

Study of the Catalytic Activity of $\text{Zr}(\text{HPO}_4)_2$ in the Synthesis of Hexahydroquinoline Derivatives under Solvent-free Conditions

Shahrzad Abdolmohammadi

Department of Chemistry, Faculty of Science, East Tehran Branch, Islamic Azad University,
P. O. Box 33955-163, Tehran, I. R. Iran

Reprint requests to Dr. Shahrzad Abdolmohammadi. Tel: +98-21-3359 4950. Fax: +98-21-3359 4332. E-mail: abdolmohammadi.sh@yahoo.com or sabdolmohammadi@qdiau.ac.ir

Z. Naturforsch. **2013**, *68b*, 195 – 200 / DOI: 10.5560/ZNB.2013-2237

Received August 27, 2012

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 $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (α -ZrP) as an effective and recyclable solid acid catalyst, in high yields.

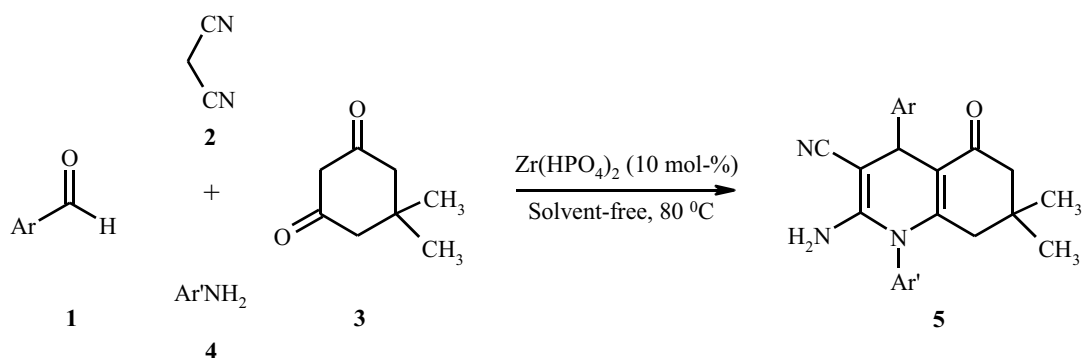
Key words: Acidic Salts, Green Method, Hexahydroquinoline-3-carbonitrile, Solvent-free, $\text{Zr}(\text{HPO}_4)_2$

Introduction

The quinoline core structure is an important heterocyclic feature that can be found in numerous biologically active compounds 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 chem-

istry, 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(HPO₄)₂·H₂O (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 compounds 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. Furthermore, 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(HPO₄)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

Entry	Catalyst (mol-%)	Solvent	Temp. (°C)	Time (h)	Yield (%) ^a
1	α -ZrP (10%)	none	80	2	98
2	α -ZrP (10%)	CH ₂ Cl ₂	70	6	51
3	α -ZrP (10%)	DMF	100	5	53
4	α -ZrP (10%)	EtOH/H ₂ O	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

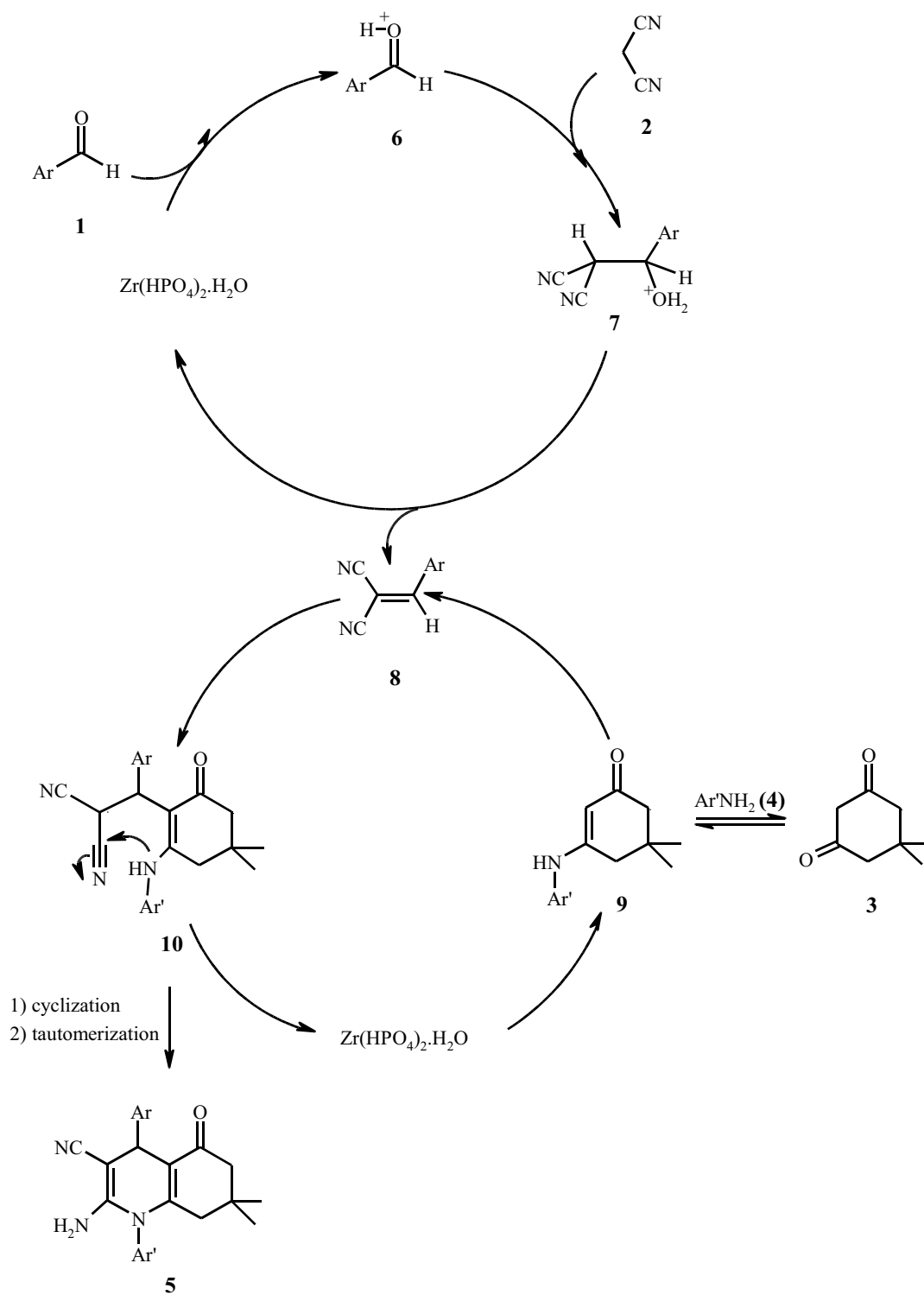
^a Isolated yield.

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

Product	Ar	Ar'	Yield (%) ^{a,b}	M. p. (°C)	
				obs.	Lit.
5a	4-BrC ₆ H ₄	C ₆ H ₅	98	277–279	275–277 [25]
5b	4-BrC ₆ H ₄	4-BrC ₆ H ₄	97	275–276	276–278 [25]
5c	4-BrC ₆ H ₄	4-CH ₃ C ₆ H ₄	98	259–261	261–263 [25]
5d	3,4-Cl ₂ C ₆ H ₃	4-BrC ₆ H ₄	96	279–281	277–279 [25]
5e	3,4-Cl ₂ C ₆ H ₃	4-CH ₃ C ₆ H ₄	98	269–271	270–272 [25]
5f	4-CH ₃ C ₆ H ₄	4-CH ₃ C ₆ H ₄	96	250–252	252–254 [25]
5g	3-NO ₂ C ₆ H ₄	C ₆ H ₅	97	268–270	268–269 [25]
5h	3-NO ₂ C ₆ H ₄	4-BrC ₆ H ₄	95	271–272	271–274 [25]
5i	3-NO ₂ C ₆ H ₄	4-CH ₃ C ₆ H ₄	98	279–280	281–283 [25]

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

Table 2. Synthesis of hexahydroquinoline-3-carbonitrile derivatives **5a–i** under solvent-free conditions at 80 °C using Zr(HPO₄)₂ as catalyst.



Scheme 2.

that Zr(HPO₄)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(HPO₄)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. ¹H NMR spectra were recorded on a Bruker DRX-500 Avance instrument at 500 MHz, using TMS as internal standard and [D₆]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), H₂O (20 mL) was added and the mixture was 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 %). – ¹H NMR: δ = 0.74 (s, 3 H, CH₃), 0.87 (s, 3 H, CH₃), 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, NH₂), 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 C₂₄H₂₂BrN₃O (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 %). – ¹H NMR: δ = 0.74 (s, 3 H, CH₃), 0.87 (s, 3 H, CH₃), 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, NH₂), 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 C₂₄H₂₁Br₂N₃O (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 %). – ¹H NMR: δ = 0.73 (s, 3 H, CH₃), 0.87 (s, 3 H, CH₃), 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, CH₃), 4.44 (s, 1 H, H-4), 5.37 (s, 2 H, NH₂), 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 C₂₅H₂₄BrN₃O (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 %). – ¹H NMR: δ = 0.73 (s, 3 H, CH₃), 0.88 (s, 3 H, CH₃), 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, NH₂), 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 C₂₄H₂₀BrCl₂N₃O (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 %). – ¹H NMR: δ = 0.73 (s, 3 H, CH₃), 0.87 (s, 3 H, CH₃), 1.74 (d, 1

H, $^2J_{\text{HH}} = 17.5$ Hz, CH), 2.01 (d, 1 H, $^2J_{\text{HH}} = 16.1$ Hz, CH), 2.17 (d, 1 H, $^2J_{\text{HH}} = 16.1$ Hz, CH), 2.20 (d, 1 H, $^2J_{\text{HH}} = 17.5$ Hz, CH), 2.40 (s, 3 H, CH₃), 4.51 (s, 1 H, H-4), 5.42 (s, 2 H, NH₂), 7.28 (m, 3 H, H_{Ar}), 7.39 (d, 2 H, $^3J_{\text{HH}} = 8.5$ Hz, H_{Ar}), 7.43 (d, 1 H, $^4J_{\text{HH}} = 2.0$ Hz, H_{Ar}), 7.60 (d, 1 H, $^3J_{\text{HH}} = 8.5$ Hz, H_{Ar}). – Anal. for C₂₅H₂₃Cl₂N₃O (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%). – ^1H NMR: $\delta = 0.74$ (s, 3 H, CH₃), 0.88 (s, 3 H, CH₃), 1.74 (d, 1 H, $^2J_{\text{HH}} = 17.5$ Hz, CH), 1.99 (d, 1 H, $^2J_{\text{HH}} = 16.1$ Hz, CH), 2.17 (s, 3 H, CH₃), 2.18 (d, 1 H, $^2J_{\text{HH}} = 16.1$ Hz, CH), 2.20 (d, 1 H, $^2J_{\text{HH}} = 17.5$ Hz, CH), 2.40 (s, 3 H, CH₃), 4.40 (s, 1 H, H-4), 5.25 (s, 2 H, NH₂), 7.13 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H_{Ar}), 7.16 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H_{Ar}), 7.24 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H_{Ar}), 7.40 (d, 2 H, $^3J_{\text{HH}} = 8.0$ Hz, H_{Ar}). – Anal. for C₂₆H₂₇N₃O (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%). – ^1H NMR: $\delta = 0.73$ (s, 3 H, CH₃), 0.88 (s, 3 H, CH₃), 1.74 (d, 1 H, $^2J_{\text{HH}} = 17.5$ Hz, CH), 2.01 (d, 1 H, $^2J_{\text{HH}} = 16.0$ Hz, CH), 2.22 (d, 1 H, $^2J_{\text{HH}} = 16.0$ Hz, CH), 2.23 (d, 1 H, $^2J_{\text{HH}} = 17.5$ Hz, CH), 4.65 (s, 1 H, H-4), 5.54 (s, 2 H, NH₂), 7.42 (d, 2 H, $^3J_{\text{HH}} = 6.8$ Hz, H_{Ar}), 7.59 (m, 4 H, H_{Ar}), 7.80 (d, 1 H, $^3J_{\text{HH}} = 7.5$ Hz, H_{Ar}), 8.10 (m, 2 H, H_{Ar}). – Anal.

for C₂₄H₂₂N₄O₃ (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%). – ^1H NMR: $\delta = 0.74$ (s, 3 H, CH₃), 0.90 (s, 3 H, CH₃), 1.75 (d, 1 H, $^2J_{\text{HH}} = 17.4$ Hz, CH), 2.01 (d, 1 H, $^2J_{\text{HH}} = 16.1$ Hz, CH), 2.16 (d, 1 H, $^2J_{\text{HH}} = 16.1$ Hz, CH), 2.26 (d, 1 H, $^2J_{\text{HH}} = 17.4$ Hz, CH), 4.62 (s, 1 H, H-4), 5.73 (s, 2 H, NH₂), 7.38 (dd, 2 H, $^3J_{\text{HH}} = 8.2$ 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 C₂₄H₂₁BrN₄O₃ (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%). – ^1H NMR: $\delta = 0.74$ (s, 3 H, CH₃), 0.94 (s, 3 H, CH₃), 1.75 (d, 1 H, $^2J_{\text{HH}} = 17.5$ Hz, CH), 2.01 (d, 1 H, $^2J_{\text{HH}} = 16.1$ Hz, CH), 2.21 (d, 1 H, $^2J_{\text{HH}} = 16.1$ Hz, CH), 2.23 (d, 1 H, $^2J_{\text{HH}} = 17.5$ Hz, CH), 2.40 (s, 3 H, CH₃), 4.65 (s, 1 H, H-4), 5.52 (s, 2 H, NH₂), 7.28 (d, 2 H, $^4J_{\text{HH}} = 7.5$ Hz, H_{Ar}), 7.43 (d, 2 H, $^3J_{\text{HH}} = 7.5$ Hz, H_{Ar}), 7.68 (m, 1 H, H_{Ar}), 7.76 (d, 1 H, $^3J_{\text{HH}} = 7.5$ Hz, H_{Ar}), 8.09 (m, 2 H, H_{Ar}). – Anal. for C₂₅H₂₄N₄O₃ (428.49): calcd. C 70.08, H 5.65, N 13.08; found C 70.21, H 5.53, N 12.96 %.

Acknowledgement

S. A. thanks the Research Council of East Tehran Branch, Islamic Azad University, for financial support of this work.

- [1] J. A. Joule, K. Mills, G. F. Smith, *Heterocyclic Chemistry*, Blackwell Science Ltd. Oxford, **1995**.
- [2] M. Q. Zhang, A. Haemers, D. V. Berghe, S. R. Pattyn, W. Bollaert, *J. Heterocycl. Chem.* **1991**, 28, 685.
- [3] K. Roy, R. P. Srivastava, B. L. Tekwani, V. C. Pandey, A. P. Bhaduri, *Bioorg. Med. Chem. Lett.* **1996**, 6, 121.
- [4] M. Reuman, S. J. Daum, B. Singh, M. P. Wentland, B. Perni, P. Pennock, P. M. Carabates, M. D. Gruett, M. T. Saindane, P. H. Droff, S. A. Coughlin, D. M. Sedlock, J. B. Rake, G. Y. Leshner, *J. Med. Chem.* **1995**, 38, 2531.
- [5] S. Bogialli, G. D'Ascenzo, A. D. Corcia, A. Lagana, S. Nicolardi, *Food Chem.* **2008**, 108, 354.
- [6] A. Kumar, S. Sharma, V. D. Tripathi, R. A. Maurya, S. P. Sirvastava, G. Bhatia, A. K. Tamrakar, A. K. Sirvastava, *Bioorg. Med. Chem.* **2010**, 18, 4138.
- [7] B. Das, B. Venkataiah, *Synthesis* **2000**, 1671.
- [8] C. Ramesh, N. Ravindranath, B. Das, *J. Org. Chem.* **2003**, 68, 7101.
- [9] M. M. Khodaei, P. Salehi, M. A. Zolfigol, S. Sirouszadeh, *Polish J. Chem.* **2004**, 78, 385.
- [10] F. Shirini, M. A. Zolfigol, A. Safari, *Indian J. Chem. Sect. B* **2005**, 44, 201.
- [11] K. Niknam, M. A. Zolfigol, M. Shayegh, R. Zare, *J. Chin. Chem. Soc.* **2007**, 54, 1067.
- [12] J. Zhang, W. L. Li, L. Q. Wu, *J. Braz. Chem. Soc.* **2011**, 22, 1236.
- [13] D. M. Poojary, B. Zhang, A. M. Clearfield, *J. Chem. Soc., Dalton Trans.* **1994**, 2453.
- [14] A. Bortun, V. V. Strelko, E. Jaimez, J. R. Garcia, *Chem. Mater.* **1995**, 34, 4611.
- [15] D. M. Poojary, A. M. Clearfield, *Inorg. Chem.* **1994**, 333, 685.

- [16] K. Segawa, Y. Ban, *Hyomen Kagaku* **1995**, 16, 80; *Chem. Abstr.* **1996**, 124, 218390.
- [17] A. Clearfield, D. S. Thakur, *Appl. Catal.* **1986**, 26, 1.
- [18] G. Alberti, M. Casciola, U. Costantino, R. Vivani, *Adv. Mater.* **1996**, 8, 291.
- [19] R. Vivani, F. Costantino, G. Alberti, M. Nocchetti, *Microporous Mesoporous Mater.* **2008**, 107, 58.
- [20] M. Curini, O. Rosati, U. Costantino, *Curr. Org. Chem.* **2004**, 8, 591.
- [21] U. Costantino, F. Fringuelli, M. Nocchetti, O. Piermatti, *Appl. Catal. A: General* **2007**, 326, 100.
- [22] U. Costantino, M. Nocchetti, F. Marmottini, R. Vivani, *Eur. J. Inorg. Chem.* **1998**, 1447.
- [23] A. Hu, H. L. Ngo, W. Lin, *J. Mol. Catal. A* **2004**, 215, 177.
- [24] X.-S. Wang, M.-M. Zhang, H. Jiang, C.-S. Yao, S.-J. Tu, *Tetrahedron* **2007**, 63, 4439.
- [25] S. Abdolmohammadi, S. Balalaie, *Tetrahedron Lett.* **2007**, 48, 3299.
- [26] S. Balalaie, S. Abdolmohammadi, H. R. Bijanzadeh, A. M. Amani, *Mol. Diversity* **2008**, 12, 85.
- [27] S. Balalaie, S. Abdolmohammadi, B. Soleimanifard, *Helv. Chim. Acta* **2009**, 92, 932.
- [28] S. Abdolmohammadi, S. Balalaie, *Comb. Chem. High Throughput Screening* **2012**, 15, 395.
- [29] S. Abdolmohammadi, M. Afsharpour, *Chin. Chem. Lett.* **2012**, 23, 257.