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EFFICIENT SYNTHESIS OF *N*-SUBSTITUTED 4-ARYLQUINOLINE DERIVATIVES USING ZnCl₂ or ZrO₂

Afsaneh Zonouzi,* Roghieh Mirzazadeh, Azadeh Peivandi, and Shahrzad Dehdari

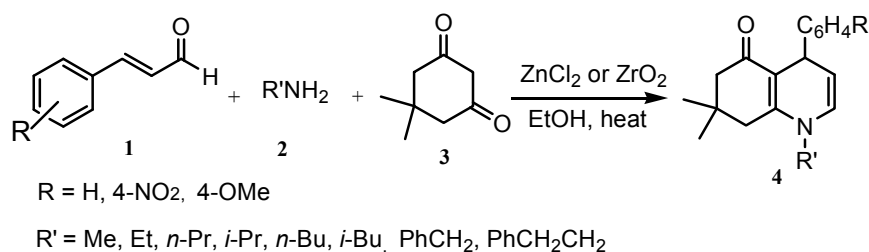
School of Chemistry, University College of Science, University of Tehran, Tehran, Iran. E-mail: zonouzi@khayam.ut.ac.ir

Abstract - *N*-Substituted 7,8-dihydro-7,7-dimethyl-4-arylquinolin-5(1*H*,4*H*,6*H*)-ones **4a-l** have been reported by one-pot reaction of cinnamaldehyde derivatives, dimedone and various amines in the presence of ZnCl₂ or ZrO₂ in fairly high yields.

The preparation of 1,4-dihydropyridines by classical Hantzsch synthesis, a one-pot condensation of an aldehyde with alkyl acetoacetate and ammonia, was developed more than one hundred years ago.¹ Up to now some reports on modification of Hantzsch reaction have been published.²⁻¹⁰ Also it has been shown some substituted 1,4-dihydropyridine derivatives exhibit biological activity.³⁻⁷ The classical methods for the synthesis of 1,4-dihydropyridines almost involved long reaction time, harsh reaction conditions, and use of a large quantity of volatile organic solvents or microwave irradiation and generally achieved the products in low to moderate yields and sometimes had been reported as by-product. In 2006 Sivamurugan and co-workers had reported the synthesis of 1,4-dihydropyridine derivatives using aldehydes, 1,3-diketones and ammonium acetate in the presence of Zn[L-proline]₂ and microwave irradiation.⁸ Wu and co-workers had reported synthesis of α -fluoro substituted amidines using ZnCl₂.⁹ They reported 1,4-dihydropyridines as by-product. In 2007 Moreau and co-workers used *p*-TSA for the synthesis of *N*-substituted 1,4-dihydropyridine derivatives.¹⁰

We have recently reported one-pot procedure for heterocyclic frameworks,¹¹⁻¹⁴ here we wish to report multi-component and one-pot reaction of cinnamaldehyde derivatives **1**, primary amine **2** and dimedone **3** (5,5-dimethyl-1,3-cyclohexanedione) in the presence of ZnCl₂, ZrO₂ and *p*-toluenesulfonic acid (*p*-TSA) as catalyst. In this reaction *N*-substituted-4-arylquinolin-5-ones **4** were achieved in fairly good yields 68-88% (Scheme 1).

In previous reports enamine was produced using ammonia and aldehyde then enamine attacked to α,β -



Scheme 1

unsaturated carbonyl compound as a nucleophile. While in this research we used α,β -unsaturated imine (produced by cinnamaldehyde derivatives and primary amines) as a Michael acceptor. Michael addition of enolate ion of dimedone **3** (1,3-dicarbonyl compound) to this imine in the presence of Lewis acid produced the *N*-substituted-4-arylquinolin-5-ones, which is a new modification of Hantzsch reaction.

Moreover dimedone **3** is still desired for the synthesis of fused heterocyclic compounds.¹⁵

We have found when cinnamaldehyde, dimedone and primary amine ($\text{PhCH}_2\text{CH}_2\text{NH}_2$) in the presence of ZnCl_2 were used simultaneously only (*E*)-3-hydroxy-5,5-dimethyl-2-(3-phenylprop-2-en-1-yl)cyclohex-2-en-1-one was produced.¹⁶ In this research, enolate ion is produced initially by using 1-2 drops of a suitable base like triethylamine then this enolate is added to imine of cinnamaldehyde and primary amine. Meanwhile we have used primary amines instead of ammonia or ammonium salts for synthesis of some *N*-substituted-4-arylquinoline derivatives.

On the other hand this one-pot reaction did not process without using acid as catalyst. Lewis acids (ZnCl_2 , ZrO_2) also *p*-TSA were used as catalyst in different amounts. Solvents (toluene, *p*-xylene, H_2O and EtOH) have been investigated in this procedure. The results for compound **4a** are compared in Table 1.

Table 1. Effect of solvents on the synthesis of compound **4a** using ZnCl_2 , ZrO_2 and *P*-TSA

Catalyst (mol %)	EtOH (Yield %)	<i>p</i> -Xylene (Yield %)	Toluene (Yield %)	H_2O (Yield %)	
ZnCl_2	5	68	52	48	-
	10	88	70	62	10
	20	87	62	55	5
ZrO_2	5	58	45	40	-
	10	76	65	58	5
	20	78	60	54	5
<i>p</i> -TSA	5	35	28	22	-
	10	42	30	25	-
	20	40	32	25	-

As shown in table 1, for the synthesis of compound **4a**, EtOH was the best solvent and *p*-TSA was not so effective, therefore, ZnCl₂ and ZrO₂ have been chosen as the catalyst and EtOH as solvent. The different amounts of ZnCl₂ and ZrO₂ on the reaction times and yields of compounds **4a-l** have been examined too (Table 2). Obviously for both catalysts 10 mol% was better than 5 mol% and 20 mol% of both catalysts was similar to 10 mol%.

Structures **4** were assigned on the basis of their elemental analysis, IR, ¹H NMR, ¹³C NMR and mass spectral data. The mass spectra of these compounds **4a-l** displayed molecular ion peaks at the appropriate *m/z* values. The ¹H NMR and ¹³C NMR spectra of **4a-l** displayed absorption in agreement with their structures. (Experimental Section)

The reaction described here is a new modification of Hantzsch reaction which represent an efficient entry for the synthesis of *N*-substituted-7,8-dihydro-7,7-dimethyl-4-arylquinolin-5(1*H*,4*H*,6*H*)-ones. Inexpensive Lewis acid (ZnCl₂ and ZrO₂) catalyzed this reaction. Further investigations of this method are currently in progress to establish its scope and utility.

EXPERIMENTAL

Chemicals and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Columns chromatography were performed on silica Gel (0.015-0.04 mm, mesh-size) and TLC on percolated plastic sheets (25 DC_{UV-254}) respectively. Melting points were measured on Barnstead Electrothermal melting point apparatus and are not corrected. Elemental analysis for C, H and N were performed using a Thermo Finnigan Flash EA1112 instrument. IR spectra were measured on a Bruker EQUINOX 55 spectrophotometer as ATR method. ¹H NMR and ¹³C NMR spectra were determined in CDCl₃ on a Bruker 500 spectrophotometer and chemical shifts were expressed in ppm downfield from tetramethyl silane. Mass spectra were recorded on a Finnigan-MAT 8430 spectrometer at an ionization potential of 70 eV.

General procedure for the synthesis of compounds **4**

To a magnetically stirred solution of cinnamaldehyde derivatives **1** (4 mmol) in EtOH (10 mL), amines **2** (4 mmol) was added gently and stirred for 20-30 min. Then a mixture of dimedone **3** (4 mmol) and 1-2 drops of triethylamine were added to the above reaction mixture. Catalyst was added according to Table 2 in this stage. The reaction mixture was refluxed for 12-14 h. The product was purified by column chromatography using silica gel and EtOAc: *n*-hexane (1:4) as co-solvent.

Table 2. Effect of catalyst (ZnCl₂, ZrO₂) and their amounts on the reaction times and yields of **4** in EtOH

4	R	R'	ZnCl ₂ 5mol%		ZnCl ₂ 10mol%		ZnCl ₂ 20mol%		ZrO ₂ 5mol%		ZrO ₂ 10mol%		ZrO ₂ 20mol%	
			Time (h)	Yield%	Time(h)	Yield%	Time(h)	Yield%	Time (h)	Yield %	Time (h)	Yield%	Time (h)	Yield%
a	H	Me	13	68	12	88	12	87	13	58	12	76	12	78
b	H	Et	14	64	14	84	14	82	14	55	14	75	14	74
c	H	<i>n</i> -Pr	12	65	12	83	12	85	12	56	12	78	12	77
d	H	<i>i</i> -Pr	14	58	14	78	14	80	14	48	14	72	14	72
e	H	<i>n</i> -Bu	13	63	13	82	13	85	13	55	13	75	13	78
f	H	<i>i</i> -Bu	14	59	14	74	14	76	14	48	14	71	14	74
g	H	PhCH ₂	12	62	12	77	12	78	12	58	12	70	12	72
h	H	Ph(CH ₂) ₂	13	61	13	77	13	77	13	51	13	78	13	75
l	4-NO ₂	Et	14	60	14	65	14	63	14	53	14	60	14	62
k	4-NO ₂	PhCH ₂	14	58	14	70	14	63	14	51	14	57	14	57
j	4-OMe	Et	14	42	14	59	14	55	14	42	14	45	14	48
i	4-OMe	PhCH ₂	14	35	14	47	14	54	14	40	14	50	14	47

7,8-Dihydro-1,7,7-trimethyl-4-phenylquinolin-5(1*H*,4*H*,6*H*)-one (4a): yellow liquid; ν_{\max} (KBr): 3024, 2958 (C-H), 1718 (C=O), 1616, 1551 (C-N) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ_{H} 1.00, 1.12 (6H, 2s, 2CH₃), 2.18-2.20 (2H, d, $J = 7.70$ Hz, 2H₈), 2.40-2.42 (2H, d, $J = 16.02$ Hz, 2H₆), 3.16 (3H, s, CH₃-N), 4.69-4.70 (1H, d, $J = 5.35$ Hz, CH-Ph), 5.07-5.09 (1H, d of d, $J = 8.12$ Hz, $J = 5.35$ Hz, H₃), 5.96-5.98 (1H, d, $J = 8.12$ Hz, H₂), 7.13-7.16, 7.26-7.32 (5H, 2m, aromatic) ppm. $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ_{C} 27.78, 30.46 (2CH₃), 29.71 (CMe₂), 38.46 (CH-Ph), 36.91, 40.32 (2CH₂), 50.30 (CH₃-N), 109.32 (olefinic carbon), 110.01 (olefinic CH), 126.32, 127.96, 128.62, 130.20 (aromatic); 148.19 (=CH-N), 152.72 (=C-N), 195.52 (C=O) ppm; MS: m/z : 267 (M⁺), 252 (M⁺-CH₃), 190 (M⁺-Ph), 175 (M⁺-CH₃, Ph), 77. Anal. Calcd for C₁₈H₂₁NO: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.84; H, 7.95; N, 5.21.

1-Ethyl-7,8-dihydro-7,7-dimethyl-4-phenylquinolin-5(1*H*,4*H*,6*H*)-one (4b): yellow liquid; ν_{\max} (KBr): 3020, 2956 (C-H), 1711 (C=O), 1612, 1552 (C-N) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ_{H} 1.02, 1.14 (6H, 2s, 2CH₃), 1.04 (3H, t, CH₃ of C₂H₅N), 2.17-2.199 (2H, d, $J = 7.72$ Hz, 2H₈), 2.41-2.43 (2H, d, $J = 16.04$ Hz, 2H₆), 3.25-3.29 (2CH₂, q, $J = 7.71$ Hz, CH₂ of C₂H₅N), 4.68-4.69 (1H, d, $J = 5.35$ Hz, CH-Ph), 5.08-5.10 (1H, d of d, $J = 8.13$ Hz, $J = 5.35$ Hz, H₃), 5.97-5.99 (1H, d, $J = 8.13$ Hz, H₂), 7.12-7.15, 7.25-7.31 (5H, 2m, aromatic) ppm. $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ_{C} 21.12, 27.73, 30.15 (3CH₃), 28.97 (CMe₂), 36.74, 40.12 (2CH₂), 38.41 (CH-Ph), 52.32 (CH₂ of C₂H₅N), 109.51 (olefinic carbon), 111.02 (olefinic CH), 126.03, 127.56, 128.42, 129.85 (aromatic), 147.61 (=CH-N), 151.93 (=C-N), 195.23 (C=O) ppm; MS: m/z : 281 (M⁺), 266 (M⁺-CH₃), 204 (M⁺-77), 77, 43. Anal. Calcd for C₁₉H₂₃NO: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.12; H, 8.26; N, 4.95.

7,8-Dihydro-7,7-dimethyl-4-phenyl-1-propylquinolin-5(1*H*,4*H*,6*H*)-one (4c): yellow liquid; ν_{\max} (KBr): 3029, 2960 (C-H), 1716 (C=O), 1616, 1550 (C-N) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ_{H} 0.94, 1.12 (6H, 2s, 2CH₃), 1.01-1.02 (3H, t, CH₃ of propyl), 1.69-1.74 (2H, m, CH₂ of propyl), 2.20-2.22 (2H, d, $J = 7.75$ Hz, 2H₈), 2.42-2.44 (2H, d, $J = 16.02$ Hz, 2H₆), 3.26-3.30, 3.48-3.52 (2H, 2m, CH₂-N), 4.71-4.72 (1H, d, $J = 5.35$ Hz, CH-Ph), 5.10-5.13 (1H, d of d, $J = 8.13$ Hz, $J = 5.35$ Hz, H₃), 6.00-6.02 (1H, d, $J = 8.12$ Hz, H₂), 7.14-7.17, 7.27-7.34 (5H, 2m, aromatic) ppm. $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ_{C} 11.49 (CH₃ of propyl), 24.17 (CH₂ of propyl), 27.72, 30.34 (2CH₃), 30.12 (CMe₂), 37.05, 39.84 (2CH₂), 37.69 (CH-Ph), 52.19 (CH₂-N), 109.39 (olefinic carbon), 110.31 (olefinic CH), 126.29, 127.99, 128.60, 129.12 (aromatic), 147.24 (=CH-N), 151.85 (=C-N), 195.59 (C=O) ppm; MS: m/z : 295 (M⁺), 280 (M⁺-CH₃), 218 (M⁺-Ph), 203 (M⁺-CH₃, Ph), 77, 43. Anal. Calcd for C₂₀H₂₅NO: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.30; H, 8.54; N, 4.77.

7,8-Dihydro-1-isopropyl-7,7-dimethyl-4-phenylquinolin-5(1*H*,4*H*,6*H*)-one (4d): yellow liquid; ν_{\max} (KBr): 3023, 2963 (C-H), 1714 (C=O), 1616, 1556 (C-N) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ_{H} 1.03, 1.14 (6H, 2s, 2CH₃), 1.47-1.56 (6H, 2d, $J = 6.68$ Hz), 2.20-2.22 (2H, d, $J = 7.75$ Hz, 2H₈), 2.40-2.42 (2H, d, $J = 16.03$ Hz, 2H₆), 3.37-3.83 (1H, m, CH-N), 4.58-4.59 (1H, d, $J = 5.35$ Hz, CH-Ph), 5.18-5.20 (1H, d

of d, $J = 8.17$ Hz, $J = 5.35$ Hz, H₃), 5.98-6.01 (1H, d, $J = 8.17$ Hz, H₂), 7.15-7.18, 7.28-7.35 (5H, 2m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ_C 25.16, 25.63 (2CH₃ of *i*-prop), 27.38, 30.16 (2CH₃), 30.23 (CMe₂), 37.13 (CH-Ph), 37.46, 40.05 (2CH₂), 52.25 (CH-N), 110.05 (olefinic carbon), 112.11 (olefinic CH), 126.13, 127.85, 128.76, 129.99 (aromatic), 150.20 (=CH-N), 154.37 (=C-N), 196.02 (C=O) ppm; MS: m/z : 295 (M⁺), 280 (M⁺-CH₃), 218 (M⁺-Ph), 203 (M⁺-Ph, Me), 77, 57. Anal. Calcd for C₂₀H₂₅NO: C, 81.31; H, 8.53; N, 4.74. Found: C, 81.32; H, 8.52; N, 4.77.

1-Butyl-7,8-dihydro-7,7-dimethyl-4-phenylquinolin-5(1H,4H,6H)-one (4e): yellow liquid; ν_{\max} (KBr): 3027, 2959 (C-H), 1717 (C=O), 1615, 1549 (C-N) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ_H 1.01, 1.12 (6H, 2s, 2CH₃), 1.02-1.03 (3H, t, CH₃ of *n*-butyl), 1.41-1.44 (2H, six, CH₂-Me of *n*-butyl), 1.62-1.67 (2H, m, CH₂-Et of *n*-butyl), 2.20-2.23 (2H, d, $J = 7.71$ Hz, 2H₈), 2.41-2.44 (2H, d, $J = 16.07$ Hz, 2H₆), 3.26-3.32, 3.48-3.54 (2H, 2m, CH₂-N), 4.69-4.70 (1H, d, $J = 5.37$ Hz, CH-Ph), 5.09-5.11 (1H, d of d, $J = 8.18$ Hz, $J = 5.37$ Hz, H₃), 5.98-6.00 (1H, d, $J = 8.18$ Hz, H₂), 7.13-7.16, 7.27-7.32 (5H, 2m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): 14.26 (CH₃ of *n*-butyl), 20.27 (CH₂-Me of *n*-butyl), 27.75, 30.12 (2CH₃), 30.32 (CMe₂), 33.06 (CH₂-Et of *n*-butyl), 32.39, 39.81 (2CH₂), 37.03 (CH-Ph), 50.38 (CH₂-N), 109.38 (olefinic carbon), 110.39 (olefinic CH), 126.30, 127.98, 128.59, 129.11 (aromatic), 148.30 (=CH-N), 151.96 (=C-N), 195.61 (C=O) ppm; MS: m/z : 309 (M⁺), 294 (M⁺-CH₃), 232 (M⁺-Ph), 176 (M⁺-Ph, C₄H₈), 77, 57, 41. Anal. Calcd for C₂₁H₂₇NO: C, 81.51; H, 8.79; N, 4.53. Found: C, 81.49; H, 8.78; N, 4.55.

7,8-Dihydro-1-isobutyl-7,7-dimethyl-4-phenylquinolin-5(1H,4H,6H)-one (4f): yellow liquid; ν_{\max} (KBr): 3025, 2958 (C-H), 1711 (C=O), 1616, 1547 (C-N) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ_H 0.99, 1.12 (6H, 2s, 2CH₃), 1.01-1.02, 1.09-1.10 (6H, 2d, $J = 3.96$ Hz, 2CH₃ of *i*-butyl), 1.94-1.99 (1H, m, CH of *i*-butyl), 2.19-2.20 (2H, d, $J = 7.72$ Hz, 2H₈), 2.26-2.28 (2H, d, $J = 16.05$ Hz, 2H₆), 3.00-3.05, 3.38-3.41 (2H, 2 d of d, $J = 14.54$ Hz, $J = 7.54$ Hz, CH₂N), 4.71-4.72 (1H, d, $J = 5.39$ Hz, CH-Ph); 5.07-5.10 (1H, d of d, $J = 7.70$ Hz, $J = 5.39$ Hz, H₃), 5.96-5.98 (1H, d, $J = 7.70$ Hz, H₂); 7.13-7.16, 7.28-7.38 (5H, 2m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ_C 20.26, 20.46 (2CH₃ of *i*-butyl) 27.56, 30.32 (2 CH₃); 30.50 (CMe₂), 32.40 (CH of *i*-butyl), 36.96 (CH-Ph), 38.14, 40.10 (2CH₂), 57.88 (CH-N), 109.20 (olefinic carbon), 109.86 (olefinic CH), 126.29, 127.98, 128.61, 129.74 (aromatic), 148.25 (=CH-N), 152.27 (=C-N), 195.81 (C=O) ppm; MS: m/z : 309 (M⁺), 2294 (M⁺-CH₃), 232 (M⁺-77), 84, 77, 43. Anal. Calcd for C₂₁H₂₇NO: C, 81.51; H, 8.79; N, 4.53. Found: C, 81.50; H, 8.77; N, 4.56.

1-Benzyl-7,8-dihydro-7,7-dimethyl-4-phenylquinolin-5(1H,4H,6H) one (4g): yellow liquid; ν_{\max} (KBr): 3031, 2978 (C-H), 1718 (C=O); 1621, 1563 (C-N) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ_H 0.93, 1.03 (6H, 2s, 2CH₃), 2.22-2.25 (2H, d, $J = 7.75$ Hz, 2H₈), 2.40-2.43 (2H, d, $J = 16.09$ Hz, 2H₆), 4.64 (2H, s, CH₂-Ph), 4.77-4.78 (1H, d, $J = 5.34$ Hz, CH-Ph), 5.14-5.16 (1H, d of d, $J = 7.51$ Hz, $J = 5.34$ Hz, H₃), 6.07-6.08 (1H, d, $J = 7.51$ Hz, H₂), 7.16-7.19, 7.27-7.31, 7.36-7.38, 7.42-7.45 (10H, 4m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ_C 27.93, 29.83 (2 CH₃); 31.98 (CMe₂), 32.49, 39.90 (2CH₂), 37.09 (CH-

Ph), 53.91 (CH₂ of benzyl), 109.33 (olefinic carbon), 110.46 (olefinic CH), 126.39, 126.44, 128.13, 128.18, 128.64, 129.45, 129.75, 137.91 (aromatic), 148.93 (=CH-N), 152.22 (=C-N), 195.88 (C=O) ppm; MS: *m/z*: 343 (M⁺), 328 (M⁺-CH₃), 252 (M⁺-91), 105 (Ph-CH₂N⁺), 91 (PhCH₂⁺), 77. Anal. Calcd for C₂₄H₂₅NO: C, 83.93; H, 7.34; N, 4.08. Found: C, 83.90; H, 7.35; N, 4.10.

7,8-Dihydro-7,7-dimethyl-1-phenethyl-4-phenylquinolin-5(1*H*,4*H*,6*H*) one (4h): yellow liquid; ν_{\max} (KBr): 3038, 2956 (C-H), 1712 (C=O); 1610, 1564 (C-N) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ_{H} 0.83, 1.02 (6H, 2s, 2CH₃), 2.09-2.12 (2H, d, *J* = 7.81 Hz, 2H₈), 2.16-2.18 (2H, d, *J* = 16.01 Hz, 2H₆), 2.91-2.98 (2H, m, -CH₂-Ph), 3.76-3.77, 4.70-4.71 (2H, 2m, CH₂-N), 4.70-4.71 (1H, d, *J* = 5.30 Hz, CH-Ph), 5.12-5.15 (1H, d of d, *J* = 7.25 Hz, *J* = 5.30 Hz, H₃), 6.00-6.01 (1H, d, *J* = 7.25 Hz, H₂), 7.15-7.18, 7.23-7.25, 7.27-7.32, 7.35-7.38 (10H, 4m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ_{C} 27.41, 30.49 (2 CH₃), 31.95 (CMe₂), 32.05, 39.87 (2CH₂), 37.04 (CH₂-benzyl), 37.12 (CH-Ph), 51.72 (CH₂-N), 109.28 (olefinic carbon), 110.77 (olefinic CH), 126.32, 127.42, 128.04, 128.48, 128.58, 129.24, 129.47, 138.12 (aromatic), 148.22 (=CH-N), 151.92 (=C-N), 195.72 (C=O) ppm; MS: *m/z*: 357 (M⁺), 342 (M⁺-CH₃), 280 (M⁺-Ph), 105 (Ph-C₂H₄⁺), 91 (PhCH₂⁺), 77. Anal. Calcd for C₂₅H₂₇NO: C, 83.99; H, 7.61; N, 3.92. Found: C, 83.98; H, 7.60; N, 3.95.

1-Ethyl-7,8-dihydro-7,7-dimethyl-4-(4-nitrophenyl)quinolin-5(1*H*,4*H*,6*H*)-one (4i): orange liquid; ν_{\max} (KBr): 3030, 2968 (C-H), 1722 (C=O), 1616, 1561 (C-N), 1525, 1340 (NO₂) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.04, 1.16 (6H, 2s, 2CH₃), 1.06 (3H, t, CH₃ of C₂H₅N), 2.18-2.21 (2H, d, *J* = 7.85 Hz, 2H₈), 2.42-2.45 (2H, d, *J* = 15.98 Hz, 2H₆), 3.27-3.31 (2CH₂, q, *J* = 8.10 Hz, CH₂ of C₂H₅N), 4.69-4.70 (1H, d, *J* = 5.85 Hz, CH-Ph), 5.21-5.23 (1H, d of d, *J* = 9.01 Hz, *J* = 5.53 Hz, H₃), 6.00-6.02 (1H, d, *J* = 8.15 Hz, H₂), 7.58-7.61, 8.32-8.36 (4H, 2m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ_{C} 21.14, 27.79, 30.28 (3CH₃), 29.01, 32.18 (3CH₃), 31.18 (CMe₂), 37.76, 40.93 (2CH₂), 41.11 (CH-Ph), 52.05 (CH₂ of C₂H₅N), 110.21 (olefinic carbon), 112.51 (olefinic CH), 124.42, 128.19, 129.56, 150.18 (aromatic), 148.63 (=CH-N), 152.98 (=C-N), 196.59 (C=O) ppm; MS: *m/z*: 326 (M⁺), 311 (M⁺-CH₃), 280 (M⁺-NO₂), 265 (M⁺-CH₃, NO₂), 107 (C₆H₅NO⁺), 43. Anal. Calcd for C₁₉H₂₂N₂O₃: C, 69.92; H, 6.7; N, 8.58. Found: C, 69.91; H, 6.78; N, 8.60.

1-Benzyl-7,8-dihydro-7,7-dimethyl-4-(4-nitrophenyl)quinolin-5(1*H*,4*H*,6*H*)-one (4j): orange liquid; ν_{\max} (KBr): 3033, 2972 (C-H), 1727 (C=O), 1617, 1563 (C-N), 1526, 1339 (NO₂) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.04, 1.17 (6H, 2s, 2CH₃), 4.65 (2H, s, CH₂Ph), 4.91-4.92 (1H, d, *J* = 5.38 Hz, CH-Ar), 5.35-5.36 (1H, d of d, *J* = 7.60 Hz, *J* = 5.51 Hz, H₃), 6.16-6.17 (1H, d, *J* = 7.50 Hz, H₂), 7.17-7.19, 7.30-7.32, 7.38-7.43, 8.32-8.36 (9H, 4m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ_{C} 27.15, 32.38, (2CH₃), 31.29 (CMe₂), 37.91, 41.02(2CH₂), 41.83 (CH-Ph), 52.19 (CH₂ of benzyl), 110.31 (olefinic carbon), 112.60 (olefinic CH), 125.00, 126.54, 128.12, 128.36, 128.50, 129.65, 150.47 (aromatic), 148.81 (=CH-N), 153.01 (=C-N), 196.59 (C=O) ppm; MS: *m/z*: 388 (M⁺), 373 (M⁺-CH₃), 297 (M⁺-Ph-CH₂), 91

(PhCH₂⁺), 77, 43. Anal. Calcd for C₂₄H₂₄N₂O₃: C, 74.21; H, 6.23; N, 7.21. Found: C, 74.20; H, 6.21; N, 7.23.

1-Ethyl-7,8-dihydro-4-(4-methoxyphenyl)-7,7-dimethylquinolin-5(1H,4H,6H)-one (4k): light yellow liquid; ν_{\max} (KBr): 3019, 2953 (C-H), 1717 (C=O), 1611, 1550 (C-N), 1211, 1198 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.02, 1.15 (6H, 2s, 2CH₃), 1.05 (3H, t, CH₃ of C₂H₅N), 2.16-2.181 (2H, d, $J = 7.75$ Hz, 2H₈), 2.42-2.44 (2H, d, $J = 15.99$ Hz, 2H₆), 3.25-3.27 (2CH₂, q, $J = 7.65$ Hz, CH₂ of C₂H₅N), 3.79 (3H, s, OCH₃) 4.68 (1H, d, $J = 5.41$ Hz, CH-Ph), 5.09-5.11 (1H, d of d, $J = 8.11$ Hz, $J = 5.34$ Hz, H₃), 5.98-6.00 (1H, d, $J = 8.13$ Hz, H₂), 7.22-7.27, 7.76-7.98 (4H, 2m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ_{C} 21.13, 27.70, 30.11 (3CH₃), 29.95 (CMe₂), 36.75, 40.27 (2CH₂), 38.43 (CH-Ph), 52.36 (CH₂ of EtN), 55.88 (OCH₃), 110.15 (olefinic carbon), 111.49 (olefinic CH), 126.73, 131.26, 131.48, 138.22, 148.75 (aromatic), 147.68 (=CH-N), 151.98 (=C-N), 195.38 (C=O) ppm; MS: m/z : 311 (M⁺), 296 (M⁺-CH₃), 280 (M⁺-OCH₃), 189 (M⁺-CH₃, Ph), 107, 43. Anal. Calcd for C₂₀H₂₅NO₂: C, 77.14; H, 8.09; N, 4.50. Found: C, 77.13; H, 8.10; N, 4.52.

1-Benzyl-7,8-dihydro-4-(4-methoxyphenyl)-7,7-dimethylquinolin-5(1H,4H,6H)-one (4l): yellow liquid; ν_{\max} (KBr): 3029, 2965 (C-H), 1723 (C=O), 1613, 1556 (C-N), 1216, 1199 (C-O) cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ_{H} 1.02, 1.16 (6H, 2s, 2CH₃), 2.17-2.19 (2H, d, $J = 7.70$ Hz, 2 H₈), 2.43-2.45 (2H, d, $J = 15.80$ Hz, 2H₆), 3.01-3.04 (2H, m, CH₂Ph), 3.77-3.79, 4.71-4.72 (2H, 2m, CH₂N), 3.81 (3H, s, OCH₃), 4.65 (1H, d, $J = 5.62$ Hz, H₂, CHPh), 5.08-5.10 (1H, d of d, $J = 8.13$ Hz, $J = 5.60$ Hz, H₃), 5.97-5.99 (1H, d, $J = 8.17$ Hz, H₂), 7.16-7.18, 7.30-7.24, 7.26-7.35, 7.40-7.67-7.99 (9H, 4m, aromatic) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ_{C} 27.93, 30.97 (2CH₃), 31.05 (CMe₂), 36.14, 39.81 (2CH₂), 38.75 (CH-Ph), 51.94 (CH₂-N), 56.91 (OCH₃), 110.26 (olefinic carbon), 112.23 (olefinic CH), 127.43, 128.06, 128.85, 129.24, 131.45, 131.63, 138.43, 149.06 (aromatic), 148.85 (=CH-N), 152.08 (=C-N), 197.01 (C=O) ppm; MS: m/z : 373 (M⁺), 358 (M⁺-CH₃), 342 (M⁺-OCH₃), 266 (M⁺-Ph), 107, 105, 92, 43. Anal. Calcd for C₂₅H₂₇NO₂: C, 80.40; H, 7.29; N, 3.75. Found: C, 80.39; H, 7.27; N, 3.78.

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