HETEROCYCLES, Vol. 85, No. 6, 2012, pp.1447 - 1455. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 18th March, 2012, Accepted, 23rd April, 2012, Published online, 2nd May, 2012
DOI: 10.3987/COM-12-12467

EFFICIENT SYNTHESIS OF *N*-SUBSTITUTED 4-ARYLQUINOLINE DERIVATIVES USING $ZnCl_2$ or ZrO_2

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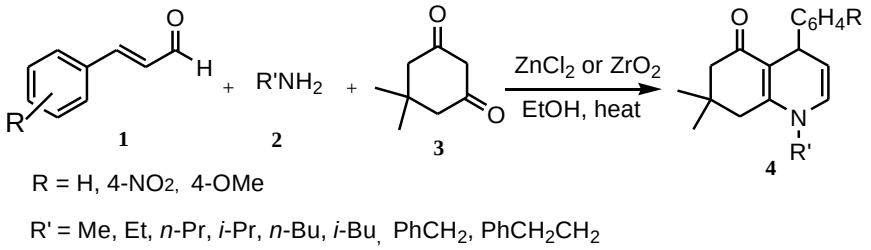
Abstract - *N*-Substituted 7,8-dihydro-7,7-dimethyl-4-arylquinolin-5(1*H*,4*H*,6*H*)-ones **4a-l** have been reported by one-pot reaction of cinnamaldehyde derivatives, dimedone and various amines in the presence of $ZnCl_2$ or ZrO_2 in fairly high yields.

The preparation of 1,4-dihydropridines 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-dihyropyridine derivatives exhibit biological activity.[3-7] The classical methods for the synthesis of 1,4-dihyropyridines almost involved long reaction time, harsh reaction conditions, and use of a large quality 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-dihyropyridine 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-flouro substituted amidines using $ZnCl_2$.[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 $ZnCl_2$, ZrO_2 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 ($PhCH_2CH_2NH_2$) 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-arylylquinoline 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 %)	*p*-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
p-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, $ZnCl_2$ and ZrO_2 have been chosen as the catalyst and EtOH as solvent. The different amounts of $ZnCl_2$ and ZrO_2 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, ^{1}H NMR, ^{13}C NMR and mass spectral data. The mass spectra of these compounds **4a-l** displayed molecular ion peaks at the appropriate *m/z* values. The ^{1}H NMR and ^{13}C 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 ($ZnCl_2$ and ZrO_2) 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. ^{1}H NMR and ^{13}C NMR spectra were determined in $CDCl_3$ 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 ($ZnCl_2$, ZrO_2) 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	*n*-Pr	12	65	12	83	12	85	12	56	12	78	12	77
d	H	*i*-Pr	14	58	14	78	14	80	14	48	14	72	14	72
e	H	*n*-Bu	13	63	13	82	13	85	13	55	13	75	13	78
f	H	*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}; ^1H NMR ($CDCl_3$, 500 MHz): δ_H 1.00, 1.12 (6H, 2s, $2CH_3$), 2.18-2.20 (2H, d, *J* = 7.70 Hz, $2H_8$), 2.40-2.42 (2H, d, *J* = 16.02 Hz, $2H_6$), 3.16 (3H, s, CH_3-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, H_3), 5.96-5.98 (1H, d, *J* = 8.12 Hz, H_2), 7.13-7.16, 7.26-7.32 (5H, 2m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 27.78, 30.46 ($2CH_3$), 29.71 (CMe_2), 38.46 (CH-Ph), 36.91, 40.32 ($2CH_2$), 50.30 (CH_3-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^+-CH_3), 190 (M^+-Ph), 175 (M^+-CH_3, Ph), 77. Anal. Calcd for $C_{18}H_{21}NO$: 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}; ^1H NMR ($CDCl_3$, 500 MHz): δ_H 1.02, 1.14 (6H, 2s, $2CH_3$), 1.04 (3H, t, CH_3 of C_2H_5N), 2.17-2.199 (2H, d, *J* = 7.72 Hz, $2H_8$), 2.41-2.43 (2H, d, *J* = 16.04 Hz, $2H_6$), 3.25-3.29 ($2CH_2$, q, *J* = 7.71 Hz, CH_2 of C_2H_5N), 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, H_3), 5.97-5.99 (1H, d, *J* = 8.13 Hz, H_2), 7.12-7.15, 7.25-7.31 (5H, 2m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 21.12, 27.73, 30.15 ($3CH_3$), 28.97 (CMe_2), 36.74, 40.12 ($2CH_2$), 38.41 (CH-Ph), 52.32 (CH_2 of C_2H_5N), 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^+-CH_3), 204 (M^+-77), 77, 43. Anal. Calcd for $C_{19}H_{23}NO$: 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}; ^1H NMR ($CDCl_3$, 500 MHz): δ_H 0.94, 1.12 (6H, 2s, $2CH_3$), 1.01-1.02 (3H, t, CH_3 of propyl), 1.69-1.74 (2H, m, CH_2 of propyl), 2.20-2.22 (2H, d, *J* = 7.75 Hz, $2H_8$), 2.42-2.44 (2H, d, *J* = 16.02 Hz, $2H_6$), 3.26-3.30, 3.48-3.52 (2H, 2m, CH_2-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, H_3), 6.00-6.02 (1H, d, *J* = 8.12 Hz, H_2), 7.14-7.17, 7.27-7.34 (5H, 2m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 11.49 (CH_3 of propyl), 24.17 (CH_2 of propyl), 27.72, 30.34 ($2CH_3$), 30.12(CMe_2), 37.05, 39.84 ($2CH_2$), 37.69 (CH-Ph), 52.19 (CH_2-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^+-CH_3), 218 (M^+-Ph), 203 (M^+-CH_3, Ph), 77, 43. Anal. Calcd for $C_{20}H_{25}NO$: 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}; ^1H NMR ($CDCl_3$, 500 MHz): δ_H 1.03, 1.14 (6H, 2s, $2CH_3$), 1.47-1.56 (6H, 2d, *J* = 6.68 Hz), 2.20-2.22 (2H, d, *J* = 7.75 Hz, $2H_8$), 2.40-2.42 (2H, d, *J* = 16.03 Hz, $2H_6$), 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, H_3), 5.98-6.01 (1H, d, *J* = 8.17 Hz, H_2), 7.15-7.18, 7.28-7.35 (5H, 2m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 25.16, 25.63 (2CH3 of *i*-prop), 27.38, 30.16 ($2CH_3$), 30.23 (CMe_2), 37.13 (CH-Ph), 37.46, 40.05 ($2CH_2$), 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^+-CH_3), 218 (M^+-Ph), 203 (M^+-Ph, Me), 77, 57. Anal. Calcd for $C_{20}H_{25}NO$: 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(1*H*,4*H*,6*H*)-one (4e): yellow liquid; ν_{max} (KBr): 3027, 2959 (C-H), 1717 (C=O), 1615, 1549 (C-N) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 1.01, 1.12 (6H, 2s, $2CH_3$), 1.02-1.03 (3H, t, CH_3 of *n*-butyl), 1.41-1.44 (2H, six, CH_2-Me of *n*-butyl), 1.62-1.67 (2H, m, CH_2-Et of *n*-butyl), 2.20-2.23 (2H, d, *J* = 7.71 Hz, $2H_8$), 2.41-2.44 (2H, d, *J* = 16.07 Hz, $2H_6$), 3.26-3.32, 3.48-3.54 (2H, 2m, CH_2-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, H_3), 5.98-6.00 (1H, d, *J* = 8.18 Hz, H_2), 7.13-7.16, 7.27-7.32 (5H, 2m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 14.26 (CH_3 of *n*-butyl), 20.27 (CH_2-Me of *n*-butyl), 27.75, 30.12 ($2CH_3$), 30.32 (CMe_2), 33.06 (CH_2-Et of *n*-butyl), 32.39, 39.81 ($2CH_2$), 37.03 (CH-Ph), 50.38 (CH_2-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^+-CH_3), 232 (M^+-Ph), 176 (M^+-Ph, C_4H_8), 77, 57, 41. Anal. Calcd for $C_{21}H_{27}NO$: 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(1*H*,4*H*,6*H*)-one (4f): yellow liquid; ν_{max} (KBr): 3025, 2958 (C-H), 1711 (C=O), 1616, 1547 (C-N) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 0.99, 1.12 (6H, 2s, $2CH_3$), 1.01-1.02, 1.09-1.10 (6H, 2d, *J* = 3.96 Hz, $2CH_3$ of *i*-butyl), 1.94-1.99 (1H, m, CH of *i*-butyl), 2.19-2.20 (2H, d, *J* = 7.72 Hz, $2H_8$), 2.26-2.28 (2H, d, *J* = 16.05 Hz, $2H_6$), 3.00-3.05, 3.38-3.41 (2H, 2 d of d, *J* = 14.54 Hz, *J* = 7.54 Hz, CH_2N), 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, H_3), 5.96-5.98 (1H, d, *J* = 7.70 Hz, H_2); 7.13-7.16, 7.28-7.38 (5H, 2m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 20.26, 20.46 ($2CH_3$ of *i*-butyl) 27.56, 30.32 (2 CH_3); 30.50 (CMe_2), 32.40 (CH of *i*-butyl), 36.96 (CH-Ph), 38.14, 40.10 ($2CH_2$), 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^+-CH_3), 232 (M^+-77), 84, 77, 43. Anal. Calcd for $C_{21}H_{27}NO$: 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(1*H*,4*H*,6*H*) one (4g): yellow liquid; ν_{max} (KBr): 3031, 2978 (C-H), 1718 (C=O); 1621, 1563 (C-N) cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H 0.93, 1.03 (6H, 2s, $2CH_3$), 2.22-2.25 (2H, d, *J* = 7.75 Hz, $2H_8$), 2.40-2.43 (2H, d, *J* = 16.09 Hz, $2H_6$), 4.64 (2H, s, CH_2-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, H_3), 6.07-6.08 (1H, d, *J* = 7.51 Hz, H_2), 7.16-7.19, 7.27-7.31, 7.36-7.38, 7.42-7.45 (10H, 4m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 27.93, 29.83 (2 CH_3); 31.98 (CMe_2), 32.49, 39.90 ($2CH_2$), 37.09 (CH-

Ph), 53.91 (CH_2 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^+-CH_3), 252 (M^+-91), 105 (Ph-CH_2N^+), 91 ($PhCH_2^+$), 77. Anal. Calcd for $C_{24}H_{25}NO$: 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 ($CDCl_3$, 500 MHz): δ_H 0.83, 1.02 (6H, 2s, $2CH_3$), 2.09-2.12 (2H, d, *J* = 7.81 Hz, $2H_8$), 2.16-2.18 (2H, d, *J* = 16.01 Hz, $2H_6$), 2.91-2.98 (2H, m, -CH_2-Ph), 3.76-3.77, 4.70-4.71 (2H, 2m, CH_2-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, H_3), 6.00-6.01 (1H, d, *J* = 7.25 Hz, H_2), 7.15-7.18, 7.23-7.25, 7.27-7.32, 7.35-7.38 (10H, 4m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 27.41, 30.49 (2 CH_3), 31.95 (CMe_2), 32.05, 39.87 ($2CH_2$), 37.04 (CH_2-benzyl), 37.12 (CH-Ph), 51.72 (CH_2-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^+-CH_3), 280 (M^+-Ph), 105 (Ph-$C_2H_4^+$), 91 ($PhCH_2^+$), 77. Anal. Calcd for $C_{25}H_{27}NO$: 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 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ_H 1.04, 1.16 (6H, 2s, $2CH_3$), 1.06 (3H, t, CH_3 of C_2H_5N), 2.18-2.21 (2H, d, *J* = 7. 85 Hz, $2H_8$), 2.42-2.45 (2H, d, *J* = 15.98 Hz, $2H_6$), 3.27-3.31 ($2CH_2$, q, *J* = 8.10 Hz, CH_2 of C_2H_5N), 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* = 5.53Hz, H_3), 6.00-6.02 (1H, d, *J* = 8.15 Hz, H_2), 7.58-7.61, 8.32-8.36 (4H, 2m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 21.14, 27.79, 30.28 ($3CH_3$), 29.01, 32.18 ($3CH_3$), 31.18 (CMe_2), 37.76, 40.93 ($2CH_2$), 41.11 (CH-Ph), 52.05 (CH_2 of C_2H_5N), 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^+-CH_3), 280 (M^+-NO_2), 265 (M^+-CH_3, NO_2), 107 ($C_6H_5NO^+$), 43. Anal. Calcd for $C_{19}H_{22}N_2O_3$: 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 (NO_2) cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ_H 1.04, 1.17 (6H, 2s, $2CH_3$), 4.65 (2H, s, CH_2Ph), 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, H_3), 6.16-6.17 (1H, d, *J* = 7.50 Hz, H_2), 7.17-7.19, 7.30-7.32, 7.38-7.43, 8.32-8.36 (9H, 4m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 27.15, 32.38, ($2CH_3$), 31.29 (CMe_2), 37.91, 41.02($2CH_2$), 41.83 (CH-Ph), 52.19 (CH_2 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^+-CH_3), 297 (M^+-Ph-CH_2), 91

($PhCH_2^+$), 77, 43. Anal. Calcd for $C_{24}H_{24}N_2O_3$: 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(1*H*,4*H*,6*H*)-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 ($CDCl_3$, 500 MHz): δ_H 1.02, 1.15 (6H, 2s, $2CH_3$), 1.05 (3H, t, CH_3 of C_2H_5N), 2.16-2.181 (2H, d, *J* = 7.75 Hz, $2H_8$), 2.42-2.44 (2H, d, *J* = 15.99 Hz, $2H_6$), 3.25-3.27 ($2CH_2$, q, *J* = 7.65 Hz, CH_2 of C_2H_5N), 3.79 (3H, S, OCH_3) 4.68 (1H, d, *J* = 5.41 Hz, CH-Ph), 5.09-5.11 (1H, d of d, *J* = 8.11 Hz, *J* = 5.34Hz, H_3), 5.98-6.00 (1H, d, *J* = 8.13 Hz, H_2), 7.22-7.27, 7.76-7.98 (4H, 2m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 21.13, 27.70, 30.11 ($3CH_3$), 29.95 (CMe_2), 36.75, 40.27 ($2CH_2$), 38.43 (CH-Ph), 52.36 (CH_2 of EtN), 55.88 (OCH_3),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^+-CH_3), 280 (M^+-OCH_3), 189(M^+-CH_3, Ph), 107, 43. Anal. Calcd for $C_{20}H_{25}NO_2$: 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(1*H*,4*H*,6*H*)-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 ($CDCl_3$, 500 MHz): δ_H 1.02, 1.16 (6H, 2s, $2CH_3$), 2.17-2.19 (2H, d, *J* = 7.70 Hz, 2 $H_{8)}$, 2.43-2.45 (2H, d, *J* = 15.80 Hz, $2H_6$), 3.01-3.04 (2H, m, CH_2Ph), 3.77-3.79, 4.71-4.72 (2H, 2m, CH_2N), 3.81 (3H, S, OCH_3), 4.65 (1H, d, *J* = 5.62 Hz, H_2, CHPh), 5.08-5.10 (1H, d of d, *J* = 8.13 Hz, *J* = 5.60 Hz, H_3), 5.97-5.99 (1H, d, *J* = 8.17 Hz, H_2), 7.16-7.18, 7.30-7.24, 7.26-7.35, 7.40-7.67-7.99 (9H, 4m, aromatic) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ_C 27.93, 30.97 ($2CH_3$), 31.05 (CMe_2), 36.14, 39.81 ($2CH_2$), 38.75 (CH-Ph), 51.94 (CH_2-N), 56.91 (OCH_3), 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^+-CH_3), 342 (M^+-OCH_3), 266 (M^+-Ph), 107, 105, 92, 43. Anal. Calcd for $C_{25}H_{27}NO_2$: C, 80.40; H, 7.29; N, 3.75. Found: C, 80.39; H, 7.27; N, 3.78.

ACKNOWLEDGEMENTS

We wish to thank the Iran National Science Foundation (INSF) for the financial support.

REFERENCES

1. A. Hantzch, *Chem. Ber.*, 1881, **14**, 1637.
2. L. M. Wang, J. Sheng, L. Zhang, J. W. Han, Z. Y. Fan, H. Tion, and C. T. Qian, *Tetrahedron*, 2005, **61**, 1539.
3. M. Khoshneviszadeh, N. Edraki, K. Javidnia, A. Alborzi, B. Pourabbas, J. Mardaneh, and R. Miri, *Bioorg. Med. Chem.*, 2009, **17**, 1579.

4. T. Li, X. Feng, C. Yao, C. Yu, B. Jiang, and S. Tu, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 453.
5. L. Bazargan, S. Fouladdel, A. Shafiee, M. Amini, S. M. Ghaffari, and E. Azizi, *Cell. Biol. Toxicol.*, 2008, **24**, 165.
6. I. O. Donkor, X. Zhou, J. Schmidt, K. C. Agrwal, and V. Kishore, *Bioorg. Med. Chem.*, 1998, **6**, 563.
7. F. Cateni, M. Zacchigna, N. Pedemonte, L. J. V. Galietta, M. T. Mazzei, P. Fossa, M. Giampieri, and M. Mazzie, *Bioorg. Med. Chem.*, 2009, **17**, 7894.
8. V. Sivamurugan, A. Vinu, M. Palanichamy, and V. Murugesan, *Heteroatom Chem.*, 2006, **17**, 267.
9. Y. M. Wu, M. Zhang, and Y. Q. Li, *J. Fluorine Chem.*, 2005, **126**, 791.
10. J. Moreau, A. Duboc, C. Hubert, J. P. Hurvios, and J. L. Renaud, *Tetrahedron Lett.*, 2007, **48**, 8647.
11. A. Zonouzi, H. Rahmani, M. Biniaz, Z. Izakian, and S. W. Ng, *J. Chem. Res.*, 2011,412.
12. A. Zonouzi, H. Rahmani, A. Kamali, and M. Biniaz, *Org. Prep. Proced. Int.*, 2011, **43**, 276.
13. A. Zonouzi, M. Biniaz, R. Mirzazadeh, M. Talebi, and S. W. Ng, *Heterocycles*, 2010, **81**, 1271.
14. A. Zonouzi, R. Mirzazadeh, M. Talebi, R. Jafarypoor, A. Peivandi, and S. W. Ng, *Heterocycles*, 2010, **81**, 2131.
15. X.-C. Wang, Y. Eie, Y.-X. Da, Z. Zhang, and Z.-J. Quan, *Heterocycles*, 2011, **83**, 2811.
16. A. Zonouzi, Z. Izakian, and S. W. Ng, *Acta Cryst.*, 2011, **E67**, 2337.