**Experimental**

**Chemistry** All melting points were measured by Electrothermal (9100) apparatus and are uncorrected. The IR spectra were determined using KBr pellets on a Perkin Elmer 1430 spectrophotometer. The NMR spectra were recorded with a Varian Mercury VXR-300 NMR spectrometer at 75 and 300 MHz (13C and 1H NMR spectra, respectively) using DMSO-*d*6 as solvent and results are expressed as δ values. Mass spectra were taken on a Shimadzu GCMS-QP 1000 Ex mass spectrometer at 70 eV. Elemental analyses were carried out at the Microanalyses Center at Cairo University and were performed on Vario EL III Elemental CHNS analyzer. Antimicrobial activity was performed at chemistry department at faculty of science in Cairo University-Giza.

**Preparation of compounds (3a-c):**

**General Procedure :**

**Conventional method A**

Solution of 3-phenyl-4-thioxo-2-thiazolidinone **1** (0.01 mol) in 10 ml of glacial acetic acid and 4-formylphenyl benzoate, 2-formyl-3-methoxyphenyl benzoate or salicyaldehyde **2a-c** (0.01 mol) with fused sodium acetate (0.015 mol) was refluxed for about 2 hr then left overnight at room temperature. The solid precipitated was filtered off, washed with water and finally dried and recrystallized from ethanol-dioxane mixture.

**Preparation of lemon juice**

Fresh lemon was purchased from the local market. The pieces were made using a knife and pressed in a fruit juicer to obtain the juice. Then the juice was filtered through filter paper to remove solid material and clear portion of juice was used as a catalyst.

**Green Method B**

Solution of 3-phenyl-4-thioxo-2-thiazolidinone **1** (0.01 mol) in 3 ml of lemon juice and 4-formylphenyl benzoate, 2-formyl-3-methoxyphenyl benzoate or salicyaldehyde **2a-c** (0.01 mol) was stirred at room temperature. After reaction completion as analyzed by TLC, the reaction mixture was quenched with cold water and stirred continuously until free flowing solid was obtained. The resulting solid was filtered, dried and recrystallization from ethanol-dioxane mixture.

**4-[(2-Oxo-3-phenyl-4-thioxothiazolidin-5-ylidene)methyl]phenyl benzoate** (**3a**).

Orange crystals, yield = 99%, m.p 220oC; νmax /cm-1 (KBr) 1717 (CO), 1584 (CO); 1H NMR (DMSO-d6) *δ*: 7.43–8.18 (m, 14H, Ar), 8.36 (s, 1H, CH); 13C NMR (DMSO) *δ* = 120.3, 122.9, 128.1, 128.2, 128.3, 128.7, 129.1, 129.6, 131.1, 131.7, 133.9, 135.7, 136.0, 152.0, 163.9, 193.9; m/z = 418 (M++1, 5.43%), 417 (M+, 18.75%), 385 (0.25%), 357 (0.25%), 312 (1.84%), 297 (1.40%), 279 (0.53%), 223 (0.47%), 181 (0.36%), 149 (0.89%), 121 (2.30%) 109 (0.50%), 191 (0.16%), 183 (0.36), 151 (0.42%), 121 (0.66%), 105 (100%), 88 (0.86%), 77 (48.34%). Anal. Calcd for C23H15NO3S2: C, 66.17; H, 3.62; N, 3.35; S, 15.36. Found: C, 66.35; H, 3.43; N, 3.13; S, 15.18%.

**2-Methoxy-4-[(2-oxo-3-phenyl-4-thioxothiazolidin-5-ylidene)methyl]phenyl benzoate** (**3b**).

Orange crystals, yield = 99%, m.p 260 oC; νmax /cm-1 (KBr) 1722 (CO), 1593 (CO); 1H NMR (DMSO-d6) *δ*: 3.86 (s, 3H, OCH3), 7.41-7.77 (m, 11H, Ar), 8.12-8.15 (m, 2H, Ar), 8.37 (s, 1H, CH); 13C NMR (DMSO) *δ* = 56.1, 115.3, 122.5, 124.1, 128.3, 128.4, 129.0, 129.3, 129.8, 132.7, 134.1, 136.3, 141.2, 151.5, 163.6, 194.0; m/z = 448 (M++1, 4.82%), 447 (M+, 16.79%), 417 (0.18%), 394 (0.16%), 356 (0.11%), 342 (1.65%), 326 (3.79%), 314 (0.57%), 278 (0.23%), 271 (0.20%), 254 (0.17%) 211 (0.25%), 191 (0.16%), 183 (0.36), 151 (0.42%), 121 (0.66%), 105 (100%), 91 (0.36%), 77 (32.7%). Anal. Calcd for C24H17NO4S2: C, 64.41; H, 3.83; N, 3.13; S, 14.33. Found: C, 64.41; H, 3.83; N, 3.13; S, 14.33%.

**5-(2-Hydroxybenzylidene)-3-phenyl-4-thioxothiazolidin-2-one**(**3c).**

Orange crystals, yield = 70%, m.p 255 oC; νmax /cm-1 (KBr) 3425 (OH), 1718 (CO); 1H NMR (DMSO-d6) *δ*: 7.31 (d, 2H, *J* = 6.9 Hz, Ar), 7.42-7.57 (m, 5H, Ar), 7.91 (d, 2H, *J* = 7.8 Hz, Ar), 8.21 (s, 1H, CH), 12.51 (s, 1H, OH); m/z = 313 (M+, 0.92%), 295 (100%), 279 (4.59%), 250 (15.18%), 190 (27.29%), 100 (21.74%), 77 (51.16%). Anal. Calcd for C16H11NO2S2: C, 61.32; H, 3.54; N, 4.47; S, 20.46. Found: C, 61.13; H, 3.37; N, 4.70; S, 20.28%.

**Preparation of cycloadducts 5a-o:**

**General Procedure :**

**Conventional method A**

A mixture of **3a-c** (0.01 mol) and *N*-arylmaleimides **4a-e** (0.01 mol) in glacial acetic acid (20 ml) was refluxed till decolourization took place, then it was left overnight at room temperature. The solid obtained was filtered off, and recrystallized from ethanol-dioxane mixture. The spectral data of compounds **5a-o** are shown below.

**Green Method B**

A mixture of **3a-c** (0.01 mol) in 3 ml of lemon juice was stirred and left overnight at room temperature. After reaction completion as analyzed by TLC, the reaction mixture was quenched with cold water and stirred continuously until free flowing solid was obtained. The resulting solid was filtered, dried and recrystallization from ethanol-dioxane mixture.

**4-((4aR,7aR,8S)-2,5,7-Trioxo-3,6-diphenyl-2,3,4a,5,6,7,7a,8-octahydropyrrolo-[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)phenyl benzoate** (**5a**).

Beige crystals, yield = 60%, m.p 232 oC; νmax /cm-1 (KBr) 1721 (CO), 1662 (CO), 1590 (CO); 1H NMR (DMSO-d6) *δ*: 4.16 (dd, 1H, *J* = 9 Hz, 6 Hz, H-6), 4.74 (d, 1H,*J* = 6 Hz, H-5), 5.21 (d, 1H, *J* = 9 Hz, H-7), 6.71-6.74 (m, 2H, Ar) 7.32-7.62 (m, 14H, Ar), 8.15-8.18 (m, 3H, Ar); Anal. Calcd for C33H22N2O5S2: C, 67.10; H, 3.75; N, 4.74; S, 10.86. Found: C, 67.30; H, 3.58; N, 4.94; S, 10.67%.

**4-((4aR,7aR,8S)-2,5,7-Trioxo-3-phenyl-6-(p-tolyl)-2,3,4a,5,6,7,7a,8-octahydropyrrolo-[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)phenyl benzoate** (**5b**).

Beige crystals, yield = 40%, m.p 200 oC; νmax /cm-1 (KBr) 1723 (CO), 1666 (CO), 1595 (CO); 1H NMR (DMSO-d6) *δ*: 3.32 (s, 3H, CH3), 4.11 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.71 (d, 1H,*J* = 6 Hz, H-5), 5.13 (d, 1H, *J* = 9 Hz, H-7), 6.62–6.63 (m, 2H, Ar), 7.32-7.64 (m, 13H, Ar), 7.66-8.15 (m, 3H, Ar). Anal. Calcd for C34H24N2O5S2: C, 67.53; H, 4.00; N, 4.63; S, 10.60. Found: C, 67.35; H, 4.19; N, 4.40; S, 10.78%.

**4-((4aR,7aR,8S)-6-(4-Methoxyphenyl)-2,5,7-trioxo-3-phenyl-2,3,4a,5,6,7,7a,8-octahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)phenyl benzoate** (**5c**).

Beige crystals, yield = 30%, m.p 220 oC; νmax /cm-1 (KBr) 1728 (CO), 1682 (CO), 1598 (CO); 1H NMR (DMSO-d6) *δ*: 3.82 (s, 3H, OCH3), 4.12 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.72 (d, 1H, *J* = 6 Hz, H-5), 5.18 (d, 1H, *J* = 9 Hz, H-7), 6.65–6.68 (m, 2H, Ar), 6.95-7.62 (m, 14H, Ar), 7.64-8.18 (m, 2H, Ar); 13C NMR (DMSO) *δ* = 55.3, 108.3, 114.2, 114.3, 121.9, 122.9, 123.7, 127.8, 127.8, 128.7, 128.8, 129.0, 129.3, 129.4, 129.6, 130.4, 133.9, 134.2, 134.3, 150.2, 159.1, 164.4, 168.7, 173.5, 173.6; m/z = 621 (M++1, 1.25%), 620 (M+, 3.11%), 587 (1.76%), 560 (3.46%), 515 (0.3%), 417 (6.1%), 383 (3.1%), 296 (1.9%), 223 (0.34%), 203 (5.3%), 188 (1.8%), 134 (1.2%), 121 (2.0%), 105 (100%), 89 (0.9%), 77 (33.26%); Anal. Calcd for C34H24N2O6S2: C, 65.79; H, 3.90; N, 4.51; S, 10.33.Found: C, 65.97; H, 3.73; N, 4.73; S, 10.51%.

**4-((4aR,7aR,8S)-6-(4-Chlorophenyl)-2,5,7-trioxo-3-phenyl-2,3,4a,5,6,7,7a,8-octahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)phenyl benzoate (5d).**

Beige crystals, yield = 36% ,m.p 235 oC; νmax /cm-1 (KBr) 1724 (CO), 1665 (CO), 1591 (CO); 1H NMR (DMSO-d6) *δ*: 4.13 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.73 (d, 1H, *J* = 6 Hz,H-5), 5.20 (d, 1H, *J* = 9 Hz, H-7), 6.76–6.79 (m, 2H, Ar), 7.29-7.78 (m, 13H, Ar), 8.16-8.18 (m, 3H, Ar); 13C NMR (DMSO) *δ* = 106.5, 107.7, 120.2, 121.8, 122.7, 127.7, 127.9, 128.3, 128.6, 128.7, 128.9, 129.2, 129.3, 129.5, 129.8, 130.2, 133.1, 133.8, 134.0, 134.1, 150.2, 164.4, 168.6, 173.0; m/z = 625 (M++1, 1.16%), 624 (M+, 40.3%), 596 (2.1%), 564 (4.1%), 443 (1.13%), 429 (4.7%), 383 (2.8%), 278 (1.24%), 207 (1.5%), 121 (1.0), 105 (100%), 89 (1.56%), 60 (1.9%), 51 (3.3%). Anal. Calcd for C33H21ClN2O5S2:C, 63.41; H, 3.39; Cl, 5.67; N, 4.48; S, 10.26. Found: C, 63.58; H, 3.20; N, 4.25; S, 10.45%.

**4-((4aR,7aR,8S)-6-(4-Bromophenyl)-2,5,7-trioxo-3-phenyl-2,3,4a,5,6,7,7a,8-octahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)phenyl benzoate** (**5e**).

Beige crystals, yield = 45%, m.p 240 oC; νmax /cm-1 (KBr) 1724 (CO), 1674 (CO), 1592 (CO); 1H NMR (DMSO-d6) *δ*: 4.15 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.78 (d, 1H, *J* = 6 Hz,H-5), 5.25 (d, 1H, *J* = 9 Hz, H-7), 6.77-6.81 (m, 2H, Ar), 7.30-7.76 (m, 13H, Ar), 8.16-8.19 (m, 3H, Ar); Anal. Calcd for C33H21BrN2O5S2:C, 59.20; H, 3.16; Br, 11.93; N, 4.18; S, 9.58. Found: C, 59.37; H, 3.35; N, 4.41; S, 9.75%.

**2-Methoxy-4-((4aR,7aR,8S)-2,5,7-trioxo-3,6-diphenyl-2,3,4a,5,6,7,7a,8-octahydropyrrolo-[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)phenyl benzoate** (**5f**).

Beige crystals, yield = 40%, m.p 200 oC; νmax /cm-1 (KBr) 1722 (CO), 1650 (CO), 1600 (CO); 1H NMR (DMSO-d6) *δ*: 3.70 (s, 3H, OCH3), 4.13 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.72 (d, 1H, *J* = 6Hz, H-5), 5.27 (d, 1H, *J* = 9 Hz, H-7), 6.74–6.76 (m, 2H, Ar), 7.07-7.75 (m, 13H, Ar), 8.14-8.17 (m, 3H, Ar); 13C NMR (DMSO) *δ* = 55.6, 107.9, 113.6, 121.5, 122.6, 122.8, 126.6, 127.8, 128.5, 128.6, 128.8, 128.9, 129.3, 129.5, 129.6, 131.2, 133.8, 134.1, 135.8, 139.1, 150.6, 163.8, 168.7, 173.3, 173.5; m/z = 622 (M++1, 0.80%), 621 (M+, 2.02%), 587 (0.87%), 560 (0.94%), 499 (2.05%), 471 (0.28%), 447 (5.64%), 352 (0.34%), 326 (1.69%), 308 (0.19), 241 (0.21%), 211 (0.28%), 173 (3.71%), 117 (1.26%), 105 (100%), 77 (33.20%); Anal. Calcd for C34H24N2O6S2: C, 65.79; H, 3.90; N, 4.51; S, 10.33. Found: C, 65.60; H, 4.07; N, 4.74; S, 10.15%.

**2-Methoxy-4-((4aR,7aR,8S)-2,5,7-trioxo-3-phenyl-6-(p-tolyl)-2,3,4a,5,6,7,7a,8-octahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)phenyl benzoate** (**5g**).

Beige crystals, yield = 43%, m.p 220 oC; νmax /cm-1 (KBr) 1733 (CO), 1655 (CO), 1591 (CO); 1H NMR (DMSO-d6) *δ*: 2.31 (s, 3H, CH3), 3.69 (s, 3H, OCH3), 4.10 (dd,1H, *J* = 9 Hz, 6 Hz,H-6), 4.70 (d, 1H, *J* = 6 Hz, H-5), 5.23 (d, 1H, *J* = 9 Hz, H-7), 6.60–6.63 (m, 2H, Ar), 7.22-7.76 (m, 13H, Ar), 8.14-8.16 (m, 2H, Ar); 13C NMR (DMSO) *δ* = 20.6, 55.7, 107.9, 113.6, 120.7, 121.5, 122.9, 126.5, 127.9, 128.5, 128.6, 128.9, 129.5, 129.6, 129.8, 134.0, 134.2, 135.9, 138.3, 139.0, 150.7, 163.8, 168.8, 173.5, 173.7; Anal. Calcd for C35H26N2O6S2: C, 66.23; H, 4.13; N, 4.41; S, 10.10. Found: C, 66.06; H, 4.30; N, 4.19; S, 10.27%.

**2-Methoxy-4-((4aR,7aR,8S)-6-(4-methoxyphenyl)-2,5,7-trioxo-3-phenyl-2,3,4a,5,6,7,7a,8-octahydropyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)phenyl benzoate** (**5h**).

Beige crystals, yield = 48%, m.p 180 oC; νmax /cm-1 (KBr) 1735 (CO), 1664 (CO), 1589 (CO); 1H NMR (DMSO-d6) *δ*: 3.73 (s, 3H, OCH3), 3.87 (s, 3H, OCH3), 4.15 (dd, 1H, *J* = 9 Hz, 6 Hz,H-6), 4.72 (d, 1H, *J* = 6 Hz,H-5), 5.29 (d, 1H, *J* = 8 Hz, H-7), 6.62–6.65 (m, 2H, Ar), 7.23-7.74 (m, 13H, Ar), 8.12-8.18 (m, 2H, Ar); Anal. Calcd for C35H26N2O7S2: C, 64.60; H, 4.03; N, 4.31; S, 9.85. Found: C, 64.78; H, 3.84; N, 4.53; S, 9.67%.

**4-((4aR,7aR,8S)-6-(4-Chlorophenyl)-2,5,7-trioxo-3-phenyl-2,3,4a,5,6,7,7a,8-octahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)-2-methoxyphenyl benzoate** (**5i**).

Beige crystals, yield = 35%, m.p 220 oC; νmax /cm-1 (KBr) 1729 (CO), 1663 (CO), 1590 (CO); 1H NMR (DMSO-d6) *δ*: 3.71 (s, 3H, OCH3), 4.13 (dd, 1H, *J* = 9 Hz, 6 Hz, H-6), 4.72 (d, 1H, *J* = 6 Hz, H-5), 5.26 (d, 1H, *J* = 9 Hz, H-7), 6.78–6.81 (m, 2H, Ar), 7.05-7.77 (m, 13H, Ar), 8.15-8.18 (m, 2H, Ar); 13C NMR (DMSO) *δ* = 55.7, 107.6, 113.6, 121.6, 122.6, 122.9, 127.9, 128.5, 128.9, 129.1, 129.4, 129.6, 129.8, 130.0, 133.4, 133.9, 134.2, 135.8, 139.2, 150.7, 164.0, 168.8, 173.2, 173.4; m/z = 657 (M++1, 0.34%), 656 (M+, 0.94%), 626 (0.57%), 596 (0.55%), 592 (0.25%), 551 (0.27%), 533 (2.87%), 503 (0.11%), 473 (0.35%), 447 (7.92%), 413 (0.27%), 386 (0.22%), 342 (0.77%), 326 (1.68%), 308 (0.28%), 271 (0.13%), 248 (0.18%), 223 (0.10%), 207 (2.82%), 183 (0.23%), 137 (1.13%), 105 (100%), 90 (1.44%), 77 (26.61%); Anal. Calcd for C34H23ClN2O6S2: C, 62.33; H, 3.54; Cl, 5.41; N, 4.28; S, 9.79. Found: C, 62.51; H, 3.35; N, 4.05; S, 9.97%.

**4-((4aR,7aR,8S)-6-(4-Bromophenyl)-2,5,7-trioxo-3-phenyl-2,3,4a,5,6,7,7a,8-octahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazol-8-yl)-2-methoxyphenyl benzoate** (**5j**).

Beige crystals, yield = 40%, m.p 245 oC; νmax /cm-1 (KBr) 1724 (CO), 1665 (CO), 1590 (CO); 1H NMR (DMSO-d6) *δ*: 3.73 (s, 3H, OCH3), 4.15 (dd, 1H, *J* = 9 Hz, 6 Hz, H-6), 4.76 (d, 1H, *J* = 6 Hz, H-5), 5.31 (d, 1H, *J* = 9 Hz, H-7), 6.77–6.83 (m, 2H, Ar), 7.09-7.80 (m, 13H, Ar), 8.16-8.19 (m, 2H, Ar); Anal. Calcd for C34H23BrN2O6S2: C, 58.37; H, 3.31; Br, 11.42; N, 4.00; S, 9.17. Found: C, 58.55; H, 3.50; N, 4.22; S, 9.34%.

**(4aR,7aR,8S)-8-(2-Hydroxyphenyl)-3,6-diphenyl-3,4a,7a,8-tetrahydropyrrolo-[3',4':5,6]thiopyrano[2,3-*d*]thiazole-2,5,7(6*H*)-trione** (**5k**).

Beige crystals, yield = 50%, m.p 250 oC; νmax /cm-1 (KBr) 3423(OH), 1717(CO), 1652 (CO); 1H NMR (DMSO-d6) *δ*: 4.12 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.44 (d, 1H, *J* = 6 Hz, H-5), 4.59 (d, 1H, *J* = 9 Hz, H-7), 6.53-7.23 (m, 14H, Ar), 9.78 (s, 1H, OH); m/z = 468 (M+, 0.19%), 414 (27.4%), 385 (8.93%), 295 (100%), 279 (28.4%), 190 (26.83%), 159 (16.2%), 132 (17.8%), 100 (22.0%); Anal. Calcd for C26H18N2O4S2: C, 64.18; H, 3.73; N, 5.76; S, 13.18. Found: C, 64.36; H, 3.54; N, 5.56; S, 13.0%.

**(4aR,7aR,8S)-8-(2-Hydroxyphenyl)-3-phenyl-6-(p-tolyl)-3,4a,7a,8-tetrahydropyrrolo-[3',4':5,6]thiopyrano[2,3-*d*]thiazole-2,5,7(6*H*)-trione** (**5l**).

Beige crystals, yield = 45%, m.p 200 oC; νmax /cm-1 (KBr) 3410 (OH), 1713 (CO), 1632 (CO); 1H NMR (DMSO-d6) *δ*: 2.32 (s, 3H, CH3), 4.32 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.51 (d, 1H, *J* = 6 Hz, H-5), 4.62 (d, 1H, *J* = 9 Hz, H-7), 6.65-7.42 (m, 13H, Ar), 9.86 (s, 1H, OH). Anal. Calcd for C27H20N2O4S2: C, 64.78; H, 4.03; N, 5.60; S, 12.81, Found: C, 64.60; H, 4.23; N, 5.37; S, 12.99%.

**(4aR,7aR,8S)-8-(2-Hydroxyphenyl)-6-(4-methoxyphenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazole-2,5,7(6*H*)-trione** (**5m**).

Beige crystals, yield = 55%, m.p 210 oC; νmax /cm-1 (KBr) 3440 (OH), 1715 (CO), 1643 (CO); 1H NMR (DMSO-d6) *δ*: 3.79 (s, 3H,OCH3), 4.44 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.72 (d, 1H, *J* = 6 Hz, H-5), 4.85 (d, 1H, *J* = 9 Hz, H-7), 6.83-7.57 (m, 13H, Ar), 9.88 (s, 1H, OH); m/z = 496 (M+2, 0.17%), 414 (28.1%), 357 (14.5%), 295 (100%), 279 (28.3%), 251 (15.7%), 159 (16.9%), 132 (17.5%), 100 (22.17). Anal. Calcd for C27H20N2O5S2: C, 62.78; H, 3.90; N, 5.42; S, 12.41, Found: C, 62.61; H, 3.72; N, 5.22; S, 12.60%.

**(4aR,7aR,8S)-6-(4-Chlorophenyl)-8-(2-hydroxyphenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazole-2,5,7(6*H*)-trione** (**5n**).

Beige crystals, yield = 50%, m.p 230 oC; νmax /cm-1 (KBr) 3436 (OH), 1714 (CO), 1650 (CO); 1H NMR (DMSO-d6) *δ*: 4.46 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.78 (d, 1H,*J* = 6 Hz, H-5), 4.89 (d, 1H, *J* =9 Hz, H-7), 6.85-7.63 (m, 13H, Ar), 9.85 (s, 1H, OH); m/z = 523 (M+, 0.23%), 385 (9.0%), 357 (13.9%), 295 (100%), 279 (29.4%), 250.9 (15.7%), 191 (27.8%), 132 (18.0%), 87.9 (37.3). Anal. Calcd for C26H17ClN2O4S2: C, 59.94; H, 3.29; Cl, 6.80; N, 5.38; S, 12.31. Found: C, 59.76; H, 3.11; N, 5.16; S, 12.50%.

**(4aR,7aR,8S)-6-(4-Bromophenyl)-8-(2-hydroxyphenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo[3',4':5,6]thiopyrano[2,3-*d*]thiazole-2,5,7(6*H*)-trione** (**5o**).

Beige crystals, yield = 55%,m.p 240oC; νmax /cm-1 (KBr) 3431 (OH), 1713 (CO), 1654 (CO); 1H NMR (DMSO-d6) *δ*: 4.43 (dd,1H, *J* = 9 Hz, 6 Hz, H-6), 4.72 (d, 1H,*J* = 6 Hz, H-5), 4.81 (d, 1H, *J* = 9 Hz, H-7), 6.73–7.42 (m, 13H, Ar), 9.89 (s, 1H, OH). Anal.Calcd for C26H17BrN2O4S2: C, 55.23; H, 3.03; Br, 14.13; N, 4.95; S, 11.34, Found: C, 55.04; H, 3.20; N, 4.74; S, 11.53%.

**Preparation of cycloadducts 7a-d, 8.**

**General procedure:**

To each of **3a-b** (0.01 mol) in glacial acetic acid (20 ml), was added acrylonitrile **6a** or ethyl acrylate **6b** (0.01 mol). The mixture was refluxed till decolourization took place, then it was left overnight at room temperature. The solid was filtered off, and recrystallized from ethanol - dioxane mixture.

**4-((6R,7S)-6-Cyano-2-oxo-3-phenyl-3,5,6,7-tetrahydro-2*H*-thiopyrano[2,3-*d*]thiazol-7-yl)phenyl benzoate** (**7a**).

Beige crystals, yield = 50%, m.p 180oC; νmax /cm-1 (KBr) 2240 (CN), 1745 (CO), 1625 (CO); 1H NMR (DMSO-d6) *δ*: 3.75-3.81 (m, 2H, H-5), 4.0 (t, 1H,*J* = 5.4 Hz, H-6), 4.5 (d, 1H, *J* = 5.4 Hz, H-7), 7.39-8.16 (m, 14H, Ar); 13C NMR (DMSO) *δ*= 103.4, 118.0, 121.7, 122.0, 124.1, 128.0, 128.7, 129.2, 129.5, 130.2, 133.8, 135.5, 150.3, 164.2, 168.3; m/z = 471 (M++1, 2.7%), 470 (M+, 8.7%), 417 (7.1%), 357 (1.0%), 295 (7.5%), 279 (2.1%), 251 (1.4%), 191 (2.1%), 159 (1.5%), 132 (2.6%), 105 (100%), 88 (4.3%), 77 (39.2%); Anal. Calcd for C26H18N2O3S2: C, 66.36; H, 3.86; N, 5.95; S, 13.63. Found: C, 66.20; H, 3.67; N, 6.18; S, 13.81%.

**4-((6R,7S)-6-Cyano-2-oxo-3-phenyl-3,5,6,7-tetrahydro-2*H*-thiopyrano[2,3-*d*]thiazol-7-yl)-2-methoxyphenyl benzoate** (**7b**).

Brown crystals,, yield = 47%, m.p 230oC; νmax /cm-1 (KBr) 2242 (CN), 1736 (CO), 1656 (CO); 1H NMR (DMSO-d6) *δ*: 3.64-3.77 (m, 2H, H-5), 3.81 (s, 3H, OCH3), 4.1 (t, 1H, *J* = 5.1 Hz, H-6), 4.5 (d, 1H, *J* = 5.1 Hz, H-7), 7.06-8.15 (m, 13H, Ar); 13C NMR (DMSO) *δ* = 56.0, 103.6, 114.2, 118.4, 120.9, 121.0, 121.3, 123.0, 124.4, 128.3, 128.7, 129.0, 129.5, 129.6, 129.8, 134.1, 137.1, 139.4, 150.8, 163.9, 168.6; Anal. Calcd for C27H20N2O4S2: C, 64.78; H, 4.03; N, 5.60; S, 12.81, Found: C, 64.60; H, 4.20; N, 5.38; S, 12.99%.

**Ethyl (6R,7S)-7-(4-(benzoyloxy)phenyl)-2-oxo-3-phenyl-3,5,6,7-tetrahydro-2*H*-thiopyrano-[2,3-*d*]thiazole-6-carboxylate** (**7c**).

Beige crystals, yield = 45%, m.p 195 oC; νmax /cm-1 (KBr) 1731 (CO), 1656 (CO), 1585 (CO); 1H NMR (DMSO-d6) *δ*: 0.73 (t, 3H, *J* = 7.2 Hz, CH3), 3.18-3.27 (m, 2H, H-5), 3.34 (t, 1H, *J* = 5.4 Hz, H-6), 3.74 (q, 2H, *J* = 7.2 Hz, CH2), 4.85 (d, 1H, *J* = 4.5 Hz, H-7), 7.34-8.14 (m, 14H, Ar); Anal. Calcd for C28H23NO5S2: C, 64.97; H, 4.48; N, 2.71; S, 12.39. Found: C, 64.82; H, 4.67; N, 2.94; S, 12.20%.

**Ethyl (6R,7S)-7-(4-(benzoyloxy)-3-methoxyphenyl)-2-oxo-3-phenyl-3,5,6,7-tetrahydro-2*H*-thiopyrano[2,3-*d*]thiazole-6-carboxylate** (**7d**).

Beige crystals, yield = 44%, m.p 210 oC; νmax /cm-1 (KBr) 1736 (CO), 1671 (CO), 1591 (CO); 1H NMR (DMSO-d6) *δ*: 0.81 (t, 3H, *J* = 7.2 Hz, CH3), 3.21-3.29 (m, 2H, H-5), 3.37 (t, 1H, *J* = 5.4 Hz, H-6), 3.76 (q, 2H, *J* = 7.2 Hz, CH2), 3.83 (s, 3H, OCH3), 4.92 (d, 1H, *J* = 4.5 Hz, H-7), 7.39-8.17 (m, 13H, Ar); Anal. Calcd for C29H25NO6S2: C, 63.60; H, 4.60; N, 2.56; S, 11.71. Found: C, 63.79; H, 4.42; N, 2.79; S, 11.91%.

**(5aR,11bS)-3-phenyl-3,5,5a,11b-tetrahydro-2*H*,6*H*-chromeno[4',3':4,5]thiopyrano[2,3-d]thiazole-2,6-dione** (**8**).

Beige crystals, yield = 83%, m.p 236 oC; νmax /cm-1 (KBr) 3447 (NH2), 1767 (CO), 1671 (CO); 1H NMR (DMSO-d6) *δ*: 3.47 (d, 2H, *J* = 3.6 Hz, H-5), 4.03 (m, 1H, H-6), 4.46 (d, 1H, *J* = 6.0 Hz, H-7), 7.16-7.53 (m, 9H, Ar); Anal. Calcd for C19H13NO3S2:C, 62.11; H, 3.57; N, 3.81; S, 17.45. Found: C, 62.29; H, 3.40; N, 3.61; S, 17.64%.

**General procedure of 9a,b and 10:**

A solution of equimolecular amounts (0.01 mol)of **3a-c** and malononitrile in ethanol (100 mL) and few drops of triethylamine was refluxed for 1hr, then left at room temperature. The solid product so obtained was filtered off and crystallized from acetic acid.

**4-(5-Amino-6-cyano-2-oxo-3-phenyl-3,7-dihydro-2*H*-thiopyrano[2,3-*d*]thiazol-7-yl)phenyl benzoate (9a).**

Beige crystals, yield = 50%, m.p 210oC; νmax /cm-1 (KBr) 3426 (NH2), 2361 (CN), 1726 (CO), 1653 (CO); 1H NMR (DMSO-d6) *δ*: 4.97 (s, 1H, H-7), 6.89-8.167(m, 16H, Ar& NH2); Anal. Calcd for C26H17N3O3S2:C, 64.58; H, 3.54; N, 8.69; S, 13.26. Found: C, 64.39; H, 3.73; N, 8.90; S, 13.09%.

**4-(5-Amino-6-cyano-2-oxo-3-phenyl-3,7-dihydro-2*H*-thiopyrano[2,3-*d*]thiazol-7-yl)-2-methoxyphenyl benzoate (9b).**

Beige crystals, yield = 39%, m.p 200 oC; νmax /cm-1 (KBr) 3452 (NH2), 2243 (CN), 1680 (CO), 1595 (CO); 1H NMR (DMSO-d6) *δ*: 3.80 (s, 3H, OCH3), 4.46 (s, 1H,H-7), 6.92-8.14 (m, 15H, Ar&NH2);13C NMR (DMSO) *δ* = 55.8, 72.1, 105.7, 111.8, 117.3, 118.5, 119.2, 123.3, 128.1, 128.6, 128.8, 129.6, 129.66, 129.7, 133.6, 133.8, 138.7, 141.2, 150.9, 151.2; Anal. Calcd for C27H19N3O4S2:C, 63.14; H, 3.73; N, 8.18; S, 12.48. Found: C, 63.33; H, 3.56; N, 8.41; S, 12.31%.

**5-Amino-3-phenyl-3,11b-dihydro-2*H*,6*H*-chromeno[4',3':4,5]thiopyrano[2,3-*d*]thiazole-2,6-dione (10).**

Beige crystals, yield = 43%, m.p 280 oC; νmax /cm-1 (KBr) 3447 (NH2), 1767 (CO), 1671 (CO); 1H NMR (DMSO-d6) *δ*: 4.40 (s, 1H,H-7), 7.08-7.61 (m, 11H, Ar&NH2); Anal. Calcd for C19H12N2O3S2: C, 59.99; H, 3.18; N, 7.36; S, 16.85. Found: C, 59.81; H, 3.35; N, 7.59; S, 16.68%.