Green approach for the synthesis of pyranopyrazoles and hexahydroquinoline-3-carboxamides using unripe grape juice (verjuice) as catalyst

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Spectral data of the new product

*6-Amino-4-isopropyl-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (**5k**)*

Yellow solid,m.p = 229-230;FT-IR (KBr): υ = 3296, 3272 (NH_2 stretch), 2956 (N-H stretch), 2869 (aromatic C-H stretch), 2235 (CN stretch), 1602 (aromatic C=C stretch), 1145 (C-O stretch), 752 (C-H out of plane bending) cm^{-1};^{1}H NMR (400 MHz, DMSO-d_6): δ =0.76 (d, 3H,*J* = 6.4), 0.82 (d, 3H,*J* = 6.8), 1.78-1.86 (m, 1H), 2.17 (s, 3H), 3.38 (d, *J* = 3.2, CH), 6.82 (s, 2H, NH_2), 12.05 (s, 1H, NH) ppm; ^{13}C NMR (100 MHz, DMSO-d6): δ = 10.94, 18.97, 18.99, 37, 39.33, 39.54, 40.37, 53.75, 97.43, 122.47, 135.16, 156.87, 163.52 ppm; Anal. Calcd. for $C_{11}H_{14}N_4O$: C, 60.54; H, 6.47, N, 25.67. Found: C, 60.42; H, 6.38, N, 25.58.

4-(2-Chlorophenyl)-2,7,7-trimethyl-5-oxo-N-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbox amide (**5n**)

White solid, m.p = 225-227 °C; FT-IR (KBr) cm^{-1}: ν = 3265 (N-H stretch), 2956 (aliphatic C-H stretch), 1677 (C=O), 1645 (C=O), 1498 (C=C stretch), 752 (aromatic C-H out of plane bending); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H), 1.06 (s, 3H), 1.95 (s, 3H), 1.98 (d, 1H, *J* = 16 Hz), 2.13 (d, 1H, *J* = 16 Hz), 2.32 (d, 1H, *J* = 17 Hz), 2.41 (d, 1H, *J* = 17 Hz), 5.35 (s, 1H), 6.97-7.29 (m, 7H), 7.53 (d, 2H, *J* = 7.6), 8.74 (s. 1H, NH), 9.72 (s, IH, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 27.1, 29.3, 32.6, 35.3, 41.2, 50.5, 108.6, 110.9, 120.3, 124.0, 127.7, 128.3, 128.9, 129.7, 131.0, 131.6, 138.1, 140.4, 143.5, 148.6, 165.8, 194.9. Elemental analysis: Calculated (%) for $C_{25}H_{25}ClN_2O_2$ (420.93): C, 71.33; H, 5.99, N, 6.66. Found: C, 71.13; H, 6.04, N, 6.59.

4-(3-Bromophenyl)-2,7,7-trimethyl-5-oxo-N-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbox amide (**5s**)

Yellow solid, m.p = 211–213 °C; FT-IR (KBr) cm^{-1}: ν = 3276 (N-H stretch), 3062 (aromatic C-H), 2956 (C-H stretch), 1674 (C=O stretch), 1643 (C=O stretch), 752 (aromatic C-H out of plane bending); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 2.13 (s, 1H), 2.18–2.20 (m, 1H), 2.22–2.28 (m, 2H), 2.36 (s, 3H, CH_3), 5.40 (s, 1H, CH), 6.09 (s,1H, NH), 7.08 (m, 1H, Ar), 7.11–7.15 (m, 1H, Ar), 7.21–7.25 (m, 1H, Ar), 7.28–7.27 (m, 2H, Ar), 7.31–7.35 (m, 2H, Ar), 7.45–7.48 (m, 2H, Ar), 7.61 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 27.3, 29.5, 32.5, 36.6, 50.8, 108.2, 111.6, 119.9, 120.0, 123.2, 127.5, 127.7, 128.8, 129.1, 131.2, 131.8, 133.9, 139.8, 139.9, 145.3, 151.4, 151.5, 167.3, 193.7 (C=O). Elemental analysis: Calculated (%) for $C_{25}H_{25}BrN_2O_2$ (465.38): C, 64.52, H, 5.41, N, 6.02. Found: C, 64.48, H, 5.46, N, 6.09.

4-(4-(Dimethylamino)phenyl)-2,7,7-trimethyl-5-oxo-N-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxamide (**5v**)

Orange solid; m.p = 248-250 °C; FT-IR (KBr) cm^{-1}: ν = 3269 (N-H stretch), 3066 (aromatic C-H), 2952 (C-H stretch), 1674 (C=O stretch), 1637 (C=O stretch), 754 (aromatic C-H out of plane bending); ^{1}H NMR: δ 0.87 (s, 3H), 1.03 (s, 3H), 2.11–2.26 (m, 4H), 2.37 (s, 3H), 2.39 (s, 6H), 4.82 (s, 1H), 6.72 (d, 2H, J = 8 Hz), 7.04 (m, 1H), 7.23–7.34 (m, 4H), 7.36 (d, 2H, J = 4 Hz), 7.52 (s, 1H, NH), 9.72 (s, 1H, NHCO); ^{13}C NMR: δ 18.0, 27.2, 29.2, 32.5, 37.0, 40.1, 40.5, 50.7, 76.8, 77.1, 77.4, 108.3, 111.0, 111.05, 112.9, 119.8, 123.8, 128.7, 128.8, 133.6, 138.3, 141.3, 149.1, 167.0, 195.0 (C=O). Elemental analysis: Calculated (%) for $C_{27}H_{31}N_3O_2$ (429.55) C, 75.50; H, 7.27, N, 9.78. Found: C, 75.33; H, 7.35, N, 9.69.

4-Isopropyl-2,7,7-trimethyl-5-oxo-N-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxamide (**5w**)

Yellow solid,m.p. = 234-236°C; FT-IR (KBr) cm^{-1}: ν = 3296 (N-H stretch), 2956 (aliphatic C-H stretch), 1664 (C=O), 1637 (C=O), 1490 (C=C stretch), 752 (aromatic C-H out of plane bending); ^{1}H NMR (400 MHz, $CDCl_3$):δ0.74 (d, 3H, J = 4.4 Hz), 0.758 (d, 3H, J = 4.4 Hz), 1.05 (s, 6H), 1.62-1.66 (m, 1H), 2.01 (s, 3H), 2.07 (d, 1H, J = 16 Hz), 2.16 (d, 1H, J = 16 Hz), 2.22 (d, 1H, J = 16.8 Hz), 2.33 (d, 1H, J = 16.8 Hz), 3.81 (d, J = 2.8 Hz), 7.00 (t, 1H, J = 6.4 Hz), 7.26 (t, 2H, J = 8 Hz), 7.62 (d, 2H, J = 8 Hz), 8.48 (s, 1H, NH), 9.62 (s, 1H, NHCO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.3, 18.2, 197, 27.01, 30.1, 32.3, 35.3, 38.2, 51.2, 107.1, 109.0, 120.1, 123.3, 128.9, 136.2, 140.1, 152.1, 169.7, 194.6 (C=O). Elemental analysis: Calculated (%) for $C_{22}H_{27}N_2O_2$ (351.46) C, 75.18; H, 7.74, N, 7.97. Found: C, 75.06; H, 7.85, N, 8.05.