Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Data

Solvent-free synthesis of polyhydroquinoline derivatives employed by mesoporous vanadium ion doped titania nanoparticles as robust heterogeneous catalyst *via* Hantzsch reaction

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Contents:

General Experimental Information:

Reagents were obtained from commercial supplier and used without further purification. The ^{1}H and ^{13}C NMR spectra of the synthesized compounds were recorded at 400 MHz and 100 MHz respectively using Bruker AVANCE 400 MHz NMR spectrometer in DMSO-d_6 and $CDCl_3$ solvent and the chemical shifts were expressed in δ (ppm) relative to TMS as internal standard and coupling constants (*J*) in Hz. Spin multiplicities are described as s (singlet), t (triplet), q (quartet) and m (multiplet). TLC is performed using precoated aluminium sheets with silica gel 60 F_{254}. XRD patterns were obtained in an X Pert Pro Diffractometer, Panalytical, Netherlands. SEM-EDAX measurements were done on a FEI instrument. N_2 BET measurements were done on ASAP 2020 of Micrometrics, USA.

Synthesis of polyhydroquinoline derivatives via Hantzsch reaction

To a mixture of methyl/ethyl acetoacetate (1.0 mmol), dimedone (1.0 mmol), arylaldehyde (1.0 mmol) and ammonium acetate (2.0 mmol), catalytic amount (2.0 mol%) of V-TiO_2 nanoparticle was added at room temperature under stirring. The reaction mixture was heated on oil bath at 80°C. The reaction advancement was monitored by TLC. After the completion of reaction, it was cooled to room temperature and the resultant reaction mixture was washed with brine and extracted with ethyl acetate. The catalyst was separated out by filtration from the extraction mixture. Organic layer was separated, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was then purified by re-crystallization from hot ethanol and water to afford 1,4-dihydroquinoline derivatives in high yield. The structures of the products were confirmed from physical and spectroscopic data (IR and ^{1}H NMR) in comparison with the literature data.

Table-1 shows the nitrogen adsorption data of (V-TiO_2 and TiO_2 NPs) synthesized nanoparticles. All the nanoparticles exhibited surface area values in between the range of 230–274 m^2/g. The increasing quantity of vanadium ion doping in TiO_2 lattices (0.1, 0.25, 0.55 and 2.0 at %) somewhat changed the values of surface area. Up to 0.55 at %, the value of surface area was found to be increased slightly and then decreased to 237 m^2/g. At minimum quantity of doping

(0.1–0.55 at %), vanadium ion might have been incorporated in the titania lattice. It also observed to have controlled the nucleation, growth, and aggregation of titania nanoparticles which facilitated the formation of more number of mesoporous relative to vanadium incorporated titania nanoparticles. On further increase of dopant concentration upto 2.0 at %, amorphous VO_x species might have partially blocked the pores which led to decreased pore volume and surface area values. This experience is also compared with already existed reported data.

Table 1: Nitrogen adsorption data of V-TiO_2 nanoparticles

Type of the nano catalyst	BET Surface area (m^2/g)	Total pore Vol. (mL/g)	Micro pore Vol. (mL/g)
Bare TiO_2	230.4	0.4	0.05
0.1 VT	234.6	0.4	0.05
0.25 VT	239.1	0.4	0.05
0.55 VT	274.6	0.5	0.05
2.0 VT	237.9	0.4	0.05

XPS data of undoped TiO_2 and doped V-TiO_2 nanoparticles are revealed in Figures **1**(a)–(c). TiO_2 sample exhibits two peaks at 459.6 and 464.9 eV, depicting Ti $2p_{3/2}$ and Ti $2p_{1/2}$ peaks (Fig. **1a**) corresponding to Ti^{+4} oxidation state . In addition to these, binding energies at 523.2 eV and 524.8 eV are also observed which are found to be the characteristics of V^{+5} states, respectively indicating peak maxima of V $2p_{1/2}$ and V $2p_{3/2}$ (Fig. **1b**). Due to similar radii vanadium ion seemed to be incorporated in TiO_2 lattice by substitutionally replacing some of Ti^{4+} ions and formed Ti O V bonds. The Ti 2p peak becomes wide and unsymmetrical after vanadium doping, which might be related to more oxygen defects appeared after vanadium doping. The O 1s peak (Fig. **1c**) of the samples is observed at ~ 530 to 532 eV for all the nanoparticles.

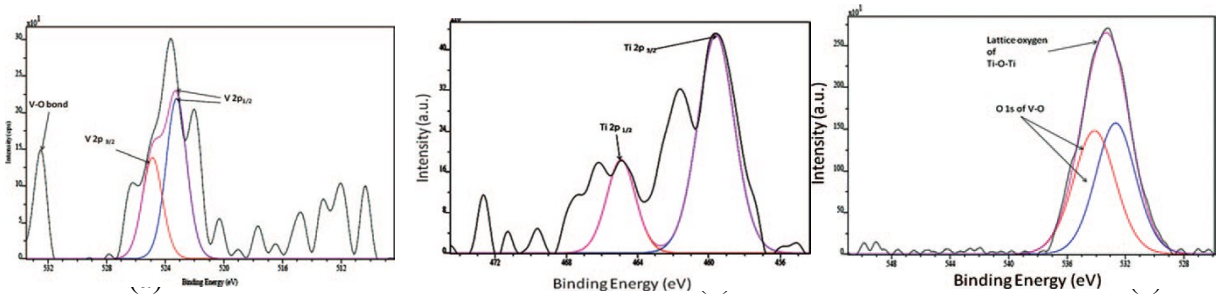


Figure 1: XPS data of TiO_2 NPs and 0.1 V-TiO_2 NPs (a-c).

Careful examination of FT-IR data (Figure 2) point towards the occurrence of 3463 cm^{-1}, 3488 cm^{-1} and 3563 cm^{-1} frequency bands which represented the presence of hydroxyl groups with different environments. These data also indicated the attachment of OH groups to both Ti^{3+} and Ti^{4+} ions. This observation further indicates the presence of oxygen vacancies in addition to surface hydroxyl groups. Collectively, surface hydroxyl groups, oxygen vacancies, Lewis acid sites, and other defects in V-TiO_2 nanoparticles play major role in the synthesis of polyhydroquinolines *via* Hantzsch hetero-annulation.

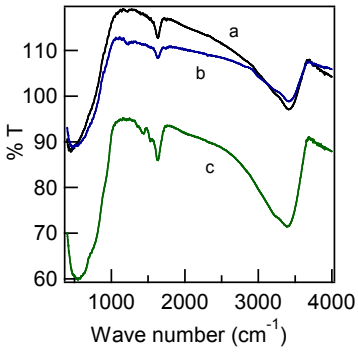
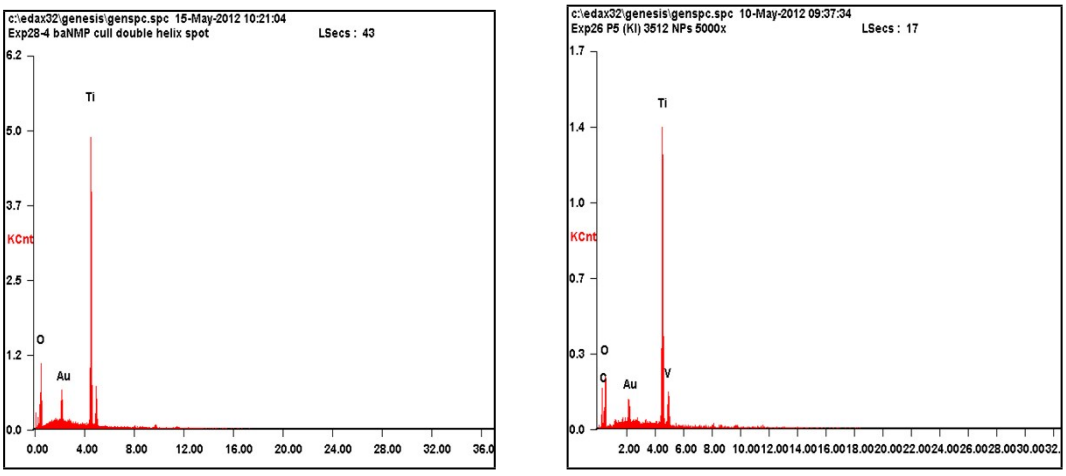


Figure 2: FT-IR data of V-TiO_2 nanoparticles.

Energy-dispersive X-ray spectroscopy (EDX) spectrum of undoped nanocrystalline TiO_2 is shown in figure 3. The EDX spectrum reveals the presence of Ti, V and O elements, which confirms that nanoparticle are TiO_2 and V-TiO_2. Au and C signals could be due to gold coating and carbon film supporting the specimen during SEM observation.



(a) (b)

Figure 3: EDX data of (a) TiO_2 and (b) V-TiO_2

Table 2:

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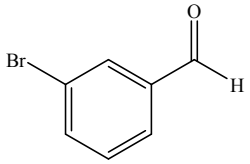
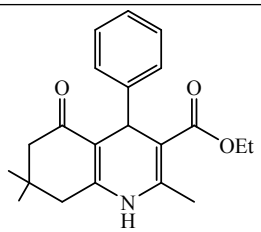
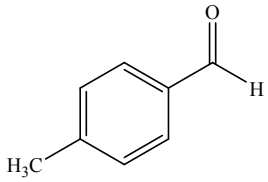
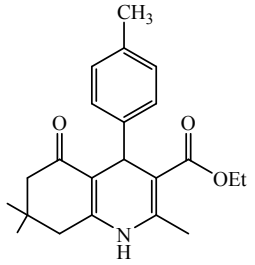
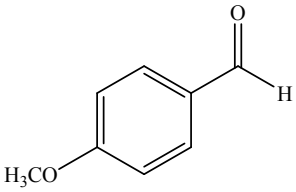
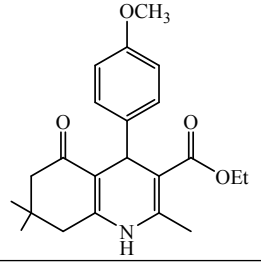
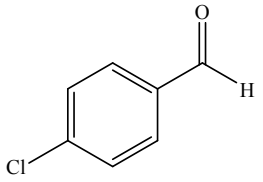
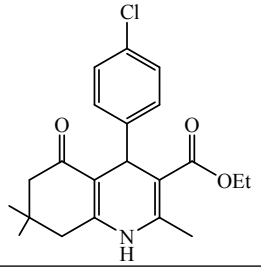
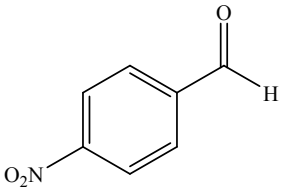
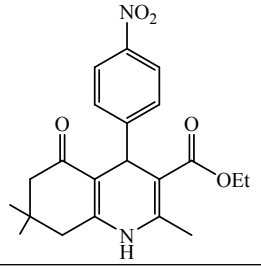
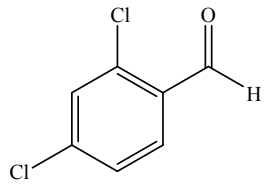
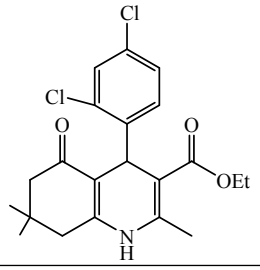
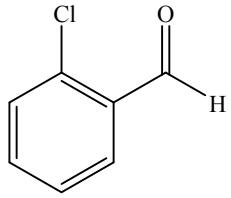
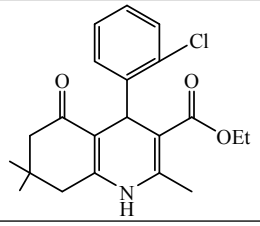
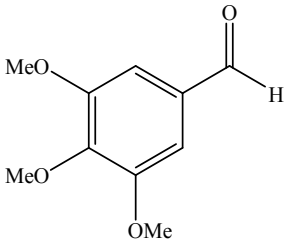
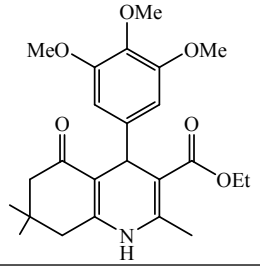
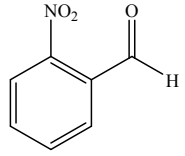
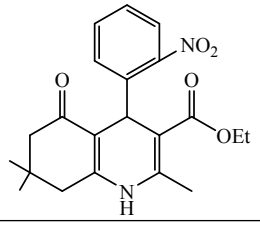
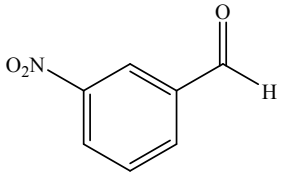
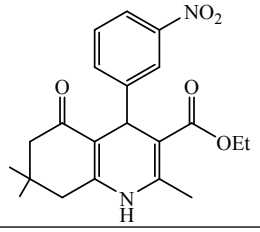
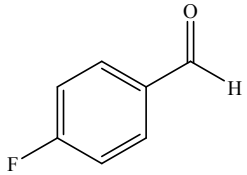
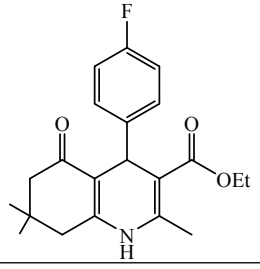
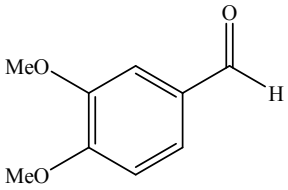
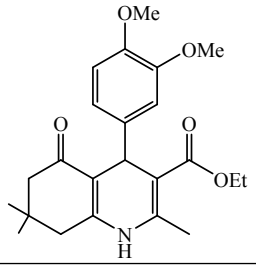
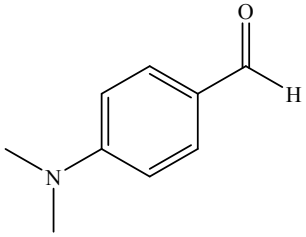
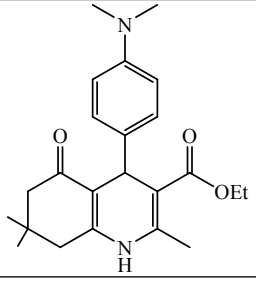
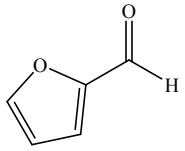
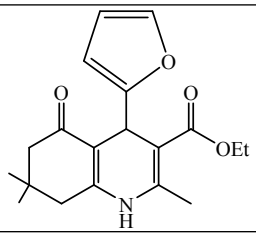
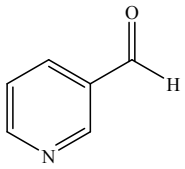
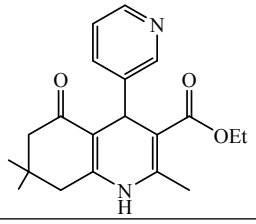
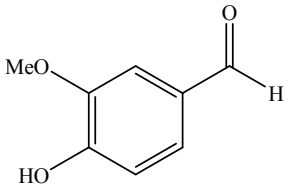
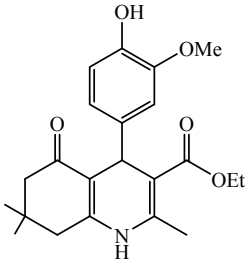
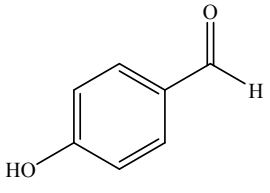
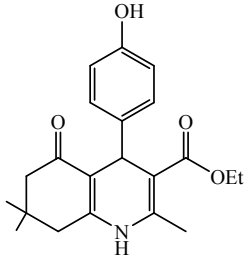
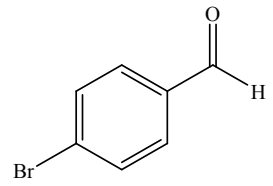
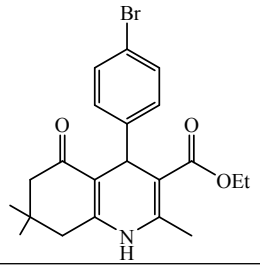
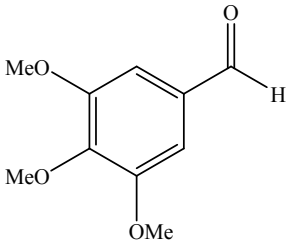
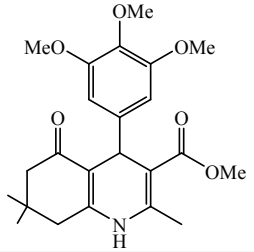
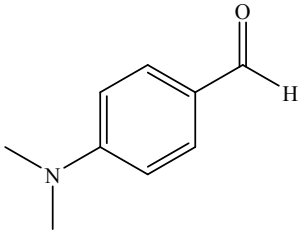
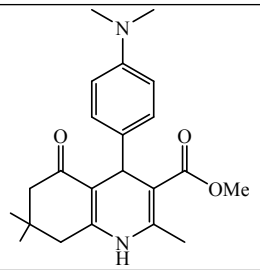
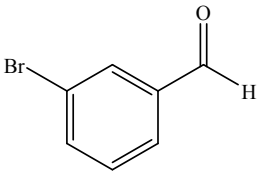
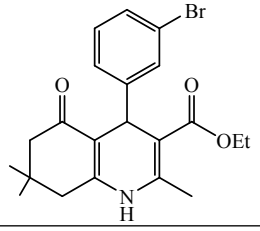
1		OEt	5a	
2		OEt	5b	
3		OEt	5c	
4		OEt	5d	
5		OEt	5e	

6		OEt	5f	
7		OEt	5g	
8		OEt	5h	
9		OEt	5i	
10		OEt	5j	
11		OEt	5k	

12		OEt	5l	
13		OEt	5m	
14		OEt	5n	
15		OEt	5o	
16		OEt	5p	
17		OEt	5q	

18		OEt	5r	
19		OMe	5s	
20		OMe	5t	
21		OEt	5u	

1*,4,5,6,7,8-Hexahydro-2,7,7-trimethyl-5-oxo-4-(4-methylphenyl)-3-quinolinecarboxyl acid ethyl ester (5b).* IR (KBr): 3290, 2975, 1708, 1636, 1612, 1486,1375, 1212, 1074, 1032, 872 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (s, 3H), 1.07 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H), 2.16-2.34 (m, 4H), 2.24 (s, 3H), 2.38 (s, 3H), 4.10 (q, J = 7.1 Hz, 2H), 5.14 (s, 1H), 6.76 (s, 1H), 7.14 (d, J = 7.9 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.25, 19.34, 21.14, 27.32, 29.43, 32.56, 36.22, 40.86, 50.87, 59.76, 106.22, 112.32, 127.90, 128.65, 135.64, 143.54, 144.24, 148.54, 167.58, 194.64.

Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(4-methoxylphenyl)-5(6H)-oxoquinolin-3-carboxylate (5c). IR (KBr): 3267, 2965, 1712, 1656, 1622, 1469, 1392, 1202, 1026, 764 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 0.98 (s, 3H), 1.06 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H), 2.04-2.18 (m, 4H), 2.28 (s, 3H), 3.76 (s, 3H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.76 (s,

1H), 6.56 (d, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 7.3 Hz, 2H), 8.56 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ 14.13, 18.25, 26.44, 29.16, 32.19, 34.71, 50.24, 50.50, 54.85, 58.98, 103.24, 110.16, 113.08, 113.12, 128.26, 128.33, 139.81, 144.66, 149.13, 157.25, 166.90, 194.28.

1,4,5,6,7,8-Hexahydro-2,7,7-trimethyl-5-oxo-4-(4-chlorophenyl)-3-quinolinecarboxyl acid ethyl ester (5d). IR (KBr): 3392, 2976, 1664, 1634, 1469, 1346, 1257, 1058, 1024, 872 cm^{-1}; ^{1}H NMR (400 MHz, CDCl^{3}): δ = 0.98 (s, 3H), 1.12 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H), 2.09-2.28 (m, 4H), 2.36 (s, 3H), 4.06 (q, *J* = 7.1 Hz, 2H), 5.12 (s, 1H), 6.32 (s, 1H), 7.23-7.36 (m, 4H), 7.34 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3): δ = 14.32, 19.22, 27.24, 29.36, 32.46, 36.32, 40.78, 50.67, 59.74, 105.44, 111.56, 122.46, 129.32, 131.56, 140.43, 147.47, 149.56, 167.76, 195.48.

1,4,5,6,7,8-Hexahydro-2,7,7-trimethyl-5-oxo-4-(2,4-dichlorophenyl)-3-quinolinecarboxyl acid ethyl ester (5f). IR (KBr): 3293, 2964, 1723, 1664, 1596, 1486,1224, 1121, 1076, 854, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 3H), 1.01 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 2.01-2.27 (m, 4H), 2.24 (s, 3H), 4.07 (m, 2H), 5.28 (s, 1H), 6.93 (s, 1H), 7.11-7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.32, 19.22, 27.32, 29.43, 32.38, 35.76, 40.95, 50.86, 59.82, 104.64, 110.75, 126.76, 129.34, 129.54, 132.12, 132.93, 133.76, 142.83, 144.24, 149.30, 167.43, 195.29.

Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(2-chlorolphenyl)-5(6H)-oxoquinolin-3-carboxylate (5g). IR (KBr): 3063, 2956, 1721, 1640, 1611, 1467, 1384, 1227, 1021, 745 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.92 (s, 3H), 1.06 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 2.12-2.32 (m, 4H), 2.42 (s, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.54 (s, 1H), 7.10-7.24 (m 4H), 7.34 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 26.52, 29.13, 31.28, 32.23, 42.64, 46.85, 48.92, 50.54, 52.97, 55.15, 101.32, 109.25, 114.28, 125.91, 127.16, 128.72, 131.13, 132.38, 141.02, 167.52, 195.71.

Ethyl 2,7,7-trimethyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (5j): IR (KBr): 3274, 2946, 1732, 1678, 1642, 1475, 1362, 1216, 1032, 772 cm^{-1}. ^{1}HNMR (400 MHz, $CDCl_3$): *d* = 0.92 (s, 3H), 1.04 (s, 3H), 1.23 (t, *J* = 7.1Hz, 3H), 2.14–2.38 (m, 7H), 3.72 (q, *J* =7.1Hz, 2H), 5.24 (s, 1H), 6.87 (s, 1H), 7.42 (t, *J* =7.9Hz, 1H), 7.76 (d, *J* =7.9Hz, 1H), 7.86 (m, 1H), 7.92 (m, 1H). ^{13}C NMR (100MHz, $CDCl_3$): *d* = 12.86, 18.12, 25.84, 28.17, 31.52, 35.78, 39.53, 49.35, 58.85, 103.78, 109.82, 119.46, 121.75, 127.63, 133.95, 143.24, 146.79, 148.61, 165.73, 194.44.

Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(4-fluorophenyl)-5(6H)-oxoquinolin-3-carboxylate (5k). IR (KBr): 3298, 2965, 1686, 1654, 1612, 1476, 1376, 1222, 1034, 762 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (s, 3H), 1.08 (s, 3H), 1.14 (t, *J* = 7.3 Hz, 3H), 2.08-2.28 (m, 4H), 2.42 (s, 3H), 4.12 (q, *J* = 7.33 Hz, 2H), 5.24 (s, 1H), 5.76

(s, 1H), 6.74-6.88 (m, 2H), 7.18 -7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.16, 18.28, 26.42, 29.08, 32.14, 35.26, 50.14, 50.38, 59.03, 103.42,110.08, 114.22, 114.31, 114.43, 129.08, 129.16, 144.11, 145.14, 149.46, 169.82, 194.29.

Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(3,4-dimethoxylphenyl)-5(6H)-oxoquinolin-3-carboxylate (5l). IR (KBr): 3243, 2959, 1686, 1648, 1616, 1476, 1373, 1216, 1046, 772 cm^{-1}. ^{1}H NMR: (400 MHz, CDCl3) δ = 0.94 (s, 3H), 1.06 (s, 3H), 1.24 (t, *J* = 7.3 Hz, 3H), 2.10-2.25 (m, 4H), 2.32 (s, 3H), 3.76 (s, 3H), 3.80 (s, 3H) 4.06 (q, *J* = 7.3 Hz, 2H), 5.12 (s, 1H), 5.78 (s, 1H, NH), 6.68 (d, *J* = 8.30 Hz, 1H), 6.72 (dd, *J* = 8.32 and 1.94 Hz, 1H), 6.78 (d, *J* = 1.96 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.26, 18.23, 26.48, 29.12, 32.07, 35.03, 50.26, 50.58, 55.23, 55.38, 59.06, 103.82, 110.15, 111.47, 111.79, 119.24, 140.42, 144.56, 146.90, 147.92, 149.44, 166.96, 194.34.

Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(4-hydroxy-3-methoxylphenyl)-5(6H)-oxoquinolin-3-carboxylate (5p). IR (KBr): 3368, 2946, 1698, 1634, 1586, 1476, 1365, 1234, 1058, 792 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.96 (s, 3H), 1.05 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 2.08-2.24 (m, 4H), 2.36 (s, 3H), 3.78 (s, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 4.86 (s, 1H), 6.72 (s, 2H), 6.84 (s, 1H), 7.86 (s, 1H), 8.54 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.25, 18.24, 26.33, 29.20, 32.18, 35.04, 50.28, 55.42, 58.97, 104.08, 110.14, 112.02, 114.95, 119.36, 119.57, 139.08, 144.34, 144.57, 146.72, 149.26, 167.08, 194.34.

1,4,5,6,7,8-Hexahydro-2,7,7-trimethyl-5-oxo-4-(4-bromophenyl)-3-quinolinecarboxyl acid ethyl ester (5r). IR (KBr): 3288, 2980, 1716, 1662, 1602, 1465,1254, 1226, 1076, 1027, 868 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (s, 3H), 1.04 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H), 2.08-2.26 (m, 4H), 2.32 (s, 3H), 4.16 (q, J = 7.1 Hz, 2H), 5.24 (s, 1H), 6.56 (s, 1H), 6.98 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.22, 19.23, 27.41, 29.14, 32.76, 36.54, 41.16, 50.67, 59.78, 105.58, 111.78, 119.54, 129.68, 130.60, 143.77, 146.51, 148.56, 167.22, 195.32.

1,4,5,6,7,8-Hexahydro-2,7,7-trimethyl-5-oxo-4-(3-bromophenyl)-3-quinolinecarboxyl acid ethyl ester (5u). IR (KBr): 3286, 2946, 1698, 1634, 1620, 1486,1456, 1222, 1082, 1074, 1043, 787 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.98 (s, 3H), 1.12 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H), 2.08-2.28 (m, 4H), 2.43 (s, 3H), 4.26-4.38 (m, 2H), 5.12 (s, 1H), 7.23 (s, 1H), 7.10-7.44 (m, 4H), 7.56 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3): δ = 14.32, 19.32, 27.54, 29.44, 32.76, 36.75, 40.86, 50.74, 59.73, 105.43, 111.38, 122.16, 126.98, 129.32, 129.44, 131.21, 144.12, 149.35, 149.43, 167.28, 195.56.