Nucleophilic heterocyclic carbene catalyzed solvent-free one-pot synthesis of polyhydroquinolines via multi-component Hantzsch reaction: an efficient and ecofriendly approach

Shahin Fatma, Preyas Ankit, Mandavi Singh, Shyam Babu Singh, Jagdamba Singh*

Environmentally Benign Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad-211002, India.

* Corresponding author.

e-mail: dr.jdsau@gmail.com

SUPPLEMENTARY DATA

Experimental

All chemicals used were of reagent grade and were used as received without further purification. All m.p. were taken in open capillary tubes and are uncorrected. The structural assignments of the synthesized products were based on elemental analysis carried out using a Coleman automatic carbon, hydrogen, and nitrogen analyzer, NMR spectra were obtained on a Bruker DRX-300 (300 MHz FTNMR) spectrometer (^1H NMR at 300 MHz, ^{13}C NMR at 75 MHz) with CDCl_3 using TMS as internal standard and mass spectra were recorded on a JEOL D-300 mass spectrometer at 70 eV.

Spectral Data

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(phenyl)-5-(6H)-oxoquinolin-3-carboxylate (4a). Mp 262-228°C (lit mp 228-229 °C)³⁶. IR (KBr): 3294, 3212, 3072, 1699, 1622, 1087, 690; ^1H NMR (CDCl_3 , 300 MHz): δ = 0.96 (s, 3H), 1.11 (s, 3H), 1.28 (t, J = 7.00 Hz, 3H), 2.06 – 2.09 (m, 4H), 2.48 (s, 3H), 4.11 (q, J = 6.8 Hz, 2H), 4.98 (s, 1H), 6.49 (br s, 1H), 7.31-7.51 (m, 5H); MS: m/z = 340 (M + H)⁺. Anal. Calcd. For $\text{C}_{21}\text{H}_{25}\text{NO}_3$; C, 74.31; H, 7.42; N, 4.13. Found; C, 74.39; H, 7.46; N, 4.17%.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(4-methoxyphenyl)-5-(6H)-oxoquinolin-3-carboxylate (4b). Mp 259-261°C (lit mp 260-262°C)³⁶. IR (KBr): 3281, 3211, 3082, 1707, 1612, 1215, 838 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 0.94 (s, 3H), 1.06 (s, 3H), 1.23 (t, J = 6.8 Hz, 3H), 2.11-2.32 (m, 4H), 2.35 (s, 3H), 3.72 (s, 3H), 4.05 (q, J = 6.9 Hz), 4.98 (s, 1H), 6.41 (br s, 1H), 6.72 (d, J = 8.4, 2H), 7.19 (d, J = 8.4Hz, 2H); MS: m/z = 370 (M + H)⁺. Anal. Calcd. For $\text{C}_{22}\text{H}_{27}\text{NO}_4$; C, 71.52; H, 7.37; N, 3.79. Found; C, 71.44; H, 7.41; N, 3.783%.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(4-chlorophenyl)-5-(6H)-oxoquinolin-3-carboxylate (4c)

Mp 243-245°C (lit. mp 245-246°C). IR (KBr): 3292, 3207, 3076, 1707, 1610, 1076, 838 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 0.93 (s, 3H), 1.05 (s, 3H), 1.26 (t, J = 6.8 Hz, 3H), 2.08 - 2.28 (m, 4H), 2.37 (s, 3H), 4.10 (q, J = 6.7 Hz, 2H), 4.99 (s, 1H), 6.42 (br s, 1H), 7.03 (d, J =

8.2Hz, 2H), 7.33 (d, J = 8.2Hz, 2H); MS: m/z = 374 (M + H)⁺. Anal. Calcd. For C₂₁H₂₄ClNO₃; C, 67.46; H, 6.47; N, 3.75. Found; C, 65.53; H, 6.51; N, 3.79%.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(4-methylphenyl)-5-(6H)-oxoquinolin-3-carboxylate

(4d). Mp 263-265°C (lit mp 265-266°C)³⁶. IR (KBr): 3282, 3197, 3076, 1694, 1604, 1215, 1063 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ = 0.92 (s, 3H), 1.07 (s, 3H), 1.22 (t, J = 7.00 Hz, 3H), 2.10(s, 3H), 2.22 - 2.42 (m, 4H), 2.40 (s, 3H), 4.06 (q, 2H, J = 7.00 Hz), 4.99 (s, 1H), 6.42 (br s, 1H), 7.00 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H); MS: m/z = 354 (M + H)⁺. Anal. Calcd. For C₂₂H₂₇NO₅; C, 71.76; H, 7.70; N, 3.96. Found; C, 71.68; H, 7.74; N, 4.00%.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(3-nitrophenyl)-5-(6H)-oxoquinolin-3-carboxylate (4e)

Mp 183-185°C (lit mp 182-184°C)³⁶ IR (KBr): 3299, 2958, 1687, 1610, 1164, 757 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) : δ = 0.92 (s, 3H), 1.05 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H), 2.10 - 2.31 (m, 4H), 2.36 (s, 3H), 4.06 (q, J = 6.8 Hz, 2H), 4.95 (s, 1H), 6.36 (br s, 1H), 6.70 (d, J = 8.4Hz, 1H), 7.02 - 7.15 (m, 2H), 7.38 (d, J = 8.4Hz, 1H); MS: m/z = 385 (M + H)⁺. Anal. Calcd. For C₂₁H₂₄N₂O₅; C, 65.61; H, 6.29; N, 7.29. Found; C, 65.53; H, 7.56; N, 7.33%.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(2-chlororophenyl)-5-(6H)-oxoquinolin-3-carboxylate

(4f). Mp 206-208°C (lit mp 208-209°C)³⁶ IR (KBr): 3282, 3199, 3077, 1698, 1600, 1218, 755 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ = 0.91 (s, 3H), 1.05 (s, 3H), 1.23 (t, J = 6.9 Hz, 3H), 2.12 (s, 3H), 2.24 (m, 4H), 4.02 (q, J = 6.9 Hz, 2H), 4.89 (s, 1H), 6.38 (br s, 1H), 7.03 - 7.22 (m, 4H); MS: m/z = 374.14 (M + H)⁺. Anal. Calcd. For C₂₁H₂₄ClNO₃; C, 67.46; H, 6.47; N, 3.75. Found; C, 67.38; H, 6.51; N, 3.79 %.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(3,4-dimethoxyphenyl)-5-(6H)-oxoquinolin-3-

carboxylate (4g). Mp 287-289°C (lit mp 288-290°C)³⁶ IR (KBr): 3280, 3201, 3074, 1693, 1614, 1018, 732 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ = 0.92 (s, 3H), 1.38 (s, 3H), 1.24 (t, J = 7.00 Hz, 3H), 2.10- 2.30 (m, 4H), 2.35 (s, 3H), 3.82 (s, 3H), 3.86 (s, 3H), 4.10 (q, J = 8.4Hz, 2H), 5.00 (s, 1H), 6.36 (br s, 1H), 6.38 (d, J = 8.3Hz), 6.76 (d, J = 8.3Hz), 6.92 (s, 1H); MS: m/z = 400 (M + H)⁺. Anal. Calcd. For C₂₃H₂₃NO₅; C, 69.15; H, 7.52; N, 3.51. Found; C, 69.07; H, 7.56; N, 3.55 %.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(4-hydroxy,3-methoxyphenyl)-5-(6H)-oxoquinolin-3-

carboxylate (4h). Mp 201-203°C(lit mp 200-202°C)³⁵. IR (KBr): 3392, 3291, 3081, 1698, 1613, 1020, 735 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ = 0.92 (s, 3H), 1.02 (s, 3H), 1.21 (t, J = 6.8 Hz, 3H), 2.12 - 2.37 (m, 4H), 2.39 (s, 3H), 3.68 (s, 3H), 4.04 (q, J = 6.8 Hz), 4.98 (s, 1H), 5.37 (br s, 1H), 6.40 (br s, 1H), 6.72 - 6.70 (m, 2H), 7.02 (d, J = 8.2Hz, 1H); MS: m/z = 386 (M + H)⁺. Anal. Calcd. For C₂₂H₂₇NO₅; C, 68.55 ;H, 7.06 ;N, 3.63 ;. Found; C, 68.47; H, 7.10; N, 3.67 %.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(2,4-dichlorophenyl)-5-(6H)-oxoquinolin-3-carboxylate

(4i).Mp 213-214°C (lit mp 216-218°C)³⁶ Solid; IR (KBr): 3291, 3203, 3088, 1702, 1605, 1100, 859 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ = 0.93 (s, 3H), 1.04 (s, 3H), 1.23 (t, J = 6.8 Hz, 3H), 2.36 - 2.60 (m, 4H), 2.93 (s, 3H), 4.09 (q, J = 6.8 Hz, 2H), 4.83 (s, 1H), 6.36 (br s,

1H), 7.69-7.73 (m, 2H), 7.82 (d, J = 8.4Hz, 1H); MS: m/z = 408.11 (M + H)⁺. Anal. Calcd. For C₂₁H₂₃Cl₂NO₃; C, 61.77 ;H, 5.68 ;N, 3.43 ;. Found; C, 61.69; H, 5.72; N, 3.47 %.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(hexanyl)-5-(6H)-oxoquinolin-3-carboxylate (4j). Mp 234- 236°C. IR (KBr): 3279, 3194, 3087, 1690, 1597, 1027, 912 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ = 0.86 (s, 3H), 1.12(s, 3H) 1.15 (t, 3H, J = 7.5 Hz), 1.21 - 1.6 (m, 11H), 2.11 (s, 3H), 2.23 - 2.40 (m, 2H), 4.01 (q, 2H, J = 7.5 Hz), 4.22 (s, 1H), 6.33 (br s, 1H); MS: m/z = 346.23 (M + H)⁺. Anal. Calcd. For C₂₁H₃₁NO₃; C, 73.01 ;H, 9.04 ;N, 4.05. Found; C, 72.93; H, 9.08; N, 4.09 %.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(4 sec butyl)-5-(6H)-oxoquinolin-3-carboxylate (4k).

Mp 244-246 °C. IR (KBr): 3284, 3193, 3083, 1699, 1594, 1032, 920 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ = 0.84 (s, 3H), 1.08(s, 3H), 1.15 (t, 3H, J = 7.5 Hz), 1.21 - 1.9 (m, 11H), 2.11 (s, 3H), 2.20 - 2.50 (m, 2H), 4.09 (q, 2H, J = 7.5 Hz), 4.27 (s, 1H), 6.36 (br s, 1H); MS: m/z = 319.21 (M + H)⁺. Anal. Calcd. For C₁₉H₂₉NO₃; C, 71.44 ;H, 9.15 ;N, 4.38 ;. Found; C, 71.36; H, 9.19; N, 4.42%.

Ethyl-1,4,7,8-tetrahydro-2,7,7,4-(4 ethyl)-5-(6H)-oxoquinolin-3-carboxylate (4l).

Mp 145-146 °C. IR (KBr): 3288, 3198, 3089, 1689, 1598, 1030, 929 cm⁻¹. ¹H NMR(300 MHz, CDCl₃): δ 0.78 (t, J = 7.5 Hz, 3H), 0.89 (s, 3H), 1.16 (s, 3H), 1.32 (q, J = 7.1 Hz, 2H), 1.40–1.49 (m, 2H), 2.18 (d, J = 7.2 Hz, 1H), 2.30 (d, J = 3.1 Hz, 2H), 2.33 (t, J = 7.5 Hz, 4H), 4.12 (t, J = 5.1 Hz, 1H), 4.19–4.23 (m, 2H), 5.57 (s, 1H). MS: m/z = 292.18 (M + H)⁺. Anal. Calcd. For C₁₇H₂₅NO₃; C, 70.07 ;H, 8.65 ;N, 4.81 ;. Found; C, 69.99; H, 8.69; N, 4.85 %.