



Original Research Article

A new application of nickel nanoparticles as a heterogeneous catalyst for synthesis of 1-amidoalkyl-2-naphthols according to green chemistry principles

Fatemeh Hakimi^{a,b,*}, Fatemeh Sadat Oreyzi^{a,b}, Fatemeh Bani Fatemeh^{a,b}, Elham Golrasan^{a,b}

^a Department of Chemistry, Payame Noor University, Tehran, P.O. Box 19395-4697, Iran

^b Research Center of Environmental Chemistry, Payame Noor University, Ardakan, Yazd, Iran

ARTICLE INFORMATION

Received: 13 January 2019

Received in revised: 14 February 2019

Accepted: 14 February 2019

Available online: 10 April 2019

DOI: 10.22034/AJGC/2020.2.1

KEYWORDS

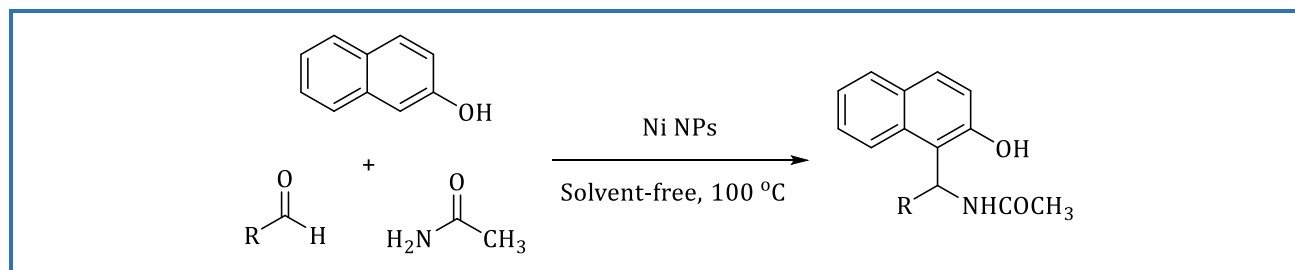
Nickel nanoparticles
1-amidoalkyl-2-naphthol
Green chemistry
Multicomponent reaction

ABSTRACT

1-amidoalkyl-2-naphthols were prepared *via* one-pot multi-component reaction of 2-naphthol, aldehydes, and amides in the presence of nickel nanoparticles as a solid phase acidic catalyst, under solvent-free condition at 100 °C. The recent literature survey reveals that the nano nickel was used as heterogeneous catalyst and received noteworthy attention because of its inexpensive, non-toxic, low corrosion, waste minimization, easy transport and disposal of the catalyst. Short reaction times, high yields, and easy work-up are the advantages of this protocol.

© 2020 by SPC (Sami Publishing Company), Asian Journal of Green Chemistry, Reproduction is permitted for noncommercial purposes.

Graphical Abstract



Introduction

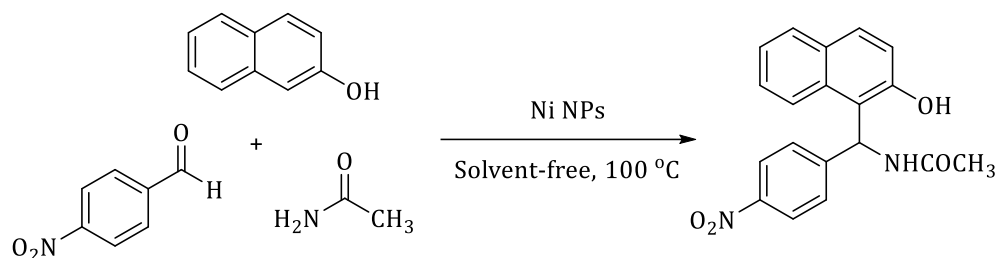
One-pot multi-component reactions (MCRs) by virtue of their convergence, productivity, facile execution and high yield have attracted considerable attention in recent years. There has been tremendous development in three or four component reaction especially the Passerine [1], Big Nellie [2], Ugi [3] and Munich [4] reactions, which have further led to renaissance of MCRs. Nevertheless, great efforts have been made to find and develop new MCRs. From the point of view of the conservation of the environment combining with economic aspects, all chemists demand the application of metal ion-free, environmentally safe and convenient reagents in the multi-component reactions [5].

Compounds bearing 1,3-amino-oxygenated functional groups are usually found in various biologically important natural products and potent drugs, including: nucleoside antibiotics and HIV protease inhibitors [6]. 1-amidoalkyl-2-naphthol derivatives exhibit important cardiovascular, bradycardiac [7] and hypertensive [8] activities. Previously, some catalysis such as nano-BF₃.SiO₂ [9], sulfonic acid functionalized imidazolium salts [10], trityl chloride [11], 1,3-disulfonic acid imidazolium hydrogen sulfate [12], saccharin sulfonic acid (SaSA) [13], silica supported molybdate phosphoric acid [14], H₃PW₁₂O₄₀ [15], H₄SiW₁₂O₄₀ [16], antimony (III) acetate [17] and silver nanoparticles [18] have been utilized for the synthesis of 1-amidoalkyl-2-naphthols.

Various researchers around the different continents are trying to prepare metal materials at the nano scales. Particularly, for the synthesis of transition metal nickel, nanoparticles (Ni-NPs) have gained tremendous importance in the last two decades, because they are efficient and reusable and are good catalysts for the synthesis of organic compounds and biological activities [19, 20]. Recent research has shown that nickel nanoparticles have been considered for non-toxicity, low corrosion, easy transfer, and catalytic disposals [21]. However, the better efficiency of heterogeneous catalysis in organic synthesis can be improved by employing nanosized catalysts because of their extremely small size and large surface to volume ratio. During the recent years, most of the work done on Ni-NPs as catalysts offer great opportunities for the wide range of applications in organic synthesis and chemical manufacturing processes, including: the chemoselective oxidative coupling of thiols [22], synthesis of tetraketones and bis-coumarins [23], reduction of *p*-nitrophenol [24], synthesis of polyhydroquinoline derivatives [25], synthesis of 1,4-dihydropyridines [26] and synthesis of bis(indolyl) methanes [27] which support hydrogen adsorption [28]. Generally, Ni-NPs are unstable and the exploration of appropriate support for stabilizing catalytic nanoparticles is a key factor in their successful and wide applications in heterogeneous catalysis [29].

We have developed an efficient procedure for the one-pot three-component synthesis of 1-amidoalkyl-2-naphthol derivatives in the presence of nickel nanoparticles as a solid phase acidic catalyst, under solvent-

free conditions at 100 °C (Scheme 1).



Scheme 1.

Experimental

Materials and methods

All chemicals were purchased from commercial suppliers and were used as received. The Ni nanoparticles were prepared according to the literature [26]. All products were identified by their spectra and physical data. Melting points were measured by using the capillary tube method with an electrothermal 9100 apparatus. The IR spectra were recorded on a Shimadzu spectrometer 883 (KBr pellets, Nujol mulls, 4000–400 cm^{-1}). ^1H NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer using TMS as an external standard.

General procedure

Preparation of 1-amidoalkyl-2-naphthols catalyzed by Ni-NPs: a mixture of 2-naphthol (1 mmol), aldehyde (1 mmol), acetamide (1.2 mmol) and Ni-NPs catalyst (0.006 g) was stirred for 12-35 minutes at 100 °C under solvent-free condition. After completion of the reaction, according to TLC analysis, the crude solid product was dissolved in CH_2Cl_2 and filtered to separate the catalyst. The catalyst was washed with EtOH (2.5 mL). The recovered catalyst was dried in vacuum and used in subsequent catalytic runs. Products were obtained by removal of the EtOH solvent under reduced pressure.

Selected spectroscopic data

N-(5-ethyl-2-hydroxyphenyl)(2-hydroxynaphthalen-1-yl)methyl)acetamide

Mp 208–210 °C, IR (KBr) (ν_{max} / cm^{-1}): 3347, 3321 and 1635. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.3 (3H, t, CH_3), 2.6 (2H, q, CH_2), 2.2 (3H, s, CH_3), 5.79 (1H, s, CH), 5.0 (2H, broad s, OH), 6.16 (1H, d, CH), 7.04-7.74 (9H, m, ArH), 8.0 (1H, NH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 13.2, 23.6, 32.7, 48.5, 112.1,

115.3, 118.7, 119.6, 121, 122, 123.9, 126.3, 128.3, 129.2, 129.4, 130.1, 133, 143, 151.8, 152.1, 173. Anal. Calcd for C₂₁H₂₁NO₃: C, 75.22; H, 6.26; N, 4.17, found: C, 75.10; H, 6.18; N, 4.14.

N-(2-hydroxynaphthalen-1-yl)(3-hydroxyphenyl)methyl)acetamide

Mp 212–214 °C, IR (KBr) (ν_{\max} / cm⁻¹): 3310, 3314 and 1620. ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.02 (3H, s, CH₃), 5.0 (2H, broad s, OH), 6.06 (1H, s, CH), 6.84–7.46 (10H, m, ArH). 8.21 (1H, NH). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 23.6, 48.5, 48.5, 115.5, 118.7, 122.6, 126, 123.9, 126.3, 128.3, 129.1, 129.6, 130.5, 133.7, 144, 152.8, 153.1, 175. Anal. Calcd for C₁₉H₁₇NO₃: C, 74.26; H, 5.53; N, 4.56, found: C, 74.50; H, 5.24; N, 4.39.

Results and Discussion

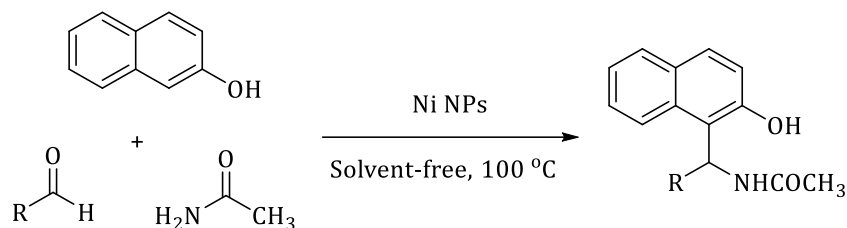
In continuation of our investigations on the applications of solid acids in organic synthesis, we have investigated the synthesis of 1-amidoalkyl-2-naphthols in the presence of Ni-NPs. The reaction of 4-nitrobenzaldehyde (1 mmol), 2-naphthol (1 mmol) and acetamide (1.2 mmol) in the presence Ni-NPs was investigated for optimization of the reaction conditions. Reaction at various solvents and different quantities of Ni-NPs revealed that the best conditions are using Ni-NPs (0.006 g) as catalyst at 100 °C under solvent-free condition (Scheme 1 and Table 1).

Table 1. Synthesis of 1-amidoalkyl-2-naphthols *via* the reaction of benzaldehyde (1 mmol), 2-naphthol (1 mmol) and acetamide (1.2 mmol) under various conditions

Entry	Catalyst (g)	Solvent	Conditions	Time (min)	Yield (%)
1	Ni-NPs (0.006 g)	EtOAc	Reflux	180	40
2	Ni-NPs (0.006 g)	EtOH	Reflux	180	60
3	Ni-NPs (0.006 g)	CHCl ₃	Reflux	180	-
4	Ni-NPs (0.006 g)	H ₂ O	Reflux	180	-
5	Ni-NPs (0.006 g)	Solvent-free	80 °C	60	80
6	Ni-NPs (0.006 g)	Solvent-free	90 °C	30	70
7	Ni-NPs (0.006 g)	Solvent-free	100 °C	15	92
8	Ni-NPs (0.003 g)	Solvent-free	100 °C	30	85
9	Ni-NPs (0.012 g)	Solvent-free	100 °C	15	90
10	Catalyst-free	Solvent-free	100 °C	120	0

As can be seen from Table 2, the reactions were carried out efficiently and the desired products were obtained in good to excellent yields (80-95%). The reaction was carried out with aromatic aldehydes containing electron releasing and withdrawing groups. The reaction of doped with

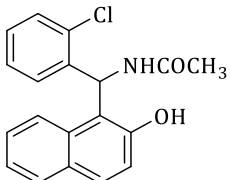
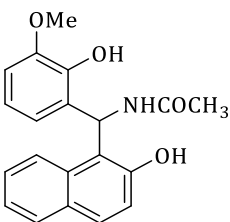
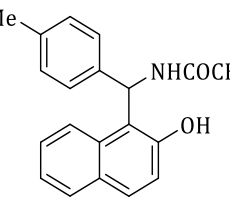
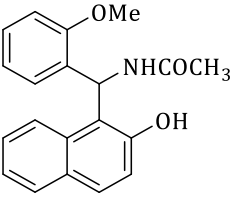
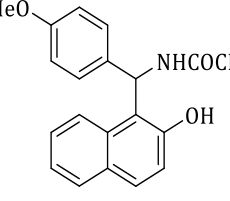
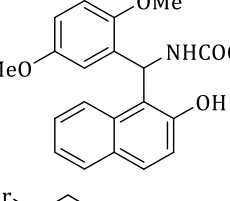
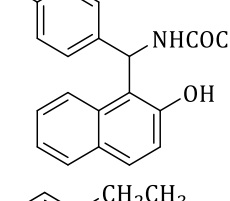
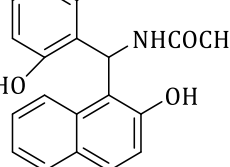
electron-releasing groups shows higher efficiency and shorter time. The reaction was carried out with some aliphatic aldehyde. Aliphatic aldehydes had no good results (Scheme 2 and Table 2).

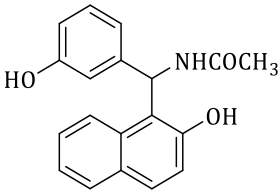
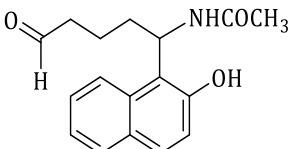


Scheme 2.

Table 2. Synthesis of 1-amidoalkyl-2-naphthols from various aldehydes catalyzed by Ni-NPs at 100 °C under solvent-free conditions^a

Entry	R	Product	Time (min)/ Yield (%) ^b	M.p. (°C) (Lit.)
1	C ₆ H ₅		15/92	246-247 243-245 [30]
2	3-NO ₂ -C ₆ H ₄		14/93	254-256 252-254 [30]
3	4-NO ₂ -C ₆ H ₄		12/95	243-245 241-242 [30]
4	4-Cl-C ₆ H ₄		15/95	228-230 226-228 [30]
5	3-Cl-C ₆ H ₄		15/94	238-240 237-238 [30]

6	2-Cl-C ₆ H ₄		15/91	196-199	198-199 [31]
7	2-OH-3-OCH ₃ -C ₆ H ₃		30/85	178-180	157-159 [32]
8	4-CH ₃ -C ₆ H ₄		20/92	221-223	222-223 [33]
9	2-OCH ₃ -C ₆ H ₄		30/80	198-200	199-202 [34]
10	4-OCH ₃ -C ₆ H ₄		20/87	182-184	183-185 [34]
11	2,5-OCH ₃ -C ₆ H ₃		35/85	248-250	251-253 [33]
12	4-Br-C ₆ H ₄		18/95	227-229	228-230 [33]
13	2-OH-5-CH ₂ CH ₃ -C ₆ H ₃		20/95	208-210	-

14	3-OHC ₆ H ₄		25/90	212-214	-
15	C ₅ H ₈ O ₂ (Glutardialdehyde)		40/35	-	-

^aThe molar ratio of 2-naphthol: aldehyde: acetamide 1:1:1.2 and Ni-NPs (0.006 g)

^b Isolated yield

Conclusions

In conclusion, we have developed an efficient procedure for the synthesis of 1-amidoalkyl-2-naphthols through the reaction of various aldehydes with 2-naphthol and acetamide using Ni-NPs as an inexpensive catalyst. The reactions under solvent-free conditions gave the desired products with good to excellent yields in short reaction times.

Acknowledgement

The Research Council of Payame Noor University is gratefully acknowledged for the financial support for this work.

Disclosure Statement

No potential conflict of interest was reported by the authors.

References

- [1]. Zhu J., Bienayme H. *Wiley-VCh Weinheim*, 2005; p. 311
- [2]. Dallinger D., Stadler A., Kappe C.O. *Pure Appl. Chem.*, 2004, **76**:1017
- [3]. Ugi I., Werner B., Domling A. *Molecules*, 2003, **8**:53
- [4]. Trost B.M. *Acc. Chem. Res.*, 2002, **35**:695
- [5]. Mullin R. *Chem. Eng. News*, 2004, **82**:29
- [6]. Wang Y.F., Lzawa T., Kobayashi S., Ohno M. *J. Am. Chem. Soc.*, 1982, **104**:6456
- [7]. Shen A.Y., Tsai C.T., Chen C.L. *Eur. J. Chem.*, 1997, **34**:877
- [8]. Cai X.H., Guo H., Xie B. *Int. J. Chem.*, 2011, **3**:119
- [9]. Mirjalili B.F., Bamoniri A., Rahmati L. *Arabian J. Chem.*, 2015, in press
<https://doi.org/10.1016/j.arabjc.2014.12.026>

- [10]. Zolfigol M.A., Khazaei A., Moosavi-Zare A.R., Zare A., Khakyzadeh V. *Appl. Catal. A: Gen.*, 2011, **400**:70
- [11]. Khazaei A., Zolfigol M.A., Moosavi-Zare A.R., Abi F., Zare A., Kaveh H., Khakyzadeh V., Kazem-Rostami M., Parhami A., Torabi-Monfared H. *Tetrahedron*, 2013, **69**:212
- [12]. Zare A., Yousofi T., Moosavi-Zare A.R. *RSC Adv.*, 2012, **2**:7988
- [13]. Zare A., Hasaninejad A., Rostami E., Moosavi-Zare A.R., Pishahang N., Roshankar M., Khedri M. *E. J. Chem.*, 2010, **7**:1162
- [14]. Hajipour A.R., Ghayeb Y., Sheikhan N., Ruoho A.E. *Tetrahedron Lett.*, 2009, **50**:5649
- [15]. Supale A.R., Gokavi G.S. *J. Chem. Sci.*, 2010, **122**:189
- [16]. Zhang Q., Luo J., Wei Y. *Green Chem.*, 2010, **12**:2247
- [17]. Hakimi F. *J. Chem. Res.*, 2016, **40**:489
- [18]. Hakimi F. *Synth. React. Inorg. M.*, 2017, **47**:994
- [19]. Mirkin C.A., Letsinger R.L., Mucic R.C., Storhoff J.J. *Nature*, 1996, **382**:607
- [20]. Storhoff J.J., Elghanian R., Mucic R.C., Mirkin C.A., Letsinger R.L. *J. Am. Chem. Soc.*, 1998, **120**:1959
- [21]. Morozov Y.G., Belousova O.V., Kuznetsov M.V. *Inorg. Mater.*, 2011, **47**:36
- [22]. Saxena A., Kumar A., Mozumdar S. *J. Mol. Catal. A: Chem.*, 2007, **269**:35
- [23]. Khurana J.M., Vij K. *J. Chem. Sci.*, 2012, **124**:907
- [24]. Jiang Z., Xie J., Jiang D., Wei X., Chen M. *Cryst. Eng. Comm.*, 2013, **15**:560
- [25]. Sapkal S., Shelke K., Shingate B., Shingare M. *Tetrahedron Lett.*, 2009, **50**:1754
- [26]. Banitaba S.H., Dehghan Khalili S., Safari J. *Iran J. Org. Chem.*, 2012, **4**:785
- [27]. Olyaei A., Vaziri M., Razeghi R., Shams B., Bagheri H. *J. Serb. Chem. Soc.*, 2013, **78**:463
- [28]. Dhakshinamoorthy A., Pitchumani K. *Tetrahedron Lett.*, 2008, **49**:1818
- [29]. Chou K., Huang K. *J. Nanopart. Res.*, 2001, **3**:127
- [30]. Luo J., Zhang Q. *Monatsh Chem.*, 2011, **141**:923
- [31]. Mirjalili B.F., Bamoniri A., Rahmati L. *Arabian J. Chem.*, 2014, **11**:653
- [32]. Habibzadeh S., Ghasemnejad H. *J. Chin. Chem. Soc.*, 2012, **59**:193
- [33]. Shaterian H.R., Yarahmadi H., Ghashang M. *Bioorg. Med. Chem. Lett.*, 2008, **18**:788
- [34]. Patil S.B., Singh P.R., Surpur M.P., Samant S.D. *Ultrason. Sonochem.*, 2007, **14**:515

How to cite this manuscript: Fatemeh Sadat Oreyzi, Fatemeh Hakimi*, Fatemeh Bani Fatemeh, Elham Golrasan. A new application of nickel nanoparticles as a heterogeneous catalyst for synthesis of 1-amidoalkyl-2-naphthols according to green chemistry principles. *Asian Journal of Green Chemistry*, 4(2) 2020, 134-141. DOI: 10.22034/AJGC/2020.2.1