

Stereoselective synthesis of spirocyclic pyrrolidine/ pyrrolizidine/ pyrrolothiazolidines, using L-proline functionalized manganese ferrite nanorod as a novel heterogeneous catalyst

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2.4 | Spectral data

2.4.1 | 1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 1). White solid, Yield: 85%; m.p.155-157 °C.IR (KBr, cm⁻¹) =3453,3142, 2912, 1765, 1723, 1609.¹H NMR (DMSO, 600 MHz): 10.75 (s, 1H), 8.03 (s, 1H),2.07(s, 3H, N1'-CH3) 3.55 (t, 1H, C5'-H, J = 8.4 Hz), 3.85 (t, 1H, C5'-H,J = 9.2 Hz), 4.67 (dd, 1H, C4'-H, J = 9.6, 8.2Hz) 7.01 –7.66 (m, 7H), ¹³C NMR (DMSO, 400 MHz): 176.7, 170.58, 168.07, 144.33, 141.60, 137.97, 134.76, 129.36, 126.74, 126.74, 125.09, 123.72, 122.80,79.35, 74.75, 58.70, 46.28, 35.14 ppm; MS: m/z=384.5 (M)Analysis calcd for C₁₈H₁₅N₃O₃S₂: C, 56.09; H, 3.92; N, 10.90; S, 10.64. Found: C, 56.11; H, 3.87; N, 10.79; S, 16.78%

2.4.2 | 7'-(thiophen-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 2). White solid, Yield: 0.43g, 89%; m.p.158-160°C IR (KBr, cm⁻¹) = 3438, 3054 , 1703 ,1683; ¹H NMR (DMSO, 600 MHz): δ: 2.70 (t, 1H, C1'-H, J= 8.8 Hz), 2.99 (dd, 1H, C1'-H, J = 9.2 Hz, 5.6 Hz), 3.76 (d, 1H, C3'-H, J = 5.6 Hz), 4.17 (d,1H, C3'-H, J = 6.0 Hz), 4.34 (d, 1H, C7'-H, J = 8.8 Hz), 4.81-4.85 (m, 1H, C7a'-H), 6.88-7.64 (m,7H, Ar-H), 8.50 (s, 1H, N1''-H), 10.40 (s, 1H, N3'''-H) ppm¹³C NMR (DMSO, 150 MHz): 176.72, 170.59, 168.02, 144.32,141.06, 137.92, 134.98, 133.41, 129.38, 110.58, 79.33, 74.73, 58.69, 46.26, 35.15, 30.25 ppm MS: m/z= 429 (M).Analysis calcd for C₁₉H₁₅N₃O₃S₃: C, 53.13; H, 3.52; N, 9.78; S, 22.13.Found: C, 53.01; H, 3.45; N, 9.70; S, 22.03%

2.4.3 | 1' -(thiophen-2-yl)-5',6',7',7a'-tetrahydro-1'H dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 3),pale Gray solid, Yield: 0.43g, 78%; m.p.195-197°C IR (KBr, cm⁻¹) = 3445, 3050,1722, 1636 cm⁻¹; ¹H NMR (DMSO, 600 MHz): δ:1.09-1.76(m, 2H, H6'-CH₂), 1.99-2.01,2.08-2.13 (m, 2H, H5'-CH₂), 2.30-2.39, 2.59-2.66 (m, 2H, H7'-CH₂), 3.45 (d, 1H, H1'-CH, J = 9.5 Hz), 4.10-4.13 (m, 1H, C7a-H),

6.78-7.94, 8.29 (m,9H, Ar-H), 7.99 (s, 1H, H₂-CH)10.01 (s, 1H, N1'-H), 10.30 (s, 1H, N1''-H), 12.10 (s, 1H, N3'''-H) ppm, ¹³C NMR (DMSO, 150 MHz): 185.36, 176.43, 176.07, 143.21, 142.33, 139.12, 137.70, 124.64, 123.82, 122.50, 121.24,118.57, 113.00, 68.23, 68.17, 60.29, 46.76, 24.25, 24.68, 24.16ppm MS: m/z= 411 (M). Analysis calcd for C₂₀H₁₇N₃O₃S₂: 58.38; H, 4.16; N, 10.21; S, 15.58. Found: C, 58.01; H, 4.45; N, 10.70; S, 15.23%

2.4.4 | 4'-(furan-2-yl)-1'-methyldispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 4).Pale yellow solid, Yield: 88%; m.p.160-162°C IR (KBr, cm⁻¹) = 3097,2978,1758, 1607, cm⁻¹H NMR (DMSO, 600 MHz):12.55 (s, 1H), 10.76 (s,1H), 2.07(s, 3H, N1'-CH₃) 3.55 (t, 1H, C5'-H, J = 8.4 Hz), 3.85 (t, 1H, C5'-H, J = 9.2 Hz), 4.67 (dd, 1H, C4'-H, J = 9.6, 8.2Hz) 7.02 –8.01 (m, 7H), ¹³C NMR (DMSO, 150 MHz):174.72, 170.52,168.02, 144.32, 141.60, 137.92, 134.86, 133.41, 129.38, 125.21, 123.63, 122.81, 110.58, 79.33, 74.75, 58.69, 46.26,35.15 MS: m/z= 369 (M). Analysis calcd for C₁₈H₁₅N₃O₄S: C, 58.53; H, 4.09; N, 11.38; S, 8.68. Found: C, 53.69; H, 3.95; N, 11.35; S, 8.53%

2.4.5 | 7'-(furan-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 5).yellow solid, Yield: 90%; m.p.186-189°C, IR (KBr, cm⁻¹) = 3430,1765, 1676 , cm⁻¹H NMR (DMSO, 600 MHz): δ: 3.04 (t, 1H, C1'-H, J= 8.8 Hz), 3.11 (dd, 1H, C1'-H, J = 9.2 Hz, 5.6 Hz), 3.44 (d, 1H, C3'-H, J = 5.6 Hz), 4.27 (d,1H, C3'-H, J = 6.0 Hz), 4.47 (d, 1H, C7'-H, J = 8.8 Hz), 5.22-5.24 (m, 1H, C7a'-H), 6.48-7.68 (m,7H, Ar-H), 10.96 (s, 1H, N1''-H), 12.45 (s, 1H, N3'''-H) ppm ¹³C NMR (DMSO, 150 MHz): 176.71, 170.58, 168.07, 141.60, 137.97, 134.76, 131.10, 129.36, 126.74, 126.68, 123.72, 122.80,110.57, 79.35, 74.75, 58.70, 46.28, 35.14, 35.74 MS: m/z= 369 (M). Analysis calcd for C₁₉H₁₅N₃O₄S₂: C, 55.19; H, 3.66; N, 10.16; S, 15.48. Found: C, 55.34; H, 3.25; N, 11.35; S, 15.53%

2.4.6 | 1' -(furan-2-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione(Table 4, entry 6).Orang solid, Yield: 0.43g, 91%; m.p.208-210°C C IR (KBr, cm⁻¹) = 3055, 2940,1740, 1692 cm⁻¹; ¹H NMR (DMSO, 600 MHz): δ:1.01-1.66(m, 2H, H6'-CH₂), 1.90-1.98,1.99-2.02 (m, 2H, H5'-CH₂), 2.37-2.43, 2.60-2.63 (m, 2H, H7'-CH₂), 3.26 (d, 1H, H1'-CH, J = 9.5 Hz), 3.26-3.45 (m, 1H, C7a'-H), 6.20-8.10 (m,7H, Ar-H), 9.93 (s, 1H, N1''-H), 12.15 (s, 1H, N3'''-H) ppm, ¹³C NMR (DMSO, 150MHz):185.44, 183.99, 174.99, 138.99,137.50,124.56, 123.93,122.60, 121.28, 118.61, 112.89, 106.60, 105.28, 74.56, 73.89, 65.29,64.51, 54.56, 28.99, 27.50ppmMS: m/z= 395 (M). Analysis calcd for C₂₀H₁₇N₃O₄S: C, 60.75; H, 4.33; N, 10.63; S, 8.11. Found: C, 60.99; H, 4.75; N, 10.37; S, 8.03%

2.4.7 | 4'-(1H-indol-3-yl)-1'-methyldispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 7).Pale Orang solid, Yield: 89%; m.p.198-200°C, IR (KBr, cm⁻¹) = 3447,2956,1703, 1607, cm⁻¹H NMR (DMSO, 600 MHz):12.53 (s, 1H,N3'''-H), 10.76 (s, 1H, N1''-H), 10.76 (s, 1H, N1'-H) ,8.01 (s,

1H, Ar-H)2.23(s, 3H, N1'-CH₃) 3.83 (t, 1H, C5'-H, J = 8.4 Hz), 4.68 (t, 1H, C5'-H, J = 9.2 Hz), 4.72 (dd, 1H, C4'-H, J = 9.6, 8.2Hz) 7.01–8.04 (m, 7H), ¹³C NMR (DMSO, 150 MHz):185.44, 176.89,176.51, 144.92, 142.22, 138.99, 137.51, 130.16, 129.14, 127.89, 124.57, 123.93, 122.59, 121.28,118.61, 113.92, 112.89,76.14, 66.97, 61.27, 46.56, 24.24 MS: m/z= 369 (M). Analysis calcd for C₂₂H₂₀N₄O₃S: C, 62.84; H, 4.79; N, 13.32; S, 7.62. Found: C, 62.09; H, 3.97; N, 13.55; S, 7.03%

2.4.8 | 7'-(1H-indol-3-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 8).Orang solid, Yield: 87%; m.p.227-230°CIR (KBr, cm⁻¹) = 3174, 3058, 2923,1765, 1694 , cm⁻¹H NMR (DMSO, 600 MHz): δ: 3.11 (t, 1H, C₁'-H, J= 8.8 Hz), 3.13 (dd, 1H, C₁'-H, J = 9.2 Hz, 5.6 Hz), 3.80 (d, 1H, C₃'-H, J = 5.6 Hz), 4.22 (d,1H, C₃'-H, J = 6.0 Hz), 4.51 (d, 1H, C7'-H, J = 8.8 Hz), 5.21-5.24 (m, 1H, C7a'-H), 6.49-7.61 (m,9H, Ar-H),7.60(s, 1H, C₂-H) 10.96 (s, 1H, N1''-H), 12.45 (s, 1H, N3'''-H) ppm ¹³C NMR (DMSO, 150 MHz): 176.71, 170.58, 168.07, 141.60, 137.97, 134.76, 131.10, 129.36, 126.74, 126.68, 123.72, 122.80,110.57, 79.35, 74.75, 58.70, 46.28, 35.14, 35.74 MS: m/z= 369 (M). Analysis calcd for C₂₃H₁₈N₄O₃S₂: C, 59.72; H, 3.92; N, 12.11; S, 13.86. Found: C, 59.64; H, 3.75; N, 12.35; S, 13.53%

2.4.9 | 1'-(1H-indol-3-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 9).Orang crystal, Yield: 80%; m.p.208-210°C:IR (KBr, cm⁻¹) = 3373,3055, 2940,1740, 1692 cm⁻¹; ¹H NMR (DMSO, 600 MHz): δ:1.07-1.75(m, 2H, H6'-CH₂), 1.99-2.13 (m, 2H, H5'-CH₂), 2.30-2.63 (m, 2H, H7'-CH₂), 3.46 (d, 1H, H1'-CH, J = 9.5 Hz), 4.11-4.13 (m, 1H, C7a-H), 6.78-7.948.29 (m,9H, Ar-H), 8.29 (s, 1H, H₂-CH)10.31 (s, 1H, N1'-H), 10.59 (s, 1H, N1''-H), 12.15 (s, 1H, N3'''-H) ppm ¹³C NMR (DMSO, 150 MHz): 185.44, 175.89, 174.99, 150.51, 142.22, 138.99, 137.51, 130.16, 129.14, 127.89, 124.57, 123.93,122.59,121.28,118.61,113.92, 112.89, 66.97, 61.27, 60.26, 46.56, 24.24, 23.68, 21.09ppm, MS: m/z= 444 (M).Analysis calcd for C₂₄H₂₀N₄O₃S: C, 64.85; H, 4.54; N, 12.60; S, 7.21. Found: C, 64.99; H, 4.65; N, 12.57; S, 7.13%

2.4.10 | 4'-(4-methoxyphenyl)-1'-methyldispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 10).Yield 77%; mp 156-158°C; IR (KBr) 1762, 1689, 1665 cm⁻¹; ¹H NMR (DMSO, 600 MHz): 11.2 (s, 1H), 9.87 (s, 1H), 6.8–7.7 (m, 8H), 4.32 (dd, 9.4, J= 8.3 Hz, 1Ha), 3.42 (dd, 12.3, J= 8.4 Hz, 1Hc), 3.35 (dd, 12.3, J= 8.4 Hz, 1Hb), 3.75 (s, 3H) 2.12 (s, 3H); ¹³C NMR (DMSO, 400 MHz) 180.2, 173.4, 168.3, 158.0, 152.2, 139.7, 131.8, 129.4, 128.5, 126.2, 124.2, 121.4, 114.5, 80.2, 69.4, 58.5, 54.5, 38.1, 33.7 ppm; m/z 408.4 (M). Analysis calcd for C₂₁H₁₉N₃O₄S: C, 61.60; H, 4.68; N, 10.26; S, 7.83. Found: C, 61.56; H, 4.66; N, 10.35; S, 7.79%

2.4.11 | 7'-(4-methoxyphenyl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 11).

yellow to white solid, Yield: 79%; m.p.189-190°C; IR (KBr, cm^{-1}) = 3160, 3148, 2911,1755, 1685 , cm^{-1} ; ^1H NMR (DMSO, 600 MHz): δ : 3.12 (t, 1H, $\text{C}_1\text{-H}$, $J = 8.8$ Hz), 3.16 (dd, 1H, $\text{C}_1\text{-H}$, $J = 9.2$ Hz, 5.6 Hz), 3.95 (d, 1H, $\text{C}_3\text{-H}$, $J = 5.6$ Hz), 4.61 (d,1H, $\text{C}_3\text{-H}$, $J = 6.0$ Hz), 4.73 (d, 1H, $\text{C}7\text{-H}$, $J = 8.8$ Hz), 5.251-5.64 (m, 1H, $\text{C}7\text{a}'\text{-H}$), 6.51-7.75 (m,8H, Ar-H),3.68(s, 3H, CH_3) 10.55 (s, 1H, $\text{N}1''\text{-H}$), 11.12 (s, 1H, $\text{N}3'''\text{-H}$) ppm ^{13}C NMR (DMSO, 150 MHz): 179.71, 172.50, 167.07, 142.70, 138.07, 134.26, 135.12, 129.18, 127.44, 125.14, 122.42, 122.89,115.37, 75.25, 72.95, 60.48,54.02, 55.08 45.38, 36.25, 35.64 MS: $m/z = 369$ (M). Analysis calcd for $\text{C}_{22}\text{H}_{19}\text{N}_3\text{O}_4\text{S}_2$: C, 58.26; H, 4.22; N, 9.27; S, 14.11. Found: C, 58.64; H, 3.75; N, 10.35; S, 14.53%

2.4.12 | 1'-(4-methoxyphenyl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 12).

white solid,70%; m.p.201-205°C:IR (KBr, cm^{-1}) = 3471,3145, 2970,1755, 1698 cm^{-1} ; ^1H NMR (DMSO, 600 MHz): δ :1.17-1.82(m, 2H, $\text{H}6'\text{-CH}_2$), 2.09-2.21 (m, 2H, $\text{H}5'\text{-CH}_2$), 2.32-2.71 (m, 2H, $\text{H}7'\text{-CH}_2$), 3.57 (d, 1H, $\text{H}1'\text{-CH}$, $J = 9.5$ Hz), 4.21-4.21 (m, 1H, $\text{C}7\text{a}'\text{-H}$), 6.89-7.48 (m,8H, Ar-H), 3.60 (s, 3H, CH_3), 11.50 (s, 1H, $\text{N}1''\text{-H}$), 12.02 (s, 1H, $\text{N}3'''\text{-H}$) ppm ^{13}C NMR (DMSO, 150 MHz): 178.44, 175.29, 172.79, 150.51, 142.22, 138.99, 137.51, 130.16, 129.14, 127.89, 124.57, 123.93, 122.59, 121.28,118.61,113.92, 112.89, 66.97, 61.27, 60.26, 46.56, 24.24, 23.68, 21.09ppm, MS: $m/z = 435$ (M).Analysis calcd for $\text{C}_{23}\text{H}_{21}\text{N}_3\text{O}_4\text{S}$: C, 63.43; H, 4.86; N, 9.65; S, 7.36.Found: C, 63.59; H, 4.75; N, 10.57; S, 7.13%

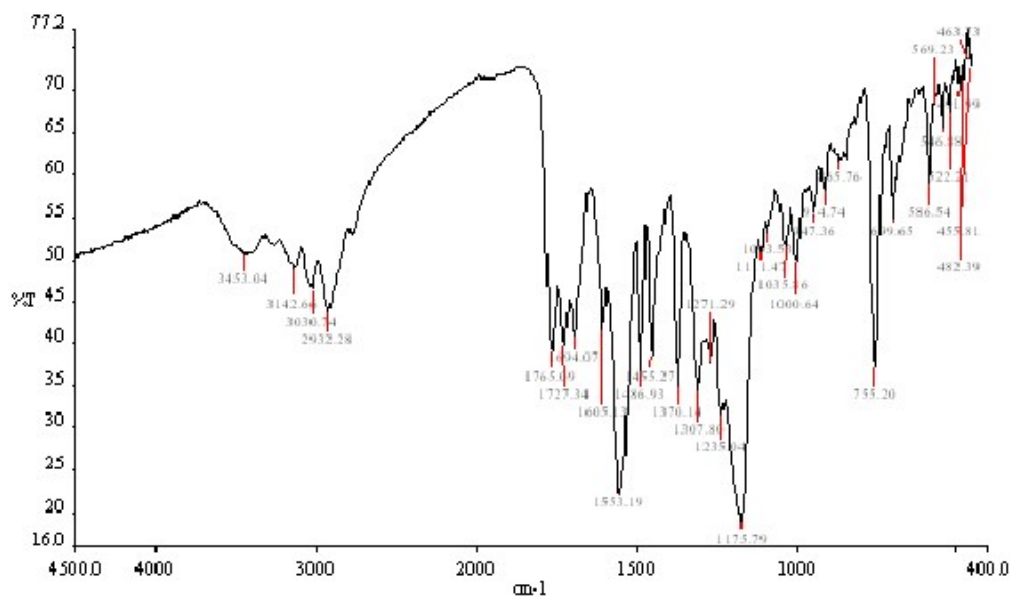


Fig1. S1a (FT-IR). 1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

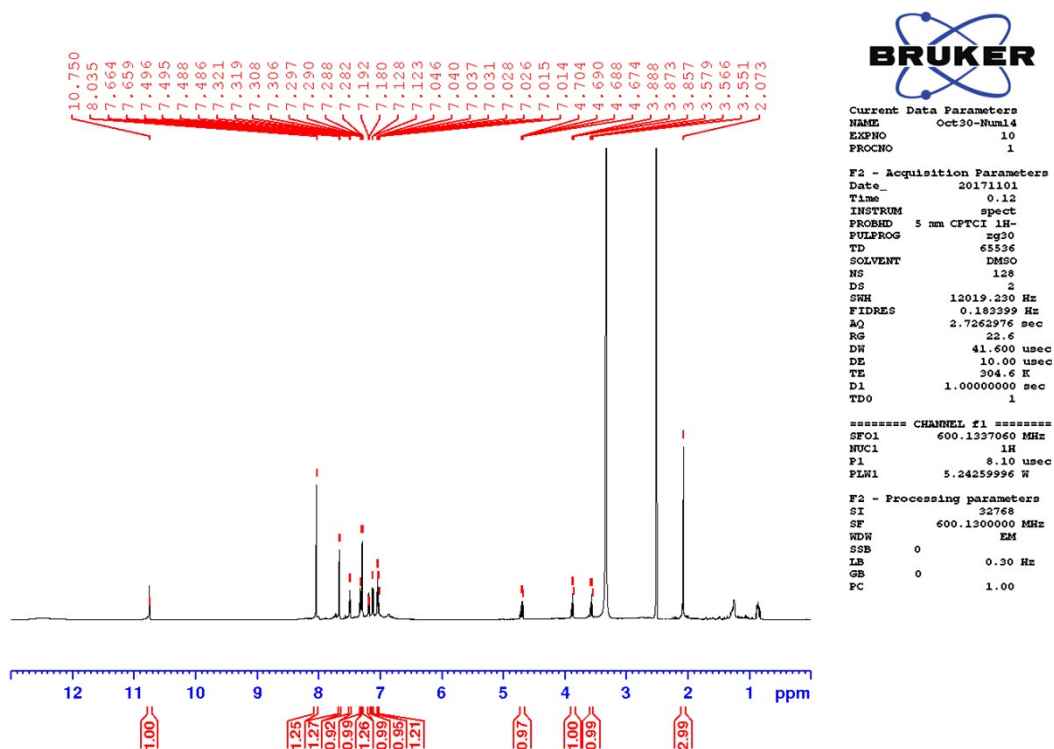


Fig2. S1a HNMR Spectra. 1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

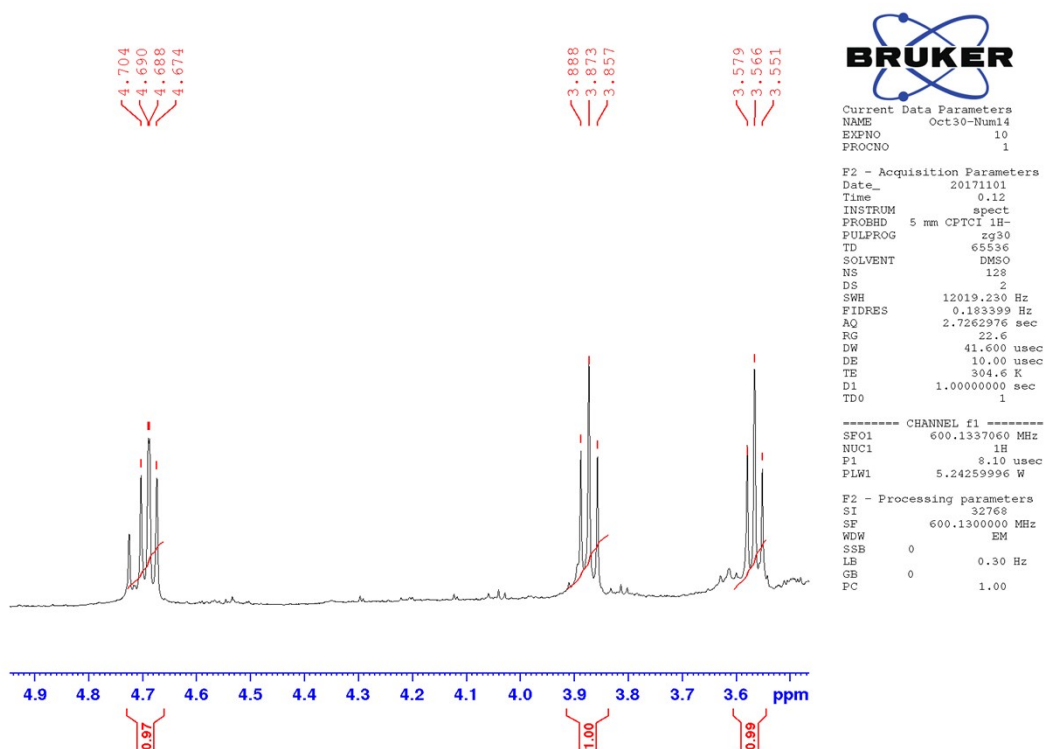


Fig3. S1a ¹H NMR Spectra expand. 1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

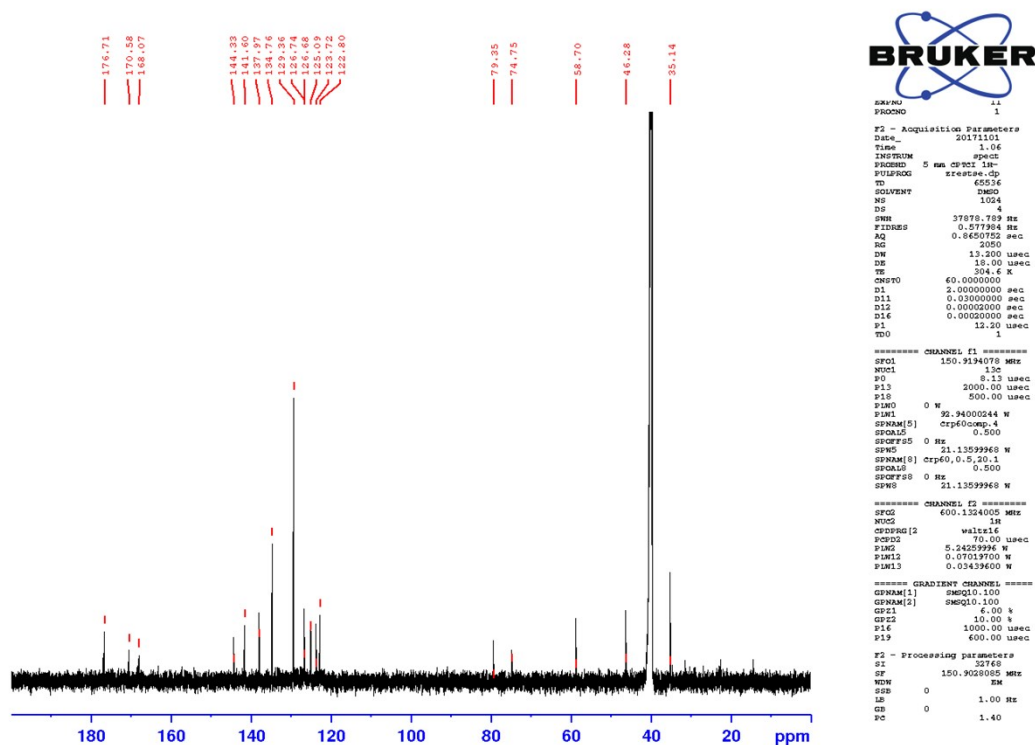


Fig4. S1a ¹³C NMR Spectra. 1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

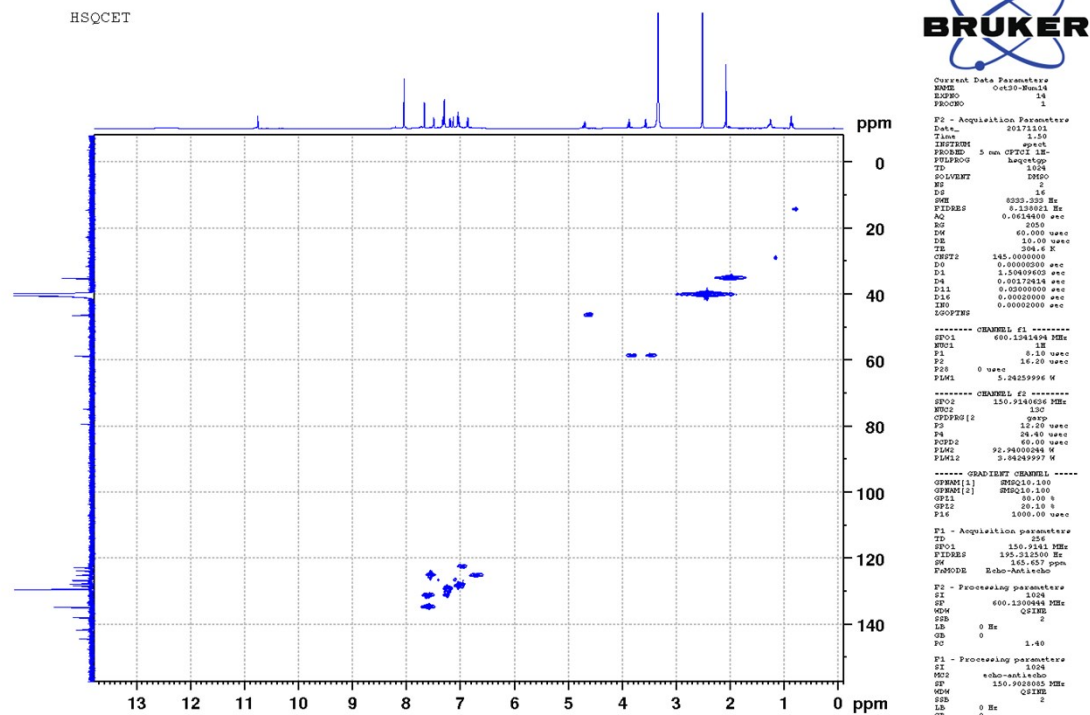


Fig5. S1a HSQC Spectra.1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5"-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

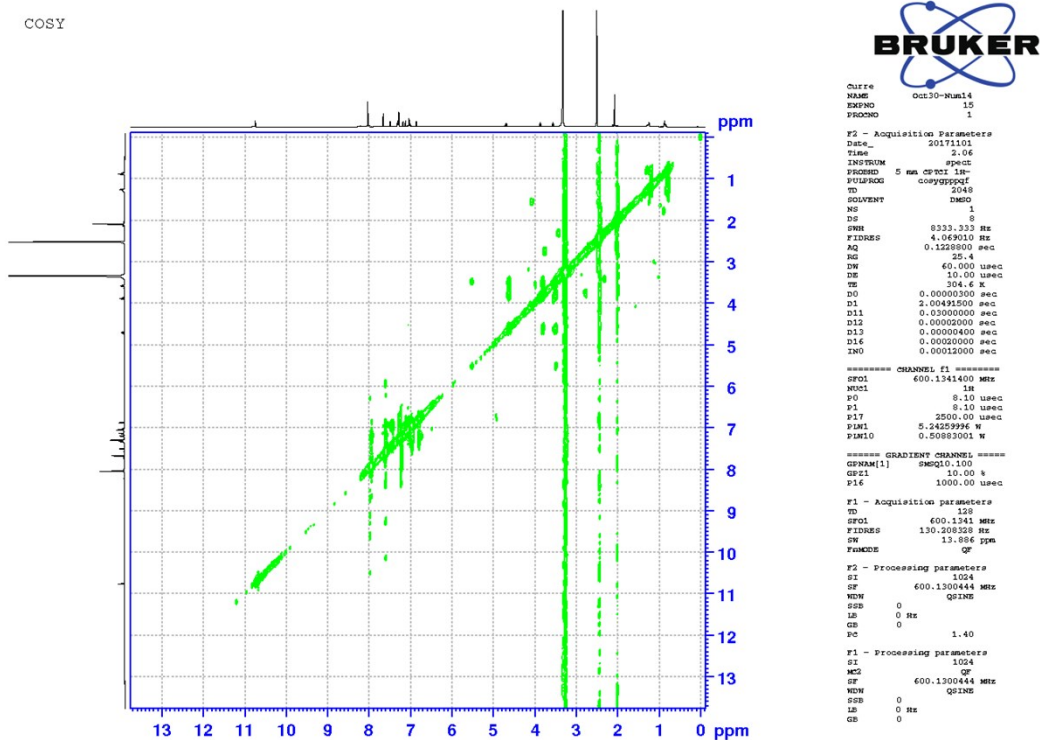


Fig6. S1a COSY Spectra.1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5"-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

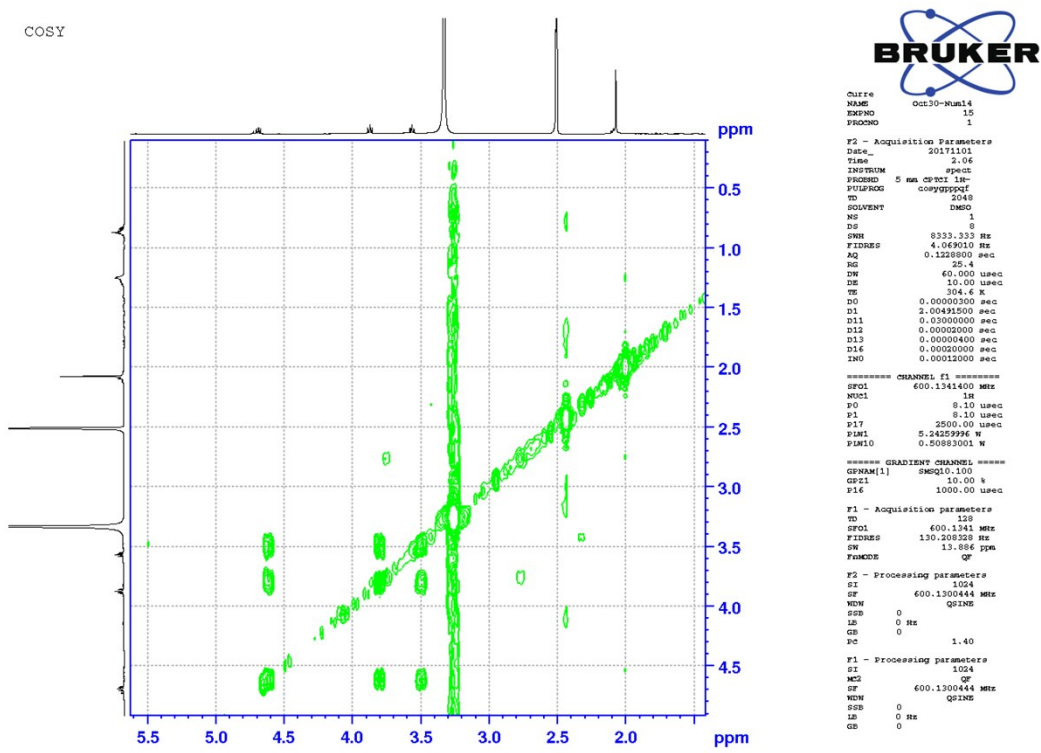


Fig7. S1a COSY Spectra. 1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5'-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

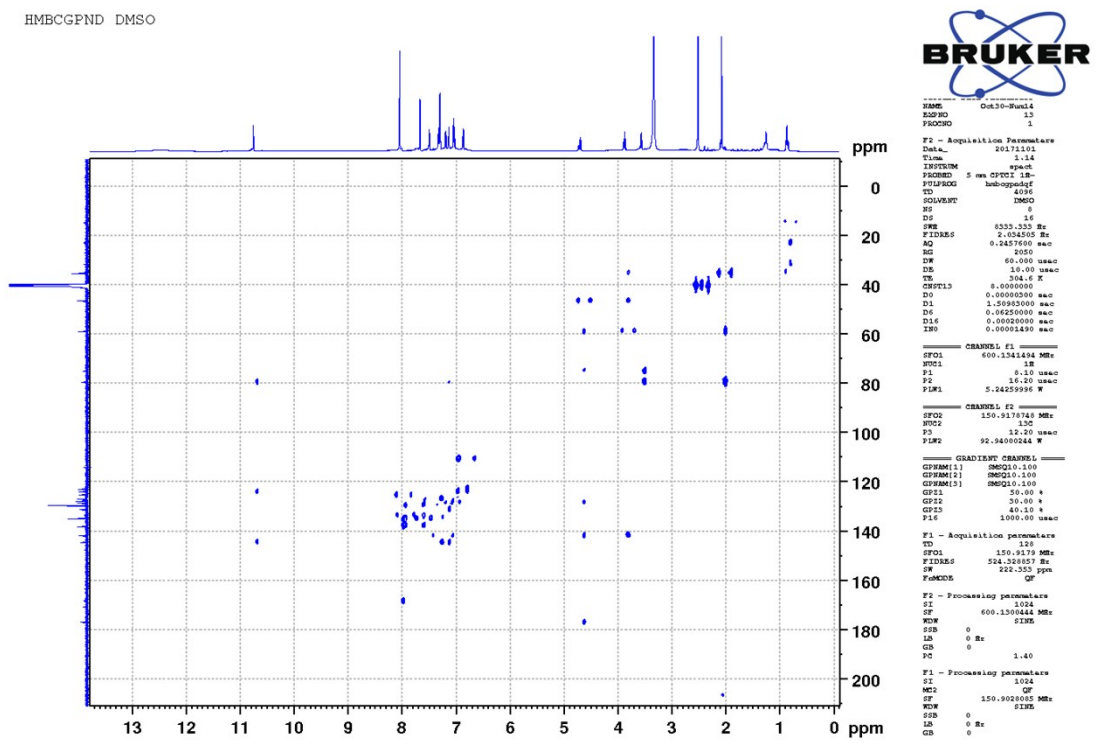


Fig8. S1a HMBC Spectra. 1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5'-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

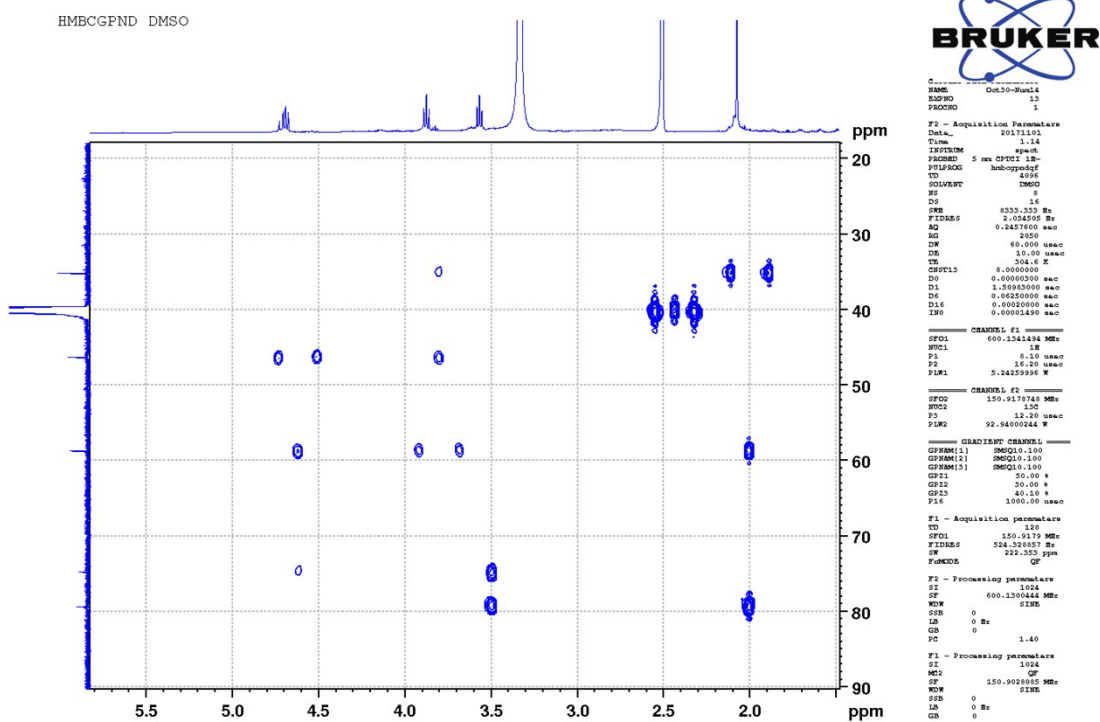


Fig9. S1a HMBC Spectra.1'-methyl-(thiophen-2-yl) dispiro[indoline-3,2'-pyrrolidine-3',5'-thiazolidine]-2,2'',4''-trione (Table 4, entry 1).

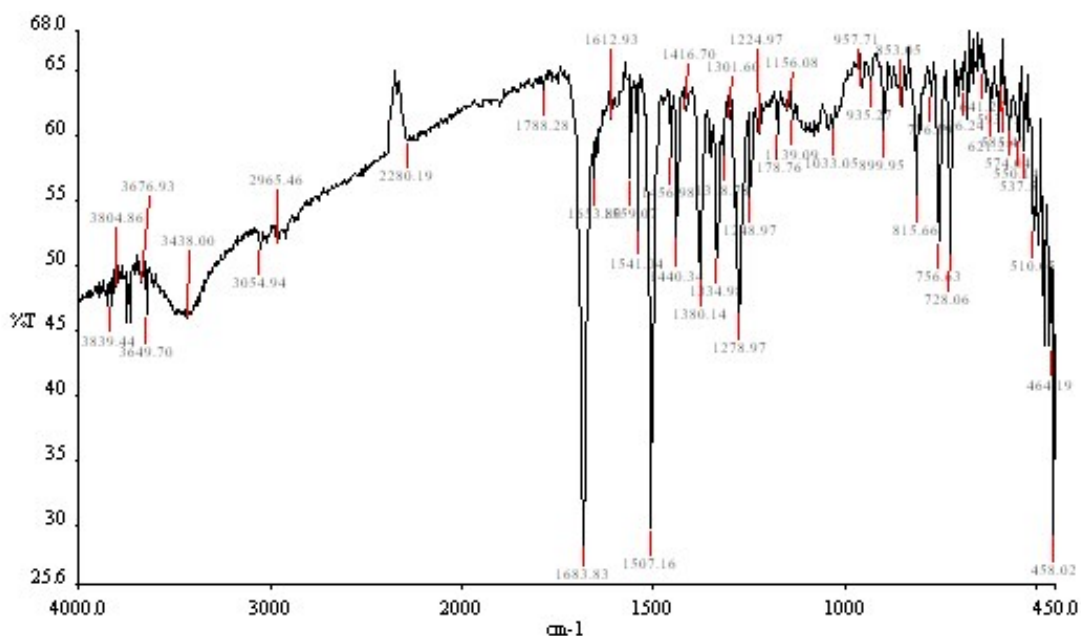


Fig10. S1b (FT-IR).7'-(thiophen-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 2).

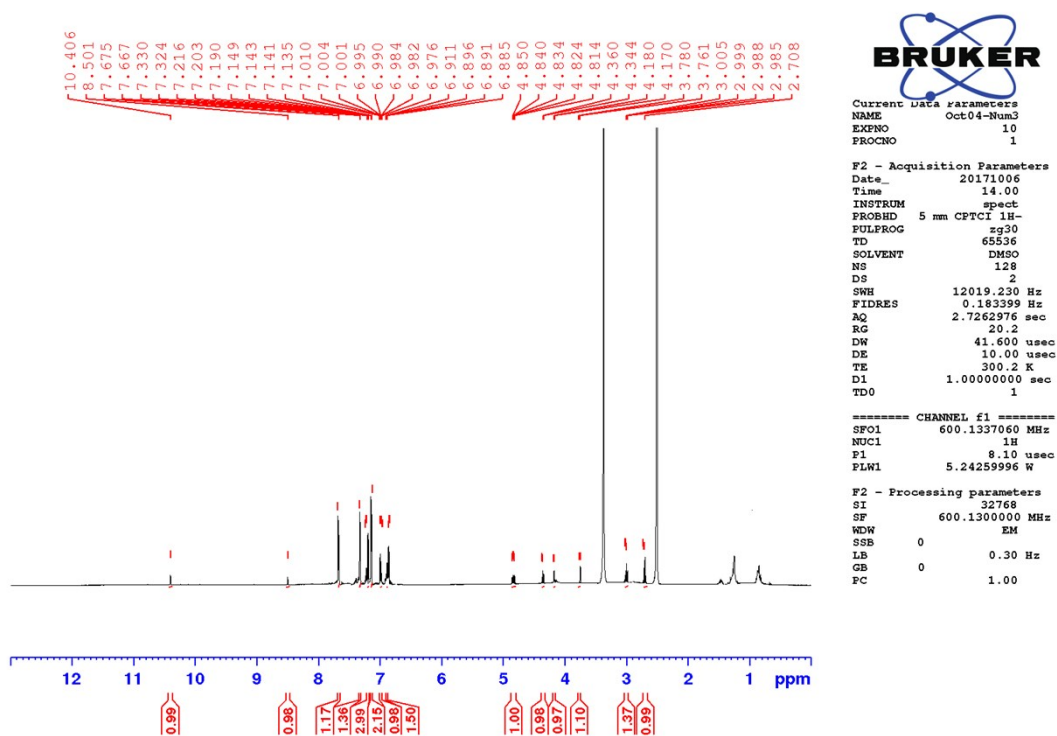


Fig11. S1b HNMR Spectra.7'-(thiophen-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 2).

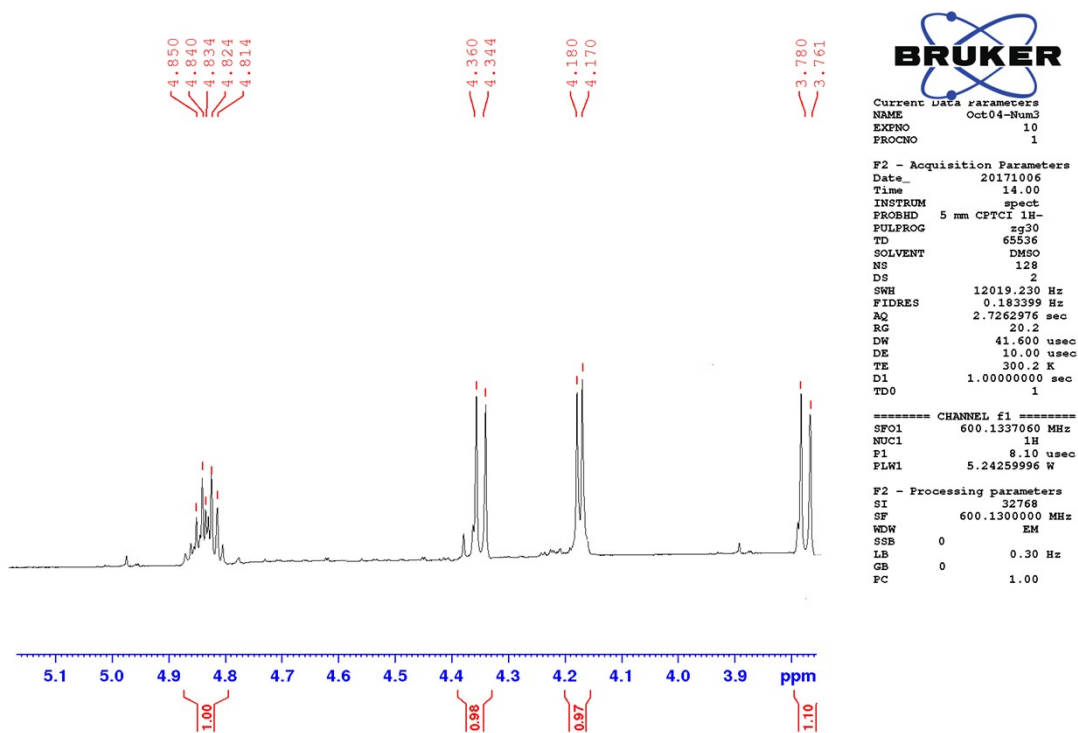


Fig12. S1b HNMR Spectra.7'-(thiophen-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 2).

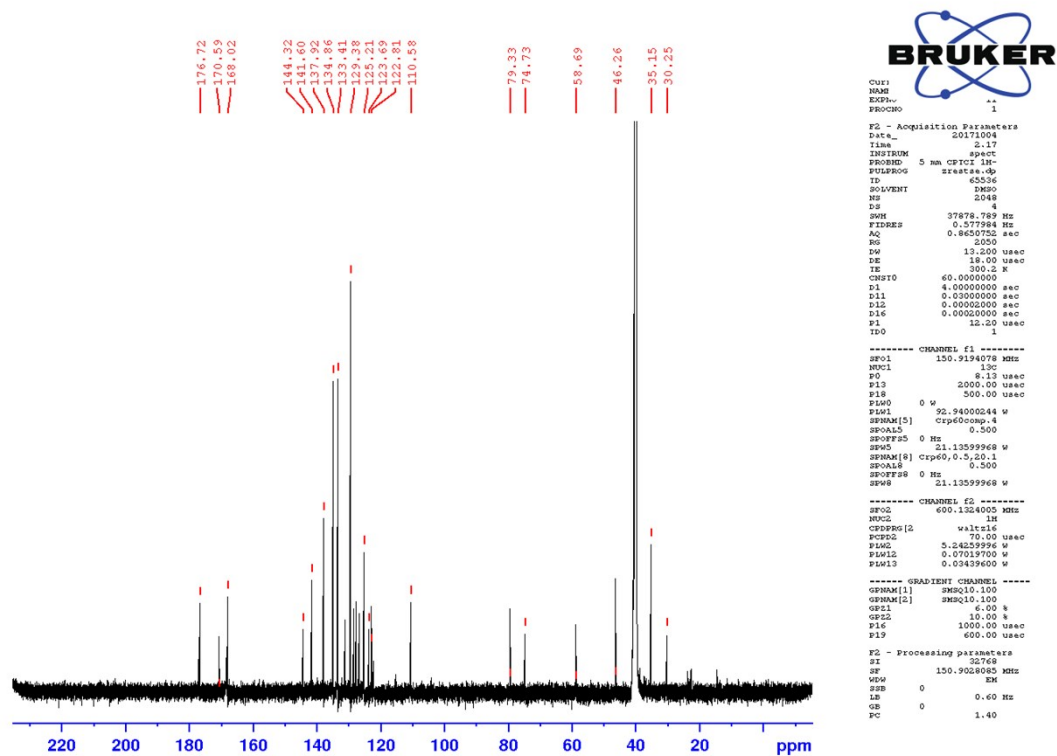


Fig13. S1b ¹³CNMR Spectra.7'-(thiophen-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 2).

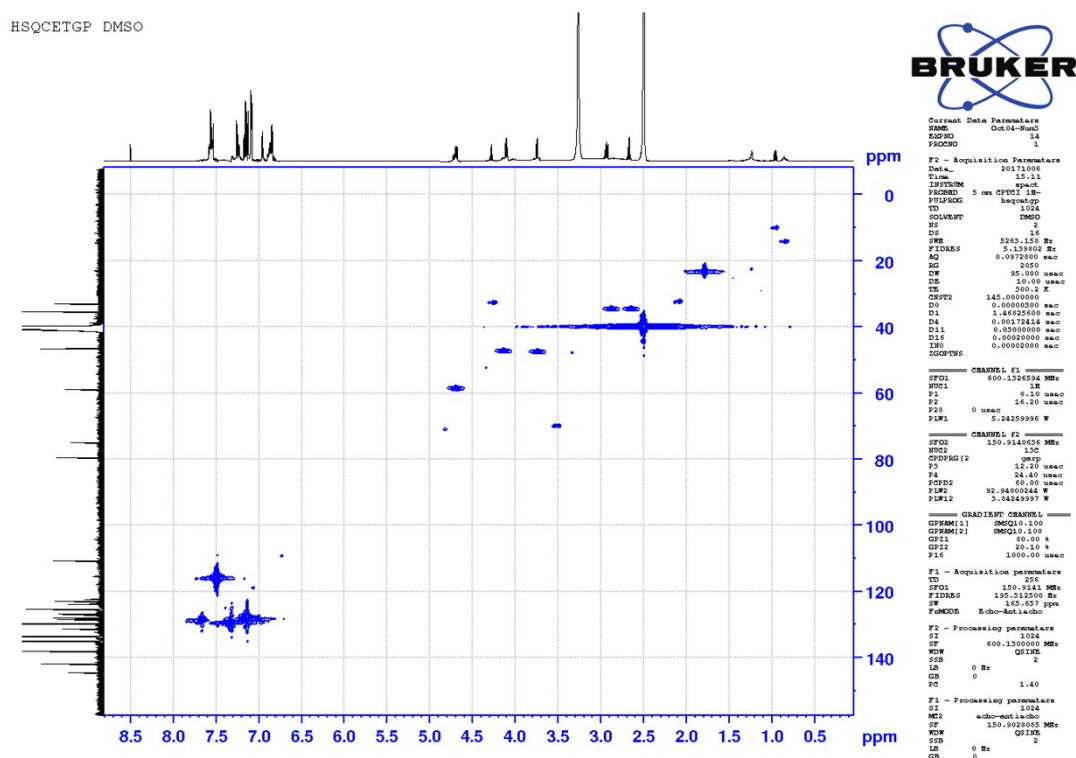


Fig14. S1b HSQC Spectra.7'-(thiophen-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 2).

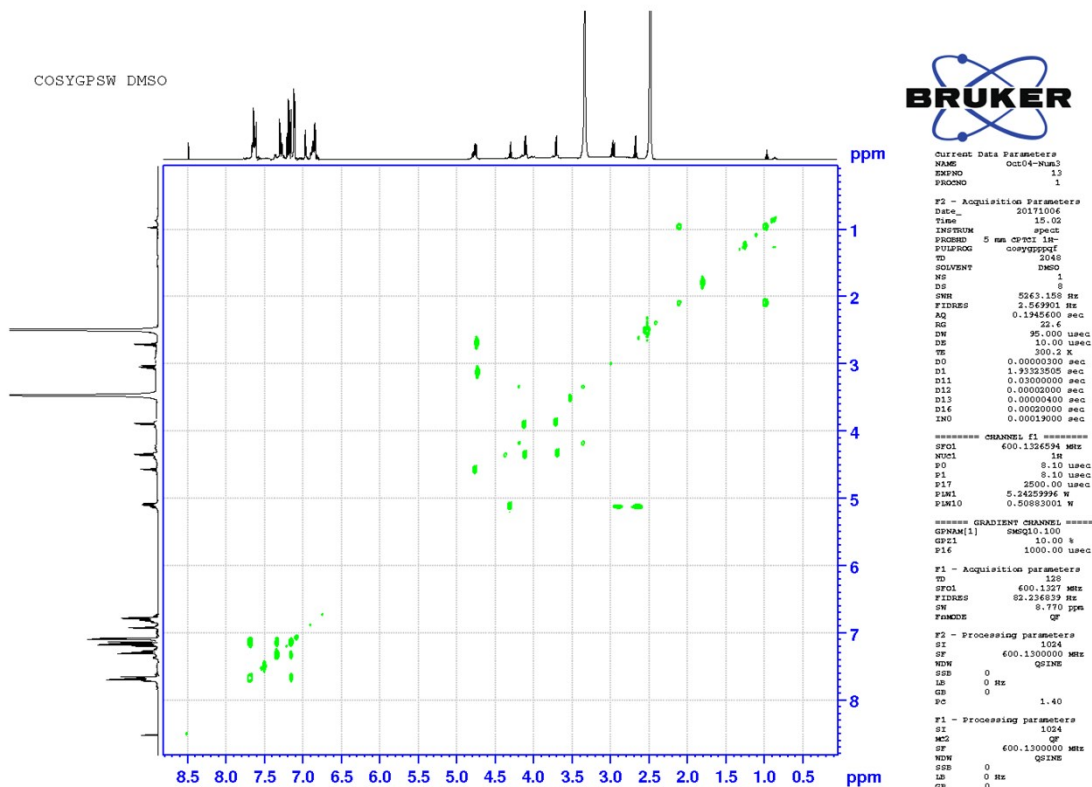


Fig15. S1b COSY Spectra.7'-(thiophen-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 2).

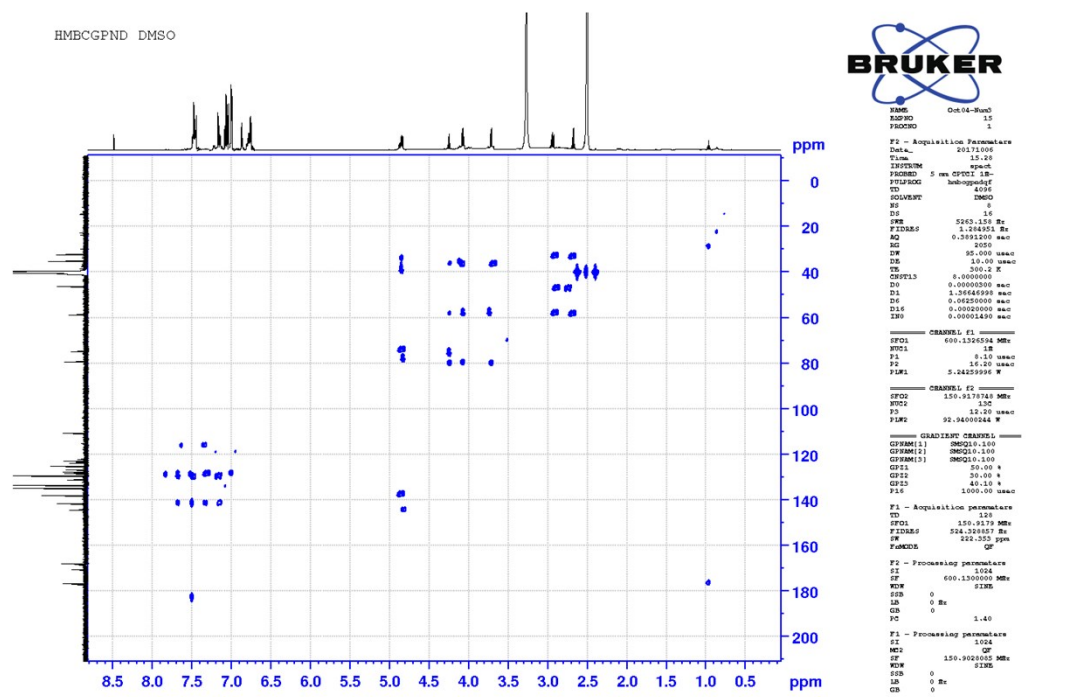


Fig16. S1b HMBC Spectra.7'-(thiophen-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 2).

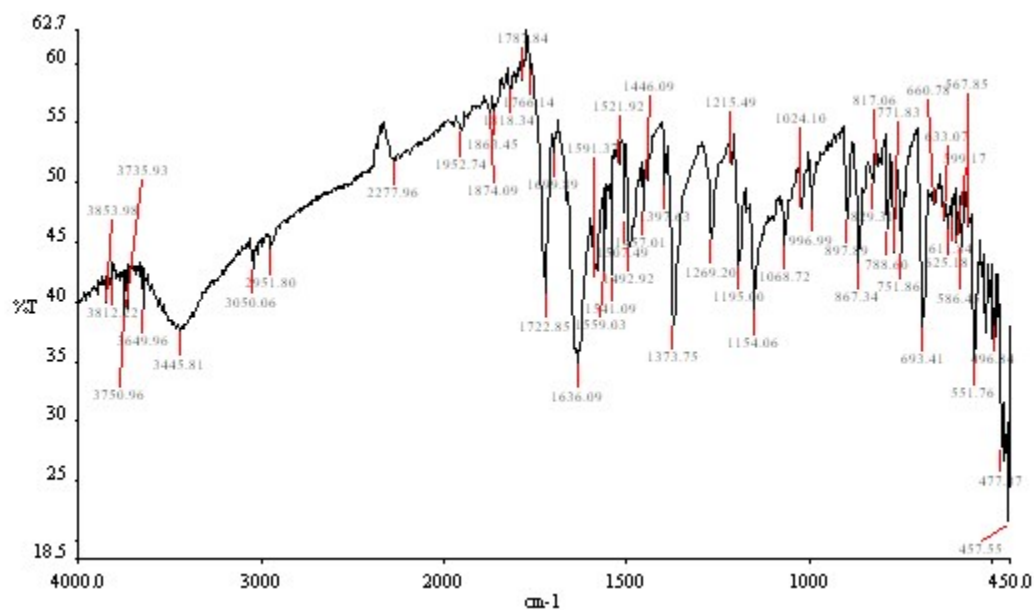


Fig17. S1c (FT-IR). 1' -(thiophen-2-yl)-5',6',7',7a'-tetrahydro-1'H dispiro[indoline-3,3'-pyrrolizine-2',5"-thiazolidine]-2,2",4"-trione (Table 4, entry 3)

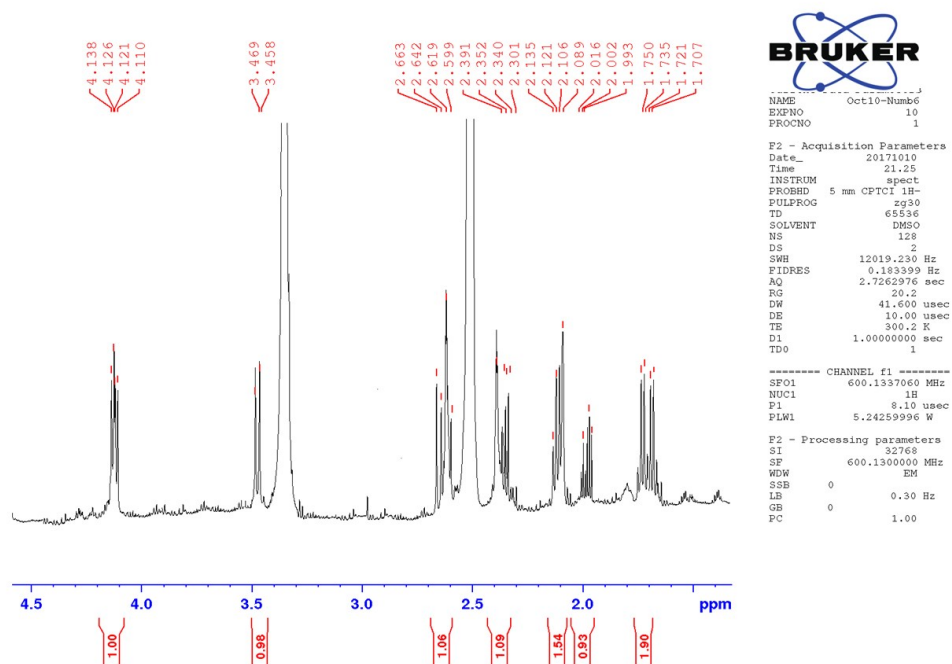


Fig18. S1b HNMR Spectra. 1' -(thiophen-2-yl)-5',6',7',7a'-tetrahydro-1'H dispiro[indoline-3,3'-pyrrolizine-2',5"-thiazolidine]-2,2",4"-trione (Table 4, entry 3)

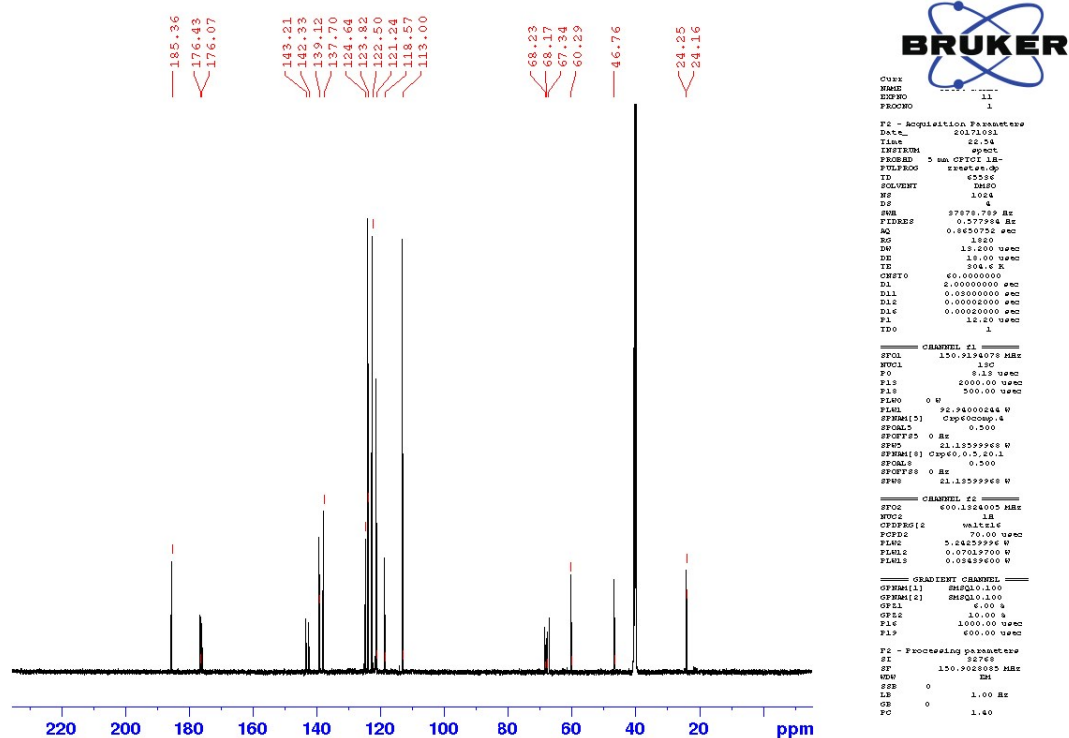


Fig19. S1b ¹³CNMR Spectra. 1'-(thiophen-2-yl)-5',6',7',7a'-tetrahydro-1'H dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 3)

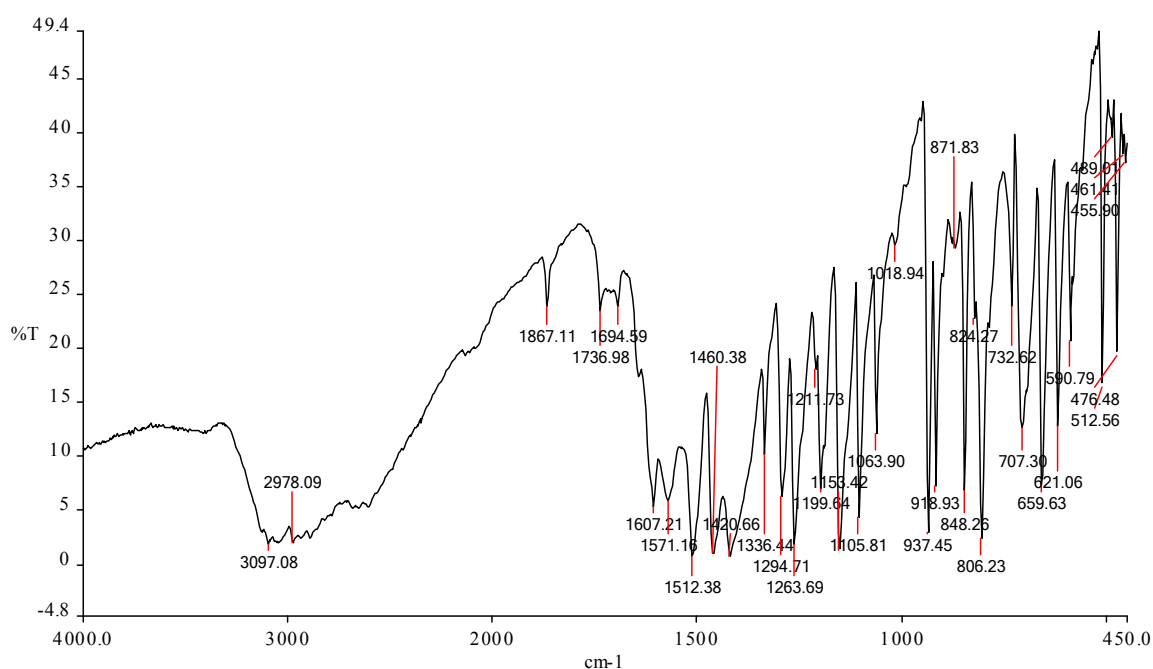


Fig20. S2a (FT-IR). 4'-(furan-2-yl)-1'-methylspiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 4).

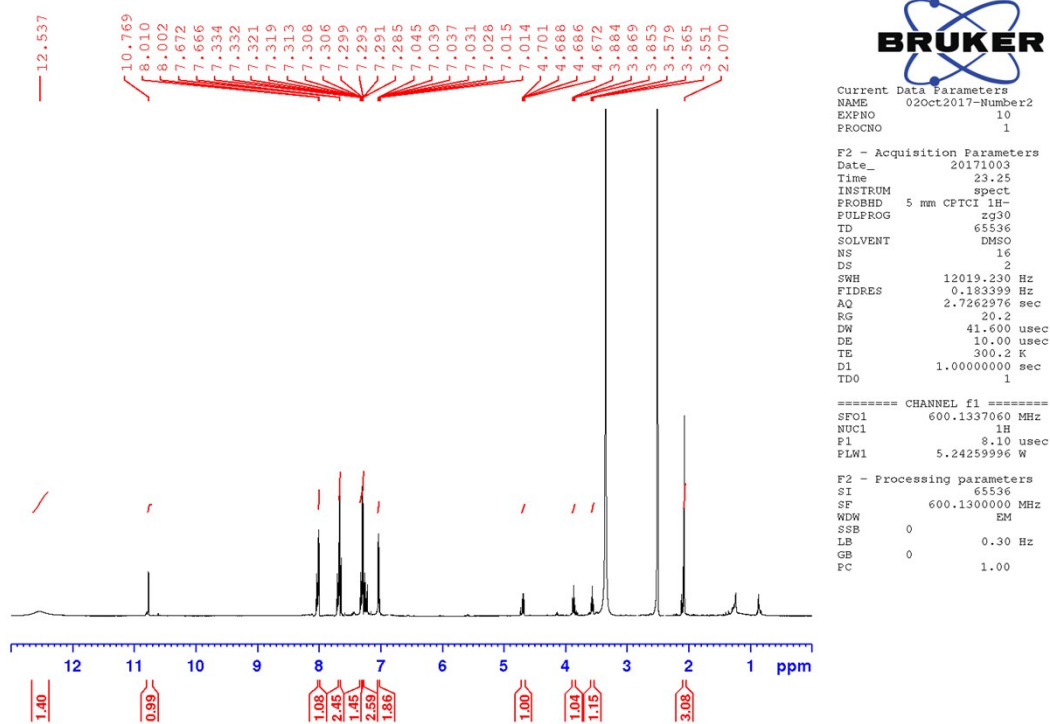


Fig21. S2a ¹H NMR Spectra. 4'-(furan-2-yl)-1'-methyl-dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 4).

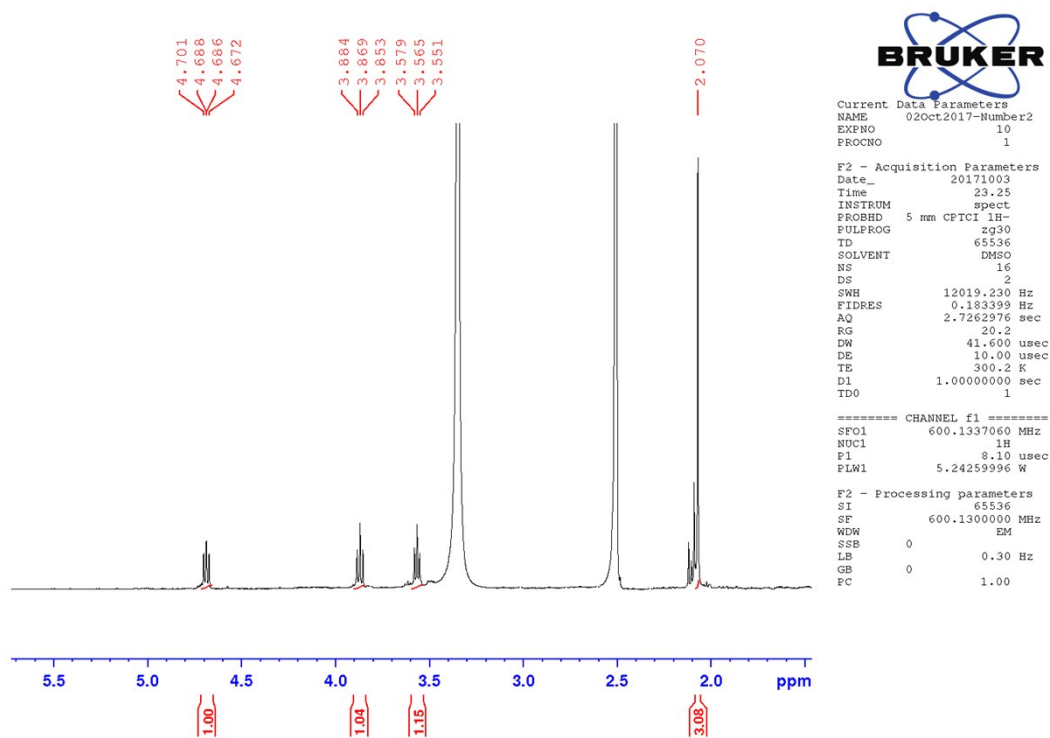
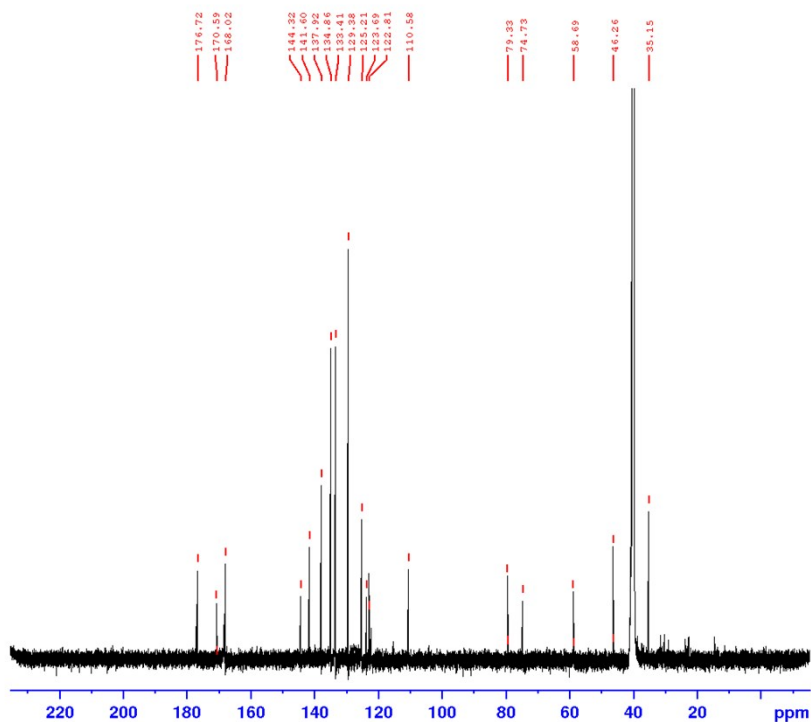


Fig22. S2a ¹H NMR Spectra. 4'-(furan-2-yl)-1'-methyl-dispiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 4).



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Fig23. S2a ^{13}C NMR Spectra.4'-(furan-2-yl)-1'-methylspiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione(Table 4, entry 4).

HSQCETGP DMS NUM2

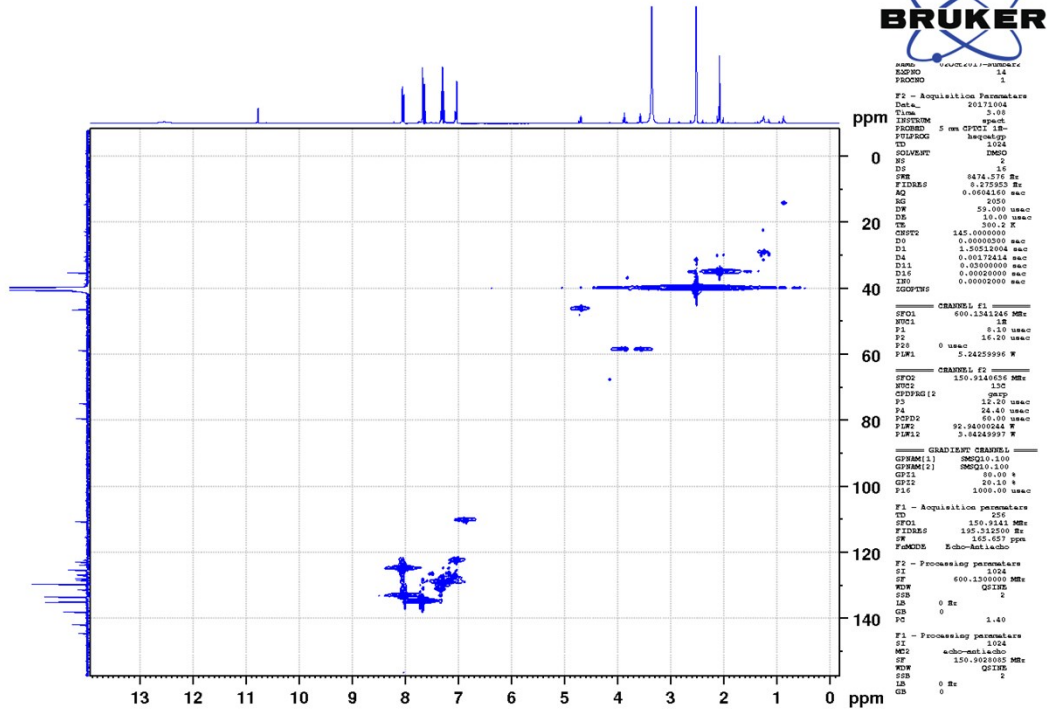


Fig24. S2a HSQC Spectra.4'-(furan-2-yl)-1'-methylspiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione(Table 4, entry 4).

COSYGPSW DMSO NUM2

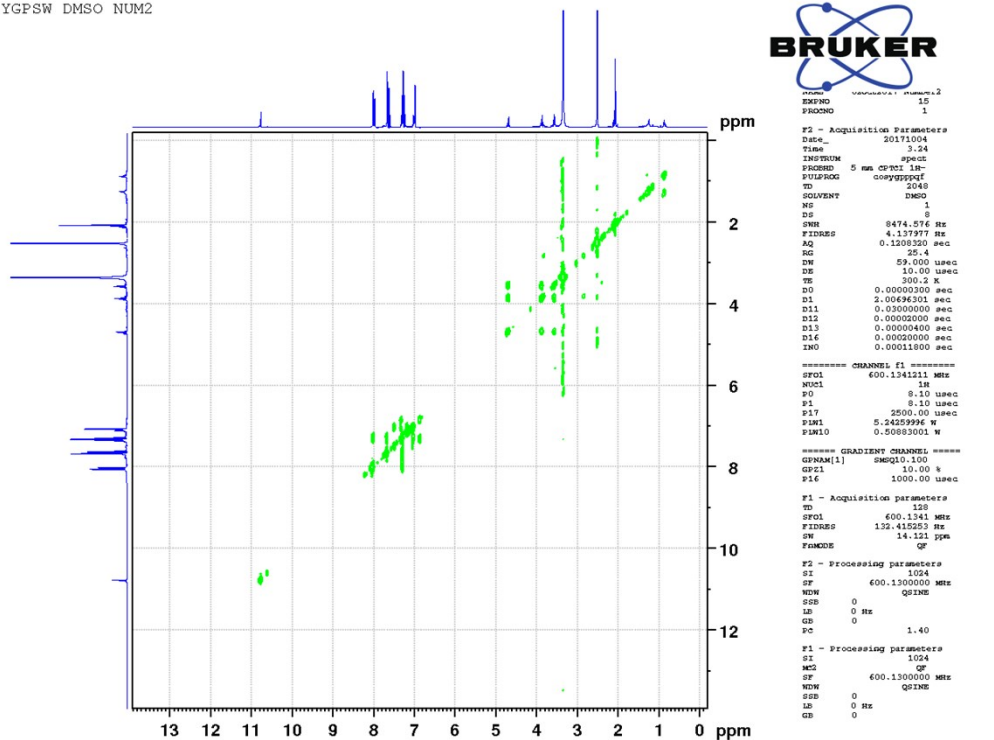


Fig25. S2a COSY Spectra. 4'-(furan-2-yl)-1'-methylspiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 4).

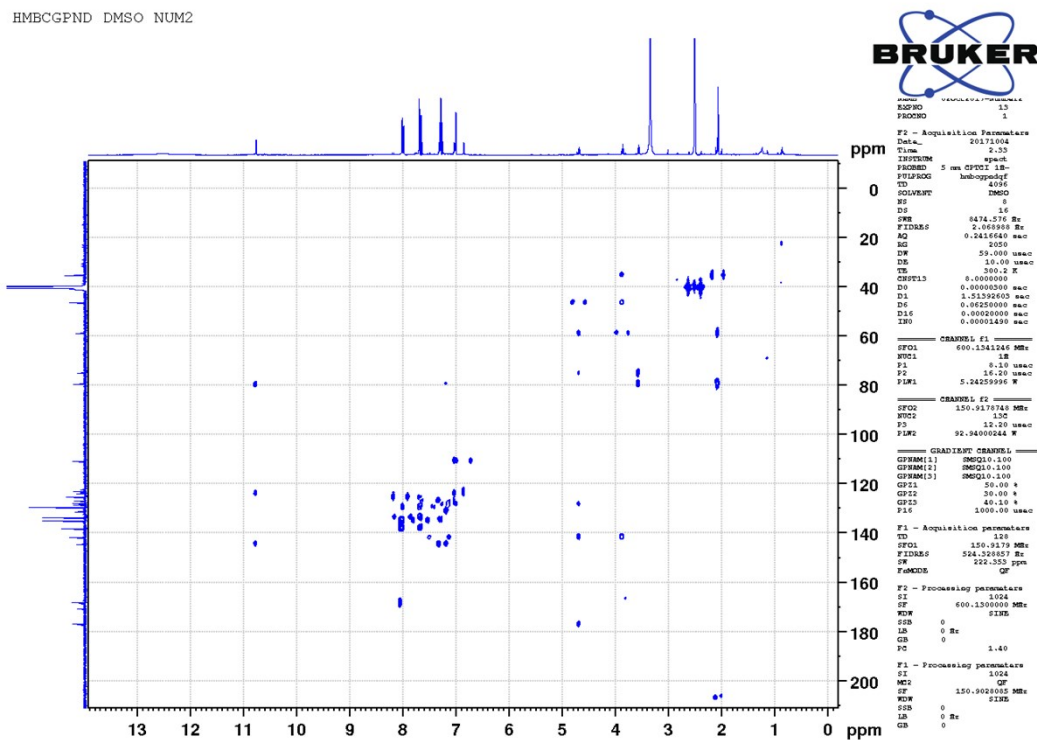


Fig26. S2aHMBC Spectra. 4'-(furan-2-yl)-1'-methylspiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 4).

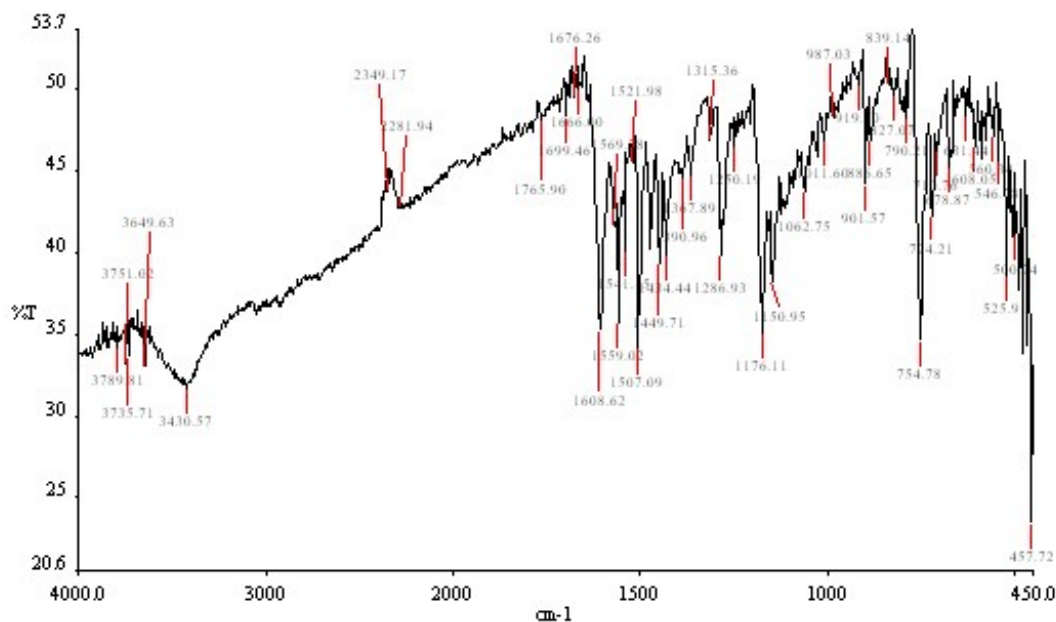


Fig26. S2b (FT-IR). 7'-(furan-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 5)

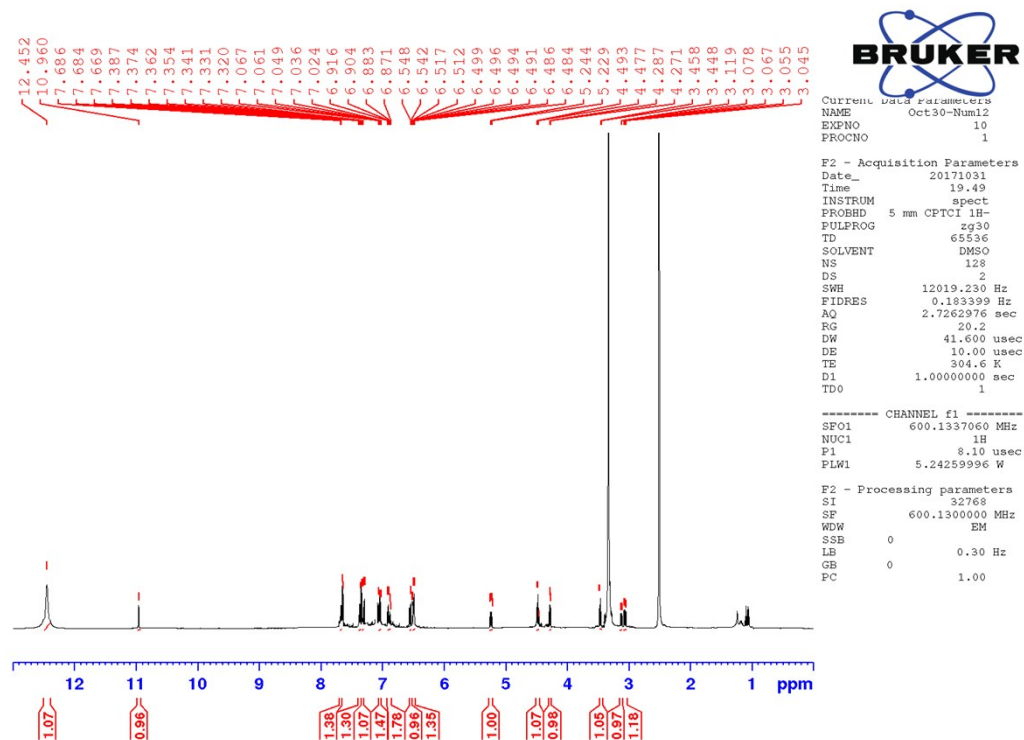


Fig27. S2b ¹H NMR Spectra. 7'-(furan-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c] thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 5)

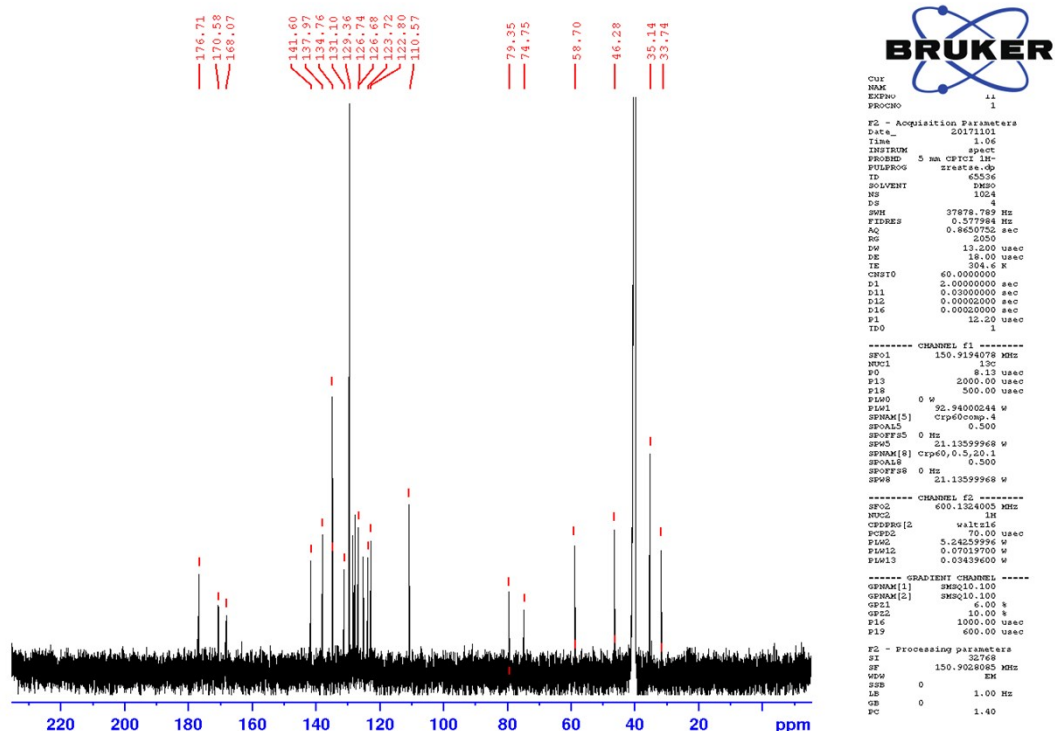


Fig28. S2b ^{13}C NMR Spectra. 7'-(furan-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 5)

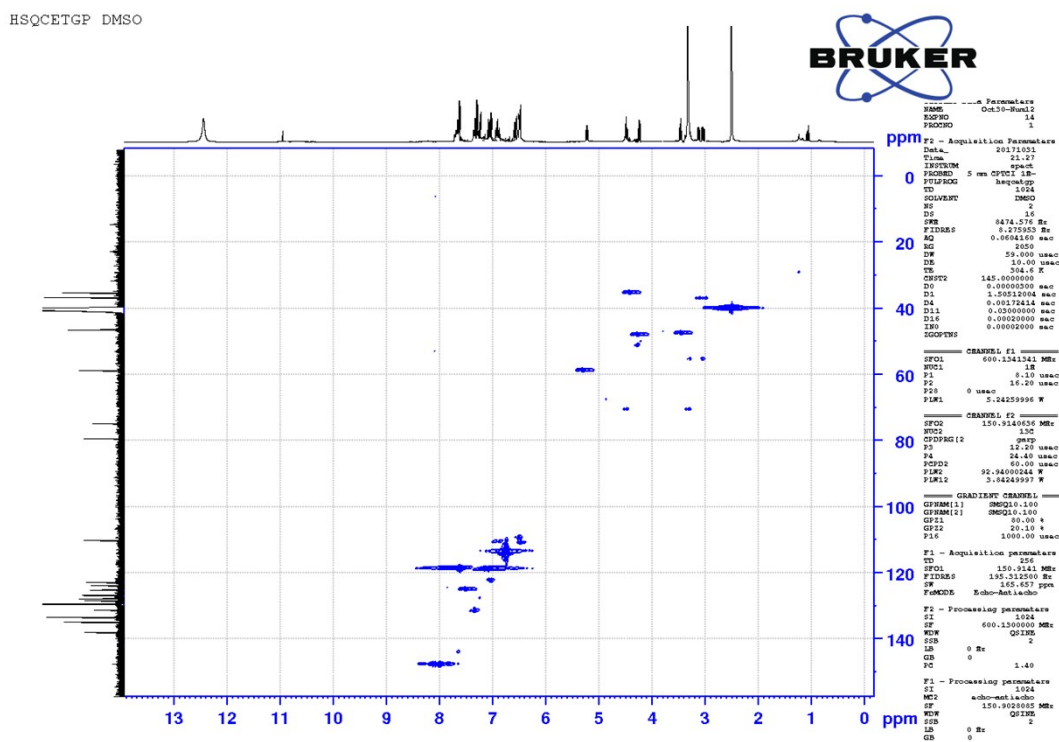


Fig29. S2b HSQC Spectra. 7'-(furan-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 5)

COSYGPSW DMSO

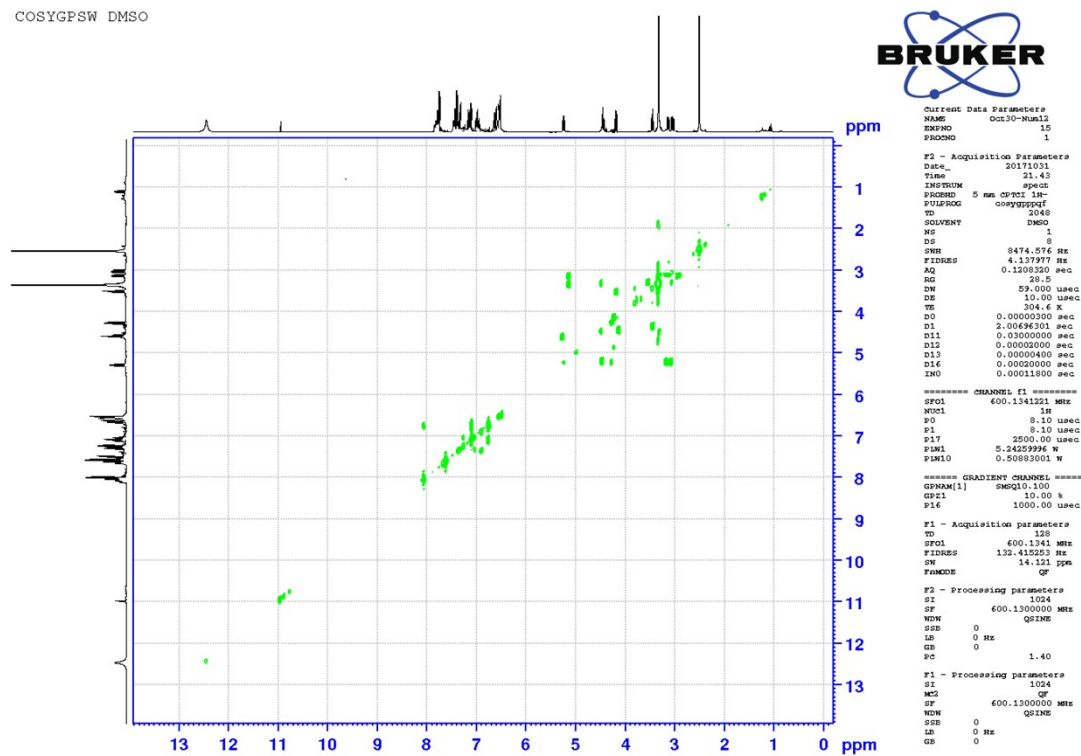


Fig30. S2b COSY Spectra. 7'-(furan-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 5)

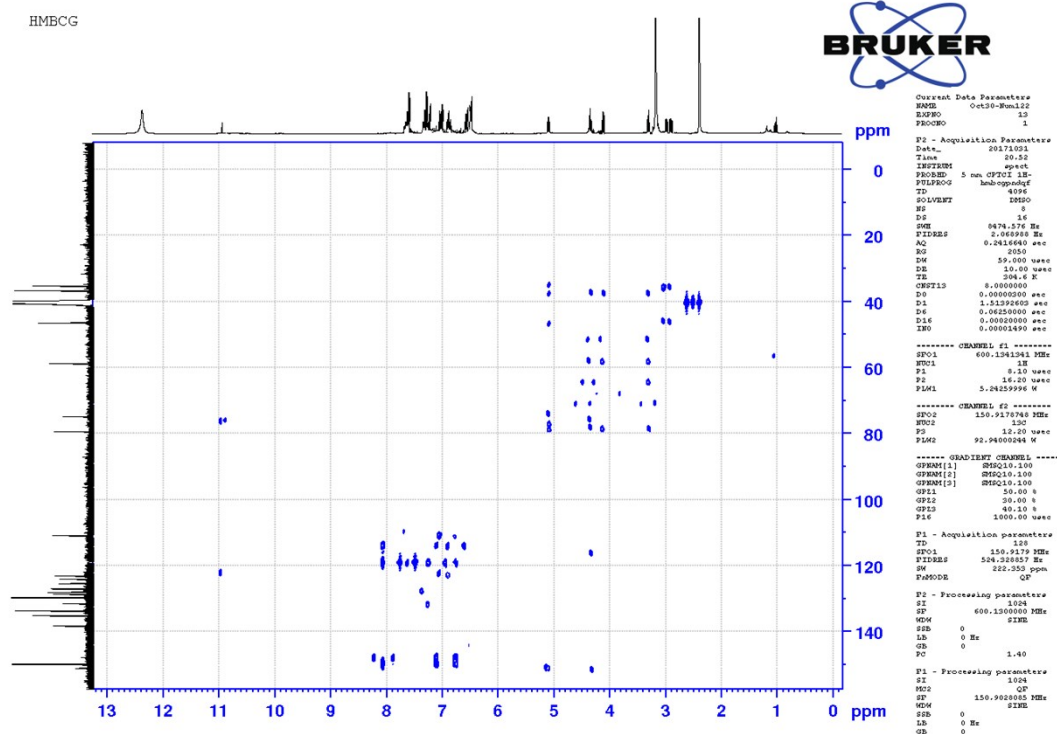


Fig31. S2b HMBC Spectra. 7'-(furan-2-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 5)

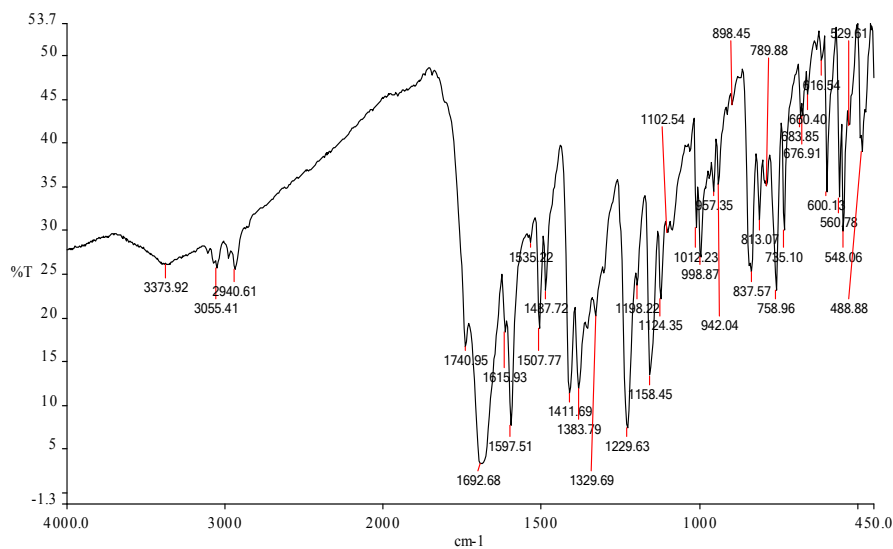


Fig32. S2c (FT-IR). 1'-(furan-2-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 6)

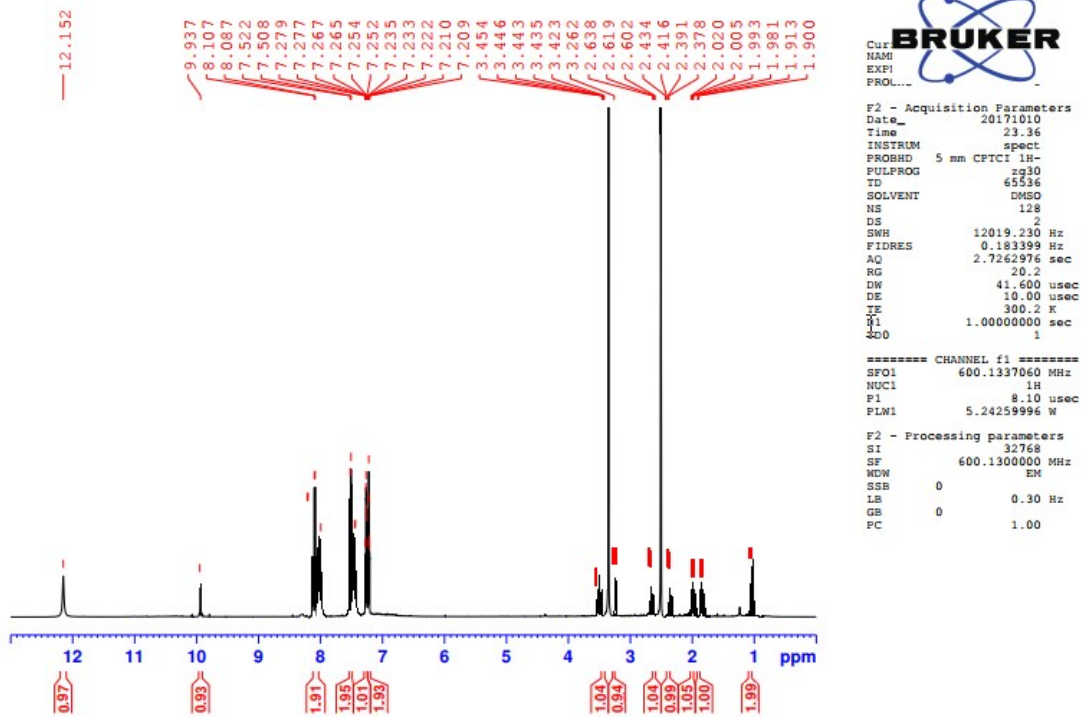


Fig33. S2c¹H NMR Spectra. (furan-2-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 6).

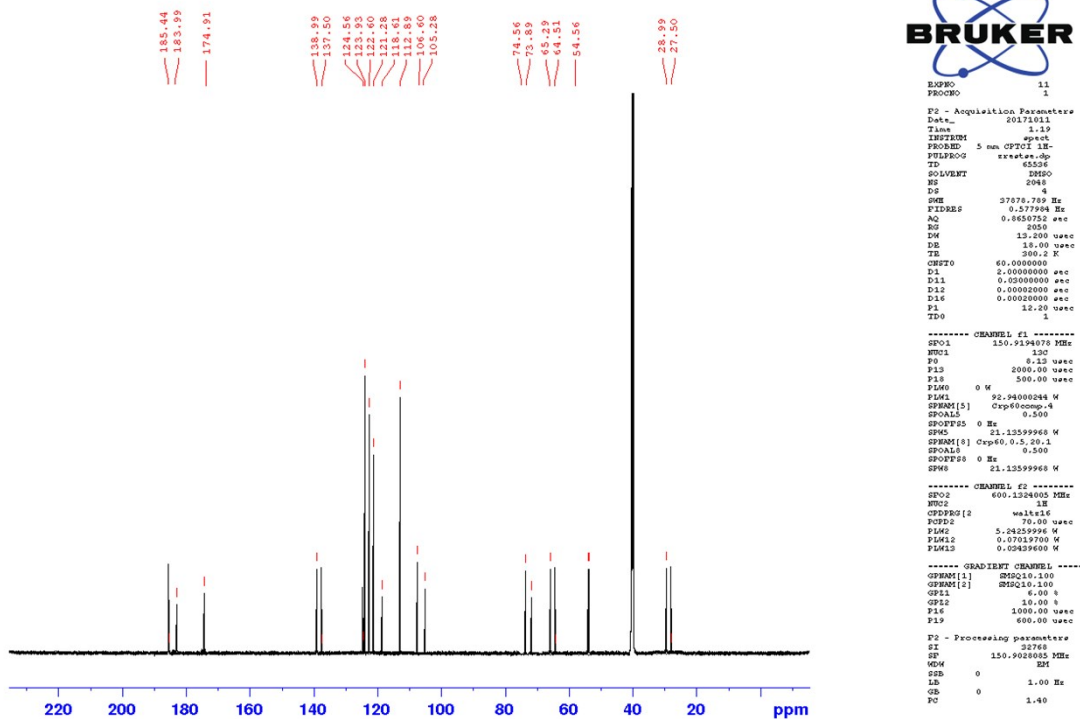


Fig34. S2c. ¹³CNMR Spectra. (furan-2-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 6).

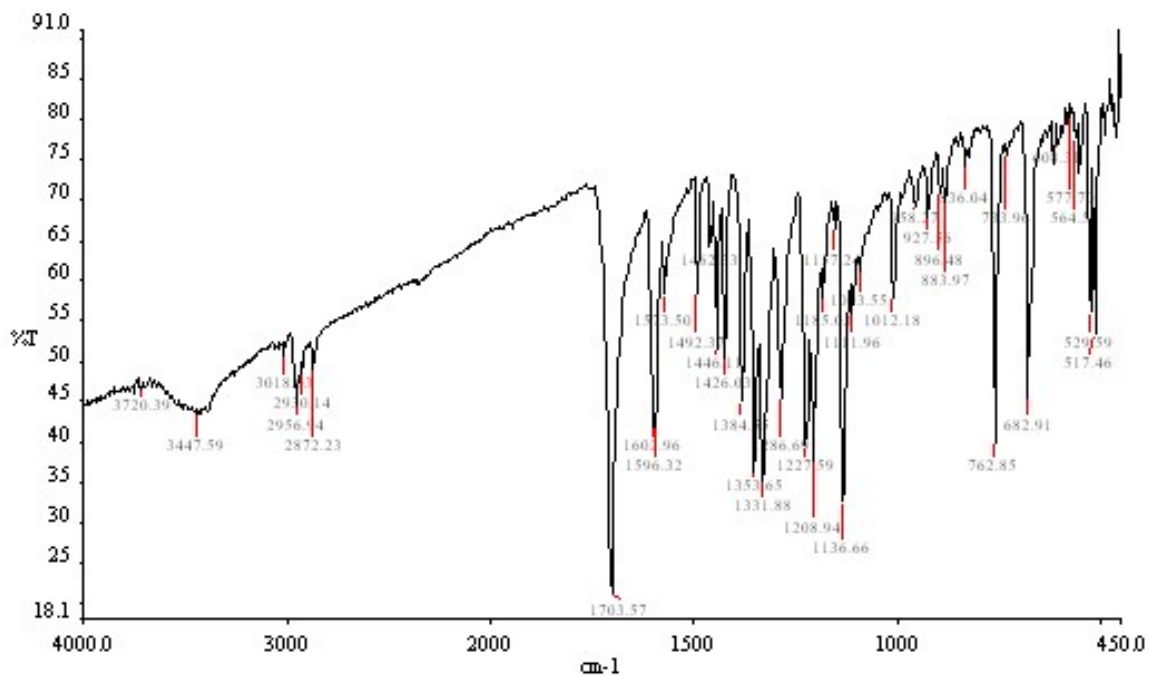


Fig35. S3a (FT-IR). 4'-(1H-indol-3-yl)-1'-methylspiro[indoline-3,2'-pyrrolidine-3',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 7).

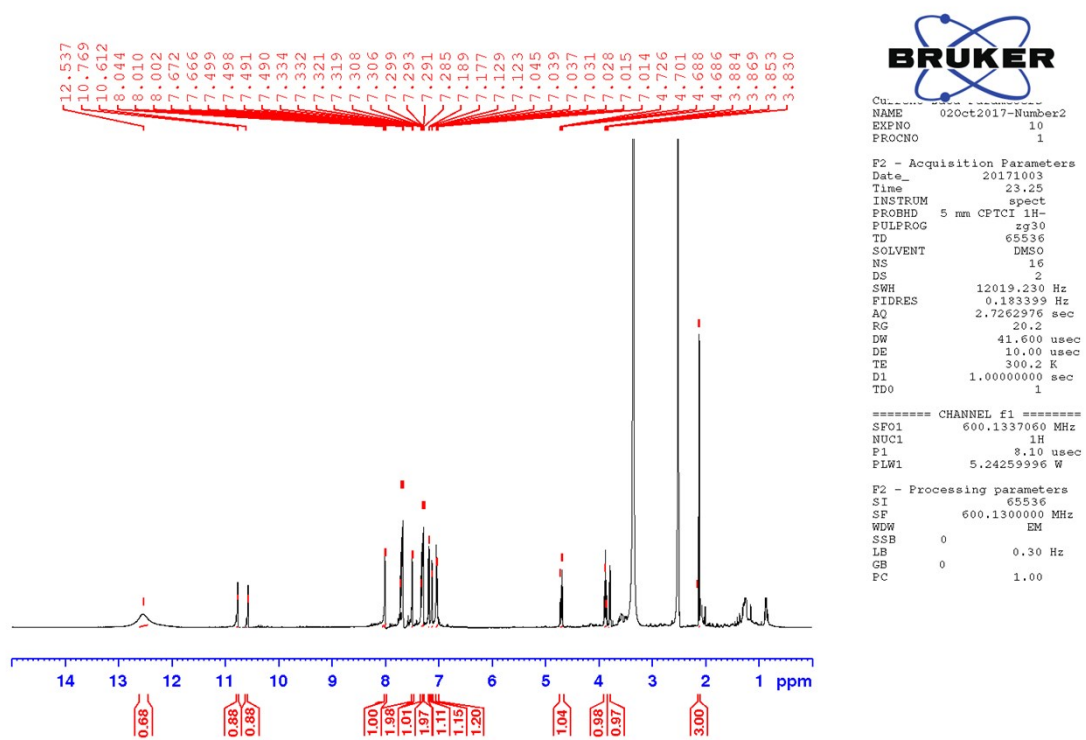


Fig36. S3a. ¹H NMR. 4'-(1H-indol-3-yl)-1'-methylspiro[indoline-3,2'-pyrrolidine-3',5'-thiazolidine]-2,2'',4''-trione (Table 4, entry 7).

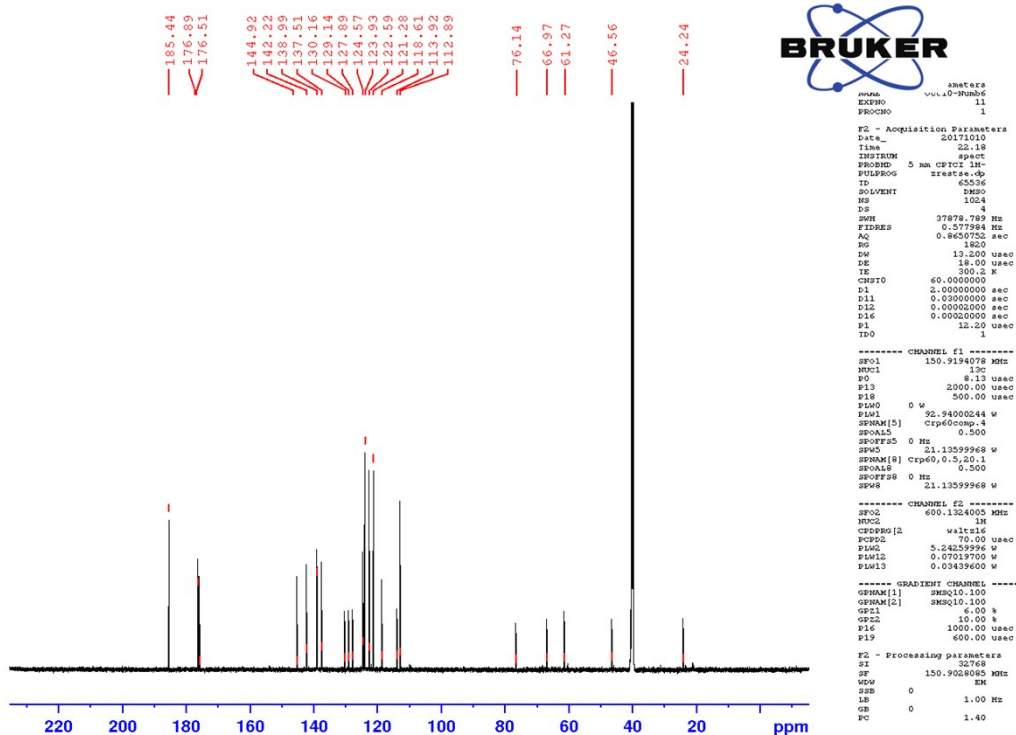
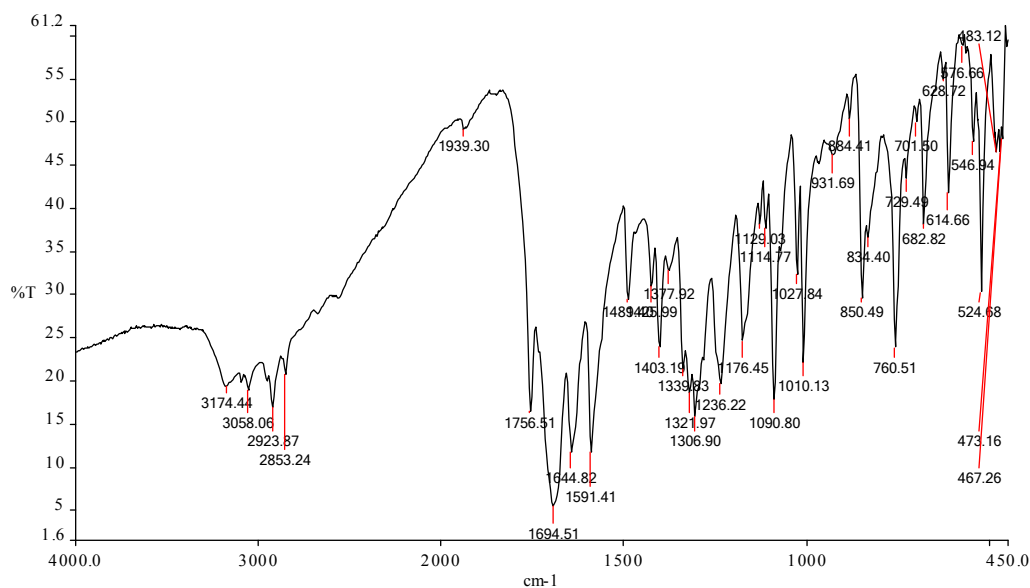


Fig37. S3a. ¹³CNMR. 4'-(1H-indol-3-yl)-1'-methylspiro[indoline-3,2'-pyrrolidine-3',5'-thiazolidine]-2,2'',4''-trione (Table 4, entry 7).



N1

Fig38. S3b (FT-IR). 7'-(1H-indol-3-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 8).

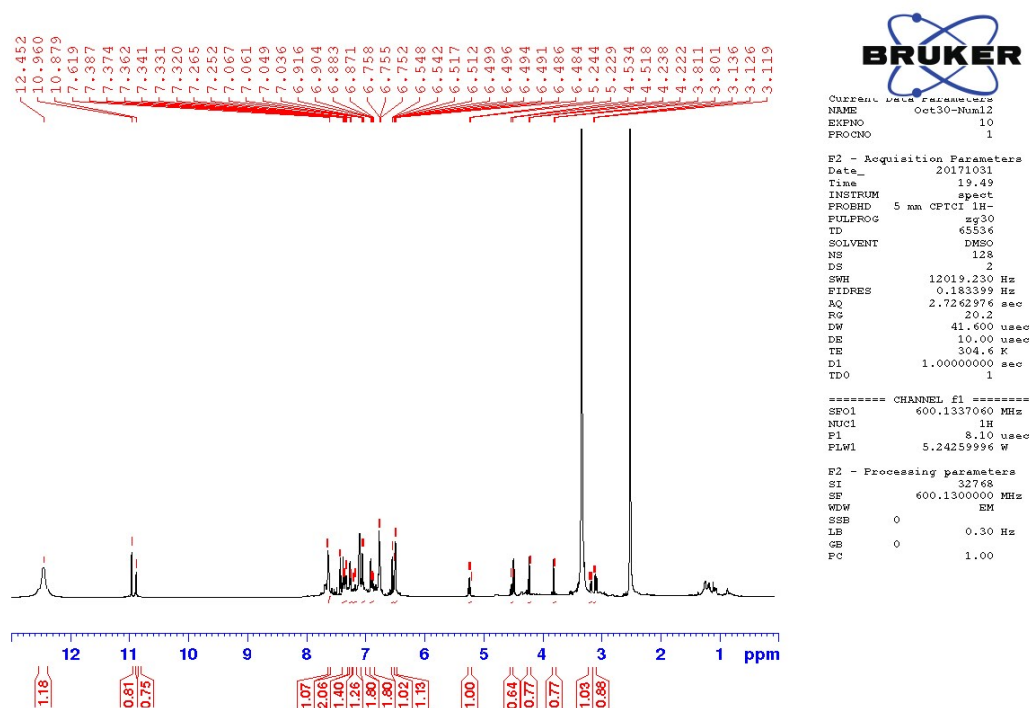


Fig39. S3b. ¹H NMR. 7'-(1H-indol-3-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 8).

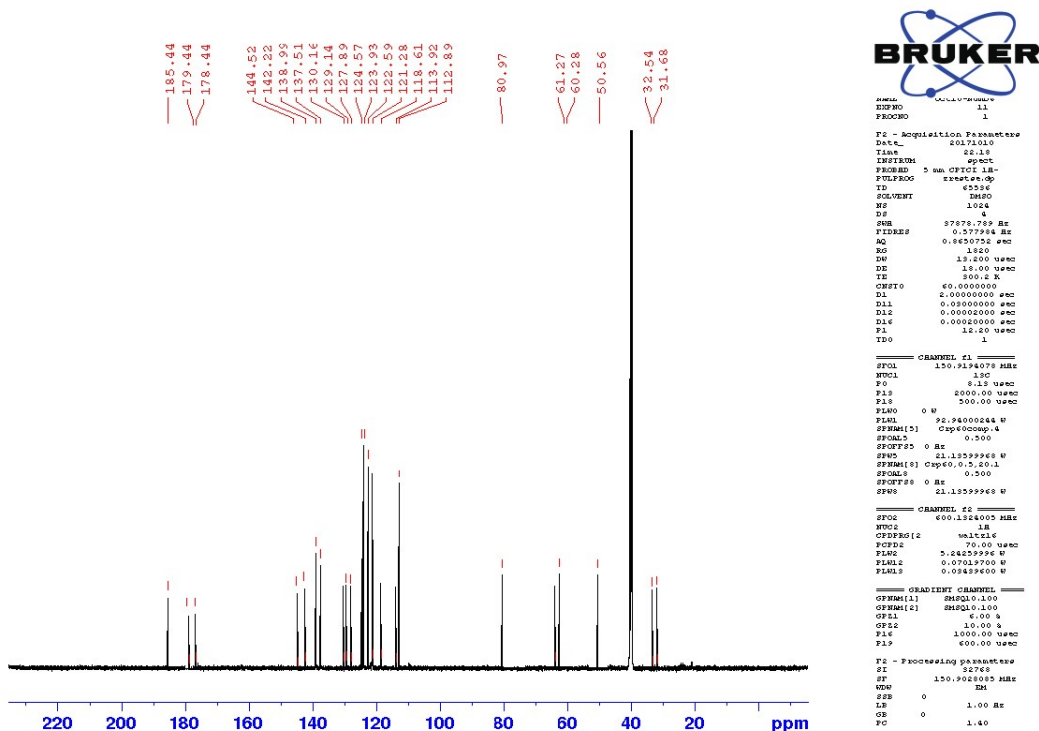


Fig40. S3b. ¹³CNMR. 7'-(1H-indol-3-yl)-7',7a'-dihydro-1'H,3'H-dispiro[indoline-3,5'-pyrrolo[1,2-c]thiazole-6',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 8).

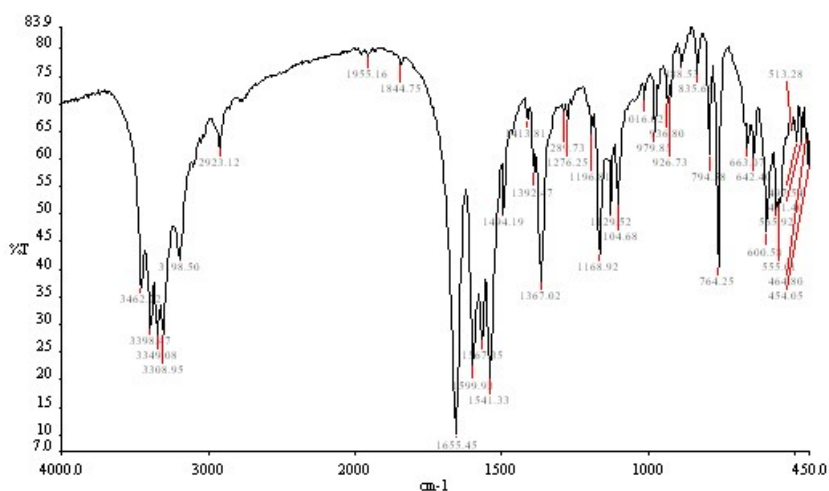


Fig41. S3b (FT-IR). 1'-(1H-indol-3-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 9).

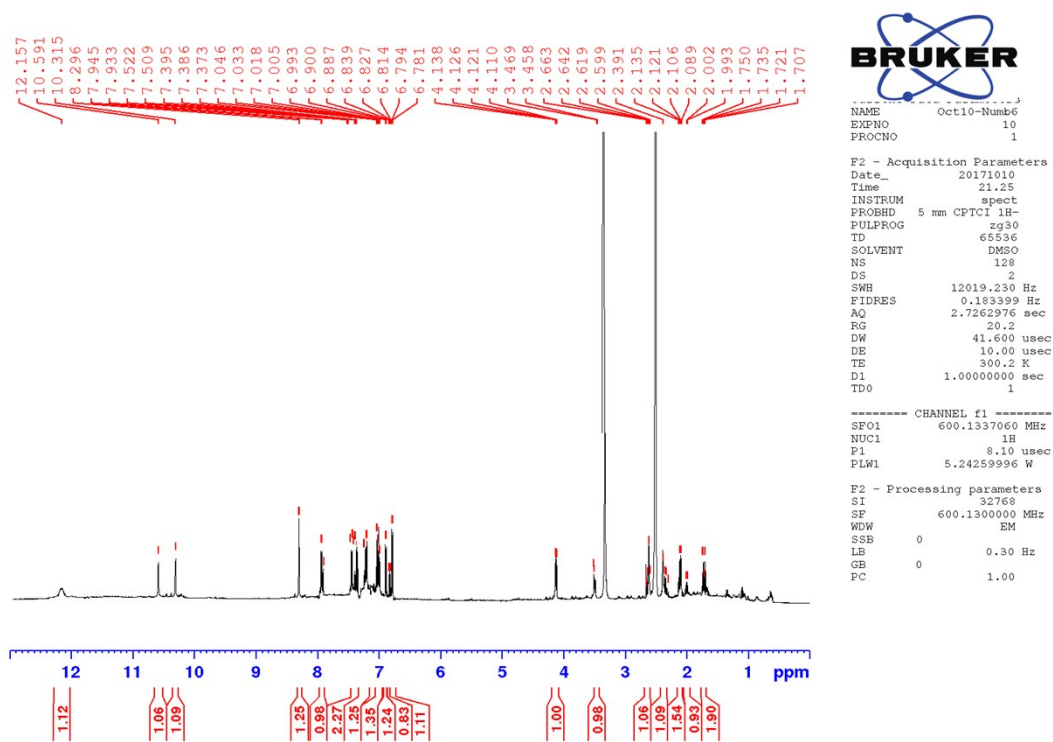


Fig42. S3C. $^1\text{H-NMR}$.1'-(1H-indol-3-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5"-thiazolidine]-2,2",4"-trione (Table 4, entry 9).



Fig43. S3C. $^1\text{H-NMR}$. 1'-(1H-indol-3-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 9).

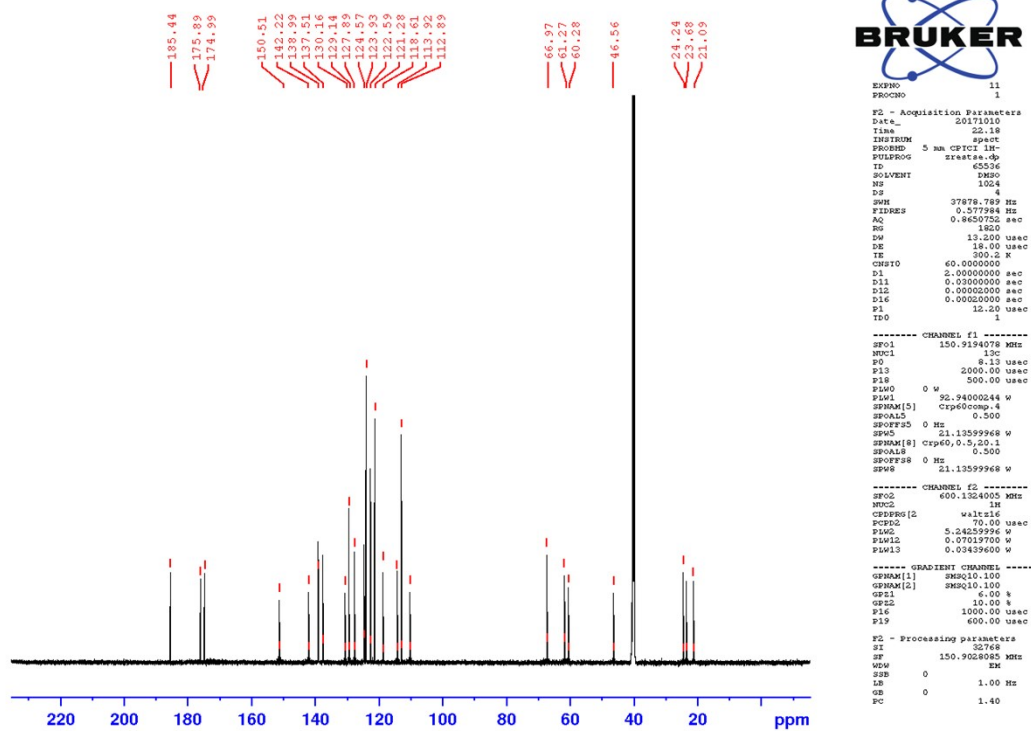


Fig43. S3C. ^{13}C NMR. 1'-(1H-indol-3-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5"-thiazolidine]-2,2",4"-trione (Table 4, entry 9).

HSQCETGP

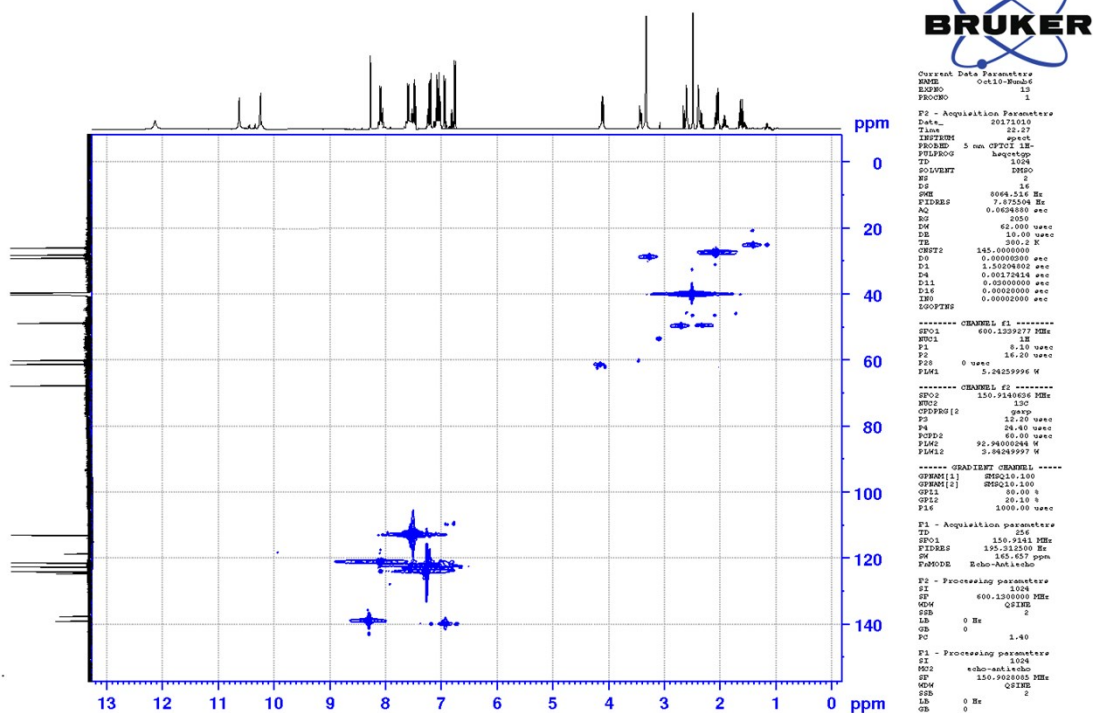


Fig43. S3C. HSQC. 1'-(1H-indol-3-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5''-thiazolidine]-2,2'',4''-trione (Table 4, entry 9).

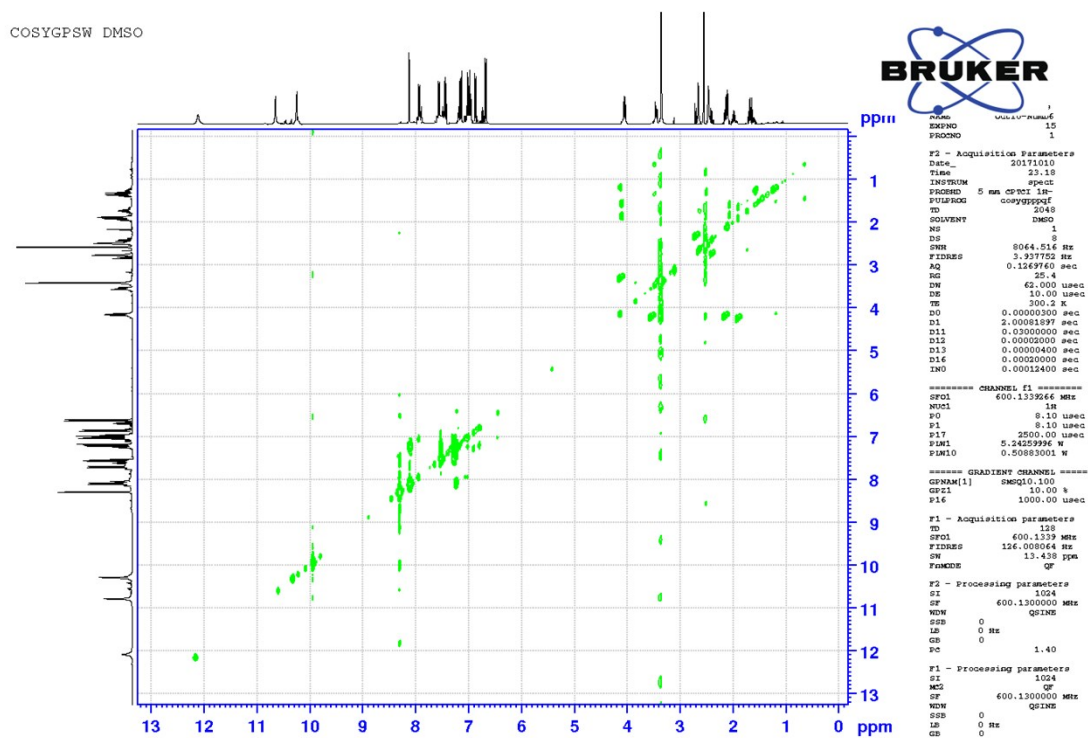


Fig43. S3C. COSY.1'- $(1H-indol-3-yl)$ -5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5"-thiazolidine]-2,2",4"-trione (Table 4, entry 9).

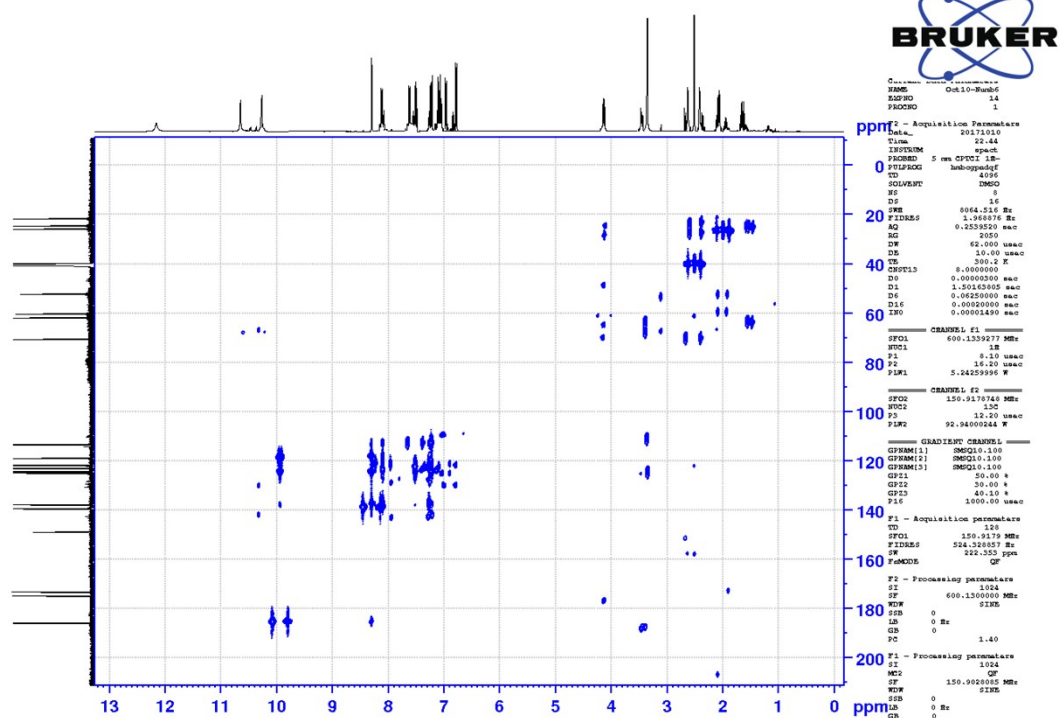


Fig43. S3C. HMBGPN. ^1H -indol-3-yl)-5',6',7',7a'-tetrahydro-1'H-dispiro[indoline-3,3'-pyrrolizine-2',5"-thiazolidine]-2,2",4"-trione (Table 4, entry 9).