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5-Pyrrolidin-2-yltetrazole promoted one-pot Hantzsch polyhydroquinoline synthesis using NH_4HCO_3 as Nitrogen-source

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Accessory Publication

Contents:

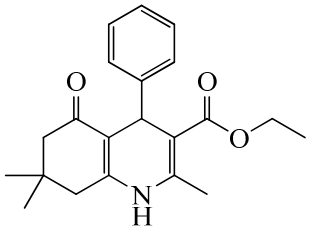
1. General Experimental Details

Melting points were obtained with a capillary melting point apparatus and uncorrected. Infrared spectra were recorded on a Thermo Nicolet Avatar 370 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at Varain–400 and Bruker Avance DRX–500 using $CDCl_3$ or DMSO as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. Mass spectra were obtained on a Trace DSQ mass spectrometer. Elemental analysis was performed on a VarioEL-3 instrument. 5-(Pyrrolidine-2-yl)tetrazole used in this work were prepa-red according to previously published work[15i], $[\alpha]_D^{25}$ -9.0 (c = 0.65, MeOH), ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 4.78 (m, 1H), 3.30 (m, 2H), 2.36 (m, 1H), 1.98-2.20(m, 3H); 13C NMR (100 MHz, DMSO-d6): δ = 157.74, 54.97, 44.64, 29.94, 23.17; MS (EI) m/z (%) = 70 (M^+, 100), 139 (20).

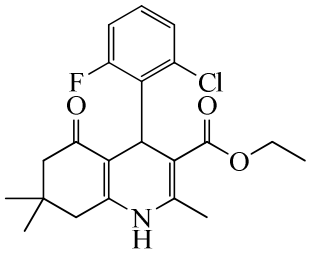
General procedure for the synthesis of 1,4-Dihydropyridines under solvent free conditions:

To a mixture of aldehyde (2 mmol), dimedone (2 mmol), ß-ketoesters (2 mmol) and ammonium bicarbona (2.4 mmol) was added 5-Pyrrolidine-2-yltetrazole (0.04 mmol) and the mixture was stirred at room temperature for the given time monitored by TLC. After the completion of the reaction, ethyl acetate (20 mL) was added and washed with brine and dried over sodium sulfate. After concentrated in vaccum, a crude solid was obtained. The pure product was obtained through crystallization from ethanol.

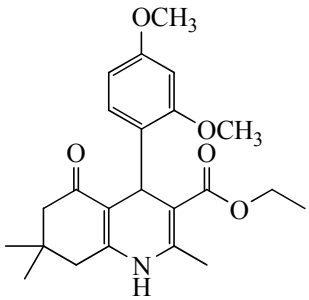
2. Experimental characterisation data for compounds



ethyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Aα)
Mp 203–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J*= 7.6 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 5.05 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 2.32-2.12 (m, 7H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.05 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 167.6, 149.1, 147.2, 143.8, 128.0, 127.9, 126.0, 111.9, 106.0, 59.8, 50.8, 40.8, 36.6, 32.7, 29.5, 27.1, 19.2, 14.2; MS (ESI): m/z (%) = 338.2 (M^+-1, 100); IR (KBr) : ν_{max}= 3288, 3078, 2962, 1698, 1610 cm^{-1}.

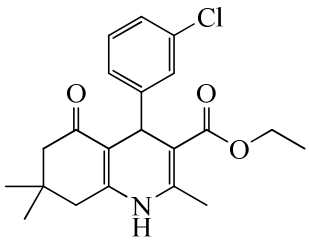


ethyl 4-(2-chloro-6-fluorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Bα)
Mp 250-253 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.05(m, 2H), 6.87 (t, 1H), 6.44 (s, 1H), 5.64 (s, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 2.08-2.29 (m, 7H), 1.14 (t, *J* = 7.2 Hz, 3H), 1.06 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 167.5, 150.2, 145.3, 135.3, 135.3, 130.9, 130.7, 127.5, 127.4, 125.7, 114.0, 113.7, 108.7, 102.1, 59.7, 50.6, 40. 8, 32.3, 31.2, 29.6, 29.3, 27.1, 19.2, 14.3; MS (ESI): m/z (%) = 392.5 (M^++1, 100), 394.5 (M^++3, 37); IR (KBr): ν_{max} = 3288, 3212, 3088, 2956, 1692, 1612 cm^{-1}. Anal. Calcd for $C_{21}H_{23}NO_3$: C, 64.37; H, 5.92; N, 3.57. Found: C, 64.30; H, 6.05; N, 3.54.



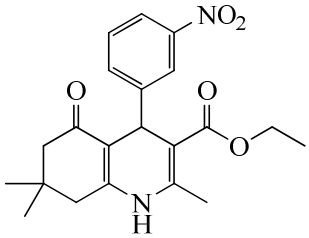
ethyl 4-(2,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Cα)
Mp 237–238 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (t, *J* = 4.0 Hz, 1H), 6.65 (s, 1H), 6.34 (m, 2H), 5.16 (s, 1H), 4.03 (q, *J* = 8.0 Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 2.26-2.06 (m, 7H), 1.19 (t, *J*

= 8.0 Hz, 3H), 1.04 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 168.1, 159.1, 158.5, 149.1, 143.2, 131.6, 127.5, 110.7, 105.1, 103.9, 98.4, 59.5, 55.3, 55.2, 50.8, 41.0, 33.0, 32.5, 29.6, 26.8, 19.1, 14.2; MS (ESI): m/z (%) = 399.2 (M^+, 25), 398.1 (M^+-1, 100); IR (KBr): ν_{max} = 3290, 3082, 2953, 2835, 1694, 1648, 1605 cm^{-1}. Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.32; N, 3.51. Found: C, 69.24; H, 7.28; N, 3.34.



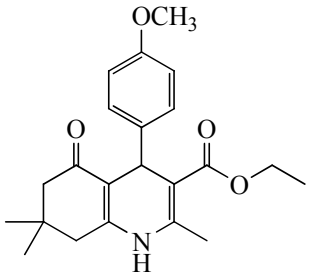
ethyl 4-(3-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Dα)

Mp 206–207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24 (m, 2H), 7.10 (m, 2H), 6.27 (s, 1H), 5.03 (s, 1H), 4.07 (m, 2H), 2.36-2.14 (m, 7H), 1.20 (t, *J* = 7.0 Hz, 3H), 1.08 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 167.2, 149.0, 148.5, 143.9, 133.7, 129.1, 128.1, 126.5, 126.2, 111.6, 105.6, 59.9, 50.7, 41.1, 36.6, 32.7, 29.4, 27.2, 19.4, 14.2; MS (ESI): m/z (%) = 372.2 (M^+-1, 100), 374.1(M^++1, 34); IR (KBr): ν_{max} = 3275, 3210, 3078, 2958, 1705, 1605 cm^{-1} ; Anal. Calcd for $C_{21}H_{24}ClNO_3$: C, 67.46; H, 6.47; N, 3.75. Found: C, 67.52; H, 6.55; N, 3.70.



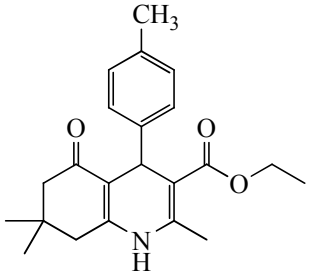
ethyl 2,7,7-trimethyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Eα)

Mp 177–178 °C; ^{1}H NMR (400 MHz, CDCl3): δ = 8.11 (s, 1H), 7.98 (m, 1H), 7.73 (d, *J* = 8.0Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 5.16 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 2H), 2.41(s, 3H), 2.13-40 (m, 4H), 1.20 (t, J = 7.2 Hz, 3H), 1.09 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl3): δ = 195.4, 166.9, 149.2, 148.8, 148.3, 144.4, 134.8, 128.5, 122.8, 121.3, 111.2, 105.1, 60.0, 50.5, 40.9, 36.9, 32.7, 28.3, 27.1, 19.4, 14.1; MS (ESI): m/z (%) = 385.2 (M^++1, 100); IR (KBr): ν_{max} = 3284, 3210, 3078, 2956, 1704, 1603 cm^{-1}.



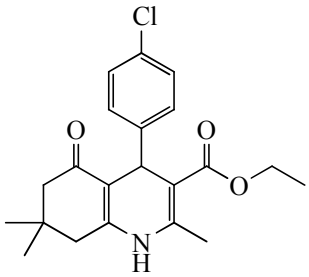
ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Fα)

Mp 256-258 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (t, 2H), 6.77 (s, 1H), 6.73 (t, 2H), 4.99 (s, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.72 (s, 3H), 2.33(s, 3H), 2.11-2.28 (m, 4H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.05 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 167.6, 157.8, 148. 8, 143.5, 139.7, 129.0, 113.2, 112.1, 106.21 59. 8, 55.1, 50.8, 40.8, 35.7, 32.64 28.5, 27.1, 19.2, 14.3; MS (ESI): m/z (%) = 368.2 (M^+-1, 100); IR (KBr): ν_{max} = 3279, 3209, 3079, 2958, 1701, 1648, 1606 cm^{-1}.



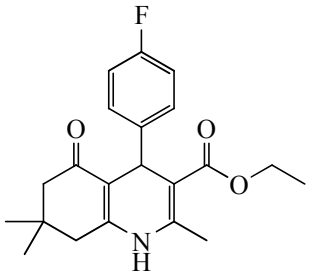
ethyl 2,7,7-trimethyl-5-oxo-4-p-tolyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Gα)

Mp 260–261 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 4.99 (s, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.72 (s, 3H), 2.34 (s, 3H), 2.28-2.12 (m, 4H), 1.21(t, *J* = 7.0 Hz, 3H), 1.05 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.8, 167.6, 157.7, 148.6, 143.4, 139.7, 128.9, 113.2, 112.1, 106.2, 59.8, 55.1, 50.8, 40.8, 35.7, 32.6, 29. 5, 27.1, 19.3, 14.2; MS (ESI):m/z (%) = 392.2 ($M+K^+$, 100); IR (KBr): ν_{max} = 3276, 3078, 2962, 1701, 1648cm^{-1}.



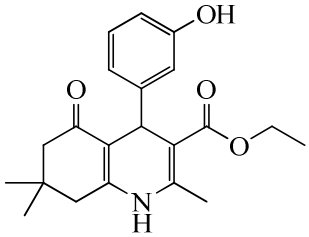
ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Hα)

Mp 242–243 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.24 (s, 1H), 5.02 (s, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.34-2.12 (m, 4H), 1.91 (t, *J* = 7.2 Hz, 3H), 1.07 (s, 3H), 0.92(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.7, 167.3, 148.9, 145.7, 143.9, 131.6, 129.4, 128.0, 111.6, 105.7, 59.9, 50.7, 40.9, 36.3, 32.7, 29. 5, 27.1, 19.3, 14.2; MS (ESI): m/z (%) = 372.3(M^+-1, 100), 374.3(M^++1, 36); IR (KBr): ν_{max} = 3277, 3209, 3079, 2960, 1706, 1648 cm^{-1}.



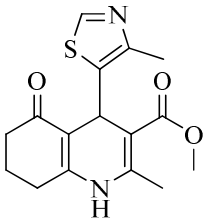
ethyl 4-(4-fluorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Iα)

Mp 185–186 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.09(s, 1H), 7.17 (m, 2H), 7.00 (m, 2H), 4.85 (s, 1H), 3.97 (q, *J* = 7.0 Hz, 2H), 2.51-1.96 (m, 7H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.00 (s, 3H), 0.83 (s, 3H).; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 194.7, 167.2, 161.8, 159.9, 149.9, 145. 7, 144.3, 144.3, 129.6, 114. 9, 114.7, 110.4, 103.9, 59.5, 50.7, 35.8, 32.6, 29.6, 26.9, 18.8, 14.6; MS (ESI): m/z (%) = 380.2 ($M+Na^+$, 100); IR (KBr): ν_{max} = 3279, 3211, 3072, 2953, 1700, 1604 cm^{-1}.



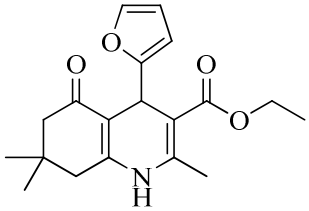
ethyl 4-(3-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carb-oxylate (5Jα)

Mp 229–230 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.09 (s, 1H), 9.03 (s, 1H), 6.95 (t, 1H), 6.59 (t, 2H), 6.45 (m, 1H), 4.79 (s, 1H), 3.99 (q, *J* = 7.0 Hz, 2H), 2.51-1.98 (m, 7H), 1.15 (t, *J* = 7.0 Hz, 3H), 1.01 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 194.7, 167.4, 157.3, 149.9, 149.4, 145.2, 129.0, 118.6, 115.0, 113.1, 110.4, 104.1, 59.5, 56.5, 50.8, 36.1, 32.6, 29.6, 27.0, 19.0, 14.6; MS (ESI): m/z (%) = 354.3(M^+-1, 100); Anal. Calcd for $C_{21}H_{25}NO_4$: C, 70.96; H, 7.09; N, 3.94. Found: C, 71.08; H, 7.18; N, 3.99.



methyl 2-methyl-4-(4-methylthiazol-5-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbo-xylate (5Lβ)

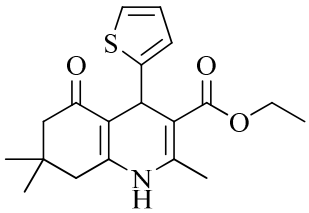
Mp 246–248 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.47 (s, 1H), 7.14 (s, 1H), 5.4 (s, 1H), 3.66 (s, 3H), 2.60-2.28 (m, 10H), 2.03-1.90 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 199.7, 172.1, 156.3, 155.2, 152.0, 150.4, 144.9, 116.2, 108.4, 56.1, 41.8, 33.8, 31.2, 26.0, 23.4, 20.1; MS (ESI): m/z (%) = 319 (M^++1, 100); Anal. Calcd for $C_{16}H_{18}N_2O_3S$: C, 60.36; H, 5.70; N, 8.80. Found: C, 60.46; H, 5.77; N, 8.83.



3-butyryl-4-(furan-2-yl)-2,7,7-trimethyl-4,6,7,8-tetrahydroquinolin-5(1H)-one (5Nα)

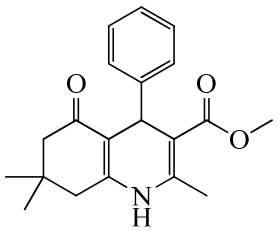
Mp 248–250 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.16 (s, 1H), 7.36 (s, 1H), 6.23 (m, 1H), 5.83 (m, 1H), 5.02 (s, 1H), 4.04 (m, 2H), 2.50-2.03(m, 7H), 1.18 (t, 3H), 1.04 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6, 167.2, 158.9, 150.9, 146.3, 141.2, 110.6, 107.1, 104.4, 101.1,

59.6, 50.7, 32.6, 30.0, 29.6, 26.8, 18.7, 14.7; MS (ESI): m/z (%) = 328.5(M^+-1, 100).



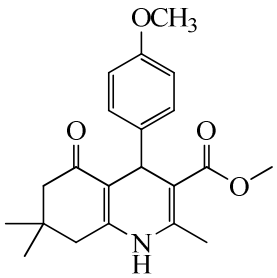
3-butyryl-2,7,7-trimethyl-4-(thiophen-2-yl)-4,6,7,8-tetrahydroquinolin-5(1H)-one (5Oα)

Mp 242–243 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (s, 1H), 7.17(d, 1H), 6.81 (t, 1H), 6.65 (d, 1H), 5.17 (s, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 2.50-2.04 (m, 7H), 1.19 (t, *J*= 7.0Hz, 3H), 1.02 (s, 3H), 0.94 (s, 3H); MS (ESI): m/z (%) = 344.5(M^+-1, 48).



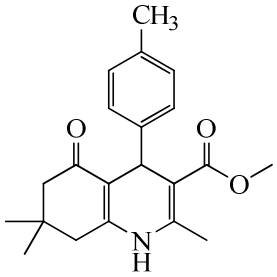
methyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Aβ)

Mp 254–256 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (m, 2H), 7.19 (t, 2H), 7.10 (t, 3H), 5.88 (s, 1H), 5.07 (s, 1H), 3.61 (s, 3H), 2.34 (s, 3H), 2.35-2.15 (m, 4H),1.08(s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 194.9, 167.8, 150.1,147.9,145.8, 128.3, 127.7, 145.8, 128.3, 127.7, 126.2, 110.5, 103.7, 51.1, 50.7, 36.1, 32.6, 29.6, 26.9, 18.8; MS (ESI):m/z (%) = 348.6 (M+Na^+, 100).



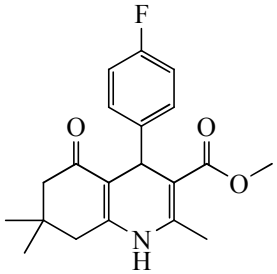
methyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Fβ)

Mp 254–256 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.05 (s, 1H), 7.03 (m, 2H), 6.74 (m, 2H), 4.80 (s, 1H), 3.67 (s, 3H), 3.52 (s, 3H), 2.51-1.96 (m, 7H), 1.00 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194. 8, 167.9, 157.8, 149.7, 145.4, 140.3, 128.7, 113.6, 110.7, 104.0, 55.3, 51.1, 50.7, 35.2, 32.6, 29.6, 26.9, 18.8; MS (ESI):m/z (%) = 354.4 (M^+-1, 100).



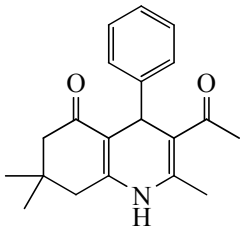
methyl 2,7,7-trimethyl-5-oxo-4-p-tolyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Gβ)

Mp 252–254 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.04 (s, 1H), 7.03 (d, 2H), 6.74 (d, 2H), 4.80 (s, 1H), 3.67 (s, 3H), 3.52 (s, 3H), 2.51-1.96 (m, 7H), 1.00 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.8, 167.9, 157.8, 149.7, 145.4, 140.3, 128. 7, 113.7, 110.7, 104.0, 55.3, 51.1, 50.7, 35.2, 32.6, 29.6, 26.9, 18.8; MS (ESI):m/z (%) = 378.2 ($M+K^+$, 100).



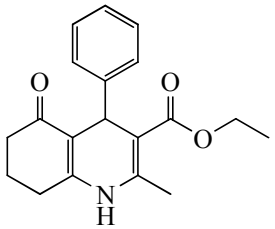
methyl 4-(4-fluorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Iβ)

Mp 235–238 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.14 (s, 1H), 7.16 (m, 2H), 7.00 (m, 2H), 4.86 (s, 1H), 3.52 (s, 3H), 2.51-1.97 (m, 7H), 1.00 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 194. 8, 167.7, 161.9, 159.9, 150.0, 146.0, 144.2, 144.1, 129.5, 129.4, 115.0, 114.8, 110.4, 103.5, 51.2, 50.6, 35.5, 32.6, 29. 6, 26.9, 18.8; MS (ESI):m/z (%) = 344.1 (M^+-1, 100); Anal. Calcd for $C_{20}H_{22}FNO_3$: C, 69.95; H, 6.46; N, 4.08. Found: C, 70.02; H, 6.53; N, 4.12.



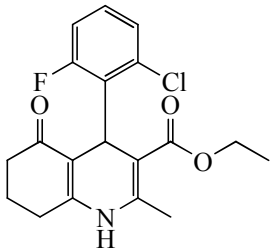
3-acetyl-2,7,7-trimethyl-4-phenyl-4,6,7,8-tetrahydroquinolin-5(1H)-one (5Aγ)

Mp 209–210 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.11 (m, 5H), 6.42 (s, 1H), 5.09 (s, 1H), 2.39 (s, 3H), 2.29-2.15 (m, 7H), 1.06 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 199.7, 195.7, 147.9, 145.7, 143.4, 128.4, 128.3, 128.2, 127.8, 126.4, 113.1, 112.7, 53.8, 50.8, 41.0, 37.1, 32.7, 29.6, 28.2, 27.0, 20.2; MS (ESI): m/z (%) = 309 (M^+-1, 100).



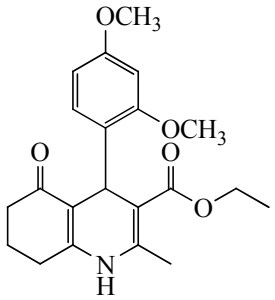
ethyl 2-methyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Aα)

Mp 240–241 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 7.30 (d, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.5Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.06 (s, 1H), 5.09 (d, 1H), 4.05 (q, *J* = 7.0 Hz, 2H), 2.44-2.30 (m, 7H), 1.95 (m, 2H), 1.18 (t, *J*= 7.0Hz, 3H). MS (ESI): m/z = 310.2 (M^++1); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 149.6, 147.1, 143.3, 128.0, 127.9, 126.0, 113.5, 106.1, 59. 8, 37.0, 36.4, 27.5, 21.0, 19.3, 14.2; MS (ESI): m/z (%) = 310.2 (M^+-1, 100).



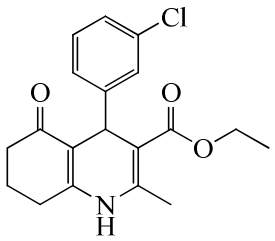
ethyl 4-(2-chloro-6-fluorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Bα)

Mp 207–208 °C; ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.08 (m, 1H), 7.03 (M, 1H), 6.95 (s, 1H), 6.87 (m, 1H), 5.65 (s, 1H), 4.04 (q, *J* = 7.2Hz, 2H), 2.36-2.23 (m, 7H), 1.92 (m, 2H), 1.14 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 167.5, 152.1, 145.2, 135.5, 131.0, 127.5, 125.8, 114.0, 109.8, 102.1, 59.7, 58.4, 39.5, 37.0, 31.3, 27.2, 23.6, 21.1, 19.1, 18.4, 14.0; Anal. Calcd for $C_{19}H_{19}ClFNO_3$: C, 62.73; H, 5.26; N, 3.85. Found: C, 62.65; H, 5.29; N, 3.78.



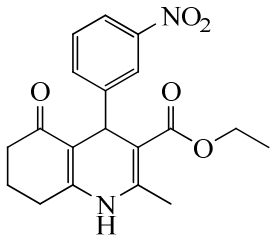
ethyl 4-(2,4-dimethoxyphenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Cα)

Mp 209–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, 1H), 6.46 (1H), 6.35 (m, 2H), 5.20 (s, 1H), 4.04 (q, *J* = 7.2Hz, 2H), 3.75 (s, 3H), 3.71 (s, 3H), 2.38-2.26 (m, 7H), 1.93 (m, 2H), 1.18 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 168.1, 159.1, 158.5, 150.5, 142.7, 131.3, 127.9, 112.2, 105.4, 104.1, 98.7, 59.6, 55.6, 55.2, 37.1, 32.6, 27.4, 21.2, 19.1, 14.2; MS (ESI):m/z (%) = 370.1 (M^+-1, 100); Anal. Calcd for $C_{21}H_{25}NO_5$: C, 67.91; H, 6.78; N, 3.77. Found: C, 67.87; H, 6.84; N, 3.72.



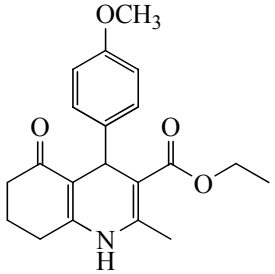
ethyl 4-(3-chlorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Dα)

Mp 209–210 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (m, 2H), 7.13 (m, 2H), 6.71 (s,1H), 5.07 (s, 1H), 4.07 (q, *J* = 7.2Hz, 2H), 2.41-1.98 (m, 7H), 1.93 (m, 2H), 1.20 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 167.3, 150.6, 149.2, 144.0, 133.7, 129.1, 128.1, 126. 5, 112.7, 105.4, 59.9, 37.0, 36.5, 29.7, 27.3, 21.0, 19.3, 14.2; MS (ESI):m/z (%) = 344.1 (M^+-1, 100); Anal. Calcd for $C_{19}H_{20}ClNO_3$: C, 65.99; H, 5.83; N, 4.05. Found: C, 65.89; H, 5.78; N, 4.12.



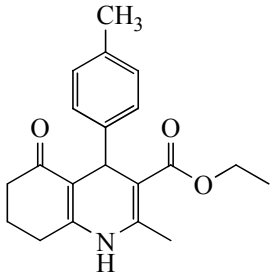
ethyl 2-methyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Eα)

Mp 198–199 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1H), 7.98(m, 1H), 7.73(d, 1H), 7.37 (t, 1H), 6.10 (s, 1H), 5.19 (s, 1H), 4.06 (q, *J* = 7.2Hz, 2H), 2.53-2.29 (m, 7H), 2.06-1.92 (m, 2H), 1.18 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 166.8, 150.0, 149.2, 148.4, 144.1, 134. 9, 128.5, 122.8, 121.3, 112.6, 105.2, 60.0, 36.8, 27.4, 21.0, 19.5, 14.1; MS (ESI):m/z (%) = 355.4 (M^+-1, 100).



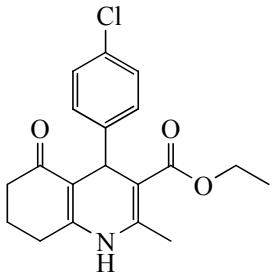
ethyl 4-(4-methoxyphenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Fα)

Mp 193–194 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 1H), 4.07 (q, *J* = 7.6 Hz, 2H), 3.72 (s, 3H), 2.38-2.29 (m, 7H), 1.98-1.90 (m, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 167.6, 157.8, 143.3, 139.8, 128.9, 113.3, 106.2, 59.8, 55.1, 37.1, 35.6, 27.3, 21.1, 19.2, 14.3; MS (ESI):m/z (%) = 340.0 (M^+-1, 100).



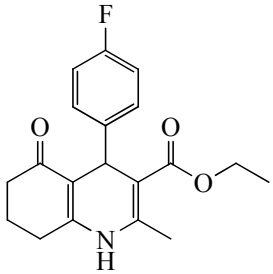
ethyl 2-methyl-5-oxo-4-p-tolyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Gα)

Mp 241–242 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.73 (s, 3H), 2.41-2.29 (m, 7H), 1.98-1.90 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.0, 167.6, 157. 8, 150.1, 143.3, 139.8, 128.9, 113.3, 113.3, 106.8, 59.8, 55.1, 37.1, 35.5, 27.8, 21.1, 19.2, 14.2; MS (ESI):m/z (%) = 364.2 ($M+K^+$, 100).



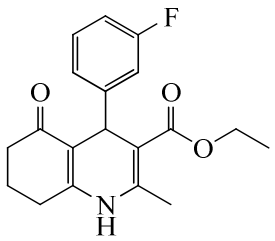
ethyl 4-(4-chlorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Hα)

Mp 234–235 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (m, 2H), 7.15 (m, 2H), 6.16 (s, 1H), 5.06 (s, 1H), 4.06 (q, *J* = 8.0 Hz, 2H), 2.44-2.30 (m, 7H), 2.01-1.93 (m, 2H), 1.20 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 167.3, 150.0, 145.7, 143.7, 131.6, 129.4, 128.0, 113.0, 105.7, 59.9, 37.0, 36.1, 29.7, 27.4, 21.0, 19.3, 14.2; MS (ESI):m/z (%) = 344.3 (M^+-1, 100).



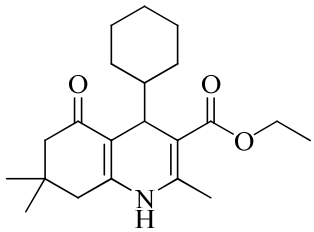
ethyl 4-(4-fluorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Iα)

Mp 243–244 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.16 (s, 1H), 7.15 (m, 2H), 7.00 (m, 2H), 4.88 (s, 1H), 3.97 (q, *J* = 7.0 Hz, 2H), 2.52-2.46 (m, 2H), 2.25 (s, 3H), 2.22-2.14 (m, 2H), 1.92-1.73 (m, 2H), 1.11 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 195.1, 167.3, 159.9, 151.9, 145.6, 144.5, 129.6, 129.5, 115.0, 114.8, 111.5, 103.9, 59.5, 37.1, 35.5, 26. 6, 21.3, 18.7, 14.6; MS (ESI):m/z (%) = 352.1 ($M+Na^+$, 100).

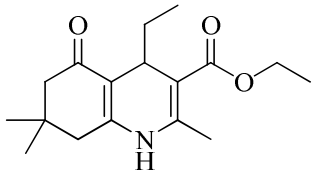


ethyl 4-(3-fluorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (7Kα)

Mp 213–214 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (m, 2H), 6.97 (d, 1H), 6.80 (t, 1H), 5.90 (s, 1H), 5.10 (s, 1H), 4.05 (q, *J* = 8.0 Hz, 2H),2.47-2.31 (m, 7H), 2.02-1.94 (m, 2H), 1.20 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.1 , 167.2, 149.5, 148.0, 143.6, 129.2, 129.1, 114.9, 114.7, 112. 8, 59.9, 50.7, 41.2, 36.5, 32.7, 29.4, 27.2, 19.5, 14.2; MS (ESI):m/z (%) = 328.1 (M^+-1, 100); Anal. Calcd for $C_{19}H_{20}FNO_3$: C, 69.29; H, 6.12; N, 5.77. Found: C, 69.36; H, 6.18; N, 5.80



ethyl 4-cyclohexyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Pα): Mp 226-228 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88 (s, 1H), 4.22-4.10 (m, 2H), 4.00 (d, *J* = 4.8 Hz, 1H), 2.36-2.20 (m, 7H), 1.66-1.55 (m, 6H), 1.29 (m, 4H), 1.13-1.05 (m, 8H), 0.93-0.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.3, 168.6, 150.6, 144.1, 109.8, 104.0, 59.6, 51.0, 45.9, 41.1, 35.0, 32.3, 30.1, 29.8, 28.2, 27.2, 26.7, 26.6, 19.0. 14.3; MS (ESI): m/z (%) = 346.3 (M^++1, 100); IR (KBr): ν_{max} = 3283, 3211, 2925, 1698, 1605 cm^{-1}.



ethyl 4-ethyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5Qα): Mp 145-146 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (s, 1H), 4.21-4.11 (m, 2H), 4.02 (t, *J* = 5.6 Hz, 1H), 2.34-2.16 (m, 7H), 1.46-1.41 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.10 (s, 6H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.1, 168.0, 150.0, 144.4, 110.6, 104.8, 59.6, 50.9, 41.1, 32.5, 31.0, 29. 7, 28. 6, 27.1, 19.2, 14.4, 9.3; MS (ESI): m/z (%) = 292.1 (M^++1, 100); IR (KBr): ν_{max} = 3294, 3222, 2955, 1696, 1605 cm^{-1}.