Study of the Catalytic Activity of $Zr(HPO_4)_2$ in the Synthesis of Hexahydroquinoline Derivatives under Solvent-free Conditions

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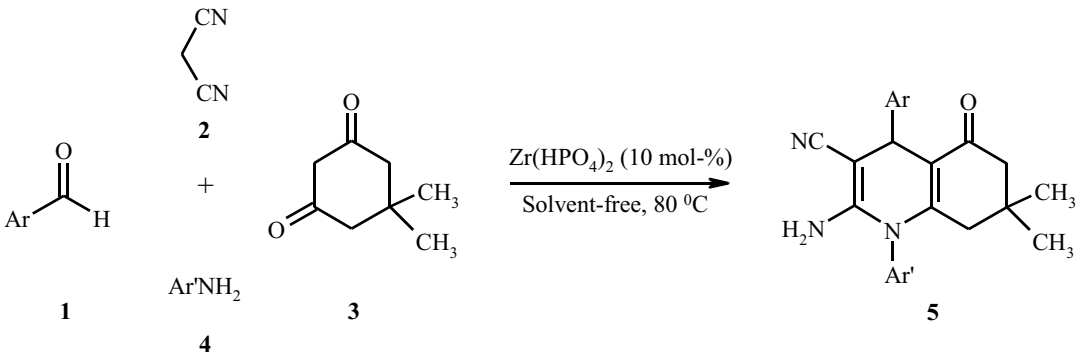
2-Amino-7,7-dimethyl-5-oxo-1,4-diaryl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile derivatives were synthesized by the one-pot four-component reaction of aromatic aldehydes, malononitrile, dimedone and arylamines in the presence of $Zr(HPO_4)_2{\cdot}H_2O$ (α-ZrP) as an effective and recyclable solid acid catalyst, in high yields.

Key words: Acidic Salts, Green Method, Hexahydroquinoline-3-carbonitrile, Solvent-free, $Zr(HPO_4)_2$

Introduction

The quinoline core structure is an important heterocyclic feature that can be found in numerous biologically active componds which exhibit a vast range of pharmacological properties such as antimalarial [1], antibacterial [2], antimicrobial [3], and anti-staphylococcal activities [4]. Meanwhile, an important class of antibiotics possesses a 4-quinolone framework in their structure [5], and also several 2,4-disubstituted polyhydroquinolines exhibit promising *in vivo* antihyperglycemic activity [6].

Recently, inorganic acidic salts have attracted the attention of researchers in organic surface chemistry, due to their low toxicity, moisture stability, ready availability at low cost, enhancement of reaction rates and eco-friendly nature. In general, these mineral salts as heterogeneous catalysts offer higher surface area and more acidic sites, which are responsible for the higher catalytic activity. The application of these acidic salts as heterogeneous catalysts in synthetic methodology has been reviewed briefly [7 – 12]. Tetravalent metal hydrogenphosphates, mainly zirconium hydrogenphosphate, are types of layered multifunctional materials which can be used as ion exchangers [13 – 15], catalysts or catalyst supports [16], adsorbents and absorbents [17], because of their chemical and thermal stability as



Scheme 1.

well as high specific surface area [18 – 23]. In this regard, we envisaged the application of zirconium hydrogenphosphate $Zr(HPO_4)_2{\cdot}H_2O$ (α-ZrP) with a layered structure, as a mild acidic catalyst in a four-component coupling reaction of aromatic aldehydes **1**, malononitrile (**2**), dimedone (**3**), and arylamines **4**, for the synthesis of 2-amino-1,4-diaryl-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitriles **5a – i** under solvent-free conditions (Scheme 1).

In view of the biological significance of quinoline heterocyclic systems, many synthetic protocols for the synthesis of these componds have been developed [24]. However, despite the potential utility of the methods published so far, our new approach reported herein provides a noticeable improvement, as this is the first time that a four-component reaction is employed for the synthesis of hexahydroquinoline-3-carbonitrile derivatives catalyzed in a very efficient manner by α-ZrP.

Results and Discussion

As part of our current studies on the development of new and green methods for the preparation of heterocyclic compounds [25 – 29], herein, we describe a convenient, simple and clean procedure to 2-amino-1,4-diaryl-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile **5** by the four-component coupling reaction in the presence of a catalytic amount of α-ZrP at 80 °C, under solvent-free conditions.

For optimization of the reaction conditions, compound **5a** was synthesized in various reaction media. As shown in Table 1, the best result was obtained under solvent-free conditions (Table 1, entries 1 – 4). It was established that the effective amount of catalyst is just 10 mol-% of α-ZrP. Furtheremore, in the absence of α-ZrP the yield of product was only 24 % after 8 h (Table 1, entries 1 and 5 – 7). The experimental conditions for the synthesis of **5a** were also explored at different temperatures. In general, the yield of product was significantly improved at 80 °C. However, further increase of the temperature above 80 °C failed to improve the yield of product (Table 1, entries 1 and 8 – 9).

Subsequently, this method was extended to benzaldehydes with different substituents and various arylamines to produce the corresponding products in high to excellent yields. The results are summarized in Table 2.

To the best of our knowledge, $Zr(HPO_4)_2$ behaves as an acid catalyst. Although the nature of its acidic sites is unclear, a mechanism for the formation of compound **5** is suggested in Scheme 2. It is reasonable to assume

Table 1. Synthesis of **5a** under different conditions.

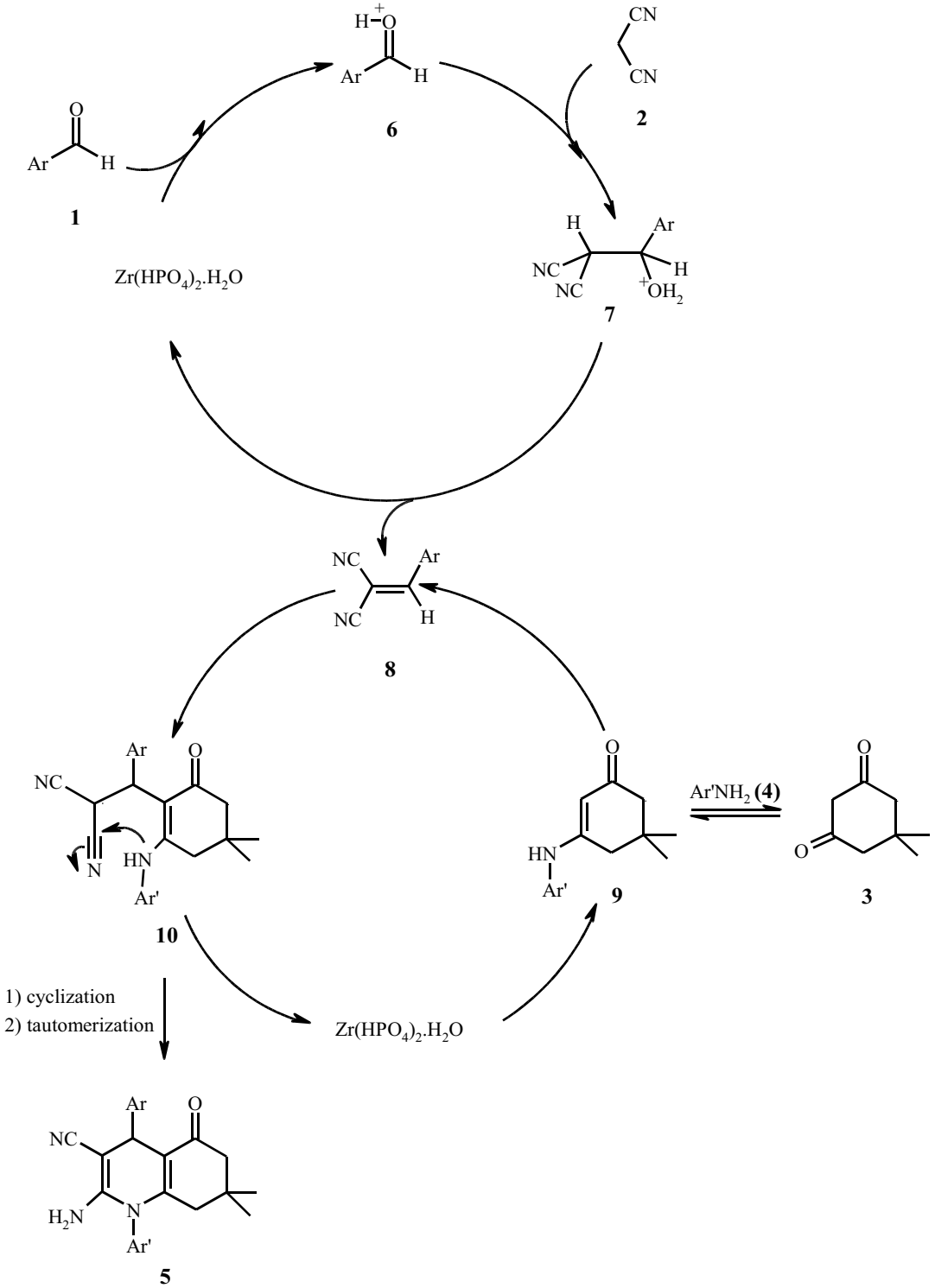
Entry	Catalyst (mol-%)	Solvent	Temp. (°C)	Time (h)	Yield (%)[a]
1	α-ZrP (10 %)	none	80	2	98
2	α-ZrP (10 %)	CH_2Cl_2	70	6	51
3	α-ZrP (10 %)	DMF	100	5	53
4	α-ZrP (10 %)	EtOH/H_2O	90	6	64
5	no catalyst	none	80	8	24
6	α-ZrP (5 %)	none	80	4	55
7	α-ZrP (15 %)	none	80	2	97
8	α-ZrP (10 %)	none	70	2	68
9	α-ZrP (10 %)	none	90	2	96

[a] Isolated yield.

Table 2. Synthesis of hexahydroquinoline-3-carbonitrile derivatives **5a – i** under solvent-free conditions at 80 °C using $Zr(HPO_4)_2$ as catalyst.

Product	Ar	Ar′	Yield (%)[a,b]	M. p. (°C)	
				obs.	Lit.
5a	4-BrC_6H_4	C_6H_5	98	277 – 279	275 – 277 [25]
5b	4-BrC_6H_4	4-BrC_6H_4	97	275 – 276	276 – 278 [25]
5c	4-BrC_6H_4	4-$CH_3C_6H_4$	98	259 – 261	261 – 263 [25]
5d	3,4-$Cl_2C_6H_3$	4-BrC_6H_4	96	279 – 281	277 – 279 [25]
5e	3,4-$Cl_2C_6H_3$	4-$CH_3C_6H_4$	98	269 – 271	270 – 272 [25]
5f	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	96	250 – 252	252 – 254 [25]
5g	3-$NO_2C_6H_4$	C_6H_5	97	268 – 270	268 – 269 [25]
5h	3-$NO_2C_6H_4$	4-BrC_6H_4	95	271 – 272	271 – 274 [25]
5i	3-$NO_2C_6H_4$	4-$CH_3C_6H_4$	98	279 – 280	281 – 283 [25]

[a] Yields refer to those of pure isolated products characterized by ^{1}H NMR spectroscopic data and elemental analysis; [b] in all cases, the reaction mixture was kept with stirring for 2 hours.


Ar
H
O
1
6
2
CN
CN
Zr(HPO4)2.H2O
H
Ar
NC
NC
H
+OH2
7
NC
Ar
NC
H
8
Ar
O
NC
N
HN
Ar'
10
1) cyclization
2) tautomerization
Zr(HPO4)2.H2O
O
HN
Ar'
9
Ar'NH2 (4)
O
O
3
Ar
O
NC
H2N
N
Ar'
5

Scheme 2.

that $Zr(HPO_4)_2$ catalyzes the formation of carbocation **6** which then undergoes a Knoevenagel condensation with malononitrile (**2**), which produces alkene **8** *via* intermediate **7**. The enamine **9**, which is obtained from the reaction of dimedone (**3**) and aryl amine **4**, adds to alkene **8** to produce the Michael adduct **10**. Intramolecular cyclization of **10** gives product **5** after tautomerization.

Conclusion

In summary, we have reported a novel green method for the synthesis of 2-amino-1,4-diaryl-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitriles *via* a one-pot four-component reaction of aromatic aldehydes, malononitrile, dimedone and arylamines, catalyzed by α-ZrP. Compared to known methods, this procedure provides noteworthy features and benefits, as $Zr(HPO_4)_2$ is not toxic or expensive, and work-up is simple. High yields and an improvement of the bond forming efficiency (BFE) and atom economy are other major advantages.

Experimental Section

Materials and methods

All of the chemical materials used in this work were purchased from Merck and used without further purification. Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker DRX-500 Avance instrument at 500 MHz, using TMS as internal standard and [D_6]DMSO as solvent. Elemental analyses were carried out using a Heraeus CHN rapid analyzer.

*General procedure for preparation of compounds **5a–g***

A mixture of aromatic aldehyde (**1**, 1 mmol), malononitrile (**2**, 1 mmol), dimedone (**3**, 1 mmol), arylamine (**4**, 1 mmol), and α-ZrP (30.1 mg, 10 mol-%) was stirred at 80 °C for 2 h. After completion of the reaction (TLC), H_2O (20 mL) was added and the mixture and filtered. The residue was washed with aqueous ethanol to generate the pure product. The filtrate was recovered for reuse by drying at 80 °C for several hours in a vacuum.

*2-Amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-1-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5a**)*

Yellow solid, yield: 0.439 g (98 %). – ^{1}H NMR: $\delta = 0.74$ (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 1.68 (d, 1 H, $^2J_{HH} = 17.4$ Hz, CH), 2.01 (d, 1 H, $^2J_{HH} = 16.0$ Hz, CH), 2.21 (d, 2 H, $^2J_{HH} = 16.7$ Hz, 2 CH), 4.45 (s, 1 H, H-4), 5.40 (s, 2 H, NH_2), 7.24 (d, 2 H, $^3J_{HH} = 8.1$ Hz, H_{Ar}), 7.39 (d, 2 H, $^3J_{HH} = 6.5$ Hz, H_{Ar}), 7.52 (d, 2 H, $^3J_{HH} = 8.1$ Hz, H_{Ar}), 7.61 (m, 3 H, H_{Ar}). – Anal. for $C_{24}H_{22}BrN_3O$ (448.36): calcd. C 64.29, H 4.95, N 9.37; found C 64.17, H 5.13, N 9.50 %.

*2-Amino-1,4-bis(4-bromophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5b**)*

Pale-yellow solid, yield: 0.511 g (97 %). – ^{1}H NMR: $\delta = 0.74$ (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 1.70 (d, 1 H, $^2J_{HH} = 17.2$ Hz, CH), 2.00 (d, 1 H, $^2J_{HH} = 16.0$ Hz, CH), 2.20 (d, 1 H, $^2J_{HH} = 16.0$ Hz, CH), 2.22 (d, 1 H, $^2J_{HH} = 17.2$ Hz, CH), 4.43 (s, 1 H, H-4), 5.58 (s, 2 H, NH_2), 7.24 (t, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.37 (t, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.50 (d, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.75 (d, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}). – Anal. for $C_{24}H_{21}Br_2N_3O$ (527.26): calcd. C 54.67, H 4.01, N 7.97; found C 54.61, H 3.93, N 8.06 %.

*2-Amino-4-(4-bromophenyl)-7,7-dimethyl-1-(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5c**)*

Pale-yellow solid, yield: 0.453 g (98 %). – ^{1}H NMR: $\delta = 0.73$ (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 1.72 (d, 1 H, $^2J_{HH} = 17.4$ Hz, CH), 1.99 (d, 1 H, $^2J_{HH} = 16.2$ Hz, CH), 2.19 (m, 2 H, 2 CH), 2.40 (s, 3 H, CH_3), 4.44 (s, 1 H, H-4), 5.37 (s, 2 H, NH_2), 7.24 (t, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.27 (t, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.41 (d, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.51 (d, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}). – Anal. for $C_{25}H_{24}BrN_3O$ (462.39): calcd. C 64.94, H 5.23, N 9.09; found C 64.99, H 5.28, N 9.16 %.

*2-Amino-1-(4-bromophenyl)-4-(3,4-dichlorophenyl)-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5d**)*

Pale-yellow solid, yield: 0.497 g (96 %). – ^{1}H NMR: $\delta = 0.73$ (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 1.74 (d, 1 H, $^2J_{HH} = 17.0$ Hz, CH), 2.01 (d, 1 H, $^2J_{HH} = 16.1$ Hz, CH), 2.19 (d, 2 H, $^2J_{HH} = 16.2$ Hz, 2 CH), 4.50 (s, 1 H, H-4), 5.63 (s, 2 H, NH_2), 7.28 (dd, 1 H, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 2.0$ Hz, H_{Ar}), 7.36 (t, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.42 (d, 1 H, $^4J_{HH} = 2.0$ Hz, H_{Ar}), 7.59 (d, 1 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.77 (d, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}). – Anal. for $C_{24}H_{20}BrCl_2N_3O$ (517.25): calcd. C 55.73, H 3.90, N 8.12; found C 55.81, H 3.97, N 8.21 %.

*2-Amino-4-(3,4-dichlorophenyl)-7,7-dimethyl-1-(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5e**)*

Pale-yellow solid, yield: 0.443 g (98 %). – ^{1}H NMR: $\delta = 0.73$ (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 1.74 (d, 1

H, $^2J_{HH} = 17.5$ Hz, CH), 2.01 (d, 1 H, $^2J_{HH} = 16.1$ Hz, CH), 2.17 (d, 1 H, $^2J_{HH} = 16.1$ Hz, CH), 2.20 (d, 1 H, $^2J_{HH} = 17.5$ Hz, CH), 2.40 (s, 3 H, CH_3), 4.51 (s, 1 H, H-4), 5.42 (s, 2 H, NH_2), 7.28 (m, 3 H, H_{Ar}), 7.39 (d, 2 H, $^3J_{HH} = 8.5$ Hz, H_{Ar}), 7.43 (d, 1 H, $^4J_{HH} = 2.0$ Hz, H_{Ar}), 7.60 (d, 1 H, $^3J_{HH} = 8.5$ Hz, H_{Ar}). – Anal. for $C_{25}H_{23}Cl_2N_3O$ (452.38): calcd. C 66.38, H 5.12, N 9.29; found C 66.29, H 5.06, N 9.36 %.

*2-Amino-7,7-dimethyl-1,4-bis(4-methylphenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5f**)*

Pale-yellow solid, yield: 0.382 g (96 %). – ^{1}H NMR: $\delta = 0.74$ (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 1.74 (d, 1 H, $^2J_{HH} = 17.5$ Hz, CH), 1.99 (d, 1 H, $^2J_{HH} = 16.1$ Hz, CH), 2.17 (s, 3 H, CH_3), 2.18 (d, 1 H, $^2J_{HH} = 16.1$ Hz, CH), 2.20 (d, 1 H, $^2J_{HH} = 17.5$ Hz, CH), 2.40 (s, 3 H, CH_3), 4.40 (s, 1 H, H-4), 5.25 (s, 2 H, NH_2), 7.13 (d, 2 H, $^3J_{HH} = 8.0$ Hz, H_{Ar}), 7.16 (d, 2 H, $^3J_{HH} = 8.0$ Hz, H_{Ar}), 7.24 (d, 2 H, $^3J_{HH} = 8.0$ Hz, H_{Ar}), 7.40 (d, 2 H, $^3J_{HH} = 8.0$ Hz, H_{Ar}). – Anal. for $C_{26}H_{27}N_3O$ (397.52): calcd. C 78.56, H 6.85, N 10.57; found C 78.64, H 6.91, N 10.66 %.

*2-Amino-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-1-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5g**)*

Yellow solid, yield: 0.402 g (97 %). – ^{1}H NMR: $\delta = 0.73$ (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 1.74 (d, 1 H, $^2J_{HH} = 17.5$ Hz, CH), 2.01 (d, 1 H, $^2J_{HH} = 16.0$ Hz, CH), 2.22 (d, 1 H, $^2J_{HH} = 16.0$ Hz, CH), 2.23 (d, 1 H, $^2J_{HH} = 17.5$ Hz, CH), 4.65 (s, 1 H, H-4), 5.54 (s, 2 H, NH_2), 7.42 (d, 2 H, $^3J_{HH} = 6.8$ Hz, H_{Ar}), 7.59 (m, 4 H, H_{Ar}), 7.80 (d, 1 H, $^3J_{HH} = 7.5$ Hz, H_{Ar}), 8.10 (m, 2 H, H_{Ar}). – Anal. for $C_{24}H_{22}N_4O_3$ (414.46): calcd. C 69.55, H 5.35, N 13.52; found C 69.68, H 5.27, N 13.59 %.

*2-Amino-1-(4-bromophenyl)-7,7-dimethyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5h**)*

Pale-yellow solid, yield: 0.469 g (95 %). – ^{1}H NMR: $\delta = 0.74$ (s, 3 H, CH_3), 0.90 (s, 3 H, CH_3), 1.75 (d, 1 H, $^2J_{HH} = 17.4$ Hz, CH), 2.01 (d, 1 H, $^2J_{HH} = 16.1$ Hz, CH), 2.16 (d, 1H, $^2J_{HH} = 16.1$ Hz, CH),), 2.26 (d, 1 H, $^2J_{HH} = 17.4$ Hz, CH), 4.62 (s, 1 H, H-4), 5.73 (s, 2 H, NH_2), 7.38 (dd, 2 H, $^3J_{HH} = 8.2$ Hz, H_{Ar}), 7.67 (m, 1 H, H_{Ar}), 7.80 (m, 3 H, H_{Ar}), 8.09 (m, 2 H, H_{Ar}). – Anal. for $C_{24}H_{21}BrN_4O_3$ (493.36): calcd. C 58.43, H 4.29, N 11.36; found C 58.51, H 4.14, N 11.28 %.

*2-Amino-7,7-dimethyl-1-(4-methylphenyl)-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (**5i**)*

Pale-yellow solid, yield: 0.420 g (98 %). – ^{1}H NMR: $\delta = 0.74$ (s, 3 H, CH_3), 0.94 (s, 3 H, CH_3), 1.75 (d, 1 H, $^2J_{HH} = 17.5$ Hz, CH), 2.01 (d, 1 H, $^2J_{HH} = 16.1$ Hz, CH), 2.21 (d, 1 H, $^2J_{HH} = 16.1$ Hz, CH), 2.23 (d, 1 H, $^2J_{HH} = 17.5$ Hz, CH), 2.40 (s, 3 H, CH_3), 4.65 (s, 1 H, H-4), 5.52 (s, 2 H, NH_2), 7.28 (d, 2 H, $^4J_{HH} = 7.5$ Hz, H_{Ar}), 7.43 (d, 2 H, $^3J_{HH} = 7.5$ Hz, H_{Ar}), 7.68 (m, 1 H, H_{Ar}), 7.76 (d, 1 H, $^3J_{HH} = 7.5$ Hz, H_{Ar}), 8.09 (m, 2 H, H_{Ar}). – Anal. for $C_{25}H_{24}N_4O_3$ (428.49): calcd. C 70.08, H 5.65, N 13.08; found C 70.21, H 5.53, N 12.96 %.

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