

Synthesis of a series of Cd(II) furan-2-thiocarboxylates: Unprecedented coordination geometry of a Cd(II) complex exhibiting catalytic efficiency for the synthesis of 3,4- dihydropyrimidine-2(1*H*)-one derivatives

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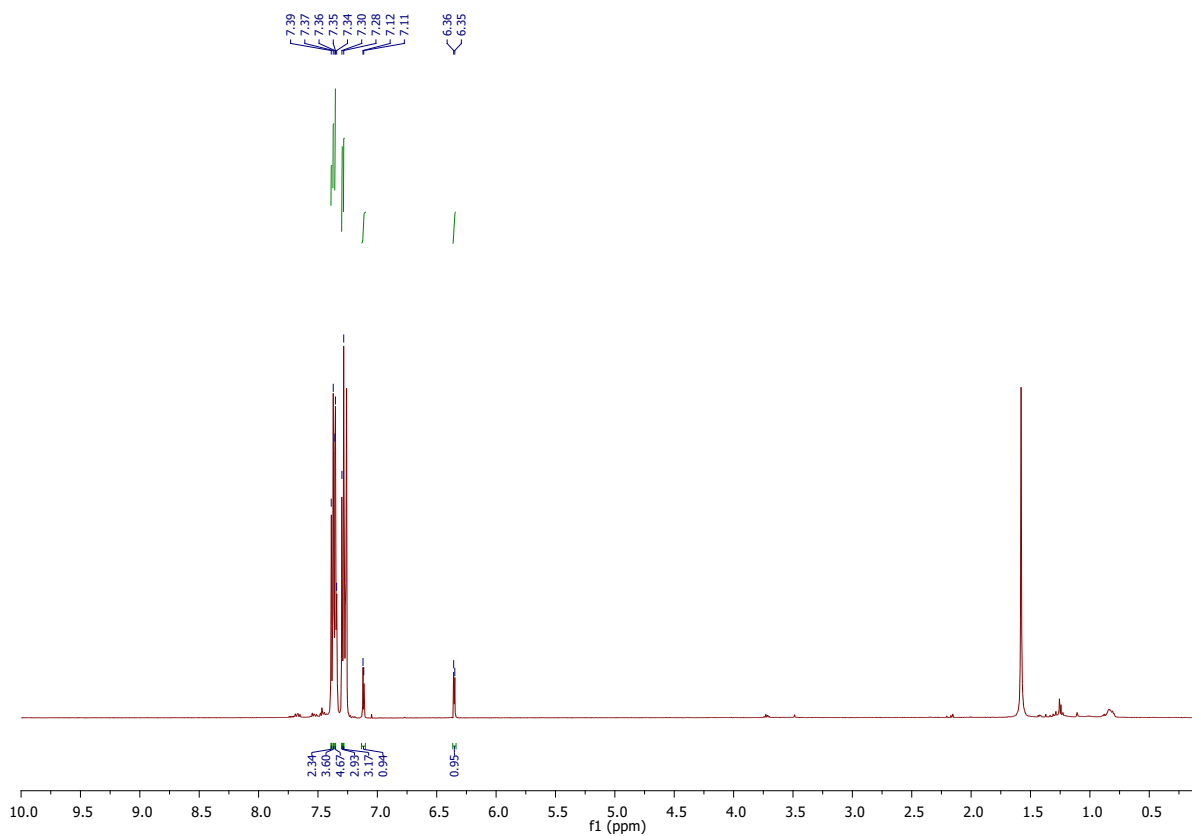
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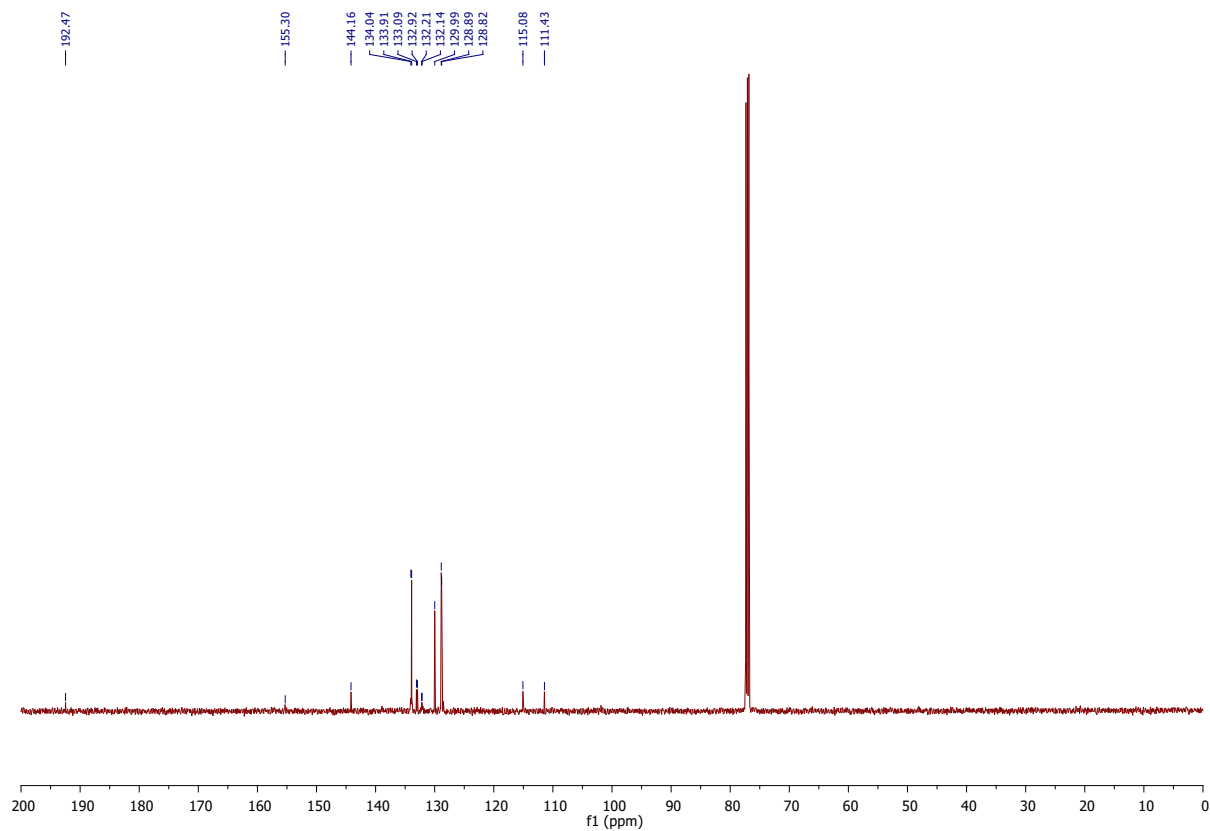
Email (SB): s_bhatt@bhu.ac.in

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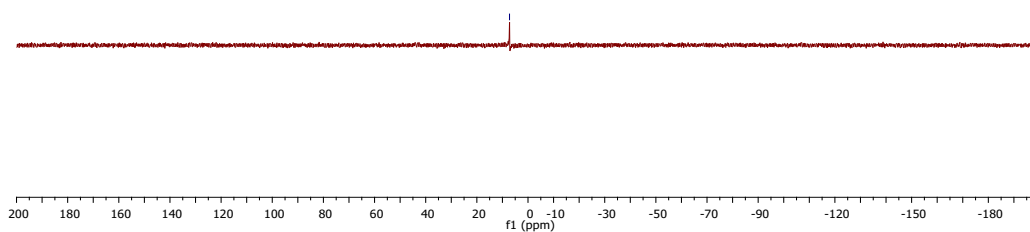
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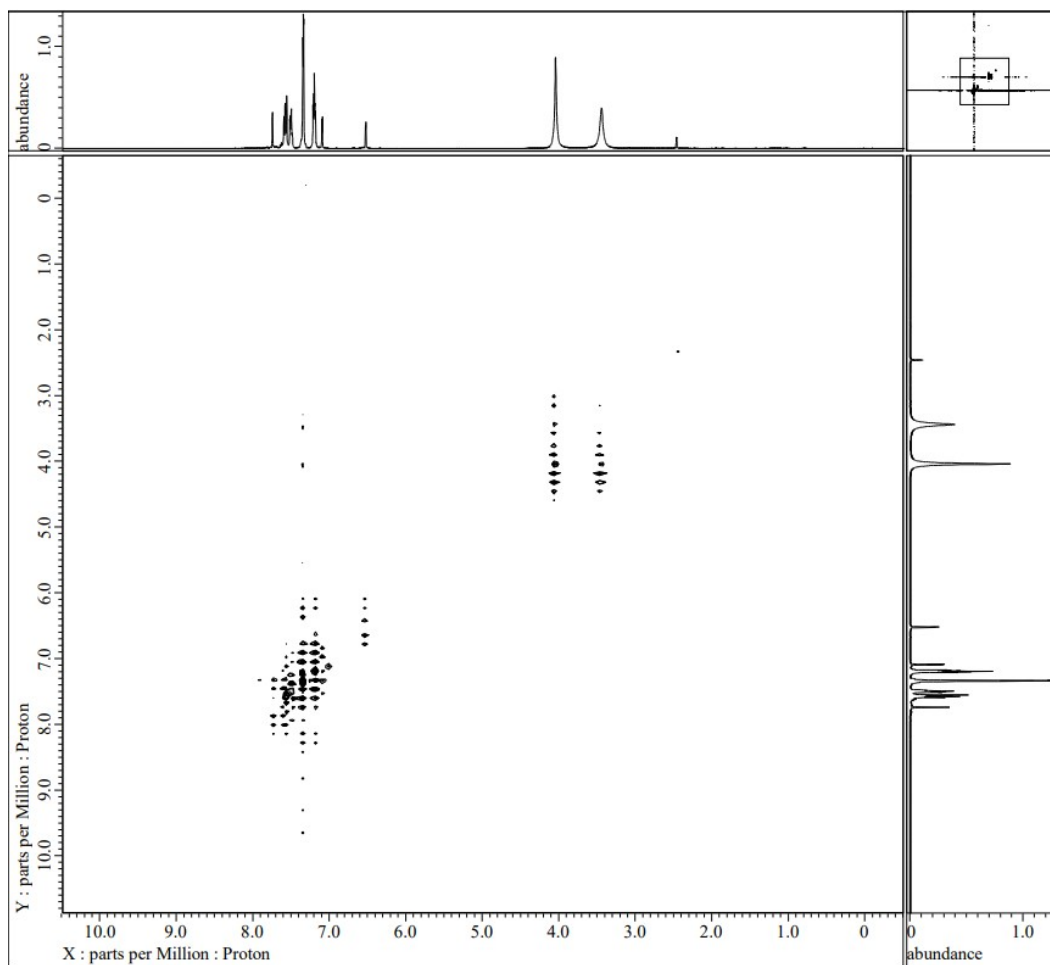
¹H NMR spectrum of 1 [(PPh₃)Cd(SCOf)₂]



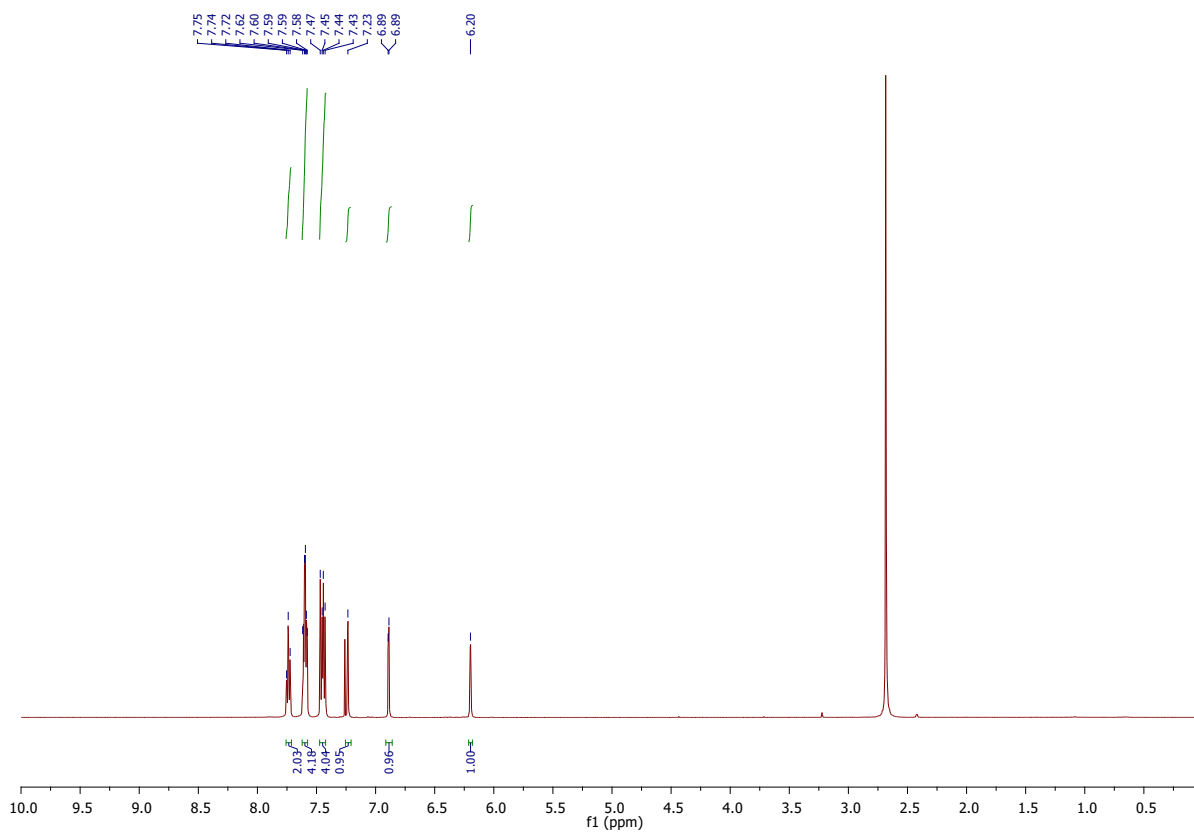
¹³C NMR spectrum of 1 [(PPh₃)Cd(SCOf)₂]



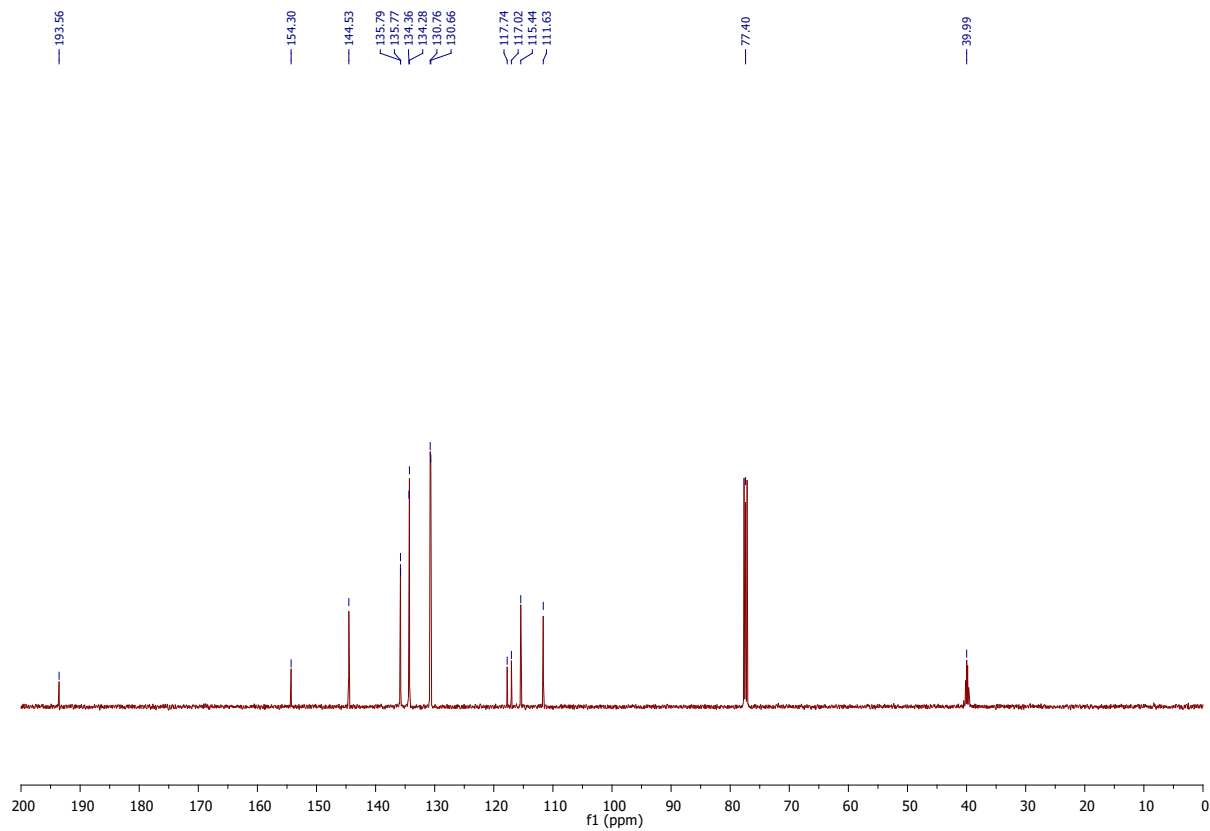
^{31}P NMR spectrum of 1 [(PPh₃)Cd(SCOf)₂]



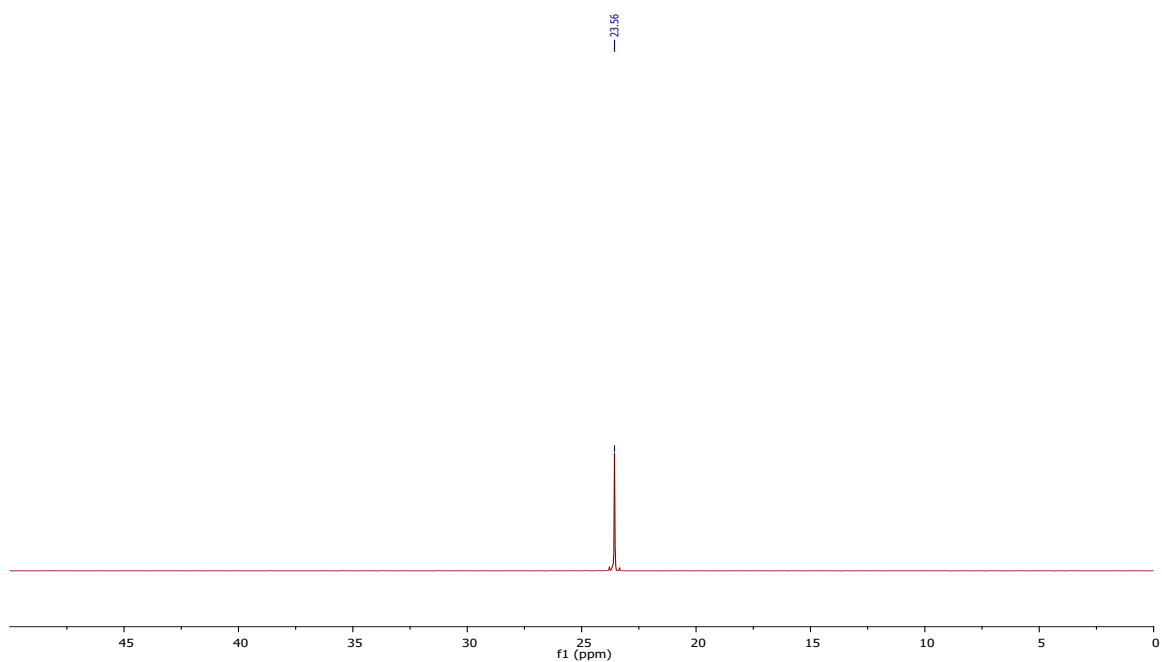
2D NOESY NMR spectrum of 1 [(PPh₃)Cd(SCOf)₂]



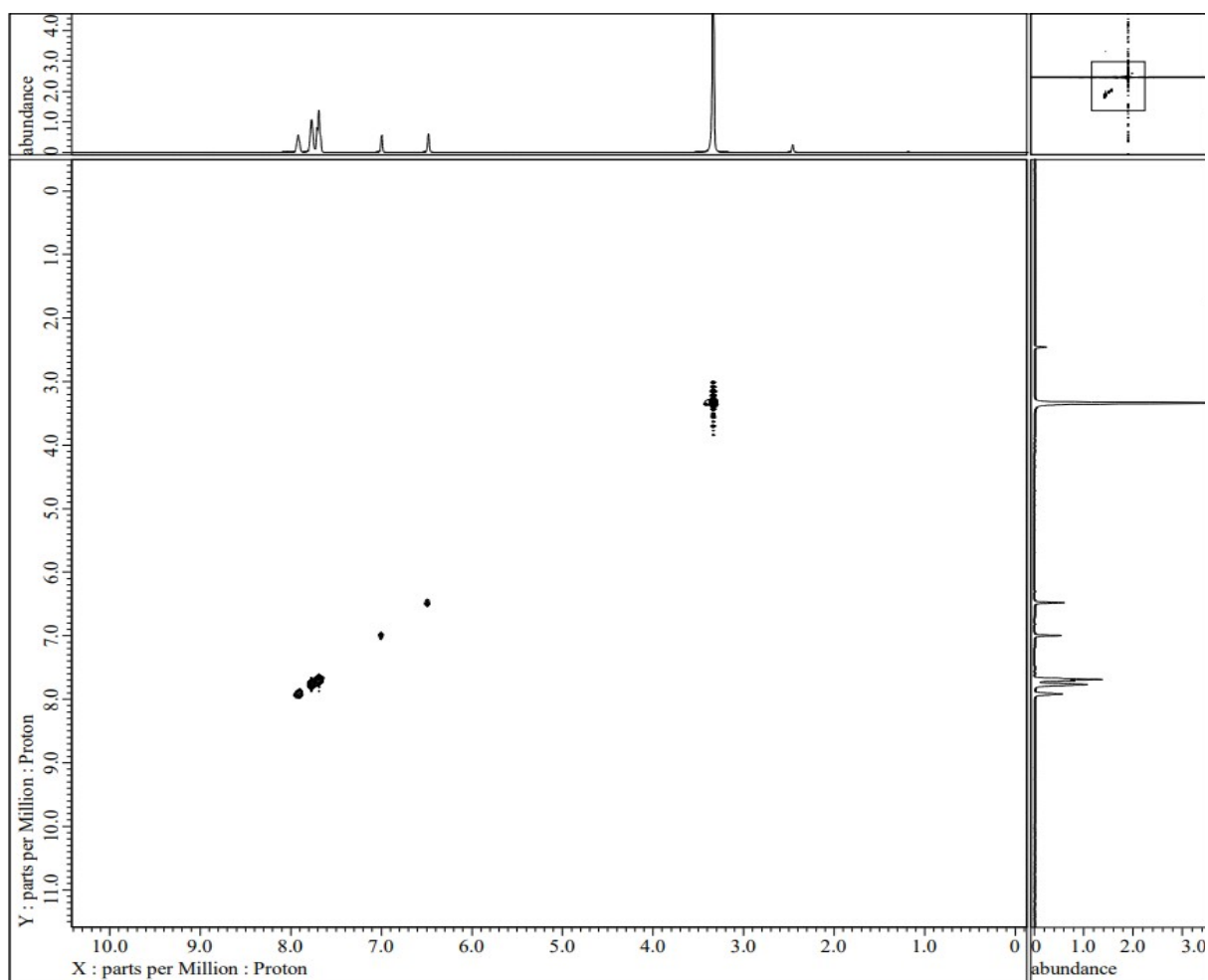
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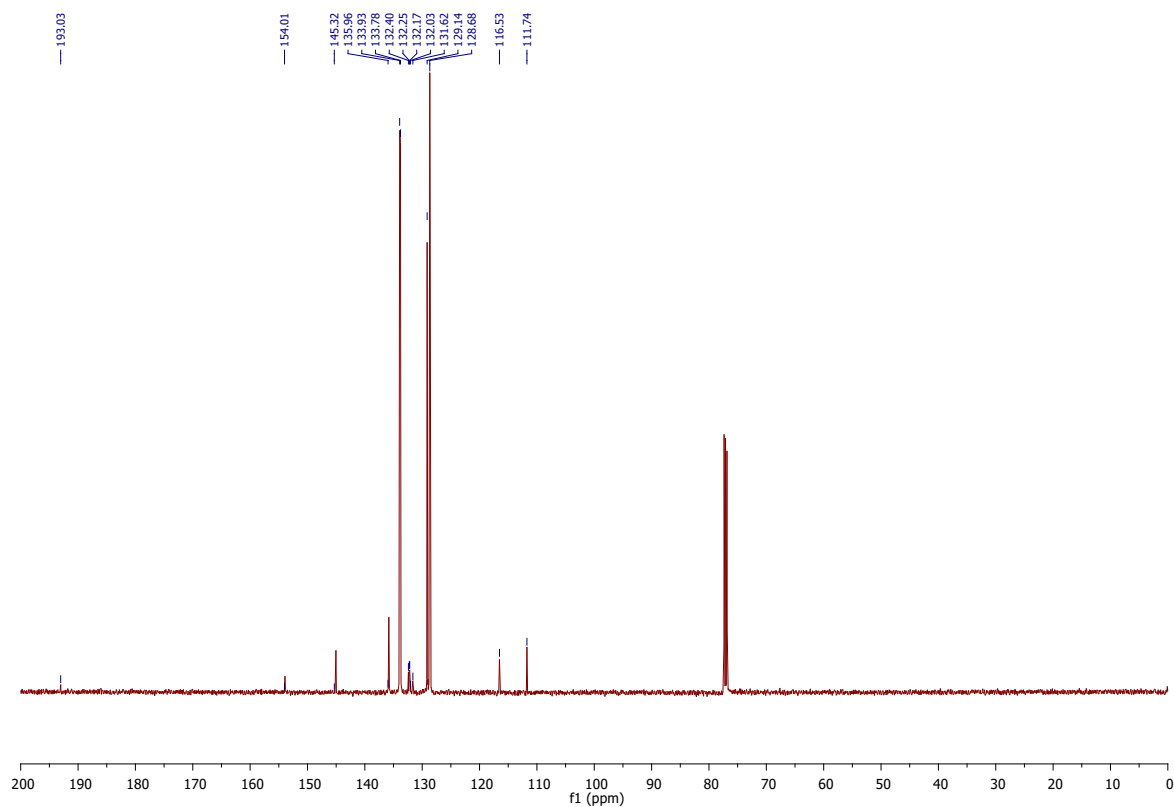
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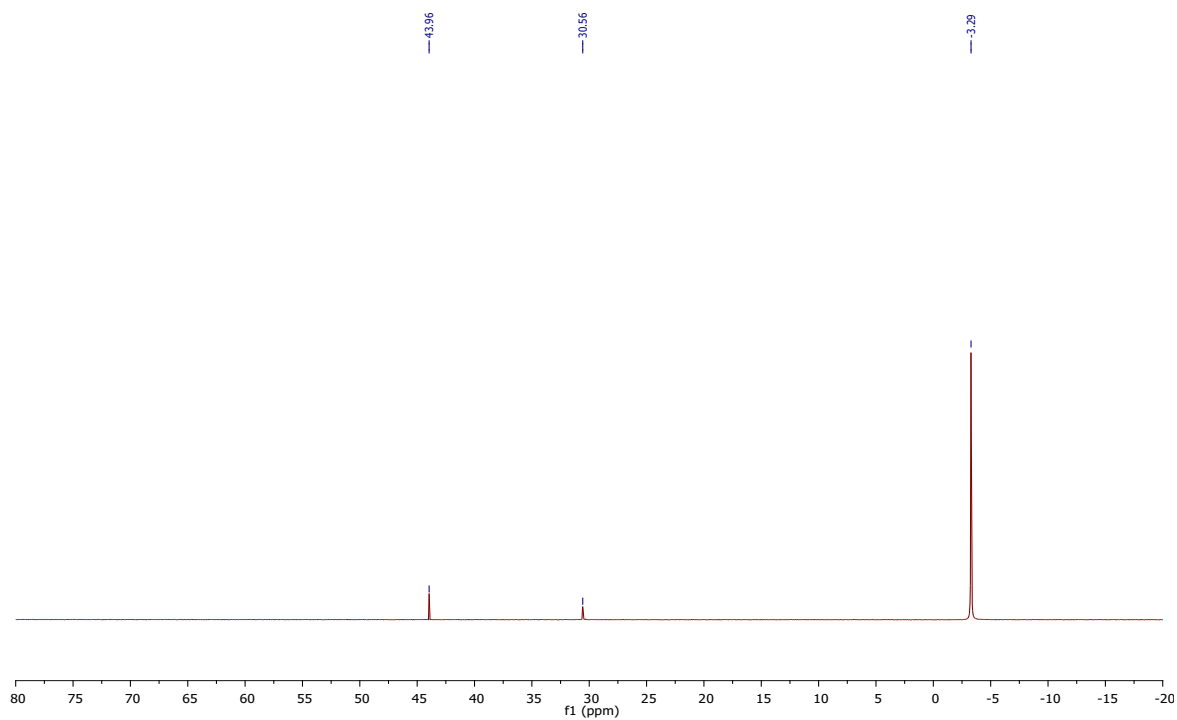
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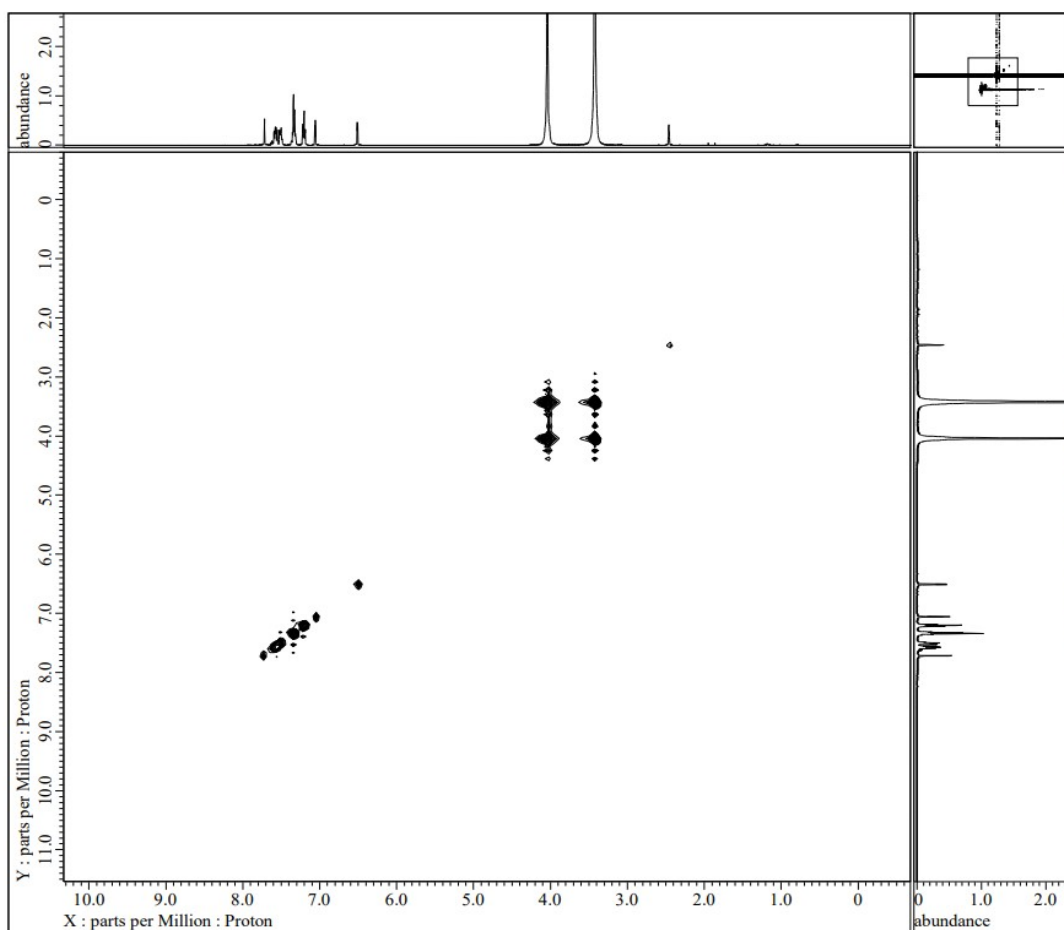
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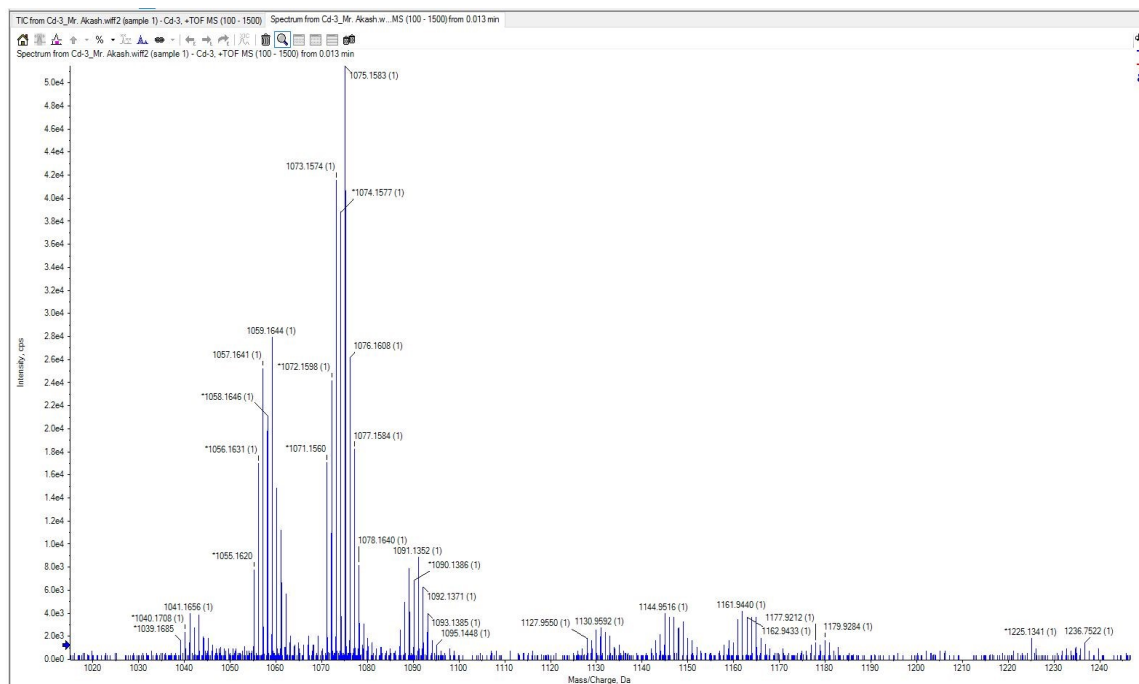
¹³C NMR spectrum of 3 [(PPh₃)₂Ag(μ₂-SCOf)₂Cd(SCOf)]



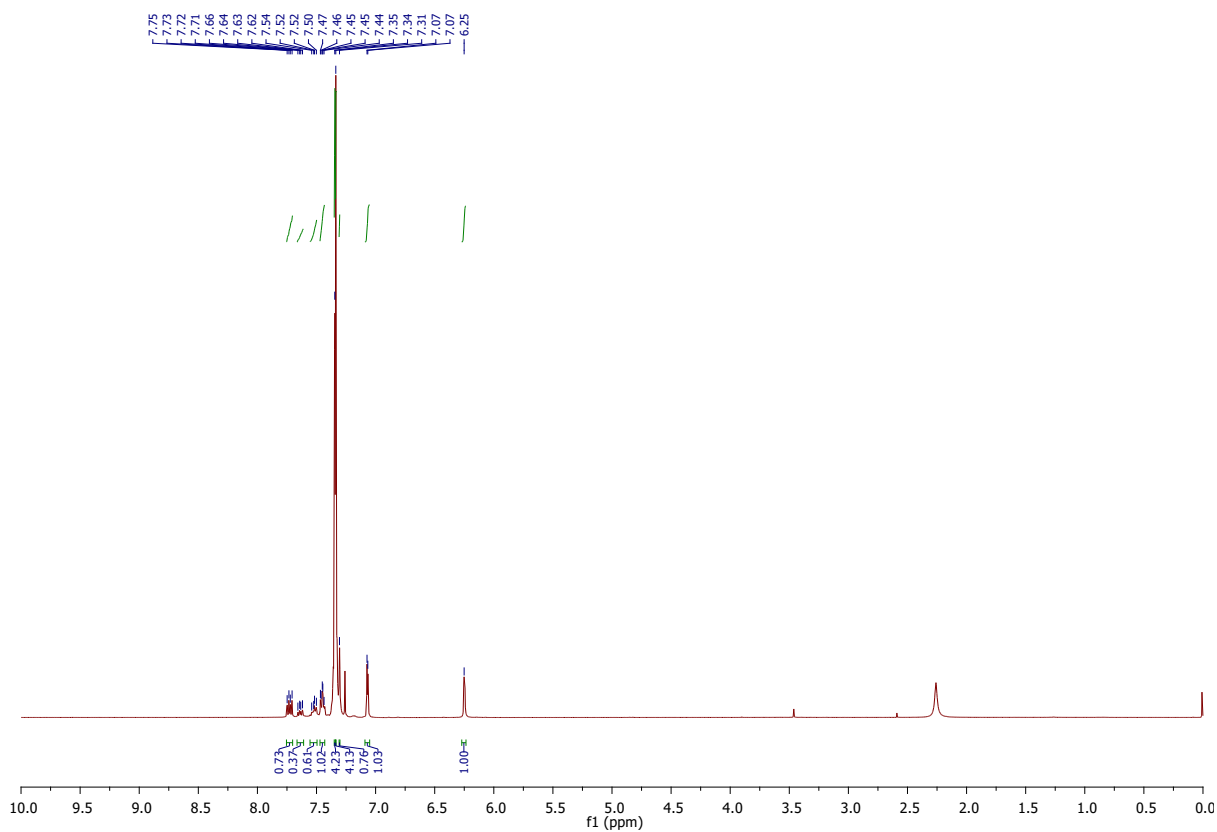
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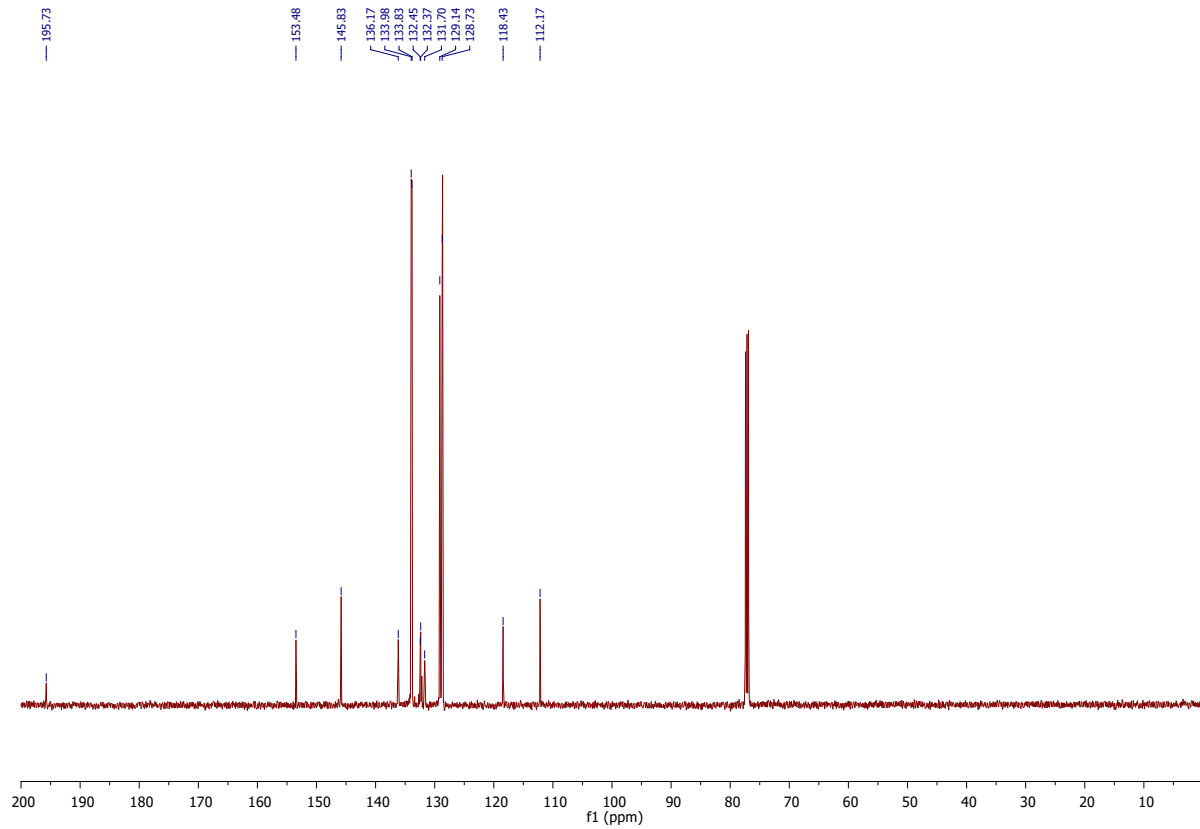
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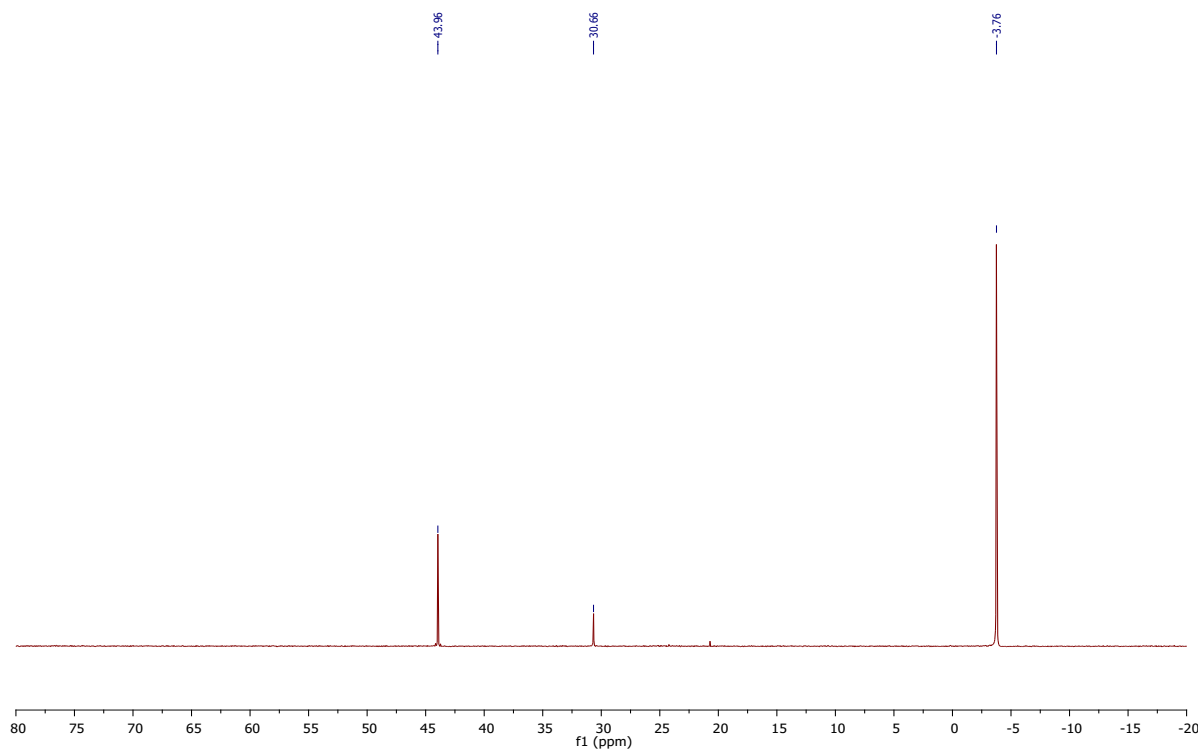
HRMS Spectrum of Complex 3



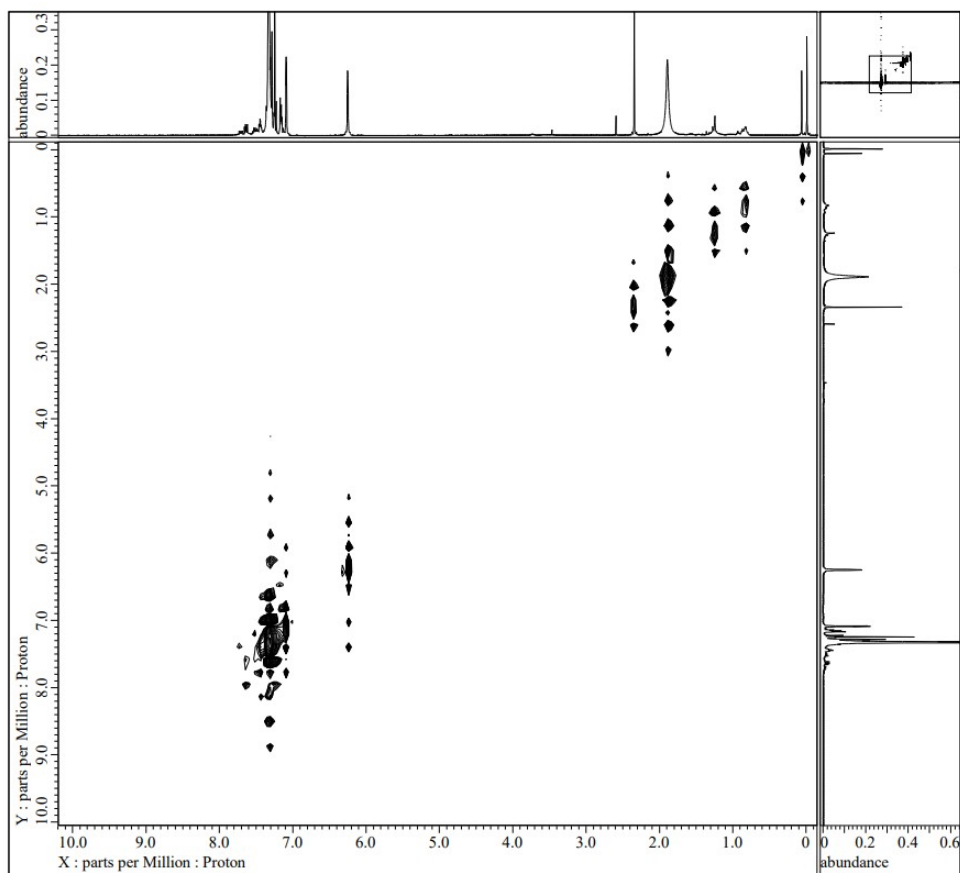
^1H NMR spectrum of $4 \text{Na}_2[(\text{PPh}_3)\text{Cd}(\text{MeOH})(\text{SCOf})_3]_2$



^{13}C NMR spectrum of $4 \text{Na}_2[(\text{PPh}_3)\text{Cd}(\text{MeOH})(\text{SCOf})_3]_2$



^{31}P NMR spectrum of $4 \text{Na}_2[(\text{PPh}_3)\text{Cd}(\text{MeOH})(\text{SCOf})_3]_2$



2D NOESY NMR spectrum of $4 \text{Na}_2[(\text{PPh}_3)\text{Cd}(\text{MeOH})(\text{SCOf})_3]_2$

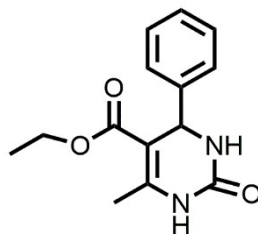
Hydrogen bond for complex 1

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C36	H36	S2	0.93	2.88	3.698 (5)	147.0
C12	H12	O1	0.93	2.64	3.429 (6)	143.1
C40	H40	S1 ¹	0.93	2.83	3.591 (5)	139.8
C22	H22	O3	0.93	2.53	3.404 (5)	156.3

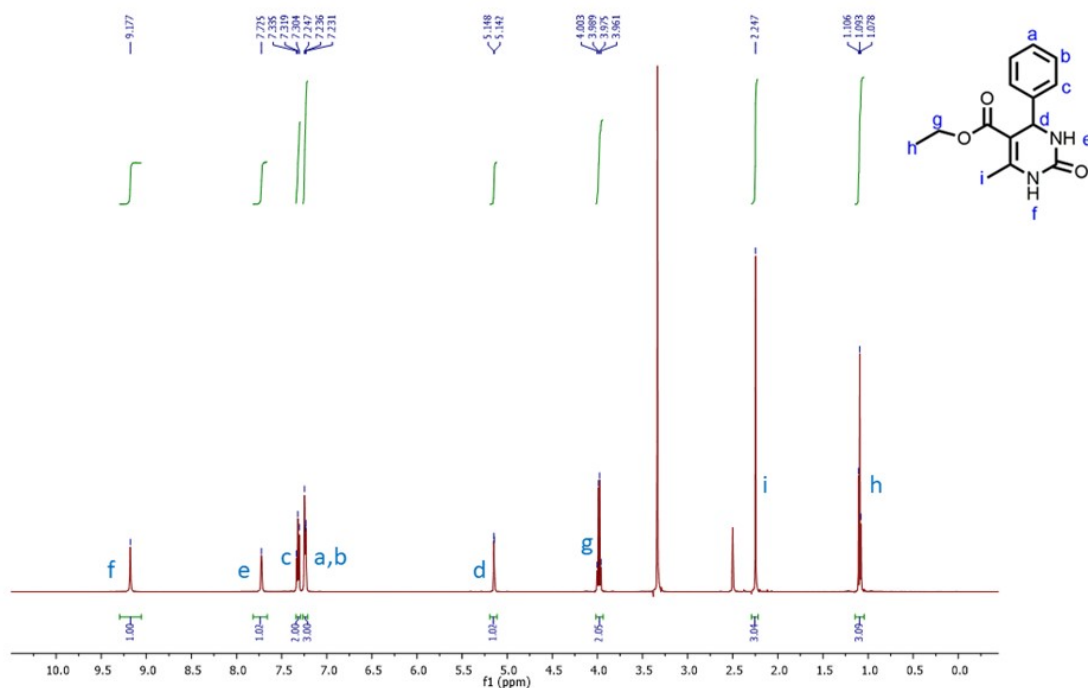
¹I/2+X,+Y,3/2-Z

Catalytic products and their NMR spectra

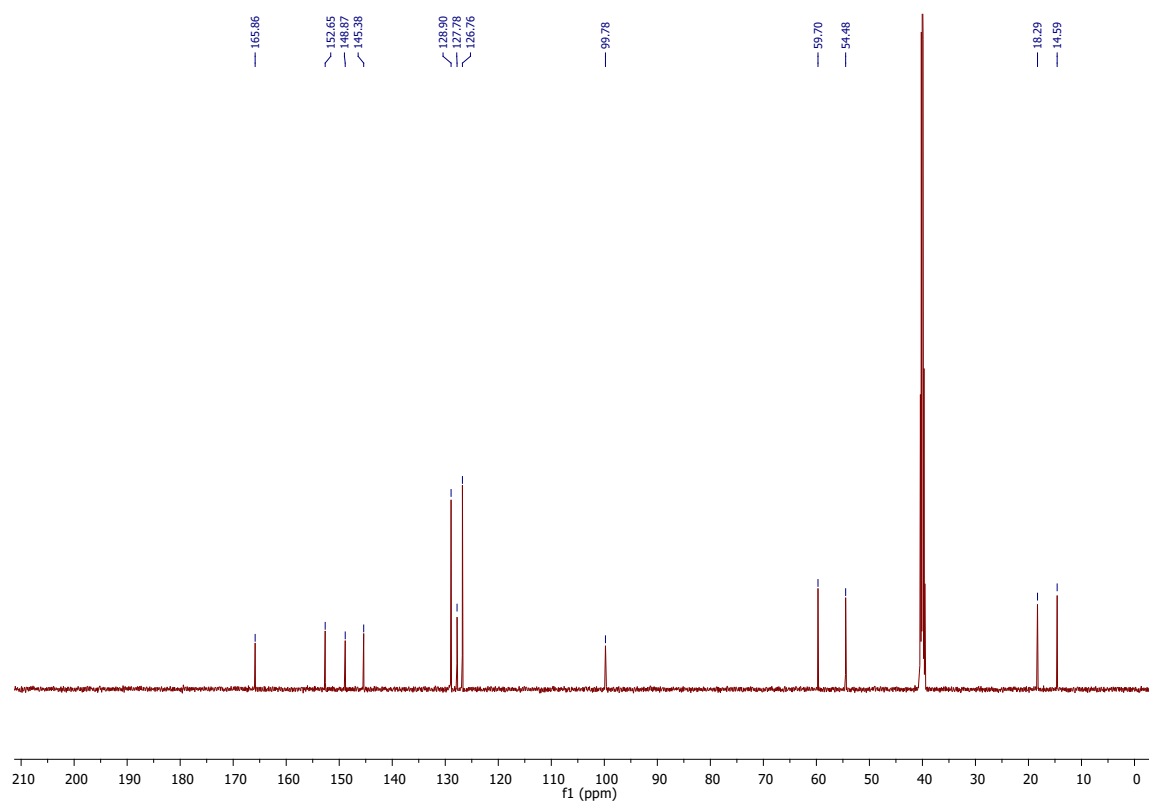
Ethyl-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5a)



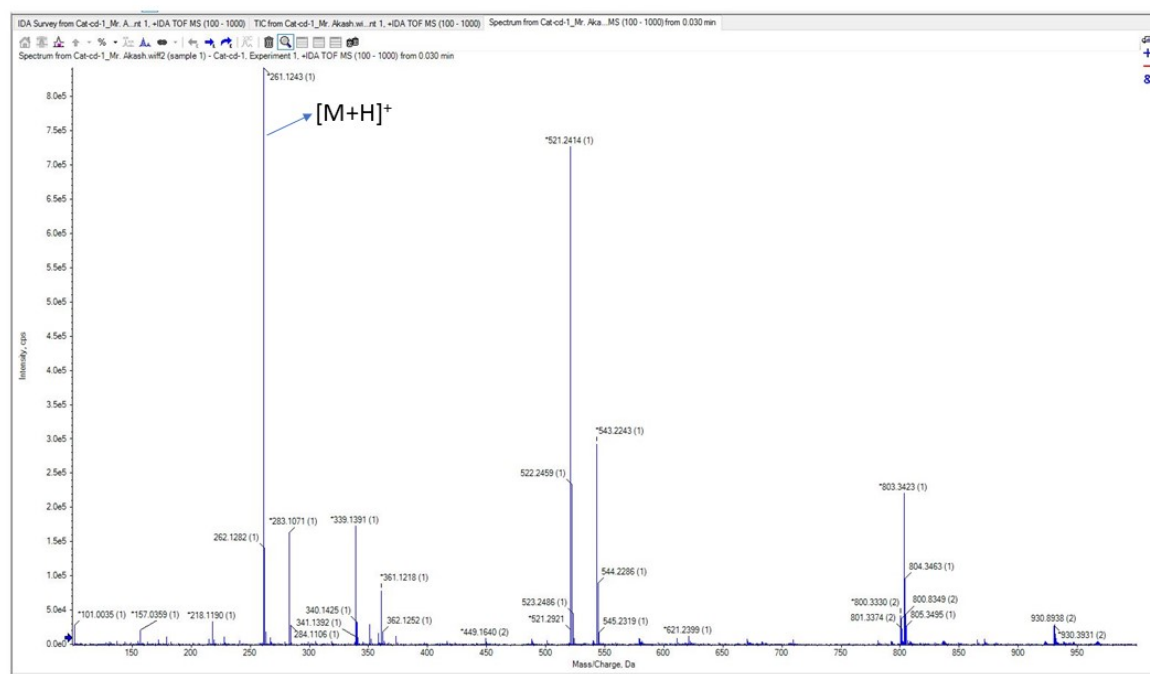
M.F. C₁₄H₁₆N₂O₃ (260.29). Yield: (0.244 g, 94%). White powder. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ 9.18 (s, 1H, NH), 7.73 (s, 1H, NH), 7.32 (t, J = 7.5 Hz 2H), 7.23(m, 3H), 5.15 (d, J = 3 Hz, 1H), 3.96-4.00 (m, 2H), 2.24 (s, 3H), 1.09 (t, J= 7.5Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆, ppm) δ 165.9, 152.7, 148.9, 145.4, 128.9, 127.8, 126.8, 99.9, 59.7,54.5, 18.3, 14.6; HRMS (ESI): calcd. for C₁₄H₁₆N₂O₃ [M + H]⁺ 261.124, found 261.124.



^1H NMR spectrum of 5a

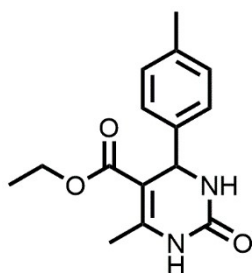


^{13}C NMR spectrum of 5a

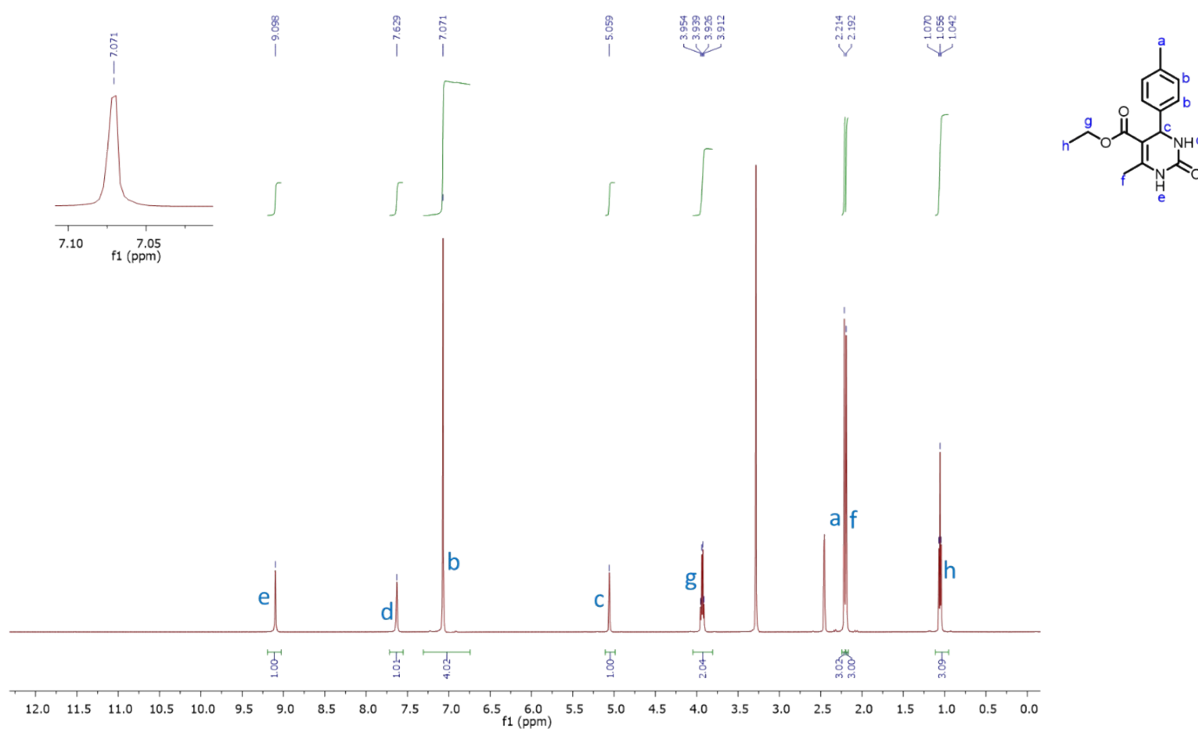


HRMS spectrum of 5a

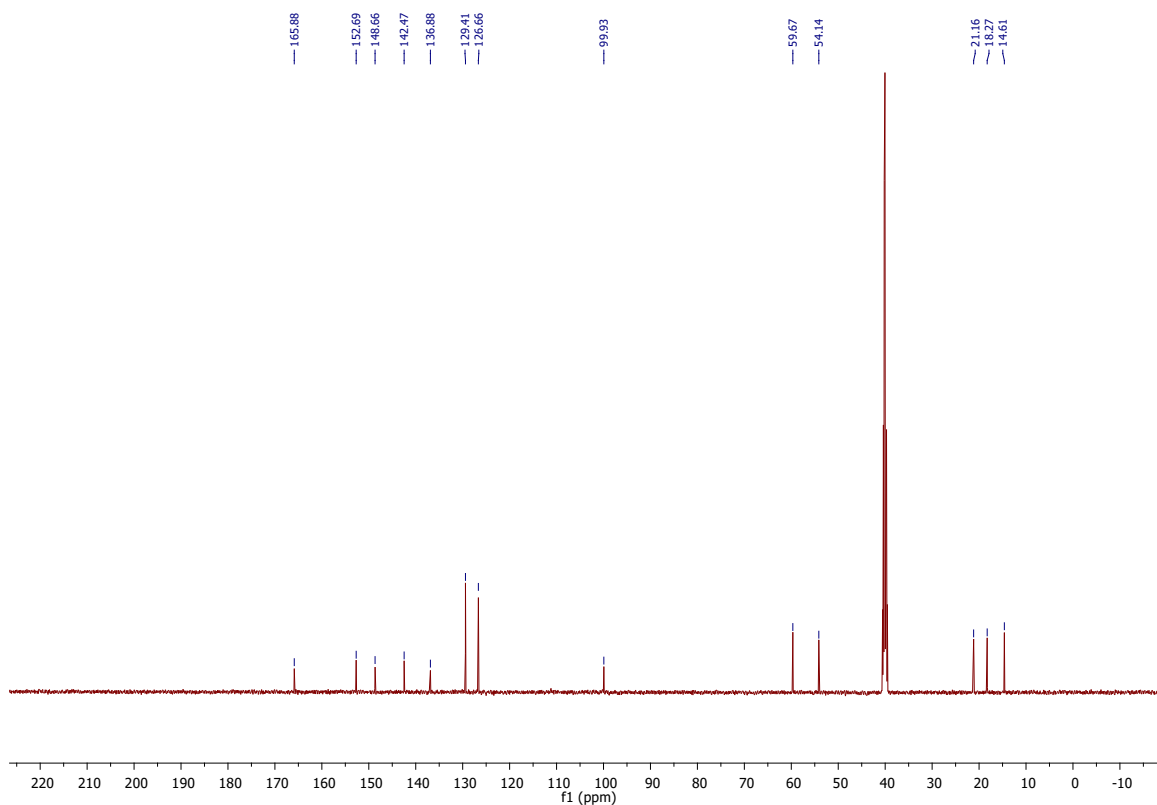
Ethyl-6-methyl-2-oxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5b)



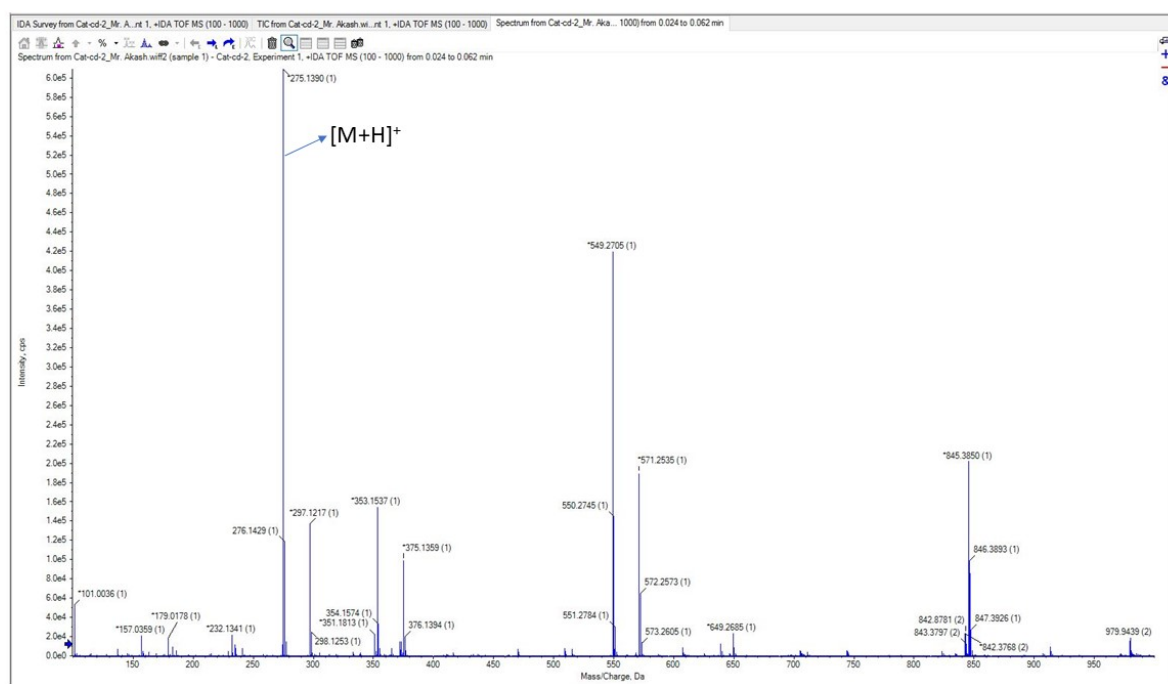
M.F. $C_{15}H_{18}N_2O_3$ (274.32). Yield: (0.252 g, 92%). White powder. 1H NMR (500 MHz, DMSO- d_6 , ppm) δ 9.10 (s, 1H, NH), 7.63 (s, 1H, NH), 7.07 (d, 4H), 5.1 (s, 1H), 3.91-3.95 (m, 2H), 2.21 (s, 3H), 2.19 (s, 3H), 1.05 (t, $J=7$ Hz, 3H); ^{13}C NMR (125 MHz, DMSO- d_6 , ppm) δ 165.9, 152.7, 148.7, 142.5, 136.9, 129.4, 126.7, 99.3, 59.7, 54.1, 21.2, 18.3, 14.6; HRMS (ESI): calcd. for $C_{15}H_{18}N_2O_3$ $[M + H]^+$ 275.139, found 275.139.



1H NMR spectrum of 5b

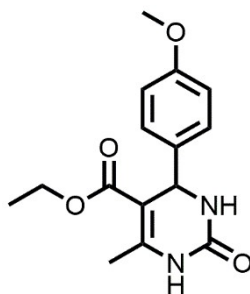


13C NMR spectrum of 5b

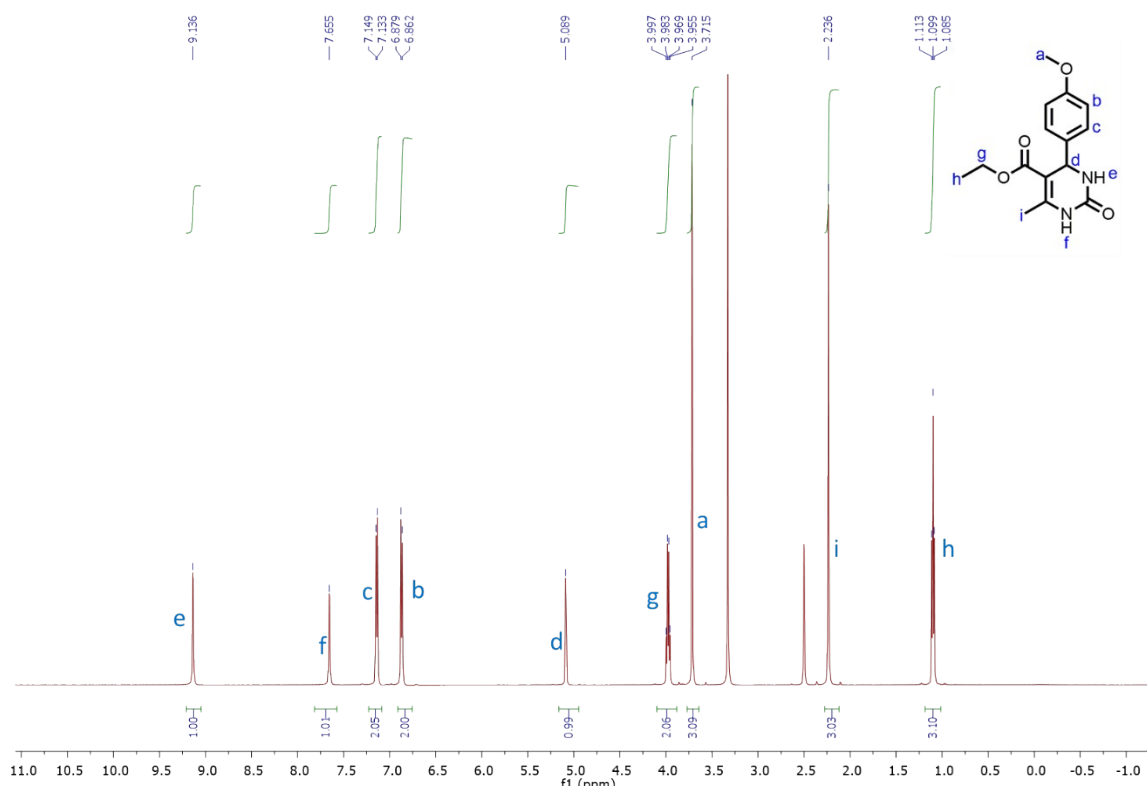


HRMS spectrum of 5b

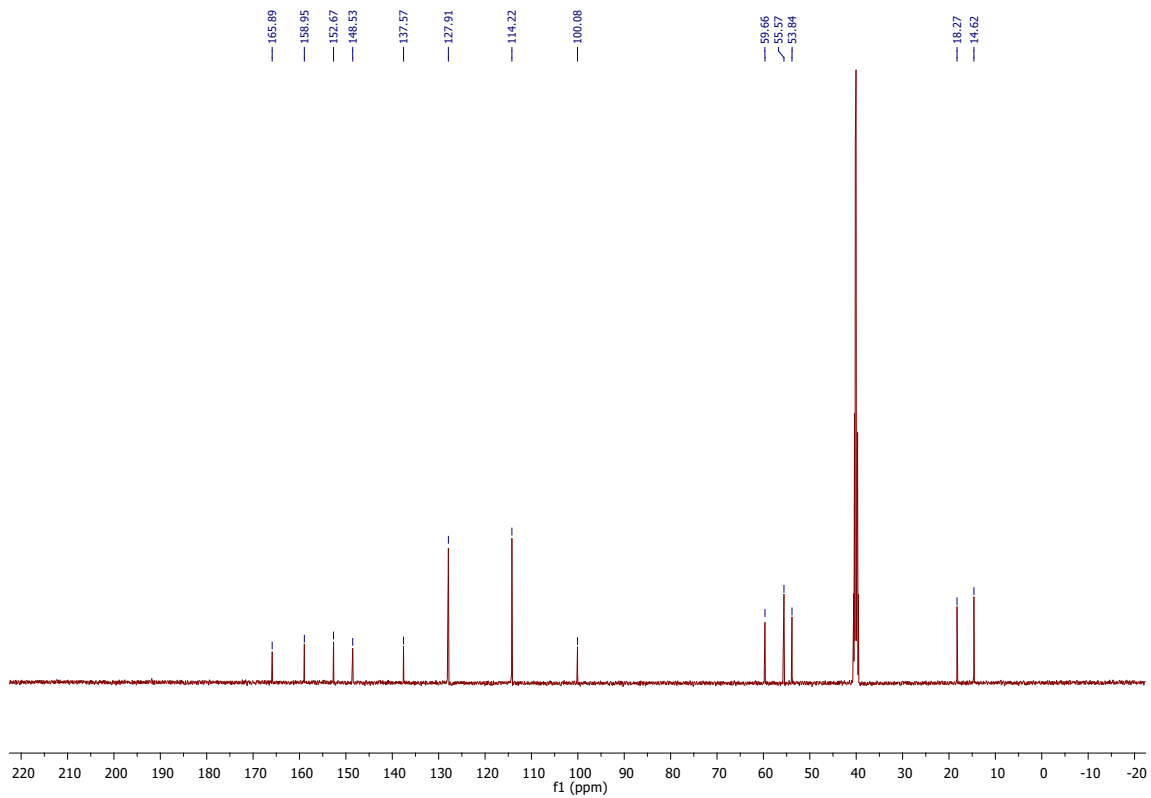
Ethyl-4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5c)



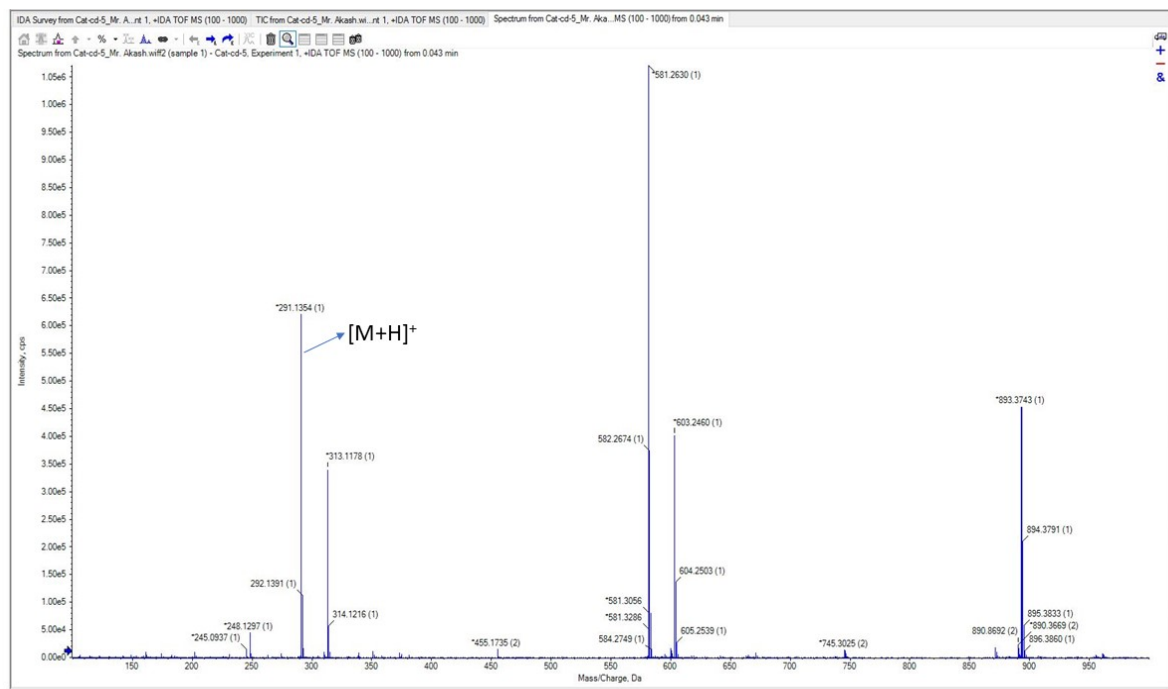
M.F. C₁₅H₁₈N₂O₄ (290.32). Yield: (0.261 g, 90%). White powder. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ 9.13 (s, 1H, NH), 7.65 (s, 1H, NH), 7.14 (d, J = 8 Hz 2H), 6.87 (d, J = 8.5Hz, 2H) 5.09 (s, 2H), 3.95-3.99 (m, 2H), 3.72(s,3H), 2.24 (s, 3H), 1.10 (t, J= 7 Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆, ppm) δ 165.9, 158.9, 152.7, 148.5, 137.6, 127.9, 114.2,100.1, 59,7,55.6, 18.3, 14.6; HRMS (ESI): calcd. for C₁₅H₁₈N₂O₄ [M + H]⁺ 291.134, found 291.135.



¹H NMR spectrum of 5c

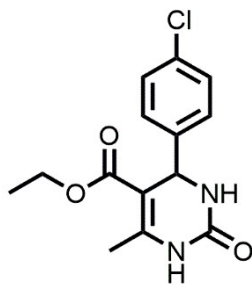


¹³C NMR spectrum of 5c

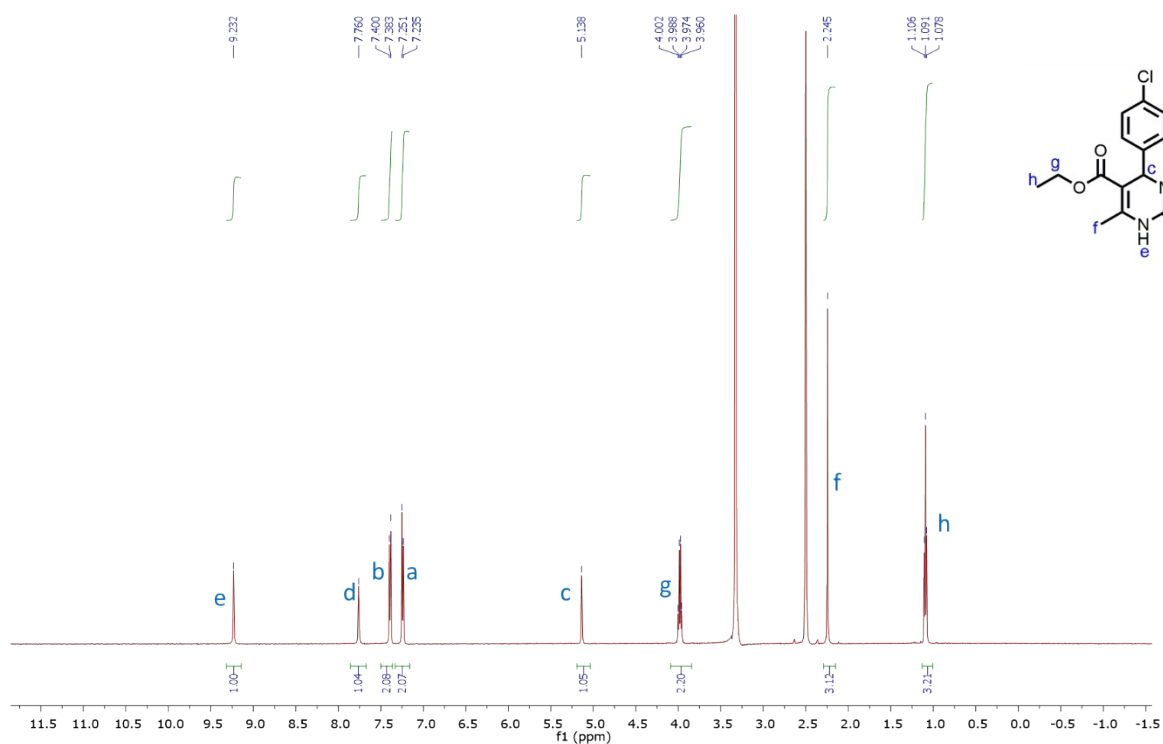


HRMS spectrum of 5c

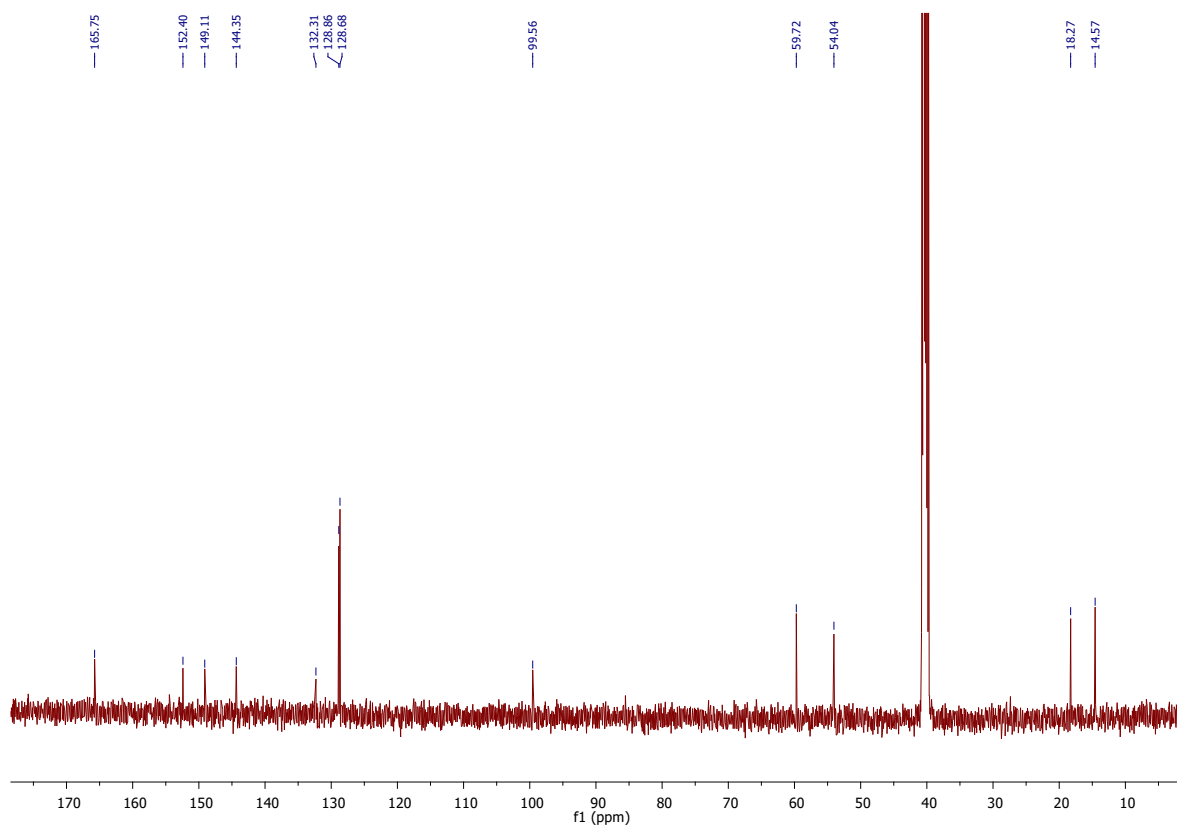
Ethyl-4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5d)



M.F. $C_{14}H_{15}N_2O_4Cl$ (294.74). Yield: (0.268 g, 91%). White powder. 1H NMR (500 MHz, DMSO- d_6 , ppm) δ 9.23 (s, 1H, NH), 7.76 (s, 1H, NH), 7.39 (d, $J = 8.5$ Hz 2H), 7.24 (d, $J = 7$ Hz, 2H) 5.14 (s, 2H), 3.96-4.00 (m, 2H), 2.24 (s, 3H), 1.09 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, DMSO- d_6 , ppm) δ 165.8, 152.4, 149.1, 144.4, 132.3, 128.9, 128.7, 126.8, 99.6, 59.7, 54.0, 18.3, 14.6

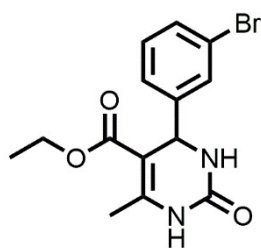


1H NMR spectrum of 5d

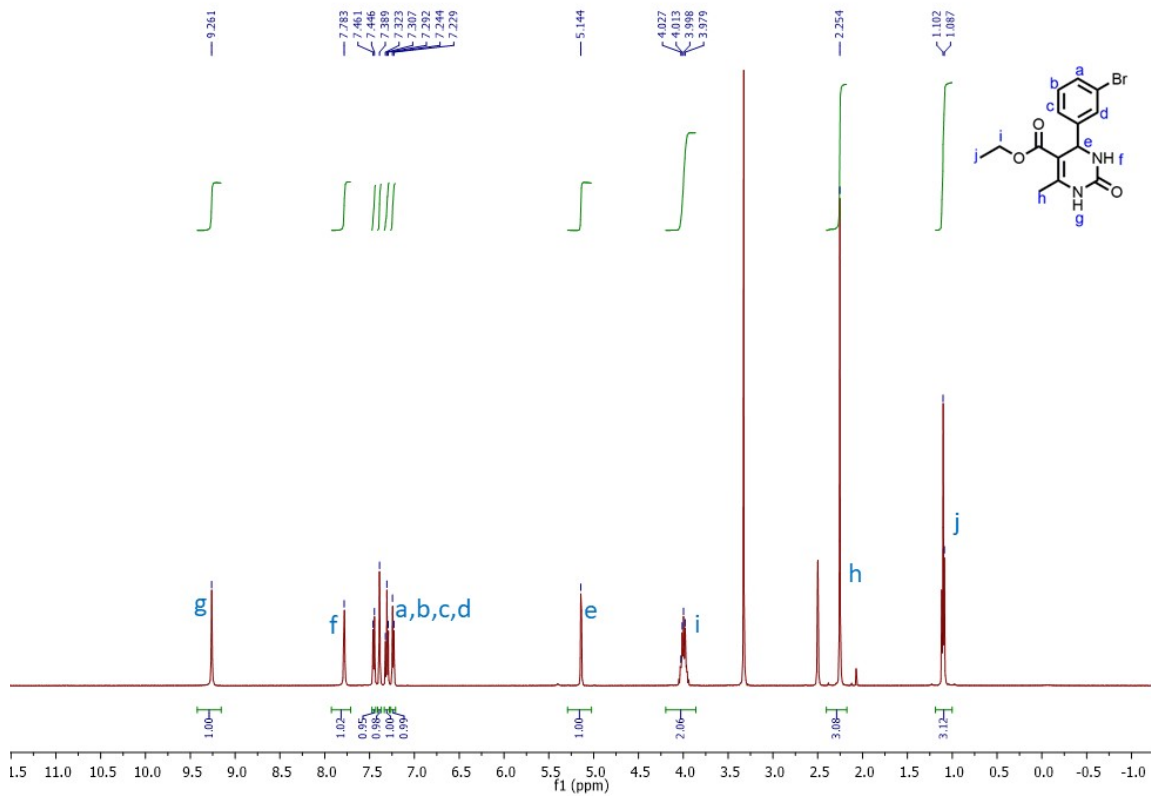


^{13}C NMR spectrum of 5d

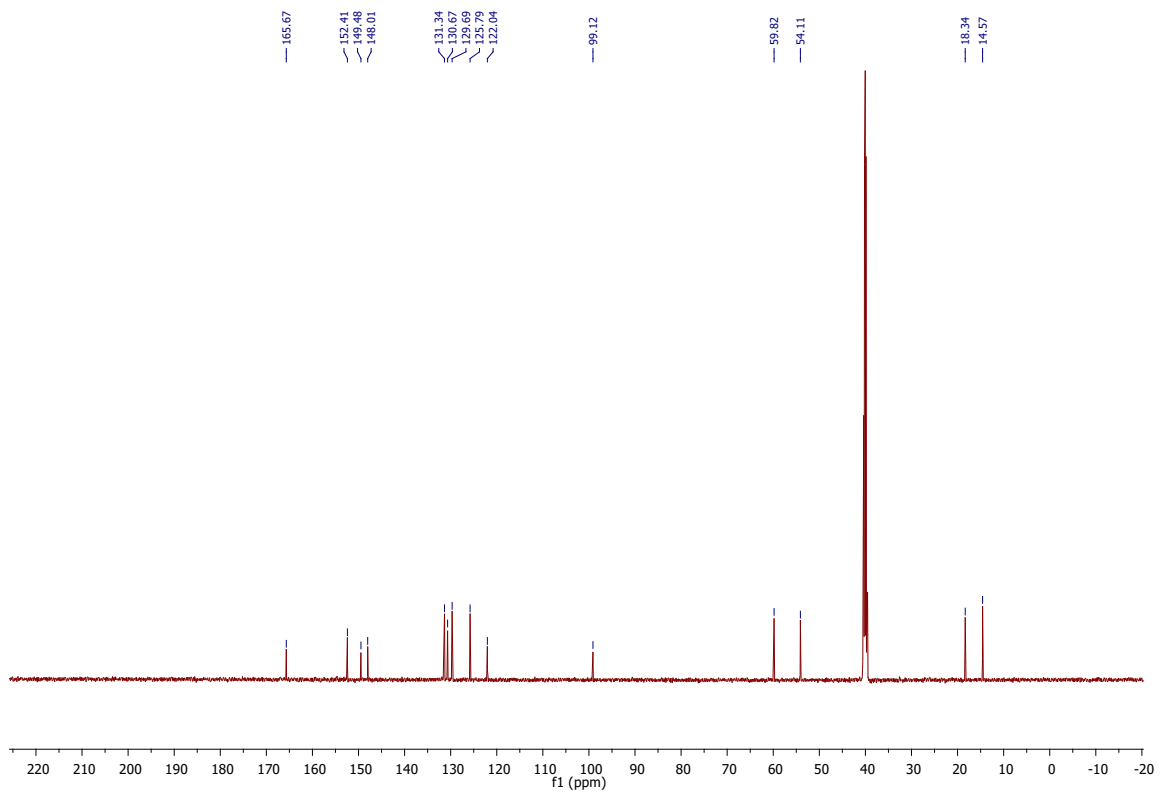
Ethyl-4-(3-bromophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5e)



M.F. $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_4\text{Br}$ (339.19). Yield: (0.305 g, 90%). White powder. ^1H NMR (500 MHz, DMSO-d_6 , ppm) δ 9.26 (s, 1H, NH), 7.78 (s, 1H, NH), 7.45 (d, $J = 7.5$ Hz 2H), 7.39 (s, 1H), 7.30 (t, $J = 7.5$, 1H), 7.23 (d, $J = 7.5$, 1H), 5.14 (s, 1H), 3.97-4.02 (m, 2H), 2.25 (s, 3H), 1.09 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6 , ppm) δ 165.7, 152.4, 149.5, 148.0, 131.3, 130.7, 129.7, 125.8, 122.0, 99.1, 59.1, 18.3, 14.6

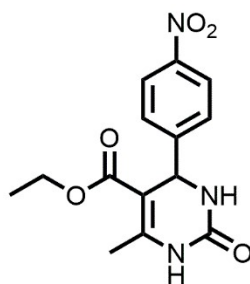


¹H NMR spectrum of 5e

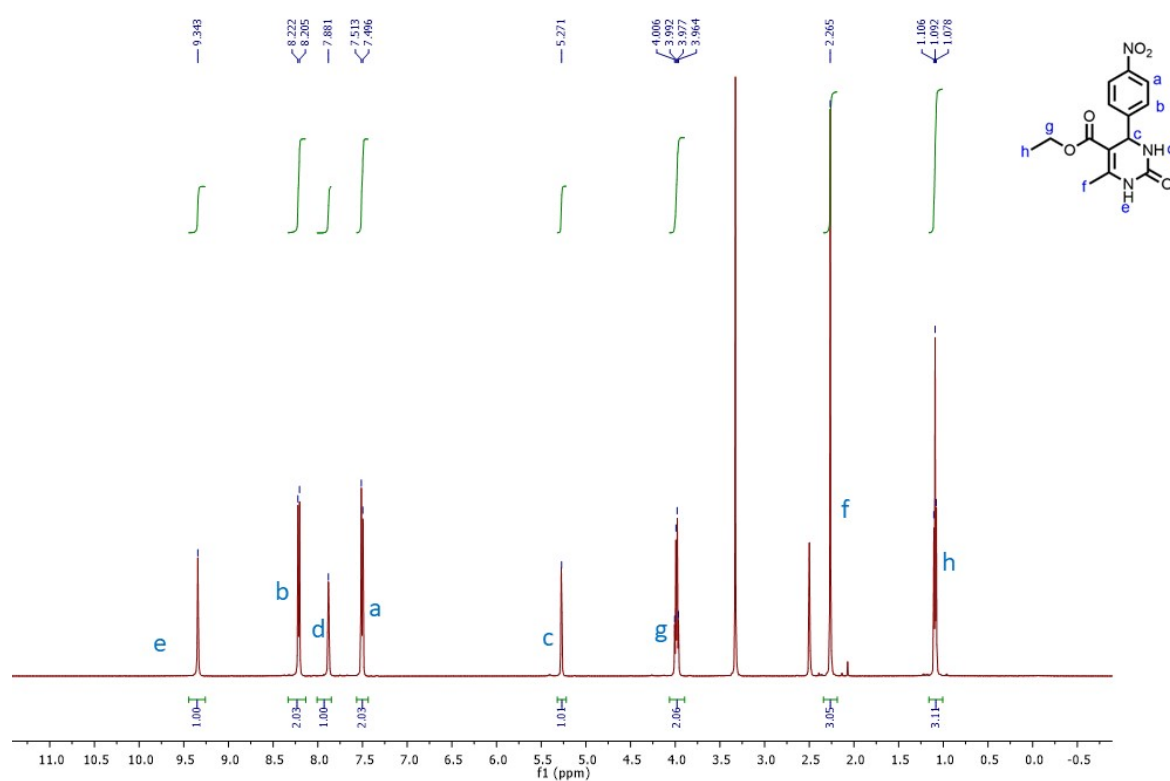


¹³C NMR spectrum of 5e

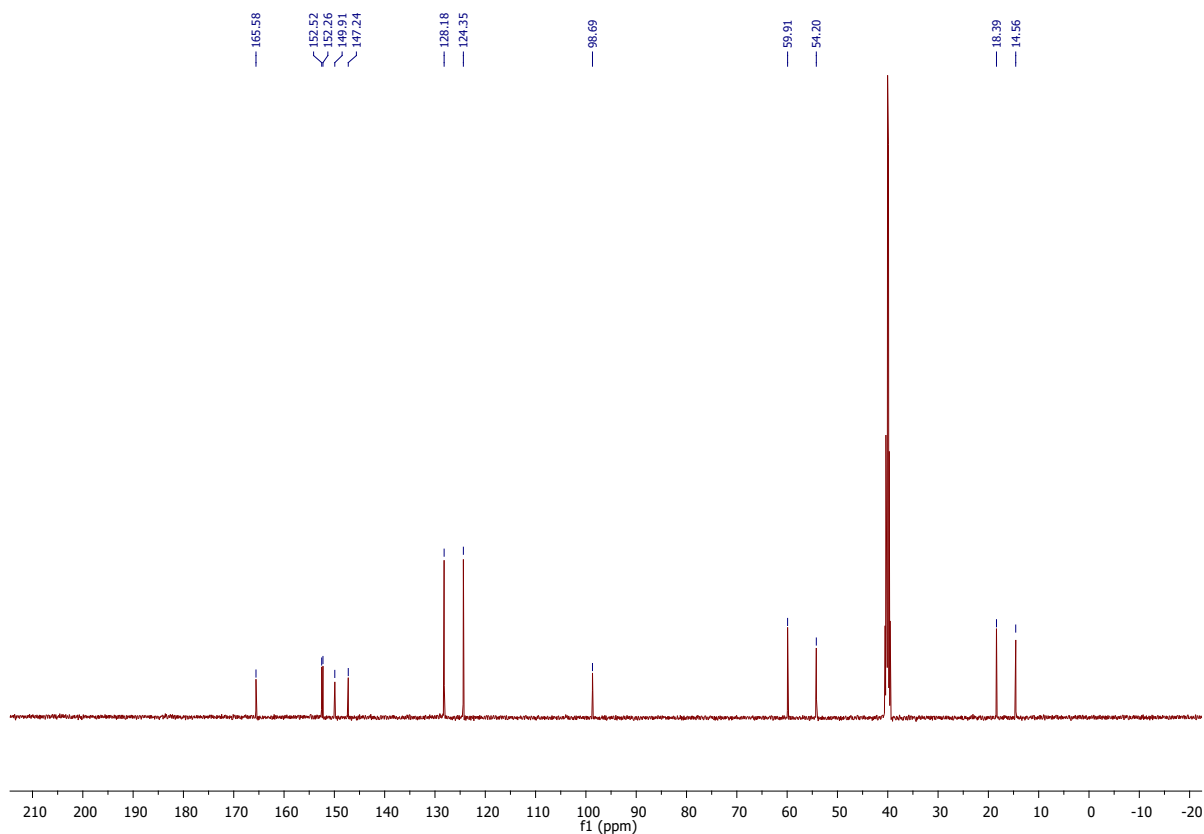
Ethyl-6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5f)



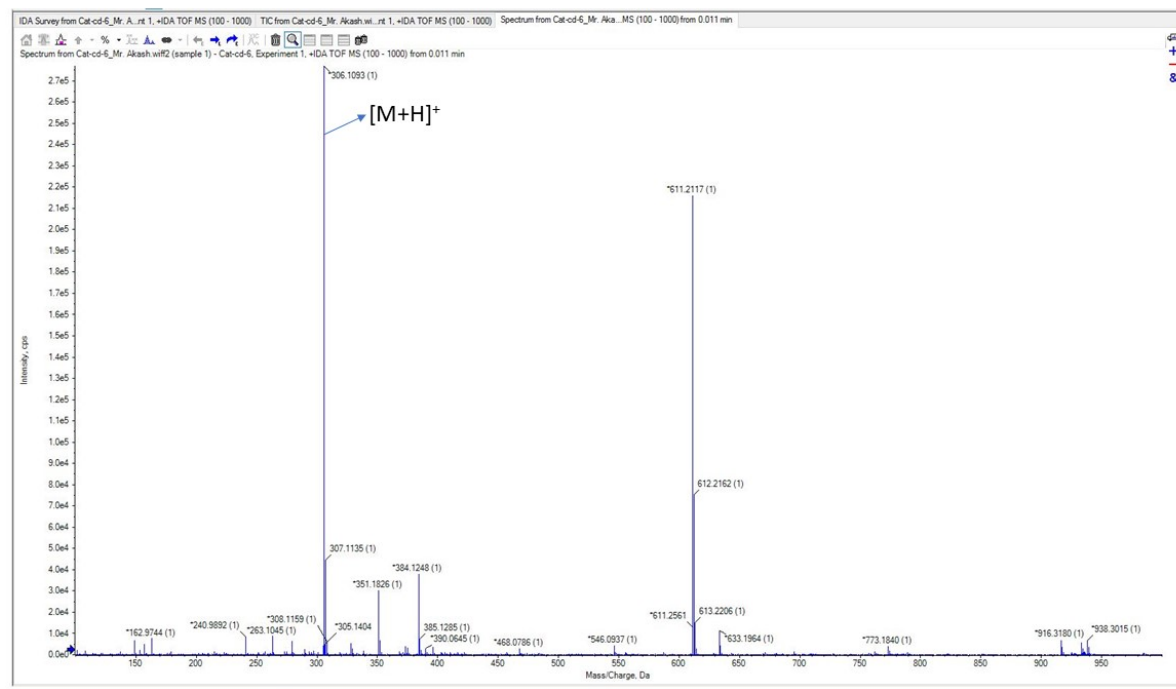
M.F. $C_{14}H_{15}N_3O_5$ (305.29). Yield: (0.275 g, 90%). White powder. 1H NMR (500 MHz, DMSO- d_6 , ppm) δ 9.34 (s, 1H, NH), 8.21 (s, 1H, NH), 7.88 (s, 1H, NH), 7.50 (d, $J = 8.5$ Hz 2H), 5.27 (d, 1H), 3.96 -4.00(m, 2H), 2.27 (s, 3H), 1.09 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, DMSO- d_6 , ppm) δ 165.6, 152.5, 152.3, 149.9, 147.2, 128.2, 124.3, 98.7, 59.9,54.2, 18.4, 14.6; HRMS (ESI): calcd. for $C_{14}H_{15}N_3O_5$ $[M + H]^+$ 306.109, found 306.109.



1H NMR spectrum of 5f

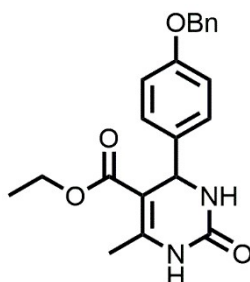


^{13}C NMR spectrum of **5f**

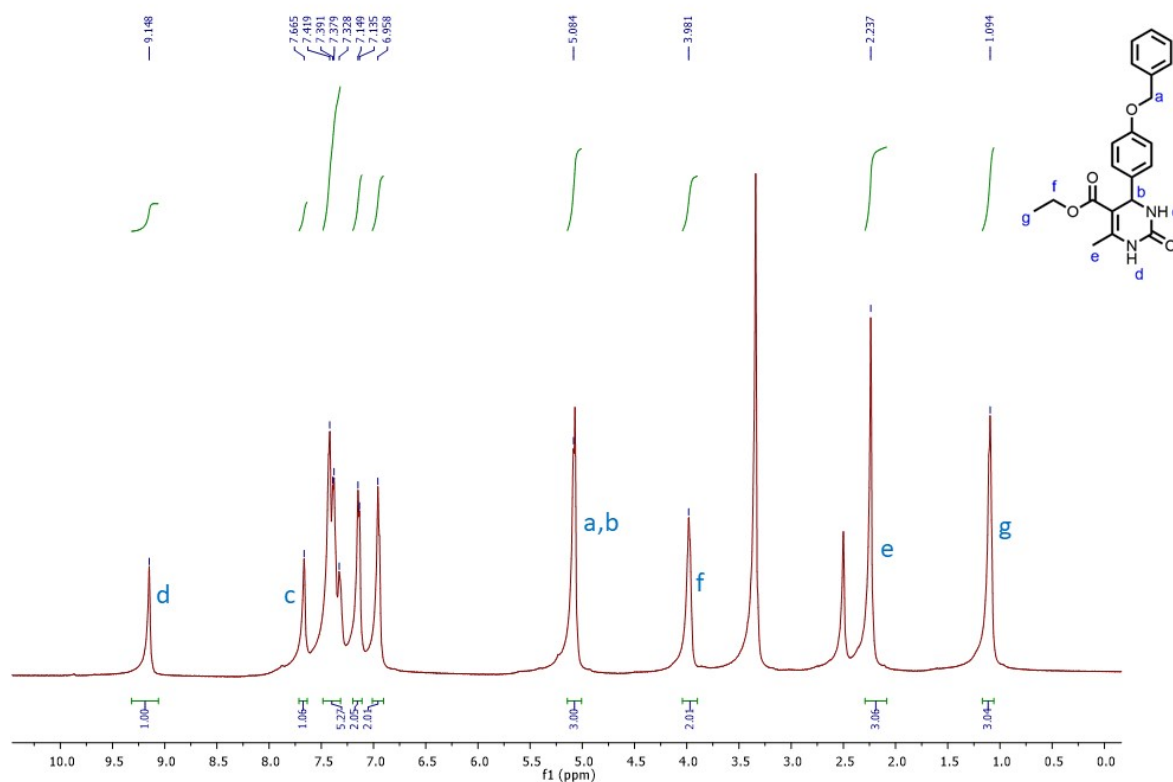


HRMS spectrum of **5f**

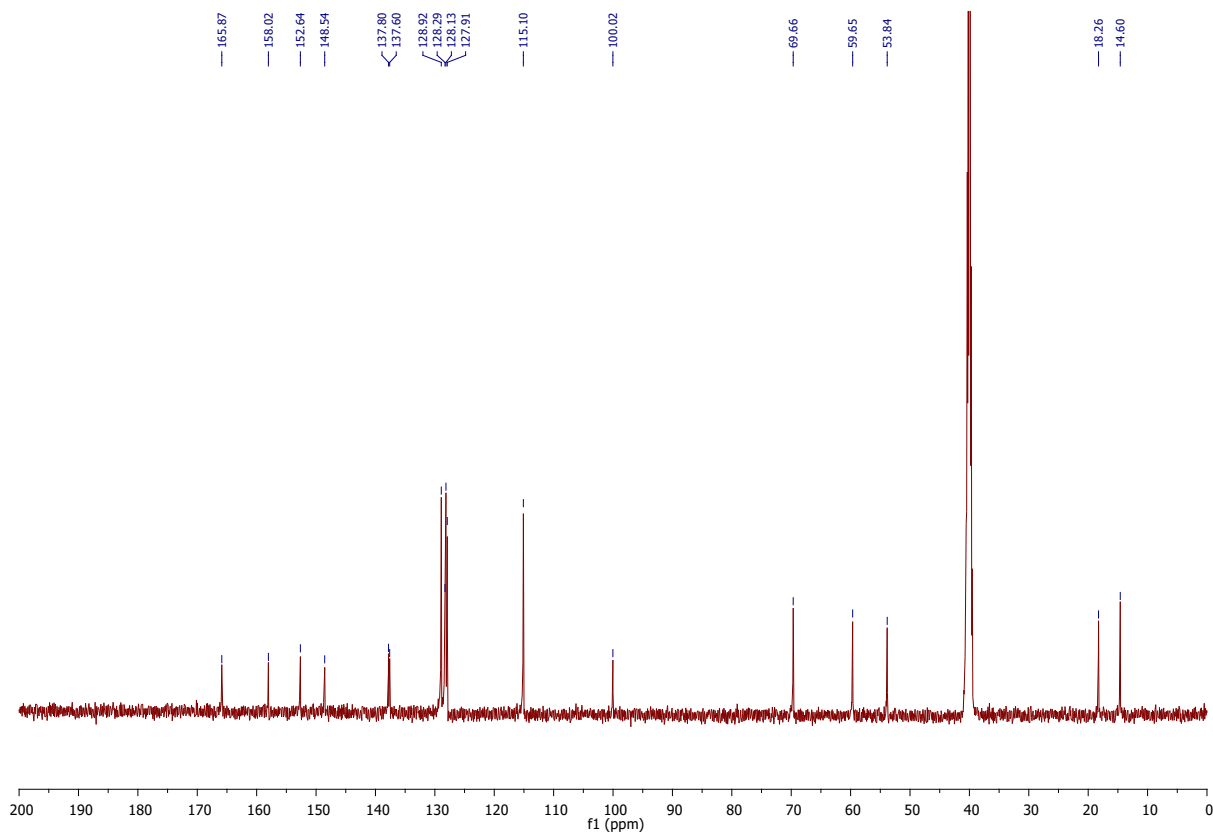
Ethyl-4-(4-(benzyloxy)phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5g)



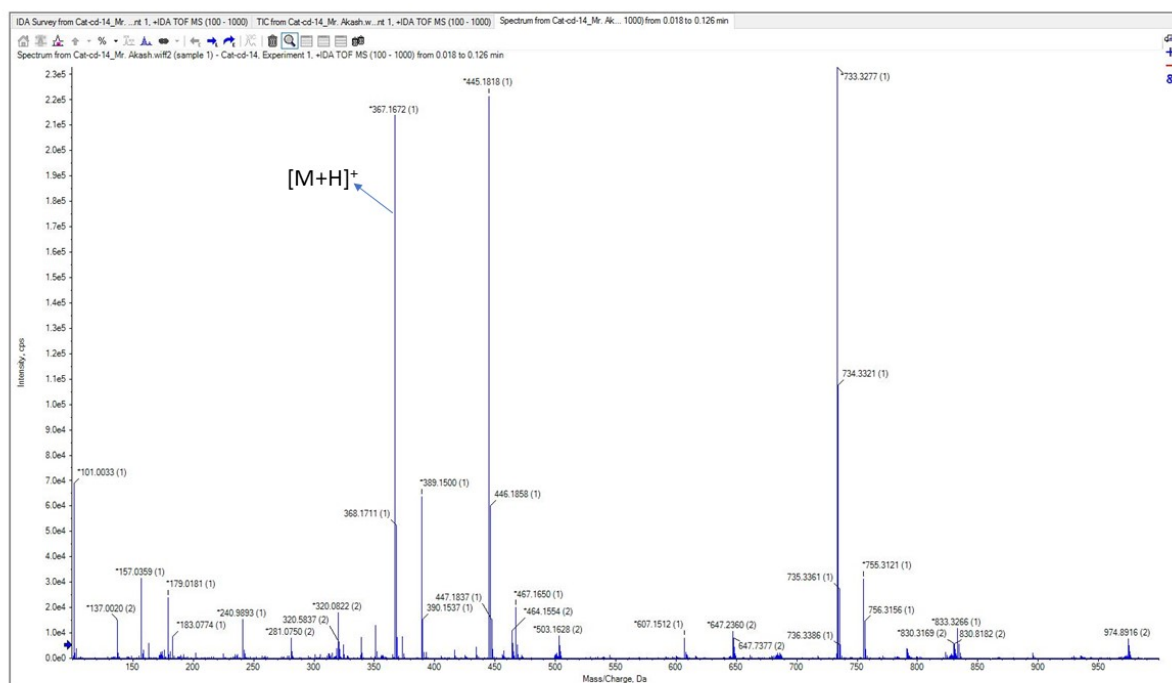
M.F. $C_{21}H_{22}N_2O_4$ (366.42). Yield: (0.325 g, 89%). White powder. 1H NMR (500 MHz, DMSO- d_6 , ppm) δ 9.15 (s, 1H, NH), 7.66 (s, 1H, NH), 7.38-7.42(5H), 7.14-7.15(2H), 6.96(2H) 5.08 (3H), 3.98 (m, 2H), 2.24 (s, 3H), 1.09 (3H); ^{13}C NMR (125 MHz, DMSO- d_6 , ppm) δ 165.9, 158.0, 152.6, 148.5, 137.8, 137.6, 128.9, 128.3, 128.1, 127.9, 115.1, 100.0, 69.7, 59.7, 53.8, 18.3, 14.6; HRMS (ESI): calcd. for $C_{21}H_{22}N_2O_4$ $[M + H]^+$ 367.166, found 367.167.



1H NMR spectrum of 5g

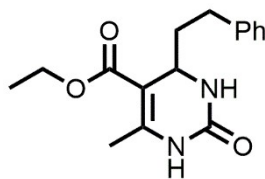


^{13}C NMR spectrum of 5g

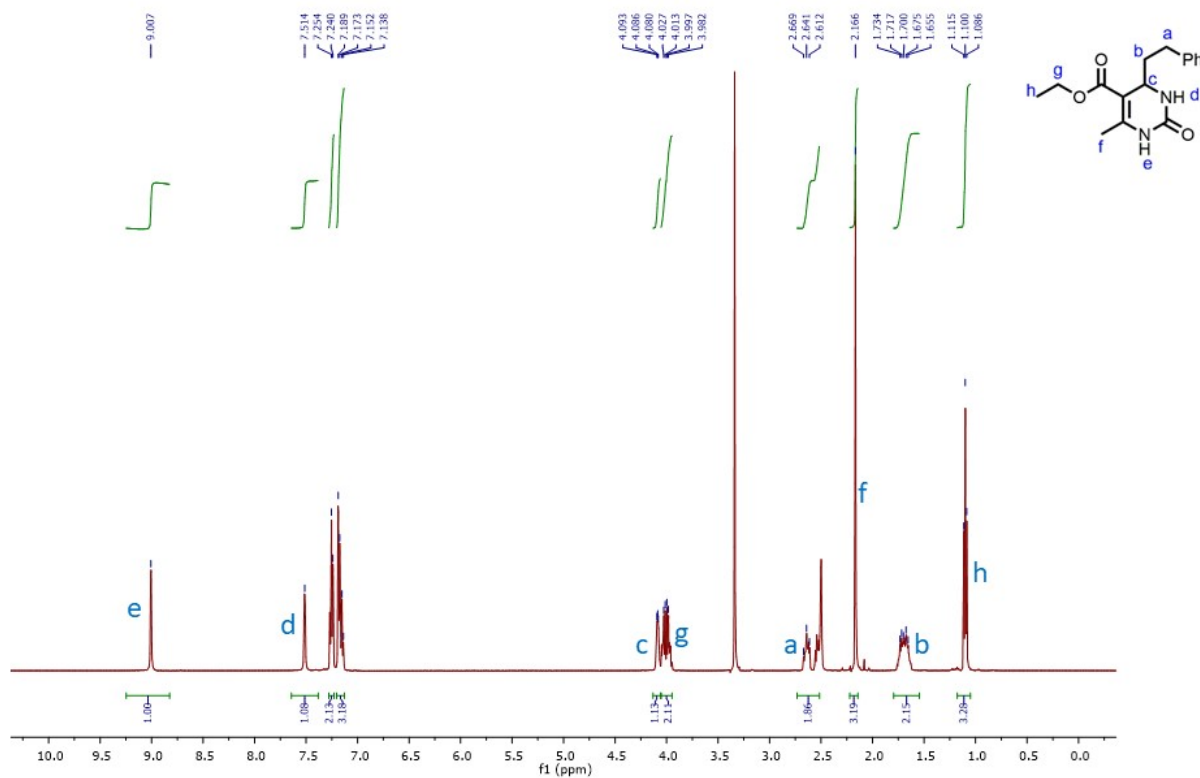


HRMS spectrum of 5g

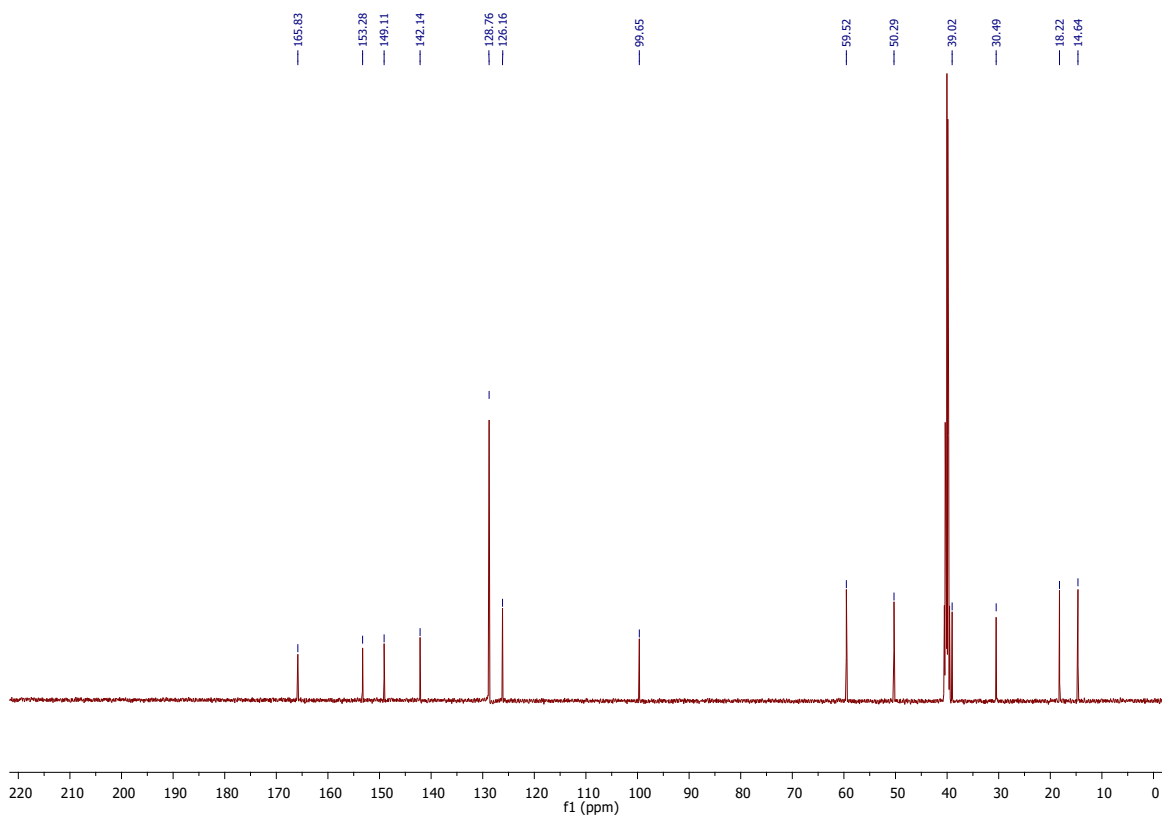
Ethyl-6-methyl-2-oxo-4-phenethyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5h)



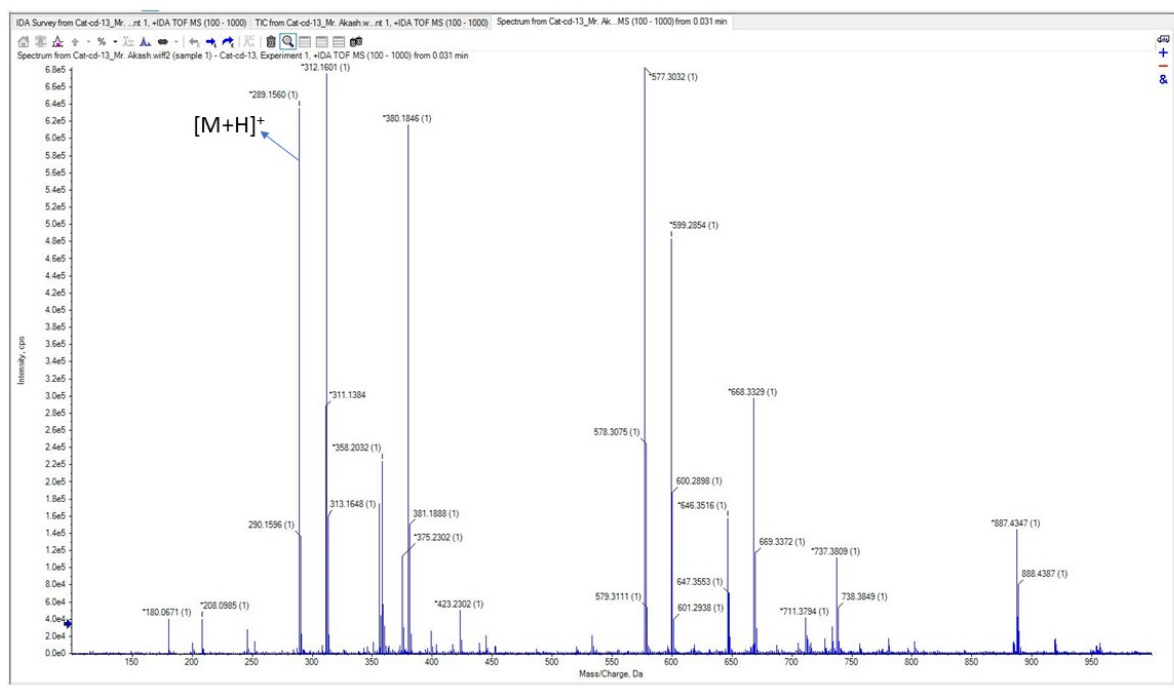
M.F. C₁₆H₂₀N₂O₃ (288.35). Yield: (0.250 g, 87%). White powder. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ 9.01 (s, 1H, NH), 7.51 (s, 1H, NH), 7.25 (t, J = 7 Hz 2H), 7.13-7.19(m, 3H), 4.08(m, 1H), 4.00(m, 2H), 2.64 (m, 2H), 2.16(s, 3H), 1.70(m, 2H), 1.10(t, J = 7.0Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆, ppm) δ 165.8, 153.3, 149.1, 142.1, 128.8, 126.2, 99.7, 59.5, 50.3, 39.0, 30.5, 18.2, 14.6; HRMS (TOF-MS): calcd. for C₁₆H₂₀N₂O₃ m/z [M + H]⁺289.155, found 289.156.



¹H NMR spectrum of 5h

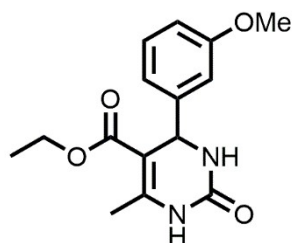


^{13}C NMR spectrum of 5h

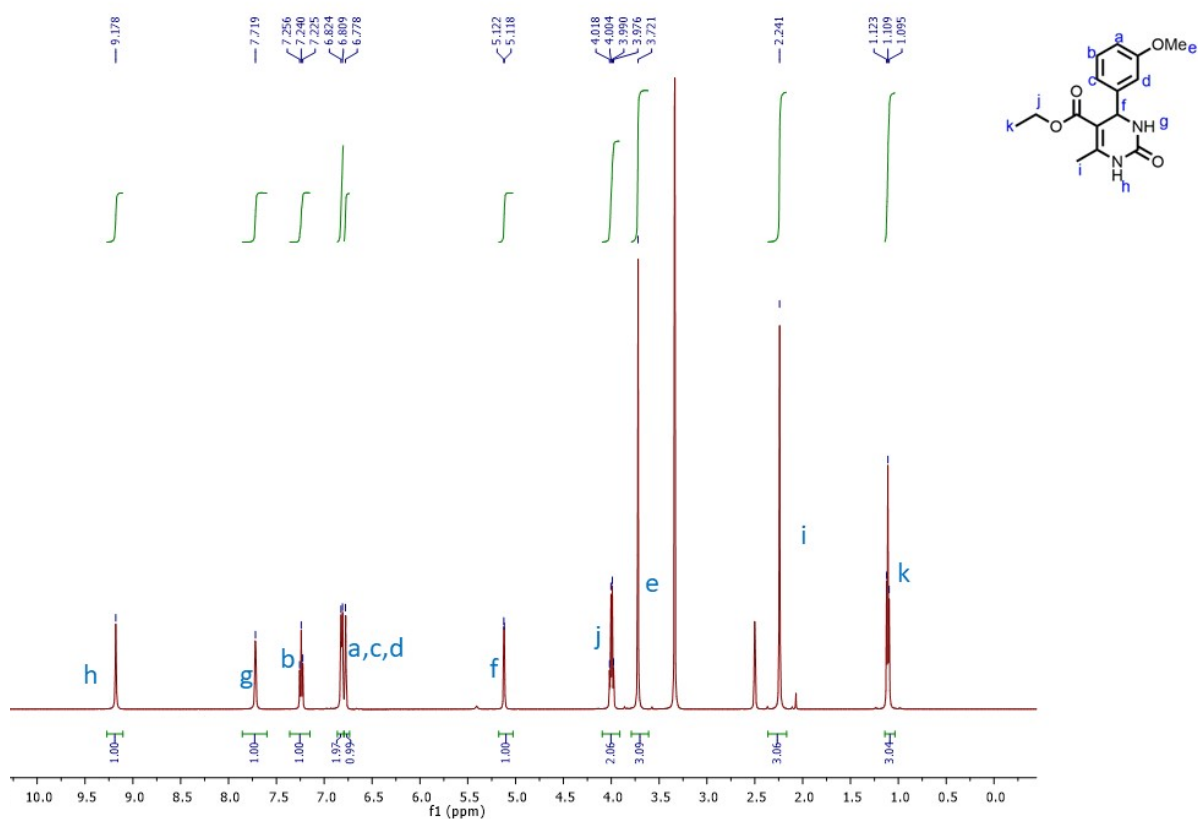


HRMS spectrum of 5h

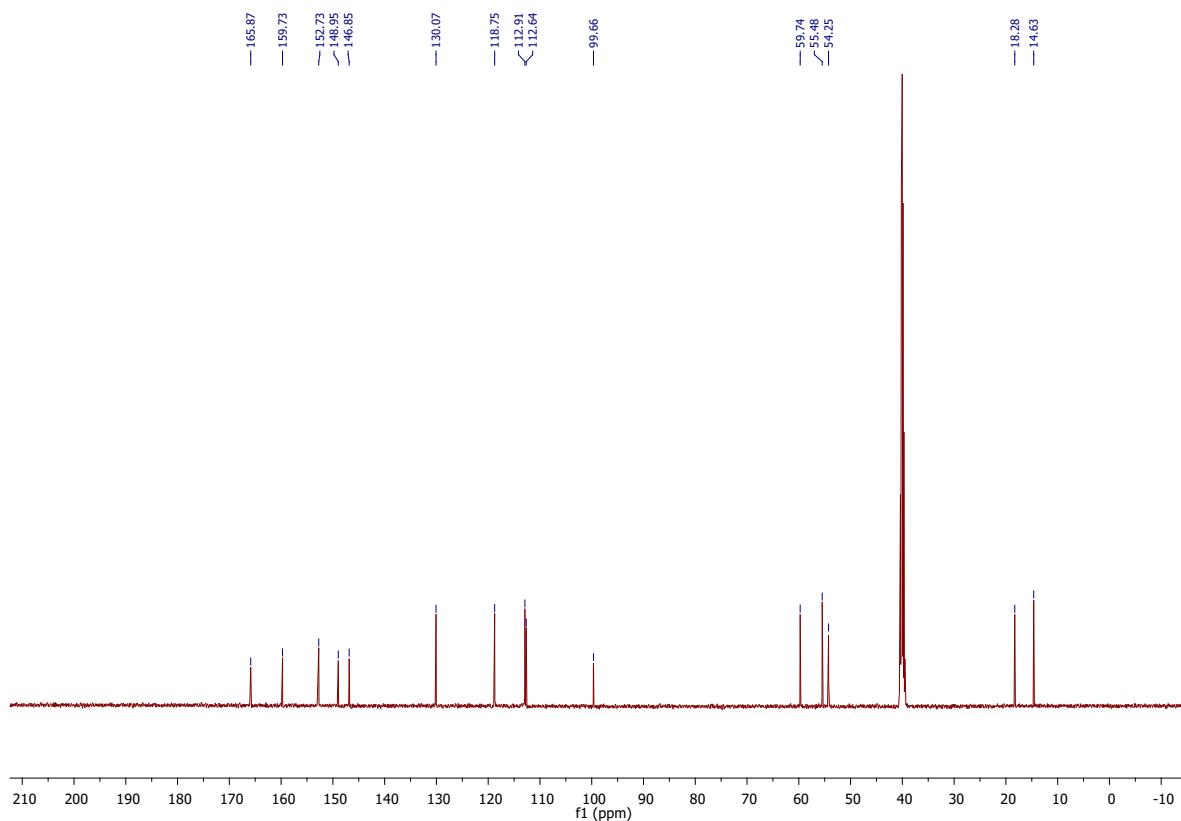
Ethyl4-(3-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5i)



M.F. C₁₅H₁₈N₂O₄ (290.32). Yield: (0.267 g, 92%). White powder. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ 9.18 (s, 1H, NH), 7.72 (s, 1H, NH), 7.24 (t, J = 7.5Hz, 1H), 6.81 (d, J = 7.5Hz, 2H), 6.78 (d, 1H), 5.12 (d, J = 6 Hz, 1H), 3.98 -4.01 (m, 2H), 3.72 (s, 3H), 2.24 (s, 3H), 1.11 (t, J = 7.0Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆, ppm) δ 165.9, 159.7, 152.7, 148.9, 146.9, 130.1, 118.7, 112.9, 112.6, 99.6, 59.7, 55.4, 54.2, 18.3, 14.6.

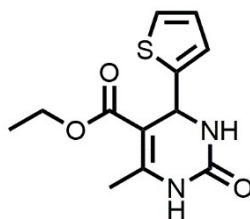


¹H NMR spectrum of 5i

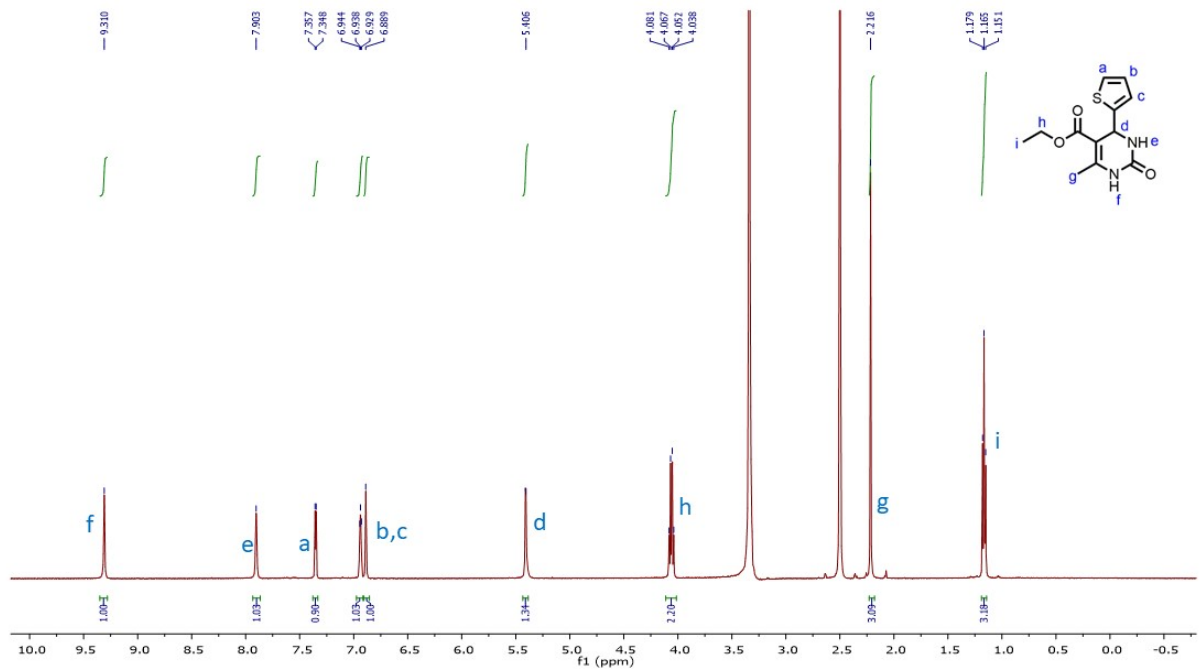


¹³C NMR spectrum of 5i

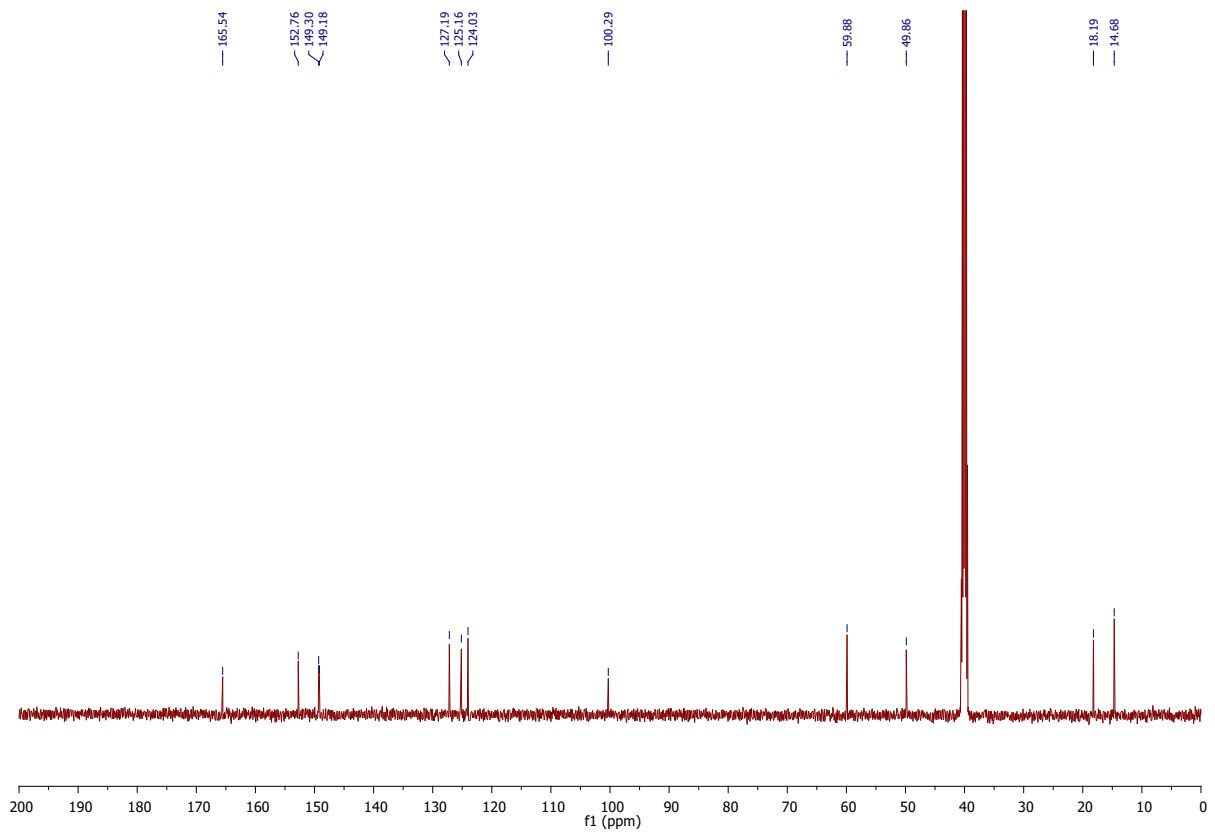
Ethyl 6-methyl-2-oxo-4-(thiophen-2-yl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5j)



M.F. C₁₂H₁₄N₂O₃S (266.32). Yield: (0.239 g, 90%). White powder. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ 9.31 (s, 1H, NH), 7.90 (s, 1H, NH), 7.35 (d, J = 4.5 Hz, 1H), 6.94 (t, J = 4.5 Hz, 1H), 6.89 (d, 1H), 5.40(d, 1H), 4.04 -4.08 (m, 2H), 2.22 (s, 3H), 1.16 (t, J= 7.0Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆, ppm) δ 165.5, 152.8, 149.3, 149.2, 127.2, 125.2, 124.0, 100.3, 59.9, 49.9, 18.2, 14.6.

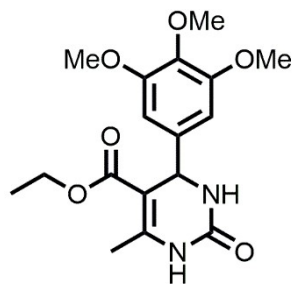


¹H NMR spectrum of 5j

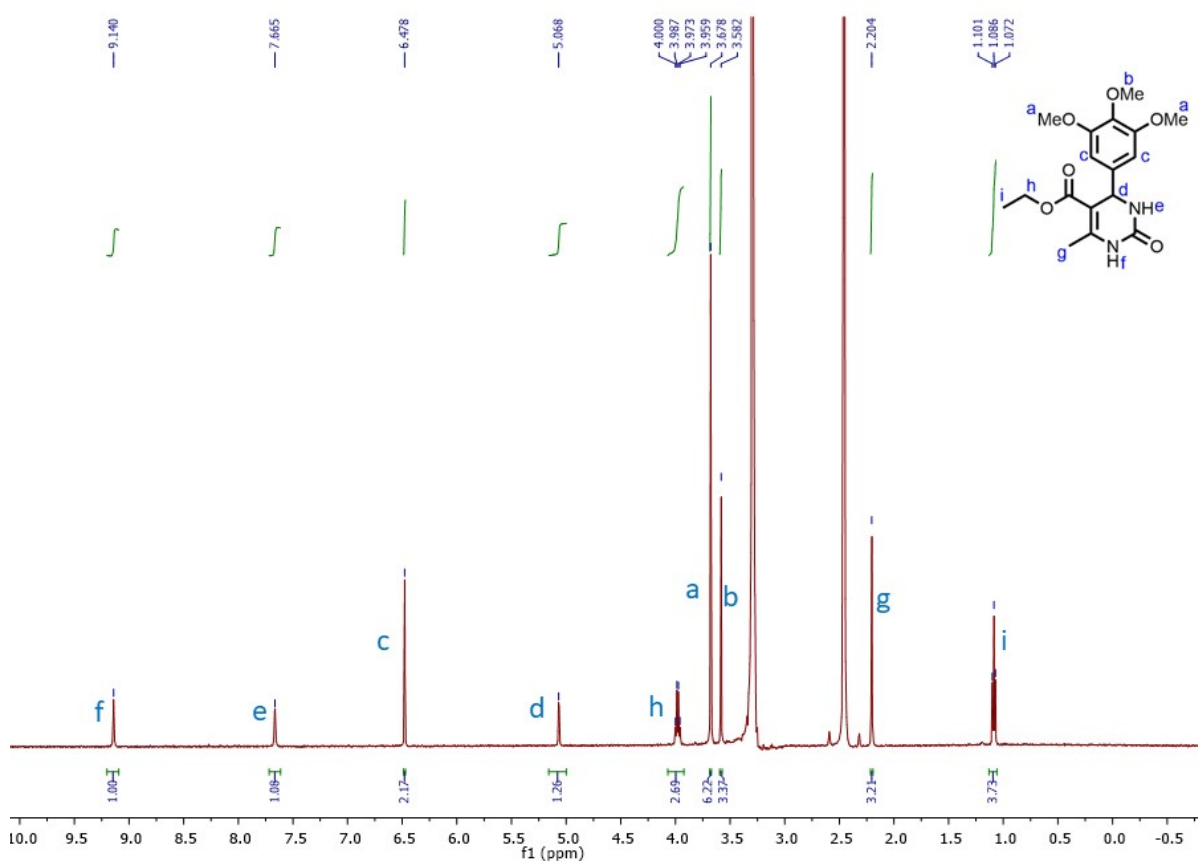


¹³C NMR spectrum of 5j

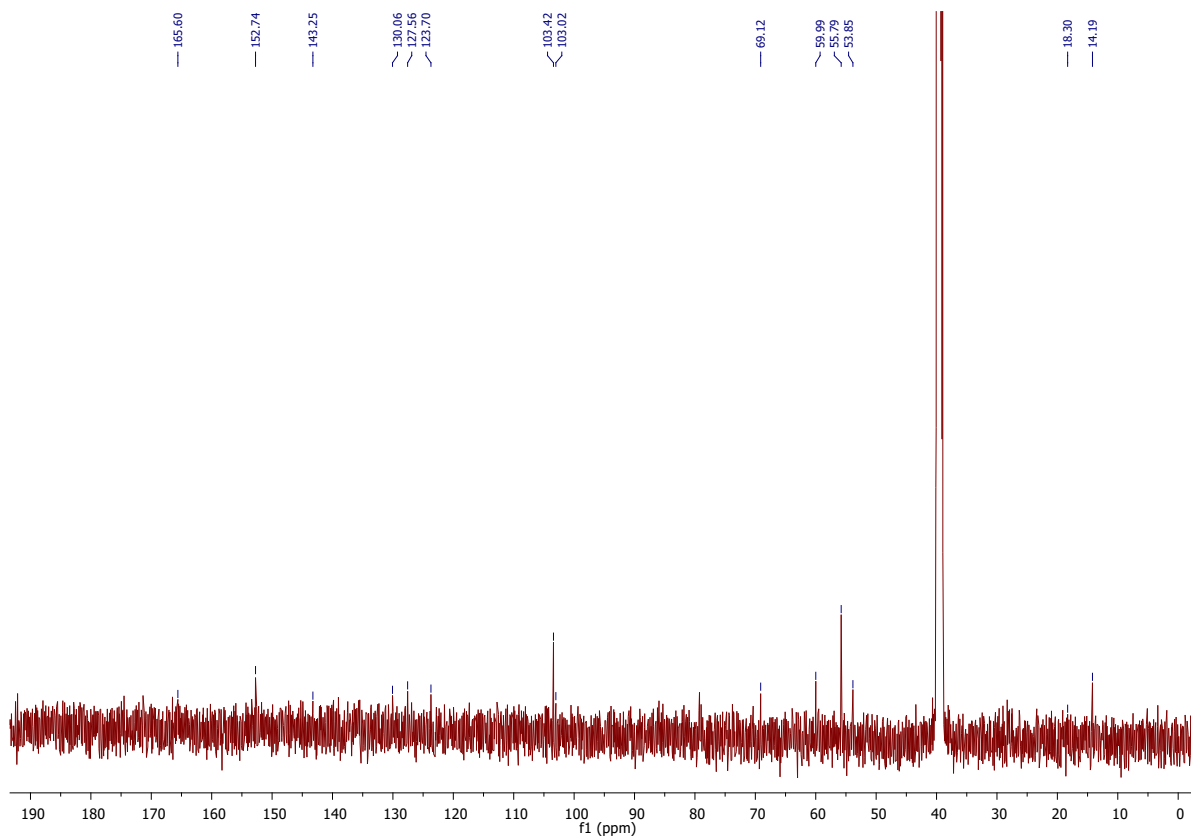
Ethyl-6-methyl-2-oxo-4-(3,4,5-trimethoxyphenyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5k)



M.F. C₁₇H₂₂N₂O₆ (350.37). Yield: (0.318 g, 91%). White powder. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ 9.14 (s, 1H, NH), 7.66 (s, 1H, NH), 6.48 (s, 2H), 5.07 (d, 1H), 3.97 - 4.00(m, 2H), 3.68 (s, 6H), 3.58 (s, 3H), 2.20 (s, 3H), 1.09 (t, J = 7.0Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆, ppm) δ 165.6, 152.7, 143.2, 130.1, 127.6, 123.7, 103.4, 103.0, 69.1, 59.9 55.8, 53.8, 18.3, 14.2.

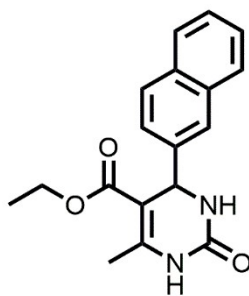


¹H NMR spectrum of 5k

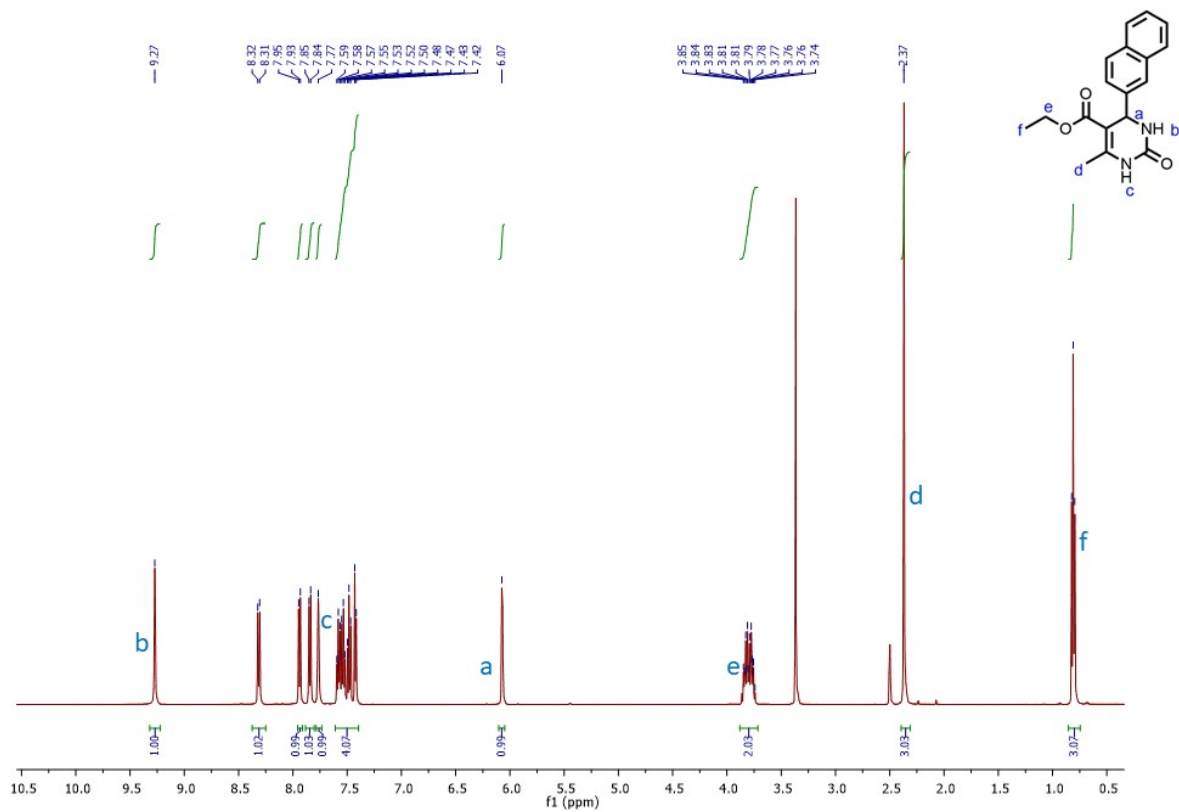


¹³C NMR spectrum of 5k

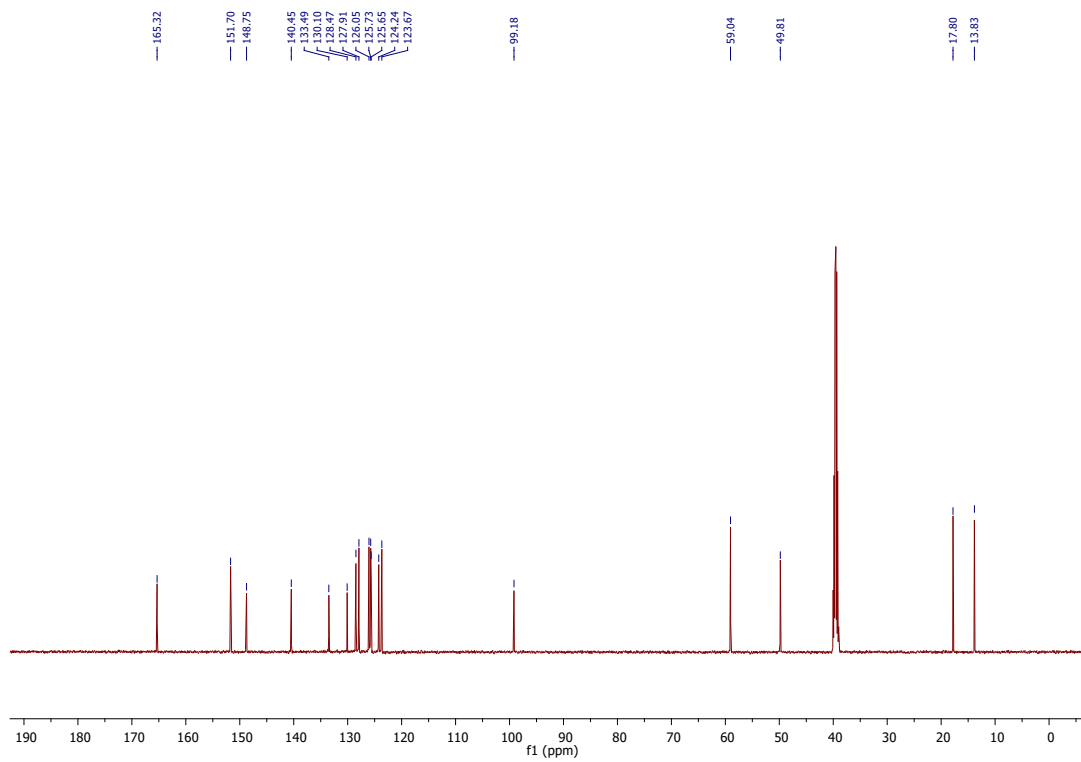
Ethyl-6-methyl-4-(naphthalen-2-yl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate(5l)



M.F. C₁₈H₁₈N₂O₃ (310.35). Yield: (0.273 g, 88%). White powder. ¹H NMR (500 MHz, DMSO-d₆, ppm) δ 9.27 (s, 1H, NH), 8.31 (d, J = 8.5 Hz 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H, NH), 7.52-7.59 (m, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 7.0 Hz, 1H) 6.07 (s, 1H), 3.74 -3.85 (m, 2H), 2.37 (s, 3H), 0.81 (t, J= 7.0 Hz, 3H); ¹³C NMR (125 MHz, DMSO-d₆, ppm) δ 165.3, 151.7, 148.7, 140.4, 133.5, 128.5, 127.9, 126.1, 125.5, 125.3, 124.2, 123.7, 99.2, 59.0,49.8, 17.8, 13.8.



¹H NMR spectrum of 51



¹³C NMR spectrum of 51

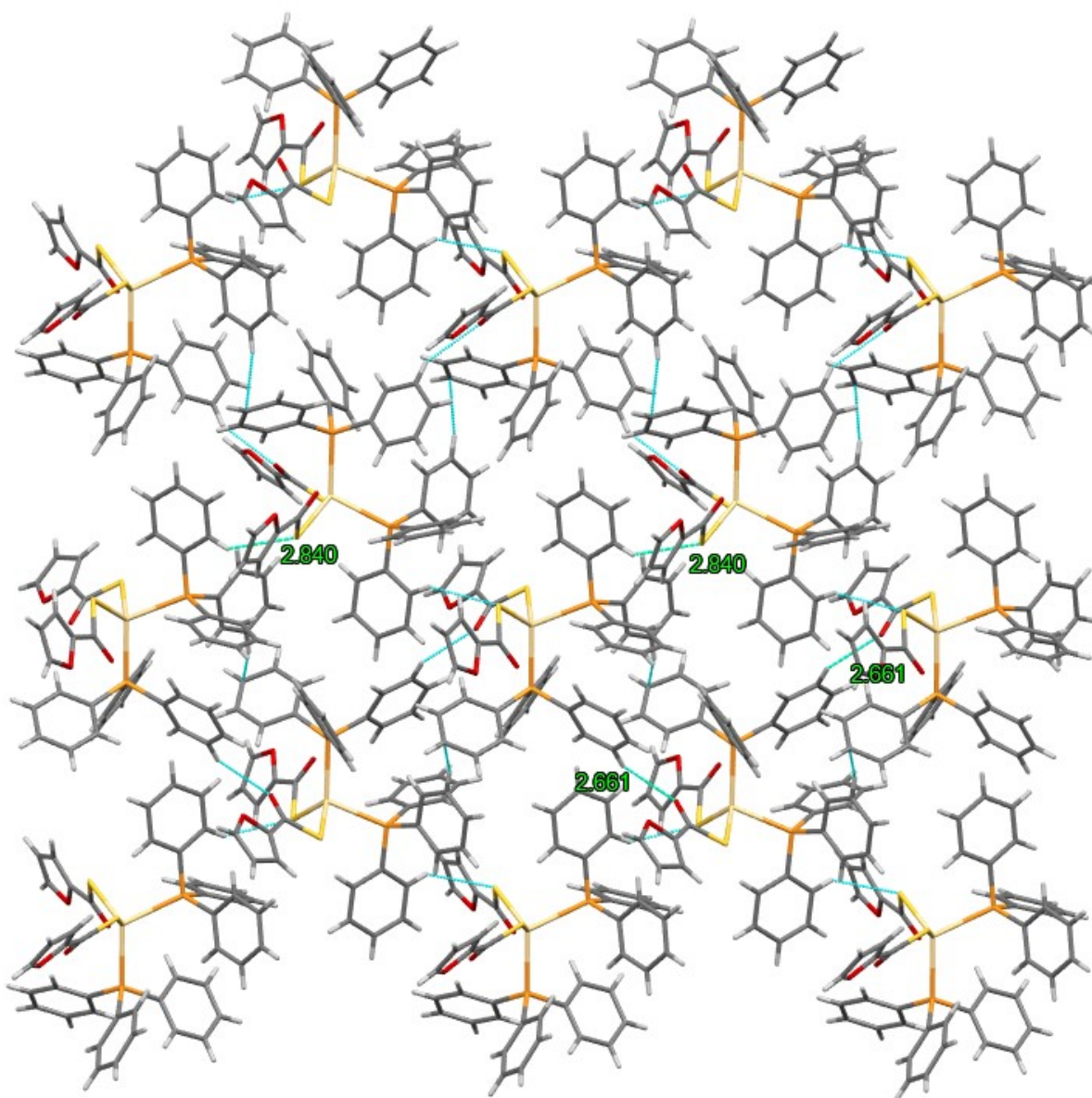


Figure S1. Packing diagram of **1** showing C-H \cdots O and C-H \cdots S interactions (green dotted line).

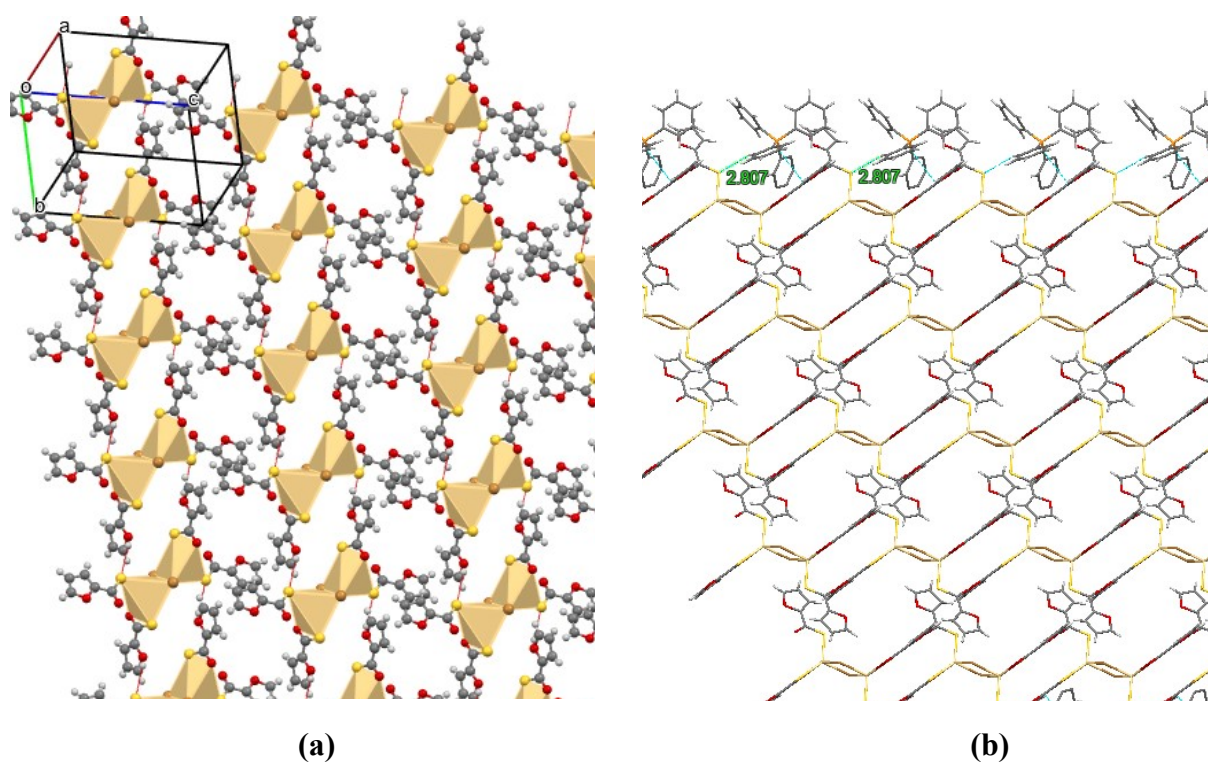


Figure S2. Packing diagrams of **2** (a) showing square pyramidal polyhedra along the *b*, *c* plane and (b) showing C-H...O and C-H...S interactions (green dotted lines).

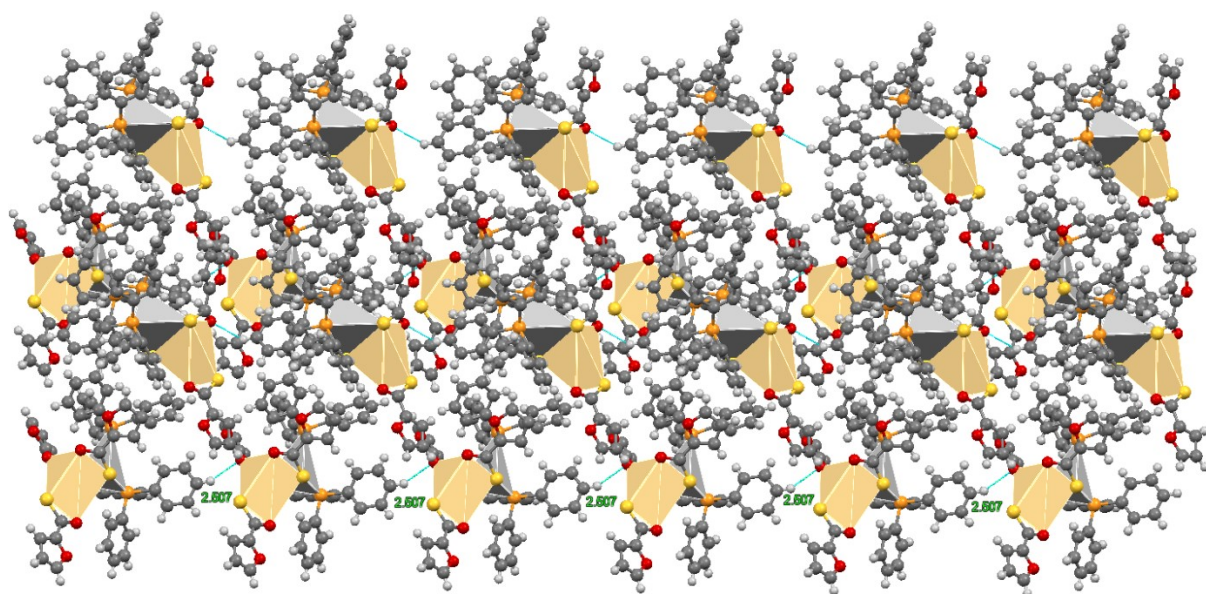


Figure S3. Packing diagram of **3** showing polyhedral core around the Cd(II) (trigonal prismatic) and Ag(I) (distorted tetrahedral) along with C-H...O hydrogen bonds.

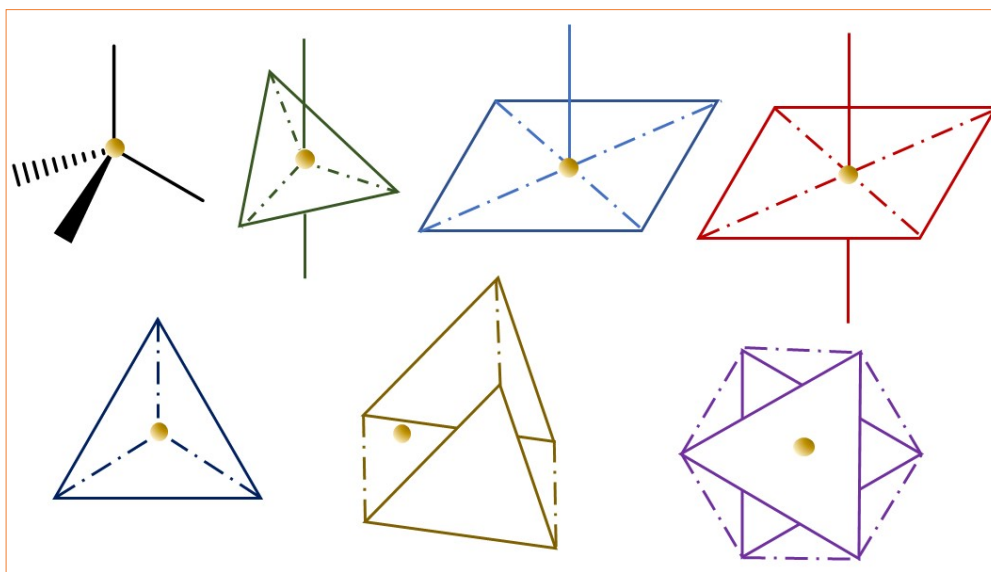


Figure S4. Earlier reported geometries of Cd(II) complexes. The above-given geometries of Cd(II) complexes are in their usual meaning.

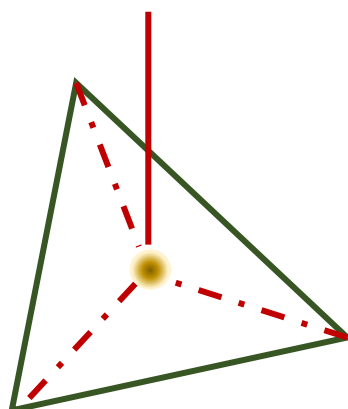


Figure S5. The above figure illustrates the trigonal pyramidal geometry of Cd(II) thiocarboxylate complex.