**SYNTHESIS OF NEW BENZOPYRANO[2,3-C]PYRAZOLES AND
3-TRIAZOLONYLIMINOCOUMARINS FROM 3-CYANO IMINOCOUMARIN
DERIVATIVES**

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Supplementary Material

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General procedure for the synthesis of benzopyrano(2,3-c)pyrazoles 1a-7a

Benzopyrano [2,3-c] pyrazole (1a)

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Benzopyrano [2,3-c] pyrazole (2a)

Pink solid, IR (cm^{-1}): $\nu = 1132$ (C=S), 1584 (C=C), 1659 (C=N), 3258/3302 (NH), 3369 (NH_2). ^1H NMR (DMSO-d_6): $\delta = 1.11$ (t, $J = 6.9$ Hz, 6H, CH_3), $\delta = 3.45$ (q, $J = 6.9$ Hz, 4H, CH_2), 6.13 (s, 1H, H_8), 6.56 (d, $J = 8.7$ Hz, 1H, H_6), 7.02 (s, 2H, NH_2), 7.27 (d, $J = 8.7$ Hz, 1H, H_5), 8.30 (s, 1H, H_4) 9.88 (s, 1H, NH). Calculated for $\text{C}_{15}\text{H}_{17}\text{N}_5\text{OS}$: %C 57.12, %H 5.43, %N 22.21. Found: %C 56.98, %H 5.52, %N 22.29.

Benzopyrano [2,3-c] pyrazole (3a)

Yellow solid, IR (cm^{-1}): $\nu = 1155$ (C=S), 1595 (C=C), 1646 (C=N), 3256 (NH) , 3359 (NH_2). ^1H NMR ($\text{CDCl}_3/\text{CF}_3\text{COOD}$): $\delta = 7.25$ (s, 1H, H_8), 7.32 (d, $J = 6.9$ Hz, 1H, H_6), 7.85 (d, $J = 6.9$ Hz, 1H, H_5), 8.60 (s, 1H, H_4). Calculated for $\text{C}_{11}\text{H}_8\text{N}_4\text{O}_2\text{S}$: %C 50.76, %H 3.10, %N 21.53. Found: %C 50.56, %H 3.06, %N 22.47.

Benzopyrano [2,3-c] pyrazole (4a)

Red-brown solid, IR (cm^{-1}): $\nu = 1160$ (C=S), 1618 (C=C), 1642 (C=N), 3255 (NH) , 3361 (NH₂). ¹H NMR (CDCl₃/CF₃COOD): $\delta = 7.48$ (d, J = 6.9 Hz, 1H, H₈), 7.65 (d, J = 6.9 Hz, 1H, H₇), 7.99 (s, 1H, H₅), 8.69 (s, 1H, H₄). Calculated for C₁₁H₇ClN₄OS : %C 47.40, %H 2.52, %N 20.10. Found: %C 47.51, %H 2.47, %N 20.15.

Benzopyrano [2,3-c] pyrazole (5a)

Orange solid, IR (cm^{-1}): $\nu = 1163$ (C=S), 1591 (C=C), 1644 (C=N), 3257 (NH) , 3361 (NH₂). ¹H NMR (DMSO-d₆): $\delta = 3.70$ (s, 3H, OCH₃), 6.65 (d, J = 8.7 Hz ,1H, H₈), 6.80 (d, J = 8.7 Hz ,1H, H₇), 6.88 (s, 1H, H₅), 6.98 (s, 2H, NH₂), 8.41 (s, 1H, H₄), 9.88 (s, 1H, NH). Calculated for C₁₂H₁₀N₄O₂S : %C 52.54, %H 3.67, %N 20.43. Found: %C 52.45, %H 3.48, %N 20.23.

Benzopyrano [2,3-c] pyrazole (6a)

Yellow solid, IR (cm^{-1}): $\nu = 1140$ (C=S), 1592 (C=C), 1656 (C=N), 3245/3318 (NH), 3370 (NH₂). ¹H NMR (CDCl₃/CF₃COOD): $\delta = 3.81$ (s, 3H, OCH₃), 6.68 (s, 1H, H₈), 6.72 (d, J = 8,7 Hz 1H, H₆), 7.40 (d, J = 8,7 Hz 1H, H₅), 8.06 (s,1H, H₄). Calculated for C₁₂H₁₀N₄O₂S : %C 52.54, %H 3.67, %N 20.43. Found: %C 52.60, %H 3.50, %N 20.35.

Benzopyrano [2,3-c] pyrazole (7a)

Yellow solid, IR (cm^{-1}): $\nu = 1133$ (C=S), 1576 (C=C), 1658 (C=N), 3288 (NH) , 3366 (NH_2).

^1H NMR (DMSO-d_6): $\delta = 3.86$ (s, 3H, OCH_3), 7.06 (s, 2H, NH_2), 7.30-7.40 (m, 2H, H_6 , H_7), 7.46 (d, $J = 8.4$ Hz, 1H, H_5), 8.06 (s, 1H, H_4), 9.86 (s, 1H, NH). Calculated for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2\text{S}$: %C 52.54, %H 3.67, %N 20.43. Found: %C 52.33, %H 3.53, %N 20.49.

General procedure for the synthesis of 3-triazolonyliminocoumarins (8a - 10a) and (8b - 10b)

A solution of 3-cyano-N-ethoxycarbonyl iminocoumarin **8-10** (5 mmoles) and 4-phenylsemicarbazid or thiosemicarbazide (5 mmoles) in 30 ml of absolute methanol was refluxed during the time indicated in Table 2. After complete reaction, the simple 3-triazolonyl iminocoumarin obtained was separated by filtration and washed with methanol.

3-triazolonyliminocoumarin (8a)

Orange solid, IR (cm^{-1}): $\nu = 1179$ (C=S), 1592 (C=C), 1644 (C=N), 1729 (C=O) , 3276 (NH).

^1H NMR ($\text{CDCl}_3/\text{CF}_3\text{COOD}$): $\delta = 1.33$ (t, $J = 6.9$ Hz, 6H, CH_3), 3.59 (q, $J = 6.9$ Hz, 4H, CH_2), 6.70 (s, 1H, H_8), 6.94 (d, $J = 9.3$ Hz, 1H, H_6), 7.64 (d, $J = 9.3$ Hz, 1H, H_5), 8.05 (s, 1H,

H₄), 8.69 (s, 1H, NH), 9.47 (s, 1H, NH). Calculated for C₁₆H₁₈N₆O₂S : %C 53.63, %H 5.03, %N 23.46. Found: %C 53.59, %H 5.08, %N 23.49.

3-triazolonyliminocoumarin (9a)

Orange-brown solid, IR (cm⁻¹): ν = 1158 (C=S), 1583 (C=C), 1629 (C=N), 1729 (C=O), 3330 (NH). ¹H NMR (CDCl₃/CF₃COOD): δ = 3.78 (s, 3H, OCH₃), 6.79 (s, 1H, H₈), 6.90 (d, J = 8.7 Hz, 1H, H₆), 7.57 (d, J = 8.7 Hz, 1H, H₅), 8.21 (s, 1H, H₄). C₁₃H₁₁N₅O₃S: %C 49.21, %H 3.49, %N 22.07. Found: %C 49.73, %H 3.56, %N 21.95.

3-triazolonyliminocoumarin (10a)

Red-brown solid, IR (cm⁻¹): ν = 1153 (C=S), 1576 (C=C), 1625 (C=N), 1729 (C=O), 3312 (NH). ¹H NMR (CDCl₃/CF₃COOD): δ = 3.96 (s, 3H, OCH₃), 6.73 (d, J = 7.8 Hz, 1H, H₇), 6.92 (t, J = 7.8 Hz, 1H, H₆), 7.49 (d, J = 7.8 Hz, 1H, H₅), 8.12 (s, 1H, H₄). C₁₃H₁₁N₅O₃S: %C 49.21, %H 3.49, %N 22.07. Found: %C 49.33, %H 3.40, %N 22.11.

3-triazolonyliminocoumarin (8b)

Orange-brown solid, IR (cm⁻¹): ν = 1584 (C=C), 1648 (C=N), 1718/ 1745 (C=O), 3126 (NH). ¹H NMR (CDCl₃/CF₃COOD): δ = 1.3 (t, J = 7.2 Hz, 6H, CH₃), δ = 3.6 (q, J = 7.2 Hz, 4H, CH₂), δ = 6.75 (d, J = 2.4 Hz, 1H, H₈), 6.99 (dd, J = 2.4 Hz, J = 9.3 Hz, 1H, H₆), 7.29 (d, J = 8.1 Hz, 1H, H_{Ar}), 7.43 (t, J = 8.1 Hz, 2H, H_{Ar}), 7.52 (d, J = 8.1 Hz, 2H, H_{Ar}), 7.65 (d, J = 9.3 Hz, 1H, H₅), 8.52 (s, 1H, H₄). C₂₂H₂₂N₆O₃: %C : 63.15, %H 5.26, %N 20.09. Found: %C : 63.22, %H 5.30, %N 19.99.

3-triazolonyliminocoumarin (9b)

Orange-brown solid, IR (cm⁻¹): ν = 1591 (C=C), 1650 (C=N), 1690/1746 (C=O), 3332 (NH). ¹H NMR (CDCl₃/CF₃COOD): δ = 3.83 (s, 3H, OCH₃), 6.81 (s, 1H, H₈), 6.89 (d, J = 8.4 Hz, 1H, H₆), 7.33 (d, J = 8,7 Hz, 1H, H_{Ar}), 7.39 (t, J = 8,7 Hz, 2H, H_{Ar}), 7.50 (d, J = 8,7 Hz, 2H, H_{Ar}), 7.53 (d, J = 8,4 Hz, 1H, H₅), 8.13 (s, 1H, H₄). C₁₉H₁₅N₅O₄: %C 60.47, %H 4.01, %N 18.56. Found: %C 60.86, %H 4.19, %N 18.41.

3-triazolonyliminocoumarin (10b)

Yellow solid, IR (cm^{-1}): ν = 1593 (C=C), 1655 (C=N), 1684/1749 (C=O), 3253/3379 (NH). ^1H NMR ($\text{CDCl}_3/\text{CF}_3\text{COOD}$): δ = 3.91 (s, 3H, OCH_3), δ = 6.70-6.90 (m, 2H, H_6 , H_7), 7.20 (d, J = 8.7 Hz, 1H, H_{Ar}), 7.34 (t, J = 8.7 Hz, 2H, H_{Ar}), 7.43 (d, J = 8.7 Hz, 2H, H_{Ar}), 7.57 (d, J = 7.2 Hz, 1H, H_5), 8.11 (s, 1H, H_4). $\text{C}_{19}\text{H}_{15}\text{N}_5\text{O}_4$: %C 60.47, %H 4.01, %N 18.56. Found: %C 60.80, %H 4.21, %N 18.38.

II. Selected of IR and ^1H NMR spectra