3-(2,5-Dioxopyrrolidin-1-yl), 3-(2,6-Dioxopiperidin-1-yl), and 3-(1,3-Dioxoisoindolin-2-yl)rhodanines. A Novel Type of Rhodanine Derivatives

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Dedicated to Prof. Dr. Klaus Hartke on the occasion of his 65th birthday

3-Aminorhodanine **2** was reacted with cyclic anhydrides yielding 3-(2,5-dioxopyrrolidin-1-yl), 3-(2,6-dioxopiperidin-1-yl), and 3-(1,3-dioxoisoindolin-2-yl)rhodanine **6-8**, which in turn were condensated in 5 position with several aldehydes yielding the new rhodanine derivatives **9-11**.

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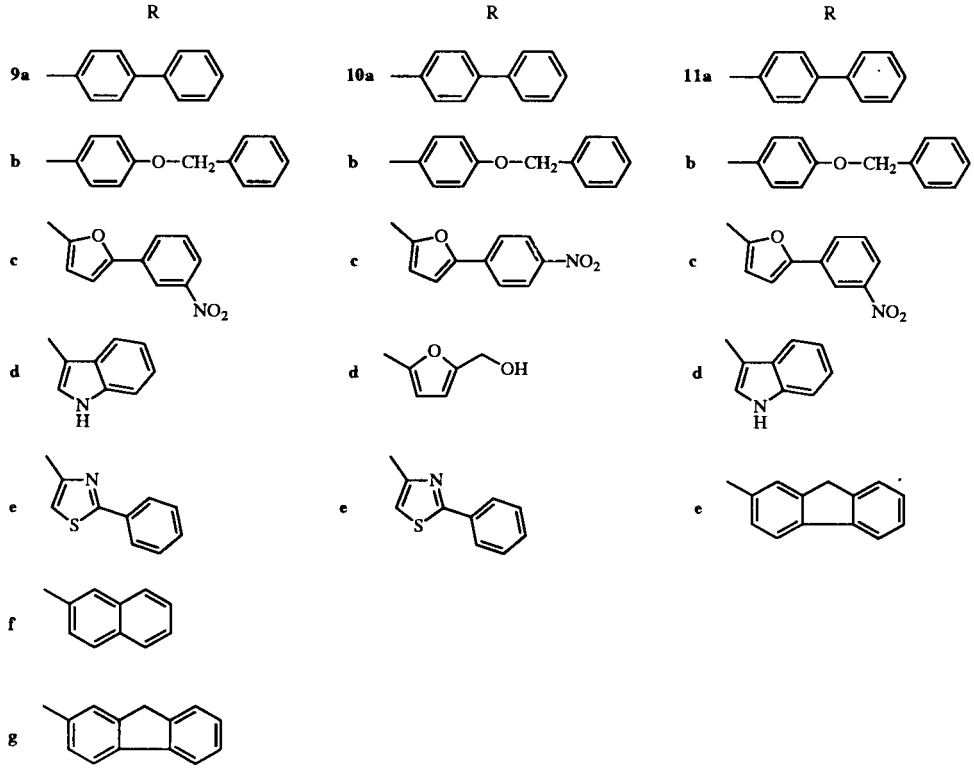
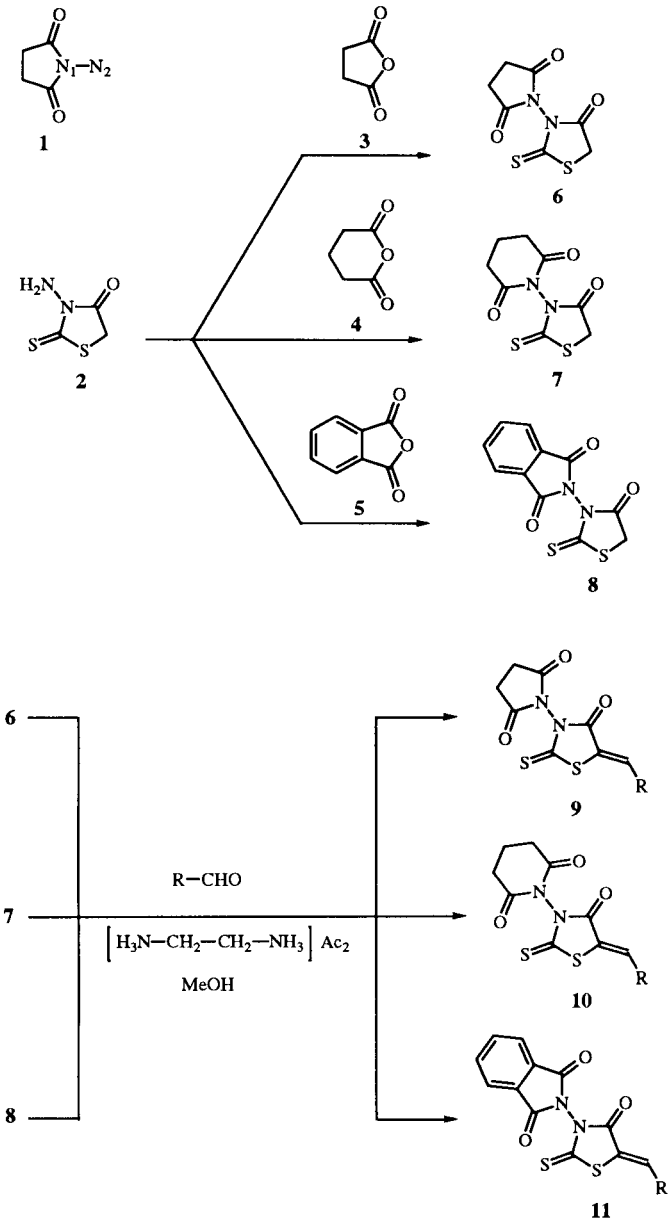
In continuation of our efforts towards the synthesis of rhodanine derivates as inhibitors of the enzyme aldose reductase [1] we wish to report the synthesis of 3-(2,5-dioxopyrrolidin-1-yl), 3-(2,6-dioxopiperidin-1-yl), and 3-(1,3-dioxoisoindolin-2-yl)rhodanines. Bisheterocyclic systems where a cyclic imide is linked *via* a N-N bridge to a second heterocycle are not very abundant in the literature. An on-line search of structure **1**, where N_2 had to be a part of a second heterocycle, in Beilstein-online retrieved only 24 references with all together 30 compounds. Our group has already published some 3-(thiazolidine-3-yl)rhodanines as examples of a novel class of rhodanine derivatives [2], possessing the unusual N-N-linkage between two heterocyles. The rhodanines **6-11** we present here are a new type of this rhodanine class hitherto unknown in literature.

The rhodanines **6-8** were obtained by refluxing 3-aminorhodanine **2** with the anhydrides **3-5** in toluene in presence of *p*-toluenesulfonic acid. The condensation of **6-8** with appropriate aldehydes to **9-11** was carried out following our standard procedure with ethylenediammonium diacetate in methanol [2,3]. The results of the pharmacological tests will be reported in due course.

EXPERIMENTAL

Column Chromatography was performed on silica gel (Silica gel 60 0.063-0.2 mm, Merck). MPLC was performed on silica





gel (silica gel 60, 0.015-0.04 mm, Merck) using B-685 medium pressure chromatography columns and a B-688 medium pressure chromatography pump by Büchi. The purity was checked by tlc on silica gel plates (silica gel 60, F_{254}, Merck). Melting points were determined on a Leitz HM Lux apparatus. Microanalyses were obtained on a Hewlett Packard CHN-Autoanalyser (N only) and a Labormatic CH-Analyser. Mass spectra were recorded on a Vacuum Generators Spectrometer 7070H with EI (70 eV). The infra red spectra were run using a Perkin Elmer PE 398 instrument. The ^1H and ^{13}C nmr spectra were recorded on a Jeol JNM-GX 400 instrument.

General Procedure for Preparation of 3-(2,5-Dioxopyrrolidin-1-yl), 3-(2,6-Dioxopiperidin-1-yl), and 3-(1,3-Dioxoisoindolin-2-yl)rhodanines **6-8**.

To a suspension of 2.96 g (0.02 mole) 3-aminorhodanine (**2**) and 0.025 moles of the anhydride **3-5** in 200 ml of toluene was added 0.4 g of *p*-toluenesulfonic acid. The mixture was refluxed for 18 hours while removing the reaction water *via* a Dean-Stark trap. Then the hot solution was filtered and the filtrate was evaporated *in vacuo*. The remaining solid was recrystallized from toluene.

3-(2,5-Dioxopyrrolidin-1-yl)-2-thioxothiazolidin-4-one (**6**).

This compound was recrystallized from toluene, yield 85%, light yellow crystals, mp 178°; ir (potassium bromide): ν 2983, 2937, 1800, 1743, 1414 cm^{-1}; ^1H nmr ([D_6]-DMSO): δ 4.69 (s, 2H), 3.08-2.97 (m, 4H); ^{13}C nmr ([D_6]-DMSO): δ 196.9, 171.3, 168.5, 34.0, 26.4; ms: m/z 230 (100, M^+).

Anal. Calcd. for $C_7H_6N_2O_3S_2$ (230.27): C, 36.51; H, 2.62; N, 12.16; S, 27.85. Found: C, 36.77; H, 2.45; N, 11.93; S, 27.85.

3-(2,6-Dioxopiperidin-1-yl)-2-thioxothiazolidin-4-one (**7**).

This compound was recrystallized from toluene, yield 86%, light yellow crystals, mp 198°; ir (potassium bromide): ν 2935, 2890, 1730, 1690, 1390, 1310 cm^{-1}; ^1H nmr ([D_6])-DMSO): δ 4.64 (s, 2H), 2.99-2.84 (m, 4H), 1.97 (m, 2H); ^{13}C nmr [D_6]-DMSO): δ 197.7, 168.9, 168.2, 33.5, 31.7, 16.3; ms: m/z 244 (100, M^+).

Anal. Calcd. for $C_8H_8N_2O_3S_2$ (244.29): C, 39.33; H, 3.30; N, 11.47; S, 26.25. Found: C, 39.50; H, 3.10; N, 11.36; S, 25.99.

3-(1,3-Dioxoisoindolin-2-yl)-2-thioxothiazolidin-4-one (**8**).

This compound was recrystallized from toluene, yield 83%, light yellow crystals, mp 205°; ir (potassium bromide): ν 2979, 2932, 1797, 1745, 1470, 1413, 1365, 1343 cm^{-1}; ^1H nmr (deuteriochloroform): δ 7.99-7.97 (m, 2H), 7.88-7.85 (m, 2H), 4.23 (s, 2H); ^{13}C nmr (deuteriochloroform): δ 194.0, 168.1, 162.3, 135.3, 129.8, 124.6, 33.4; ms: m/z 278 (100, M^+).

Anal. Calcd. for $C_{11}H_6N_2O_3S_2$ (278.31): C, 47.47; H, 2.17; N, 10.07; S, 23.04. Found: C, 47.26; H, 2.07; N, 9.93; S, 22.81.

General Procedure for the Preparation of the 5-Condensed Rhodanines **9-11**.

To a stirred solution of 4 mmoles of **6**, **7** or **8** and ethylenediammonium diacetate (560 mg, 3.1 mmoles) in 50 ml of dry methanol were added 3.1 mmoles of the aldehyde in portions. The consumption of the aldehyde was followed by tlc. After 12-24 hours at room temperature the formed solid was collected, washed with cold methanol and purified by column chromatography and/or recrystallisation.

3-(2,5-Dioxopyrrolidin-1-yl)-5-(4-phenylbenzylidene)-2-thioxothiazolidin-4-one (**9a**).

This compound was recrystallized from toluene, yield 79%, yellow crystals, mp 223°; ir (potassium bromide): ν 2986, 1735, 1592, 1412, 1297, 1251, 1174, 772 cm^{-1}; ^1H nmr ([D_6]-DMSO): δ 8.12 (s, 1H), 7.92-7.90 (m, 2H), 7.83-7.77 (m, 4H), 7.54-7.50 (m, 2H), 7.44 (m, 1H), 3.19-3.06 (m, 4H); ^{13}C nmr ([D_6]-DMSO): δ 187.8, 172.0 162.0, 143.8, 139.1, 137.3, 132.4, 131.9, 129.6, 129.0, 128.2, 127.4, 118.1, 27.2; ms: m/z 394 (54, M^+), 210 (100).

Anal. Calcd. for $C_{20}H_{14}N_2O_3S_2$ (394.49): C, 60.89; H, 3.58; N, 7.10; S, 16.26. Found: C, 60.96; H, 3.52; N, 7.16; S, 16.03.

3-(2,5-Dioxopyrrolidin-1-yl)-5-(4-benzyloxybenzylidene)-2-thioxothiazolidin-4-one (**9b**).

This compound was recrystallized from toluene/dioxane, yield 81%, yellow crystals, mp 221°; ir (potassium bromide): ν 3015, 2944, 2873, 1748, 1711, 1577, 1511, 1256, 1182 cm^{-1}; ^1H

nmr ([D$_6$]-DMSO): δ 8.02 (s, 1H), 7.73-7.71 (m 2H), 7.49-7.47 (m, 2H), 7.43-7.40 (m, 2H), 7.36 (m, 1H), 7.25-7.23 (m, 2H), 5.25 (s, 2H), 3.15-3.05 (m, 4H); ^{13}C nmr ([D$_6$]-DMSO): δ 187.3, 171.3, 161.4, 137.1, 136.2, 133.5, 128.3, 127.9, 127.6, 125.0, 116.0, 114.4, 69.6, 26.5; ms: m/z 424 (10, M$^+$), 91 (100).

Anal. Calcd. for $C_{21}H_{16}N_2O_4S_2$ (424.49): C, 59.42; H, 3.80; N, 6.60; S, 15.10. Found: C, 59.19; H, 3.87; N, 6.62; S, 15.07.

3-(2,5-Dioxopyrrolidin-1-yl)-5-[(5-(3-nitrophenyl)-2-furyl)-methylene]-2-thioxothiazolidin-4-one (**9c**).

This compound was recrystallized from toluene/dioxane, yield 72%, orange crystals, mp 285°; ir (potassium bromide): ν 3052, 1743, 1601, 1527, 1349, 1240, 1176, 804 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 8.62 (s, 1H), 8.28-8.25 (m, 2H), 7.95 (s, 1H), 7.86 (m, 1H), 7.64 (d, 1H), 7.52 (d, 1H), 3.12-3.05 (m, 4H); ^{13}C nmr ([D$_6$]-DMSO): δ 187.9, 171.4, 161.1, 156.4, 149.7, 148.5, 131.0, 130.4, 129.7, 124.9, 123.6, 121.4, 119.0, 114.6, 112.5, 26.5; ms: m/z 429 (55, M$^+$), 245 (100).

Anal. Calcd. for $C_{18}H_{11}N_3O_6S_2$ (429.46): C, 50.34; H, 2.58; N, 9.79; S, 14.93. Found: C, 50.38; H, 2.73; N, 9.65; S, 14.72.

3-(2,5-Dioxopyrrolidin-1-yl)-5-(3-indolylmethylene)-2-thioxo-thiazolidin-4-one (**9d**).

This compound was recrystallized from dioxane, yield 74%, orange crystals, mp >330°; ir (potassium bromide): ν 3393, 1742, 1702, 1592, 1572, 1231 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 12.43 (br s, 1H), 8.31 (s, 1H), 8.09 (s, 1H), 8.02 (d, 1H), 7.55 (d, 1H), 7.33-7.28 (m, 2H) 3.19-3.06 (m, 4H); ^{13}C nmr ([D$_6$]-DMSO): δ 186.9, 171.6, 161.1, 136.5, 130.1, 126.7, 123.7, 121.9, 118.7, 112.7, 111.0, 109.1, 26.5; ms: m/z 357 (35, M$^+$), 173 (100).

Anal. Calcd. for $C_{16}H_{11}N_3O_3S_2$ (357.41): C, 53.77; H, 3.10; N, 11.76; S, 17.94. Found: C, 53.60; H, 3.11; N, 11.94; S, 17.65.

3-(2,5-Dioxopyrrolidin-1-yl)-5-[(2-phenyl-1,3-thiazol-4-yl)-methylene]-2-thioxothiazolidin-4-one (**9e**).

This compound was recrystallized from dioxane, yield 70%, yellow crystals, mp >240°; ir (potassium bromide): ν 1744, 1463, 1292, 1245 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 8.55 (s, 1H), 8.06 (s, 1H), 8.04-8.01 (m, 2H), 7.60-7.57 (m, 3H), 3.17-3.06 (m, 4H); ^{13}C nmr ([D$_6$]-DMSO): δ 191.5, 171.4, 168.7, 161.7, 149.8, 131.7, 131.2, 130.3, 129.4, 127.2, 126.5, 119.8, 26.6; ms: m/z 401 (56, M$^+$), 217 (100).

Anal. Calcd. for $C_{17}H_{11}N_3O_3S_3$ (401.49): C, 50.86; H, 2.76; N, 10.47; S, 23.96. Found: C, 50.59; H, 2.86; N, 10.27; S, 23.64.

3-(2,5-Dioxopyrrolidin-1-yl)-5-(2-naphthylmethylene)-2-thioxo-thiazolidin-4-one (**9f**).

This compound was chromatographically purified (dichloromethane:hexane 2:1), yield 65%, yellow crystals, mp 241-243°; ir (potassium bromide): ν 1742, 1600, 1591, 1302, 1265, 1242, 1221, 1175 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 8.33 (s, 1H), 8.18 (s, 1H), 8.11-8.07 (m, 2H), 8.00 (d, 1H), 7.75 (dd, 1H), 7.70-7.62 (m, 2H), 3.19-3.06 (m, 4H); ^{13}C nmr ([D$_6$]-DMSO): δ 187.4, 171.4, 161.4, 137.2, 133.8, 132.8, 132.6, 129.9, 129.2, 129.1, 128.8, 127.7, 127.3, 126.2, 118.0, 26.6; ms: m/z 368 (38, M$^+$), 184 (100).

Anal. Calcd. for $C_{18}H_{12}N_2O_3S_2$ (368.43): C, 58.68; H, 3.28; N, 7.61; S, 17.40. Found: C, 58.41; H, 3.29; N, 7.68; S, 17.36.

3-(2,5-Dioxopyrrolidin-1-yl)-5-(2-fluorenylmethylene)-2-thioxo-thiazolidin-4-one (**9g**).

This compound was chromatographically purified (MPLC, dichloromethane:hexane 19:1, p = 2 bar), yield 62% yellow crystals, mp 163°; ir (potassium bromide): ν 1746, 1591, 1298, 1266, 1237, 1215, 1171 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 8.08 (s, 1H), 8.07 (m, 1H), 8.00 (m, 1H), 7.87 (s, 1H), 7.73 (m, 1H), 7.64 (m, 1H), 7.46-7.39 (m, 2H), 4.02 (s, 2H), 3.19-3.06 (m, 4H); ^{13}C nmr ([D$_6$]-DMSO) δ 187.3, 171.4, 161.4, 144.8, 144.3, 144.1, 139.6, 137.6, 130.9, 130.6, 128.2, 127.5, 127.0, 125.2, 121.1, 121.0, 116.3, 36.4, 26.6; ms: m/z 406 (62, M$^+$), 222 (100).

Anal. Calcd. for $C_{21}H_{14}N_2O_3S_2$ (406.48): C, 62.05; H, 3.47; N, 6.89; S, 15.78. Found: C, 62.08; H, 3.47; N, 7.00; S, 15.65.

3-(2,6-Dioxopiperidin-1-yl)-5-(4-phenylbenzylidene)-2-thioxo-thiazolidin-4-one (**10a**).

This compound was recrystallized from toluene/dioxane, yield 88%, yellow crystals, mp 204°; ir (potassium bromide): ν 1727, 1593; 1485, 1302, 1260 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 8.07 (s, 1H), 7.91-7.89 (m, 2H), 7.81-7.75 (m, 4H), 7.53-7.49 (m, 2H), 7.44 (m, 1H), 3.07-2.91 (m, 4H), 2.08-2.01 (m, 2H); ^{13}C nmr ([D$_6$]-DMSO): δ 188.0, 168.3, 161.8, 143.0, 138.5, 135.9, 131.7, 131.4, 129.0, 128.4, 127.5, 126.8, 117.8, 31.7, 16.3; ms: m/z 408 (35, M$^+$), 210 (100).

Anal. Calcd. for $C_{21}H_{16}N_2O_3S_2$ (408.50): C, 61.75; H, 3.95; N, 6.86; S, 15.70. Found: C, 61.77, H, 3.84, N, 6.92, S, 15.69.

3-(2,6-Dioxopiperidin-1-yl)-5-(4-benzyloxybenzylidene)-2-thioxothiazolidin-4-one (**10b**).

This compound was recrystallized from toluene/dioxane, yield 95%, yellow crystals, mp 189°; ir (potassium bromide): ν 1734, 1591, 1509, 1262 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 7.95 (s, 1H), 7.68 (d, 2H), 7.47-7.45 (m, 2H), 7.42-7.32 (2m, 3H), 7.21 (d, 2H), 5.21 (s, 2H), 3.04-2.88 (m, 4H), 2.06-1.99 (m, 2H); ^{13}C nmr ([D$_6$]-DMSO): δ 188.2, 168.3, 161.9, 161.2, 136.4, 136.2, 133.4, 128.4, 128.0, 127.7, 125.1, 116.0, 114.9, 69.6, 31.7, 16.3; ms: m/z 438 (16, M$^+$), 91 (100).

Anal. Calcd. for $C_{22}H_{18}N_2O_4S_2$ (438.52): C, 60.26; H, 4.14; N, 6.39; S, 14.62. Found: C, 60.19; H, 4.07; N, 6.50; S, 14.70.

3-(2,6-Dioxopiperidin-1-yl)-5-[(5-(4-nitrophenyl)-2-furyl)-methylene]-2-thioxothiazolidin-4-one (**10c**).

This compound was recrystallized from toluene/dioxane, yield 57%, orange powder, mp >340°; ir (potassium bromide): ν 3039, 1723, 1611, 1597, 1511, 1329, 1272, 1242 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 8.43-8.40 (m, 2H), 8.14-8.12 (m, 2H), 7.94 (s, 1H), 7.66 (d, 1H), 7.54 (d, 1H), 3.11-2.91 (m, 4H), 2.11-2.01 (m, 2H); ^{13}C nmr ([D$_6$]-DMSO): δ 188.7, 168.3, 161.5, 156.3, 150.5, 147.1, 133.9, 125.4, 124.6, 124.5, 120.1, 115.7, 113.8, 31.7, 16.3; ms: m/z 443 (42, M$^+$), 245 (100).

Anal. Calcd. for $C_{19}H_{13}N_3O_6S_2$ (443.46): C, 51.46; H, 2.95; N, 9.48; S, 14.46. Found: C, 51.23; H, 3.01; N, 9.72; S, 14.43.

3-(2,6-Dioxopiperidin-1-yl)-5-[(5-hydroxymethyl-2-furyl)-methylene]-2-thioxothiazolidin-4-one (**10d**).

This compound was chromatographically purified (MPLC, dichloromethane:ethyl acetate 7:1, p = 4 bar), yield 73%, yellow crystals, mp 115°; ir (potassium bromide): ν 3444, 1725, 1611, 1243, 1128 cm^{-1}; ^{1}H nmr ([D$_6$]-DMSO): δ 7.83 (s, 1H), 7.31 (d, 1H), 6.66 (d, 1H), 5.55 (br, 1H), 4.56 (d, 2H), 3.04-2.89 (m, 4H), 2.08-1.99 (m, 2H); ^{13}C nmr ([D$_6$]-DMSO): δ 189.5, 168.3, 162.8, 161.6, 148.5, 123. 6, 121.6, 113.7, 111.2, 56.0, 31.7, 16.3; ms: m/z 352 (48, M$^+$), 154 (100).

Anal. Calcd. for $C_{14}H_{12}N_2O_5S_2$ (352.39): C, 47.72; H, 3.43;

N, 7.95; S, 18.20. Found: C, 47.44; H, 3.65; N, 7.94; S, 18.10.

3-(2,6-Dioxopiperidin-1-yl)-5-[(2-phenyl-1,3-thiazol-4-yl)-methylene]-2-thioxothiazolidin-4-one (**10e**).

This compound was recrystallized from toluene/dioxane, yield 66%, yellow crystals, mp 284°; ir (potassium bromide): ν 3106, 1727, 1610, 1305, 1263, 1240 cm^{-1}; ^1H nmr ([D_6]-DMSO): δ 8.52-8.51 (m, 1H), 8.04-7.99 (2m, 3H), 7.60-7.55 (m, 3H), 3.06-2.92 (m, 4H), 2.08-2.05 (m, 2H); ^{13}C nmr ([D_6]-DMSO): δ 192.4, 168.7, 168.3, 162.2, 149.9, 131.8, 131.2, 129.8, 129.4, 126.5 (2C), 120.3, 31.8, 16.4; ms: m/z 416 (15, M^+), 217 (100).

Anal. Calcd. for $C_{18}H_{13}N_3O_3S_3$ (415.51): C, 52.03; H, 3.15; N, 10.12; S, 23.15. Found: C, 52.00; H, 3.10; N, 10.01; S, 23.10.

3-(1,3-Dioxoisoindolin-2-yl)-5-(4-phenylbenzylidene)-2-thioxothiazolidin-4-one (**11a**).

This compound was recrystallized from toluene, yield 95%, yellow crystals, mp 260-262°; ir (potassium bromide): ν 1756, 1587, 1255, 1231, 1177 cm^{-1}; ^1H nmr ([D_6]-DMSO): δ 8.19, (s, 1H), 8.18-8.16 (m, 2H), 8.11-8.08 (m, 2H), 7.95-7.93 (m, 2H), 7.87-7.85 (m, 2H), 7.81-7.79 (m, 2H), 7.55-7.51 (m, 2H), 7.47-7.43 (m, 1H); ^{13}C nmr ([D_6]-DMSO): δ 188.0, 162.0, 161.9, 143.2, 138.4, 137.0, 136.3, 131.8, 131.3, 128.9, 128.5, 128.4, 127.5, 126.7, 124.8, 117.4; ms: 443 (12, M^+), 210 (100).

Anal. Calcd. for $C_{24}H_{14}N_2O_3S_2$ (442.54): C, 65.14; H, 3.19; N, 6.33; S, 14.49. Found: C, 64.96; H, 3.25; N, 6.58; S, 14.38.

3-(1,3-Dioxoisoindolin-2-yl)-5-(4-benzyloxybenzylidene)-2-thioxothiazolidin-4-one (**11b**).

This compound was chromatographically purified (dichloromethane) yield, 76%, yellow crystals, mp 195-197°; ir (potassium bromide): ν 1754, 1736, 1591, 1259 cm^{-1}; ^1H nmr ([D_6]-DMSO): δ 8.16-8.13 (m, 2H), 8.09-8.06 (m, 3H), 7.75-7.72 (m, 2H), 7.49-7.45 (m, 2H), 7.44-7.40 (m, 2H), 7.39-7.33 (m, 1H), 7.27-7.24 (m, 2H), 5.25 (s, 2H); ^{13}C nmr ([D_6]-DMSO): δ 188.2, 162.2, 162.1, 161.5, 137.6, 136.4, 136.2, 133.7, 128.5, 128.4, 128.0, 127.7, 125.1, 124.9, 116.1, 114.3, 69.7; ms: m/z 472 (21, M^+), 91 (100).

Anal. Calcd. for $C_{25}H_{16}N_2O_4S_2$ (472.54): C, 63.54; H, 3.41; N, 5.93; S, 13.57. Found: C, 63.53; H, 3.43; N, 6.01; S, 13.44.

3-(1,3-Dioxoisoindolin-2-yl)-5-[(5-(3-nitrophenyl)-2-furfuryl)-methylene]-2-thioxothiazolidin-4-one (**11c**).

This compound was chromatographically purified (MPLC, dichloromethane:hexane 2:1, p = 2 bar), yield 66%, orange crystals, mp 303°; ir (potassium bromide): ν 3036, 1754, 1727, 1602, 1529, 1348, 1239, 702 cm^{-1}; ^1H nmr ([D_6]-DMSO): δ 8.68 (s, 1H), 8.34-8.27 (m, 2H), 8.16-8.14 (m, 2H), 8.09-8.07 (m, 2H), 8.03 (s, 1H), 7.89 (t, 1H), 7.68 (d, 1H), 7.57 (d, 1H); ^{13}C nmr ([D_6]-DMSO): δ 188.9, 162.2, 161.7, 156.6, 149.8, 148.6, 136.4, 131.1, 130.5, 129.8, 128.6, 125.1, 124.9, 123.7, 121.8, 119.1, 114.6, 112.6; ms: m/z 477 (52, M^+), 245 (100).

Anal. Calcd. for $C_{22}H_{11}N_3O_6S_2$ (477.50): C, 55.34; H, 2.32; N, 8.80; S, 13.43. Found: C, 55.33; H, 2.41; N, 8.81; S, 13.30.

3-(1,3-Dioxoisoindolin-2-yl)-5-(3-indolyl-methylene)-2-thioxothiazolidin-4-one (**11d**).

This compound was chromatographically purified (MPLC, dichloromethane:hexane 19:1, p = 2 bar), yield 72%, orange crystals, mp >315°; ir (potassium bromide): ν 3386, 1746, 1726, 1597, 1578, 1285, 1233, 1184 cm^{-1}; ^1H nmr ([D_6]-DMSO): δ 8.37 (s, 1H), 8.17-8.14 (2m, 3H), 8.09-8.07 (m, 2H), 8.04 (m, 1H), 7.6 (m, 1H), 7.34-7.25 (m, 2H); ^{13}C nmr ([D_6]-DMSO): δ 187.7, 162.3, 161.6, 136.4, 136.2, 132.4, 130.5, 128.6, 126.7, 124.7, 123.6, 121.9, 118.7, 112.6, 111.0, 108.9; ms: m/z 405 (56, M^+), 173 (100).

Anal. Calcd. for $C_{20}H_{11}N_3O_3S_2$ (405.47): C, 59.24; H, 2.73; N, 10.37; S, 15.82. Found: C, 58.98; H, 2.70; N, 10.44; S, 15.68.

3-(1,3-Dioxoisoindolin-2-yl)-5-(2-fluorenylmethylene)-2-thioxothiazolidin-4-one (**11e**).

This compound was recrystallized from toluene, yield 77%, yellow crystals, mp 312°; ir (potassium bromide): ν 1748, 1591, 1257, 1241, 1220 cm^{-1} ; ^1H nmr ([D_6]-DMSO): δ 8.19 (s, 1H), 8.17-8.14 (m, 2H), 8.11 (m, 1H), 8.09-8.06 (m, 2H), 8.03 (m, 1H), 7.97 (s, 1H), 7.81 (m, 1H), 7.67 (m, 1H), 7.48-7.43 (m, 2H), 4.08 (s, 2H); ms: m/z 455 (15, M^+), 222 (100).

Anal. Calcd. for $C_{25}H_{14}N_2O_3S_2$ (454.53): C, 66.06; H, 3.10; N, 6.16; S, 14.11. Found: C, 65.89; H, 3.24; N, 6.39; S, 14.16.

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