

Supplementary data

Design and Synthesis of benzothiazole/thiophene-4*H*-chromene hybrids

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India.

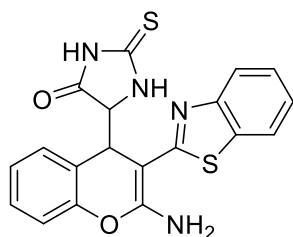
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Experimental section

General information: All chemicals were reagent grade purchased from Sigma Aldrich, Merck and Alfa Aesar used without purification. The reactions were monitored by thin layer chromatography (TLC) on pre-coated Aluminium plate of silica gel G/UV-254 of 0.25 mm thickness (Merck 60 F-254), spot were visualised under short UV light. NMR spectra were recorded on a Bruker Avance-II 400FT spectrometer at 400 MHz (¹H) and 100(¹³C) IN DMSO using TMS as an internal reference. Mass spectra were recorded on a Water UPLC-TQD mass spectrometer. Melting points were determined by open glass capillary method and were uncorrected.

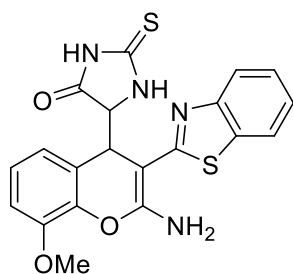
4. General procedure for synthesis of 5-(2-amino-3-(benzo[d]thiazol-2-yl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one derivatives. To a stirred solution of ethanol were added a mixture of thiohydantoin (1.0equiv), benzothiazole acetonitrile (1.2equiv) and salicylaldehyde (1.0equiv) derivatives at room temperature with vigorous stirring for appropriate time (scheme 2). The precipitate was filtered, washed with ethanol 5ml x2. The product were obtained uncontaminated by TLC and spectral techniques.

4a. 5-(2-amino-3-(benzo[d]thiazol-2-yl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one:



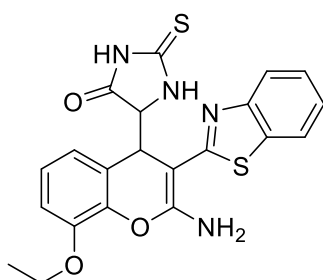
Pale yellow solid, yield 95%; m.p.=248-249°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.18(s,1H,NH), 10.37(s,1H,NH), 8.56(s,2H,NH₂), 7.96(d, J=7.6Hz, 1H), 7.78(d, J=8.0, Hz, 1H), 7.42-7.32(m,3H), 7.24-7.20(m, 1H), 7.15-7.12(m,1H), 7.07(d, J=8.4Hz, 1H), 4.40(d, J=3.2Hz, 1H), 4.17(d, J=2.8Hz, 1H); ¹³CNMR (DMSO-d₆, 100 MHz)δ(ppm)=182.4, 174.0, 167.9, 157.5, 153.4, 149.4, 131.0, 129.0, 128.7, 126.1, 123.8, 122.5, 121.4, 119.7, 118.6, 115.7, 74.2, 63.8; HR-MS m/z: calcd for C₁₉H₁₄N₄O₂S₂ [M+H]⁺:395.0631 ; found:395.0634

4b. 5-(2-amino-3-(benzo[d]thiazol-2-yl)-8-methoxy-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one



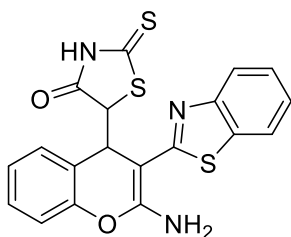
Yellow solid, yield 87%; m.p.=265-266°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.56(s, 1H,NH), 10.27(s,1H,NH), 8.57(s, 2H,NH₂),7.97(q, J=4.0,7.2Hz, 1H), 7.79(d, J=8.0Hz, 1H), 7.42-7.38(m, 1H), 7.24-7.20(m,1H), 7.08-7.03(m, 2H), 6.69(q, J=2.0, 4.8Hz, 1H),4.54(d, J=2Hz, 1H), 4.28(d, j=2.0Hz, 1H), 3.84(s,3H);¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=183.2, 175.0, 167.6, 157.2, 153.5, 147.0, 139.7, 131.0, 126.1, 124.0, 122.6, 121.5, 119.7, 119.7, 119.2, 111.8, 75.6, 65.9, 55.7, 48.6, 40.6.HR-MS m/z: calcd forC₂₀H₁₆N₄O₃S₂ [M+H]⁺:425.0737; found:425.0730.

4c. 5-(2-amino-3-(benzo[d]thiazol-2-yl)-8-ethoxy-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one



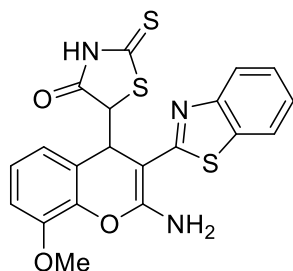
Pale yellow solid, yield 83%; m.p.=256-257°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.55(s,1H,NH), 10.28(s,1H,NH), 8.52(s,2H, NH₂), 7.97(d, J=7.6Hz, 1H), 7.79(d, J=8.0Hz, 1H), 7.42-7.38(m,1H), 7.24-7.20(m, 1H), 7.05-7.00(m, 2H), 6.68(q, J=2.8,3.6Hz, 1H), 4.54(d, J=1.6Hz, 1H), 4.28(d, J=2.0Hz, 1H), 4.11(q, J=6.8,3.6Hz, 2H), 1.37(t, J=6.8,6.8Hz, 3H);¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=183.1, 175.0, 1167.6, 157.2, 153.5, 146.1, 140.0, 131.0, 126.1, 124.0, 122.6, 121.5, 119.7, 119.7, 119.2, 113.0, 75.7, 66.0, 64.2, 40.7, 14.7.HR-MS m/z: calcd for C₂₁H₁₈N₄O₃S₂ [M+H]⁺:439.0893;found:439.0899.

4d. 5-(2-amino-3-(benzo[d]thiazol-2-yl)-4H-chromen-4-yl)-2-thioxothiazolidin-4-one



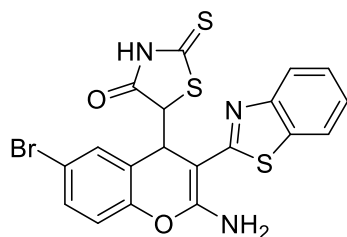
Yellow solid, yield 88%; m.p.=240-241°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=8.42(s,1H,NH₂), 7.98(d, J=7.6Hz, 1H), 7.77(d, J=8.0Hz, 1H), 7.41-7.37(m, 1H), 7.35-7.27(m, 1H), 7.24(t, J=0.8,7.2Hz, 1H), 7.21-7.17(m, 1H), 7.11-7.06(m, 2H), 4.81(d, J=3.2Hz, 1H), 4.61(d, J=2.8Hz, 1H);¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=211.8, 188.9, 167.8, 156.5, 153.3, 150.4, 131.0, 128.6, 126.0, 124.0, 122.6, 1215, 120.4, 119.8, 115.4, 78.5, 66.2, 44.3.HR-MS m/z: calcd for C₁₉H₁₃N₃O₂S₃ [M+H]⁺:412.0243; found:412.0243.

4e. 5-(2-amino-3-(benzo[d]thiazol-2-yl)-8-methoxy-4H-chromen-4-yl)-2-thioxothiazolidin-4-one



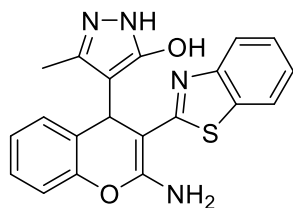
Yellow solid, yield 85%; m.p.=253-254°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=13.17(s,1H,NH), 8.59(s,2H,NH₂), 7.99(d, J=7.6Hz,1H), 7.80(d, J=8.0Hz, 1H), 7.43-7.39(m,1H), 7.27-7.22(m, 1H), 7.13-7.06(m, 2H),6.73(q, J=1.6,5.6Hz, 1H),5.28(d, J=3.2Hz, 1H), 4.70(d, J=2.8Hz, 1H), 3.85(s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=176.9, 167.2, 156.7, 153.3, 147.0, 139.7, 131.5, 126.7, 124.4, 122.9, 121.6, 120.0, 119.9, 119.2, 112.1, 76.5, 63.0, 55.7, 48.6, 40.5. HR-MS m/z: calcd for C₂₀H₁₅N₃O₃S₃[M+H]⁺:442.0348; found:442.0348.

4f. 5-(2-amino-3-(benzo[d]thiazol-2-yl)-6-bromo-4H-chromen-4-yl)-2-thioxothiazolidin-4-one



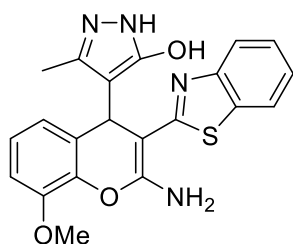
Yellow solid, yield 70%; m.p.=272-273°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=8.43(s,2H,NH₂), 7.98(d, J=7.6Hz, 1H), 7.78(d, J=7.6Hz,1H), 7.80-7.40(m, 1H), 7.38(d, J=1.2Hz, 1H), 7.30(d, J=2.4Hz, 1H), 7.25-7.21(m, 1H), 7.06(d, J=8.8Hz, 1H), 4.82(d, J=3.2Hz, 1H), 4.58(d, J=2.8Hz, 1H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=211.8, 189.1, 167.5, 156.1, 153.2, 149.8, 131.3, 131.1, 131.0, 126.1, 122.9, 122.7, 121.5, 119.9, 117.7, 115.4, 78.0, 66.3,HR-MS m/z: calcd for C₁₉H₁₂BrN₃O₂S₃ [M+H]⁺: 489.9348; found:489.9344.

4g. 4-(2-amino-3-(benzo[d]thiazol-2-yl)-4H-chromen-4-yl)-3-methyl-1H-pyrazol-5-ol



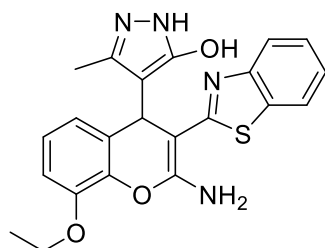
White solid, yield 93%; m.p.=245-246°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=10.47(s, 2H, NH,OH), 8.37(s, 2H, NH₂), 7.87(d, J=8.0Hz, 1H), 7.74(d, J=8.4Hz, 1H), 7.34(t, J=7.2, 7.6Hz, 1H), 7.29(d, J=7.6Hz, 1H), 7.22-7.14(m, 2H), 7.07(q, J=7.2, 6.4Hz, 2H), 4.88(s, 1H), 2.04(s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=169.2, 159.4, 155.5, 152.9, 147.9, 136.1, 131.7, 129.9, 127.4, 125.7, 125.4, 124.2, 122.3, 121.1, 119.6, 115.4, 105.3, 78.14, 31.0, 10.1. HR-MS m/z: calcd for C₂₀H₁₆N₄O₂S [M+H]⁺: 377.1067; found: 377.1069.

4h. 4-(2-amino-3-(benzo[d]thiazol-2-yl)-8-methoxy-4H-chromen-4-yl)-3-methyl-1H-pyrazol-5-ol



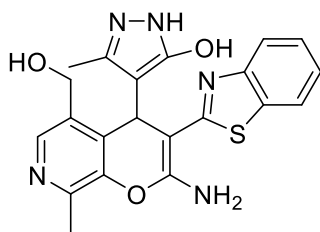
Pink solid, yield 83%; m.p.=263-264°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=10.45(s, 2H, NH,OH), 8.41(s, 2H, NH₂), 7.86(d, J=8 Hz, 1H), 7.74(d, J=8Hz, 1H), 7.34(t, J=7.6, 7.6Hz, 1H), 7.15(t, J=7.6, 7.6Hz, 1H), 7.00(t, J=8.0, 7.6Hz, 1H), 6.87(q, J=8.4, 5.2Hz, 2H), 4.86(s, 1H), 3.83(s, 3H), 2.03(s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=169.2, 159.4, 155.5, 152.9, 146.7, 137.3, 136.1, 131.7, 126.1, 125.7, 123.8, 122.2, 121.1, 120.3, 119.6, 109.8, 105.2, 78.0, 55.6, 31.0, 10.1. HR-MS m/z: calcd for C₂₁H₁₈N₄O₃S [M+H]⁺: 407.1172; found: 407.1181.

4i. 4-(2-amino-3-(benzo[d]thiazol-2-yl)-8-ethoxy-4H-chromen-4-yl)-3-methyl-1H-pyrazol-5-ol



Pink solid, yield 78%; m.p.=218-219°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=10.44(s, 2H, NH,OH), 8.37(s, 2H, NH₂), 7.86(d, J=7.6Hz, 1H), 7.74(d, J=8.0Hz, 1H), 7.36-7.32(m, 1H), 7.18-7.14(m, 1H), 6.97(t, J=10.8, 4.8Hz, 1H), 6.85(t, J=9.6, 8.4Hz, 2H), 4.85(s, 1H), 4.10(q, J=7.2, 6.8Hz, 2H), 2.03(s, 3H), 1.38(t, J=7.2, 6.8Hz, 3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=169.2, 159.4, 155.5, 152.9, 145.9, 137.6, 136.1, 131.7, 126.2, 125.7, 13.8, 122.2, 121.1, 120.3, 119.5, 111.0, 105.3, 78.0, 64.0, 31.1, 14.7, 10.1. HR-MS m/z: calcd for C₂₂H₂₀N₄O₃S [M+H]⁺: 421.1329 ; found: 421.1334.

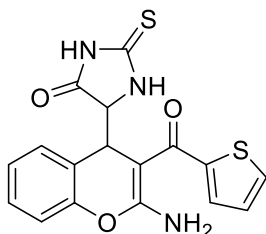
4j. 4-(2-amino-3-(benzo[d]thiazol-2-yl)-5-(hydroxymethyl)-8-methyl-4H-pyrano[2,3-c]pyridin-4-yl)-3-methyl-1H-pyrazol-5-ol



Pale yellow solid, yield 91%; m.p.=260-261°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=10.97(s, 1H,NH), 9.87(s, 1H, OH), 8.35(s, 2H, NH₂), 8.16(s, 1H), 7.89(d, J=8.0, 1H), 7.74(d, J=8.0Hz,1H), 7.35(t, J=7.6,7.6Hz, 1H), 7.18(t, J=7.6,7.2Hz, 1H), 5.31(s, 1H, OH), 4.91(s, 1H), 4.70(d, J=14Hz, 1H), 4.39(d, J=14Hz, 1H), 2.53(s, 3H),2.15(s, 3H);¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=169.0, 159.3, 155.3, 152.9, 144.2, 143.5, 142.3, 136.7, 132.6, 131.5, 129.1, 125.8, 122.4, 121.1, 119.6, 130.0, 78.8, 58.0, 27.8, 18.7 , 10.2.HR-MS m/z: calcd forC₂₁H₁₉N₅O₃S [M+H]⁺: 422.1281; found:422.1289.

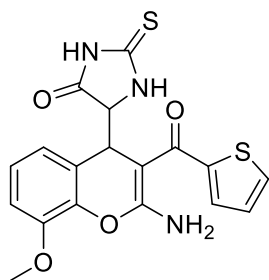
7. General procedure for synthesis of 5-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one derivatives. To a stirred solution of ethanol and water (1:1) ratio were added a mixture of 2-thenoyl acetonitrile(3-oxo-3-(thiophen-2-yl)propanenitrile) (1.2 equiv), thiohydantoin(1.0 equiv) and salicylaldehyde(1.0 equiv) derivatives at ambient temperature with vigorous stirring for appropriate time (scheme 5). The precipitate was filtered, washed with ethanol and water (1:1) ratio 10x3. The product were obtained, uncontaminated by TLC and spectral techniques.

7a. 5-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one



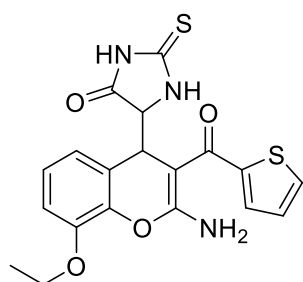
White solid, yield 92%; m.p.=233-234°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.49(s,1H,NH), 10.21(s,1H,NH), 9.37(s,2H,NH₂), 7.78(d, J=4.8Hz,1H), 7.72(d, J=3.2Hz, 1H), 7.34-7.30(m,1H), 7.20(t, J=4.0,4.4Hz, 1H), 7.14-7.07(m, 3H), 4.90(d, J=0.8Hz,1H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=183.1, 180.3, 174.8, 165.0, 150.2, 146.2, 130.4, 1290, 128.2, 128.0, 127.9, 124.4, 120.0, 115.6, 83.90, 68.33, 37.95, HR-MS m/z: calcd for C₁₇H₁₃N₃O₃S₂ [M+H]⁺: 372.0471; found: 372.048.

7b. 5-(2-amino-8-methoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one



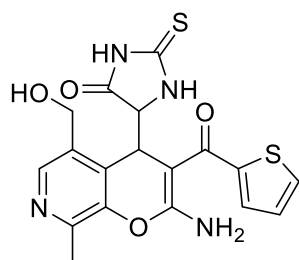
Yellow solid, yield 90%; m.p.=268-269°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.50(s,1H,NH), 10.21(s,1H,NH), 9.42(s,2H,NH₂), 7.77(d, J=4.4Hz,1H), 7.70(d, J=9.6Hz,1H), 7.20(t, J=4.4,4.0Hz,1H), 7.04(d, J=6.0Hz,2H), 6.65(d, J=5.6Hz,1H), 4.89(d, J=7.2Hz, 1H), 4.32(d, J=8.0Hz, 1H), 3.83(s,3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=183.1, 180.3, 174.8, 164.0, 146.8, 146.2, 139.4, 130.5, 128.0, 127.9, 124.3, 121.0, 119.4, 111.9, 83.7, 68.3, 55.9, 37.8. : HR-MS m/z: calcd for C₁₈H₁₅N₃O₄S₂ [M+H]⁺: 402.0577; found: 402.0584.

7c. 5-(2-amino-8-ethoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one



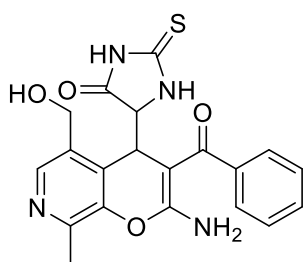
Yellow solid, yield 80%; m.p.=262-263°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.49(s,1H,NH), 10.22(s,1H,NH), 9.41(s,2H,NH₂), 7.77(d, J=4.8Hz, 1H), 7.71(d, J=3.6Hz, 1H), 7.19(t, J=4.4,4.4Hz, 1H), 7.01(t, J=2.4,3.2Hz, 2H), 6.64(q, J=3.2,2.4Hz, 1H), 4.89(d, J=1.6Hz, 1H), 4.32(s, 1H), 4.10(q, J=7.2,6.8Hz, 2H), 1.35(t, J=6.8Hz, 3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=183.1, 180.2, 174.8, 164.8, 146.3, 146.0, 139.7, 130.5, 128.0, 127.9, 124.3, 121.0, 119.4, 113.3, 83.8, 68.4, 64.3, 37.9, 25.5, 14.6. HR-MS m/z: calcdfor C₁₉H₁₇N₃O₄S₂ [M+H]⁺: 416.0733; found: 416.0743.

7d. 5-(2-amino-5-(hydroxymethyl)-8-methyl-3-(thiophene-2-carbonyl)-4H-pyrano[2,3-c]pyridin-4-yl)-2-thioxoimidazolidin-4-one



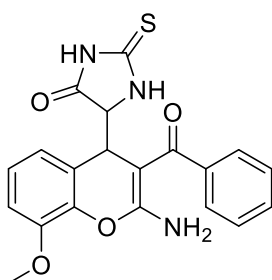
Pink solid, yield 89%; m.p.=259-260°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.50(s,1H,NH), 9.86(s,1H,NH), 8.87(s,2H,NH₂), 8.25(s,1H), 7.69(t, J=4.4,0.8Hz,1H), 7.52(d, J=3.2Hz,1H), 7.06(q, J=4.0,0.8Hz, 1H), 5.46(d, J=4.8Hz,1H), 5.25(s, 1H), 4.66(d, J=4.8Hz, 1H), 4.61(d,J=4.0Hz, 1H), 4.36(d, J=0.8Hz, 1H), 2.51(s,3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=183.4, 181.9, 173.5, 164.8, 145.8, 145.7, 145.4, 143.9, 131.4, 129.9, 129.8, 128.4, 127.2, 79.6, 66.6, 58.6, 34.8, 18.6. HR-MS m/z: calcd for C₁₈H₁₆N₄O₄S₂ [M+H]⁺: 417.0686; found: 417.0695.

7e. 5-(2-amino-3-benzoyl-5-(hydroxymethyl)-8-methyl-4H-pyrano[2,3-c]pyridin-4-yl)-2-thioxoimidazolidin-4-one



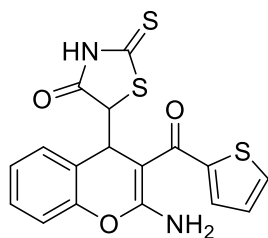
Pale yellow solid, yield 91%; m.p.=238-239°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.50(s,1H,NH), 9.76(s,1H,NH), 8.80(s, 2H,NH₂), 8.23(s, 1H), 7.37-7.30(m, 5H), 5.38(t, J=4.8,4.4Hz, 1H), 4.72(d, J=2.8Hz, 1H), 4.52(d, J=3.6Hz, 2H), 4.29(s, 1H), 2.52(s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)= 191.9, 183.4, 173.4, 164.8, 146.0, 145.9, 143.7, 140.5, 131.2, 130.3, 129.6, 127.9, 127.8, 79.5, 66.5, 58.5, 35.5, 18.7. HR-MS m/z: calcd for C₂₀H₁₈N₄O₄S [M+H]⁺: 411.1122; found: 411.1119.

7f. 5-(2-amino-3-benzoyl-8-methoxy-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one



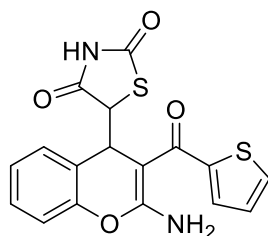
Yellow solid, yield 83%; m.p.=214-215°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=11.35(s,1H,NH), 9.95(s, 1H,NH), 9.13(s, 2H,NH₂), 7.45-7.42(m, 3H), 7.36(q, J=3.6,3.6Hz,2H), 7.02(t, J=0.8,4.4Hz,2H), 6.54(t, J=4.4,4.8Hz, 1H), 4.29(d, J=2.8Hz, 1H), 3.9(d, J=1.6Hz, 1H), 3.83(s,3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=192.1, 183.0, 174.1, 164.1, 146.9, 141.5, 139.7, 129.0, 128.4, 126.2, 124.2, 121.4, 119.5, 111.8, 82.7, 68.4, 55.8, 38.4. HR-MS m/z: calcd for C₂₀H₁₇N₃O₄S [M+H]⁺: 396.1013; found: 396.1021.

7g. 5-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxothiazolidin-4-one



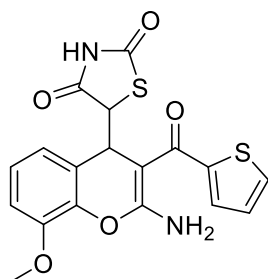
Yellow solid, yield 86%; m.p.=208-209°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=13.07(s,1H,NH), 9.28(s, 2H,NH₂), 7.81(t, J=5.2, 4.4Hz, 2H), 7.38-7.35(m, 1H), 7.23-7.13(m, 4H)5.29(d, J=3.2Hz, 1H), 4.95(d, J=3.2Hz, 1H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=203.1, 180.9, 176.6, 164.1, 150.0, 145.5, 130.8, 129.4, 128.4, 128.2, 128.0, 124.7, 120.2, 115.8, 84.1, 65.1,38.0 HR-MS m/z: calcd for. C₁₇H₁₂N₂O₃S₃ [M+H]⁺: 389.0083; found: 389.0090.

7h. 5-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)thiazolidine-2,4-dione



White solid, yield 78%; m.p.=223-224°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=12.03(s, 1H, NH), 9.30(s, 2H, NH₂), 7.83(q, J=3.2,8.8Hz, 2H), 7.40-7.36(m, 1H), 7.23-7.14(m,4H), 5.31(d, J=2.8Hz,1H), 4.82(d, J=2.8Hz,1H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=180.8, 174.4, 171.5, 164.2, 150.2, 145.7, 130.9, 129.4, 128.4, 128.3, 128.1, 124.7, 120.0, 115.8, 84.2, 62.1, 37.8. HR-MS m/z: calcd for C₁₇H₁₂N₂O₄S₂ [M+H]⁺: 373.0311; found: 373.0322.

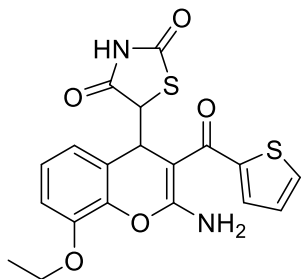
7i. 5-(2-amino-8-methoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)thiazolidine-2,4-dione



Yellow solid, yield 72%; m.p.=249-250°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=12.02(s,1H, NH), 9.36(s,2H, NH₂), 7.84-7.81(m, 2H), 7.22(q, J=4.0,5.2Hz, 1H), 7.13-7.06(m, 2H), 6.70(q, J=2.0, 5.2Hz, 1H), 5.30(d, J=3.2Hz, 1H), 4.82(d, J=3.2Hz, 1H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=180.8, 174.3, 171.5, 164.1, 146.9, 145.6, 139.3,

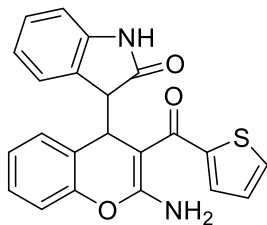
130.8, 128.3, 128.1, 124.6, 121.0, 119.4, 112.1, 84.1, 62.0, 55.7, 37.9. HR-MS m/z : calcd for $C_{18}H_{14}N_2O_5S_2$ $[M+H]^+$: 403.0417; found: 403.0426.

7j. 5-(2-amino-8-ethoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)thiazolidine-2,4-dione



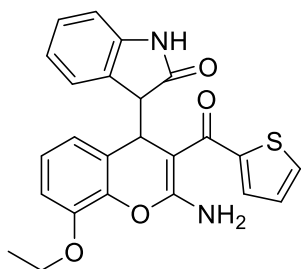
Yellow solid, yield 70%; $m.p.$ =236-237°C; 1H NMR (400 MHz, $DMSO-d_6$): δ (ppm)=12.02(s,1H,NH), 9.35(s,2H, NH_2), 7.83(q, J =3.6,4.8Hz, 2H), 7.22(q, J =4.0,1.2Hz, 1H), 7.07(t, J =4.4,2.0Hz, 2H), 6.69(q, J =2.8,3.6Hz,1H), 5.29(d, J =2.8Hz, 1H), 4.82(d, J =3.2Hz, 1H), 4.13(q, J =7.2,3.6Hz, 2H), (t, J =6.8,6.8Hz, 3H); ^{13}C NMR ($DMSO-d_6$, 100 MHz) δ (ppm)=180.0, 174.4, 171.6, 164.1, 146.1, 145.7, 139.6, 130.9, 128.3, 128.1, 124.6, 121.1, 119.5, 113.3, 84.2, 64.3, 62.1, 37.9, 14.6. HR-MS m/z : calcd for $C_{19}H_{16}N_2O_5S_2$ $[M+H]^+$: 417.0573; found: 417.0555.

7k. 3-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)indolin-2-one



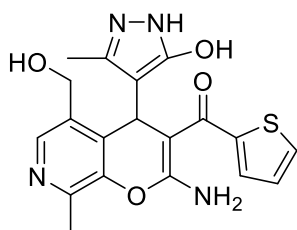
Pale yellow solid, yield 80%; $m.p.$ =256-257°C; 1H NMR (400 MHz, $DMSO-d_6$): δ (ppm)=10.41(s,1H,NH), 9.45(s, 2H, NH_2), 8.08(d, J =3.6Hz, 1H), 7.81(q, J =0.4,4.4Hz, 1H), 7.24(q, J =3.6,1.2Hz, 1H), 7.20(q, J =1.6,6.4Hz, 1H), 7.10-7.06(m,2H), 7.02-6.97(m,2H), 6.82-6.77(m,2H), 6.52(d, J =8.0Hz, 1H), 5.14(d, J =3.2Hz,1H), 3.67(d, J =3.2Hz, 1H); ^{13}C NMR ($DMSO-d_6$, 100 MHz) δ (ppm)=180.6, 176.9, 164.6, 148.9, 146.9, 142.8, 131.0, 128.4, 128.4, 127.9, 126.5, 124.1, 123.8, 121.5, 121.0, 115.1, 109.0, 85.1, 62.0, 54, 37.0, 25.5. HR-MS m/z : calcd for $C_{22}H_{16}N_2O_3S$ $[M+H]^+$: 389.0954; found: 388.0935.

7l. 3-(2-amino-8-ethoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)indolin-2-one



Yellow solid, yield 74%; m.p.=271-272°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=10.40(s,1H, NH),9.51(s,2H,NH₂),8.07(d, J=3.2Hz, 1H), 7.81(q, J=0.8,4.4Hz, 1H), 7.23(q, J=4.0,1.2Hz, 1H), 7.06(d, J=7.6Hz, 1H), 7.00(t, J=7.6,7.6Hz, 1H), 6.90(t, J=8.0,7.6Hz, 1H), 6.81-6.75(m,3H), 6.55(d, J=8.0Hz, 1H), 5.13(d, J=6.8Hz, 1H), 3.93(q, J=6.8,10.4Hz, 2H), 3.66(d, J=28Hz, 1H), 1.20(t, J=6.8,68Hz, 3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=180.6, 176.8, 164.5, 146.9, 145.5, 142.8, 138.7, 131.0, 128.4, 128.3, 127.9, 126.5, 124.0, 123.8, 122.7, 121.0, 119.6, 113.1, 109.0, 85.0, 64.3, 54.1, 37.0, 14.5. HR-MS m/z: calcd for C₂₄H₂₀N₂O₄S [M+H]⁺: 433.1217; found: 433.1225.

7m. (2-amino-4-(5-hydroxy-3-methyl-1H-pyrazol-4-yl)-5-(hydroxymethyl)-8-methyl-4H-pyrano[2,3-c]pyridin-3-yl)(thiophen-2-yl)methanone



Pink solid, yield 84%; m.p.=235-236°C; ¹H NMR (400 MHz, DMSO-d₆): δ(ppm)=10.92(s,1H,OH), 9.46(s, 1H,NH), 8.90(s, 2H,NH₂), 8.11(s,1H), 7.71(d, J=4.8Hz, 1H), 7.59(d, J=3.6Hz, 1H), 7.12(t, J=4.4, 4.0Hz, 1H), 5.54(s,1H), 5.29(s, 1H), 4.48(q, J=5.2,8.0Hz, 1H), 4.30(d, J=11.6Hz, 1H), 1.52(s,3H); ¹³C NMR (DMSO-d₆, 100 MHz)δ(ppm)=183.5, 163.2, 144.9, 144.3, 144.2, 142.6, 132.2, 131.1, 129.0, 127.8, 127.2, 104.6, 86.4, 58.1, 56.0, 25.9, 18.5,18.5, 8.7. HR-MS m/z: calcd for C₁₉H₁₈N₄O₄S [M+H]⁺: 399.1122; found: 399.1132.

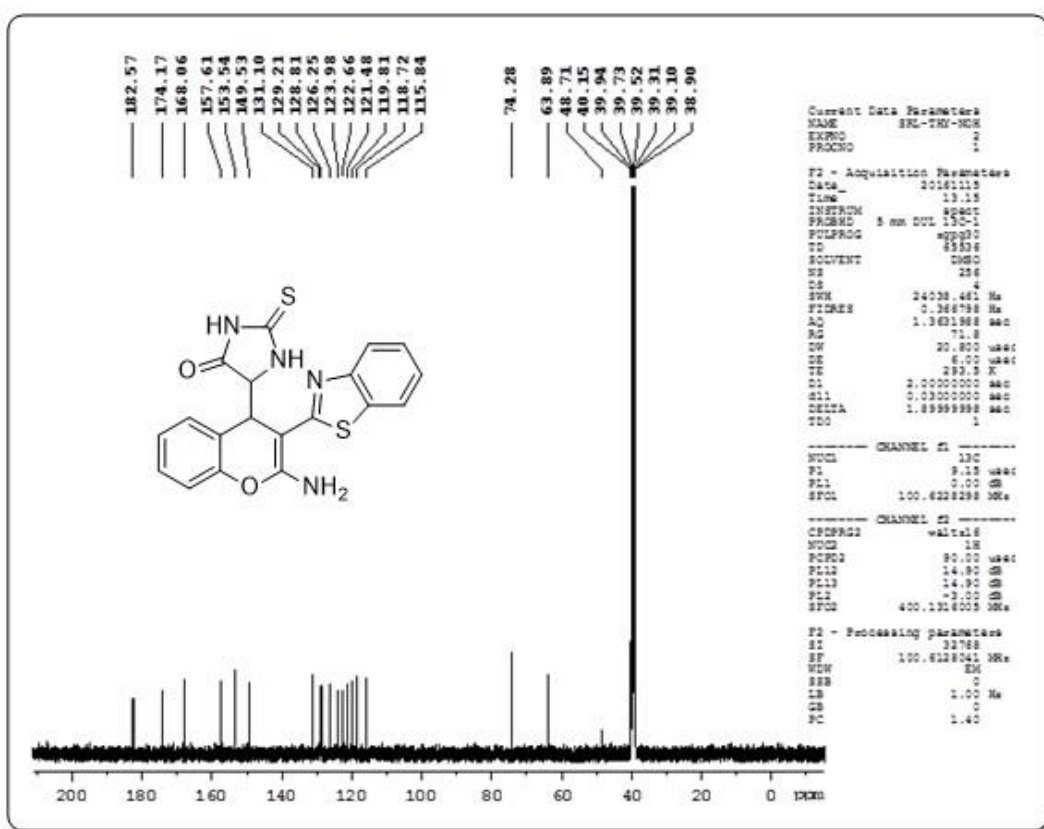
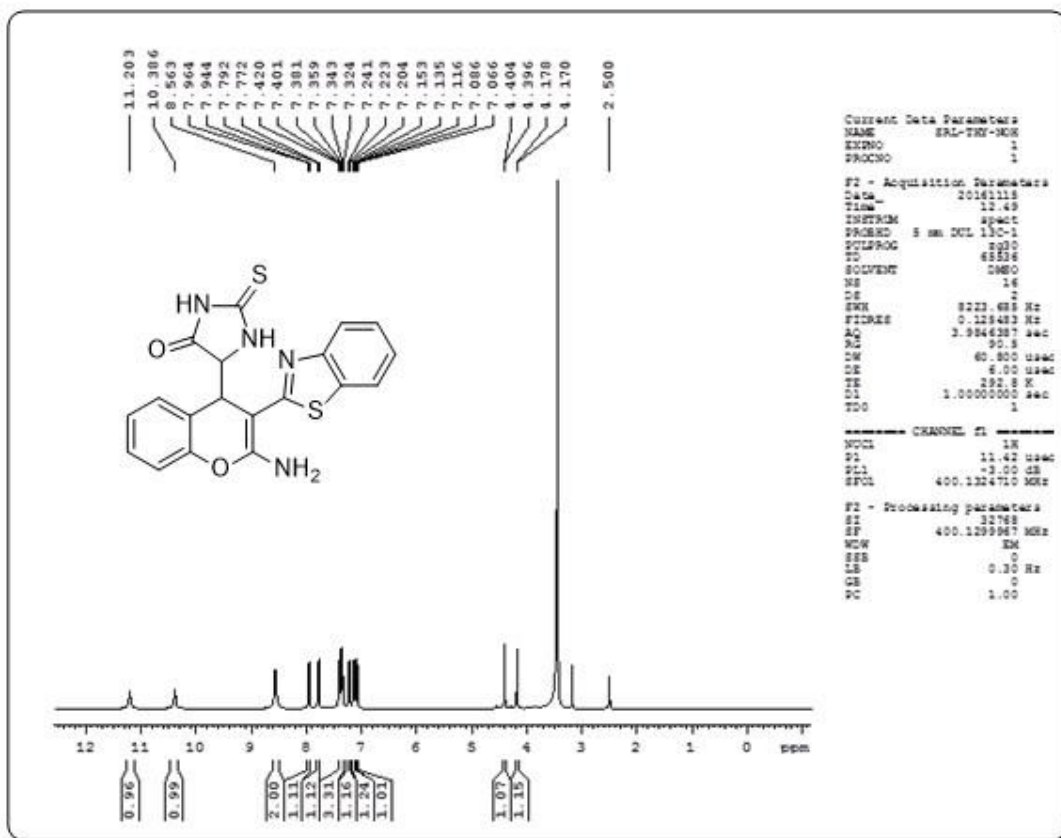


Fig 5: ^1H , ^{13}C spectrum of 5-(2-amino-3-(benzo[d]thiazol-2-yl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one **4a**

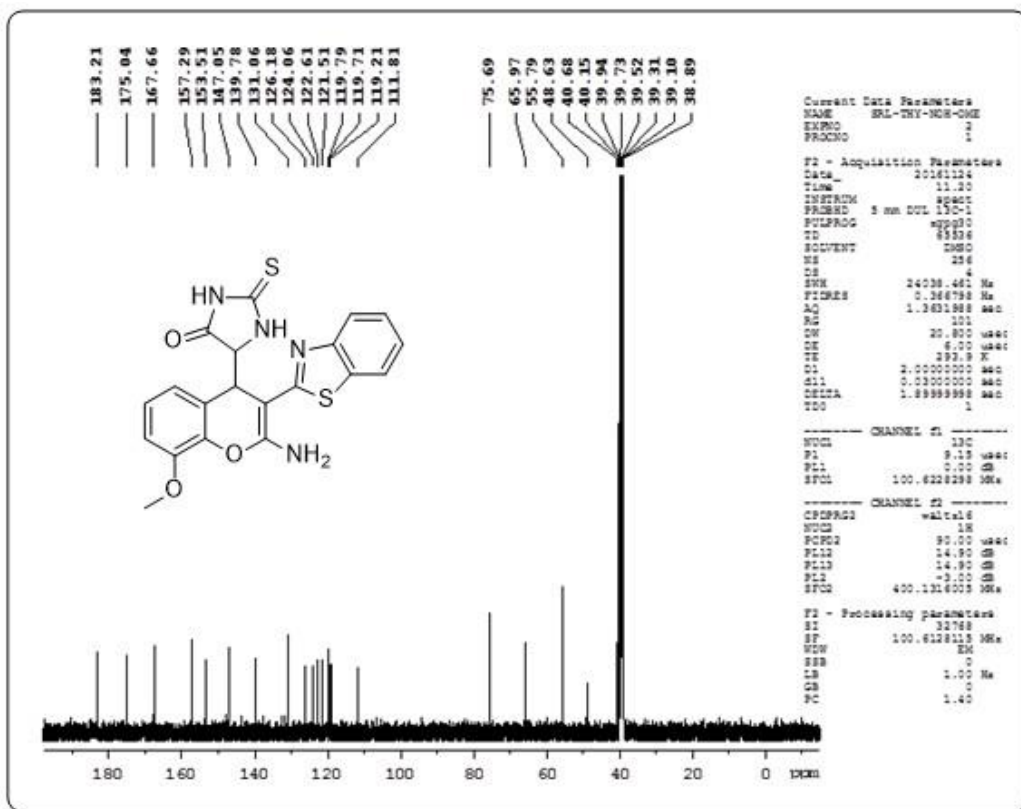
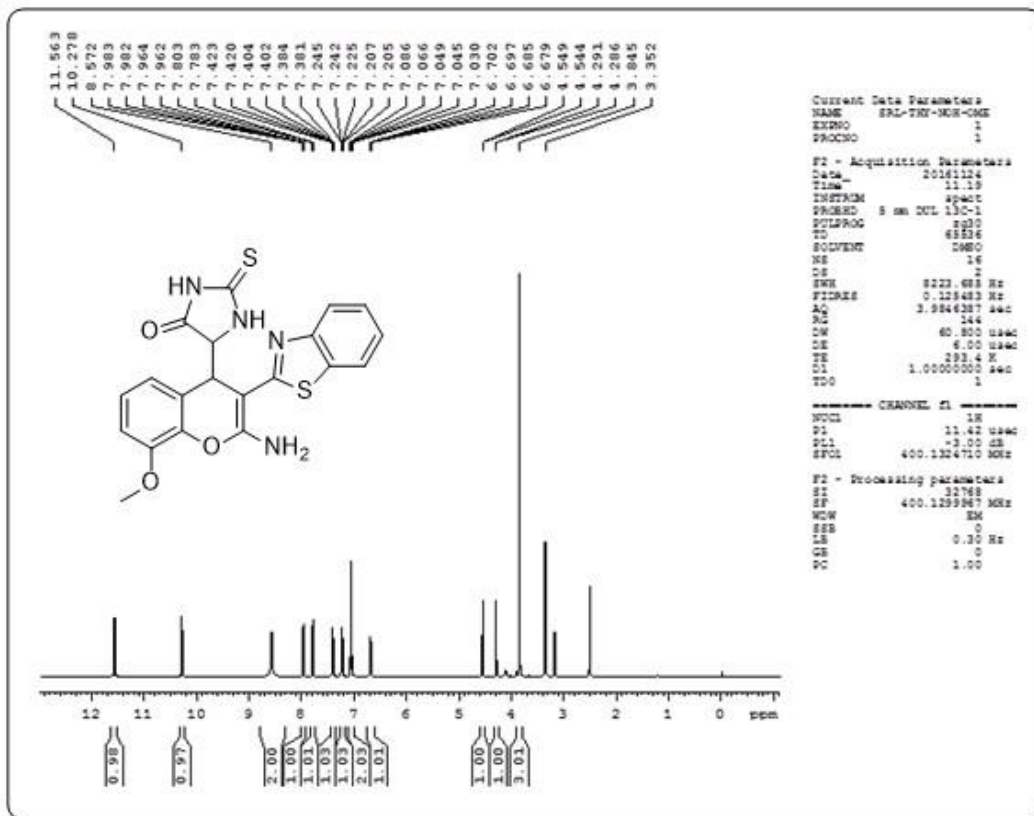


Fig 6: ^1H , ^{13}C spectrum of 5-(2-amino-3-(benzo[d]thiazol-2-yl)-8-methoxy-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one **4b**

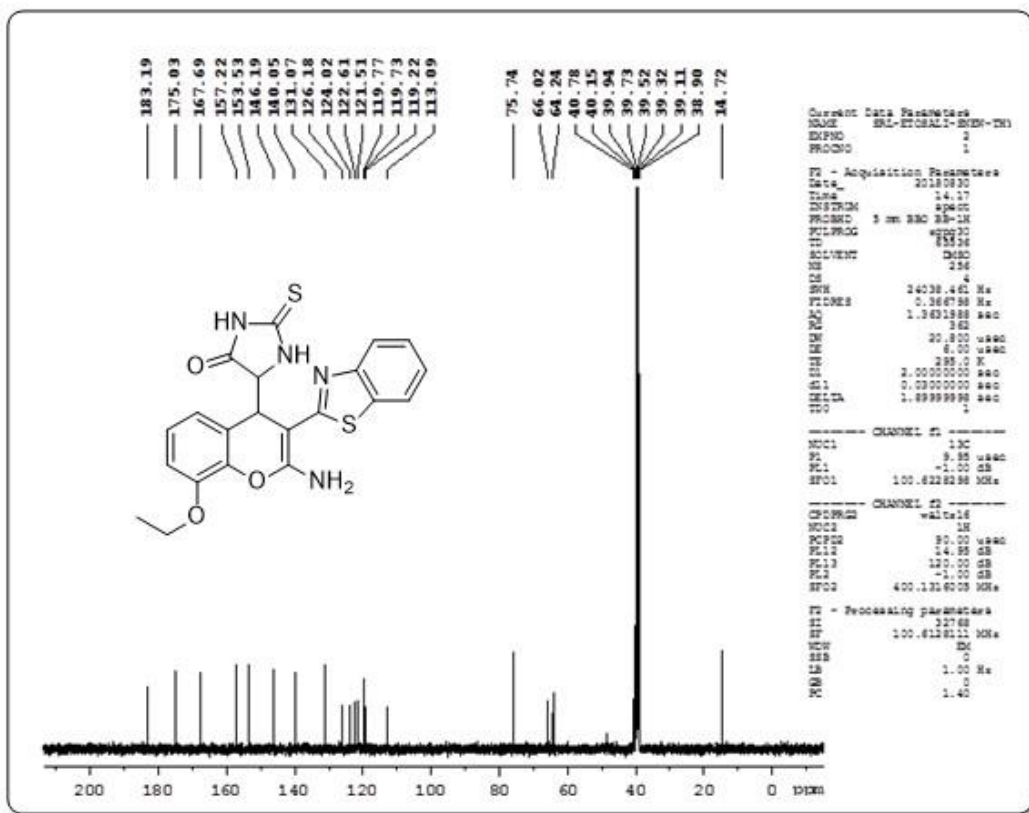
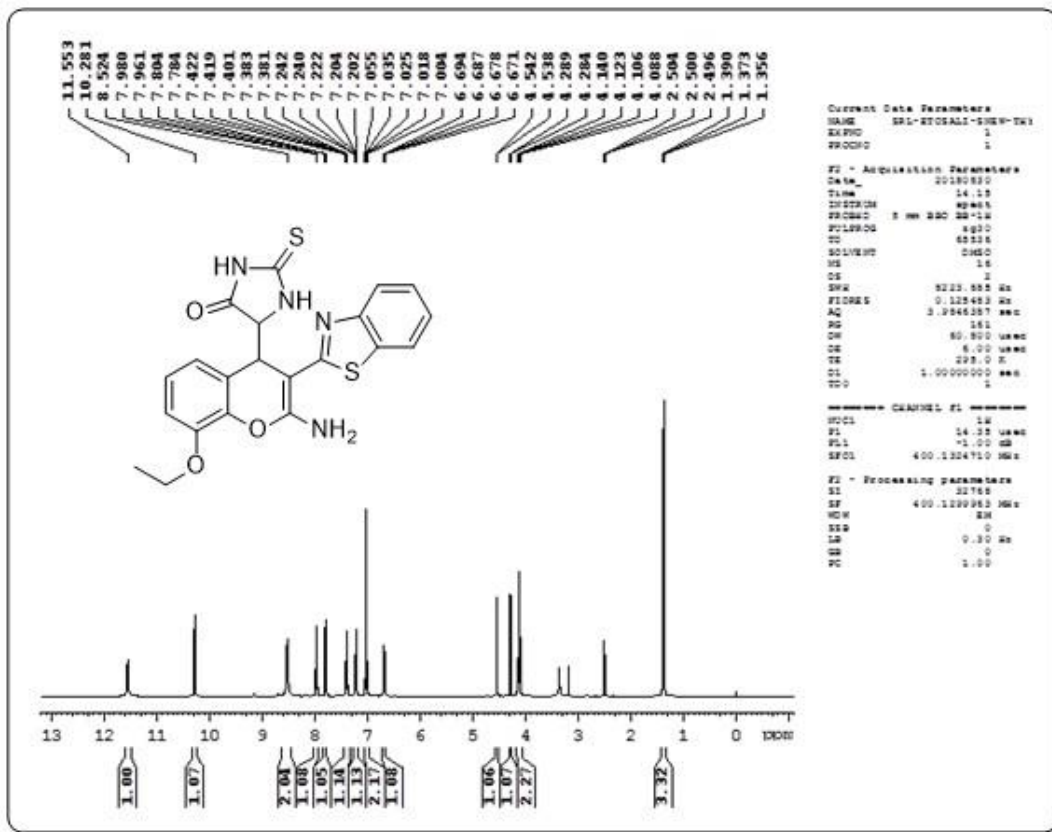


Fig 7: ^1H , ^{13}C spectrum of 5-(2-amino-3-(benzo[d]thiazol-2-yl)-8-ethoxy-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one **4c**

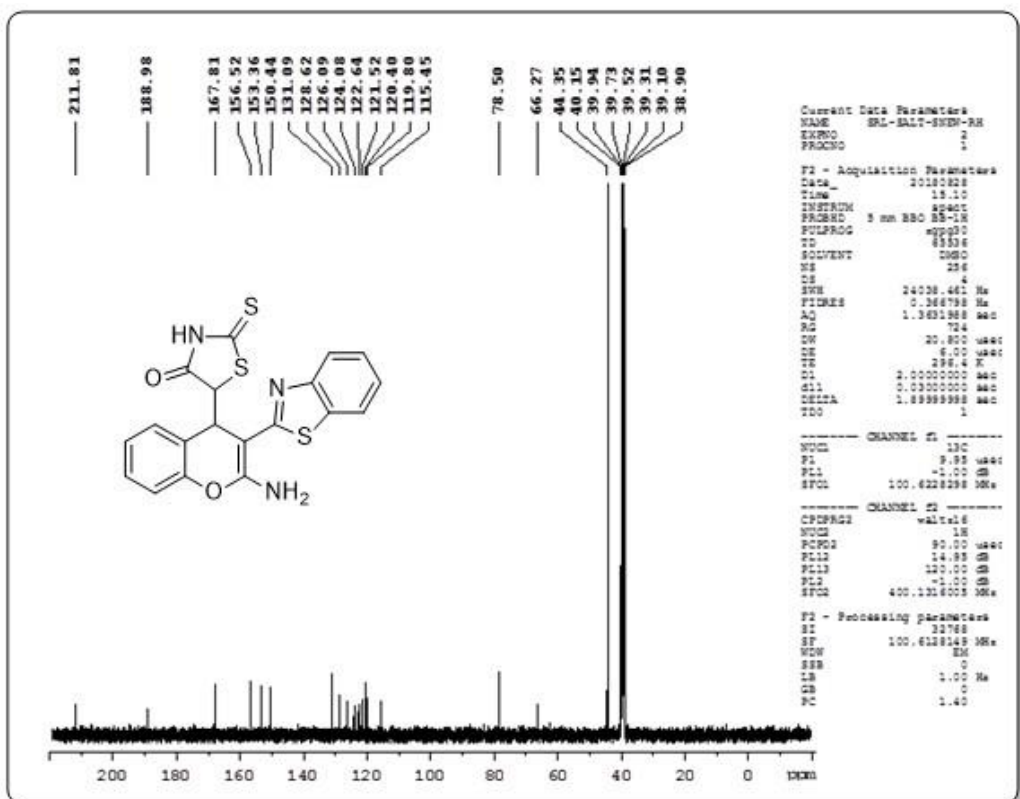
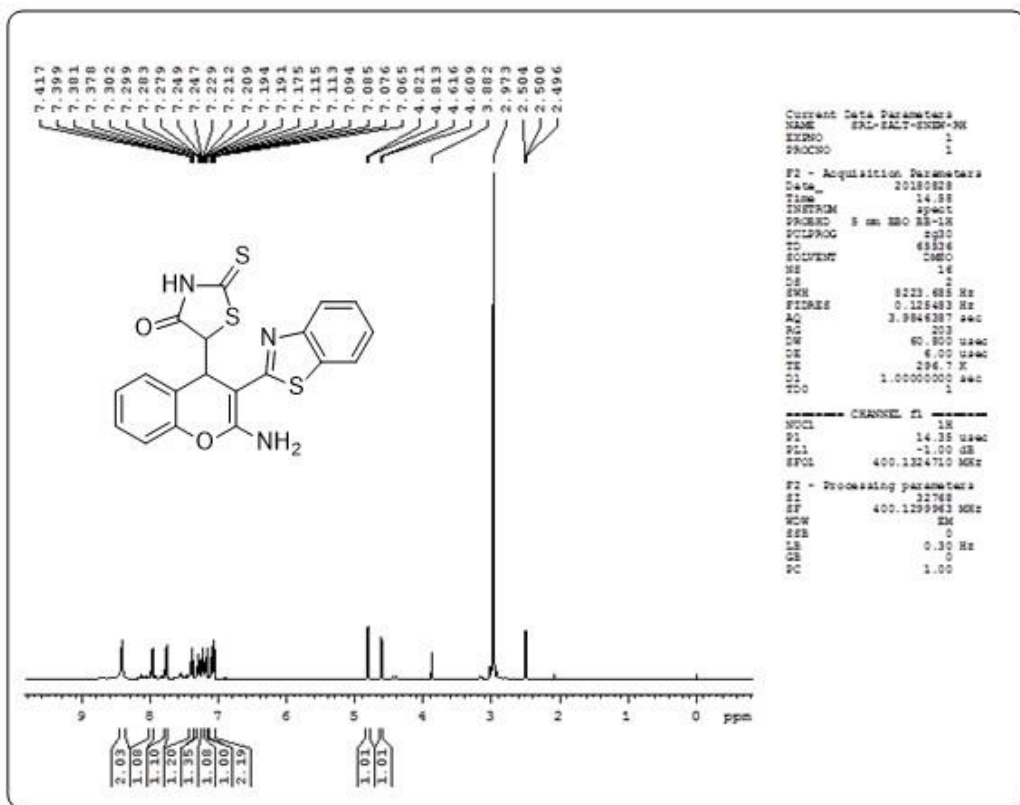


Fig 8: ^1H , ^{13}C spectrum of 5-(2-amino-3-(benzo[d]thiazol-2-yl)-4H-chromen-4-yl)-2-thioxothiazolidin-4-one **4d**

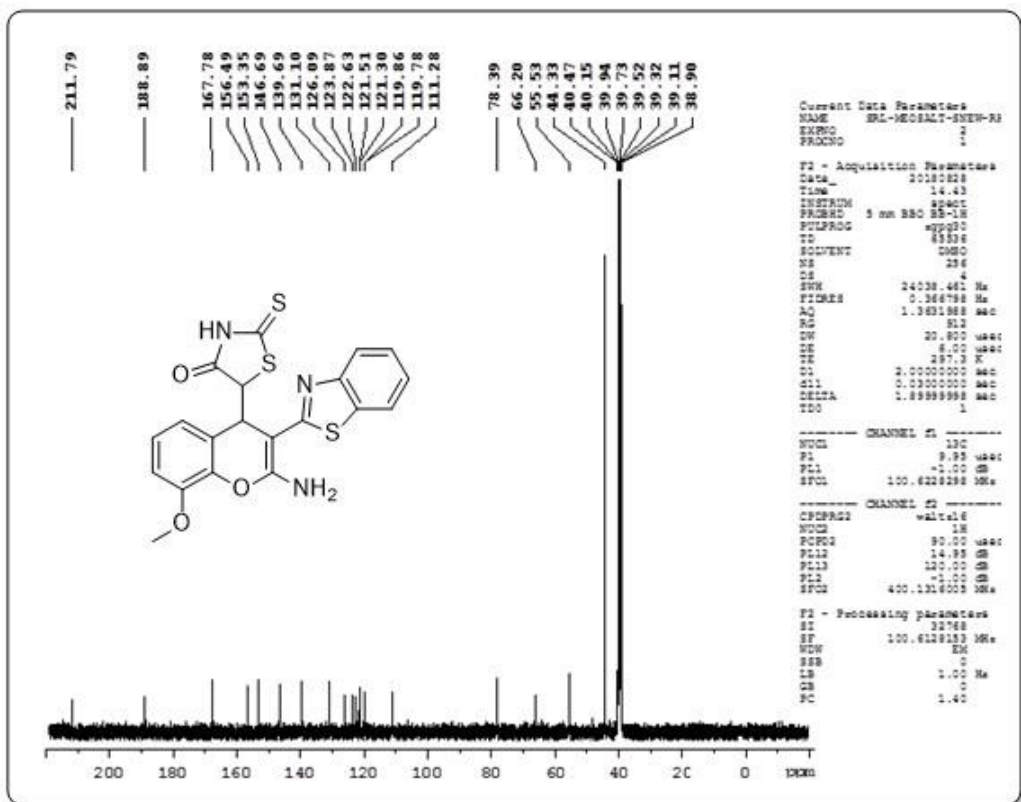
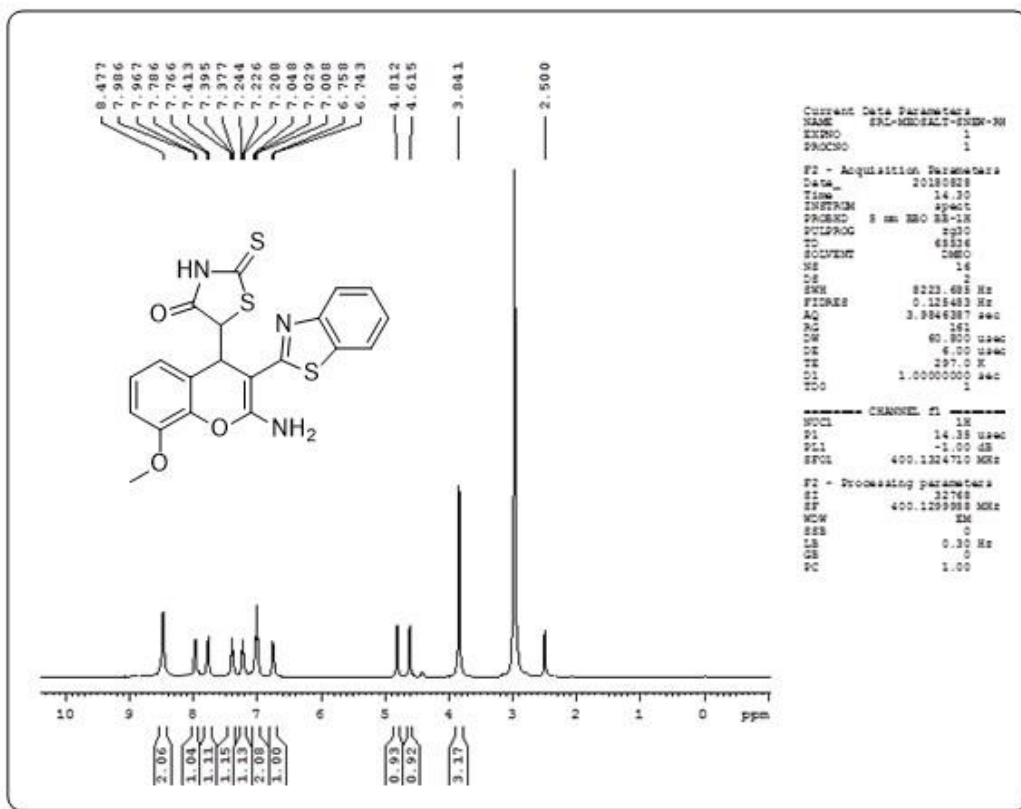


Fig 9: ^1H , ^{13}C spectrum of 5-(2-amino-3-(benzo[d]thiazol-2-yl)-8-methoxy-4H-chromen-4-yl)-2-thioxothiazolidin-4-one **4e**

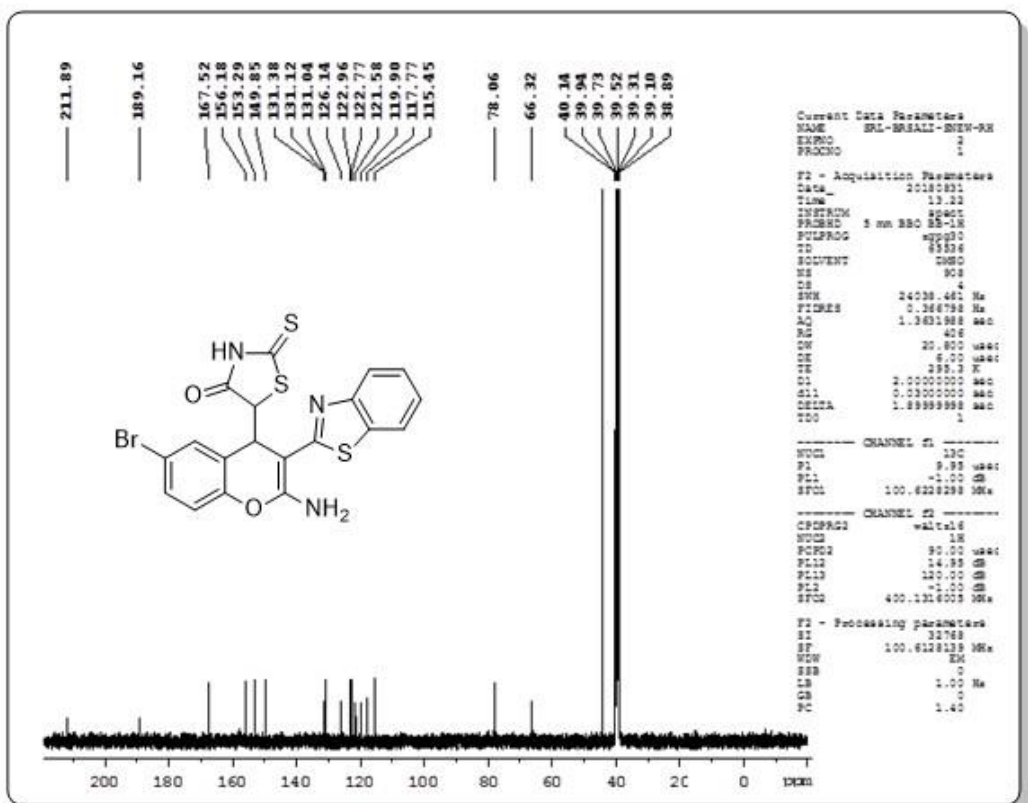
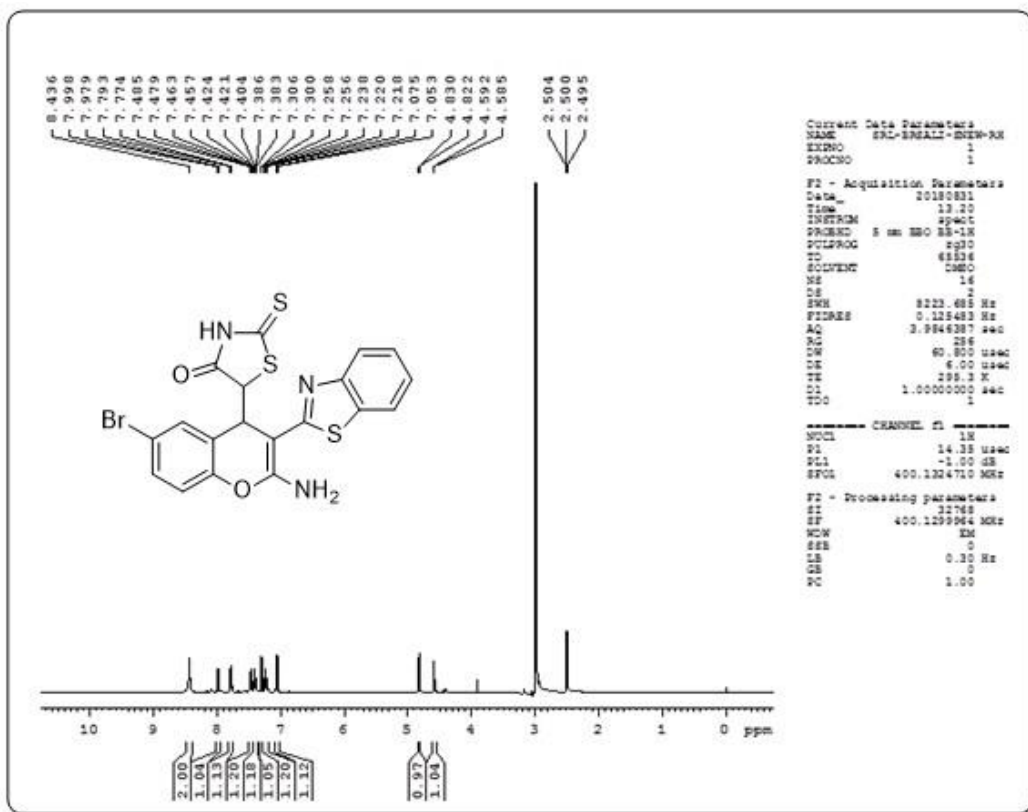


Fig 10: ^1H , ^{13}C spectrum of 5-(2-amino-3-(benzo[d]thiazol-2-yl)-6-bromo-4H-chromen-4-yl)-2-thioxothiazolidin-4-one **4f**

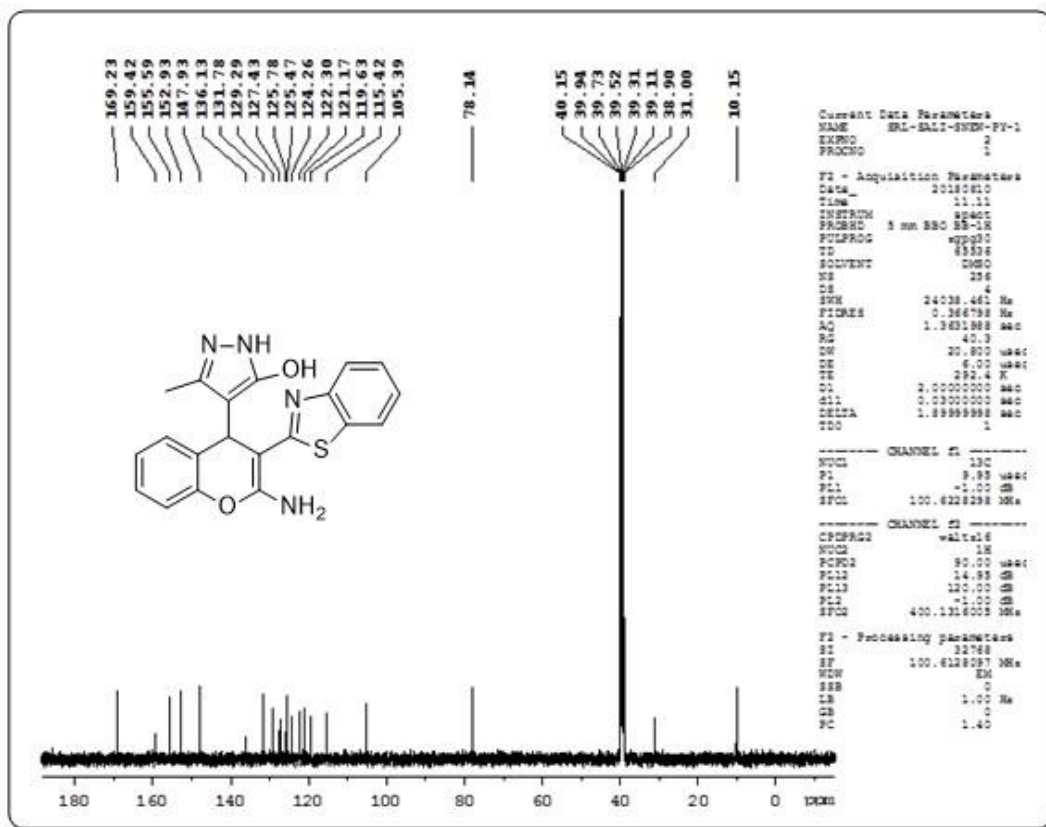
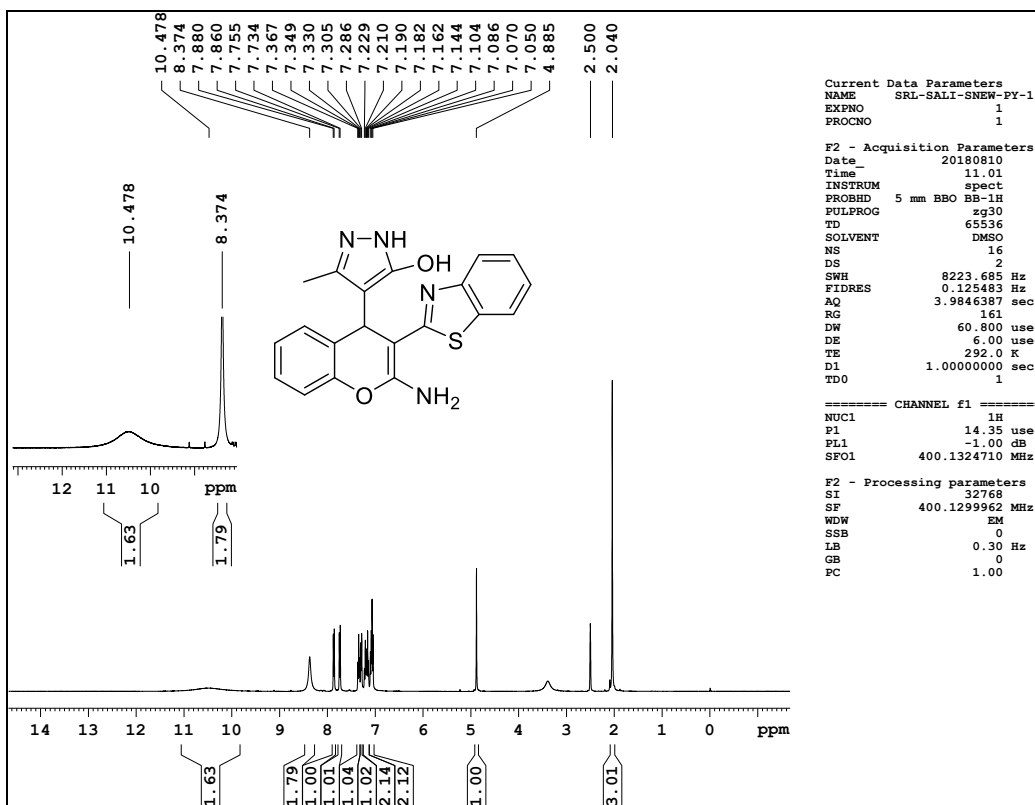


Fig 11. ^1H , ^{13}C spectrum of 4-(2-amino-3-(benzo[d]thiazol-2-yl)-4H-chromen-4-yl)-3-methyl-1H-pyrazol-5-ol **4g**

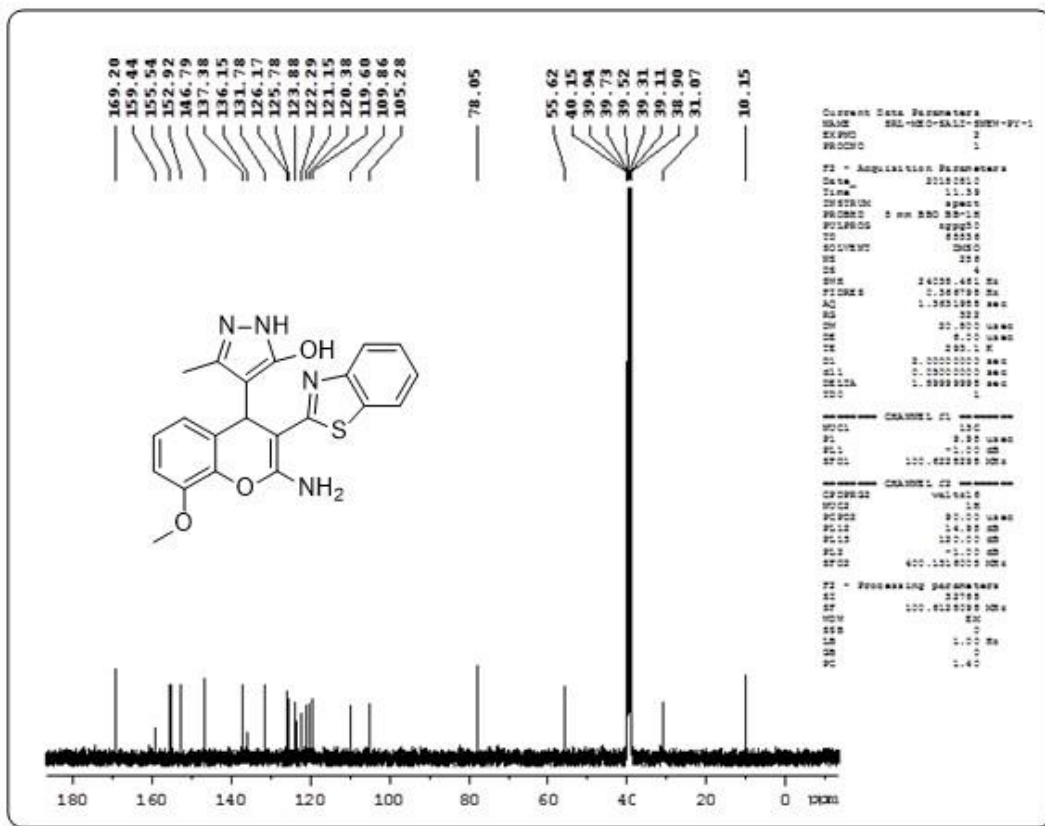
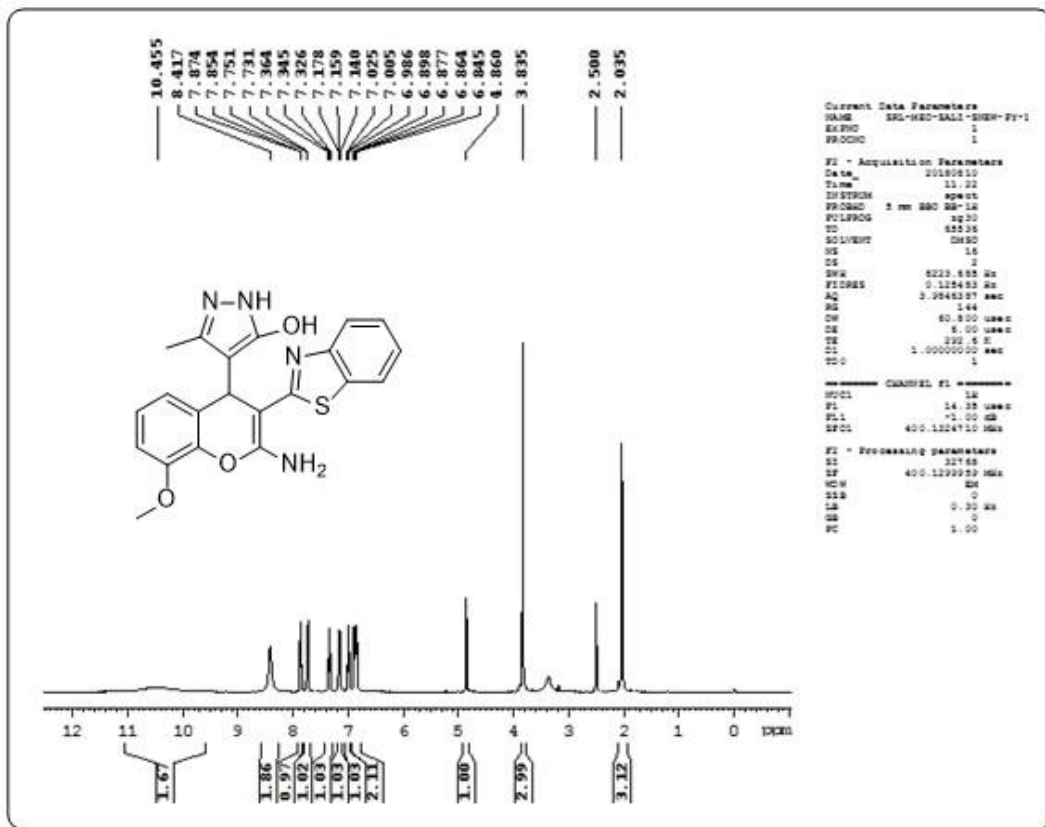


Fig 12: ^1H , ^{13}C spectrum of 4-(2-amino-3-(benzo[d]thiazol-2-yl)-8-methoxy-4H-chromen-4-yl)-3-methyl-1H-pyrazol-5-ol **4h**

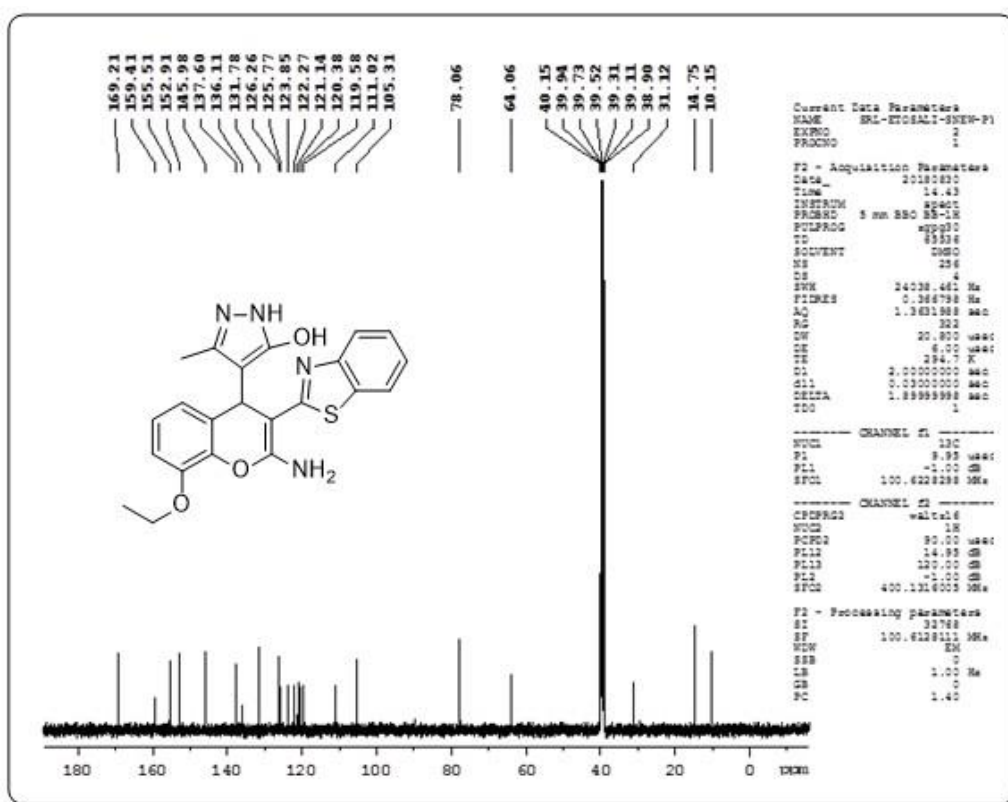
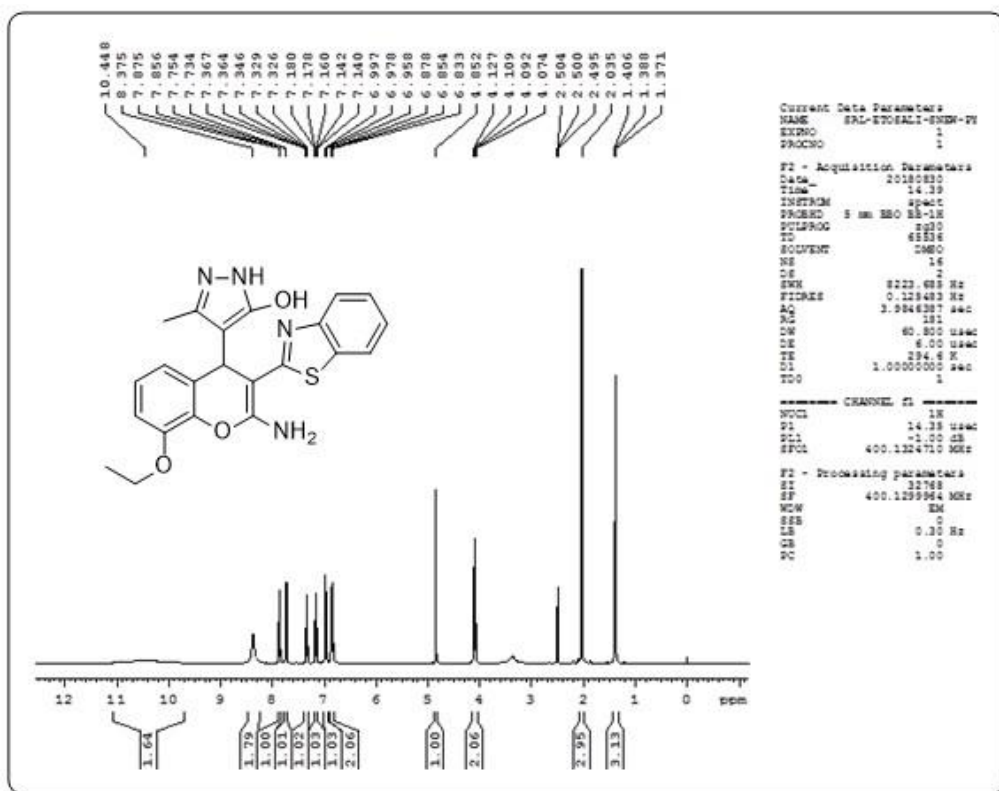


Fig 13: ^1H , ^{13}C spectrum of 4-(2-amino-3-(benzo[d]thiazol-2-yl)-8-ethoxy-4H-chromen-4-yl)-3-methyl-1H-pyrazol-5-ol **4i**

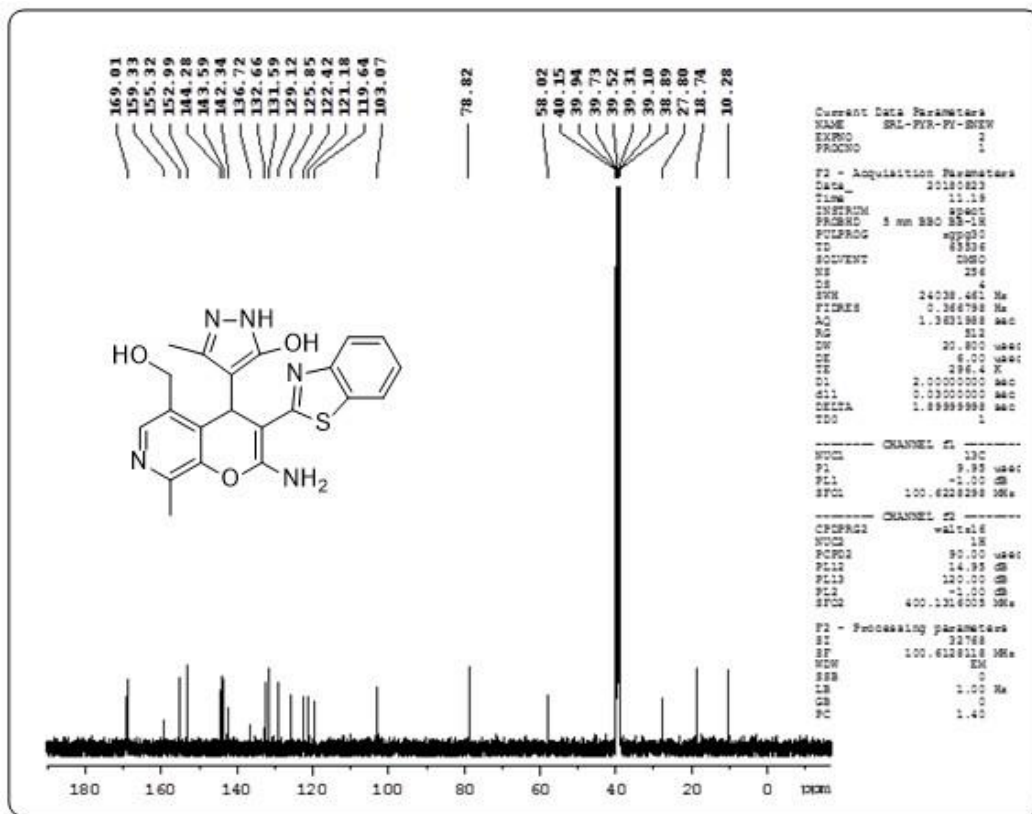
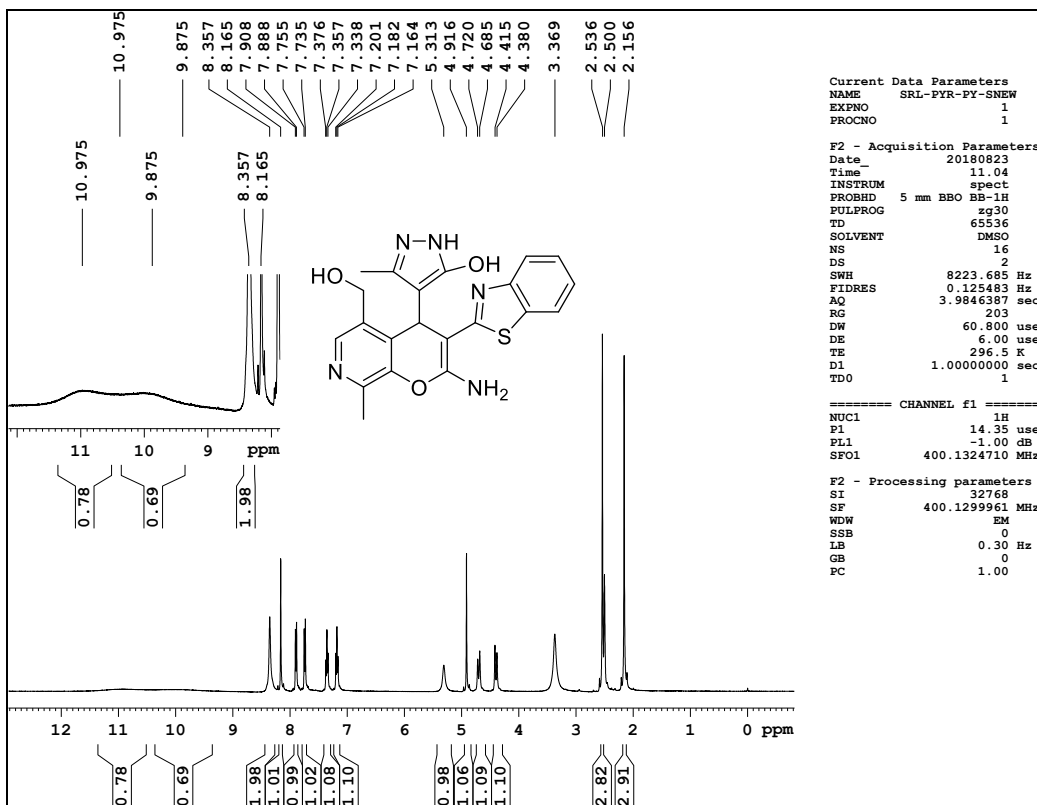


Fig 14: ^1H , ^{13}C spectrum of 4-(2-amino-3-(benzo[d]thiazol-2-yl)-5-(hydroxymethyl)-8-methyl-4H-pyrano[2,3-c]pyridin-4-yl)-3-methyl-1H-pyrazol-5-ol **4j**

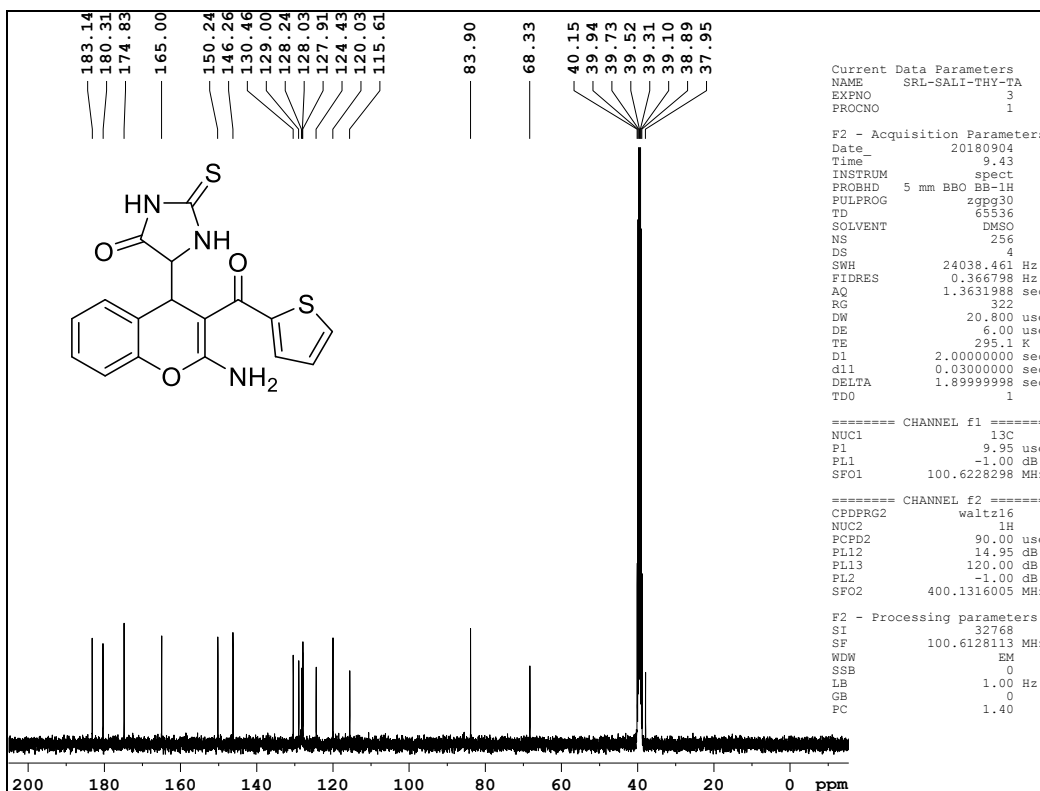
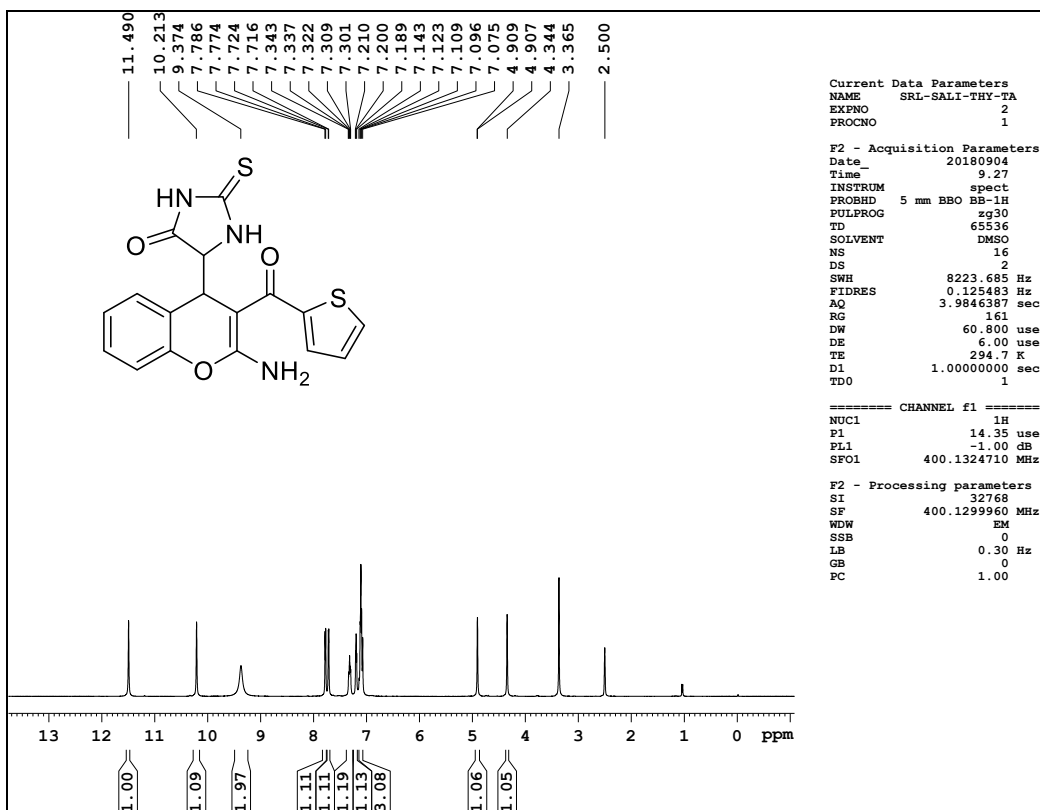


Fig 15: ^1H , ^{13}C spectrum of 5-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one **7a**

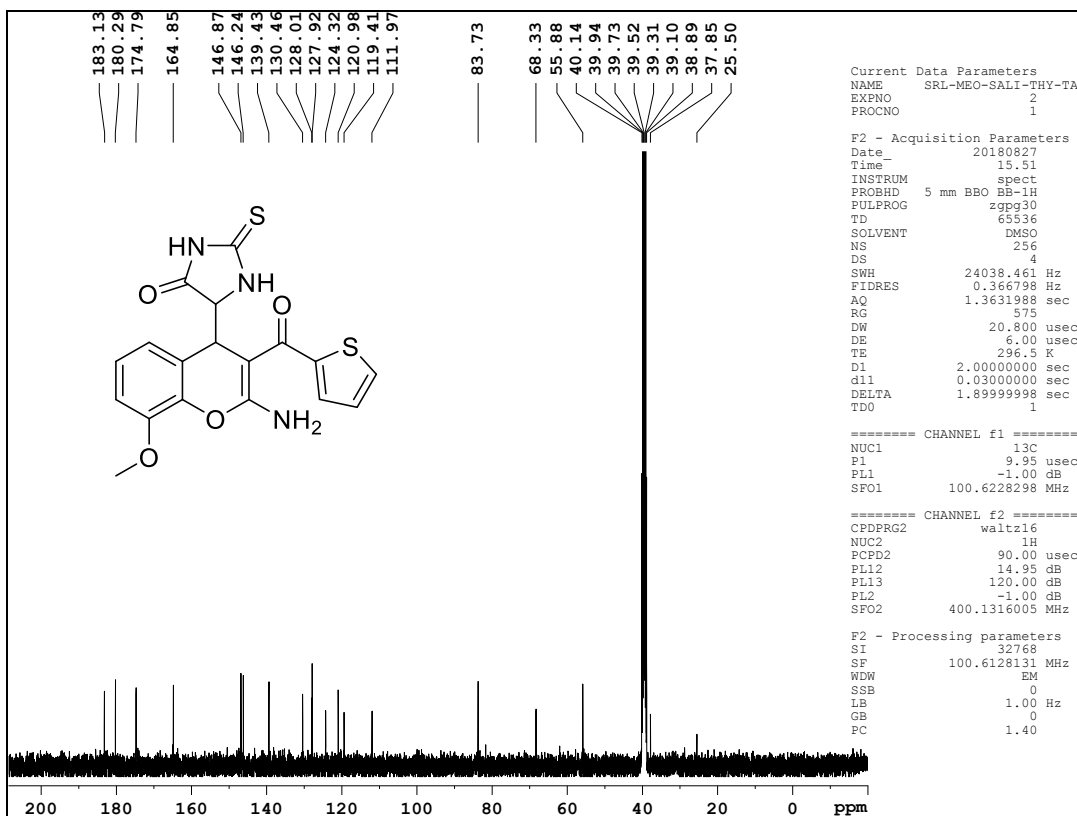
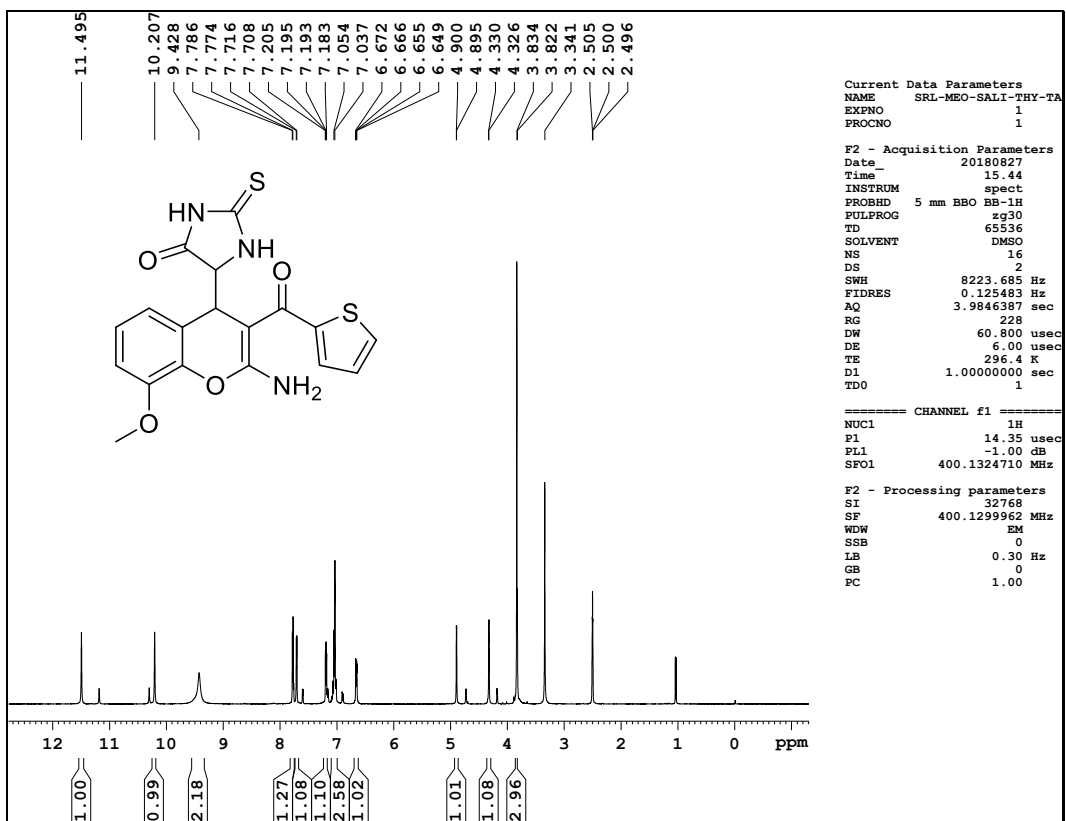


Fig 16: ^1H , ^{13}C spectrum of 5-(2-amino-8-methoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one **7b**

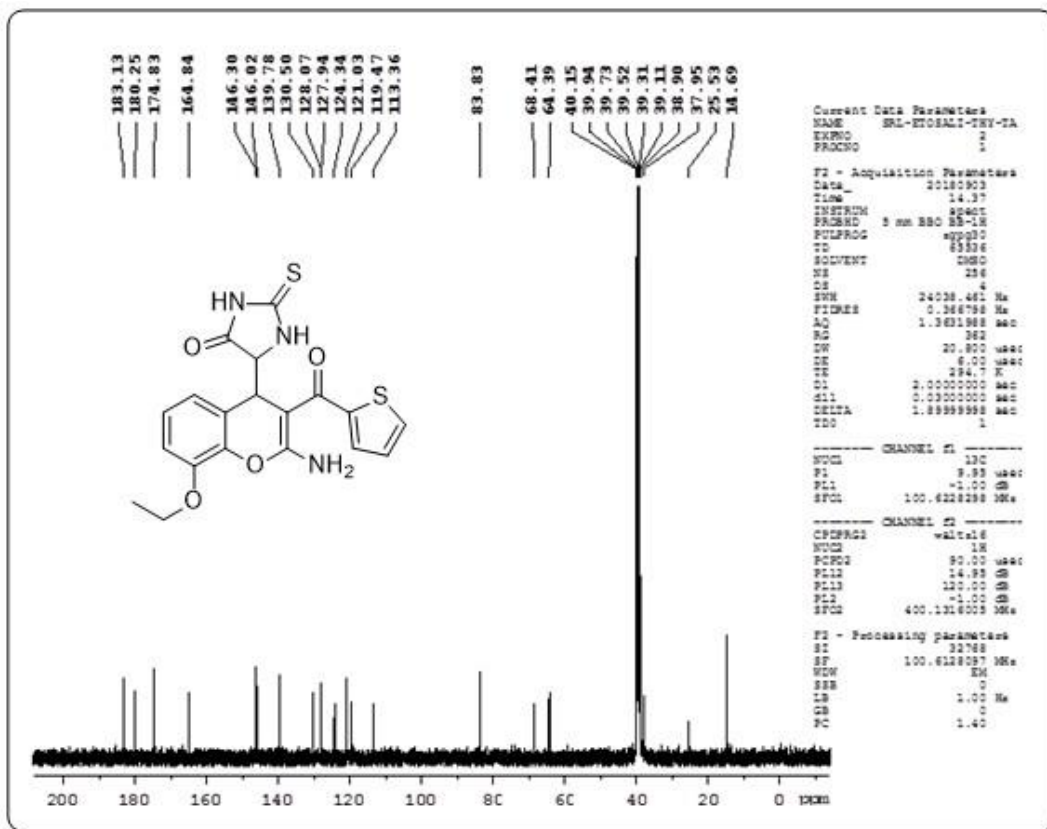
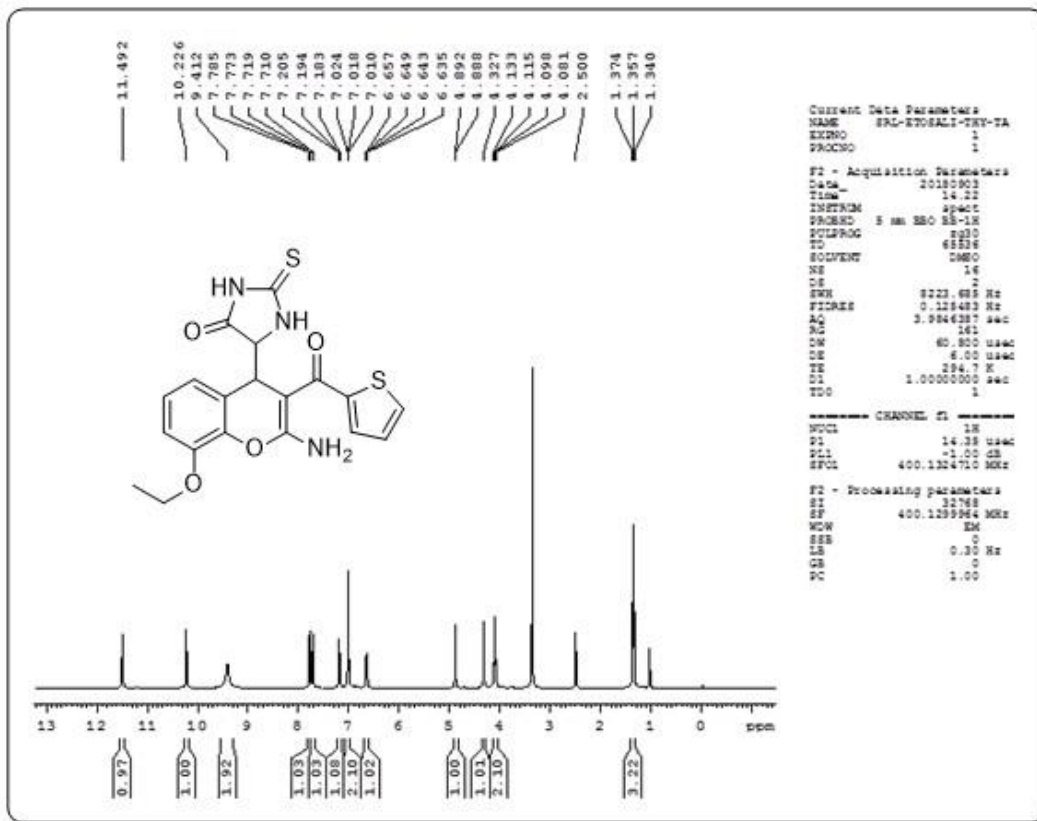


Fig 17: ¹H, ¹³C spectrum of 5-(2-amino-8-ethoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one **7c**

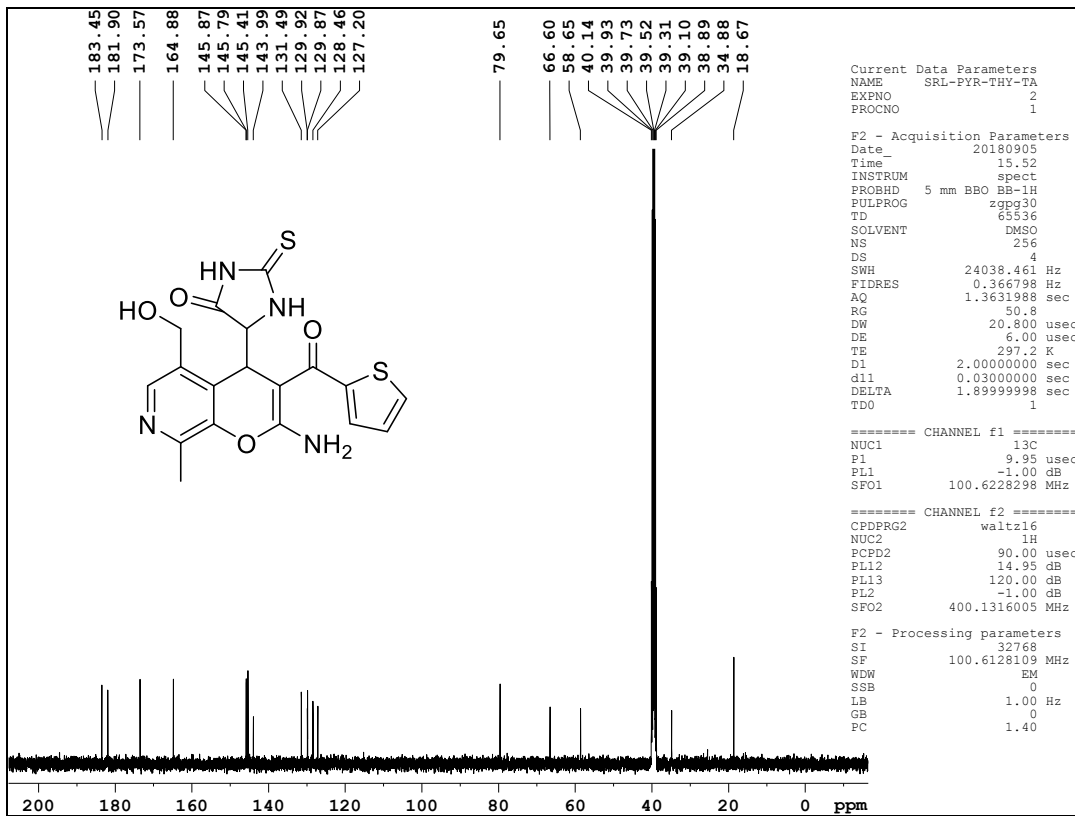
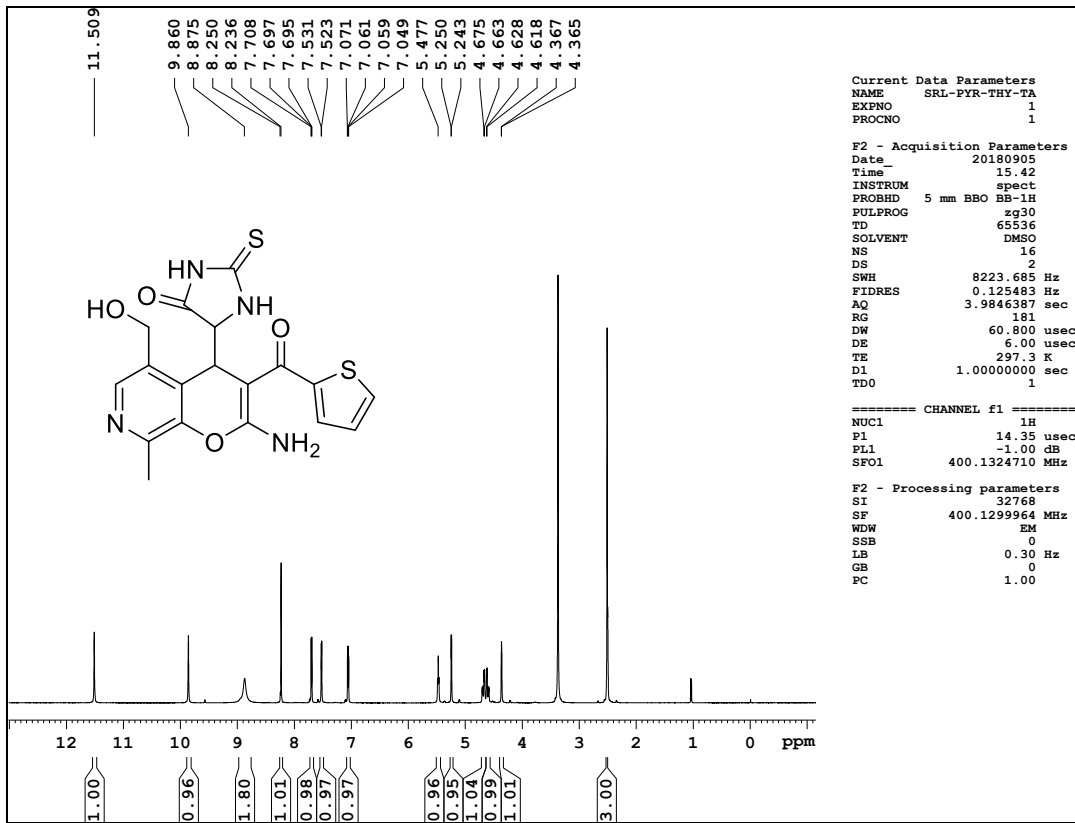


Fig 18: ^1H , ^{13}C spectrum of 5-(2-amino-5-(hydroxymethyl)-8-methyl-3-(thiophene-2-carbonyl)-4H-pyrano[2,3-c]pyridin-4-yl)-2-thioxoimidazolidin-4-one **7d**

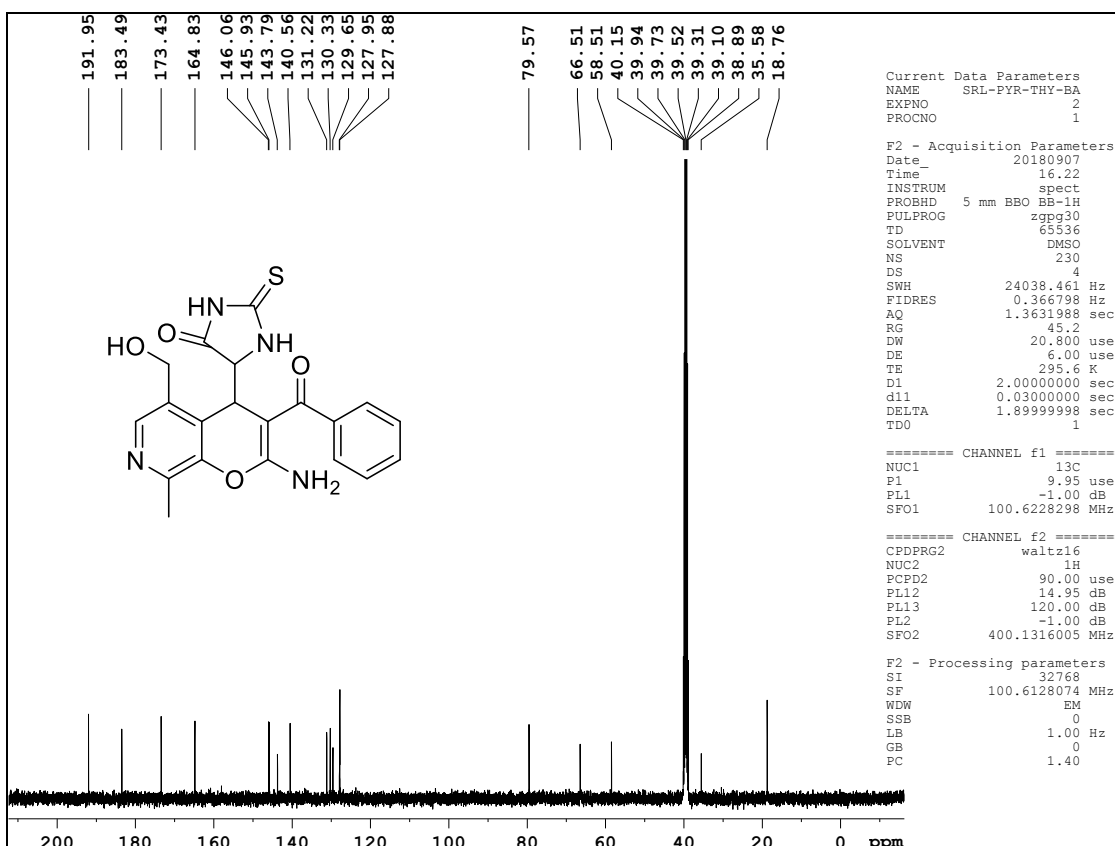
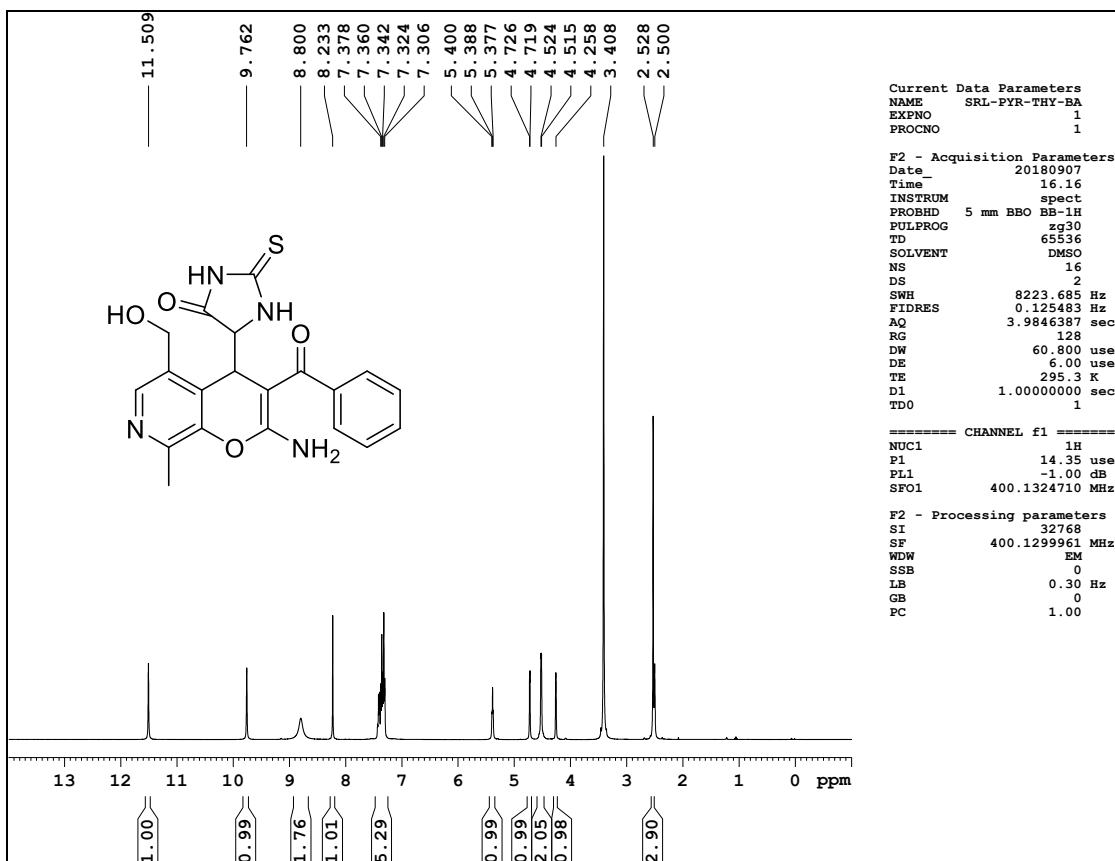


Fig 19: ¹H, ¹³C spectrum of 5-(2-amino-3-benzoyl-5-(hydroxymethyl)-8-methyl-4H-pyrano[2,3-c]pyridin-4-yl)-2-thioxoimidazolidin-4-one **7e**

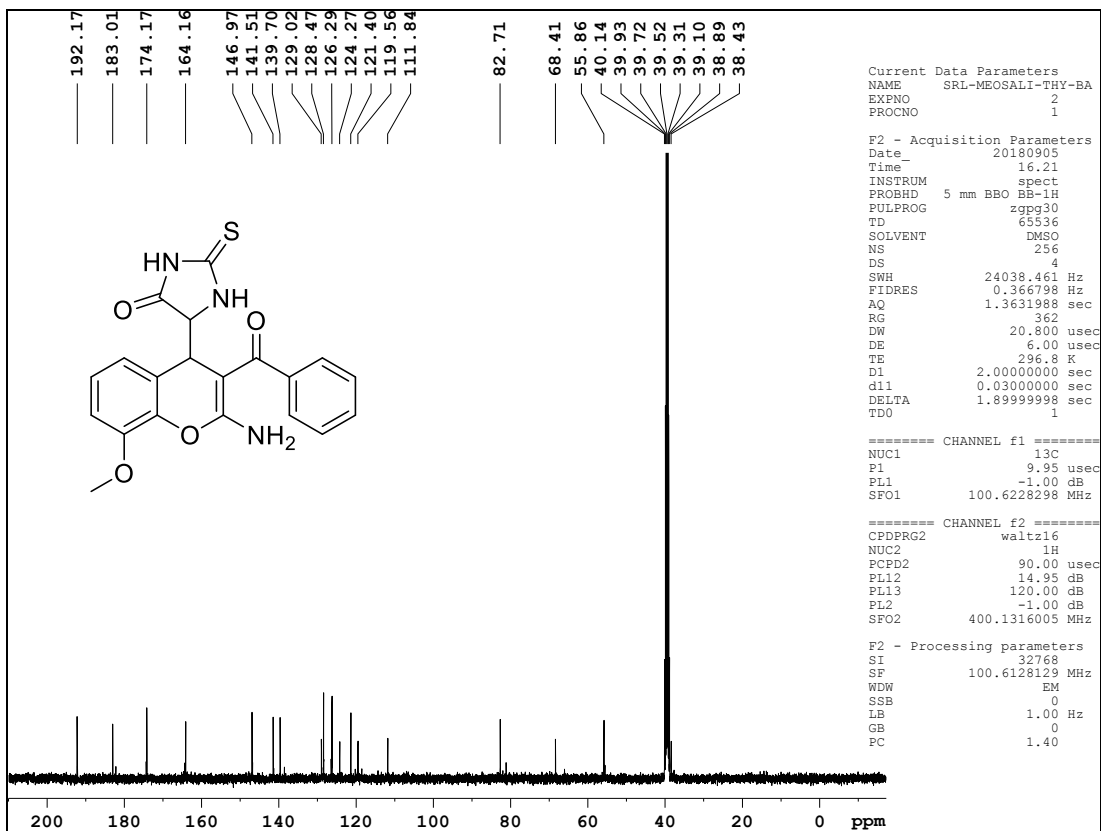
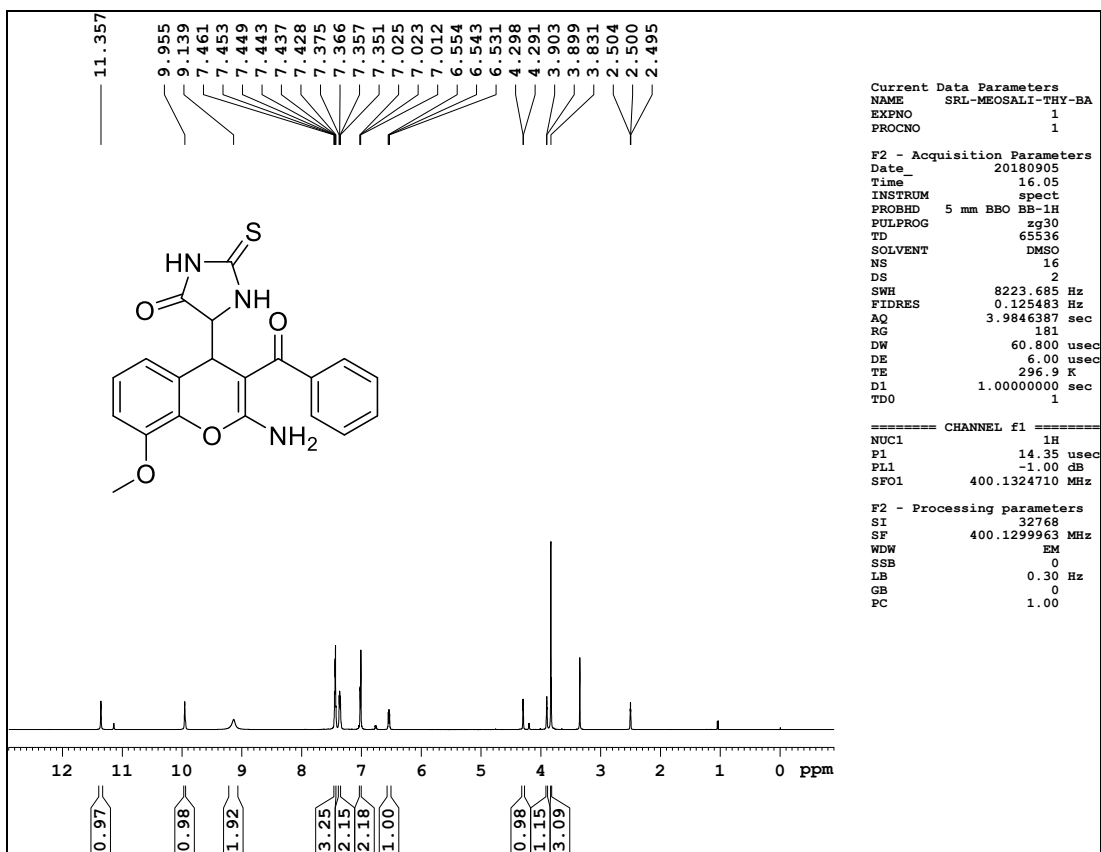


Fig 20: ¹H, ¹³C spectrum of 5-(2-amino-3-benzoyl-8-methoxy-4H-chromen-4-yl)-2-thioxoimidazolidin-4-one **7f**

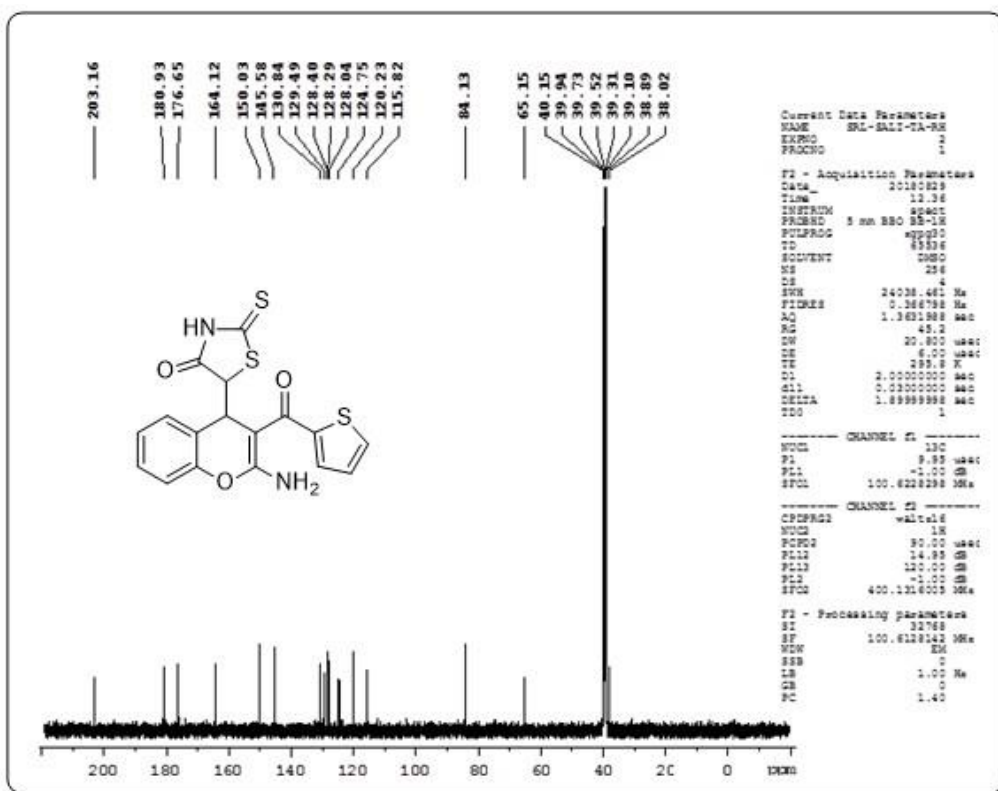
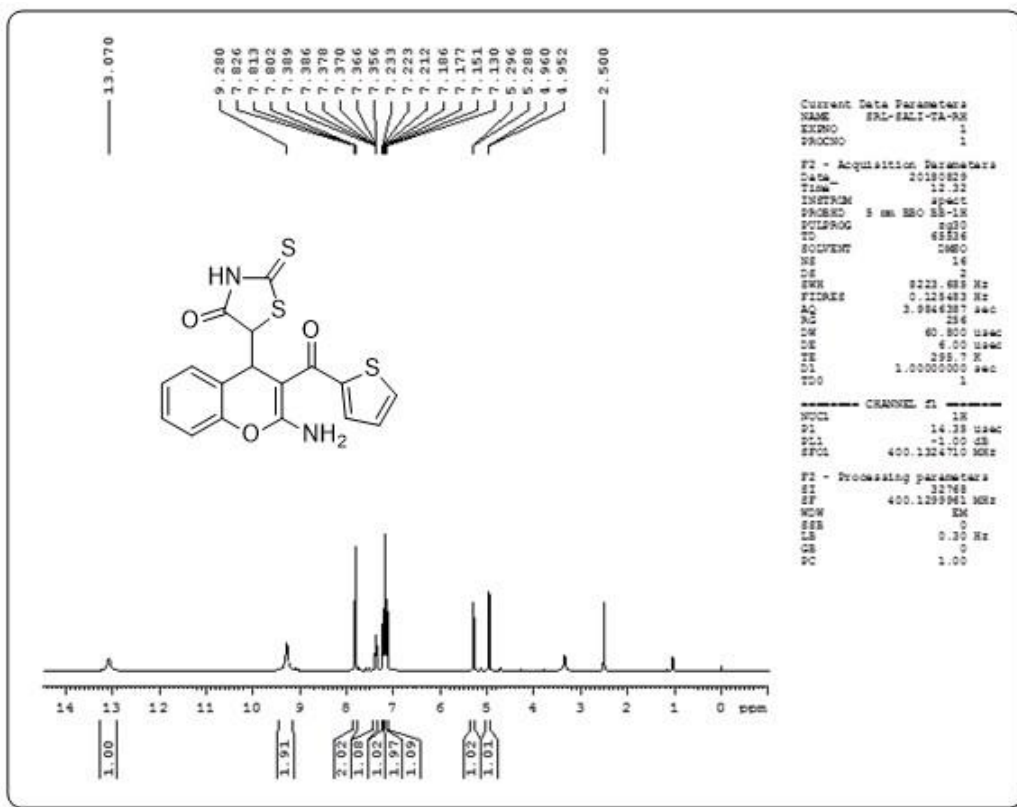


Fig 21: ¹H, ¹³C spectrum of 5-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)-2-thioxothiazolidin-4-one **7g**

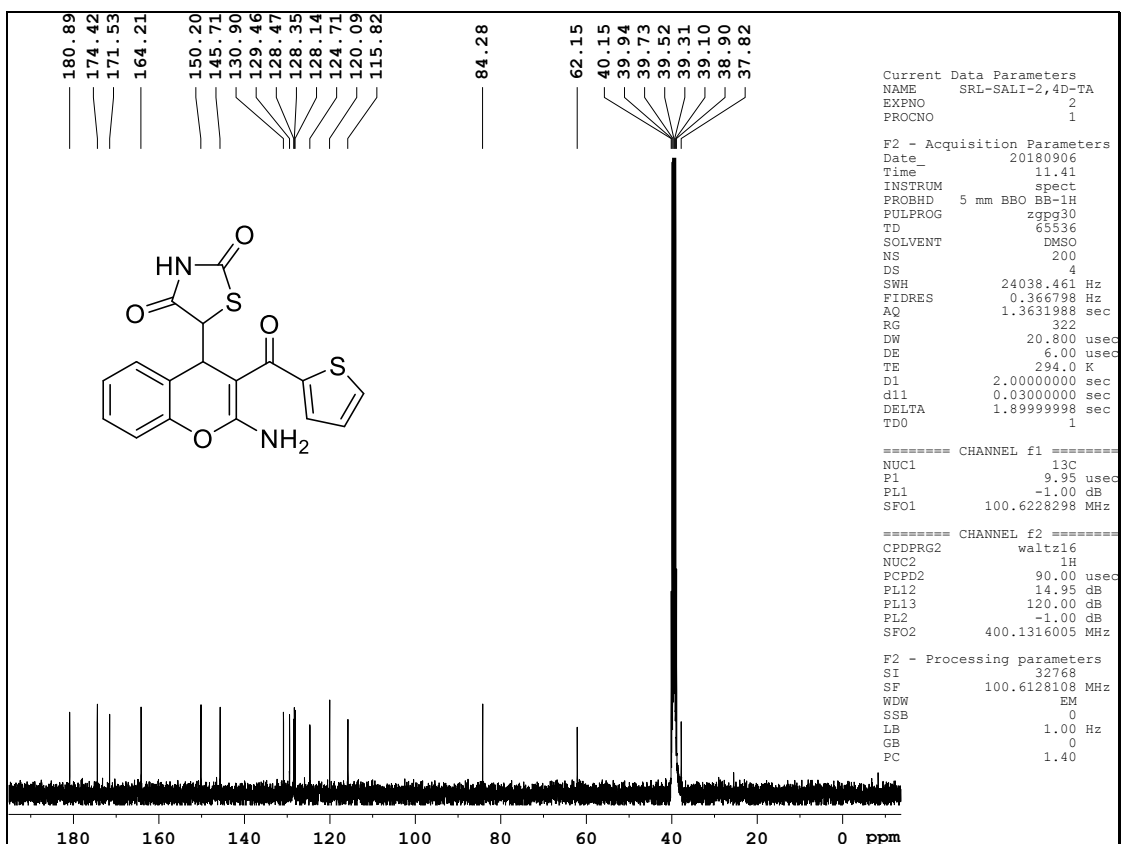
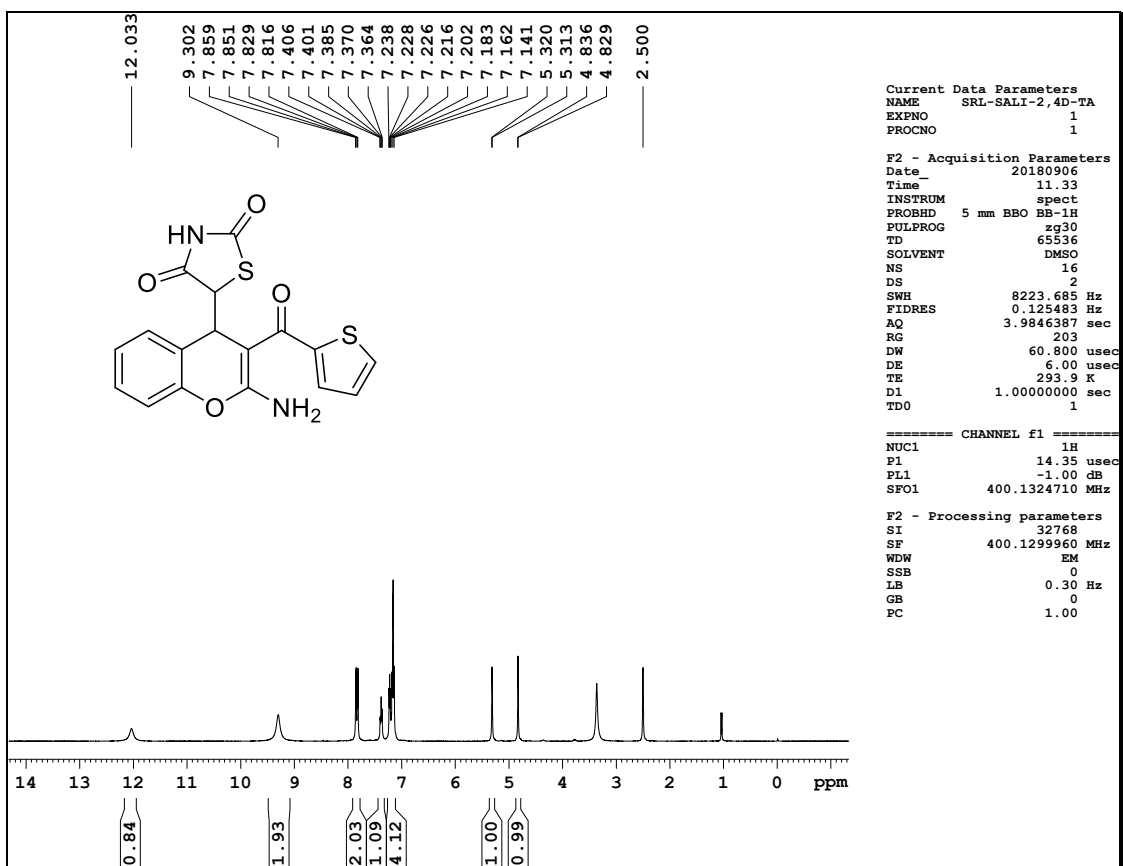


Fig 22: ¹H, ¹³C spectrum of 5-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)thiazolidine-2,4-dione **7h**

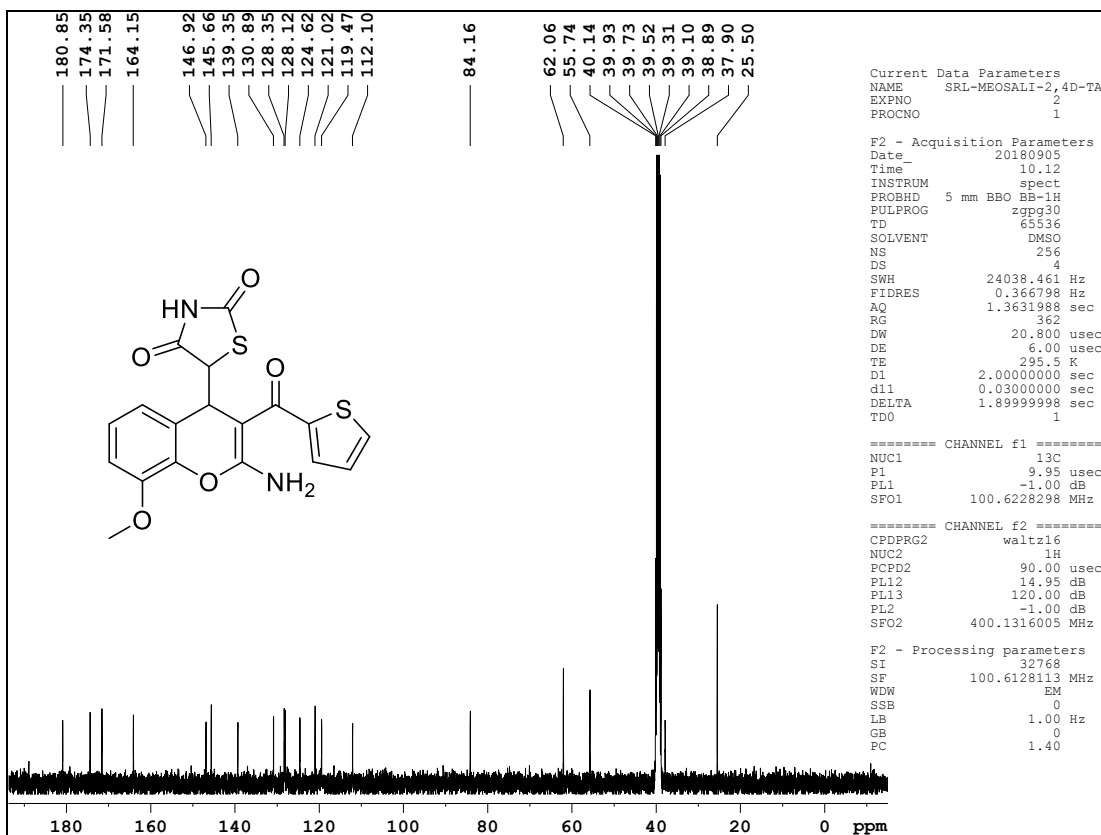
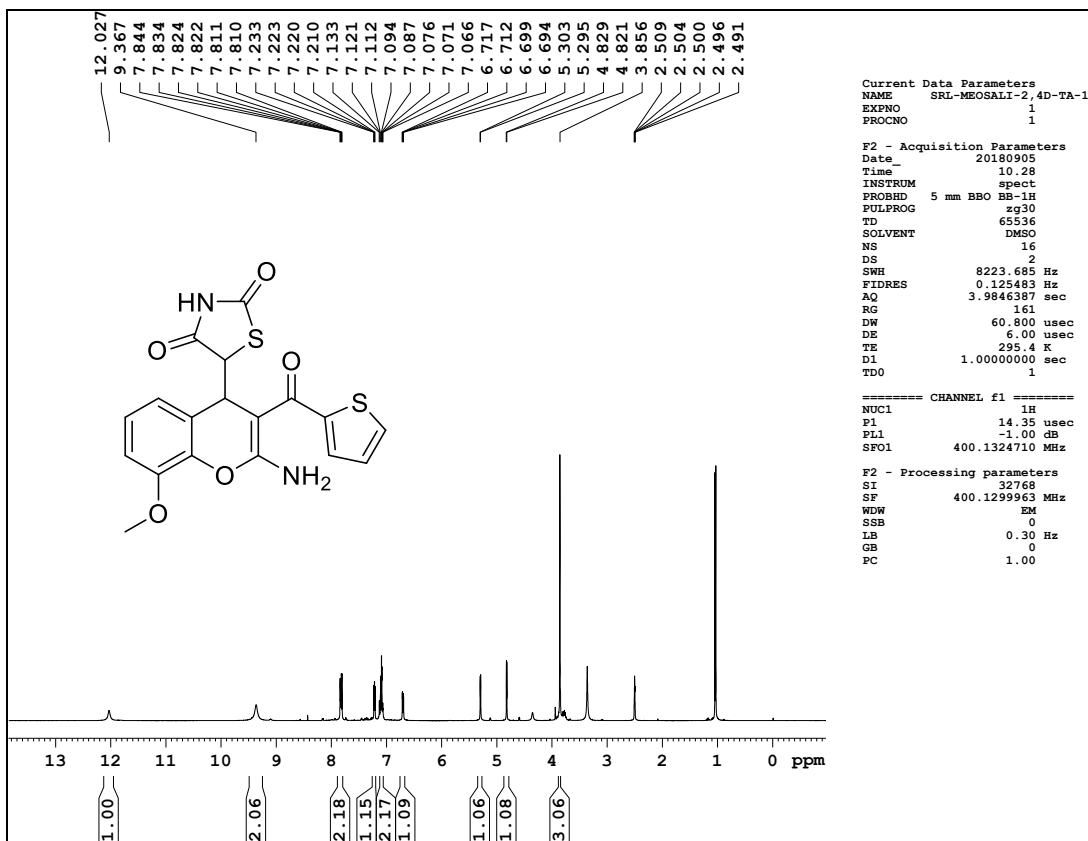


Fig 23: ^1H , ^{13}C spectrum of 5-(2-amino-8-methoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)thiazolidine-2,4-dione **7i**

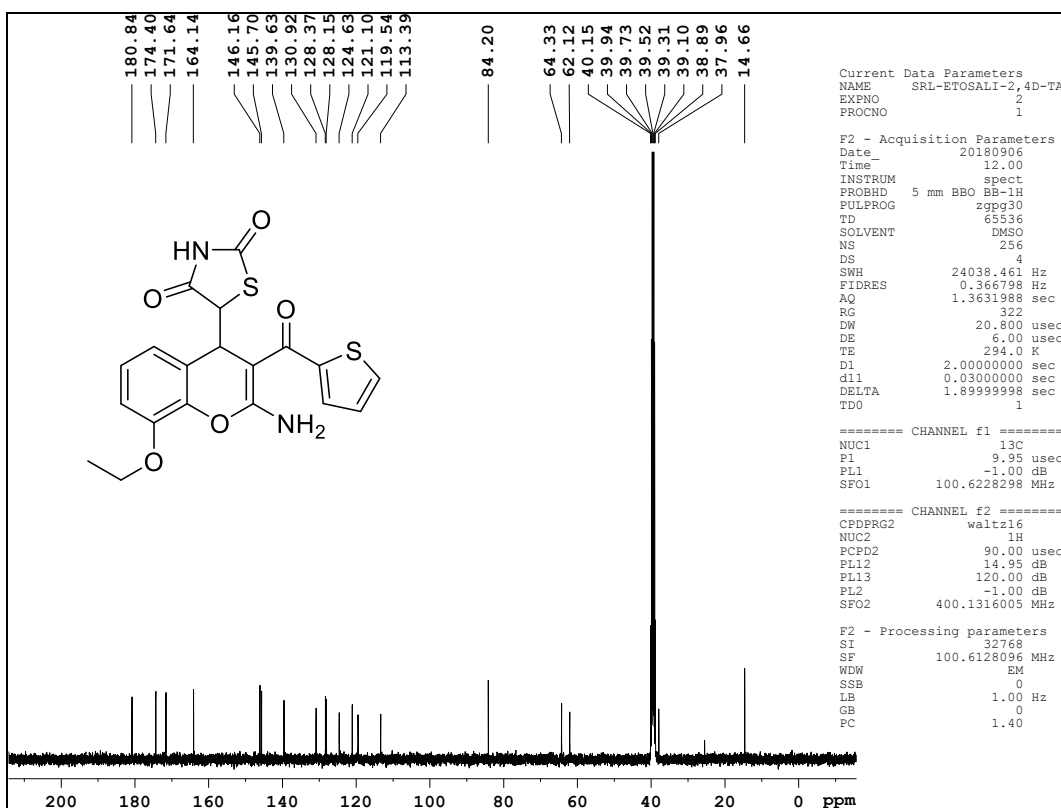
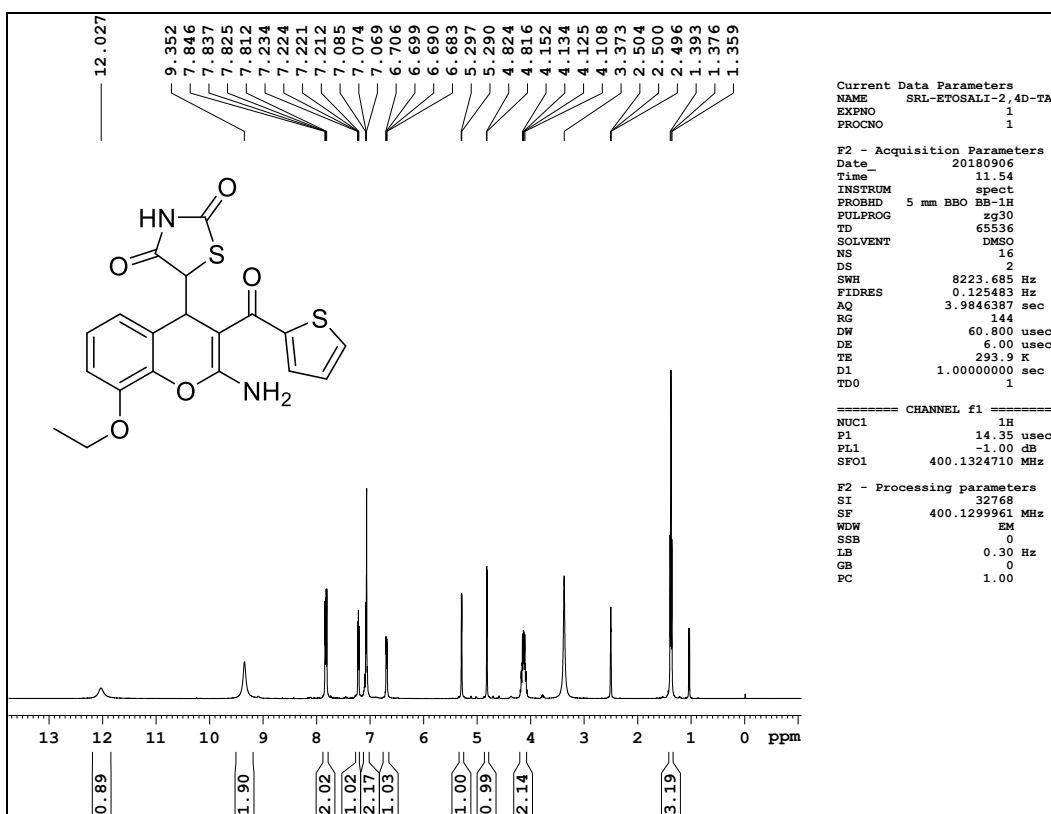


Fig 24: ^1H , ^{13}C spectrum of 5-(2-amino-8-ethoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)thiazolidine-2,4-dione **7j**

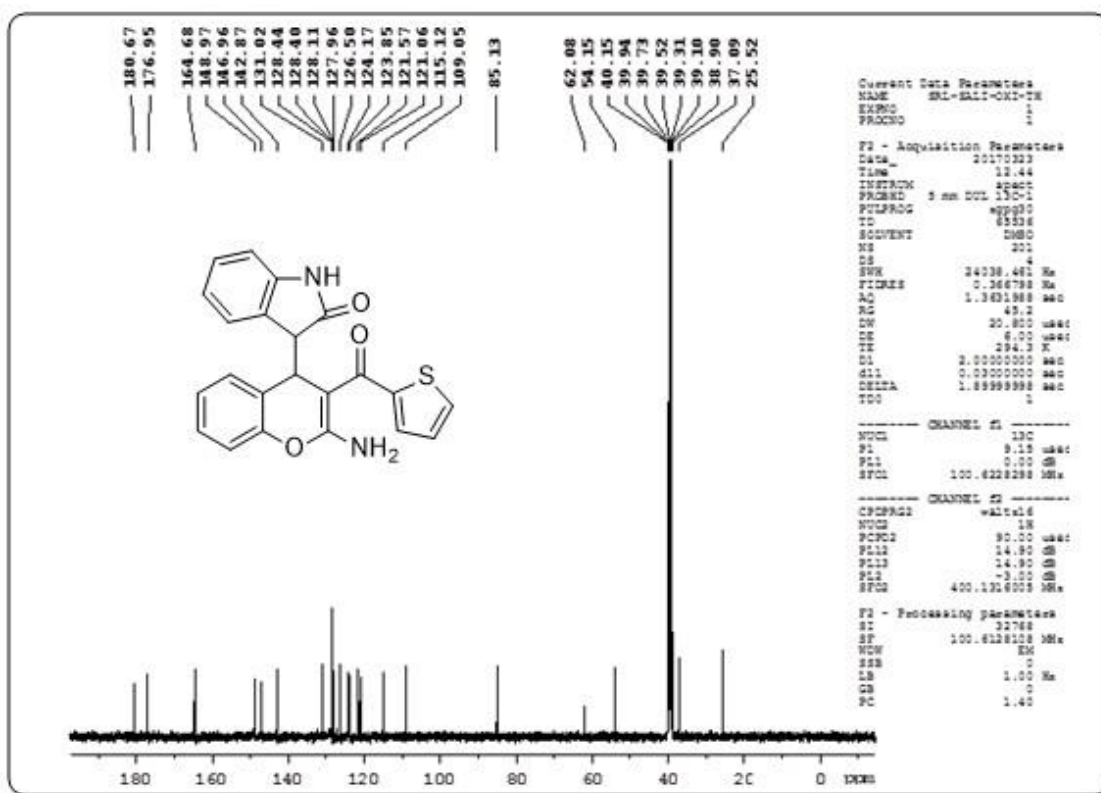
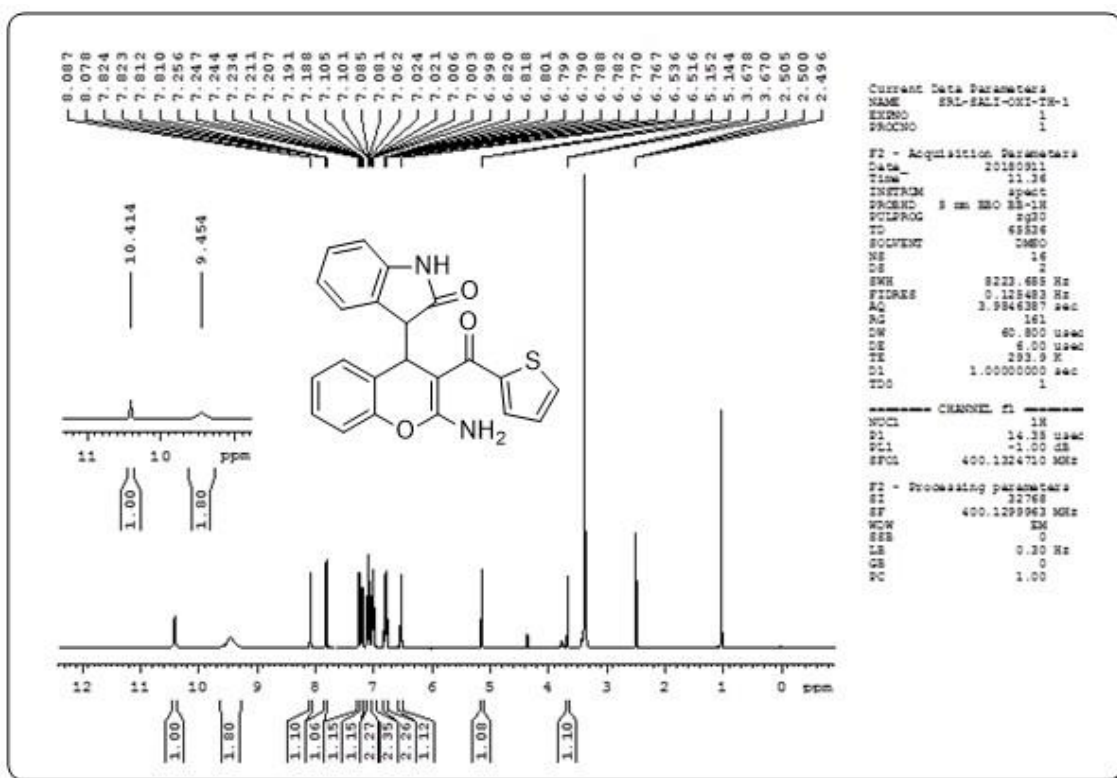


Fig 25: ^1H , ^{13}C spectrum of 3-(2-amino-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)indolin-2-one **7k**

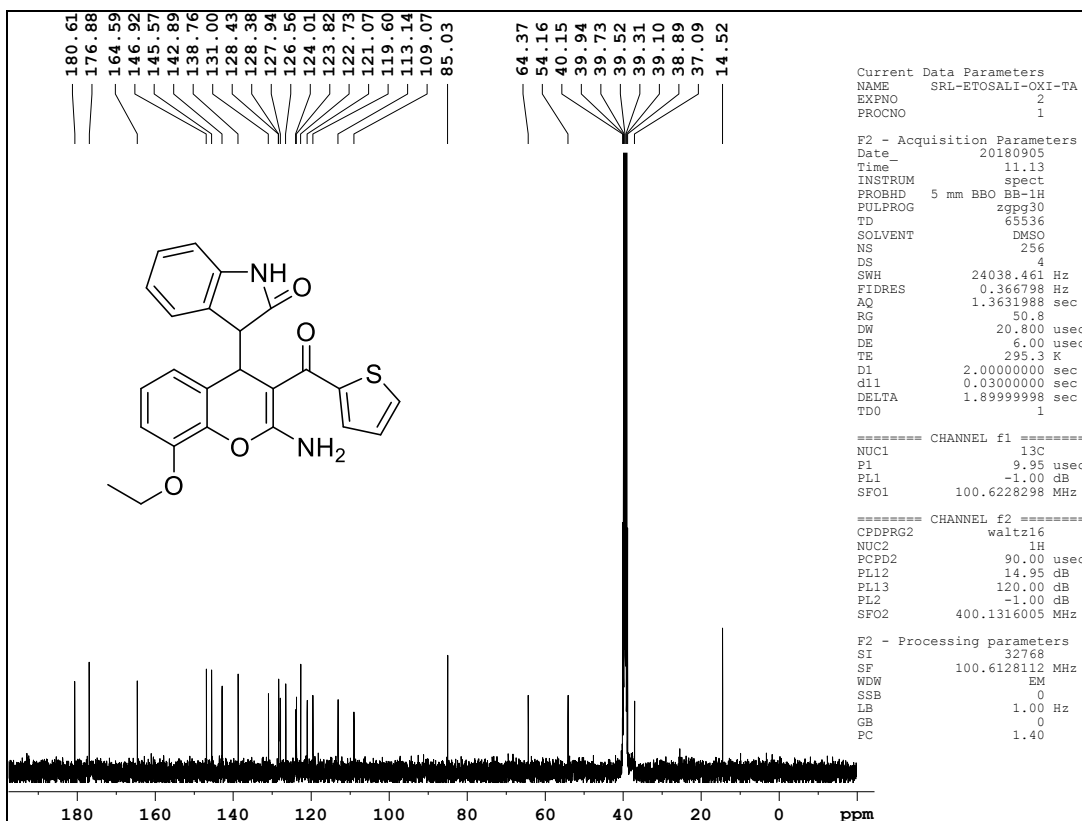
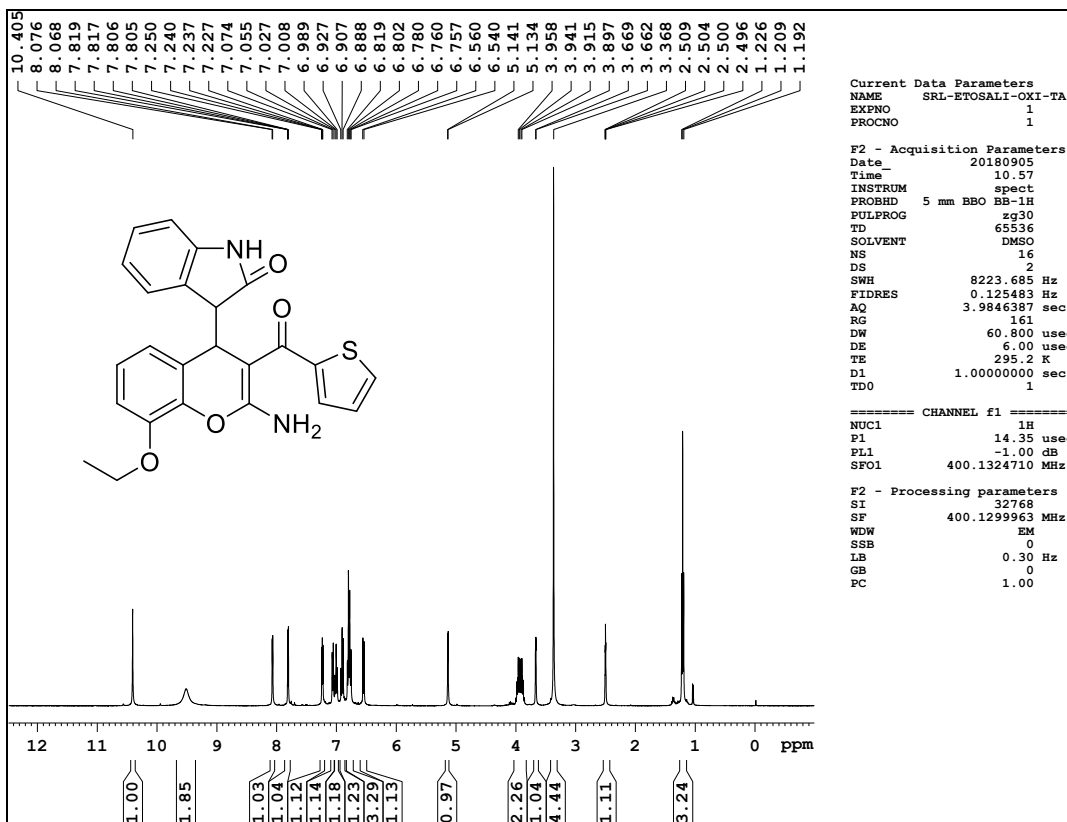


Fig 26: ^1H , ^{13}C spectrum of 3-(2-amino-8-ethoxy-3-(thiophene-2-carbonyl)-4H-chromen-4-yl)indolin-2-one **71**

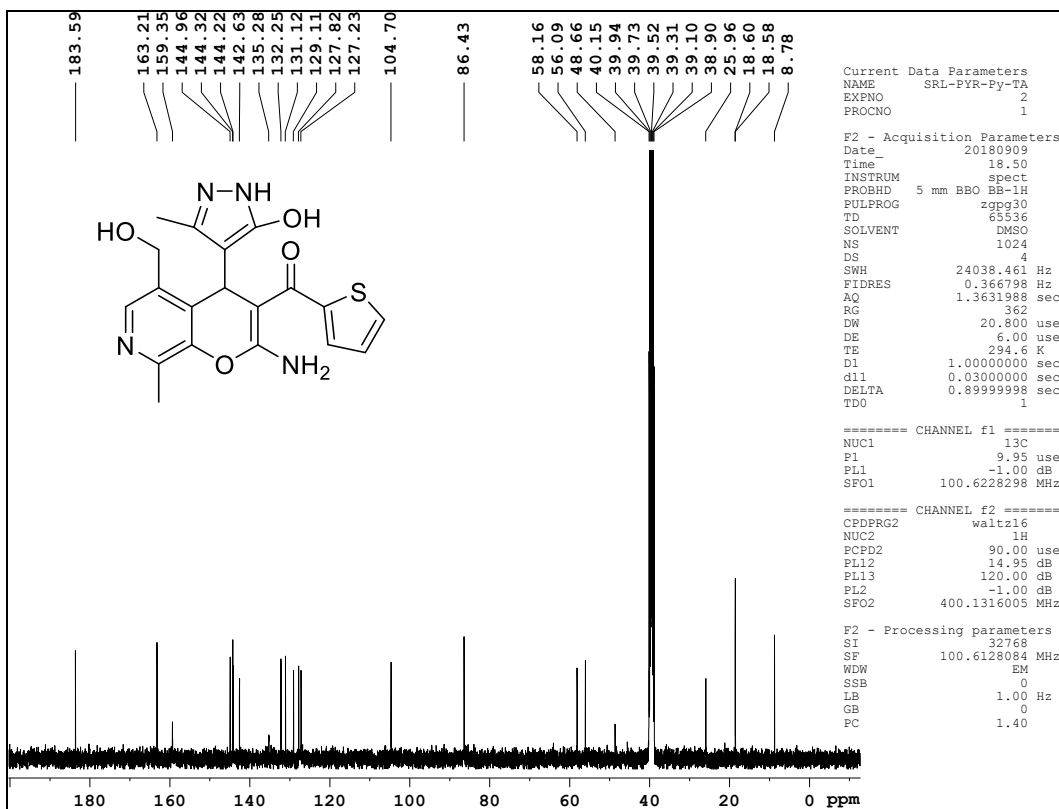
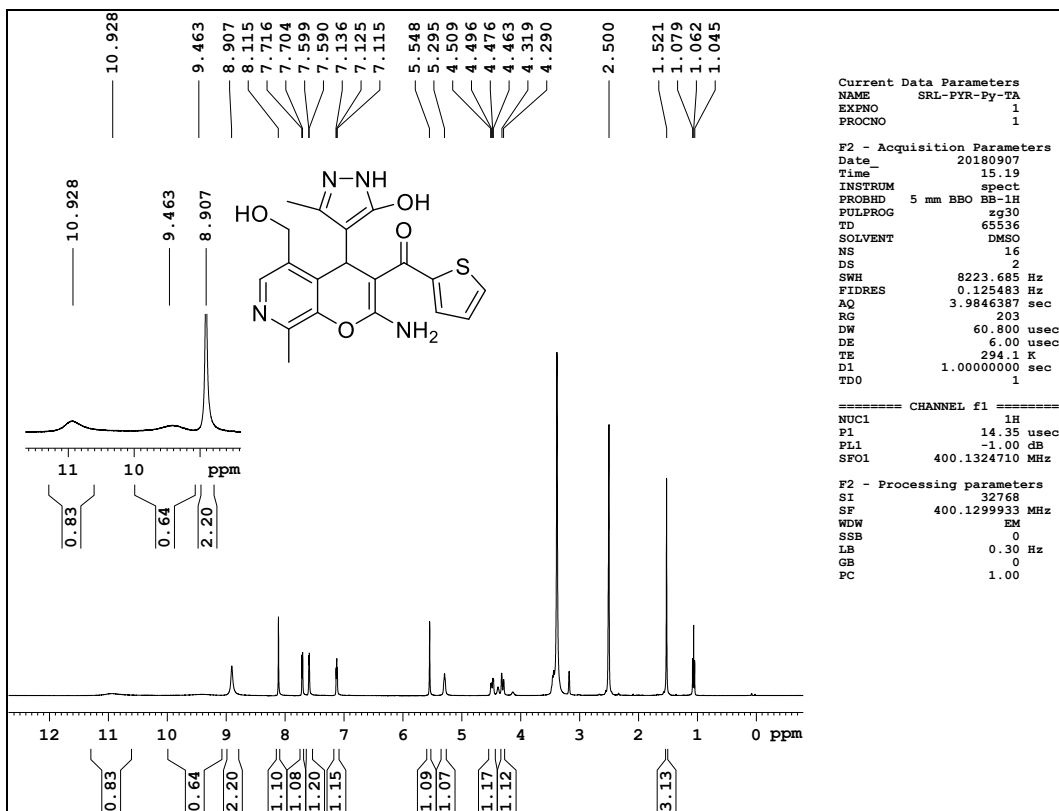


Fig 27: ^1H , ^{13}C spectrum of (2-amino-4-(5-hydroxy-3-methyl-1H-pyrazol-4-yl)-5-(hydroxymethyl)-8-methyl-4H-pyrano[2,3-c]pyridin-3-yl)(thiophen-2-yl)methanone **7m**

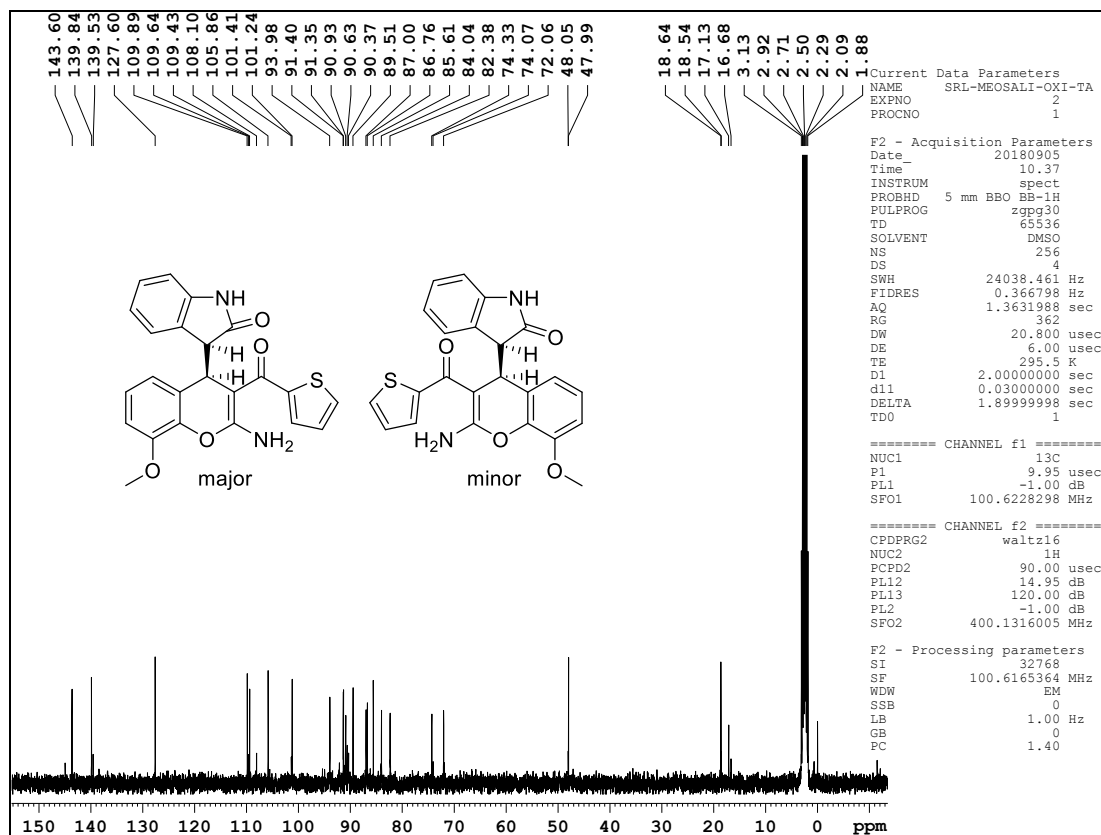
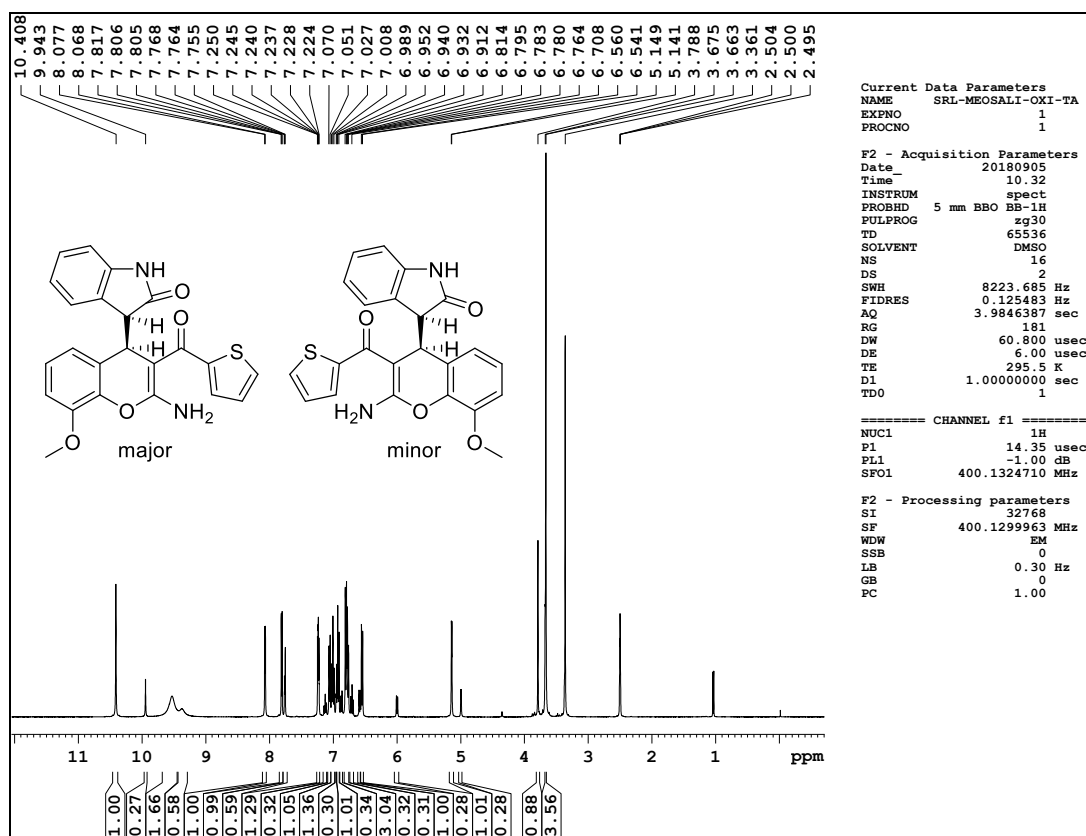


Fig 27: ^1H , ^{13}C spectrum of 3-(2-amino-8-methoxy-3-(thiophene-2-carbonyl)-4*H*-chromen-4-yl)indolin-2-one **7n**