An efficient method for the preparation of 2,2,4-trisubstituted 1,2-dihydroquinolines using catalytic amount $Bi(OTf)_3$ as catalyst

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Abstract
Substituted 1,2-dihydroquinolines have been synthesised from substituted anilines and methyl pyruvate using catalytic amounts of commercially available $Bi(OTf)_3$ as a catalyst under microwave-assisted conditions. This method is simple, easy to work up, inexpensive, with a broad substrate scope and short reaction times. The reaction provides 1,2-dihydroquinolines (19 examples) in good yields (34-97% yields).

Keywords: Aryl amines, bismuth (III) triflate, α-ketoesters, Lewis acids, microwave irradiation, Skraup synthesis, 1,2-dihydroquinolines

Introduction

1,2-Dihydroquinoline derivatives have been found in numerous natural products and many of them have been shown to have biological activity.[1-2] In addition, 1,2-dihydroquinoline derivatives are versatile intermediates in organic chemistry. They can be readily transformed to 1,2,3,4-tetrahydroquinolines[3-4] and quinolines[5-6] which are of great value in medicinal chemistry.[7-8] In the literature, numerous methods describe the synthesis of 1,2-dihydroquinolines. Typically aryl amines were reacted with a range of different compounds such as ketones,[9] α,β-unsaturated ketones[10], 2,2-dimethoxy propane,[11] aldehyde,[12] alkynes,[13] alcohol,[14] glycerine,[15] α-ketoester[16-17] in the presence of Lewis acid or Brønsted acid catalysts. To date there have been few methods published for the synthesis of 1,2-dihydroquinoline derivatives using α-ketoesters. Waldman *et al*[16] have reported the formation of 1,2- dihydroquinolines using α-keto ester in the presence of $AuCl_3$ (5 mol%)/$AgSbF_6$ (15 mol%) as catalyst. However, large amounts of gold and silver salts have to be applied which is expensive. Recently, Ji *et al*[17] reported the preparation of these compounds using Brønsted acid (HNO_3, 10 mol%) in combination with $In(OTf)_3$ (1 mol%). Additionally, harsh reaction conditions are required which limits the substrate scope.

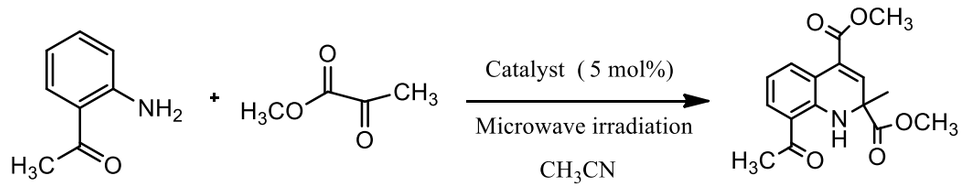
We now report the synthesis of substituted 1,2-dihydroquinolines employing anilines and methyl pyruvates. The reactions are catalysed using catalytic amounts of commercially available $Bi(OTf)_3$ under microwave-assisted conditions.

Results and Discussion

Due to the pharmaceutical importance of 1,2- dihydroquinolines and inspired by Waldman *et al*[16] we endeavoured to identify more appropriate and easier methods for the synthesis of these compounds. Initially various Lewis acids and protic acids were investigated. As demonstrated, Lewis acid or Bronsted acids are needed for the synthesis of 1,2- dihydroquinolines, as no reaction occurs without a catalyst. In this study $Bi(OTf)_3$ has been selected as the catalyst since it is cheap and stable in the presence of air and moisture. Furthermore, it has been demonstrated

that $Bi(OTf)_3$ is a good catalyst for many transformations, including Friedel-Crafts alkylation,[18] synthesis of 1,2-dihydroquinolines,[19] deprotection of O,O acetals,[20] and the aza-Cope rearrangement.[21] As seen in Table 1, various Lewis acids [$Sc(OTf)_3$, $Cu(OTf)_2$, Zn $(OTf)_3$, $Yb(OTf)_3$, $Bi(OTf)_3$] were tested in this synthesis. Among these $Bi(OTf)_3$ was the most effective catalyst which gave the products in very high yields (71%) (Table 1, entry 5). Additionally, various protic acids were also evaluated. However, inferior yields were observed (Table 1, entries 6-9). When 15 mol % trifluoromethanesulfonic acid was used a slight increase in yield was observed (Table 1, entry 7). However, the use of trifluoromethanesulfonic acid is not desirable as it is typically difficult to handle and in certain solvents is less soluble due to droplet formation. No product was observed in the absence of a catalyst after five hours (Table 1, entry 10).

Table 1. Effect of catalyst on reaction between *o*-acetyl aniline and methyl pyruvate



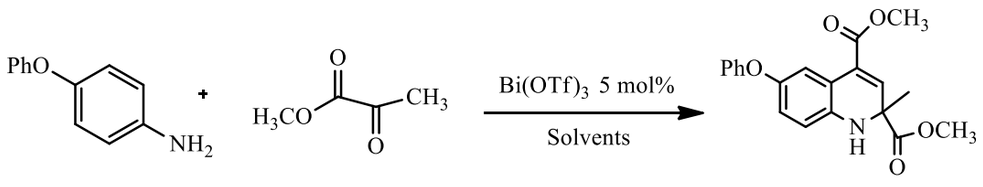
1a **2** **3a**

Entry[a]	Catalyst	Time (h)	Yield (%)[b]
1	$Cu(OTf)_2$	5	43
2	$Sc(OTf)_3$	5	56
3	$Zn(OTf)_3$	5	27
4	$Yb(OTf)_3$	5	43
5	$Bi(OTf)_3$	5	71
6	CF_3SO_2OH	5	53
7	CF_3SO_2OH	5	60[c]
8	CH_3SO_2OH	5	39
9	$PhSO_2OH$	5	44
10	None	5	_

[a]Reaction were carried out with ortho-acetyl aniline (1 eq), methyl pyruvate (2.2 eq).
[b]Isolated yield after silica gel chromatography.
[c]15 mol% acid was used.

Several solvents were employed in the reaction of para-phenoxy aniline and methyl pyruvate (Table 2). Acetonitrile was found to be an effective solvent[22] and a high yield of (**3b)** (70%) was observed after of 3.5 hours (Table 2, entry 3). When the reaction was refluxed in acetonitrile the yield slightly improved (75%) but the reaction took longer (7 hours) (Table 2, entry 5). In this reaction toluene was observed to be as effective as acetonitrile (Table 2, entry 2).

Table 2. Effect of solvent on reaction between *p*-phenoxy aniline and methyl pyruvate



1b **2b** **3b**

Entry[a]	Solvent	Time	Reaction conditions	Yield (%)[b]
1	DMF	3.5 h	MW, 85 ^oC, 10 bar, 150 Watt	52
2	Toluene	3 h	MW, 85 ^oC, 10 bar, 150 Watt	68

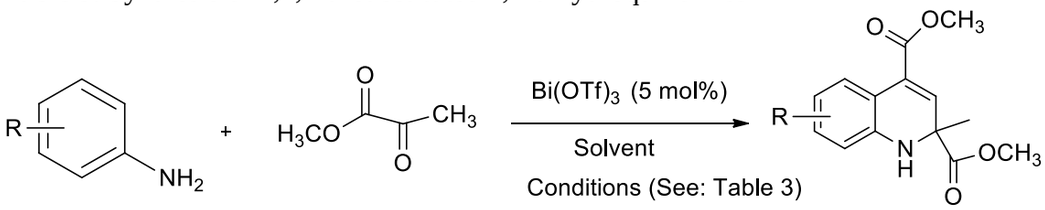
Table 2. Continued

Entry[a]	Solvent	Time	Reaction conditions	Yield (%)[b]
3	CH_3CN	3.5 h	MW, 85°C, 10 bar, 150 Watt	70
4	CH_3NO_2	2 h	MW, 85°C, 10 bar, 150 Watt	60
5	CH_3CN	7 h	Reflux, 82°C	75
6	CH_3NO_2	7 h	Heat, 82°C	63
7	$CHCl_3$	6 d	RT	62

[a]Reactions were carried out with para-phenoxy aniline (1 eq), methyl pyruvate (2.2 eq).
[b]Isolated yield after silica gel chromatography.

When the condensation reaction of the aniline derivatives with methyl pyruvate was investigated at room temperature a moderate yield was observed after a long period of time (Table 3). When performed in chloroform, the condensation of 2,5-dimethoxyaniline with methyl pyruvate provided a low yield (10 %) after six days (Table 3, entry 10). The condensation of *o*-acetyl aniline with methyl pyruvate provided trace amounts of product after 2 days (Table 3, entry 1). When the same reaction was performed in acetonitrile **3a** was obtained in low yield (22%) (Table 3, entry 1). When various electron withdrawing groups, such as para-cyano, nitro and acetyl aniline, were tested no product was obtained after 3-4 days (Table 3, entries 24, 26 and 28). When electron withdrawing groups were present on aniline at room temperature, either no reaction occurred or a reaction with very low yield was observed (Table 3, entries 1, 2, 24, 26 and 28).

Table 3. Synthesis of 2,2,4-trisubstituted 1,2-dihydroquinolines



1a-r **3a-3r**

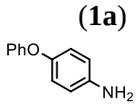
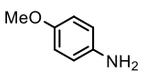
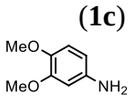
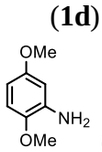
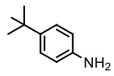
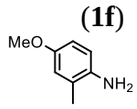
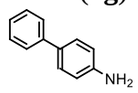
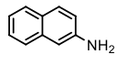
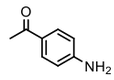
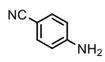
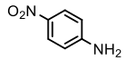
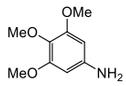
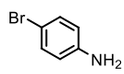
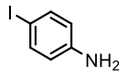
Entry[a]	Anilines, R =	Time	Solvents	Conditions (Compd. No)	Yields[b]
1	**(1a)** 2-acyl-	2 d	$CHCl_3$	RT (**3a**)	Trace
2	(**1a**)	2 d	CH_3CN	RT (**3a**)	22
3	(**1a**)	5 h	CH_3CN	MW (**3a**)	71
4	 (**1b**)	6 d	$CHCl_3$	RT (**3b**)	62
5	(**1b**)	7.5 h	CH_3CN	MW (**3b**)	77
6	 (**1c**)	2 d	$CHCl_3$	RT (**3c**)	60
7	(**1c**)	12 h	CH_3CN	MW (**3c**)	58
8	 (**1d**)	2 d	$CHCl_3$	RT (**3d**)	65
9	(**1d**)	4 h	CH_3CN	MW (**3d**)	62
10	 (**1e**)	6 d	$CHCl_3$	RT **(3e)**	10

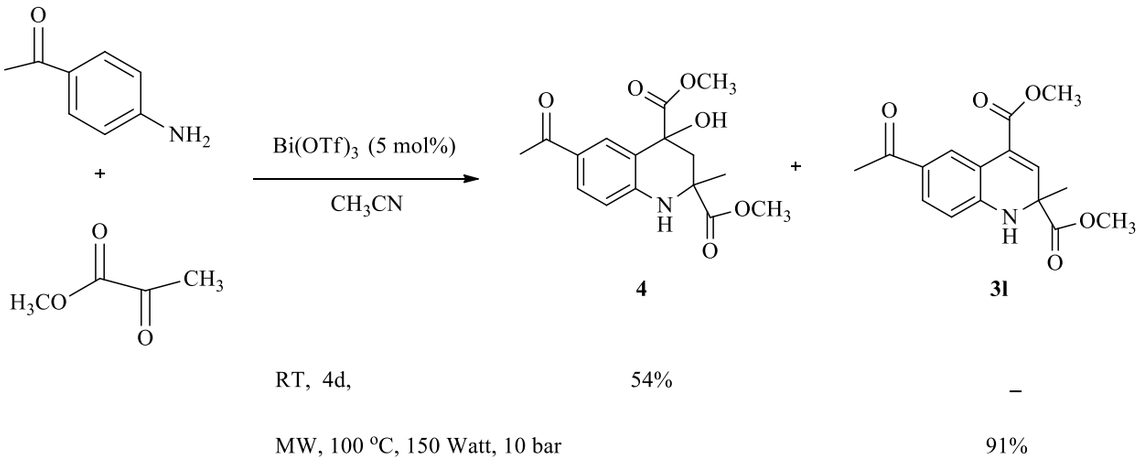
Table 3. Continued

Entry[a]	Anilines, R =	Time	Solvents	Conditions (Compd. No)	Yields[b]
11	(**1e**)	3 h	CH_3CN	MW (**3e**)	45
12	 (**1f**)	6 d	$CHCl_3$	RT **(3f)**	66
13	(**1f**)	11 h	CH_3CN	MW (**3f**)	73
14	 (**1g**)	6 d	$CHCl_3$	RT **(3g)**	36
15	(**1g**)	10 h	CH_3CN	MW (**3g**)	77
16	 (**1h**)	7 d	$CHCl_3$	RT **(3h)**	68
17	(**1h**)	8.5 h	CH_3CN	MW (**3h**)	65
18	 (**1i**)	7 d	$CHCl_3$	RT **(3i)**	73
19	(**1i**)	4 h	CH_3CN	MW (**3i**)	53
20	 (**1j**)	7 d	$CHCl_3$	RT (**3j**)	51
21	(**1j**)	2.5 h	CH_3CN	MW **(3j)**	53
22	 (**1k**)	6 d	$CHCl_3$	RT **(3k)**	62
23	(**1k**)	5 h	CH_3CN	MW (**3k**)	60
24	 (**1l**)	4 d	CH_3CN	RT **(3l)**	-
25	(**1l**)	3 h	CH_3CN	MW (**3l**)	91
26	 (**1m**)	3 d	CH_3CN	RT **(3m)**	-
27	(1**m**)	10 h	CH_3CN	MW (**3m**)	97
28	 (**1n**)	3 d	CH_3CN	RT **(3n)**	-
29	(**1n**)	10 h	CH_3CN	MW (**3n**)	71
30	 (**1o**)	8 h	CH_3CN	MW (**3o**)	63
31	 (**1p**)	4 h	CH_3CN	MW (**3p**)	83
32	 (**1q**)	10 h	CH_3CN	MW (**3q**)	81
33	 (**1r**)	7 h	CH_3CN	MW (**3r**)	34

[a]Reactions were carried out with aniline derivatives (1 eq), methyl pyruvate (2.2 eq).
[b]Isolated yield after silica gel chromatography.
MW: Microwave, RT: Room temperature

As seen in Tables 1, 2, and 3, the best results for the synthesis of 1,2- dihydroquinolines were observed with acetonitrile, $Bi(OTf)_3$ (5 mol%) and a microwave irridation system. For this reason, the condensation of aniline derivatives with methyl pyruvate was tried using microwave irridiation/acetonitrile /$Bi(OTf)_3$ (5 mol%). The results are seen in Table 3. In the presence of

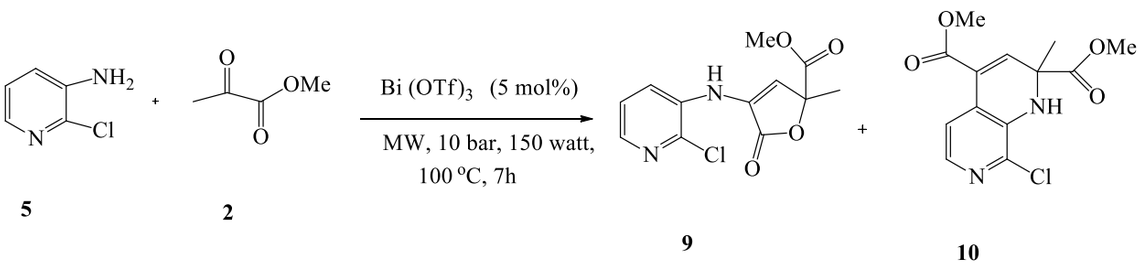
electron withdrawing or donating groups on aniline, the expected 1,2- dihydroquinolines derivatives were obtained in very good yields and in shorter time (Table 3, entries 3, 11, 15, 25, 27 and 29). At the end of the reaction of para acetyl aniline with methyl pyruvate at room temperature, instead of the expected product (**3l**), intermediate product (**4**) was produced in 54% yield (Scheme 1). When the reaction was repeated using microwave irridation, the expected product (**3l**) was produced in 91% yield (Table 3, entry 25).



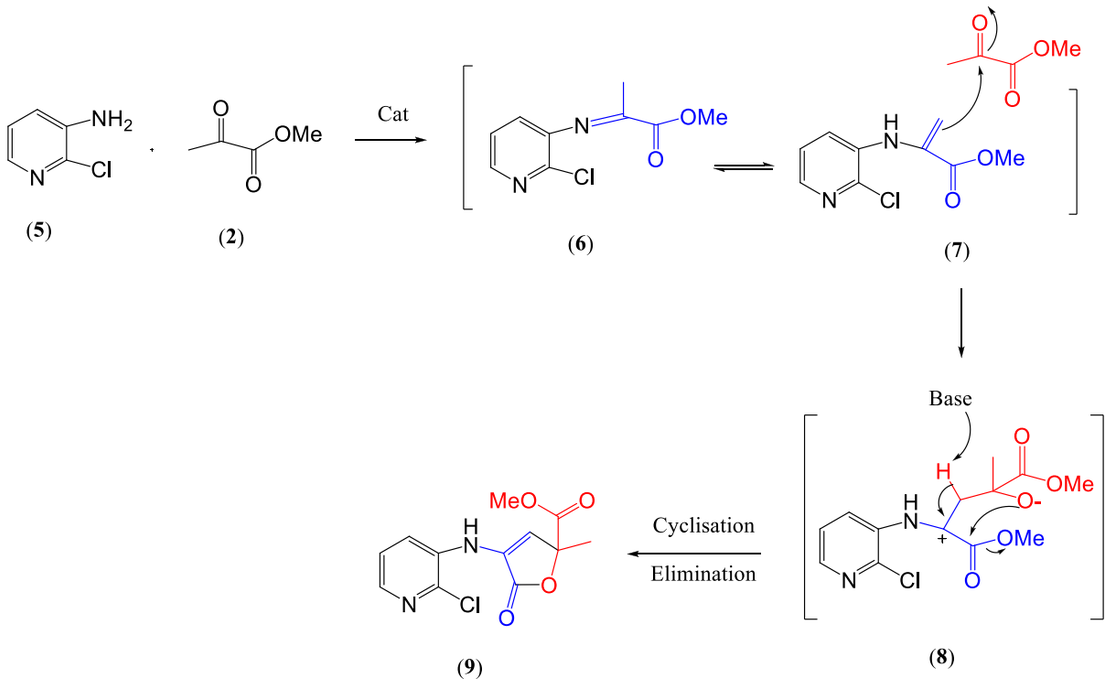
Scheme 1. Reaction of p-acetyl aniline (1 eq) and methyl pyruvate (2.2 eq).

The mechanism of the reaction was explained by Waldman[16] and Ji[17]. Ji suggests that imines or enamines are formed as a result of the reaction of *p*-methoxyaniline and methyl pyruvate as 39% imine and a trace amount of enamine were isolated. Neither Waldman[16] nor Ji[17] isolated intermediate product (**4)** which can be synthesised through the ring opening of lactone.[23] Our experiments support the formation of enamines and imines but these intermediate products are rapidly transformed to product (**4**) in 54% yield (Scheme 1). The structures of 3a[24], 3k[25], 3o[26], 3p[27], 3l[28] and 3q[29] were determined by X-ray crystallography.

When the same conditions were used with 2-chloro 3-amino pyridine, instead of the expected product (**10**), by-product (**9**) was produced in 23% yield (Scheme 2). The mechanism for the formation of **9** involves the initial generation of intermediate (**6)**, then imine intermediate (**6**) is transformed into enamine intermediate (**7**). As seen in Scheme 3, by-product (**9**) was obtained from enamine (**7**) which with a second mol of methyl pyruvate forms an intermediate alcohol by a 1,2-addition which subsequently cyclises to the product (**9**) (Scheme 3). The X-ray structure of by-product (**9**)[30] was shown in Figure 1.



Scheme 2. Synthesis of lactone (**9**).



Scheme 3. Proposed mechanism for synthesis of lactone (**9**).

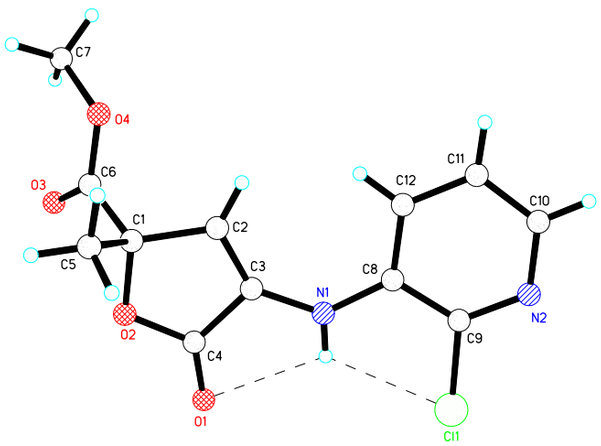


Figure 1. X-ray structure of (**9**).[30]

Conclusions

In this study we report the effective $Bi(OTf)_3$ (5 mol%) catalysed synthesis of 1,2-dihydroquinolines. Microwave irridation was found to be most effective to provide a series of 1,2-dihydroquinolines with both electron withdrawing and electron donating substituents. Characteristics of this study include: (*i*) one-pot reaction providing products in good yield, (*ii*) the starting materials are cheap and easily obtained, (*iii)* performing reactions using microwave irridation is safer and easier than under reflux, (*iv)* the products can easily be purified by column chromatography, (*v)* the 1,2-dihydroquinolines (**3a-3r**) obtained are useful in medicinal chemistry.

Experimental Section

General. Acetonitrile, chloroform were distilled from calcium hydride immediately prior to use. Dimethyl formamide, toluene , nitromethane were distilled before use. All aniline derivatives, $Bi(OTf)_3$ and methyl pyruvate are commercially available. Compounds **3a,**[16] **3n, 3o, 3i and**

3c[17] previously reported in the literature. Column chromatography was performed using MN silica gel (particle size 0.040-0.063 mm). For thin-layer chromatography (TLC), silica gel coated aluminium plates (Merck, silica gel 60 F_{254}) were used and chromatography was performed using silica gel Merck 60 (particle size 0.063-0.20 mm), visualised by UV irradiation. ^{1}H-NMR and ^{13}C-NMR were recorded on a Mercury 300 or 400 spectrometer in $CDCl_3$ or MeOD. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated bs (broadened singlet), s (singlet), d (doublet), m (multiplet), dd (double doubled); coupling constants (*J*) are in Hertz (Hz). ^{13}C NMR spectra were acquired on a broad band decoupled mode. Mass spectra was conducted on GC-MS Shimadzu QP2010 (column: Equity®-5, length × I.D. 30 m × 0.25 mm, df 0.25 μm, lot # 28089-U, Supelco). HRMS were measured on a Finnigan MAT 95 or LTQ Orbitrap XL spectrometer. IR spectra were measured in a Perkin-Elmer ATR apparatus and are reported in terms of frequency of absorption (cm^{-1}). Microwave, CEM marked, Discover SP-D With explorer 12 Hybrid was used. This work was presented in 25th National Chemistry Congress as a poster.[31]

General procedure for the synthesis of 1,2-dihydroquinolines under room temperature
The N-substituted aniline (100 mg, 1 eq) was dissolved in acetonitrile (1.5 ml) in a screw-capped test tube and $Bi(OTf)_3$ (5 mol%, 0.05 eq) and methyl pyruvate (2.2 eq) was added to the mixture. This mixture were stirred at room temperature (For the time see: Table 3) until the starting material was completely consumed as monitored by tlc. The resultant residue was direcly purified by flash chromatography on silica (EtOAc:Cyclohexane 2:98). All solid products were recrystallized over pentan and ethyl acetate.

General procedure for the synthesis of 1,2-dihydroquinolines under microvawe conditions
N-Substituted aniline (100 mg, 1 eq) was dissolved in acetonitrile (1.5 ml) then $Bi(OTf)_3$ (5 mol%, 0.05 eq) and methyl pyruvate (2.2 eq) were added to the solution. This mixture were heated by microwave irradiation (10 bar, 150 watt, 100ºC, See for the time: Table 1,2 and 3). The progress of the reaction was monitored through tlc. The resultant residue was direcly purified by flash chromatography on silica (EtOAc:Cyclohexane 2:98). All solid products were recrystallized over pentan and ethyl acetate. By this method the following compounds were prepared.

Dimethyl 8-acetyl-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3a).[16] Yellow crystalline solid; yield (71%); R_f 0.5 (2:1 Cyclohexane/EtOAc); mp 101-102 ºC.
IR (KBr) 3268 (NH), 1718, 1639 (CO) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.63 (s, 3H, CH_3), 2.59 (s, 3H, $COCH_3$), 3.76 (s, 3H, $COOCH_3$), 3.85 (s, 3H, $COOCH_3$), 6.59-6.64 (m, 1H, Ar-H), 6.65-6.66 (d, 1H, *J* 1.9 Hz, C=CH), 7.65-7.68 (dd, 1H, *J* 8.1 and 1.4 Hz, Ar-H), 7.9-8.0 (m, 1H, Ar-H) 9.6 (bs, 1H, NH). ^{13}C-NMR (400 MHz, $CDCl_3$): 28.1 ($\underline{C}H_3$), 28.7 ($CO\underline{C}H_3$), 52.2, 52.9 (2x$COO\underline{C}H_3$), 58.6 (C2), 115.1 (C8), 116.7 (C6), 117.6 (C10), 127.3 (C7), 131.8 (C5). 132.0 (C3), 132.7 (C4), 146.0 (C9), 165.7 (CO), 172.9 (CO), 200.4 (CO). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.41; H, 5.83; N, 4.61. MS m/z (EI) 303.1 (M^+, 3%), 245.1 (39), 244.1 (100), 228.1 (8), 226.1 (28), 185.1 (15), 167.1 (13), 142.1 (10), 115.0 (8), 59.2 (4).
Dimethyl 6-phenoxy-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3b). Yellow solid; yield (77%); R_f 0.43 (2:1 Cyclohexane/EtOAc); mp 78-79 ºC. IR (KBr) 3379 (NH), 1721 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 3H, CH_3), 3.76 (s, 3H, $COOCH_3$), 3.81 (s, 3H, $COOCH_3$), 4.49 (br, 1H, NH), 6.61-6.63 (d, 1H, *J* 8.3 Hz, Ar-H), 6.73 (bs, 1H, -C=CH), 6.80-6.83 (dd, 1H, *J* 8.7 and 2.6 Hz, Ar-H), 6.92-6.94 (m, 2H, Ar-H), 6.98-7.0 (m, 1H, Ar-H), 7.25-7.29 (m, 1H, Ar-H), 7.61 (bs, 1H, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): 27.4 ($\underline{C}H_3$), 52.1, 52.8 (2x$COO\underline{C}H_3$), 58.7 (C2), 114.9 (C8), 117.1 (C7), 117.3 (C5), 118.6 (C10), 121.6 (C6′). 121.9 (C2′), 127.4 (C4′), 129.4 (C3′and C5′), 133.7 (C3), 138.9 (C4), 148.2 (C9), 157.0 (C6), 158.6 (C1′), 165.6 (CO), 174.2 (CO). Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96. Found: C, 67.93; H, 5.54; N, 3.92; MS *m/z* (EI) 353.1 (M^+, 4%), 295.1 (19), 294.1 (100), 235.1 (4), 77.2 (5), 59.3 (2).

Dimethyl 6-methoxy-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3c).[17] Yellow oil; yield (58%); R_f 0.33 (2:1 Cyclohexane/EtOAc). IR (kapilar) 3368 (NH), 1726 (CO) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.53 (s, 3H, CH_3), 3.72, 3.74, 3,85 (s, 9H, COOMe and 6-OMe), 4.34 (bs, 1H, NH), 6.57-6.59 (d,1H, *J* 8.6Hz, Ar-H), 6.69-6.73 (dd, 1H, *J* 8.6 and 2.8 Hz, Ar-H), 6.74 (bs, 1H, -C=CH), 7.48-7.49 (d, 1H, H 2.8 Hz, Ar-H). ^{13}C-NMR (300 MHz, $CDCl_3$): δ = 26.9 ($\underline{C}H_3$), 52.0, 52.7 (COO$\underline{C}H_3$), 55.7 (OCH_3), 58.5 (C2), 111.5 (C8), 114.4 (C5), 115.1 (C10), 116.2 (C7), 127.9 (C3), 134.2 (C4), 136.6 (C9), 152.6 (C6), 166.0 (CO), 174.6 (CO). Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.62; H, 6.031; N, 5.060. MS *m/z* (EI) 291.2 (M^+, 11%), 233.3 (26), 232.2 (100), 173.2 (7), 131.2 (6), 116.2 (4).

Dimethyl 6,7-dimethoxy-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3d). Yellow oil; yield (62%); R_f 0.16 (2:1 Cyclohexane/EtOAc). IR (kapilar) 3367 (NH), 1725 (CO) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 3H, CH_3), 3.72, 3.80, 3,82, 3.83 (s, 12H, COO$\underline{C}H_3$ and 6,7-O$\underline{C}H_3$), 4.36 (bs, 1H, NH), 6.21 (s,1H, Ar-H), 6.57 (s, 1H, Ar-H), 7.54 (s, 1H, -C=CH). ^{13}C-NMR (300 MHz, $CDCl_3$): δ = 26.9 ($\underline{C}H_3$), 51.9, 52.6 (COO$\underline{C}H_3$), 55.6, 56.4 (OCH_3), 58.5 (C2), 98.4 (C8), 108.6 (C5), 110.5 (C9), 127.4 (C3), 130.6 (C4), 137.7 (C6), 1141.9 (C10), 150.5 (C7), 166.1 (CO), 174.9 (CO). Anal. Calcd for $C_{16}H_{19}NO_6$: C, 59.81; H, 5.96; N, 4.36. Found: C, 55.65; H, 5.810; N, 3.918. MS *m/z* (EI) 321.2 (M^+, 14%), 263.2 (25), 262.2 (100), 246.1 (16), 218.2 (7), 203.2 (5), 131.1 (6).

Dimethyl 5,8-dimethoxy-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3e). Yellow solid; yield (45%); R_f 0.23 (2:1 Cyclohexane/EtOAc); mp 100-101°C. IR (KBr) 3381 (NH), 1727 (CO) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.53 (s, 3H, CH_3), 3.70, 3.71, 3,78, 3.81 (s, 12H, COO$\underline{C}H_3$ and 5,8-O$\underline{C}H_3$), 4.9 (bs, 1H, NH), 6.0 (s, 1H, -C=CH), 6.14-6.16 (d,1H, *J* 8.8 Hz, Ar-H), 6.65-6.67 (d, 1H, *J* 8.8 Hz, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 26.8 ($\underline{C}H_3$), 52.0, 52.6 (COO$\underline{C}H_3$), 56.1, 56.2 (OCH_3), 57.6 (C2), 99.6 (C10), 107.6 (C6), 111.4 (C7), 126.4 (C8), 129.2 (C3), 134.0 (C4), 141.1 (C9), 149.8 (C5), 169.4 (CO), 174.5 (CO). Anal. Calcd for $C_{16}H_{19}NO_6$: C, 59.81; H, 5.96; N, 4.36. Found: C, 59.30; H, 5.61; N, 4.26. MS *m/z* (EI) 321.1 (M^+, 5%), 263.1 (16), 262.1 (100), 247.1 (6), 232.1 (33), 202.1 (4), 173.1 (3).

Dimethyl 6-*t*-butyl-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3f). Yellow solid; yield (73%); R_f 0.66 (2:1 Cyclohexane/EtOAc); m.p: 140-141 °C. IR (KBr) 3360 (NH), 1740, 1718 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 9H, ^{t}Bu), 1.54 (s, 3H, CH_3), 3.73 (s, 3H, $COOCH_3$), 3.86 (s, 3H, $COOCH_3$), 4.43 (bs, 1H, NH), 6.56-6.58 (d, 1H, *J* 8.0, Ar-H), 6.65 (bs, 1H, -C=CH), 7.11-7.13 (d, 1H, *J* 8.0, Ar-H), 7.86 (br, 1H, Ar-H). ^{13}C-NMR (400MHz, $CDCl_3$): 27.6 ($\underline{C}H_3$), 31.0, 31.2, 31.3 (-C($\underline{C}H_3$)$_3$), 31.5 (-$\underline{C}$(CH_3)$_3$), 52.0, 52.7 (2xCOO$\underline{C}H_3$), 58.5 (C2), 113.6 (C8), 120.4 (C10), 123.2 (C5), 126.6 (C7), 128.3 (C3). 132.5 (C4), 140.0 (C6), 141.1 (C9), 166.1 (CO), 174.5 (CO). Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41. Found: C, 67.73; H, 7.44; N, 4.33. MS *m/z* (EI) 317.2 (M^+, 4%), 259.2 (18%), 258.2 (100), 243.2 (10), 242.2 (15), 228.1 (6), 199.1 (3).

Dimethyl 6-methoxy-2,8-dimethyl-1,2-dihydroquinoline-2,4-dicarboxylate (3g).
Yellow solid; yield (77%); R_f 0.5 (2:1 Cyclohexane/EtOAc); mp 82-83 °C. IR (KBr) 3382 (NH), 1740, 1718 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 3H, CH_3), 2.2 (s, 3H, CH_3), 3.70 (s, 3H, $COOCH_3$), 3.73 (s, 3H, OCH_3), 3.84 (s, 3H, $COOCH_3$), 6.63-6.64 (d, 1H, *J* 2.6, Ar-H), 6.70 (br, 1H, -C=CH), 7.33-7.34 (d, 1H, *J* 2.6, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 17.3 (CH_3), 27.2 ($\underline{C}H_3$), 52.0, 52.8 (COO$\underline{C}H_3$), 55.7 (OCH_3), 58.5 (C2), 109.0 (C5), 117.0 (C10), 117.9 (C7), 122.7 (C8), 128.3 (C3). 133.6 (C4), 134.8 (C9), 151.7 (C6), 166.0 (CO), 174.8 (CO). Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.84; H, 6.42; N, 4.59. MS *m/z* (EI) 305.1 (M^+, 6%), 247.2 (20), 246.1 (100), 203.1 (8), 187.1 (7), 145.1 (4).

Dimethyl 6-phenyl-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3h). Yellow solid; yield (65%); R_f 0.56 (2:1 Cyclohexane/EtOAc); mp 109-110 °C. IR (KBr) 3364 (NH), 1712 (CO) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 3H, CH_3), 3.76 (s, 3H, $COOCH_3$), 3.88 (s, 3H, $COOCH_3$), 4.58 (bs, 1H, NH), 6.69-6.72 (bs, 2H, -C=CH and Ar-H), 7.23-7.31 (m, 1H, Ar-H), 7.31-7.40 (m, 3H, Ar-H), 7.52-7.55 (m, 2H, Ar-H), 8.1 (br, 1H, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): 27.7 ($\underline{C}H_3$), 52.1, 52.9 (2xCOO$\underline{C}H_3$), 58.7 (C2), 114.4 (C8), 116.5 (C10), 125.2 (C2′), 126.1 (C7), 126.2 (C6′). 126.4 (C4′), 127.3 (C5), 128.2 (C3), 128.3 (C5′), 128.5 (C3′), 131.5 (C6), 132.9 (C4), 141.0 (C1′), 141.8 (C9), 165.9 (CO), 174.2 (CO). Anal. Calcd for $C_{20}H_{19}NO_4$:

C, 71.20; H, 5.68; N, 4.15. Found: C, 70.99; H, 5.77; N, 4.11. MS *m/z* (EI) 337.2 (M^+, 7%), 279.2 (21), 278.2 (100), 219.2 (7), 139.2 (4), 59.3 (2).

Compound (3i).[17] Yellow solid; yield (53%); R_f 0.56 (2:1 Cyclohexane/EtOAc); mp 121-122ºC. IR (KBr) 3396 (NH), 1720 (CO) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.62 (s, 3H, CH_3), 3.77 (s, 3H, $COOCH_3$), 3.89 (s, 3H, $COOCH_3$), 5.0 (bs, 1H, NH); 6.5-6.6 (d, 1H, *J* 8.5 Hz, Ar-H), 6.68 (s, 1H, C=CH), 7.21-7.24 (d, 1H, *J* 8.7 Hz, Ar-H), 7.43-7.47 (m, 2H, Ar-H), 7.73-7.76 (m, 1H, Ar-H), 7.83-7.87 (m, 1H, Ar-H), 7.87-7.89 (d, 1H, *J* 8.7 Hz, Ar-H). ^{13}C-NMR (300 MHz, $CDCl_3$): 27.3 (CH_3), 52.0, 52.9 (2x$COO\underline{C}H_3$), 58.6 (C2), 111.1 (C13), 117.8 (C6), 119.9 (C5), 122.2 (C12), 123.9 (C9). 125.2 (C8), 126.4 (C7), 128.5 (C3), 129.0 (C3), 130.2 (C11), 134.2 (C4), 137.9 (C14), 166.5 (CO), 174.4 (CO). Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.40; H, 5.55; N, 4.47. MS *m/z* (EI) 311.1 (M^+, 16%), 253.2 (35), 252.1 (100), 192.1 (21), 59.3 (2).

Compound (3j). Yellow solid; yield (67%); R_f 0.43 (2:1 Cyclohexane/EtOAc); mp 173-175 ºC. IR (KBr) 3351 (NH), 1716 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 3H, CH_3), 3.73 (s, 3H, $COOCH_3$), 3.80 (s, 3H, $COOCH_3$), 6.44 (s, 1H, -C=CH), 6.96-6.99 (d, 1H, *J* 8.7 Hz, Ar-H), 7.21-7.25 (m, 1H, Ar-H), 7.33-7.40 (m, 2H, Ar-H), 7.63-7.69 (m, 2H, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): 25.5 ($\underline{C}H_3$), 52.3, 52.8 (2x$COO\underline{C}H_3$), 57.8 (C2), 110.4 (C10), 117.0 (C7), 122.4 (C5), 123.4 (C9), 126.1 (C8). 127.1 (C12), 128.6 (C13), 129.5 (C6), 129.9 (C3), 130.3 (C14), 130.9 (C4), 142.0 (C11), 169.4 (CO), 174.3 (CO). Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.52; H, 5.70; N, 4.45; MS *m/z* (EI) 311.1 (M^+, 5%), 253.1 (19), 252.1 (100), 193.1 (10), 118.6 (4), 59.3 (3).

Dimethyl 2,6,8-trimethyl -1,2-dihydroquinoline-2,4-dicarboxylate (3k). Pale yellow crystalline solid; yield (60%); R_f 0.25 (2:1 Cyclohexane/EtOAc); mp 147-148 ºC. IR (KBr) 3352 (NH), 1740, 1709 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.50 (s, 3H, CH_3), 2.1, 2.2 (s, 6H, 2xCH_3), 3.70, 3.80 (s, 6H, 2x$COO\mathit{CH_3}$), 6.3 (s, 1H, Ar-H), 6.42 (bs, 2H, Ar-H and -C=CH). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 20.5, 21.3 (2XCH_3), 26.9 ($\underline{C}H_3$), 52.2, 52.7 ($COO\underline{C}H_3$), 57.7, (C2), 113.5(C10), 123.3 (C8), 130.4, 130.9 (C5 and C6), 134.7 (C7), 139.4 (C4), 143.4 (C9), 169.0 (CO), 174.3 (CO). Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.41; H, 6.69; N, 4.86. MS *m/z* (EI) 289.1 (M^+, 5%), 231.2 (28), 230.1 (100), 198.1 (8), 171.1 (15), 170.1 (9), 128.1 (6).

Dimethyl 6- acetyl-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3l). Yellow crystalline solid; yield (91%); R_f 0.31 (2:1 Cyclohexane/EtOAc); m.p: 152-153 ºC. IR (KBr) 3329 (NH), 1742, 1664 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 3H, CH_3), 2.49 (s, 3H, $COCH_3$), 3.74 (s, 3H, $COOCH_3$), 3.86 (s, 3H, $COOCH_3$), 5.0 (br, 1H, NH); 6.5-6.6 (d, 1H, *J* 8.5 Hz, Ar-H), 6.69 (br, 1H, C=CH), 7.71-7.74 (dd, 1H, *J* 8.5 and 2.0 Hz, Ar-H), 8.49-8.50 (d, 1H, *J* 2.0 Hz, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): 26.1 ($\underline{C}H_3$), 28.2 ($CO\underline{C}H_3$), 52.2, 53.0 (2x$COO\underline{C}H_3$), 58.9 (C2), 113.5 (C8), 114.5 (C10), 127.3 (C6), 127.8 (C5), 128.1 (C3). 130.3 (C7), 132.4 (C4), 146.5 (C9), 165.5 (CO), 173.3 (CO), 196.3 (CO). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.42; H, 5.70; N, 4.63. MS *m/z* (EI) 303.2 (M^+, 3%), 245.2 (14), 244.2 (100), 201.2 (7), 186.2 (4), 114.9 (3), 59.4 (1).

Dimethyl 6- cyano-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3m). White solid; yield (71%); R_f 0.23 (2:1 Cyclohexane/EtOAc); mp 140-141ºC. IR (KBr) 3351 (NH), 1724, 1718 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.59 (s, 3H, CH_3), 3.78 (s, 3H, $COOCH_3$), 3.87 (s, 3H, $COOCH_3$), 4.9 (br, 1H, NH), 6.58-6.60 (d, 1H, *J* 8.3 Hz, Ar-H), 6.75 (br, 1H, -C=CH), 7.30-7.33 (dd, 1H, *J* 8.3 and 1.8 Hz, Ar-H), 8.19-8.20 (d, 1H, *J* 1.8, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): 28.4 ($\underline{C}H_3$), 52.4, 53.2 (2x$COO\underline{C}H_3$), 58.9 (C2), 100.7 (C6), 114.0 (C8), 115.6 (C10), 119.9 (CN), 126.4 (C7). 131.0 (C3), 133.4 (C4), 133.5 (C5), 145.6 (C9), 165.0 (CO), 173.1 (CO). Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79. Found: C, 62.96; H, 4.82; N, 9.81. MS *m/z* (EI) 386.1 (M^+, 1%), 228.1 (15%), 227.1 (100), 199.1 (5), 168.0 (20), 167.1 (6), 140.1 (6), 59.2 (4).

Dimethyl 6-nitro-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3n).[17] Yellow solid; yield (97%); R_f 0.23 (2:1 Cyclohexane/EtOAc); mp135-136 ºC. IR (KBr) 3347 (NH), 1721 (CO) cm^{-1}. ^{1}H-NMR (300MHz, $CDCl_3$): δ = 1.62 (s, 3H, CH_3), 3.80 (s, 3H, $COOCH_3$), 3.90 (s, 3H, $COOCH_3$), 5.22 (bs, 1H, NH), 6.5-6.6 (d, 1H, *J* 8.9 Hz, Ar-H), 6.78 (d, 1H, *J* 1.54 Hz ,

C=CH), 7.9-8.0 (dd, 1H, *J* 8.9 and 2.5 Hz, Ar-H), 8.83-8.84 (d, 1H, *J* 2.5, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): 28.6 ($\underline{C}H_3$), 52.5, 53.3 (2xCOO$\underline{C}H_3$), 59.3 (C2), 113.3 (C8), 114.4 (C10), 123.4 (C5), 126.2 (C7), 126.4 (C3). 133.3 (C4), 139.1 (C6), 147.6 (C9), 164.9 (CO), 172.7 (CO). Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.61; N, 9.15. Found: C, 54.84; H, 4.45; N, 9.15. MS *m/z* (EI) 306.1 (M^+, 1%), 248.1 (15), 247.1 (100), 201.1 (47), 186.1 (12), 142.1 (9), 59.3 (5).

Dimethyl 2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3o).[17] Yellow solid; yield (63%); R_f 0.53 (2:1 Cyclohexane/EtOAc); mp 73 ºC. IR (KBr) 3365 (NH), 1710 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.55 (s, 3H, CH_3), 3.7 (s, 3H, COOMe), 3.8 (s, 3H, COOMe), 4.5 (bs, 1H, NH), 6.61-6.63 (m,1H, Ar-H), 6.66 (s, 1H, -C=CH), 6.71-6.74 (m, 1H, Ar-H), 7.0-7.10 (m, 1H, Ar-H), 7.77-7.79 (m, 1H, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): δ = 27.6 ($\underline{C}H_3$), 52.0, 52.8 (COO$\underline{C}H_3$), 58.5 (C2), 114.1 (C5), 116.3 (C8), 118.6 (C6), 126.4 (C10), 128.1 (C7), 129.6 (C3), 132.5 (C4), 142.4 (C9), 166.0 (CO), 174.2 (CO). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.43; H, 5.81; N, 5.41. MS *m/z* (EI) 261.1 (M^+, 3%), 203.1 (15), 202.1 (100), 188.1 (4), 174.1 (5), 143.1 (18), 142.1 (7), 115.1 (7), 59.1(5).

Dimethyl 5,6,7-trimethoxy-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3p).
White crystalline solid; yield (83%); R_f 0.16 (2:1 Cyclohexane/EtOAc); mp 120-121 ºC.
IR (KBr) 3359 (NH), 1739 (CO) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 3H, CH_3), 3.69, 3.71, 3,79, 3.80 (s, 15H, COO$\underline{C}H_3$ and 5,6,7-O$\underline{C}H_3$), 4.42 (bs, 1H, NH), 5.85 (bs, 1H, Ar-H), 5.99 (s, 1H, -C=CH). ^{13}C-NMR (300 MHz, $CDCl_3$): δ = 26.9 ($\underline{C}H_3$), 52.1, 52.6 (COO$\underline{C}H_3$), 55.7, 58.0 (2xOCH_3), 58.0(C2), 60.9 (OCH_3), 93.7 (C8), 104.3 (C10), 123.8 (C3), 129.0 (C4), 134.2 (C9), 139.7 (C5), 149.8 (C6), 155.1 (C7), 170.3 (CO), 174.9 (CO). Anal. Calcd for $C_{17}H_{21}NO_7$: C, 58.11; H, 6.02; N, 3.99. Found: C, 57.73; H, 5.91; N, 3.93. MS *m/z* (EI) 351.2 (M^+, 7%), 293.1 (19), 292.2 (100), 262.1 (6), 217.1 (7), 133.1 (3).

Dimethyl 6-bromo-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3q). Yellow crystalline solid; yield (81%); R_f 0.5 (2:1 Cyclohexane/EtOAc); mp 106-107 ºC. IR (KBr) 3352 (NH), 1724 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.54 (s, 3H, CH_3), 3.74 (s, 3H, $COOCH_3$), 3.85 (s, 3H, $COOCH_3$), 4.51 (bs, 1H, NH), 6.4-6.5 (d, 1H, *J* 8.5 Hz, Ar-H), 6.71 (bs, 1H, -C=CH), 7.14-7.17 (dd, 1H, *J* 8.5 and 2.1 Hz, Ar-H), 7.97-7.98 (d, 1H, *J* 2.1, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): 27.5 ($\underline{C}H_3$), 52.4, 52.9 (2xCOO$\underline{C}H_3$), 58.6 (C2), 110.4 (C6), 115.6 (C8), 117.9 (C9), 127.0 (C7), 129.0 (C3). 132.1 (C5), 133.8 (C4), 141.4 (C9), 165.4 (CO), 173.9 (CO). Anal. Calcd for $C_{14}H_{14}BrNO_4$: C, 49.43; H, 4.15; N, 4.12. Found: C, 49.38; H, 4.01; N, 4.13. MS *m/z* (EI) 339.0 (M^+, 5%), 283.0 (12%), 282.0 (97), 280.0 (100%), 221.0 (7), 201.1 (11), 142.1 (6), 115.1 (6), 59.2 (6).

Dimethyl 6-iodo-2-methyl-1,2-dihydroquinoline-2,4-dicarboxylate (3r). Yellow crystalline solid; yield (34%); R_f 0.56 (2:1 Cyclohexane/EtOAc); mp 120 ºC. IR (KBr) 3350 (NH), 1723 (CO) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.54 (s, 3H, CH_3), 3.74 (s, 3H, $COOCH_3$), 3.86 (s, 3H, $COOCH_3$), 4.51 (bs, 1H, NH), 6.3-6.4 (d, 1H, *J* 8.4 Hz, Ar-H), 6.68-6.69 (d, 1H, *J* 2.0 Hz, -C=CH), 7.32-7.35 (dd, 1H, *J* 8.4 and 2.0 Hz, Ar-H), 8.13-8.14 (d, 1H, *J* 2.0, Ar-H). ^{13}C-NMR (400 MHz, $CDCl_3$): 27.6 ($\underline{C}H_3$), 52.24, 52.97 (2xCOO$\underline{C}H_3$), 58.5 (C2), 116.15 (C8), 118.4 (C10), 126.9 (C3), 133.5 (C4), 134.8 (C5). 138.0 (C7), 142.0 (C9), 165.4 (CO), 173.9 (CO). Anal. Calcd for $C_{14}H_{14}INO_4$: C, 43.43; H, 3.64; N, 3.62. Found: C, 43.81; H, 3.58; N, 3.56. MS *m/z* (EI) 387.1 (M^+, 7%), 329.0 (11), 328.0 (100), 201.2 (20), 142.2 (4), 59.3 (2).

Dimethyl 6-acetyl-4-hydroxy-2-methyl-1,2,3,4-tetrahydroquinoline-2,4-dicarboxylate (4). White solid; yield (54%); R_f 0.35 (1:1 Cyclohexane/EtOAc); mp 200-201 ºC. IR (KBr) 3325 (NH), 1743 (CO) cm^{-1}. ^{1}H-NMR (300MHz, MeOD): δ = 1.52 (s, 3H, CH_3), 2.27.2.64 (AB, 2H, J_{AB} 13.7 Hz, -CH_2), 2.43 (s, 3H, $COCH_3$), 3.6 (s, 3H, $COOCH_3$), 3.77 (s, 3H, $COOCH_3$), 6.71-6.73 (d, 1H, *J* 8.4 Hz, Ar-H), 7.59-7.60 (d, 1H, *J* 2.0 Hz, Ar-H), 7.72-7.75 (dd, 1H, *J* 8.6 and 2.0 Hz, Ar-H). MS *m/z* (EI) 321.2 (M^+, 21%), 263.2 (5), 262.2 (28), 245.2 (20), 244.2 (100), 202.2 (29). 160.2 (7), 130.2 (4), 59.2 (4). HRMS-EI calcd. for $C_{16}H_{19}NO_6$ [M+]: 321.12069; Found: 321.12115.

Lactone (**9**). MW (10 bar, 150 watt, 100 ºC, 7 hrs). Pale purple solid; yield (23%); R_f 0.4 (1:1 Cyclohexane/EtOAc); mp 98-99 ºC. ^{1}H-NMR (300MHz, $CDCl_3$): δ = 1.79 (s, 3H, CH_3), 3.80 (s, 3H, OMe), 6.40 (s, 1H, =CH), 6.94 (1H, br, NH), 7.27-7.30 (1H, dd, *J* 5.0 and 8.0, Ar-H), 7.50-7.52 (1H, dd, *J* 1.3 and 8.0 Hz, Ar-H), 8.03-8.04 (1H, dd, *J* 1.4 and 4.6 Hz, Ar-H). ^{13}C-

NMR (400 MHz, $CDCl_3$): 23.1 ($\underline{C}H_3$), 53.34 (OCH_3), 84.81 (C2), 115.17 (C3), 122.8 (C5'), 123.2 (C4'), 128.3 (C6'), 133.9 (C2'), 139.9 (C3'), 141,6 (C4), 168.2 (CO), 169.4 (CO). Crystal data for **9**: $C_{12}H_{11}ClN_2O_4$, M = 282.68, crystallizes as colourless blocks, crystal dimensions 0.50 x 0.30 x 0.20 mm. Monoclinic, a = 7.5735(10) Å, b = 14.407(2) Å, c = 11.6615(14) Å, β = 96.641(10)°, V = 1263.9(3) $Å^3$, z = 4, D_c= 1.486 Mgm^{-3}, space group $P2_1/c$ (No. 14), MoK_α radiation (λ = 0.71073), μ = 0.314 mm^{-1}, F(000) = 584.
The X-ray data were collected at 293(2) K in the range 4.5° < 2θ < 56° on a Nicolet P3/F diffractometer by the Wyckoff scan method. The 3044 unique reflections were corrected for Lorentzian polarization effects, but not for absorption. Intensity of 1647 reflections were larger than 2σ(I). The structure was solved by Direct Methods and refined by full matrix least squares methods of F^2 with SHELXTL-97 program package. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0850 (wR_2 = 0.1548, I>2σ(I), 179 parameters, mean and maximum δ/σ 0.000 and 0.000), with allowance of anisotropic displacement parameters for all non-hydrogen atoms. Minimum and maximum final rest-electron density is –0.255 and 0.263 $eÅ^{-3}$.

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