**Synthesis Of New 3-Carboxamidine Iminocoumarins
And Benzopyrano[2,3-d]pyrimidines**

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Supplementary Material

Table of Contents

I. Analytical data of compounds.....	S - 2
General procedure for the synthesis of 3-carboxamidine iminocoumarins 12-18.....	S - 2
General procedure for the synthesis of benzopyranopyrimidines 19-22	S - 5
II. Selected of IR, ¹H NMR, ¹³C NMR and MS spectra.....	S - 8

I. Analytical data of compounds

General procedure for the synthesis of 3-carboxamidine iminocoumarins 12-18

A mixture of 3-cyano-iminocoumarins (**1-7**) (0.05 mol) and cyanamide (0.05 mol), were stirred in 30 ml of methanol. After total dissolution 0.05 mol of piperidine was added and the reaction mixture was stirred at room temperature during the time indicated in Table 1. After complete reaction, the simple 3-carboxamidine iminocoumarins obtained was separated by filtration and washed with methanol.

N-cyano-2-imino-8-methoxy-2H-chromene-3-carboxamidine (**12**)

Yellow solid, IR Spectrum (ν : cm^{-1}): 1597 (C=C), 1620/1660 (C=N), 2211 ($\text{C}\equiv\text{N}$), 3312/3342/3438 (NH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, *J*: Hz): 3.89 (s, 3H, OCH_3), 7.18-7.34 (m, 3H, H_5 , H_6 , H_7), 8.52 (s, 1H, H_4), 9.04 (s, 1H, NH), 9.20 (s, 1H, NH), 10.88 (s, 1H, NH). Calculated for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$: %C 59.50, %H 4.16, %N 23.13. Found: %C 59.43, %H 4.21, %N 23.17.

***N*-cyano-7-(diethylamino)-2-imino-2H-chromene-3-carboxamidine (13)**

Orange-brown solid, IR Spectrum (ν : cm^{-1}): 1582 (C=C), 1623/1657 (C=N), 2213 ($\text{C}\equiv\text{N}$), 3311/3332/ 3344 (NH). ^1H NMR Spectrum (300 MHz, DMSO), (δ : ppm, J : Hz): 1.10 (t, $^3J = 7.2$ Hz, 6H, CH_3), $\delta = 3.43$ (q, $^3J = 7.2$ Hz, 4H, CH_2), 6.26 (s, 1H, H_8), 6.63 (d, $^3J = 8.7$ Hz, 1H, H_6), 7.34 (d, $^3J = 8.7$ Hz, 1H, H_5), 8.16 (s, 1H, H_4) 8.43 (s, 1H, NH), 8.62 (s, 1H, NH), 9.86 (s, 1H, NH). Calculated for $\text{C}_{15}\text{H}_{17}\text{N}_5\text{O}$: %C 63.60, %H 6.00, %N 24.72. Found: %C 63.67, %H 5.92, %N 24.67.

***N*-cyano-2-imino-7-methoxy-2H-chromene-3-carboxamidine (14)**

Yellow solid, IR Spectrum (ν : cm^{-1}): 1584 (C=C), 1621/1662 (C=N), 2220 ($\text{C}\equiv\text{N}$), 3300/3324/3392 (NH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, J : Hz): 3.84 (s, 3H, OCH_3), 6.74 (s, 1H, H_8), 6.92 (d, $^3J = 8.4$ Hz, 1H, H_6), 7.64 (d, $^3J = 8.4$ Hz, 1H, H_5), 8.58 (s, 1H, H_4). 8.83 (s, 1H, NH), 9.07 (s, 1H, NH), 10.60 (s, 1H, NH). Calculated for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$: %C 59.50, %H 4.16, %N 23.13. Found: %C 59.57, %H 4.07, %N 23.09.

***N*-cyano-2-imino-6-methoxy-2H-chromene-3-carboxamidine (15)**

15

Orange solid, IR Spectrum (ν : cm^{-1}): 1595 (C=C), 1618/1658 (C=N), 2218 ($\text{C}\equiv\text{N}$), 3304/3329/3348 (NH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, J : Hz): 3.78 (s, 3H, OCH_3), 7.16 (d, $^3J = 8.7$ Hz, 1H, H_8), 7.24 (d, $^3J = 2.1$ Hz, 1H, H_5), 7.32 (dd, $^3J = 2.1$ Hz, $^3J = 8.7$ Hz, 1H, H_7), 8.38 (s, 1H, H_4), 8.92 (s, 1H, NH), 9.13 (s, 1H, NH), 10.54 (s, 1H, NH). Calculated for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$: %C 59.50, %H 4.16, %N 23.13. Found: %C 59.45, %H 4.28, %N 23.07.

6-chloro-*N*-cyano-2-imino-2H-chromene-3-carboxamidine (16)

16

Red-brown solid, IR Spectrum (ν : cm^{-1}): 1583 (C=C), 1628/1668 (C=N), 2220 ($\text{C}\equiv\text{N}$), 3307/3322/3341 (NH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, J : Hz): 7.42 (d, $^3J = 6.9$ Hz, 1H, H_8), 7.64 (dd, $^4J = 1.8$ Hz, $^3J = 6.9$ Hz, 1H, H_7), 7.73 (d, $^4J = 1.8$ Hz, 1H, H_5), 8.34 (s, 1H, H_4), 9.05 (s, 1H, NH), 9.23 (s, 1H, NH), 10.89 (s, 1H, NH). Calculated for $\text{C}_{11}\text{H}_7\text{ClN}_4\text{O}$: %C 53.55, %H 2.84, %N 22.71. Found: %C 53.61, %H 2.80, %N 22.78.

***N*-cyano-7-hydroxy-2-imino-2H-chromene-3-carboxamidine (17)**

17

Yellow solid, IR Spectrum (ν : cm^{-1}): 1586 (C=C), 1632/1672 (C=N), 2211 ($\text{C}\equiv\text{N}$), 3312/3332 (NH), 3428 (OH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, J : Hz): 6.56 (s, 1H, H_8), 6.69 (d, $^3J = 7.2$ Hz, 1H, H_6), 7.43 (d, $^3J = 7.2$ Hz, 1H, H_5), 8.29 (s, 1H, H_4), 8.64 (s, 1H, NH), 8.83 (s, 1H, NH), 9.34 (s, 1H, OH) 9.74 (s, 1H, NH). Calculated for $\text{C}_{11}\text{H}_8\text{N}_4\text{O}_2$: %C 57.89, %H 3.53, %N 24.55. Found: %C 57.82, %H 3.60, %N 24.45.

***N*-cyano-2-imino-5,6-phenyl-2H-chromene-3-carboxamidine (18)**

18

Orange-brown solid, IR Spectrum (ν : cm^{-1}): 1596 (C=C), 1625/1671(C=N), 2219 ($\text{C}\equiv\text{N}$), 3310/3334/3378 (NH). ^1H NMR Spectrum (300 MHz, DMSO), (δ : ppm, J : Hz): 7.58 (d, $^3J = 8.2$ Hz, 1H, H_8), 7.72-8.62 (m, 5H, H_7 , H_{Ar}), 8.98 (s, 1H, H_4), 9.13 (s, 1H, NH), 9.25 (s, 1H, NH), 10.80 (s, 1H, NH). Calculated for $\text{C}_{15}\text{H}_{10}\text{N}_4\text{O}$: %C 68.70, %H 3.82, %N 21.37. Found: %C 68.95, %H 3.75, %N 21.29.

General procedure for the synthesis of benzopyrano[2,3-d]pyrimidines 19-22

A mixture of 3-cyano-N-ethoxycarbonyl iminocoumarins **8-11** (0.05 mol) and cyanamide (0.05 mol) in 30 ml of absolute methanol was refluxed during the time indicated in Table 2. The precipitate was filtered and washed with methanol.

***N*-cyano-8-diethylamino-4-imino-2-oxo-2H-Benzopyrano[2,3-d]pyrimidine (19)**

Pink solid, IR Spectrum (ν : cm^{-1}): 1531 (C=C), 1618/1647 (C=N), 1709 (C=O), 2189 (C $\equiv$ N), 3130 (NH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, J : Hz): 1.20 (t, $^3J = 6$ Hz, 6H, CH₃), 3.61 (q, $^3J = 6$ Hz, 4H, CH₂), 6.86 (d, $^4J = 3$ Hz, 1H, H₉), 7.03 (dd, $^4J = 3$ Hz, $^3J = 9.3$ Hz, 1H, H₇), 7.79 (d, $^3J = 9$ Hz, 1H, H₆), 8.86 (s, 1H, H₅), 11.58 (s, 1H, NH). ^{13}C NMR Spectrum (75MHz, DMSO), (δ : ppm): 12.88, 45.59, 97.16, 102.72, 111.17, 113.39, 115.31, 133.92, 143.25, 155.54, 155.87, 157.88, 160.50, 167.36. Calculated for C₁₆H₁₅N₅O₂ : %C 62.13, %H 4.85, %N 22.65. Found: %C 62.19, %H 4.96, %N 22.55. The mass spectrum was m/z 310.4 [(M+H)⁺].

***N*-cyano-8-methoxy-4-imino-2-oxo-2H-Benzopyrano[2,3-d]pyrimidine (20)**

Pink solid, IR Spectrum (ν : cm^{-1}): 1530 (C=C), 1617/1643 (C=N), 1703 (C=O), 2211 (C $\equiv$ N), 3223 (NH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, J : Hz): 3.32 (s, 3H, OCH₃), 6.70 (d, 4J = 2.4 Hz, 1H, H₉), 6.94 (dd, 4J = 2.4 Hz, 3J = 9.3 Hz, 1H, H₇), 7.74 (d, 3J = 9.3 Hz, 1H, H₆), 8.62 (s, 1H, H₅), 11.13 (s, 1H, NH). ^{13}C NMR Spectrum (75MHz, DMSO), (δ : ppm): 55.90, 98.13, 104.20, 109.23, 110.89, 117.12, 126.92, 132.25, 158.24, 160.17, 160.88, 161.50, 166.86. Calculated for C₁₃H₈N₄O₃ : %C 58.21, %H 3.01, %N 20.89. Found: %C 58.14, %H 3.09, %N 20.84.

***N*-cyano-7- methoxy-4-imino-2-oxo-2H-Benzopyrano[2,3-*d*]pyrimidine (21)**

Pink solid, IR Spectrum (ν : cm^{-1}): 1532 (C=C), 1623/1638 (C=N), 1708 (C=O), 2179 (C $\equiv$ N), 3200 (NH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, J : Hz): 3.58 (s, 3H, OCH₃), 6.82 (d, 3J = 7.4 Hz, 1H, H₉), 7.08 (s, 1H, H₆), 7.72 (d, 3J = 7.4 Hz, 1H, H₈), 8.62 (s, 1H, H₅), 10.98 (s, 1H, NH). ^{13}C NMR Spectrum (75MHz, DMSO), (δ : ppm): 55.30, 104.92, 109.22, 111.64, 114.13, 115.17, 115.31, 139.05, 155.29, 156.11, 159.11, 161.23, 166.69. Calculated for C₁₃H₈N₄O₃ : %C 58.21, %H 3.01, %N 20.89. Found: %C 58.28, %H 3.07, %N 20.79.

***N*-cyano-9- methoxy-4-imino-2-oxo-2H-Benzopyrano[2,3-*d*]pyrimidine (22)**

Pink solid, IR Spectrum (ν : cm^{-1}): 1528 (C=C), 1613/1645 (C=N), 1693 (C=O), 2189 (C $\equiv$ N), 3134 (NH). ^1H NMR Spectrum (300MHz, DMSO), (δ : ppm, J : Hz): 3.82 (s, 3H, OCH₃), 7.68-7.83 (m, 3H, H₆, H₇, H₈), 8.68 (s, 1H, H₅), 11.62 (s, 1H, NH). ^{13}C NMR Spectrum(75MHz, DMSO), (δ : ppm): 59.98, 102.22, 112.27, 115.21, 118.23, 122.11, 125.69, 142.76, 149.09, 152.56, 158.01, 159.55, 165.89. Calculated for C₁₃H₈N₄O₃ : %C 58.21, %H 3.01, %N 20.89. Found: %C 58.15, %H 2.91, %N 20.96.

II. Selected of IR, ^1H NMR, ^{13}C NMR and MS spectra