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AZAHETEROCYCLIC DERIVATIVES OF α-PYRONO[2,3-*f*]ISOFLAVONES

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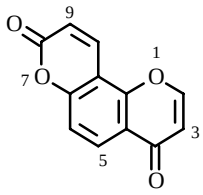
9-Azahetaryl-3-arylpyrano[2,3-f]chromen-4,8-diones were synthesized by condensation of 7-hydroxy-8-formylisoflavones with 2-azahetarylacetonitriles followed by acid hydrolysis.

Key words: isoflavones, 2-azahetarylacetonitriles, condensation, α-pyrono[2,3-*f*]isoflavones.

The broad class of natural complicated flavonoids contains compounds with α- and γ-pyrone cores in a single molecule, in particular, derivatives of pyrano[2,3-*f*]chromen-4,8-dione (**1**). Roots of *Clausena heptaphylla* afforded clausenidine (**2**) [1, 2]; the powdery film from the leaf surface of the fern *Pityrogramma calomelanos*, calomelanol D (**3**) [3-7], which are partially hydrogenated derivatives of **1**.



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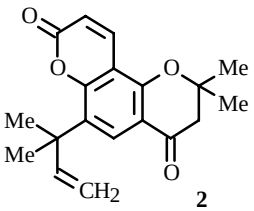

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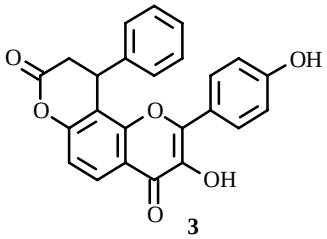

3

Synthetic derivatives of α-pyrono[2,3-*f*]chromones have been proposed as monofunctional photoreagents for DNA [8]. α-Pyrono[2,3-*f*]flavones, their heteroanalogs, and isoflavones exhibit bactericidal activity [9, 10].

The pyrano[2,3-*f*]chromen-4,8-dione system can be synthesized via annellation of the γ-pyrone core to the coumarin core [9-13] or, on the other hand, by annellation of the α-pyrone ring to the chromone ring [9, 14-18]. α-Pyrono[2,3-*f*]isoflavones were prepared through both pathways, by acylation of 5-hydroxy-6-arylacetylcoumarin using the Kostanetsky reaction [11] and starting with 7-hydroxy-8-formylchromones under forcing Perkin reaction conditions [9, 15]. Derivatives of this system with heterocyclic substituents in the α-pyrone ring are known. Therefore, it seemed interesting to modify α-pyrono[2,3-*f*]isoflavones by adding pharmacophoric azaheterocyclic groups.

Thus, we investigated the reaction of 7-hydroxy-8-formylisoflavones **4-7** with 2-azahetarylacetonitriles. The starting materials for synthesizing the formyl derivatives were the natural isoflavone formononetin (**8**) and its synthetic analogs **9-11** that are unsubstituted and substituted at the 2- and 6-positions. 8-Formylformononetin (**4**) was synthesized previously from **8** using the Duff reaction [19, 20]. We used this method to synthesize 7-hydroxy-8-formylisoflavones **4-7**. Reaction of **8-11** with an excess of hexamethylenetetramine in acetic acid with subsequent work up with dilute HCl produced in good yields (60-73%) **4-7**.

PMR spectra of **4-7** in DMSO-d_6 contained a singlet at 6.8 ppm that was characteristic of H-8 in starting isoflavones **8-11**. The formyl proton resonated at 10-53-10.59 ppm. A broad singlet for the 7-OH was shifted to weak field by almost 2 ppm as a result of the formation of an intramolecular H-bond with the O atom of the 8-CHO group. The chelate structure of the products was also confirmed by their characteristic red-brown color in alcohol solution with $FeCl_3$ [14, 19] and the presence of a broad band at 3070-3100 cm^{-1} in the IR spectra. Formyl C=O and isoflavone carbonyl stretching vibrations were observed as a strong broad band at 1640-1650 cm^{-1}.

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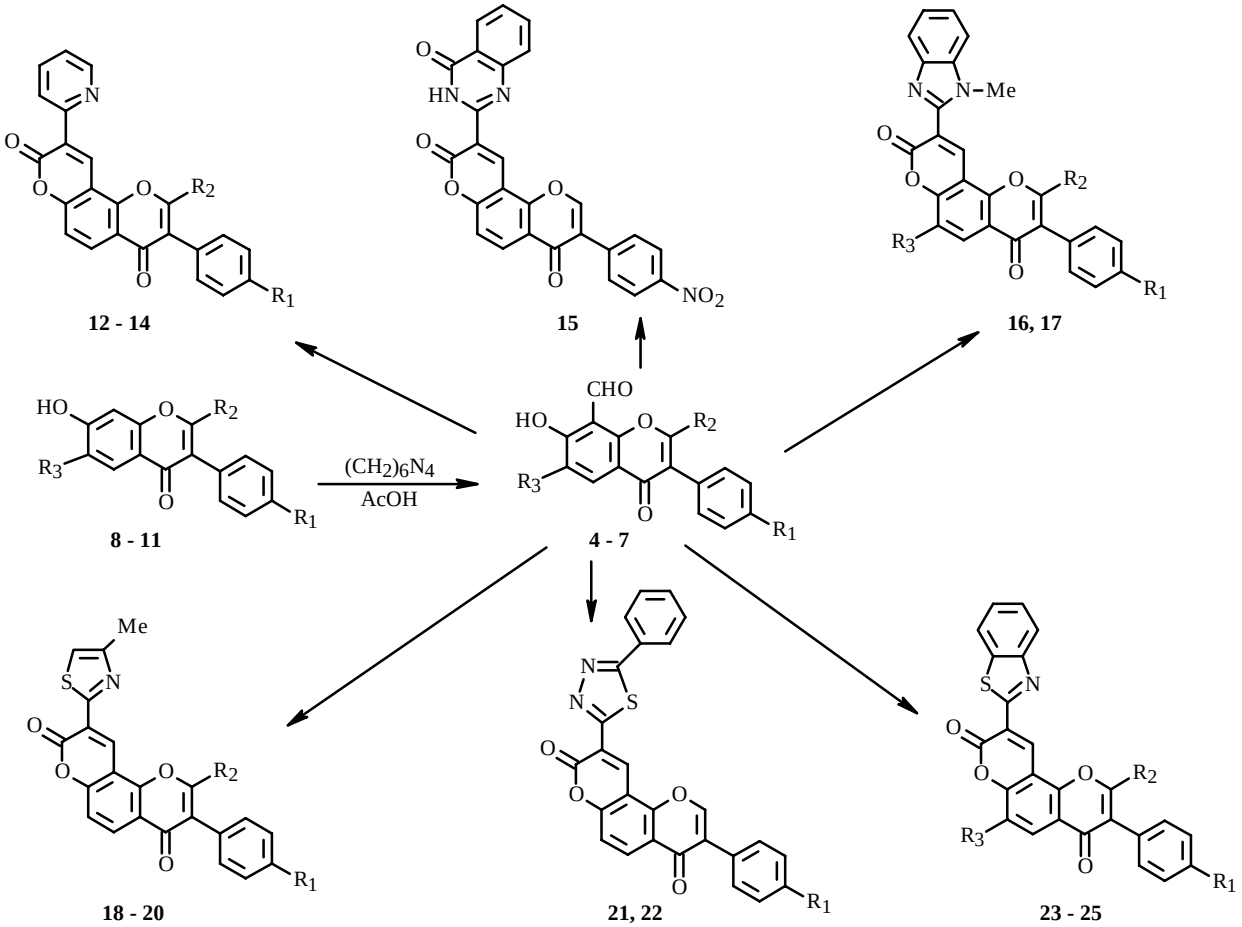

4: R_1 = OMe, R_2 = R_3 = H; **5:** R_1 = NO_2, R_2 = R_3 = H; **6:** R_1 = Cl, R_2 = Me, R_3 = H; **7:** R_1 = F, R_2 = Me, R_3 = Et;
8: R_1 = OMe, R_2 = R_3 = H; **9:** R_1 = NO_2, R_2 = R_3 = H; **10:** R_1 = Cl, R_2 = Me, R_3 = H; **11:** R_1 = F, R_2 = Me, R_3 = Et;
12: R_1 = OMe, R_2 = H; **13:** R_1 = NO_2, R_2 = H; **14:** R_1 = Cl, R_2 = Me; **16:** R_1 = NO_2, R_2 = R_3 = H; **17:** R_1 = F, R_2 = Me, R_3 = Et;
18: R_1 = OMe, R_2 = H; **19:** R_1 =NO_2, R_2 = H; **20:** R_1 = Cl, R_2 = Me; **21:** R_1 = OMe; **22:** R_1 = NO_2; **23:** R_1 = OMe, R_2 = R_3 = H;
24: R_1 = NO_2, R_2 = R_3 = H; **25:** R_1 = F, R_2 = Me, R_3 = Et

7-Hydroxy-8-formylisoflavones **4-7** underwent a Knoevenagel reaction with 2-cyanomethyl derivatives of azines (pyridine and quinazolin-4-one) and azoles (1-methylbenzimidazole, 4-methylthiazole, 5-phenyl-1,3,4-thiadiazole, and benzothiazole) in DMF in the presence of catalytic amounts of piperidine at room temperature. Hydrolysis of the condensation products by H_2SO_4 (3%) for 5 h isolated in high yields 9-azahetaryl-3-arylpyrano[2,3-*f*]chromen-4,8-diones **12-14**, **16-20**, **24**, and **25**. Longer boiling in H_2SO_4 (30%) was required to form **15** and **21-23**. Compounds **12-25** are high melting and poorly soluble in organic solvents.

PMR spectra of **12-25** in CF_3CO_2D contained signals characteristic of the isoflavone protons and the azaheterocyclic part of the molecules in addition to a weak-field singlet at 9.43-10.15 ppm for H-10 of pyrano[2,3-*f*]chromen-4,8-dione that was deshielded by the azaheterocycle N atom. Formation of the α-pyrone ring was confirmed by the appearance in IR spectra of **12-25** of a strong band for C=O stretches of a lactone carbonyl at 1710-1750 cm^{-1}. The chromone C=O was located at 1640-1660 cm^{-1}, which agreed with previous results for α-pyronochromones [10, 17].

Thus, reaction of 7-hydroxy-8-formylisoflavones with 2-azahetarylacetonitriles under mild conditions produced new derivatives of α-pyrono[2,3-*f*]isoflavone with an azaheterocyclic substituent in the α-pyrone ring.

EXPERIMENTAL

The purity of the products was monitored by TLC on Silufol UV-254 plates using $CHCl_3$:CH_3OH (9:1). PMR spectra were recorded in DMSO-d_6 and CF_3CO_2D on a Varian Mercury 400 spectrometer relative to TMS (internal standard). IR spectra were recorded on a UR-20 instrument in KBr disks. Elemental analyses of all compounds agreed with those calculated.

General Method for Synthesizing 7-Hydroxy-8-formylisoflavones 4-7. A solution of **8-11** (5 mmol) and hexamethylenetetramine (7 g, 50 mmol) in acetic acid (20 mL) was heated on a water bath for 6-8 h, poured into HCl:H_2O (1:1, 24 mL), boiled for 10 min, and diluted with water (40 mL). After several hours the resulting precipitate was filtered off and recrystallized from EtOH.

7-Hydroxy-8-formyl-4′-methoxyisoflavone (4). Yield 60%, mp 178°C (lit. [19] mp 166°C, [20] 165-185°C), $C_{17}H_{12}O_5$. PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 3.82 (3H, s, CH_3O-4′), 6.97 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 7.07 (1H, d, J = 8.8, H-6), 7.52 (2H, d, J = 8.8, H_{Ar}-3′, H_{Ar}-5′), 8.28 (1H, d, J = 8.8, H-5), 8.37 (1H, s, H-2), 10.55 (1H, s, CHO-8), 12.25 (1H, s, OH-7). IR spectrum (KBr, ν, cm^{-1}): 3080 (CHO...HO), 1640 (C=O).

7-Hydroxy-8-formyl-4′-nitroisoflavone (5). Yield 70%, mp 182°C, $C_{16}H_9NO_6$. PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.12 (1H, d, J = 8.8, H-6), 7.92 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 8.27 (3H, d, J = 8.8, H-5, H_{Ar}-3′, H_{Ar}-5′), 8.68 (1H, s, H-2), 10.53 (1H, s, CHO-8), 12.26 (1H, s, OH-7). IR spectrum (KBr, ν, cm^{-1}): 3080 (CHO...HO), 1650 (C=O).

7-Hydroxy-2-methyl-8-formyl-4′-chloroisoflavone (6). Yield 72%, mp 165°C, $C_{17}H_{11}ClO_4$. PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 2.36 (3H, s, CH_3-2), 7.04 (1H, d, J = 8.8, H-6), 7.28 (2H, d, J = 8.4, H_{Ar}-2′, H_{Ar}-6′), 7.44 (2H, d, J = 8.4, H_{Ar}-3′, H_{Ar}-5′), 8.17 (1H, d, J = 8.8, H-5), 10.56 (1H, s, CHO-8), 12.22 (1H, s, OH-7). IR spectrum (KBr, ν, cm^{-1}): 3100 (CHO...HO), 1640 (C=O).

7-Hydroxy-2-methyl-8-formyl-6-ethyl-4′-fluoroisoflavone (7). Yield 73%, mp 183°C, $C_{19}H_{15}FO_4$. PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 1.27 (3H, t, J = 7.6, CH_3CH_2-6), 2.35 (3H, s, CH_3-2), 2.73 (2H, q, J = 7.6, CH_3CH_2-6), 7.20 (2H, t, $J_{H\text{-}3',H\text{-}2'} = J_{H\text{-}3',F} = 8.4$, H_{Ar}-3′, H_{Ar}-5′), 7.30 (2H, dd, $J_{H\text{-}2',H\text{-}3'} = 8.4$, $J_{H\text{-}2',F} = 5.6$, H_{Ar}-2′, H_{Ar}-6′), 8.05 (1H, s, H-5), 10.59 (1H, s, CHO-8), 12.80 (1H, s, OH-7). IR spectrum (KBr, ν, cm^{-1}): 3070 (CHO...HO), 1640 (C=O).

General Method for Synthesizing 9-Azahetaryl-3-arylpyrano[2,3-*f*]chromen-4,8-diones 12-25. A solution of **4-7** (1 mmol) in DMF (2 mL) was treated with the appropriate 2-azahetarylacetonitrile (1 mmol) and piperidine (3 drops), heated for 5 min, held at room temperature for 12 h, treated with H_2SO_4 (10 mL, 3%), boiled for 5 h (for **15** and **21-23**, for 15 h in 30% H_2SO_4), and cooled. The precipitate was filtered off and recrystallized from DMF.

3-(4-Methoxyphenyl)-9-(pyridin-2-yl)pyrano[2,3-*f*]chromen-4,8-dione (12). Yield 79%, mp 217°C, $C_{24}H_{15}NO_5$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 3.85 (3H, s, OCH_3-4′), 6.98 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 7.28 (2H, d, J = 8.8, H_{Ar}-3′, H_{Ar}-5′), 7.53 (1H, d, J = 9.2, H-6), 7.97 (1H, t, J = 6.8, H_{Py}-4″), 8.22 (1H, s, H-2), 8.61-8.66 (3H, m, H-5, H_{Py}-3″, H_{Py}-5″), 8.77 (1H, d, J = 5.6, H_{Py}-6″), 9.44 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1740 ($C{=}O_\alpha$), 1660 ($C{=}O_\gamma$).

3-(4-Nitrophenyl)-9-(pyridin-2-yl)pyrano[2,3-*f*]chromen-4,8-dione (13). Yield 51%, mp >300°C, $C_{23}H_{12}N_2O_6$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 7.79 (1H, d, J = 9.2, H-6), 7.84 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 8.21 (1H, t, J = 6.8, H_{Py}-4″), 8.47 (2H, d, J = 8.8, H_{Ar}-3′, H_{Ar}-5′), 8.57 (1H, s, H-2), 8.83-8.90 (3H, m, H-5, H_{Py}-3″, H_{Py}-5″), 9.01 (1H, d, J = 5.6, H_{Py}-6″), 9.68 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1750 ($C{=}O_\alpha$), 1645 ($C{=}O_\gamma$).

2-Methyl-9-(pyridin-2-yl)-3-(4-chlorophenyl)pyrano[2,3-*f*]chromen-4,8-dione (14). Yield 75%, mp 267°C, $C_{24}H_{14}ClNO_4$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 2.61 (3H, s, CH_3-2), 7.30 (2H, d, J = 8.4, H_{Ar}-2′, H_{Ar}-6′), 7.55 (2H, d, J = 8.4, H_{Ar}-3′, H_{Ar}-5′), 7.76 (1H, d, J = 8.8, H-6), 8.21 (1H, m, H_{Py}-4′), 8.81-8.84 (3H, m, H-5, H_{Py}-3″, H_{Py}-5″), 9.01 (1H, d, J = 5.6, H_{Py}-6″), 9.67 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1730 ($C{=}O_\alpha$), 1650 ($C{=}O_\gamma$).

3-(4-Nitrophenyl)-9-(4-oxo-3,4-dihydroquinazolin-2-yl)pyrano[2,3-*f*]chromen-4,8-dione (15). Yield 83%, mp >300°C, $C_{26}H_{13}N_3O_7$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 7.79 (1H, d, J = 9.2, H-6), 7.83 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 8.01 (1H, t, J = 7.6, H-7″), 8.17 (1H, d, J = 8.0, H-8″), 8.26 (1H, t, J = 7.6, H-6″), 8.47 (2H, d, J = 8.8, H_{Ar}-3′, H_{Ar}-5′), 8.51 (1H, s, H-2), 8.61 (1H, d, J = 8.0, H-5″), 8.97 (1H, d, J = 9.2, H-5), 10.15 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1710 ($C{=}O_\alpha$), 1670 ($C{=}O_q$), 1645 ($C{=}O_\gamma$).

9-(1-Methylbenzimidazol-2-yl)-3-(4-nitrophenyl)pyrano[2,3-*f*]chromen-4,8-dione (16). Yield 82%, mp 291°C, $C_{26}H_{15}N_3O_6$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 4.32 (3H, s, N–CH_3), 7.79 (1H, d, J = 9.2, H-6), 7.86 (5H, m, H_{Ar}-2′, H_{Ar}-6′, H_{Bzi}-5″, H_{Bzi}-6″, H_{Bzi}-7″), 8.00 (1H, d, J = 8.0, H_{Bzi}-4″), 8.48 (2H, d, J = 8.0, H_{Ar}-3′, H_{Ar}-5′), 8.56 (1H, s, H-2), 8.90 (1H, d, J = 9.2, H-5), 9.43 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1735 ($C{=}O_\alpha$), 1660 ($C{=}O_\gamma$).

2-Methyl-9-(1-methylbenzimidazol-2-yl)-3-(4-fluorophenyl)-6-ethylpyrano[2,3-*f*]chromen-4,8-dione (17). Yield 83%, mp >300°C, $C_{29}H_{21}FN_2O_4$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 1.52 (3H, t, J = 7.6, $\underline{CH_3}CH_2$-6), 2.58 (3H, s, CH_3-2), 3.17 (2H, q, J = 7.6, $CH_3\underline{CH_2}$-6), 4.32 (3H, s, N–CH_3), 7.27 (2H, t, $J_{H\text{-}3',H\text{-}2'} = J_{H\text{-}3',F}$ = 8.4, H_{Ar}-3′, H_{Ar}-5′), 7.37 (2H, dd, $J_{H\text{-}2',H\text{-}3'}$ = 8.4, $J_{H\text{-}2',F}$ = 5.6, H_{Ar}-2′, H_{Ar}-6′), 7.87-8.01 (4H, m, H_{Bzi}-4″, H_{Bzi}-5″, H_{Bzi}-6″, H_{Bzi}-7″), 8.70 (1H, s, H-5), 9.44 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1720 (C=O_α), 1630 (C=O_γ).

9-(4-Methylthiazol-2-yl)-3-(4-methoxyphenyl)pyrano[2,3-*f*]chromen-4,8-dione (18). Yield 78%, mp 271°C, $C_{23}H_{15}NO_5S$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 2.58 (3H, s, CH_3-4″), 3.85 (3H, s, OCH_3-4′), 6.98 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 7.28 (2H, d, J = 8.8, H_{Ar}-3′, H_{Ar}-5′), 7.51 (1H, d, J = 9.2, H-6), 7.56 (1H, s, H-5″), 8.21 (1H, s, H-2), 8.64 (1H, d, J = 9.2, H-5), 9.43 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1735 (C=O_α), 1650 (C=O_γ).

9-(4-Methylthiazol-2-yl)-3-(4-nitrophenyl)pyrano[2,3-*f*]chromen-4,8-dione (19). Yield 74%, mp 292°C, $C_{22}H_{12}N_2O_6S$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 2.82 (3H, s, CH_3-4″), 7.78 (1H, d, J = 9.2, H-6), 7.79 (1H, s, H-5″), 7.84 (2H, d, J = 8.4, H_{Ar}-2′, H_{Ar}-6′), 8.46 (2H, d, J = 8.4, H_{Ar}-3′, H_{Ar}-5′), 8.58 (1H, s, H-2), 8.87 (1H, d, J = 9.2, H-5), 9.75 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1740 (C=O_α), 1660 (C=O_γ).

2-Methyl-9-(4-methylthiazol-2-yl)-3-(4-chlorophenyl)pyrano[2,3-*f*]chromen-4,8-dione (20). Yield 76%, mp 275°C, $C_{23}H_{14}ClNO_4S$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 2.60 (3H, s, CH_3-2), 2.80 (3H, s, CH_3-4″), 7.29 (2H, d, J = 8.4, H_{Ar}-2′, H_{Ar}-6′), 7.54 (2H, d, J = 8.4, H_{Ar}-3′, H_{Ar}-5′), 7.73 (1H, d, J = 8.8, H-6), 7.78 (1H, s, H-5″), 8.81 (1H, d, J = 8.8, H-5), 9.73 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1725 (C=O_α), 1660 (C=O_γ).

3-(4-Methoxyphenyl)-9-(5-phenyl-[1,3,4]thiadiazol-2-yl)pyrano[2,3-*f*]chromen-4,8-dione (21). Yield 87%, mp >300°C, $C_{27}H_{16}N_2O_5S$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 3.85 (3H, s, OCH_3-4′), 6.99 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 7.30 (2H, d, J = 8.8, H_{Ar}-3′, H_{Ar}-5′), 7.54-7.59 (3H, m, H-6, H_{Ph}-3″, H_{Ph}-5″), 7.73 (1H, t, J = 7.6, H_{Ph}-4″), 7.93 (2H, d, J = 7.6, H_{Ph}-2″, H_{Ph}-6″), 8.26 (1H, s, H-2), 8.65 (1H, d, J = 9.2, H-5), 9.65 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1725 (C=O_α), 1640 (C=O_γ).

3-(4-Nitrophenyl)-9-(5-phenyl-[1,3,4]thiadiazol-2-yl)pyrano[2,3-*f*]chromen-4,8-dione (22). Yield 88%, mp >300°C, $C_{26}H_{13}N_3O_6S$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 7.79 (3H, m, H-6, H_{Ph}-3″, H_{Ph}-5″), 7.84 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 7.94 (1H, t, J = 7.6, H_{Ph}-4″), 8.16 (2H, d, J = 7.6, H_{Ph}-2″, H_{Ph}-6″), 8.47 (2H, d, J = 8.8, H_{Ar}-3′, H_{Ar}-5′), 8.60 (1H, s, H-2), 8.87 (1H, d, J = 9.2, H-5), 9.90 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1725 (C=O_α), 1660 (C=O_γ).

9-Benzothiazol-2-yl-3-(4-methoxyphenyl)pyrano[2,3-*f*]chromen-4,8-dione (23). Yield 89%, mp >300°C, $C_{26}H_{15}NO_5S$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 4.09 (3H, s, OCH_3-4′), 7.23 (2H, d, J = 8.4, H_{Ar}-2′, H_{Ar}-6′), 7.53 (2H, d, J = 8.4, H_{Ar}-3′, H_{Ar}-5′), 7.66 (1H, d, J = 8.8, H-6), 7.95 (1H, t, J = 8.4, H-6″), 8.03 (1H, t, J = 8.4, H-5″), 8.31 (1H, d, J = 8.4, H-7″), 8.40 (1H, d, J = 8.4, H-4″), 8.49 (1H, s, H-2), 8.94 (1H, d, J = 8.8, H-5), 9.89 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1735 (C=O_α), 1645 (C=O_γ).

9-Benzothiazol-2-yl-3-(4-nitrophenyl)pyrano[2,3-*f*]chromen-4,8-dione (24). Yield 78%, mp >300°C, $C_{25}H_{12}N_2O_6S$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 7.81 (1H, d, J = 8.8, H-6), 7.86 (2H, d, J = 8.8, H_{Ar}-2′, H_{Ar}-6′), 7.96 (1H, t, J = 8.4, H-6″), 8.04 (1H, t, J = 8.4, H-5″), 8.32 (1H, d, J = 8.4, H-7″), 8.40 (1H, d, J = 8.4, H-4″), 8.48 (2H, d, J = 8.8, H_{Ar}-3′, H_{Ar}-5′), 8.62 (1H, s, H-2), 8.94 (1H, d, J = 8.8, H-5), 9.90 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1725 (C=O_α), 1650 (C=O_γ).

9-Benzothiazol-2-yl-2-methyl-3-(4-fluorophenyl)-6-ethylpyrano[2,3-*f*]chromen-4,8-dione (25). Yield 85%, mp >300°C, $C_{28}H_{18}FNO_4S$. PMR spectrum (400 MHz, CF_3CO_2D, δ, ppm, J/Hz): 1.49 (3H, t, J = 7.6, $\underline{CH_3}CH_2$-6), 2.61 (3H, s, CH_3-2), 3.16 (2H, q, J = 7.6, $CH_3\underline{CH_2}$-6), 7.24 (2H, t, $J_{H\text{-}3',H\text{-}2'} = J_{H\text{-}3',F}$ = 8.4, H_{Ar}-3′, H_{Ar}-5′), 7.34 (2H, dd, $J_{H\text{-}2',H\text{-}3'}$ = 8.4, $J_{H\text{-}2',F}$ = 5.6, H_{Ar}-2′, H_{Ar}-6′), 7.93 (1H, t, J = 8.4, H-6′), 8.00 (1H, t, J = 8.4, H-5″), 8.29 (1H, d, J = 8.4, H-7″), 8.35 (1H, d, J = 8.4, H-4″), 8.72 (1H, s, H-5), 9.87 (1H, s, H-10). IR spectrum (KBr, ν, cm^{-1}): 1725 (C=O_α), 1645 (C=O_γ).

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