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# Efficient One-Pot Synthesis of Polyhydroquinoline Derivatives Using Silica Sulfuric Acid as a Heterogeneous and Reusable Catalyst Under Conventional Heating and Energy-Saving Microwave Irradiation

Akbar Mobinikhaledi [a], Naser Foroughifar [a], Mohammad Ali Bodaghi Fard [a], Hassan Moghanian [a], Sattar Ebrahimi [a] & Mehdi Kalhor [a]

[a] Department of Chemistry, Faculty of Sciences, Arak University, Arak, Iran

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# Efficient One-Pot Synthesis of Polyhydroquinoline Derivatives Using Silica Sulfuric Acid as a Heterogeneous and Reusable Catalyst Under Conventional Heating and Energy-Saving Microwave Irradiation

**Akbar Mobinikhaledi, Naser Foroughifar, Mohammad Ali Bodaghi Fard, Hassan Moghanian, Sattar Ebrahimi, and Mehdi Kalhor**
Department of Chemistry, Faculty of Sciences, Arak University, Arak, Iran

**Abstract:** An efficient Hantzsch four-component condensation reaction for the synthesis of polyhydroquinoline derivatives was reported under two conditions: solvent-free conventional heating and energy-saving microwave irradiation. The process is simple and environmentally benign, and the use of a heterogeneous and reusable catalyst, high yields, and short reaction times are the key features of this protocol.

**Keywords:** Heterogeneous, polyhydroquinoline, silica sulfuric acid

## INTRODUCTION

In recent years, much attention has been focused on the synthesis of 1,4-dihydropyridyl compounds because of their significant biological activities.[1,2] Cardiovascular agents such as nifedipine, nicardipine, and other related derivatives are dihydropyridyl compounds, which are effective in the treatment of hypertention.[3] They are also common

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Address correspondence to Akbar Mobinikhaledi, Department of Chemistry, Faculty of Sciences, Arak University, Arak 38156-879, Iran. E-mail: akbar_mobini@yahoo.com

features of various bioactive compounds such as vasodilator, bronchodilator, antiatherosclerotic, antitumor, geroprotective, hepatoprotective, and antidiabetic agents.[4–7] Numerous methods have been reported for the synthesis of polyhydroquinoline (PHQ) derivatives, because of biological importance associated with these compounds. The classical method involves a three-component coupling of an aldehyde, ethylacetoacetate, and ammonia in acetic acid or in refluxing ethanol.[8,9] However, these methods suffer from several disadvantages such as long reaction times, use of volatile and excess organic solvents, low product yields, and harsh reaction conditions. Thus, chemists have developed several efficient methods for the synthesis of PHQ derivatives, which includes the use of ionic liquids,[10,11] microwave irradiation,[12–14] TMSCl,[15] polymers,[16] $I_2$,[17] $HClO_4 \cdot SiO_2$,[18] ceric ammonium nitrate (CAN),[19] metal triflates,[20] and heteropolyacid.[21] However, the use of high temperatures, expensive metal precursors, and environmentally harmful catalysts limit the use of these methods. Thus development of a simple and efficient method for preparation of PHQ derivatives is an active research area, and there is a scope for further improvement involving milder and less hazardous reaction conditions. In recent years, the preparation of silica sulfuric acid (SSA) as a heterogeneous stable acidic reagent[22] and some of its catalytic activities in synthetic methodology have been reported.[23–29]

Because of the unique catalyst features of SSA, we investigated the use of SSA for the synthesis of PHQ derivatives (Fig. 1).

## RESULTS AND DISCUSSION

We optimized the conditions by examining the reaction involving *p*-chlorobenzaldehyde, ethylacetoacetate, dimedone, and ammonium acetate to afford the appropriate PHQ (**4c**). A summary of the obtained results is provided in Table 1. Entry 5 describes the yields of three consecutive condensations leading to PHQ (**4c**, Table 2) and refers to the

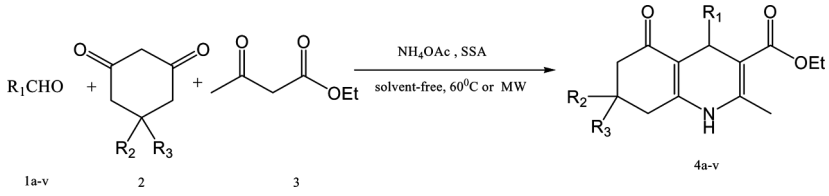


***Figure 1.*** Synthesis of polyhydroquinoline derivatives with the promotion of SSA.

**Table 1.** Optimization of reaction conditions

| Entry | Solvent[a] | Catalyst | Yield (%) |
|---|---|---|---|
| 1 | $CH_2Cl_2$ | SSA | 35 |
| 2 | $CH_3CN$ | SSA | 67 |
| 3 | $C_2H_5OH$ | SSA | 73 |
| 4 | Toluene | SSA | 39 |
| 5 | None[b] | SSA | 91,93,90[d] |
| 6 | None[c] | None | 43 |

[a]Refluxed for 6 h.
[b]60 °C for 40 min.
[c]100 °C for 3 h.
[d]Isolated yield after three consecutive runs.



reusability of SSA. Entry 6 shows the catalytic effect of SSA in this reaction. The reactions proceeded efficiently and smoothly at 60 °C (oil bath) and were completed within 30 min–2 h. Table 2 shows the generality of the present protocol, which is equally effective for aromatic, aliphatic, unsaturated, and heterocyclic aldehydes. Moreover, the experimental procedure is very simple, and there was no undesirable side product.

Recently Bose and coworkers have developed an energy-efficient protocol for a solvent-free reaction that is mildly exothermic but not spontaneous. They found that many of these reactions require a short burst of energy for the initiation of the reaction. After such initiation, the exothermic reaction proceeds on its own to completion without additional energy input.[30] We used this protocol for the synthesis of PHQ derivatives using a domestic oven at medium high power in the presence of SSA as a catalyst. Interestingly, we found that this method was very efficient, and the products were prepared in high yields in a short time with only a short burst of microwave energy needed. A summary of obtained data is provided in Table 3.

## CONCLUSION

In conclusion, we have demonstrated that the four-component Hantzsch reaction can effectively synthesize PHQ derivatives with the promotion of SSA, which provides a simple and efficient method in two conditions. Mild reaction conditions, high yields, generality, and simplicity of the procedure; stability and reusability of the catalyst, and avoidance of harmful organic solvents are features of this new protocol.

**Table 2.** SSA catalyzed the synthesis of polyhydroquioline derivatives through Hantzsch reaction with various aldehydes and 1,3-diketone under conventional method

| Entry | 1 | $R_1$ | $R_2$ | $R_3$ | Product | Time (min) | Yield (%)[a] | Mp (found)[b] | Mp (reported)[Lit.] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1a | Ph | H | H | **4a** | 45 | 92 | 243–245 | 240–241[18] |
| 2 | 1b | 4-Me–$C_6H_4$ | H | H | **4b** | 50 | 92 | 242–243 | 241–242[18] |
| 3 | 1c | 4-Cl–$C_6H_4$ | H | H | **4c** | 40 | 91 | 234–236 | 234–235[18] |
| 4 | 1d | 4-MeO–$C_6H_4$ | H | H | **4d** | 50 | 94 | 194–196 | 193–195[18] |
| 5 | 1e | 2-$NO_2$–$C_6H_4$ | H | H | **4e** | 60 | 90 | 192–194 | 190–191[18] |
| 6 | 1f | 3-$NO_2$–$C_6H_4$ | H | H | **4f** | 80 | 90 | 200–201 | 198–200[18] |
| 7 | 1g | Ph | $CH_3$ | $CH_3$ | **4g** | 30 | 94 | 203–205 | 202–204[19] |
| 8 | 1h | 4-Me–$C_6H_4$ | $CH_3$ | $CH_3$ | **4h** | 40 | 94 | 261–263 | 260–261[19] |
| 9 | 1i | 4-Cl–$C_6H_4$ | $CH_3$ | $CH_3$ | **4i** | 30 | 91 | 242–244 | 245–246[17] |
| 10 | 1j | 2-$NO_2$–$C_6H_4$ | $CH_3$ | $CH_3$ | **4j** | 60 | 92 | 203–206 | 206–207[17] |
| 11 | 1k | 3-$NO_2$–$C_6H_4$ | $CH_3$ | $CH_3$ | **4k** | 60 | 90 | 178–180 | 178–179[17] |
| 12 | 1l | 4-$NO_2$–$C_6H_4$ | $CH_3$ | $CH_3$ | **4l** | 90 | 91 | 242–244 | 243–244[17] |
| 13 | 1m | 4-OH–$C_6H_4$ | $CH_3$ | $CH_3$ | **4m** | 80 | 96 | 231–233 | 230–231[17] |
| 14 | 1n | 4-Br–$C_6H_4$ | $CH_3$ | $CH_3$ | **4n** | 30 | 93 | 253–255 | 253–255[19] |
| 15 | 1o | 4-N(Me)$_2$–$C_6H_4$ | $CH_3$ | $CH_3$ | **4o** | 40 | 96 | 260–262 | 262–263[17] |
| 16 | 1p | 4-MeO–$C_6H_4$ | $CH_3$ | $CH_3$ | **4p** | 30 | 94 | 252–255 | 256–257[17] |
| 17 | 1q | 2-Cl–$C_6H_4$ | $CH_3$ | $CH_3$ | **4q** | 60 | 91 | 202–205 | 207–208[17] |
| 18 | 1r | 3,4-(OMe)$_2$–$C_6H_3$ | $CH_3$ | $CH_3$ | **4r** | 30 | 92 | 201–203 | 198–199[17] |
| 19 | 1s | 2,4-(Cl)$_2$–$C_6H_3$ | $CH_3$ | $CH_3$ | **4s** | 25 | 95 | 240–243 | 241–243[19] |
| 20 | 1t | $C_6H_5$-CH=$CH_2$ | $CH_3$ | $CH_3$ | **4t** | 75 | 89 | 200–202 | 204–206[19] |
| 21 | 1u | *n*–$C_3H_7$ | $CH_3$ | $CH_3$ | **4u** | 30 | 91 | 146–148 | 147–148[19] |
| 22 | 1v | 5-Me-2-Thienyl | $CH_3$ | $CH_3$ | **4v** | 40 | 92 | 228–230 | 226–229[19] |

[a]Isolated yield.
[b]Melting points are not corrected.

**Table 3.** SSA catalyzed the synthesis of polyhydroquioline derivatives through Hantzsch reaction with various aldehydes and 1,3-diketone under short bursts of MW irradiation

| Entry | 1 | $R_1$ | $R_2$ | $R_3$ | Product | Irradiation time (min) | Total time (min) | Yield (%)[a] | Mp (found)[b] | Mp (reported)[Lit.] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1a | Ph | H | H | **4a** | 1 | 20 | 91 | 242–244 | 240–241[18] |
| 2 | 1b | 4-Me-$C_6H_4$ | H | H | **4b** | 1 | 20 | 90 | 241–243 | 241–242[18] |
| 3 | 1c | Ph | $CH_3$ | $CH_3$ | **4c** | 1 | 15 | 93 | 204–205 | 202–204[19] |
| 4 | 1d | 4-Me-$C_6H_4$ | $CH_3$ | $CH_3$ | **4d** | 1 | 15 | 94 | 260–263 | 260–261[19] |
| 5 | 1e | 4-Br-$C_6H_4$ | $CH_3$ | $CH_3$ | **4e** | 1 | 20 | 92 | 252–254 | 253–255[19] |
| 6 | 1f | 2-$NO_2$-$C_6H_4$ | $CH_3$ | $CH_3$ | **4f** | 1 | 25 | 90 | 204–206 | 206–207[17] |
| 7 | 1g | 4-$NO_2$-$C_6H_4$ | $CH_3$ | $CH_3$ | **4g** | 1 | 25 | 89 | 242–245 | 243–244[17] |
| 8 | 1h | 4-N$(Me)_2$-$C_6H_4$ | $CH_3$ | $CH_3$ | **4h** | 1 | 20 | 93 | 261–263 | 262–263[17] |
| 9 | 1i | 3,4-$(OMe)_2$-$C_6H_3$ | $CH_3$ | $CH_3$ | **4i** | 1 | 15 | 94 | 202–204 | 198–199[17] |

[a]Isolated yield.
[b]Melting points are not corrected.

## EXPERIMENTAL

### General

All of the products are known compounds and were characterized by comparison of their physical and spectroscopic data with those reported in the literature. Melting points were obtained in open capillaries on an Electrothermal 5000 digital apparatus and are not corrected. A National microwave oven, model no. NN-K571MF (1000 W), was used for microwave-assisted reactions. Infrared (IR) spectra were recorded on a Galaxy series Fourier transform infrared (FT-IR) 5000 spectrometer. NMR spectra were recorded on a Brucker 300-MHz spectrometer in dimethyl sulfoxide (DMSO-$d_6$) with tetramethylsilane (TMS) as an internal standard. Silica sulfuric acid was prepared according to the reported procedure.[22] Progress of the reactions was followed by dissolving a sample in ethyl acetate and monitoring by thin-layer chromatography (TLC) using *n*-hexane/EtOAc (2:1 v/v) as an eluent.

### General Procedure for the Synthesis of 4a–v (Table 2) Under Solvent-Free Conventional Heating Conditions

A mixture of aldehyde (1.0 mmol), dimedone or 1,3-cyclohexanedione (1.0 mmol), ethyl acetoacetate (1.0 mmol), ammonium acetate (2.0 mmol), and silica sulfuric acid (0.08 g, 0.20 mmol) was heated at 60 °C for an appropriate time (TLC). The resulting solid product was treated with hot ethanol or acetonitrile and then filtered. The filtrate was concentrated to afford the crude product. The pure product was obtained by recrystallization from absolute ethanol.

### General Procedure for the Synthesis of 4a–i (Table 3) Under MW Irradiation

A mixture of aldehyde (1.0 mmol), dimedone or 1,3-cyclohexanedione (1.0 mmol), ethyl acetoacetate (1.0 mmol), ammonium acetate (2.0 mmol), and SSA (0.08 g, 0.20 mmol) was mixed and irradiated by microwaves for 1 min and then allowed to go to completion. The resulting solid product was treated with hot ethanol or acetonitrile and then filtered. The filtrate was concentrated to afford the crude product. The pure product was obtained by recrystallization from absolute ethanol.

**Physical and Spectroscopic Data for Selected Compounds**

Ethyl-1,4,7,8-tetrahydro-2-methyl-4-(phenyl)-5(6H)-oxoquinoline-3-carboxylate (Table 2, **4a**)

Mp 243–245 °C; IR (KBr) ($\nu_{max}$): 3284, 3140, 1691, 1608, 1479, 1379, 1222, 1180, 1072 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$H: 1.12 (3H, t, $J = 7.0$ Hz, $CH_3$), 1.87–2.27 (6H, m, $CH_2$), 2.46 (3H, s, $CH_3$), 3.97 (2H, q, $J = 7.0$ Hz, $CH_2$), 4.90 (1H, s, CH), 7.04–7.20 (5H, m, Ar), 9.14 (1H, s, NH) ppm.

Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(phenyl)-5(6H)-oxoquinoline-3-carboxylate (Table 2, **4g**)

Mp 203–205 °C; IR (KBr) ($\nu_{max}$): 3288, 2962, 1699, 1610, 1485, 1381, 1211,1072 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$H: 0.84 (3H, s, $CH_3$), 1.00 (3H, s, $CH_3$), 1.13 (3H, t, J = 7.1 Hz, $CH_3$), 2.14–2.50 (4H, m, $CH_2$), 3.97 (2H, q, J = 7.1 Hz, $CH_2$), 4.84 (1H, s, CH), 7.03–7.20 (5H, m, Ar), 9.07 (1H, s, NH) ppm.

Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(4-methylphenyl)-5(6H)-oxoquinoline-3-carboxylate (Table 2, **4h**)

Mp 261–262 °C; IR (KBr) ($\nu_{max}$): 3277, 3207, 3078, 2962, 1701, 1647, 1604, 1493, 1381, 1280, 1215, 1090 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$H: 0.84 (3H, s, $CH_3$), 1.00 (3H, s, $CH_3$), 1.14 (3H, t, J = 7.1 Hz, $CH_3$), 1.98–2.44 (4H, m, $CH_2$), 2.24 (3H, s, $CH_3$), 2.29 (3H, s, $CH_3$), 3.96 (2H, q, J = 7.1 Hz, $CH_2$), 4.79 (1H, s, CH), 6.95–7.03 (4H, m, Ar), 9.03 (1H, s, NH) ppm.

Ethyl-1,4,7,8-tetrahydro-2,7,7-trimethyl-4-(4-bromophenyl)-5(6H)-oxoquinoline-3-carboxylate (Table 2, **4n**)

Mp 253–255 °C; IR (KBr) ($\nu_{max}$): 3280, 3217, 3065, 2951, 1695, 1637, 1608, 1489, 1381, 1263, 1210, 1092 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): $\delta$H: 0.82 (3H, s, $CH_3$), 1.00 (3H, s, $CH_3$), 1.12 (3H, t, J = 7.0 Hz, $CH_3$), 1.94–2.44 (4H, m, $CH_2$), 2.29 (3H, s, $CH_3$), 3.96 (2H, q, J = 7.0 Hz, $CH_2$), 4.82 (1H, s, CH), 7.08–7.39 (4H, m, Ar), 9.12 (1H, s, NH) ppm.

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## REFERENCES


1. Mauzerall, D.; Westheimer, F. H. 1-Benzyldihydronicotinamide—A model for reduced DPN. *J. Am. Chem. Soc.* **1955**, *77*, 2261–2264.
2. Shan, R.; Velazquez, C.; Knaus, E. E. Syntheses, calcium channel agonist–antagonist modulation activities, and nitric oxide release studies of nitrooxyalkyl 1,4-dihydro-2,6-dimethyl-3-nitro-4-(2,1,3-benzoxadiazol-4-yl)pyridine-5-carboxylate racemates, enantiomers, and diastereomers. *J. Med. Chem.* **2004**, *47*, 254–261.
3. Buhler, F. R.; Kiowski, W. Calcium antagonists in hypertension. *J. Hypertens.* **1987**, *5*, S3–10.
4. Sausins, A.; Duburs, G. Synthesis of 1,4-dihydropyridines by cyclocondensation reactions. *Heterocycles* **1988**, *27*, 269–289.
5. Mannhold, R.; Jablonka, B.; Voigdt, W.; Schoenafinger, K.; Schraven, K. Calcium- and calmodulin-antagonism of elnadipine derivatives: Comparative SAR. *Eur. J. Med. Chem.* **1992**, *27*, 229–235.
6. Bossert, F.; Meyer, H.; Wehinger, E. 4-Aryldihydropyridines, a new class of highly active calcium antagonists. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 762–769.
7. Nakayama, H.; Kanaoka, Y. Chemical identification of binding sites for calcium channel antagonists. *Heterocycles* **1996**, *42*, 901–909.
8. Loev, B.; Snader, K. M. The Hantzsch reaction, I: Oxidative dealkylation of certain dihydropyridines. *J. Org. Chem.* **1965**, *30*, 1914–1916.
9. Dondoni, A.; Massi, A.; Minghini, E.; Bertolasi, V. Multicomponent Hantzsch cyclocondensation as a route to highly functionalized 2- and 4-dihydropyridylalanines, 2- and 4-pyridylalanines, and their N-oxides: Preparation via a polymer-assisted solution-phase approach. *Tetrahedron* **2004**, *60*, 2311–2326.
10. Ji, S.-J.; Jiang, Z.-Q.; Lu, J.; Loh, T.-P. Facile ionic liquids–promoted one-pot synthesis of polyhydroquinoline derivatives under solvent free conditions. *Synlett* **2004**, *5*, 831–835.
11. Sridhar, R.; Perumal, P. T. A new protocol to synthesize 1,4-dihydropyridines by using 3,4,5-trifluorobenzeneboronic acid as a catalyst in ionic liquid: Synthesis of novel 4-(3-carboxyl-1H-pyrazol-4-yl)-1,4-dihydropyridines. *Tetrahedron* **2005**, *61*, 2465–2470.
12. Khadilkar, B. M.; Gaikar, V. G.; Chitnavis, A. A. Aqueous hydrotrope solution as a safer medium for microwave enhanced Hantzsch dihydropyridine ester synthesis. *Tetrahedron Lett.* **1995**, *36*, 8083–8086.
13. Ohberg, L.; Westman, J. An efficient and fast procedure for the Hantzsch dihydropyridine synthesis under microwave conditions. *Synlett* **2001**, *8*, 1296–1298.
14. Agarwal, A.; Chauhan, P. M. S. Solid supported synthesis of structurally diverse dihydropyrido[2,3-d]pyrimidines using microwave irradiation. *Tetrahedron Lett.* **2005**, *46*, 1345–1348.
15. Sabitha, G.; Reddy, G. S. K. K.; Reddy, C. S.; Yadav, J. S. A novel TMSI-mediated synthesis of Hantzsch 1,4-dihydropyridines at ambient temperature. *Tetrahedron Lett.* **2003**, *44*, 4129–4131.

16. Breitenbucher, J. G.; Figliozzi, G. Solid-phase synthesis of 4-aryl-1,4-dihydropyridines via the Hantzsch three-component condensation. *Tetrahedron Lett.* **2000**, *41*, 4311–4315.
17. Ko, S.; Sastry, M. N. V.; Lin, C.; Yao, C.-F. Molecular iodine–catalyzed one-pot synthesis of 4-substituted-1,4-dihydropyridine derivatives via Hantzsch reaction. *Tetrahedron Lett.* **2005**, *46*, 5771–5774.
18. Maheswara, M.; Siddaiah, V.; Damu, G. L. V.; Rao, C. V. An efficient one-pot synthesis of polyhydroquinoline derivatives via Hantzsch condensation using heterogeneous catalyst under solvent-free conditions. *Arkivoc* **2006**, *2*, 201–206.
19. Ko, S.; Yao, C.-F. Ceric ammonium nitrate (CAN) catalyzes the one-pot synthesis of polyhydroquinoline via the Hantzsch reaction. *Tetrahedron* **2006**, *62*, 7293–7299.
20. Wang, L.-M.; Sheng, J.; Zhang, L.; Han, J.-W.; Fan, Z.-Y.; Tian, H.; Qian, C.-T. Facile $Yb(OTf)_3$ promoted one-pot synthesis of polyhydroquinoline derivatives through Hantzsch reaction. *Tetrahedron* **2005**, *61*, 1539–1543.
21. Heravi, M. M.; Bakhtiari, K.; Javadi, N. M.; Bamoharram, B. B.; Saeedi, M.; Oskooie, H. A. $K_7[PW_{11}CoO_{40}]$-catalyzed one-pot synthesis of polyhydroquinoline derivatives via the Hantzsch three-component condensation. *J. Mol. Catal. A. Chem.* **2007**, *264*, 50–52.
22. Zolfigol, M. A. Silica sulfuric acid/$NaNO_2$ as a novel heterogeneous system for production of thionitrites and disulfides under mild conditions. *Tetrahedron* **2001**, *57*, 9509–9511.
23. Salehi, P.; Zolfigol, M. A.; Shirini, F.; Baghbanzadeh, M. Silica sulfuric acid and silica chloride as efficient reagents for organic reactions. *Curr. Org. Chem.* **2006**, *10*, 2171–2189.
24. Salehi, P.; Dabiri, M.; Zolfigol, M. A.; Bodaghi Fard, M. A. Silica sulfuric acid: An efficient and reusable catalyst for the one-pot synthesis of 3,4-dihydropyrimidin-2(1H)-ones. *Tetrahedron Lett.* **2003**, *44*, 2889–2891.
25. Salehi, P.; Dabiri, M.; Zolfigol, M. A.; Baghbanzadeh, M. A new approach to the facile synthesis of mono- and disubstituted quinazolin-4(3H)-ones under solvent-free conditions. *Tetrahedron Lett.* **2005**, *46*, 7051–7053.
26. Salehi, P.; Dabiri, M.; Zolfigol, M. A.; Otokesh, S.; Baghbanzadeh, M. Selective synthesis of 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles in water at ambient temperature. *Tetrahedron Lett.* **2006**, *47*, 2557–2560.
27. Seyyedhamzeh, M.; Mirzaei, P.; Bazgir, A. Solvent-free synthesis of aryl-14H-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydro-xanthenes using silica sulfuric acid as catalyst. *Dyes and Pigments* **2008**, *76*, 836–839.
28. Hari, G. S.; Nagaraju, M.; Murthy, M. M. Silica sulfuric acid–catalyzed Friedel–Crafts alkylation of indoles with nitro olefins. *Synth. Commun.* **2008**, *38*, 100–105.
29. Srihari, G.; Nagaraju, M.; Murthy, M. M. Solvent-free one-pot synthesis of amidoalkyl naphthols catalyzed by silica sulfuric acid. *Helv. Chim. Acta* **2007**, *90*, 1497–1504.
30. Manhas, M. S.; Ganguly, S. N.; Mukherjee, S.; Jain, A. K.; Bose, A. K. Microwave initiated reactions: Pechmann coumarin synthesis, Biginelli reaction, and acylation. *Tetrahedron Lett.* **2006**, *47*, 2423–2425.