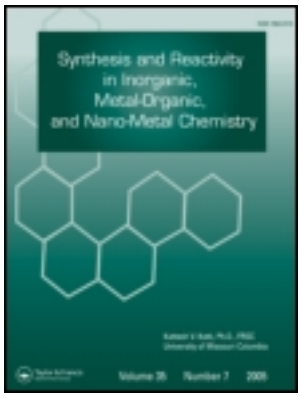

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A Simple Method for Preparation of ZnO Nanoparticles as a Highly Efficient Nanocatalyst for N-Formylation of Primary and Secondary Amines under Solvent-Free Condition

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A Simple Method for Preparation of ZnO Nanoparticles as a Highly Efficient Nanocatalyst for N-Formylation of Primary and Secondary Amines under Solvent-Free Condition

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A convenient reaction between alky, aryl, and heteroalkyl amines and formic acid as a formylating agent in the presence of catalytic amount of mechanochemically synthesized zinc oxide nanoparticles under solvent-free condition for the synthesis of corresponding *N*-formyl derivatives is described.

Keywords amines, formic acid, *N*-formylation, solvent-free, ZnO nanoparticles

INTRODUCTION

Designing of new specific catalysts and exploring their catalytic activity has caused profound effects in optimizing the efficiency of a wide range of organic synthesis. Development of such catalysts has resulted in more economical and environmentally friendly chemistry through replacing nonselective, unstable, or toxic catalysts.[1] Surface of metal oxides exhibit both Lewis acid and Lewis base characters. This is characteristic of many metal oxides, especially TiO_2, Al_2O_3, and ZnO, and they are excellent adsorbents for a wide variety of organic compounds and increase reactivity of the reactants.[2]

Nanoscale oxide particles are gaining increasing technical importance for classic areas of application such as catalysts, passive electronic components, or ceramic materials.[3,4] Metal oxide nanoparticles are also widely used in industrial applications as catalysts, ceramic, pigments, and so on. Zinc oxide nanoparticles are certainly some of the most interesting multifunctional of metal oxides, because they have surface properties that suggest that a very rich organic chemistry may occur there. So far, a variety of techniques have been applied to the preparation of nanocrystalline ZnO with different particle morphologies and sizes.[5–8] However, most of these methods involve a strictly controlled synthesis environment, expensive equipment and complicated procedures.

Mechanochemical processing is a novel method for the production of nanosized materials, where separated nanoparticles can be prepared. The method has been widely applied to synthesize a large variety of nanoparticles, including ZnS, CdS, ZnO, $LiMn_2O_4$, SiO_2, and CeO_2.[9–12] Milling of precursor powders leads to the formation of a nanoscale composite structure of the starting materials that react during milling or subsequent heat treatment to form a mixture of separated nanocrystals of the desired phase.

Formamides are important intermediates in the synthesis of pharmaceutically valuable compounds,[13] fungicides and herbicides,[14] formamidines,[15] isocyanides,[16] and can be used as a catalyst in some reactions such as allylation[17] and hydrosilylation[18] of carbonyl compounds. A number of methods have been reported for the formylation of amines. Some of the formylation reagents are chloral,[19] activated formic acid using DCC or EDCI,[20] formic acid esters,[21] ammonium format,[22] Lewis acids,[23] solid-supported reagents,[24] aq. 85% formic acid using ZnO,[25] aq. formic acid in protic ionic liquid,[26] indium-formic acid[27] and formic acid at 80°C.[28] Many of these methods have disadvantages such as expensive and toxic reagents and catalysts, long reaction times, high temperature, side products formation, tedious work-up procedure, and difficult accessibility to reagents. Thus, a mild, convenient, high-yield, experimental simplicity and effectiveness procedure using inexpensive catalyst would be valuable.

ZnO under solvent-free conditions have proved to be useful to chemists due to the reaction rate enhancement, selectivity, easier work-up, and recyclability of the supports.[25]

As the part of our research, we are trying to synthesize and use nanoparticles having catalytic activities, which are economic for large-scale preparation. Here we describe the use of ZnO nanoparticles (NAP-ZnO) as a simple and efficient heterogeneous eco-friendly catalyst for *N*-formylation of different amines (Scheme 1).

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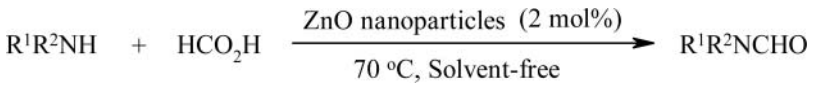

SCH. 1. *N*-Formylation of amines with formic acid catalyzed by ZnO-nanoparticles.

EXPERIMENTAL

Materials were purchased from Merck, Germany. The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck, 230–400 mesh, Germany) and were identified by comparison of their spectra (^{1}H NMR, ^{13}C NMR, IR) and physical data with those of the authentic samples. Nuclear magnetic resonance spectra were recorded on a Bruker DRX-400 AVANCE spectrometer (Germany) in $CDCl_3$ or DMSO as solvent. Melting points were determined using an Electrothermal Thermo Scientific IA9200 apparatus (USA). Mass spectra were obtained on an Agilent technologies instrument (USA) and IR spectra were determined on a Shimadzu instrument (Kyoto, Japan). Powder X-ray diffraction data were obtained using a Shimadzu XD-D1 diffractometer (Kyoto, Japan) using Cu Ka radiation ($\lambda = 1.5418$ Å). The transmission electron micrographs (TEM) were obtained with a Philips CM10 microscope (The Netherlands).

Preparation of ZnO Nanoparticles

To prepare nanosized particles of zinc oxide,[29] we used the method of mechanochemical synthesis from salt systems. Zinc acetate [$Zn(CH_3CO_2)_2.2H_2O$] and oxalic acid [$H_2C_2O_4.2H_2O$] were used as the main raw materials. Zinc acetate was dried at 120°C in air for 24 h prior to use. In a typical synthesis, starting materials [$Zn(CH_3COO)_2.2H_2O$ and $H_2C_2O_4.2H_2O$] were put in an agate mortar with molar ratio of 2:3 and mixed and milled for 45 min at room temperature. The white powders (precursor) were calcined at 450°C in air in a porcelain crucible for 30 min to prepare the ZnO nanoparticles. The results obtained from XRD pattern and TEM micrograph of the ZnO nanoparticles show that the mean particle size is 15 nm.

General Procedure

To a mixture of aq. 98% formic acid (3 mmol, 0.11 mL) and ZnO nanoparticles (2 mol%, 0.0016 g) was added an amine (1 mmol). The reaction mixture was heated in an oil bath at 70°C with continuous stirring. The progress of the reaction was monitored by TLC. After completion of the reaction, CH_2Cl_2 or EtOAc was added to the cooled reaction mixture, and then filtered to remove the ZnO nanoparticles. The organic solvent was washed with H_2O (2×10 mL) and a saturated solution of $NaHCO_3$ and dried over anhydrous Na_2SO_4. After removal of the solvent, the pure product was obtained. This was further purified by recrystallization with suitable solvent (Table 1).

RESULTS AND DISCUSSION

In this study, we prepared nanosized ZnO catalyst[29] and used it successfully in the synthesis of *N*-formylation of amines. X-ray diffraction pattern of the mechanochemically synthesized zinc oxide is shown in Figure 1. The diffraction angle and intensity of the characteristic peaks of the samples is well consistent with that of the standard JCPDS card No. 36–1451. The value of 15.8 nm was calculated from XRD data for average particle size of this crystalline ZnO using Scherrer's equation.[30] Figure 2 shows a typical TEM micrograph of the ZnO nanoparticles. It can be observed that the particles are almost 10–20 nm, which is in good agreement with XRD crystal sizes.

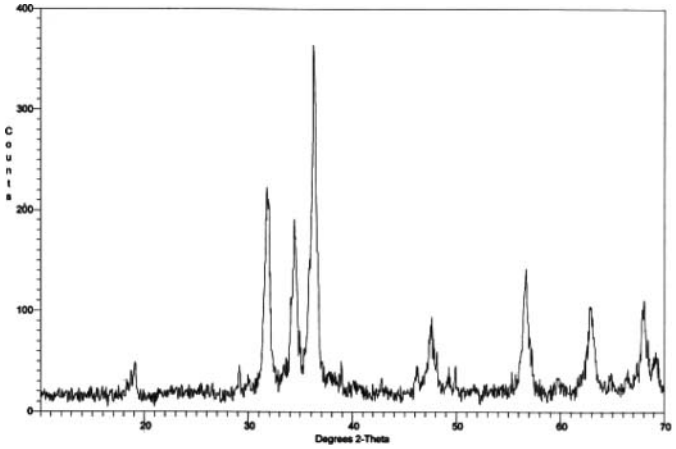

FIG. 1. X-ray diffraction pattern of ZnO nanoparticles.

Encouraged with the initial success in the *N*-formylation reaction, we carried out formylation of aniline (1 mmol) with aq.

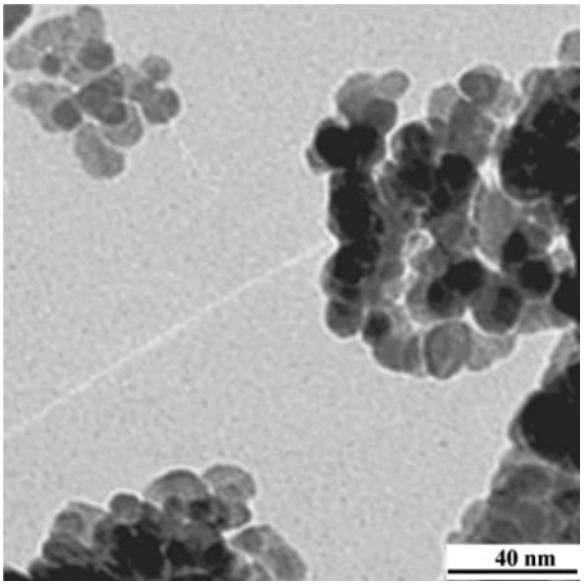

FIG. 2. TEM micrograph of synthesis ZnO nanoparticle.

TABLE 1
N-Formylation of amines with formic acid catalyzed by ZnO-nanoparticles[a]

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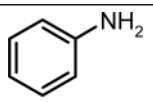
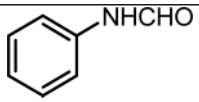
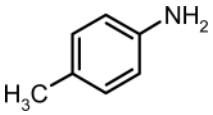
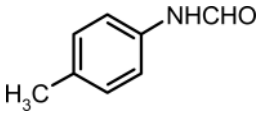
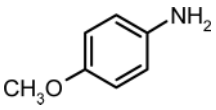
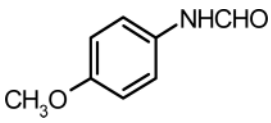
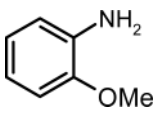
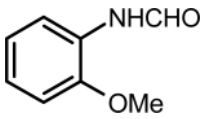
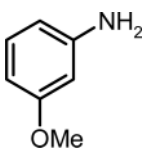
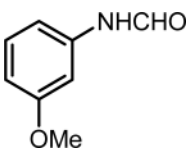
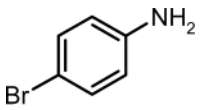
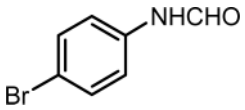
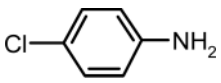
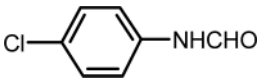
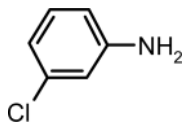
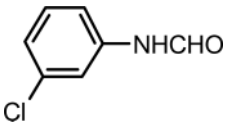
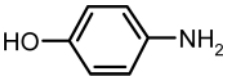
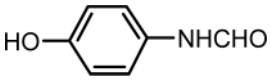
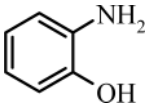
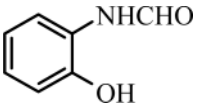
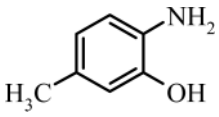
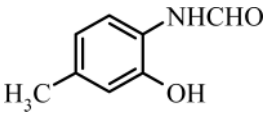
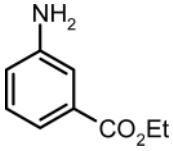
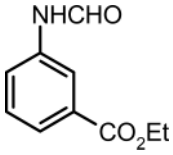
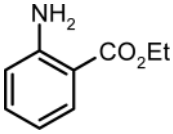
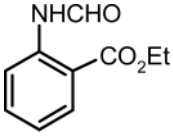
1		7		98	[25]
2		6		95	[31]
3		3		94	[24]
4		25		92	[32]
5		6		94	[33]
6		35		93	[25]
7		30		95	[31]
8		15		94	[34]
9		30		98	[25]
10		25		95	[25]
11		40		96	[25]
12		42		96	[35]
13		60		89	[36]

(Continued on next page)

TABLE 1
N-Formylation of amines with formic acid catalyzed by ZnO-nanoparticles[a] *(Continued)*

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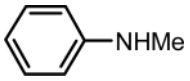
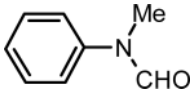
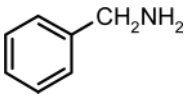
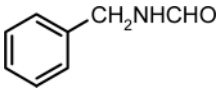
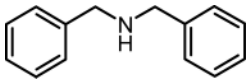
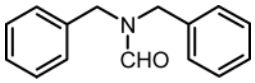
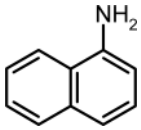
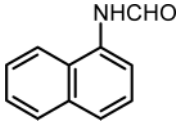
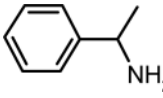
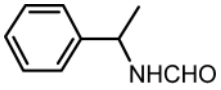
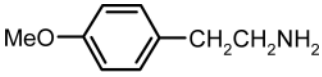
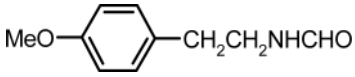
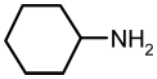
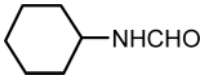
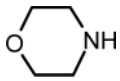
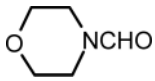
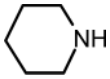
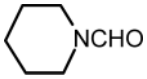
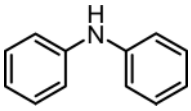
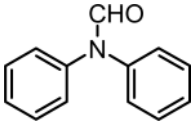
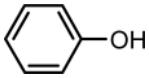
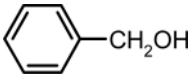
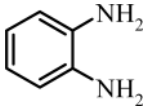
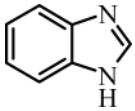
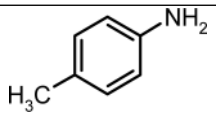
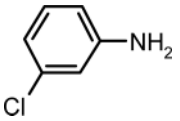
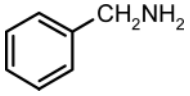
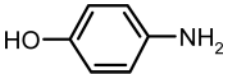
14		45		93	[37]
15		20		95	[24]
16		360		81	[24]
17		90		98	[38]
18		15		92	[39]
19		30		90	[40]
20		20		91	[31]
21		20		93	[25]
22		30		93	[39]
23		360		85	[25]
24		-	No reaction	-	-
25		-	No reaction	-	-
26		6		97	[41]

[a]Reaction conditions: formic acid (3 mmol, 0.11 mL), amine (1 mmol), and ZnO nanoparticles (2 mol%, 0.0016 g) at 70°C.
[b]Yields refer to isolated pure products.

98% formic acid (3 mmol) under solvent-free condition. In the process of optimization of this reaction, we explored different amount of NAP-ZnO and formic acid with various solvents at different temperatures. In the absence of the catalyst, formamide was obtained in trace amount after 2 h at 70°C, while good results were obtained in the presence of NAP-ZnO (2 mol%) after 7 min. In continuation, we optimized the catalyst amount. With inclusion of 1 mol% of NAP-ZnO the reaction took longer time. Using more than 2 mol% of NAP-ZnO (5, 7, and 10 mol%) has less effect on the yield and time of the reaction. Thus, we

TABLE 2
Comparison nano-ZnO with other catalysts for N-formylation of amines

Entry	Amine	Nano-ZnO		Other catalysts			
		Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
1		6	95	20	92[a]	30	98[b]
2		15	94	25	93[a]	-	-
3		20	95	150	85[c]	90	90[b]
4		30	98	50	93[a]	330	92[c]

[a]ZnO.[23]
[b]$ZnCl_2$.[25]
[c]Sodium formate.[39]

found that 2 mol% of NAP-ZnO could effectively catalyze the reaction for synthesis of the desired product. Then, the effect of temperature was studied by carrying out the model reaction in the presence of NAP-ZnO (2 mol%) at room temperature, 50°C, and 70°C. It was observed that the best yield obtained at 70°C. Also we investigated the effect of different solvents (CH_2Cl_2 and CH_3CN) on the reaction, the results showed the reaction needed longer time (90 and 150 min, respectively) than solventless condition, therefore the solvent free condition was selected. Finally, we surveyed the different amount of formic acid (1, 2, and 3 mmol) in the reaction and the best reaction time and yield was obtained using 3 mmol of formic acid.

Aliphatic and aromatic primary and secondary amines (1 mmol) converted to their *N*-formyl derivatives in an easy route in the presence of NAP-ZnO (2 mol%) in formic acid (3 mmol) at 70°C under solvent free condition (Table 1).

To widen the scope, we subjected a series of other aromatic amine derivatives having electron-donating as well as electron-withdrawing substituents to obtain the corresponding formamides with excellent yields under the optimized reaction conditions. Previously, the *N*-formylation of anilines having electron-withdrawing groups was found to be difficult.[31] When anilines are substituted at the 4-position with electron-donating (ED) groups, higher reaction rates are observed than the one bearing electron-withdrawing (EW) groups at that position (Table 1, entries 2, 3, 6, 7, and 9). On the other hand, in the *N*-formylation reaction of amines using NAP-ZnO, 2-substituted anilines with either EW or ED groups (Table 1, entries 4, 10, 11, and 13) exhibit a decrease of reaction time when compared with the corresponding 3 or 4-substituted anilines, which may be ascribed to the steric hindrance for the unidirectional entry of reacting species (Table 1, entries 3, 5, and 8).

O-Formylation of benzylalcohol and phenol under this reaction condition was not successful (Table 1, entries 24 and 25). Also, the formylation of amines occurred selectively in the presence of hydroxyl group (Table 1, entries 9–11). Therefore, the described catalytic formylating system is chemoselective.

Heterocyclic amines are easily formylated to the corresponding formamides in high to excellent yields (Table 1, entries 21 and 22).

When *o*-phenylenediamine was used, instead of *N*-formylation, cyclization occurred to give benzimidazole as a product (Table 1, entry 26).

In order to show the advantages and the drawbacks of nano-ZnO for the *N*-formylation of amines, we have compared the results with some of those reported with other catalysts in Table 2. The results clearly signify the usefulness of the present catalyst for the synthesis of formamides. Although, Hosseini and coworkers[25] described formylation of amines with 50 mol% ZnO, but, in comparison of our method, it is evident that, the catalytic activity of the nano-ZnO is much greater than that of the bulk-ZnO.

Furthermore, NAP-ZnO can also be recovered by filtration. It was washed with distilled water and dichloromethane, dried for 2 h under vacuum and reused as a catalyst in the formylation reaction. The NAP-ZnO recycled for four runs without loss of its activity.

CONCLUSION

In conclusion, we have shown that the synthesized NAP-ZnO catalyze the *N*-formylation of amines with formic acid in high to excellent yields and in short duration. Our protocol avoids the use of expensive reagents and the reaction performed under solvent free condition serves as an efficient method. We believe that the present methodology could be an important addition to the existing methodologies. The NAP-ZnO was well characterized by transmission electron microscopy (TEM) and powder X-ray diffraction (powder XRD). The advantages of the present method are (a) the ease of preparation of NAP-ZnO; (b) using NAP-ZnO as a reusable, nontoxic, and inexpensive heterogeneous nanocatalyst; (c) mild reaction conditions; (d) easy and clean work-up; (e) more convenient and environmentally benign; (f) high to excellent product yields and (g) excellent chemoselectivity.

The physical and spectral data (mp, IR, ^{1}H NMR, and ^{13}C NMR) of selected products 5, 10, 11, and 17 are given subsequently.

3-methoxyformanilide (entry 5): Light yellow viscous oil. IR (KBr): 3110, 2890, 1660, 1570, 1140 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 50:50 (*cis/trans*), δ 8.71 (d, 1H, J = 11.6 Hz, *cis*), 8.38 (s, 1H, *trans*), 8.13 (brd, 1H, *cis*), 7.41 (brd, 1H, *trans*), 6.63–6.76 (m, 4H, Ar-H), 7.01–7.32 (m, 4H, Ar-H), 3.85 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 55.35 (CH_3, *trans*), 55.41 (CH_3, *cis*), 104.98 (CH, *trans*), 105.85 (CH, *cis*), 110.42 (CH, *trans*), 110.59 (CH, *cis*), 110.95 (CH, *trans*), 111.99 (CH, *cis*), 129.82 (CH, *trans*), 130.64 (CH, *cis*), 137.89 (C, *trans*), 138.05 (C, *cis*), 158.96 (C=O, *trans*), 160.17 (C, *trans*), 160.71 (C, *cis*), 162.42 (C=O, *cis*).

Ethyl 3-formamidobenzoate (entry 10): White powder, m.p = 73–76°C. IR (KBr): 3318, 3012, 1687, 1612, 1483, 1098 cm^{-1}. ^{1}H NMR (400 MHz, DMSO): 19:81 (*cis/trans*), δ 10.45 (s, 1H), 8.85 (d, 0.19H, *J* = 11.2 Hz, *cis*), 8.32 (s, 0.81H, *trans*), 8.25 (s, 1H, Ar-H), 7.46–7.82 (m, 3H, Ar-H), 4.31 (q, 2H, J = 7.2 Hz), 1.31 (t, 3H, J = 7.2 Hz). ^{13}CNMR (400 MHz, DMSO): δ = 14.61 (CH_3), 61.30 (CH_2, *cis*), 61.36 (CH_2, *trans*), 118.4 (CH, *cis*), 119.98 (CH, *trans*), 122.0 (CH, *cis*), 124.0 (CH, *trans*), 124.6 (CH, *cis*), 124.7 (CH, *trans*), 129.8 (CH, *cis*), 130.3 (CH, *trans*), 130.96 (C, *cis*), 131.5 (C, *trans*), 139.0 (C, *cis*), 139.3 (C, *trans*), 160.4 (C=O, ester, *cis*), 163.0 (C=O, ester, *trans*), 165.8 (C=O, formyl, *cis*), 165.9 (C=O, formyl, *trans*).

Ethyl 2-formamidobenzoate (entry 11): Creme powder, m.p = 61–64°C. IR (KBr): 3281, 2996, 1693, 1591, 1526, 1082 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 22:78 (*cis/trans*), δ 11.05 (brd, 0.22H, cis), 10.51 (brs, 0.78H, *trans*), 8.96 (d, 0.22H, *J* = 11.2 Hz, *cis*), 8.71 (d, 0.78H, *J* = 8.4 Hz, *trans*), 8.52 (m, 1H, Ar-H), 7.13–8.06 (m, 3H, Ar-H), 4.39 (q, 2H, J = 7.2), 1.43 (t, 3H, J = 7.2). ^{13}CNMR (400 MHz, $CDCl_3$): δ = 14.17 (CH_3), 61.52 (CH_2), 115.5 (C, *trans*), 115.7 (C, *cis*), 121.2 (CH), 123.1 (CH, *trans*), 123.3 (CH, *cis*), 130.9 (CH, *trans*), 131.9 (CH, *cis*), 134.3 (CH, *trans*), 134.6 (CH, *cis*), 140.5 (C), 159.5 (C=O, ester, *trans*), 161.3 (C=O, ester, *cis*), 168.0 (C=O, formyl).

N-(4-methoxyphenyl) ethylformamide (entry 17): Light yellow viscous oil. IR (KBr): 3390, 2938, 1658, 1112, cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 19: 81 (*cis/trans*), δ 8.4 (brd, 1H), 8.15 (s, 0.81H, *cis*), 8.15 (d, 0.19H, *trans*), 7.14 (d, 2H, J = 6.4, Ar-H), 7.14 (d, 2H, J = 6.8, Ar-H), 6.8 (d, 2H, J = 6.4, Ar-H), 6.2 (brd, 1H), 3.8 (s, 3H), 3.51 (dd, 2H, *J* = 6.4, 6.8 Hz, *trans*), 3.40 (dd, 0.5H, *J* = 6.4, 6.8 Hz, *cis*), 2.77 (t, 2H, *J* = 6.8 Hz, *trans*), 2.74 (t, 0.44H, *J* = 6.8 Hz, *cis*). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 34.6 (CH_2, *trans*), 36.86 (CH_2, *cis*), 39.4 (CH_2, *trans*), 43.29 (CH_2, *cis*), 55.29 (CH_3, *trans*), 55.31 (CH_3, *cis*), 114.14 (CH, *trans*), 114.28 (CH, *cis*), 128.24 (C), 129.71 (CH, *trans*), 129.84 (CH, *cis*), 130.37 (C), 161.11 (C=O, *trans*), 164.42 (C=O, *cis*).

REFERENCES

1. (a) Singh, R.; Kissling, M.R.; Letellier, A.M.; Nolan, P.S. *J. Org. Chem.* **2004**, *69*, 209. (b) Anastas, P.T.; Bartlett, L.B.; Kirchhof, M.M.; Williamson, C.T. *Catal. Today* **2000**, *55*, 11.
2. Tanabe, K. *Solid Acids and Bases*; Academic Press, New York, **1970**.
3. Feldmann, C.; Jungk, H. *Angew. Chem. Int. Ed.* **2001**, *40*, 359.
4. Wang, Y.; Ma, C.; Sun, X.; Li, H. *Inorg. Chem. Commun.* **2002**, *5*, 751.
5. Palkar, V.R. *Nanostruct. Mater.* **1999**, *11*, 369.
6. Park, H.K.; Kim, D.K.; Kim, C.H. *J. Am. Ceram. Soc.* **1997**, *80*, 743.
7. Kodas, T.T. *Adv. Mater.* **1989**, *6*, 180.
8. Zhang, B.P.; Binh, N.T.; Wakatsuki, K.; Segawa, Y.; Yamada,Y.; Usami, N.; Kawasaki, M.; Koinuma, H. *J. Phys. Chem. B* **2004**, *108*, 10899.
9. Li, F.; Yu, X.; Pan, H.; Wang, M.; Xin, X. *Solid State Sci.* **2000**, *2*, 767.
10. Soiron, S.; Rougier, A.; Aymard, L.; Tarascon, J. *J. Power Sources* **2001**, *97/98*, 402.
11. Yang, H.; Hu, Y.; Tang, A.; Jin, S.; Qiu, G. *J. Alloys Compd.* **2004**, *363*, 271.
12. (a) Jackson, A.; Meth-Cohn, O. *J. Chem. Soc. Chem. Commun.* **1995**, 1319. (b) Kobayashi, K.; Nagato, S.; Kawakita, M.; Morikawa, O.; Konishi, H. *Chem. Lett.* **1995**, 575. (c) Kakehi, A.; Ito, S.; Hayashi, S.; Fujii, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3573. (d) Lohray, B.B.; Baskaran, S.; Rao, B.S.; Reddy, B.Y.; Rao, I.N. *Tetrahedron Lett.* **1999**, *40*, 4855.
13. Tsuzuki, T.; McCormick, P.G. *Scripta Mater.* **2001**, *44*, 1731.
14. Chen, B.C.; Bednarz, M.S.; Zhao, R.; Sundeen, J.E.; Chen, P.; Shen, Z.; Skoumbourdis, A.P.; Barrish, J.C. *Tetrahedron Lett.* **2000**, *41*, 5453.
15. Han, Y.; Cai, L. *Tetrahedron Lett.* **1997**, *38*, 5423.
16. Effenberger, F.; Eichhorn, J. *Tetrahedron: Asymmetry* **1997**, *8*, 469.
17. Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620.
18. Kobayashi, S.; Yasuda, M.; Hachiya, I. *Chem. Lett.* **1996**, 407.
19. (a) Waki, M.; Meienhofer, J. *J. Org. Chem.* **1977**, *42*, **2019**. (b) Chen, F.M. F.; Benoiton, N.L. *Synthesis* **1979**, 709.
20. (a) Yale, H.L. *J. Org. Chem.* **1971**, *36*, 3238. (b) Kisfaludy, L.; Laszlo, O. *Synthesis* **1987**, 510. (c) Duezek, W.; Deutsch, J.; Vieth, S.; Niclas, H.J. *Synthesis* **1996**, 37.
21. Blicke, F.F.; Lu, C.J. *J. Am. Chem. Soc.* **1952**, *74*, 3933.
22. Reddy, P.G.; Kumar, G.D. K.; Baskaran, S. *Tetrahedron Lett.* **2000**, *41*, 9149.

23. (a) Desai, B.; Danks, T.N.; Wagner, G. *Tetrahedron Lett.* **2005**, *46*, 955. (b) Das, B.; Krishnaiah, M.; Balasubramanyam, P.; Veeranjaneyulu, B.; Nandankumar, D. *Tetrahedron Lett.* **2008**, *49*, 2225.
24. Chandra Shekhar, A.; Ravi Kumar, A.; Sathaiah, G.; Luke Paul, V.; Sridhar, M.; Shanthan Rao, P. *Tetrahedron Lett.* **2009**, *50*, 7099.
25. Hosseini-Sarvari, M.; Sharghi, H. *J. Org. Chem.* **2006**, *71*, 6652.
26. Akbari, J.; Hekmati, M.; Sheykhan, M.; Heydari, A. *ARKIVOC* **2009**, 123.
27. Kim, J.G.; Jang, D.O. *Synlett* **2010**, 1231.
28. Rahman, M.; Kundu, D.; Hajra, A.; Majee, A. *Tetrahedron Lett.* **2010**, *51*, 2896.
29. Shen, L.; Bao, N.; Yanagisawa, K.; Domen, K.; Gupta, A.; Grimes, C.A. *Nanotechnology* **2006**, *17*, 5117.
30. Cullity, B.D. *Elements of X-ray Diffraction*, vol. 1; Addison-Wesley, Boston, **1978**.
31. Pratap, T.V.; Baskaran, S. *Tetrahedron Lett.* **2001**, *42*, 1983.
32. Ikawa, T.; Barder, T.E.; Biscoe, M.R.; Buchwald, S.L. *J. Am. Chem. Soc.* **2007**, *129*, 13001.
33. Kavalek, J.; Sterba, V. *Collect. Czech. Chem. Commun.* **1975**, *40*, 1924.
34. Tumma, H.; Nagaraju, N.; Reddy, K.V. *J. Mol. Catal. A.* **2009**, *310*, 121.
35. Connolly, T.J.; Durst, T. *Can. J. Chem*. **1997**, *75*, 536.
36. Cai, L.; Han, Y.; Ren, S.; Huang, L. *Tetrahedron* **2000**, *56*, 8253.
37. Jung, S.H.; Ahn, J.H.; Park, S.K.; Choi, J.K. *Bull. Korean Chem. Soc.* **2002**, *23*, 149.
38. Saito, I.; Takami, M.; Matsuura, T. *Bull. Chem. Soc. Japan* **1975**, *48*, 2865.
39. Hill, D.R.; Hasiao, C.N.; Kurukulasuriya, R.; Wittenberger, S. *Org. Lett.* **2002**, *4*, 111.
40. Sawa, Y.; Kato, T.; Masuda, T.; Hori, M.; Fujimura, H. *Yakugaku Zasshi*, **1975**, *95*, 251.
41. Alinezhad, H.; Salehian, F.; Biparva, P. *Syn. Commun.* **2012**, *42*, 102.