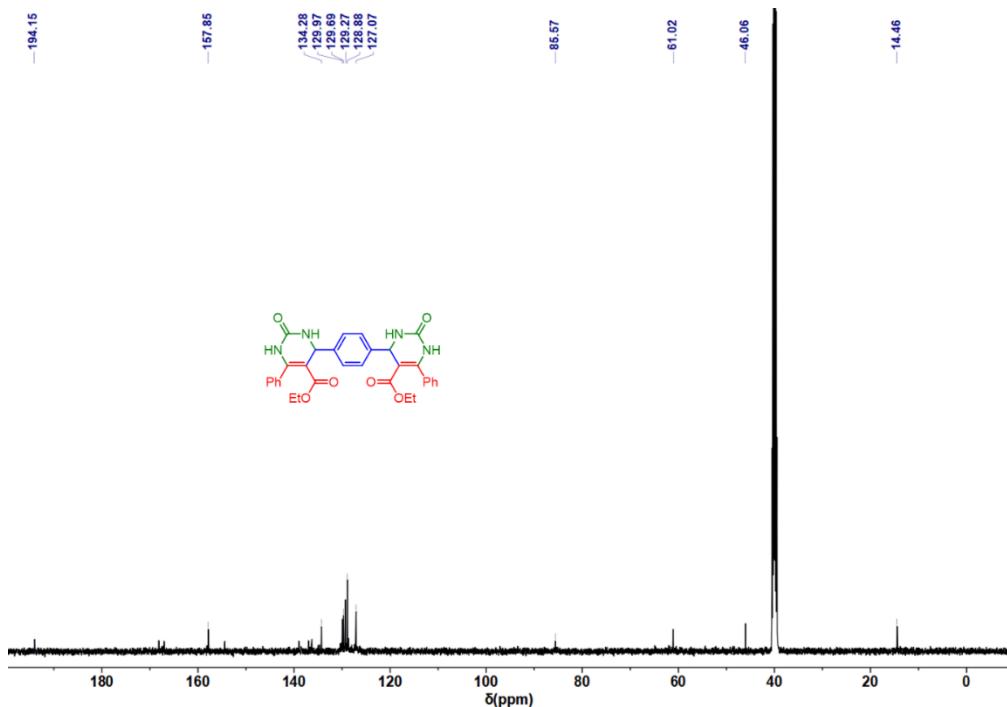


Figure S21. ^{13}C spectrum of 5-pyrimidinecarboxylic acid, 4,4'-(1,4-phenylene)bis[1,2,3,4-tetrahydro-6-phenyl-2-oxo-, 5,5'-diethyl ester].

Table S3. ^1H and ^{13}C NMR spectral data of some synthesized dihydropyrimidine-2-thione.

1		208-210 [208-210] ^a	^1H NMR (500 MHz, DMSO- D_6) δ 10.33 (s, 1H), 9.65 (s, 1H), 7.35 (t, J = 7.3 Hz, 2H), 7.28 (m, 1H), 7.22 (m, 2H), 5.17 (d, J = 3.8 Hz, 1H), 4.01 (d, J = 7.3 Hz, 2H), 2.29 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H). ^{13}C NMR (500 MHz, DMSO- D_6) δ 174.79, 165.67, 145.57, 144.04, 129.10, 128.22, 126.93, 101.26, 60.12, 54.59, 17.69, 14.54.
2		178-180 [179-180] ^a	^1H NMR (500 MHz, DMSO- D_6) δ 10.38 (s, 1H), 9.67 (s, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 5.17 (d, J = 3.8 Hz, 1H), 4.00 (m, 2H), 2.29 (s, 3H), 1.10 (t, J = 7.0 Hz, 3H). ^{13}C NMR (500 MHz, DMSO- D_6) δ 174.79, 165.53, 145.92, 142.92, 132.81, 129.25, 128.86, 100.83, 60.20, 53.99, 17.72, 14.54
3		200-202 [201-203] ^b	^1H NMR (500 MHz, DMSO- D_6) δ 10.37 (s, 1H), 9.66 (s, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.16 (d, J = 3.8 Hz, 1H), 3.99 (m, 2H), 2.28 (s, 3H), 1.09 (t, J = 7.0 Hz, 3H). ^{13}C NMR (500 MHz, DMSO- D_6) δ 174.26, 165.00, 145.39, 142.39, 132.27, 128.60, 128.32, 100.29, 59.66, 53.45, 17.19, 14.00.
4		108-110 [109-111] ^b	^1H NMR (500 MHz, DMSO) δ 10.37 (s, 1H), 9.34 (s, 1H), 8.22 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 5.29 (d, J = 3.5 Hz, 1H), 4.00 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (500 MHz, DMSO- D_6) δ 184.33, 179.98, 132.06, 130.83, 129.18, 124.63, 62.09, 61.87, 26.75, 17.74, 14.41.

5		192-194 [192-194] ^b	¹ H NMR (500 MHz, DMSO) δ 10.38 (s, 1H), 9.67 (s, 1H), 7.14 (s, 4H), 5.12 (d, <i>J</i> = 3.4 Hz, 1H), 4.00 (q, <i>J</i> = 7.1 Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 1.12 (t, <i>J</i> = 7.1 Hz, 3H). ¹³ C NMR (500 MHz, DMSO- <i>D</i> ₆) δ 174.26, 165.00, 145.39, 142.39, 132.27, 128.60, 128.32, 100.29, 59.66, 53.45, 21.10, 17.19, 14.00.
6		151-153 [150-152] ^b	¹ H NMR (500 MHz, DMSO) δ 10.33 (s, 1H), 9.65 (s, 1H), 7.17 (d, <i>J</i> = 8.7 Hz, 2H), 6.90 (d, <i>J</i> = 8.8 Hz, 2H), 5.12 (d, <i>J</i> = 3.4 Hz, 1H), 4.01 (q, <i>J</i> = 7.1 Hz, 2H), 3.75 (s, 3H), 2.27 (s, 3H), 1.13 (t, <i>J</i> = 7.1 Hz, 3H). ¹³ C NMR (500 MHz, DMSO- <i>D</i> ₆) δ 184.37, 167.47, 132.37, 132.21, 132.06, 129.20, 128.15, 115.07, 61.87, 60.10, 56.25, 14.41.

^a Javidi J.; Esmaeilpour M.; Dodeji F. N. Immobilization of phosphomolybdic acid nanoparticles on imidazole functionalized Fe₃O₄@SiO₂: A novel and reusable nanocatalyst for one-pot synthesis of Biginelli-type 3,4-dihydro-pyrimidine-2-(1*H*)-ones/thiones under solvent-free conditions, *Rsc Adv.* **2015**, *5*, 308–315.

^b Stadler A.; Kappe C. O. Automated library generation using sequential microwave-assisted chemistry. Application toward the Biginelli multicomponent condensation *J. Comb. Chem.* **2001**, *3*, 624–630.

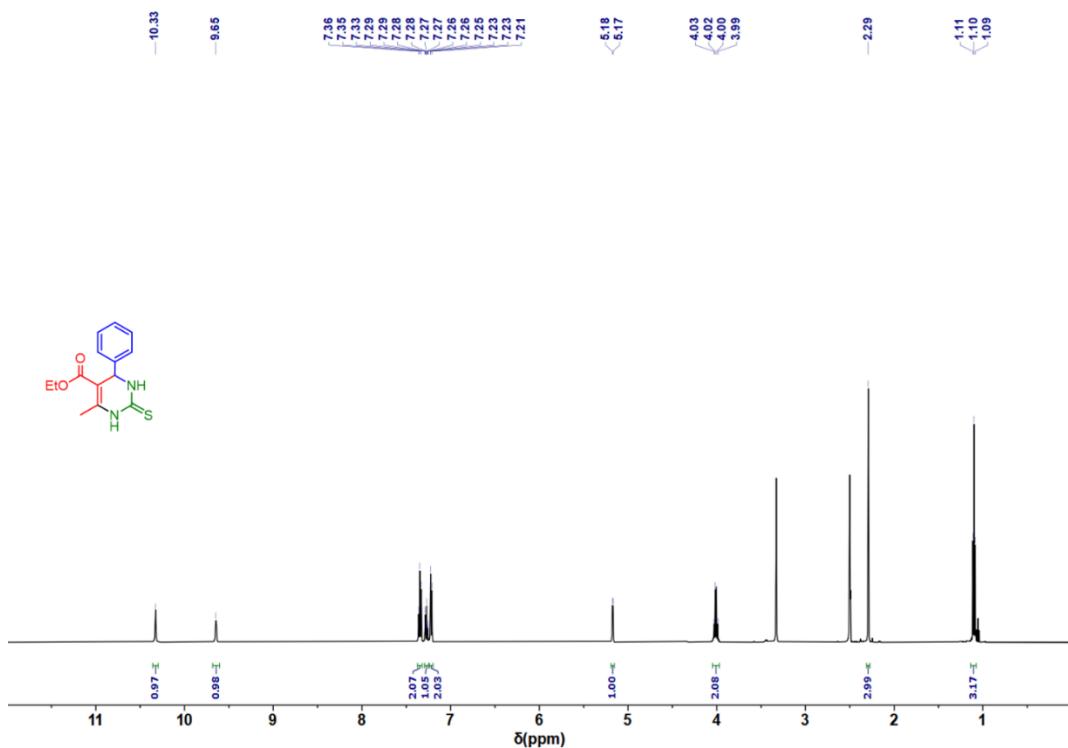
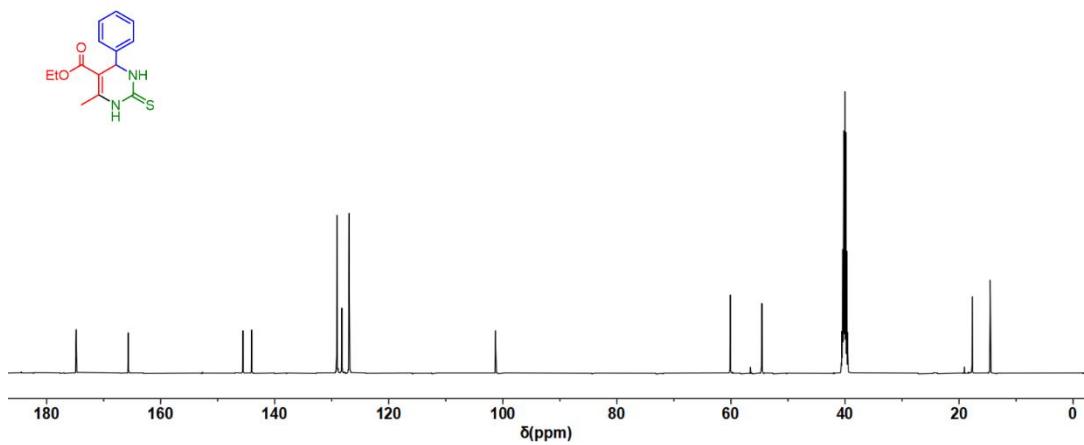


Figure S22. ^1H NMR spectrum of ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

MRM-AP-TUBENZ
single pulse decoupled gated NOE



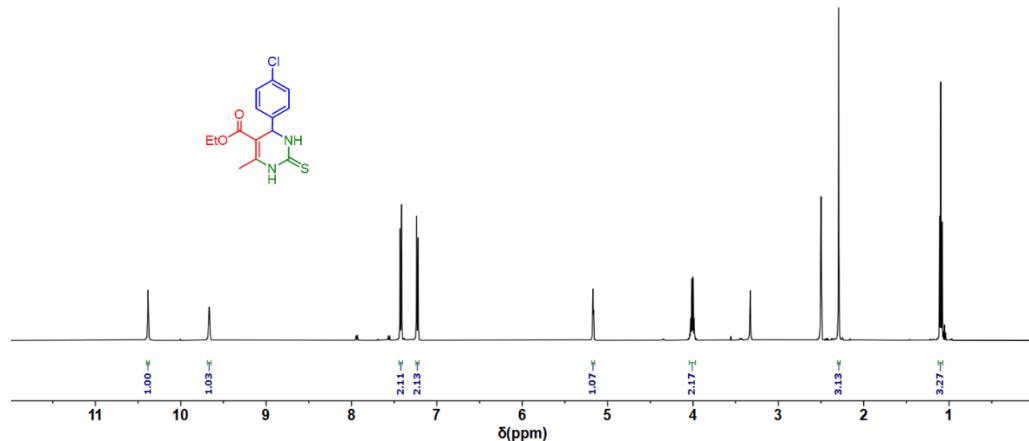


Figure S24. ¹H NMR spectrum of ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

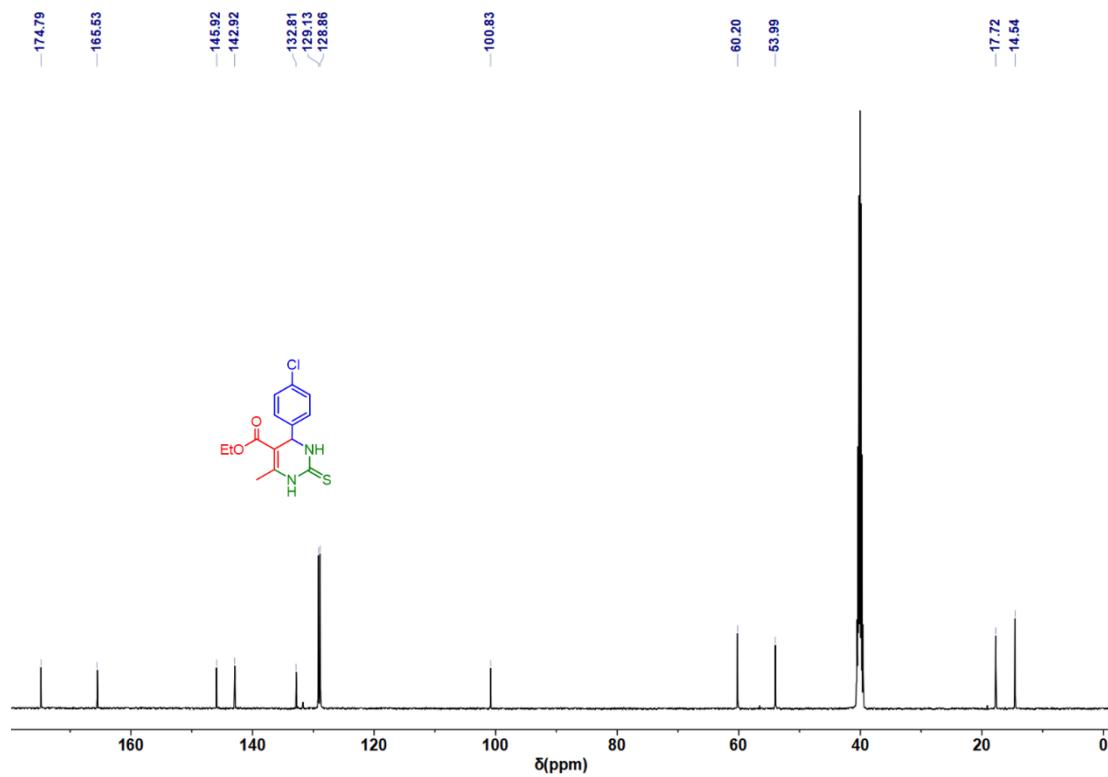


Figure S25. ¹³C NMR spectrum of ethyl 4-(4-chlorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

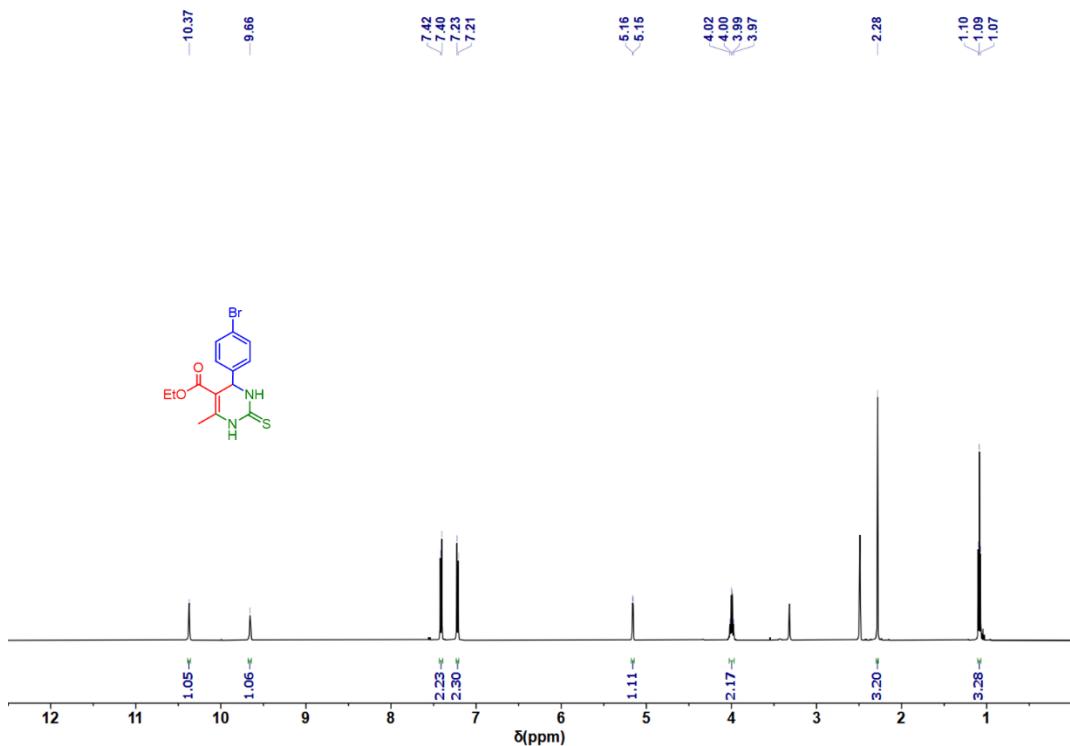


Figure S26. ^1H NMR spectrum of ethyl 4-(4-bromophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

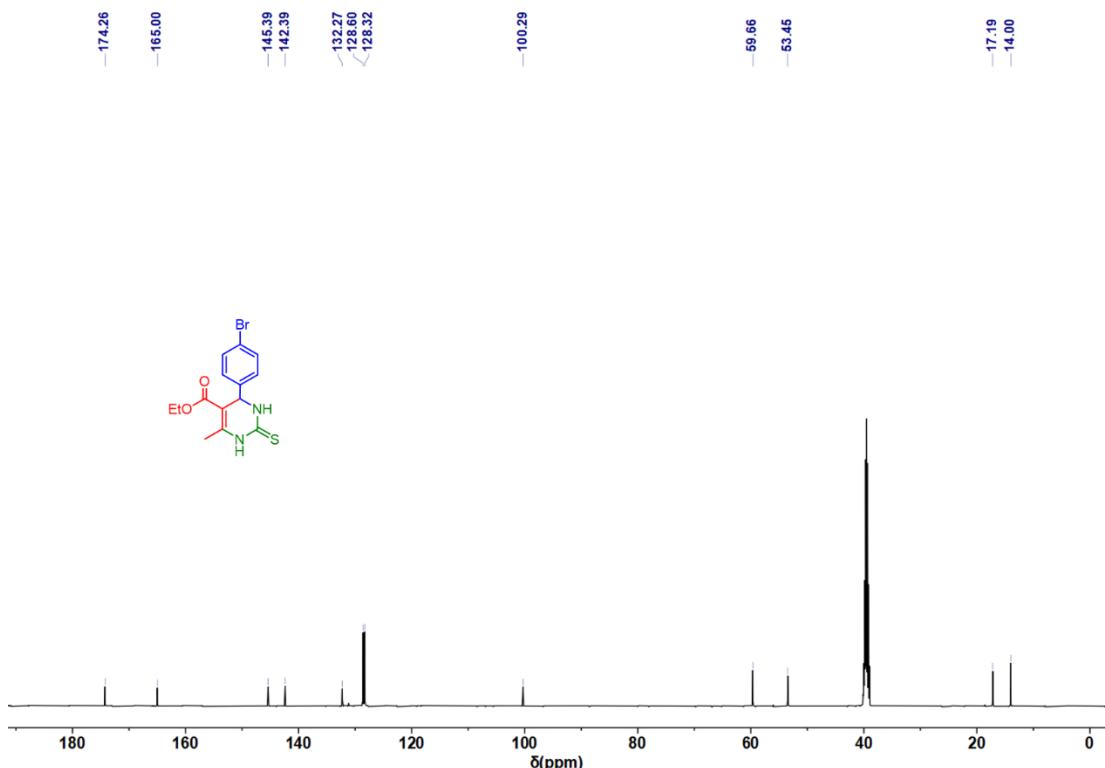


Figure S27. ^{13}C NMR spectrum of ethyl 4-(4-bromophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

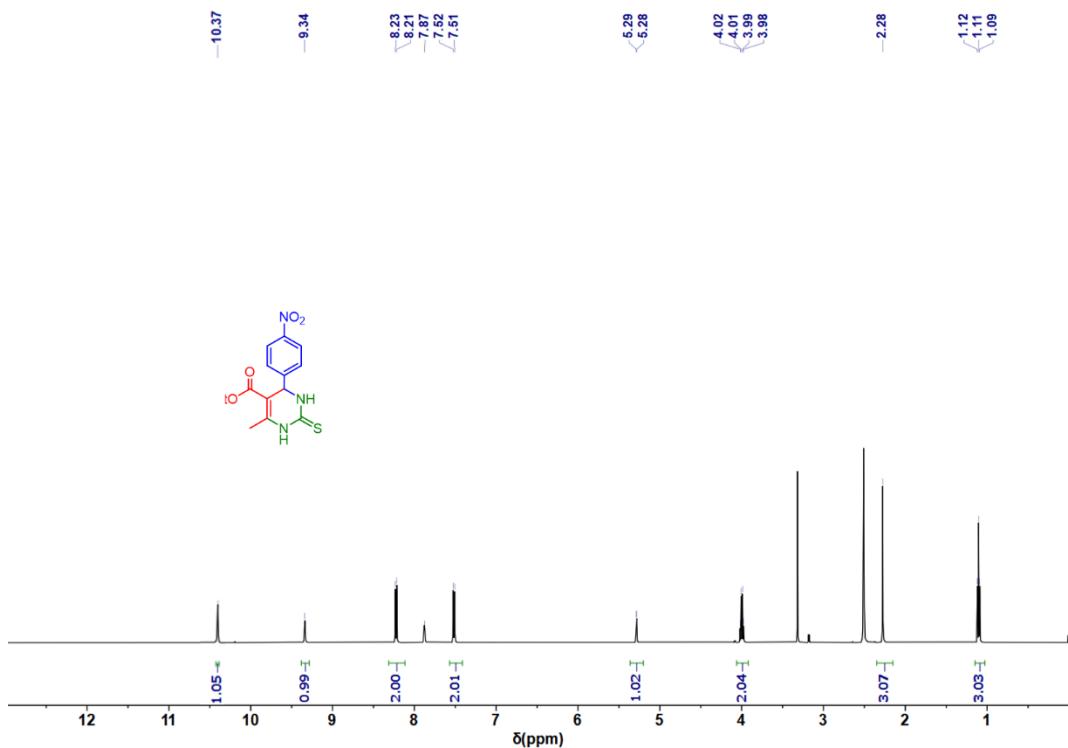


Figure S28. ^1H NMR spectrum of ethyl 4-(4-nitrophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

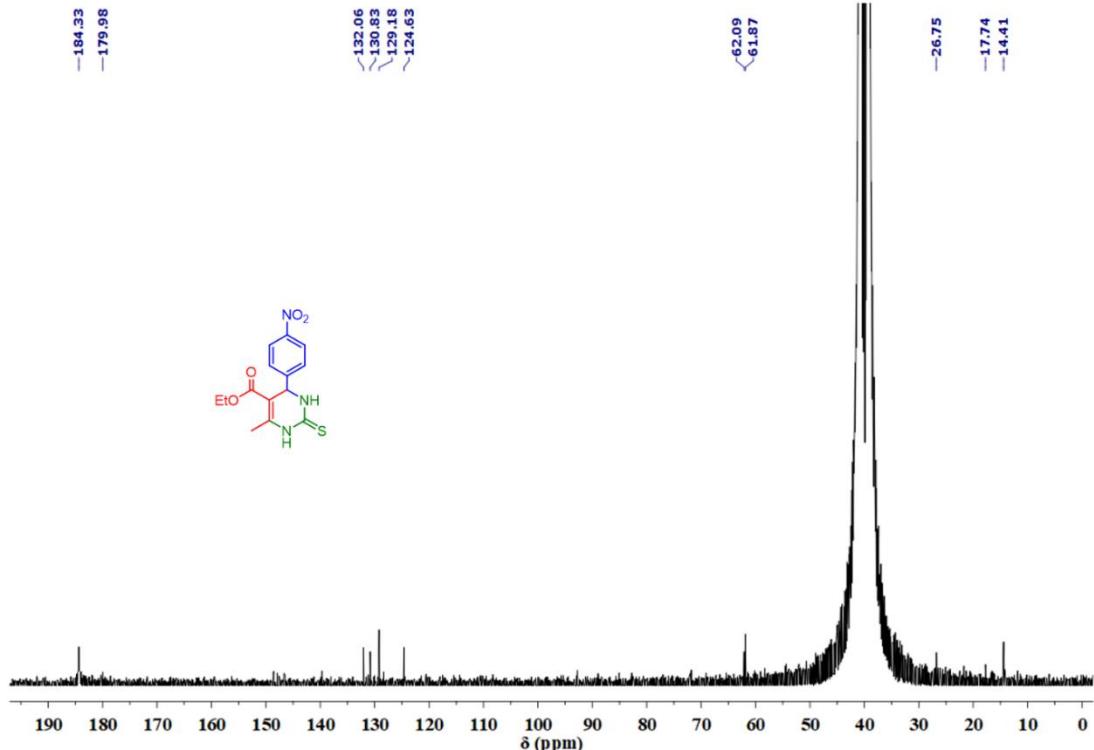


Figure S29. ^{13}C NMR spectrum of ethyl 4-(4-nitrophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

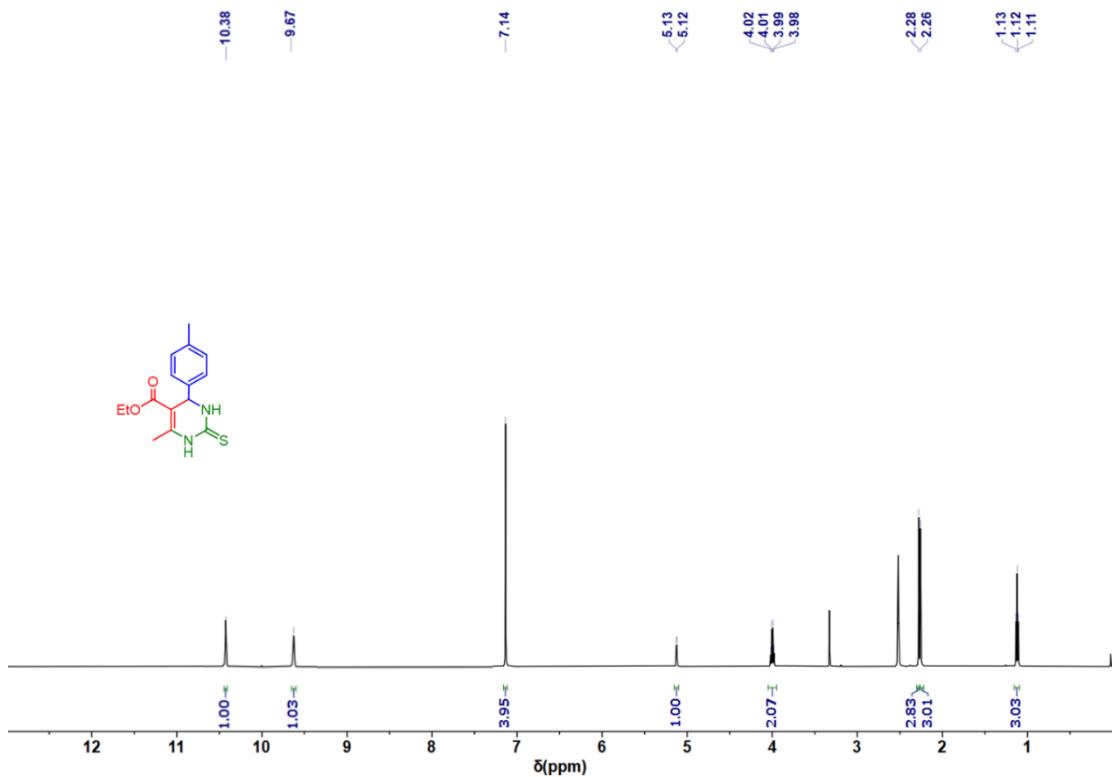


Figure S30. ^1H NMR spectrum of ethyl 6-methyl-2-thioxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

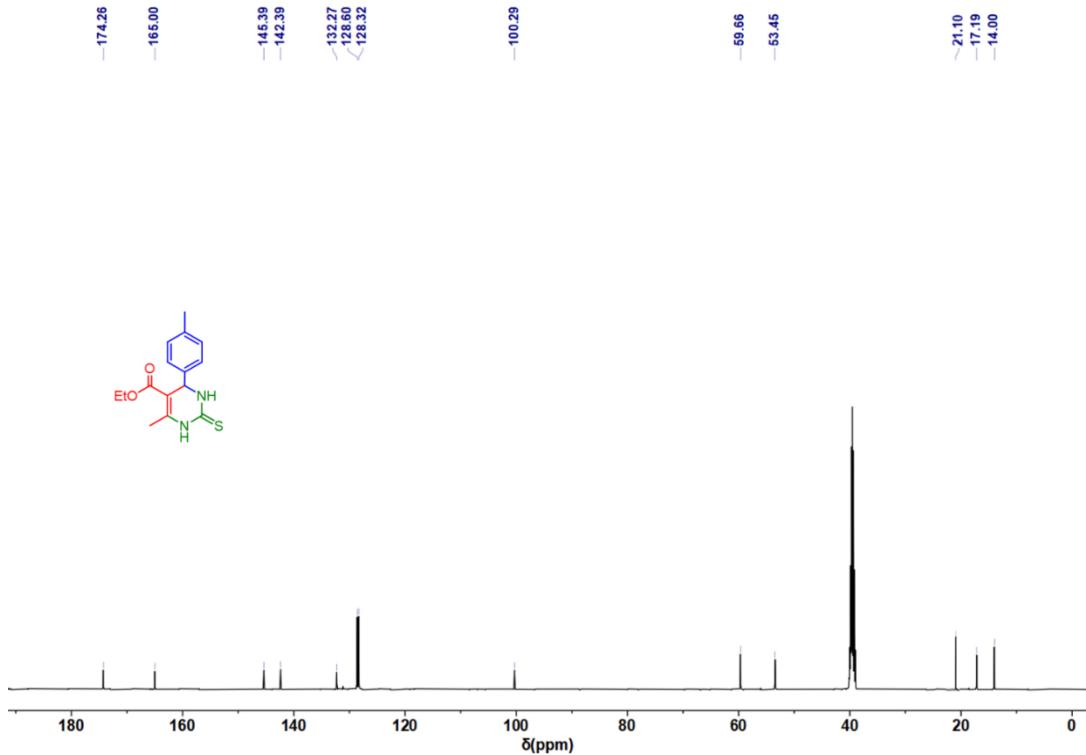


Figure S31. ^{13}C NMR spectrum of ethyl 6-methyl-2-thioxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

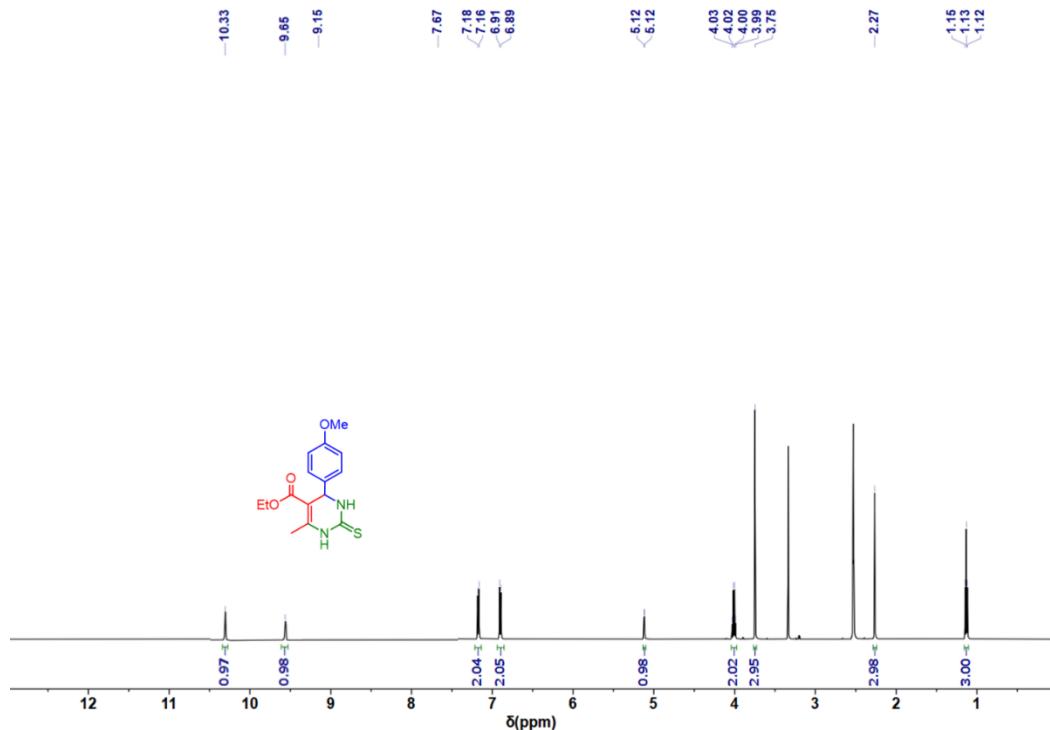


Figure S32. ^1H NMR spectrum of ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

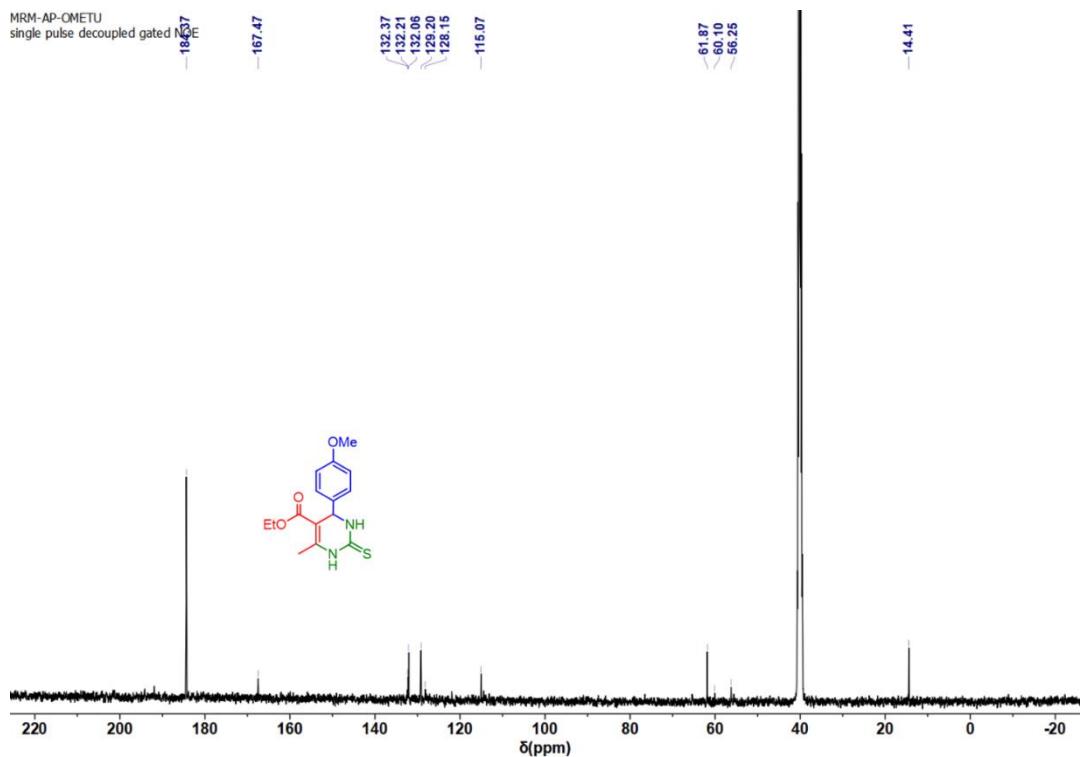


Figure S33. ^{13}C NMR spectrum of ethyl 4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate.

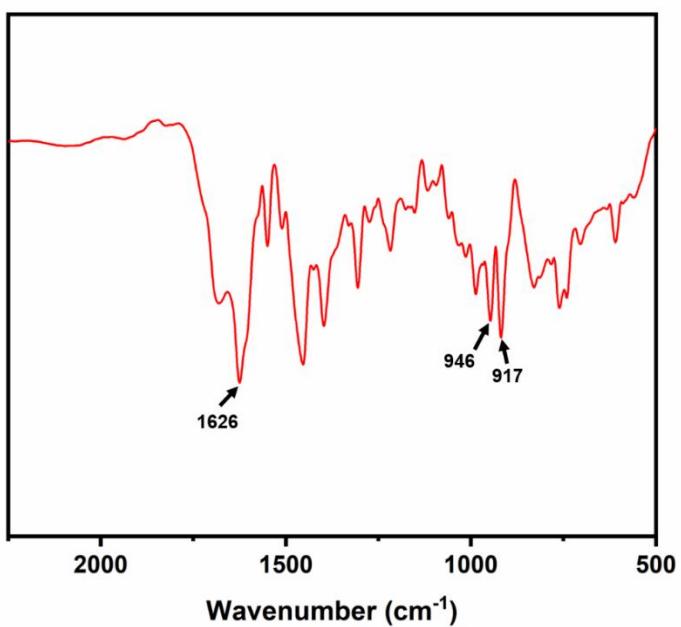


Figure S34. IR spectrum of catalyst **2** after the first catalytic cycle.

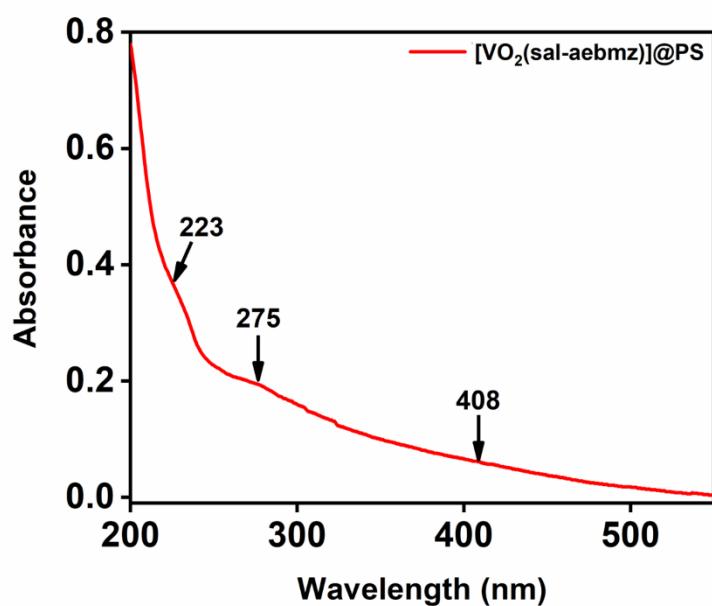


Figure S35. UV-visible spectrum of catalyst **2** recorded in Nujol after the first cycle.
