

Supporting information

Heterogeneous catalyst NiCoSe₂ & NiCo₂S₄ for the effective synthesis of dihydropyrimidine-2-ones/thiones

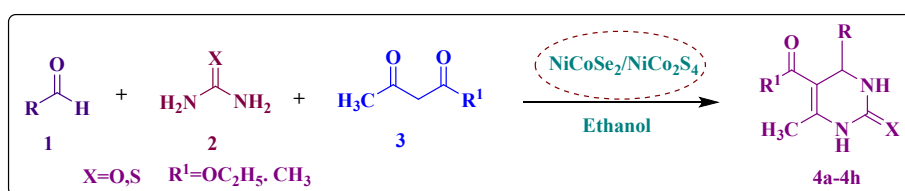
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Ethyl-1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate, (4a):

Yield 95%: ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.59 (s, 1H), 7.32 (m, 5H), 5.49 (s, 1H), 5.25 (s, 1H), 4.10 (q, 2H), 2.32 (s, 3H), 1.10 (t, 3H). ¹³C NMR (400 MHz, DMSO-*d*₆) δ 165.8, 153.2, 145.1, 143.3, 128.2, 127.4, 126.2, 101.1, 60.3, 54.7, 18.8, 14.5. MS: Cald. for C₁₄H₁₆N₂O₂S: *m/z*: 277.1011 [M⁺⁺H], Found: 277.00.

Ethyl 4-(2-fluorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4b):

Yield 92 %: ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.36 (s, 1H), 9.58 (s, 1H), 7.37 – 7.30 (m, 1H), 7.27 – 7.22 (m, 1H), 7.21 – 7.14 (m, 2H), 5.45 (d, 1H), 3.98 – 3.91 (m, 2H), 2.30 (s, 3H), 1.05 (t, 3H). ¹³C NMR (400 MHz, DMSO-*d*₆) 180.8, 167.8, 160.5, 159.6, 129.6, 128.9, 128.9, 124.4, 104.4, 115.8, 61.9, 43.8, 15.6, 14.5. MS: Cald. for C₁₄H₁₅FN₂O₂S *m/z*: 295.0971 [M⁺⁺H], Found =295.0896.

Ethyl-4-(2,4-difluorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4c):

Yield 90 % : ^1H NMR (400 MHz, DMSO- d_6) δ 10.38 (s, 1H), 9.2 (s, 1H), 7.2 – 7.15 (m, 2H), 7.16 – 7.08 (m, 1H), 5.38 (d, 1H), 3.95 – 3.90 (m, 2H), 2.35 (s, 3H), 1.01(t, 3H). ^{13}C NMR (400 MHz, DMSO- d_6) 173.10, 164.34, 147.39, 144.38, 134.73, 133.54, 128.84, 127.42, 121.10, 100.25, 60.24, 53.63, 17.66, 14.43. MS: Cald. for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{N}_2\text{O}_2\text{S}$ m/z : 313.0434 [M^++H], Found=313.0534.

Ethyl-4-(4-bromo-3-chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate, (4d):

Yield 80 % : ^1H NMR (400 MHz, DMSO- d_6) δ 10.28 (s, 1H), 9.42 (s, 1H), 7.22 – 7.10 (m, 2H), 7.1 1– 7.01 (m, 1H), 5.22 (d, 1H), 3.82 – 3.89 (m, 2H), 2.18 (s, 3H), 1.05 (t, 3H). ^{13}C NMR (400 MHz, DMSO- d_6) 173.78, 164.23, 145.28, 145.23, 133.62, 132.43, 128.88, 127.31, 120.17, 100.08, 60.12, 53.49, 17.63, 14.31. MS: Cald. for $\text{C}_{14}\text{H}_{14}\text{BrClN}_2\text{O}_3$ m/z : 307.1116 [M^++H], Found = 307.1016.

Ethyl-4-(2-chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate, (4e)

Yield 74% : ^1H NMR (400 MHz, DMSO- d_6) δ 10.26 (s, 1H), 9.45 (s, 1H), 7.27 – 7.32 (m, 1H), 7.17 – 7.14 (m, 1H), 7.11 – 7.08 (m, 2H), 5.35 (d, 1H), 3.48 – 3.84 (m, 2H), 2.20 (s, 3H), 1.01 (t, 3H). ^{13}C NMR (400 MHz, DMSO- d_6) 182.8, 168.8, 161.5, 159.2, 128.6, 127.1, 128.2, 124.2, 103.4, 115.3, 61.5, 42.2, 14.5, 14.3. MS: Cald. for $\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{O}_3$ m/z : 333.0434 [M^++Na], Found =333.0334.

1-(4-(2,4-difluorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidin-5-yl)ethanone, (4f)

Yield 85% : ^1H NMR (400 MHz, DMSO- d_6) δ 10.38 (s, 1H), 9.2 (s, 1H), 7.2 – 7.15 (m, 2H), 7.16 – 7.08 (m, 1H), 5.38 (d, 1H), 2.35 (s, 3H), 1.71(t, 3H). ^{13}C NMR (400 MHz, DMSO- d_6) 195.5, 180.01, 163.10, 161.34, 157.2, 135.39, 123.02, 111.01, 103.9, 104.38, 43.73, 26.54, 15.84. MS: Cald. for $\text{C}_{13}\text{H}_{12}\text{F}_2\text{N}_2\text{OS}$ m/z : 281.0617 [M^+-H], Found= 281.0286.

1-(4-(4-bromo-3-chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidin-5-yl)ethanone, (4g)

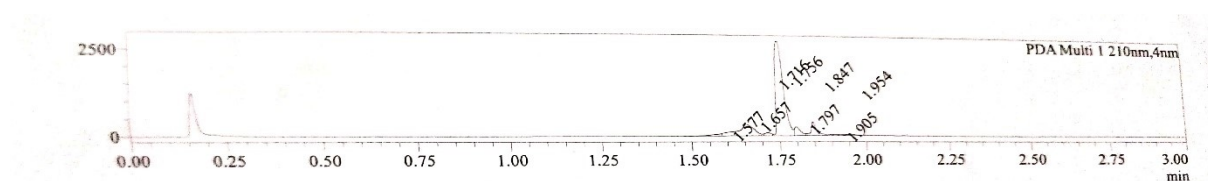
Yield 91 %: ^1H NMR (400 MHz, DMSO- d_6) δ 10.18 (s, 1H), 9.02 (s, 1H), 7.12 – 7.08 (m, 2H), 7.11– 7.01 (m, 1H), 5.22 (d, 1H), 2.08 (s, 3H), 1.25 (t, 3H). ^{13}C NMR (400 MHz, DMSO- d_6) 193.78, 182.23, 160.28, 157.23, 143.0, 132.62, 126.9, 129.2, 115.43, 104.88, 53.0, 28.1, 15.2. MS: Cald. for $\text{C}_{13}\text{H}_{12}\text{BrClN}_2\text{OS}$ m/z : 380.9621 [M^++H], Found= 380.9431.

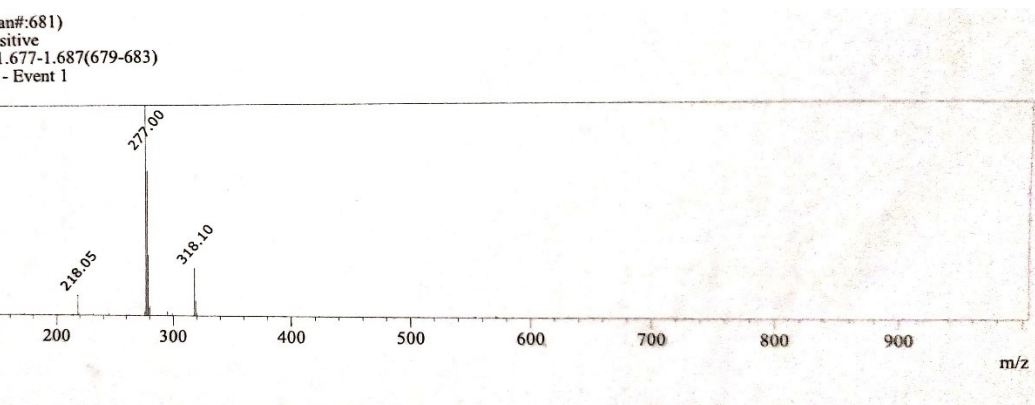
Ethyl 4-(2,4-difluorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate, (4h)

Yield 88 % : ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10.35 (s, 1H), 9.2 (s, 1H), 7.0 – 7.05 (m, 2H), 7.14 – 7.01 (m, 1H), 5.25 (d, 1H), 3.85 – 3.88 (m, 2H), 2.33 (s, 3H), 1.01(t, 3H). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) 173.10, 164.34, 147.39, 144.38, 134.73, 133.54, 128.84, 127.42, 121.10, 100.25, 60.24, 53.63, 17.66, 14.43. MS: Cald. for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{N}_2\text{O}_3$ m/z : 319.0870 [$\text{M}^+ + \text{Na}$], Found=319.0770.

Ethyl-4-(4-bromo-3-chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4i)

Yield 89% : ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 10.28 (s, 1H), 9.42 (s, 1H), 7.22 – 7.10 (m, 2H), 7.11– 7.01 (m, 1H), 5.32 (d, 1H), 3.89 – 3.94 (m, 2H), 2.25 (s, 3H), 1.02 (t, 3H). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$) 174.79, 165.25, 146.28, 145.33, 134.72, 133.53, 128.81, 127.21, 121.17, 100.18, 60.22, 53.59, 17.65, 14.41. MS: Cald. for $\text{C}_{14}\text{H}_{14}\text{BrClN}_2\text{O}_2\text{S}$ m/z : 389.0708 [$\text{M}^+ + \text{H}$], Found= 389.0208.

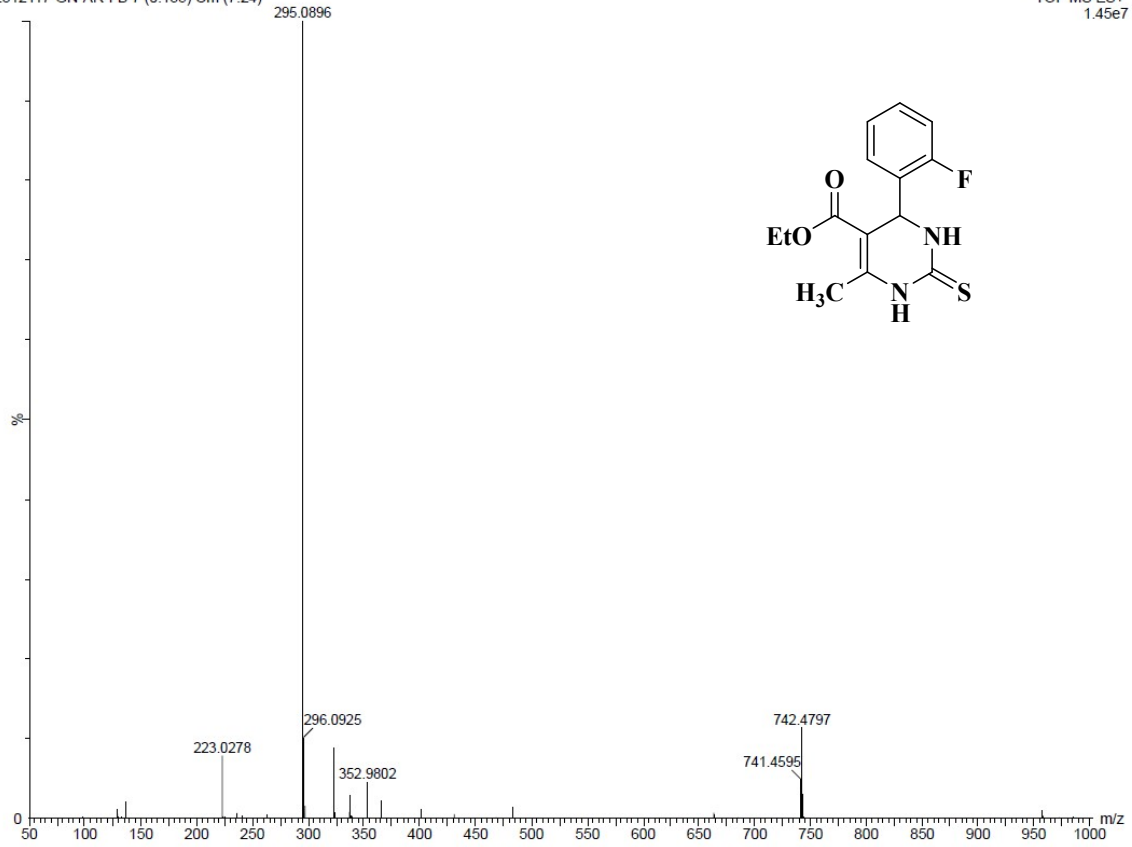




Spectrum 1: LCMS of ethyl-1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate, (4a):

2312117-GN-AR-FB 7 (0.135) Cm (7:24)

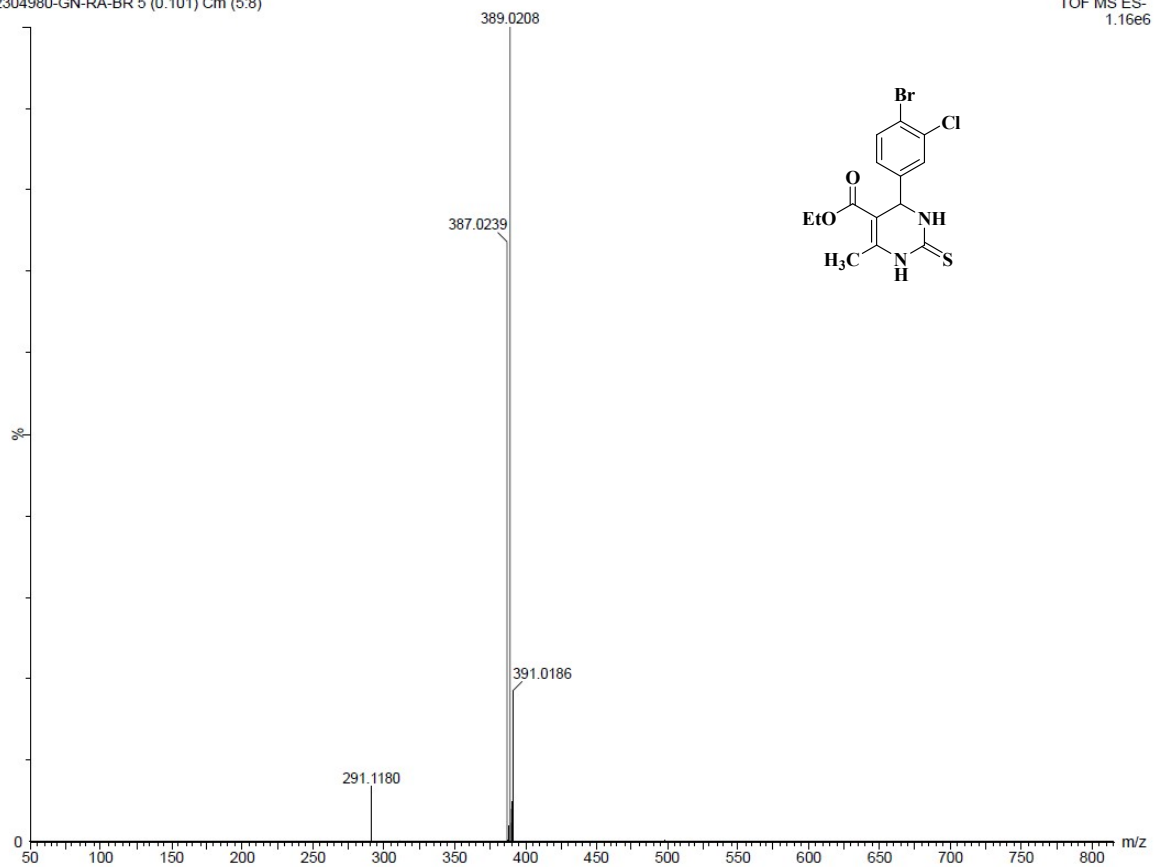
TOF MS ES+
1.45e7



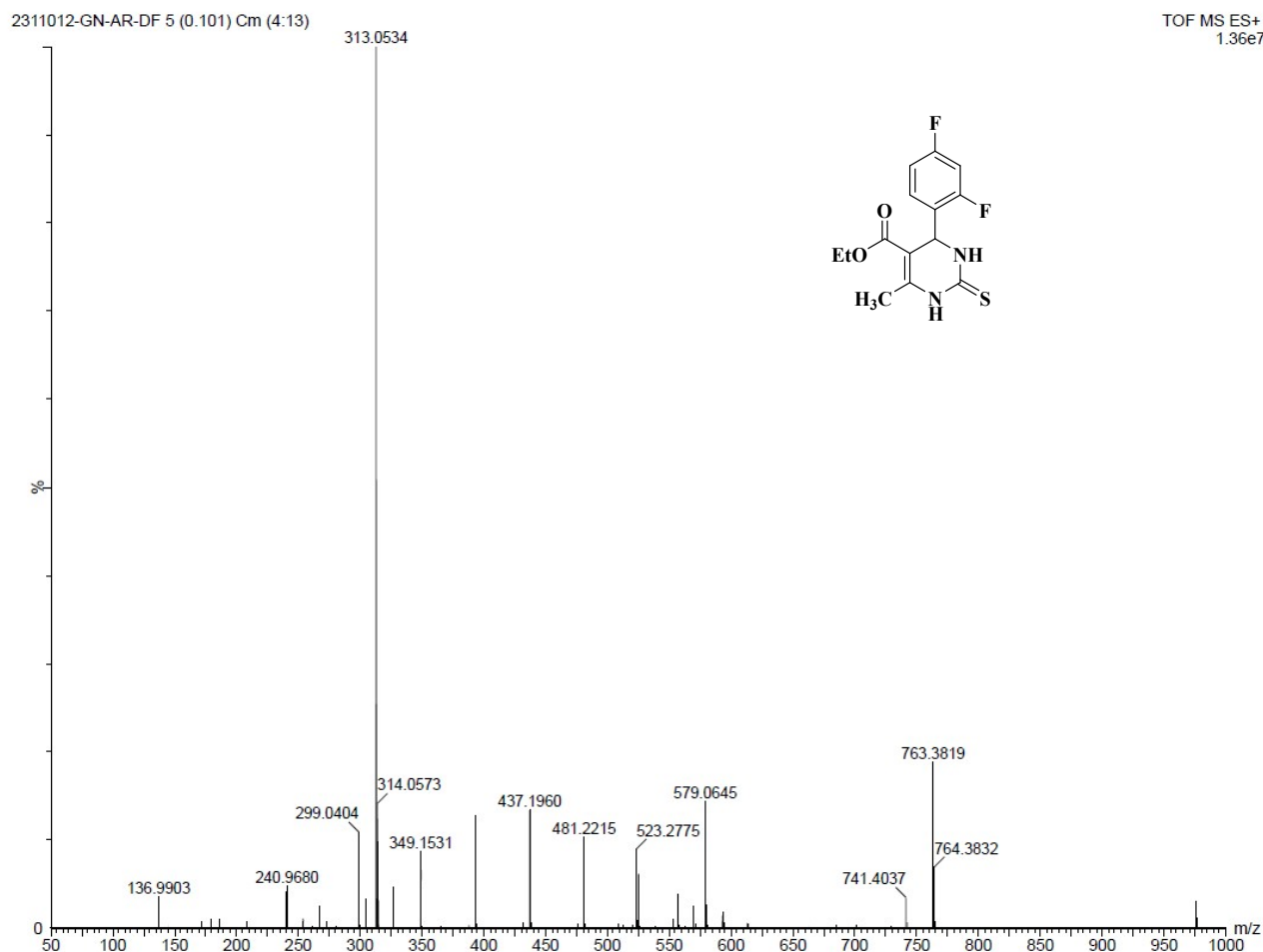
Spectrum 2: HRMS of ethyl 4-(2-fluorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4b)

2304980-GN-RA-BR 5 (0.101) Cm (5:8)

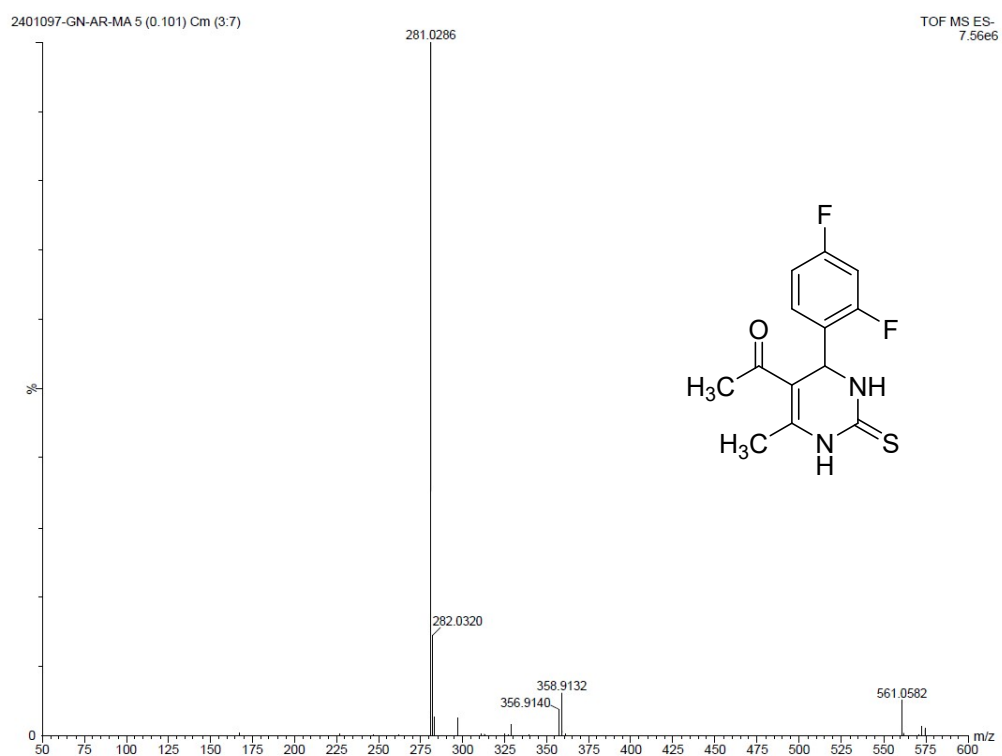
TOF MS ES-
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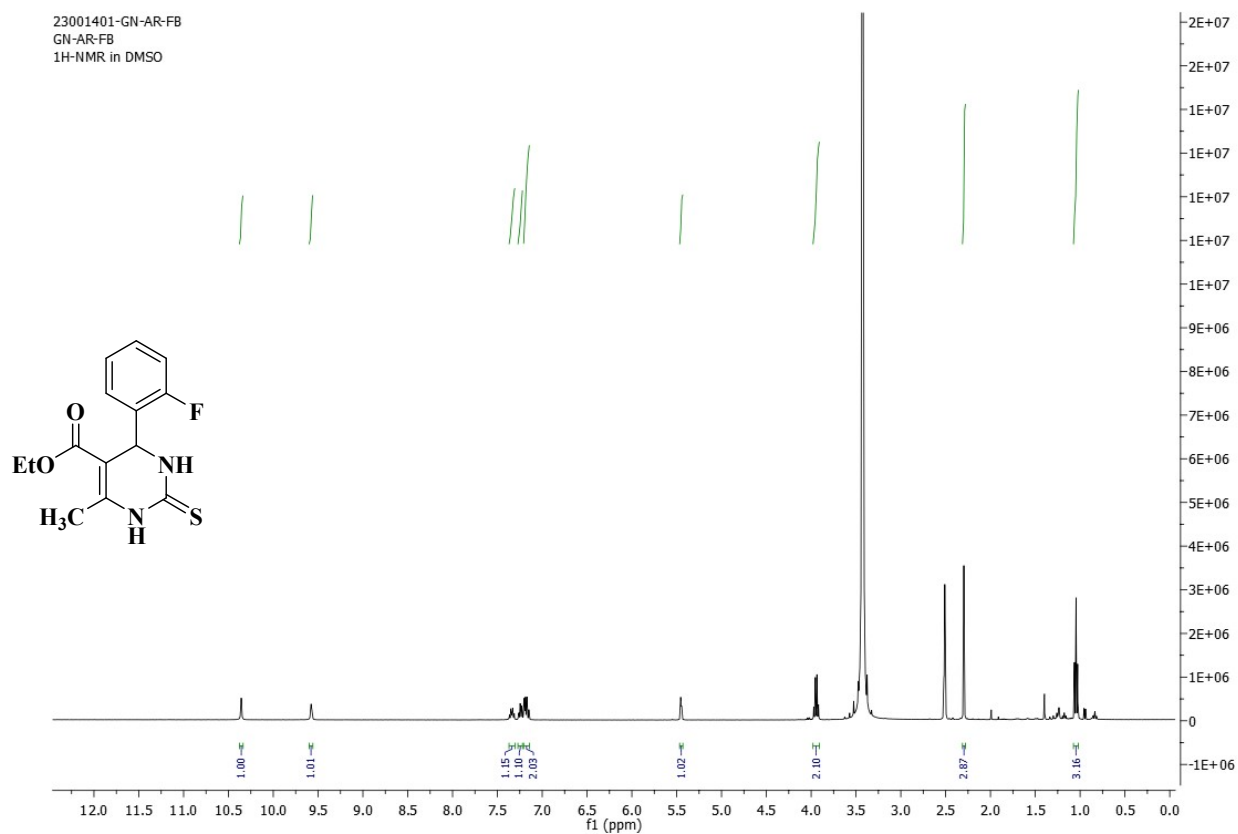
Spectrum 3: HRMS of ethyl-4-(4-bromo-3-chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate, (4d)



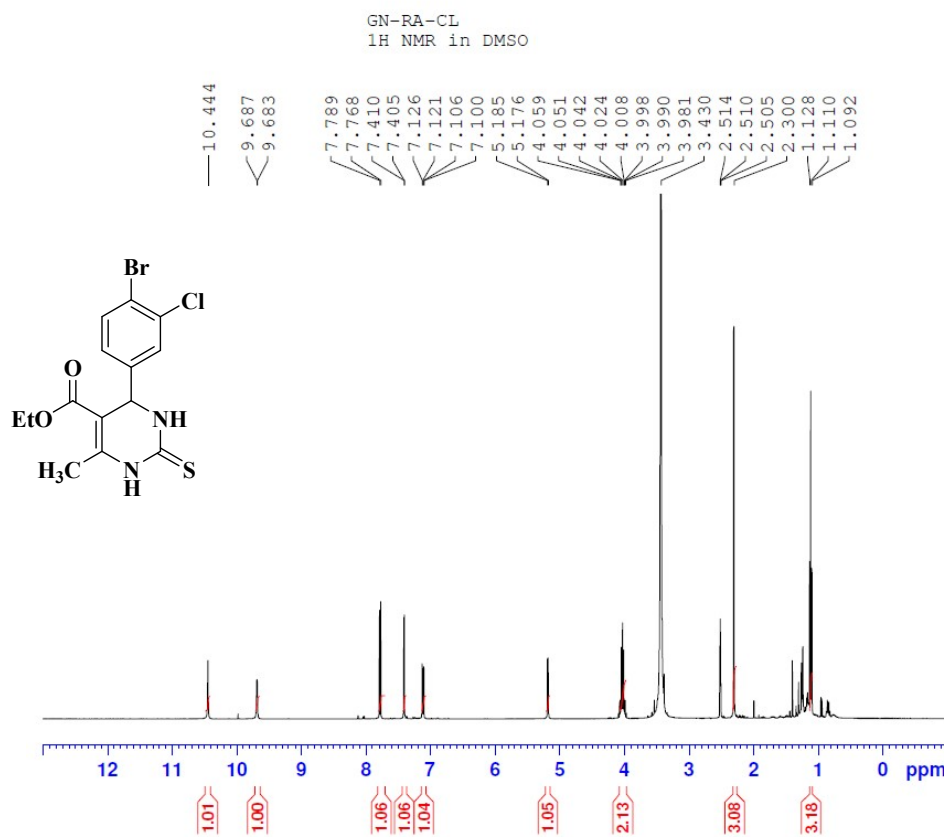
Spectrum 4: HRMS of ethyl-4-(2,4-difluorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4c)



Spectrum 5: HRMS of 1-(4-(2,4-difluorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethan-1-one,(4f)



Spectrum 6: ¹H NMR of Ethyl 4-(2-fluorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4b)

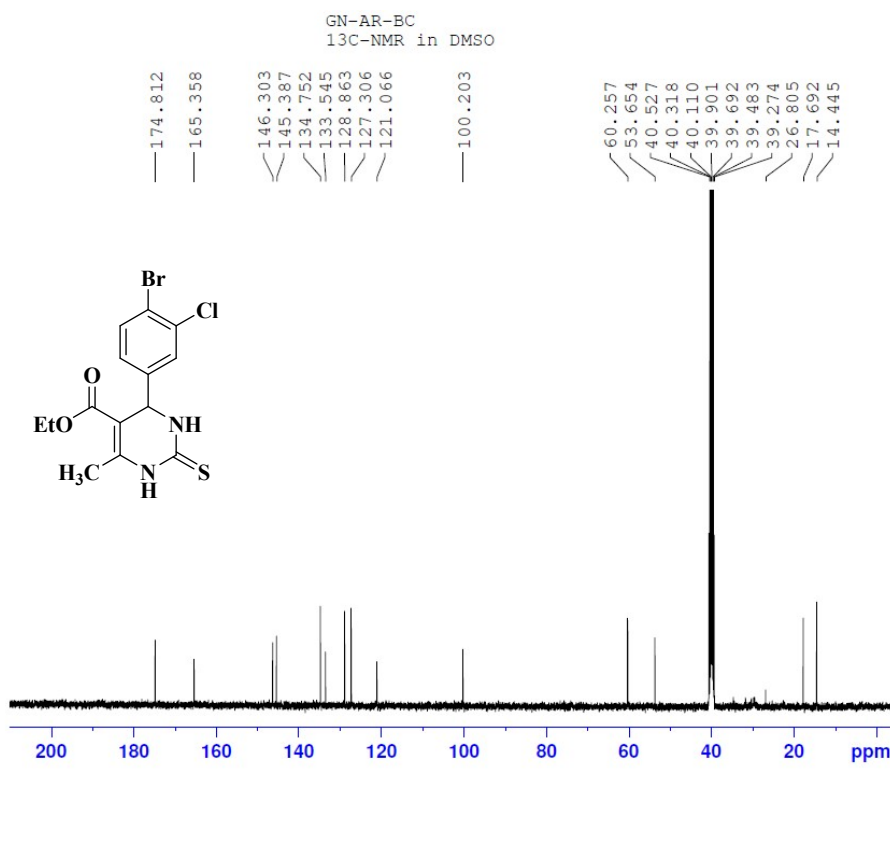


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PROCNO 1

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TE 296.9 K
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NUC1 1H
PO 4.67 usec
P1 14.00 usec
PLW1 11.28999996 W

F2 - Processing parameters
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Spectrum 7: ¹H NMR of ethyl-4-(4-bromo-3-chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4d)

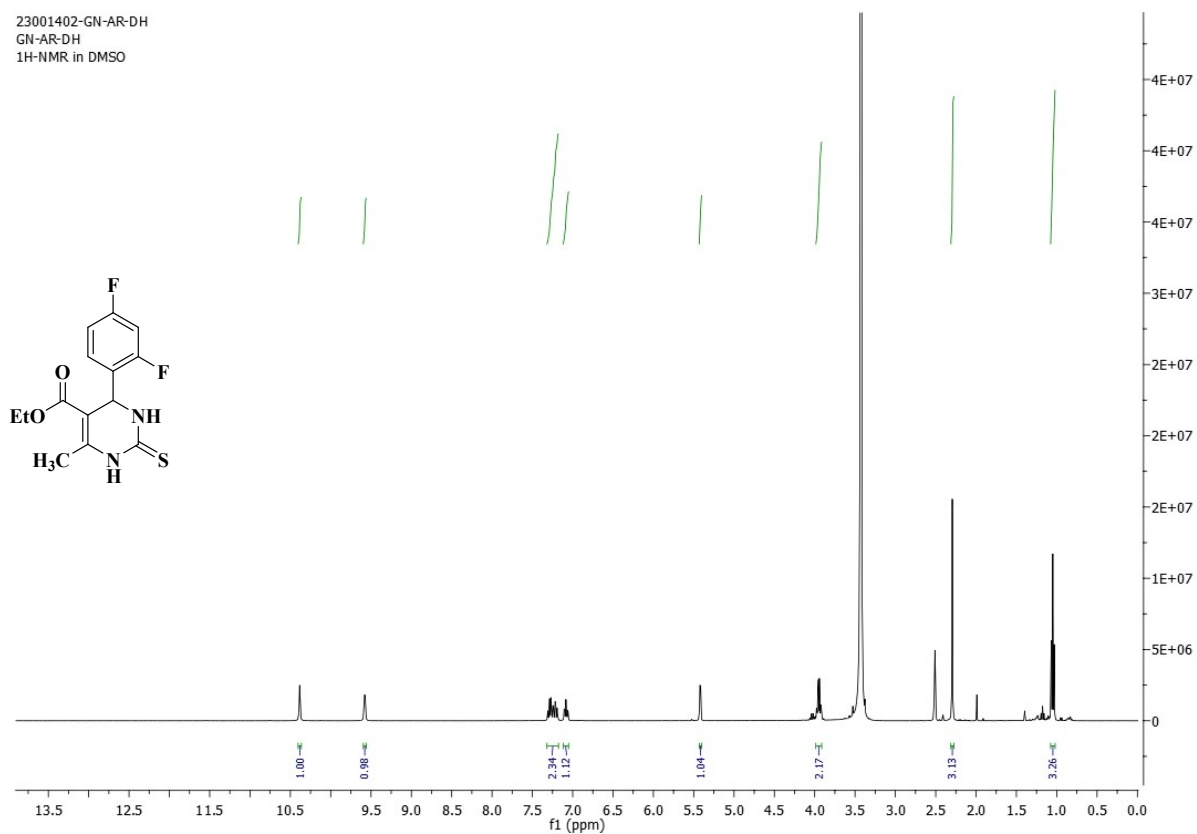


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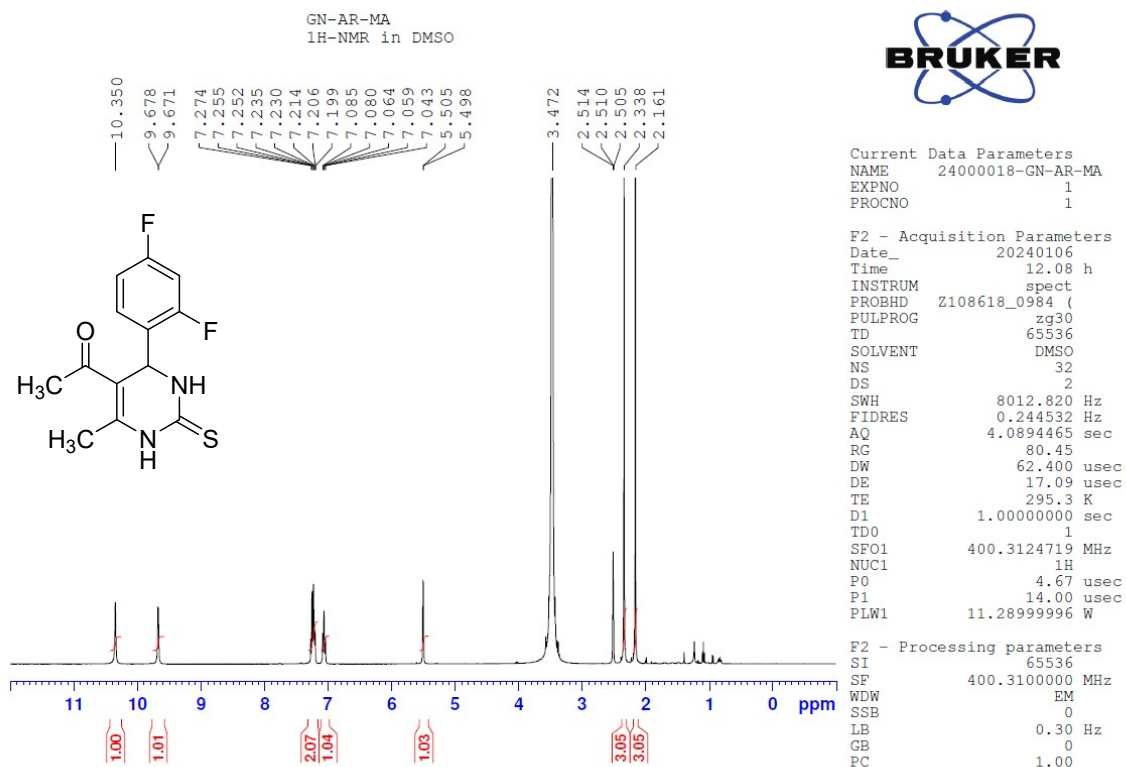
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PLW2 11.28999996 W
PLW12 0.27318001 W
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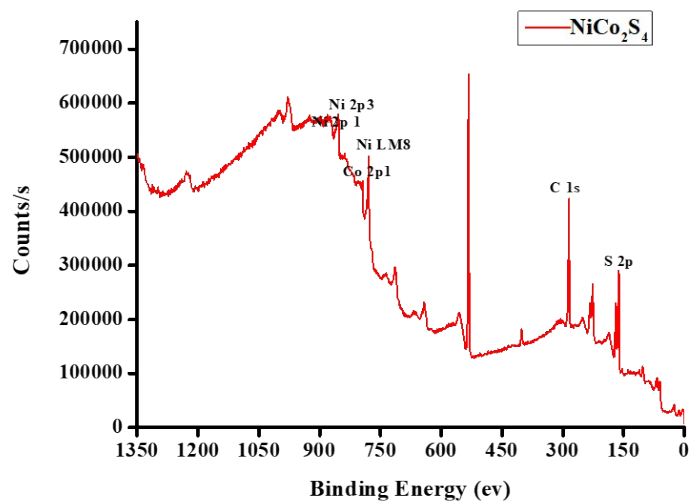
Spectrum 8: ^{13}C NMR of ethyl-4-(4-bromo-3-chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4d)



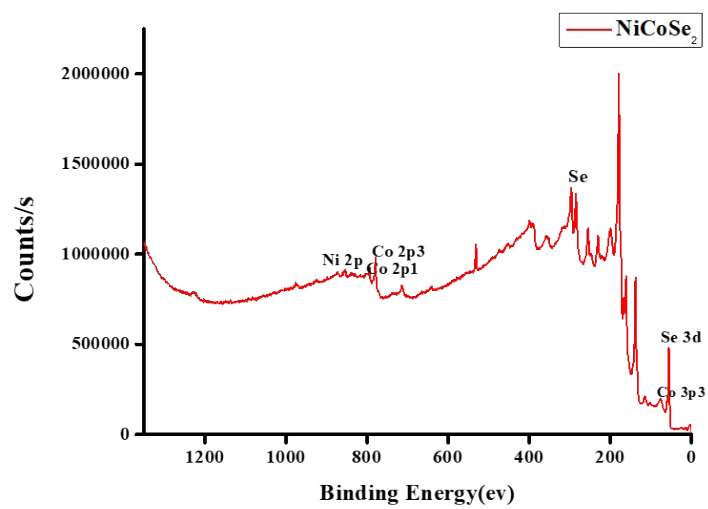
Spectrum 9: ^1H NMR of ethyl-4-(2,4-difluorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-thioxopyrimidine-5-carboxylate, (4c)



Spectrum 10: ^1H NMR of 1-(4-(2,4-difluorophenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidin-5-yl)ethan-1-one,(4f)



XPS survey spectrum for NiCo_2S_4 .



XPS survey spectrum for NiCoSe₂.

