


1-1-2010

## Friedel-Crafts acylation of arenes with carboxylic acids using silica gel supported $AlCl_3$

KAVEH PARVANAK

Follow this and additional works at: <https://journals.tubitak.gov.tr/chem>

 Part of the [Chemistry Commons](#)

---

### Recommended Citation

PARVANAK, KAVEH (2010) "Friedel-Crafts acylation of arenes with carboxylic acids using silica gel supported  $AlCl_3$ ," *Turkish Journal of Chemistry*. Vol. 34: No. 4, Article 14. <https://doi.org/10.3906/kim-0912-359>

Available at: <https://journals.tubitak.gov.tr/chem/vol34/iss4/14>

This Article is brought to you for free and open access by TÜBİTAK Academic Journals. It has been accepted for inclusion in Turkish Journal of Chemistry by an authorized editor of TÜBİTAK Academic Journals. For more information, please contact [academic.publications@tubitak.gov.tr](mailto:academic.publications@tubitak.gov.tr).

# Friedel-Crafts acylation of arenes with carboxylic acids using silica gel supported $\text{AlCl}_3$

Kaveh PARVANAK BOROUJENI

*Department of Chemistry, Shahrekord University, Shahrekord 115, IRAN*

*e-mail: parvanak-ka@sci.sku.ac.ir*

Received 12.12.2009

Aromatic compounds react smoothly with carboxylic acids in the presence of silica gel supported aluminium trichloride to afford the corresponding ketones with high regioselectivity in high to excellent yields. The catalyst is stable (as a bench top catalyst) and can be easily recovered and reused without appreciable change in its efficiency.

**Key Words:** Acylation, aluminium trichloride, ketones, silica gel

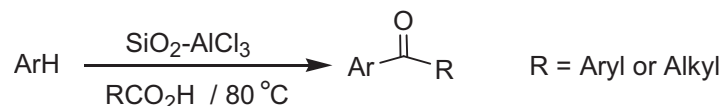
## Introduction

In recent years, the use of heterogeneous catalysts has received considerable attention in different areas of organic synthesis. The high selectivity, nontoxicity, easy separation from the reaction media, recyclability, moisture and air tolerance, and easier handling make the use of heterogeneous catalysts an attractive alternative to conventional homogeneous catalysts.<sup>1</sup>

Friedel-Crafts acylation reactions are of great importance in both laboratory work and industrial processes to synthesize aromatic ketones.<sup>2,3</sup> Usually, these reactions are performed using acid chlorides or acid anhydrides in the presence of protic acids or Lewis acids.<sup>4–12</sup> The major disadvantages associated with the reported methods for the acylation of arenes are the use of toxic acid chlorides or anhydrides as acylating agents, a need for the use of stoichiometric or excessive amounts of catalyst in reactions, tedious work-up, environmental pollution, and the use of moisture sensitive, unrecyclable, hazardous, or difficult-to-handle catalysts. These disadvantages could be avoided by performing the acylation of arenes with carboxylic acids as acylating agents over recoverable solid acid catalysts. The Friedel-Crafts acylation of arenes using carboxylic acids is preferable to acylation via acid chlorides and anhydrides because the former reaction produces only water as a by-product, which meets recent requirements for environmentally benign chemical processes. Furthermore, carboxylic acids are stable and more available compounds, and their handling is much easier than that of corresponding acid chlorides and

anhydrides. However, the aromatic acylation using carboxylic acids, especially in the presence of heterogeneous Lewis acid catalysts, is scarcely reported.<sup>13–25</sup>

In a continuation of our ongoing program to develop environmentally benign methods using heterogeneous Lewis acid catalysts, we found that silica gel supported aluminium trichloride (SiO<sub>2</sub>-AlCl<sub>3</sub>) was a good catalyst for the Friedel-Crafts sulfonylation of aromatic compounds.<sup>26</sup> Along this line, we now wish to report that SiO<sub>2</sub>-AlCl<sub>3</sub> is also an effective and highly chemoselective catalyst for the acylation of aromatic compounds with carboxylic acids under mild reaction conditions (Scheme 1).



**Scheme 1.** Acylation of arenes with carboxylic acids using SiO<sub>2</sub>-AlCl<sub>3</sub>.

## Experimental

**General:** Chemicals were either prepared in our laboratory or purchased from Merck and Fluka. Capacity of the catalyst was determined by the gravimetric method and atomic absorption technique using a Philips atomic absorption instrument. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica gel polygram SILG/UV<sub>254</sub> plates. Gas chromatography was performed in an apparatus from Shimadzu with a flame ionization detector and SE-30 coated (5% on Chromosorb W-HP) packed 3-ft column. The temperature was programmed to rise from 80 to 280 °C at 10 °C/min (injection temperature: 300 °C). IR spectra were run on a Shimadzu model 8300 FTIR spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer.

### Preparation of SiO<sub>2</sub>-AlCl<sub>3</sub>

Anhydrous AlCl<sub>3</sub> (5.1 g) was added to silica gel (Merck, grade 60, 230-400, washed with 1 M HCl and dried under vacuum at 80 °C for 72 h, 10.2 g) in carbon tetrachloride (30 mL). The mixture was stirred using a magnetic stirrer under reflux conditions for 2 days in an N<sub>2</sub> atmosphere and filtered and washed with 50 mL of dry CCl<sub>4</sub>, and then dried under vacuum at 60 °C for 3 h. The determined loading of AlCl<sub>3</sub> was 1.3 mmol/g.<sup>27</sup>

### Typical experimental procedure

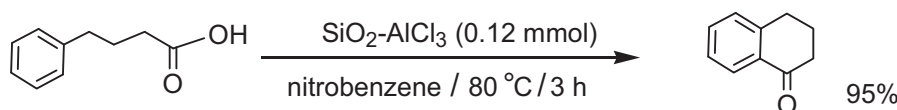
To a solution of *o*-xylene (5 mmol) and heptanoic acid (4 mmol), 0.4 mmol of SiO<sub>2</sub>-AlCl<sub>3</sub> was added, and the reaction mixture was stirred magnetically at 80 °C. After completion of the reaction (monitored by TLC and GC), the catalyst was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was washed with an aqueous solution of sodium bicarbonate and water, and the organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated on a rotary evaporator under reduced pressure to give the corresponding ketone: <sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>)δ 0.82-0.91 (m, 3H), 1.23-1.41 (m, 6H), 1.63-1.74 (m, 2H), 2.26-2.33 (m, 6H), 2.80 (t, J = 7.2 Hz, 0.1H, 2,3-dimethyl isomer), 2.90 (t, J = 7.2 Hz, 1.9H, 3,4-dimethyl isomer), 7.11 (t, J = 7.2 Hz, 0.05H, 2,3-dimethyl isomer), 7.13-7.20 (m, 1H), 7.25 (d, J = 7.2 Hz, 0.05H, 2,3-dimethyl isomer), 7.65 (d, J = 7.2 Hz, 0.95H, 3,4-dimethyl isomer), 7.70

(d,  $J = 7.2$  Hz, 0.95H, 3,4-dimethyl isomer); IR (KBr)  $\nu$ :  $1685\text{ cm}^{-1}$  (C=O). Whenever required, the products were purified by column chromatography (silica gel) using petroleum ether-ethyl acetate as an eluent so as to afford the pure ketone.

## Results and discussion

$\text{SiO}_2\text{-AlCl}_3$  was prepared by reacting silica gel with aluminium trichloride in refluxing carbon tetrachloride. Using catalytic amounts of this catalyst in the Friedel-Crafts acylation of arenes with carboxylic acids as acylating agents in solvent-free conditions, high to excellent yields of product were obtained (Table 1). The optimum molar ratio of  $\text{SiO}_2\text{-AlCl}_3$  to carboxylic acid was 0.1:1. From the results, it is clear that  $\text{SiO}_2\text{-AlCl}_3$  is capable of catalyzing not only the acylation of activated arenes but also that of deactivated arenes (Table 1, entries 1-23). The methodology showed the excellent positional selectivity as the para-substituted product was formed exclusively. Naphthalene, 2-methoxynaphthalene, and anthracene underwent acylation with high regioselectivity in 88%-91% yields (Table 1, entries 24-30). It was pleasing to observe that even heterocyclic compounds such as furan, thiophene, and pyrrole were smoothly converted into the corresponding ketones, a conversion which is otherwise problematic in the presence of strong acid catalysts (Table 1, entries 31-36). These reactions were regioselective, producing only the 2-acyl product in high to excellent yields. The acylation of indoles with carboxylic acids in the presence of  $\text{SiO}_2\text{-AlCl}_3$  was also studied, and the corresponding indolyl aryl ketones were obtained with high regioselectivity in high to excellent yields. For example, indole and 5-bromoindole were converted to their corresponding ketones with benzoic acid in 89% and 90% yields, respectively (Table 1, entries 37-38). No *N*-substituted products were observed under these reaction conditions. Acylation of highly deactivated arenes such as nitrobenzene and 1,2-dichlorobenzene failed. Side product formation was not observed in the reactions we studied.  $\text{SiO}_2\text{-AlCl}_3$  was stable under the reaction conditions, and during the reactions no leaching of acid moieties was observed due chemical bonding to the support.

One notable achievement of this solid acid catalyst is intramolecular Friedel-Crafts acylation. For example, 4-phenylbutanoic acid cyclized in nitrobenzene at  $80\text{ }^\circ\text{C}$  in the presence of  $\text{SiO}_2\text{-AlCl}_3$  to give the desired 1-tetralone in 95% yield (Scheme 2).



**Scheme 2.** Intramolecular Friedel-Crafts acylation using  $\text{SiO}_2\text{-AlCl}_3$ .

Following these results, we further investigated the potential of  $\text{SiO}_2\text{-AlCl}_3$  for the selective acylation of different types of substituted benzenes. The results showed that  $\text{SiO}_2\text{-AlCl}_3$  is able to discriminate between aromatic compounds containing electron donating and electron withdrawing groups, a transformation that is difficult to accomplish via conventional methods. For example, toluene was selectively converted to the corresponding ketone in the presence of chlorobenzene (Scheme 3). Furthermore, it was also observed that the catalyst is efficient for the selective acylation of anisole over toluene. Although the reason for the observed chemoselectivities is not exactly clear, it is possibly due to the mild catalytic activity of the solid catalyst.

Table 1. Acylation of arenes with carboxylic acids catalyzed by SiO<sub>2</sub>-AlCl<sub>3</sub>.<sup>a</sup>


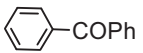
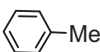
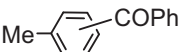
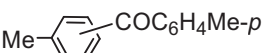
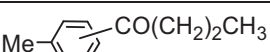
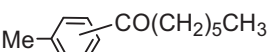
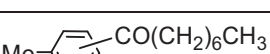

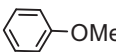
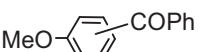
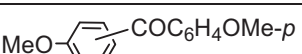
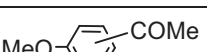
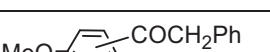
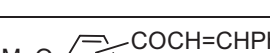
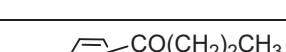
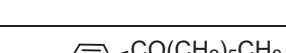
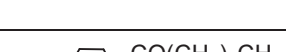
Entry	Arene	Carboxylic acid	Product	Time (h)	Yield (%) ( <i>o:m:p</i> ) <sup>b</sup>
1		PhCO <sub>2</sub> H		2	90 <sup>20,28</sup>
2		PhCO <sub>2</sub> H		1.8	91(5:4:91) <sup>25</sup>
3	"	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> COOH		1.7	91(5:0:95) <sup>29</sup>
4	"	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H		1.7	95(4:0:96) <sup>13</sup>
5	"	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CO <sub>2</sub> H		1.7	94(4:0:96) <sup>13</sup>
6	"	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CO <sub>2</sub> H		1.8	90(3:0:97) <sup>13</sup>
7	"	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> H		1.9	89(3:0:97) <sup>13</sup>
8		PhCO <sub>2</sub> H		1.6	93(6:3:91) <sup>25</sup>
9	"	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H		1.5	95(6:3:91) <sup>15,25</sup>
10	"	MeCO <sub>2</sub> H		1.5	96(6:4:90) <sup>30,31,32</sup>
11	"	PhCH <sub>2</sub> CO <sub>2</sub> H		1.6	95(6:3:91) <sup>33</sup>
12	"	PhCH=CHCO <sub>2</sub> H		1.9	90(4:0:96) <sup>25,34</sup>
13	"	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H		1.5	92(5:4:91) <sup>16,18</sup>
14	"	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CO <sub>2</sub> H		1.6	91(5:0:95) <sup>16,18</sup>
15	"	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CO <sub>2</sub> H		1.6	90(3:0:97) <sup>16,18</sup>

Table 1. Continued

Entry	Arene	Carboxylic acid	Product	Time (h)	Yield (%) ( <i>o:m:p</i> ) <sup>b</sup>
16	"	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> H		1.7	90(3:0:97) <sup>16,18</sup>
17		CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CO <sub>2</sub> H		1.7	90(95:5) <sup>c,21</sup>
18		PhCO <sub>2</sub> H		1.8	91 <sup>25</sup>
19	"	MeCO <sub>2</sub> H		1.7	92 <sup>18,35</sup>
20		PhCO <sub>2</sub> H		1.8	88(3:4:93) <sup>d,28</sup>
21		PhCO <sub>2</sub> H		1.6	90(7:0:93) <sup>28,29</sup>
22		PhCO <sub>2</sub> H		2	89(5:0:95) <sup>28</sup>
23	"	MeCO <sub>2</sub> H		1.9	87(4:3:93) <sup>28</sup>
24		PhCO <sub>2</sub> H		2.5	91(7:93) <sup>d,e,28</sup>
25		PhCO <sub>2</sub> H		2.4	90 <sup>d,25</sup>
26	"	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H		2.5	89 <sup>d,25</sup>
27	"	MeCO <sub>2</sub> H		2.2	91 <sup>d,18,36</sup>

Table 1. Continued

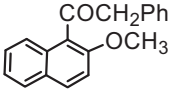
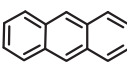
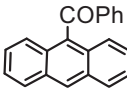
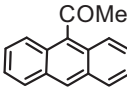

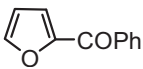
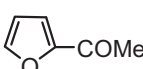

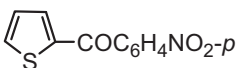
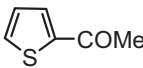
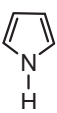
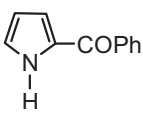
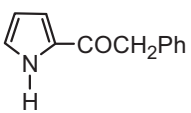
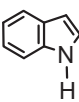
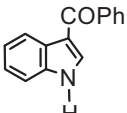
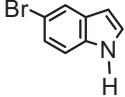
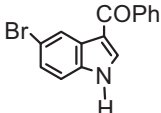
Entry	Arene	Carboxylic acid	Product	Time (h)	Yield (%) ( <i>o:m:p</i> ) <sup>b</sup>
28	"	PhCH <sub>2</sub> CO <sub>2</sub> H		2.3	91 <sup>d,18,37</sup>
29		PhCO <sub>2</sub> H		2.7	88 <sup>d,25</sup>
30	"	MeCO <sub>2</sub> H		2.6	90 <sup>d,18,36</sup>
31		PhCO <sub>2</sub> H		2.3	90 <sup>f,20,38</sup>
32	"	MeCO <sub>2</sub> H		2.2	90 <sup>f,5,39</sup>
33		<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H		2.5	93 <sup>f,5</sup>
34	"	MeCO <sub>2</sub> H		2.5	95 <sup>f,5,40</sup>
35		PhCO <sub>2</sub> H		2.3	88 <sup>f,5,41</sup>
36	"	PhCH <sub>2</sub> CO <sub>2</sub> H		2.3	89 <sup>f,5,18</sup>
37		PhCO <sub>2</sub> H		3	90 <sup>d,42,43,44</sup>

Table 1. Continued

Entry	Arene	Carboxylic acid	Product	Time (h)	Yield (%) ( <i>o:m:p</i> ) <sup>b</sup>
38		PhCO <sub>2</sub> H		3.1	89 <sup>d,42,43,44</sup>

<sup>a</sup>All reactions carried out at 80 °C in the absence of solvent, unless otherwise indicated. The molar ratio of SiO<sub>2</sub>-AlCl<sub>3</sub> to carboxylic acid is 0.1:1.

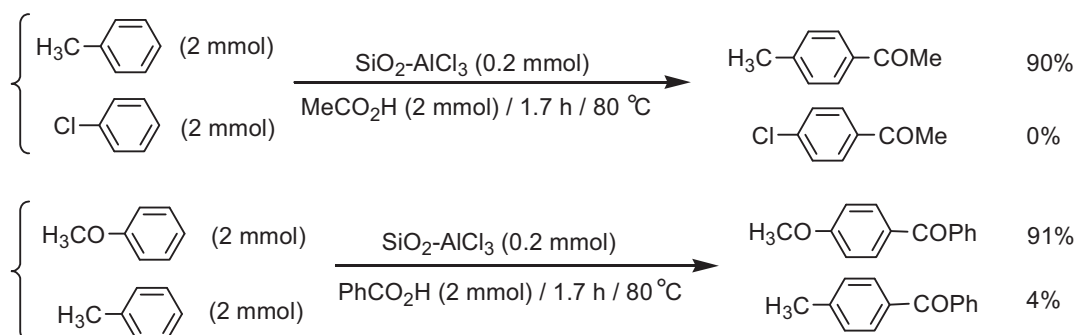
<sup>b</sup>Isolated yields. Isomer distribution based on <sup>1</sup>H-NMR spectroscopy and GC. All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples.

<sup>c</sup>Isomer distribution of 3,4-dimethylphenyl isomer to 2,3-dimethylphenyl isomer.

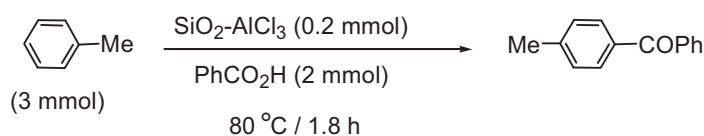
<sup>d</sup>The reaction was performed in 1,2-dichloroethane.

<sup>e</sup> $\alpha:\beta$  ratio.

<sup>f</sup>The reaction was performed at 60 °C.



**Scheme 3.** Selective acylation of different types of substituted benzenes using SiO<sub>2</sub>-AlCl<sub>3</sub>.



Use <sup>a</sup>	1	2	3	4	5
Yield (%)	91	91	90	90	89

<sup>a</sup>Recovered catalyst was used successively (Use 2,3,4,...)

**Scheme 4.** Acylation of toluene using recovered SiO<sub>2</sub>-AlCl<sub>3</sub>.

SiO<sub>2</sub>-AlCl<sub>3</sub> can be used several times with negligible loss of catalytic activity and there is no need for regeneration (Scheme 4). The capacity of the catalyst after 5 uses was 1.3 mmol AlCl<sub>3</sub> per gram.



A comparison of the efficiency of  $\text{SiO}_2\text{-AlCl}_3$  catalyst with some of those reported in the literature is given in Table 2. As it is seen, in addition to having the general advantages attributed to the solid supported catalysts,  $\text{SiO}_2\text{-AlCl}_3$  has a good efficiency compared to other recently reported catalysts.

**Table 2.** Comparison of the catalytic activity of  $\text{SiO}_2\text{-AlCl}_3$  against other reported catalysts for the acylation of anisole and toluene with carboxylic acids.

Arene	Carboxylic acid	Catalyst	Temp. ( $^{\circ}\text{C}$ )	Time (h)	Yield (%) ( <i>o</i> : <i>p</i> )
Anisole	Benzoic acid	$\text{SiO}_2\text{-AlCl}_3$	80	1.6	93(6:91)
"	"	$\text{AlPW}_{12}\text{O}_{40}$	120	10	92 <sup>18</sup>
"	"	$\text{AlPW}_{12}\text{O}_{40}/\text{TFAA}^a$	25	2.5	96 <sup>18</sup>
"	"	$\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$	85	5	65 <sup>25</sup>
Anisole	Heptanoic acid	$\text{SiO}_2\text{-AlCl}_3$	80	1.7	91(5:95)
"	"	HZSM-5 zeolite	150	48	5 <sup>14</sup>
"	"	$\text{Eu}(\text{NTf}_2)_3$	250	6	87(3:97) <sup>21</sup>
Anisole	Octanoic acid	$\text{SiO}_2\text{-AlCl}_3$	80	1.6	90(3:97)
"	"	$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	110	5	45(1:73) <sup>16</sup>
"	"	Beta zeolite	155	6	42.6(1:38) <sup>22</sup>
Anisole	Dodecanoic acid	$\text{SiO}_2\text{-AlCl}_3$	80	1.7	90(3:97)
"	"	$\text{FePW}_{12}\text{O}_{40}$	160	1	97(2:98) <sup>24</sup>
Toluene	Octanoic acid	$\text{SiO}_2\text{-AlCl}_3$	80	1.8	90(3:97)
"	"	CeNaY zeolite	150	48	75(3:94) <sup>13</sup>

<sup>a</sup>Trifluoroacetic anhydride.

## Conclusion

A convenient and chemoselective method of acylation of aromatic compounds has been devised. The significant advantages of this methodology are mild reaction conditions, high to excellent yields, short reaction times, solvent-free conditions, low cost, and easy preparation and handling of the catalyst. In addition, the use of  $\text{SiO}_2\text{-AlCl}_3$  resulted in a reduction in the unwanted and hazardous waste that is produced during conventional homogeneous processes. Finally, the reaction work-up is effected through a simple filtration process, and the catalyst recovered after a reaction can be washed with solvent and used again at least 5 times with no impaired yield.

## Acknowledgements

The author thanks the Research Council of Shahrekord University for partial support of this work.

## References

- Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815-4195, and references cited therein.
- Jensen, R.; Goldman, G. In *Friedel-Crafts and Related Reactions*, vol. III; Olah, G., Ed.; Wiley Interscience, New York, 1964.
- Franck, H. G.; Stadelhofer, J. W. *Industrial Aromatic Chemistry*, Springer-Verlag, Berlin, 1988.
- Hosseini Sarvari, M.; Sharghi, S. *J. Org. Chem.* **2004**, *69*, 6953-6956.
- Kantam, M. L.; Ranganath, K. V. S.; Sateesh, M.; Kumar, K. B. S.; Choudary, B. M. *J. Mol. Catal. A; Chem.* **2005**, *225*, 15-20.
- Earle, M. J.; Hakala, U.; Hardacre, C.; Karkkainen, J.; McAuley, B. J.; Rooney, D. W.; Seddon, K. R.; Thompson, J. M.; Wahala, K. *Chem. Commun.* **2005**, 903-905.
- Gopalakrishnan, M.; Sureshkumar, P.; Kanagarajan, V.; Thanusu, J. *Catal. Commun.* **2005**, *6*, 753-756.
- Jang, D. O.; Moon, K. S.; Cho, D. H.; Kim, J. G. *Tetrahedron Lett.* **2006**, *47*, 6063-6066.
- Sartori, G.; Maggi, R. *Chem. Rev.* **2006**, *106*, 1077-1104.
- Li, C.; Liu, W.; Zhao, Z. *Catal. Commun.* **2007**, *8*, 1834-1837.
- Zayed, F.; Greiner, L.; Schulz, P. S.; Lapkin, A.; Leitner, W. *Chem. Commun.* **2008**, 79-81.
- de Noronha, R. G.; Fernandes, A. C.; Romao, C. C. *Tetrahedron Lett.* **2009**, *50*, 1407-1410.
- Chiche, B.; Finiels, A.; Gauthier, C.; Geneste, P. *J. Org. Chem.* **1986**, *51*, 2128-2130.
- Wang, Q. L.; Ma, Y.; Ji, X.; Yan, H.; Qiu, Q. *J. Chem. Soc., Chem. Commun.* **1995**, 2307-2308.
- Ma, Y.; Wang, Q. L.; Jiang, W.; Zuo, B. *Appl. Catal. A: General* **1997**, *165*, 199-206.
- Kaur, J.; Kozhevnikov, I. V. *Chem. Commun.* **2002**, 2508-2509.
- Cui, D. M.; Kawamura, M.; Shimada, S.; Hayashi, T.; Tanaka, M. *Tetrahedron Lett.* **2003**, *44*, 4007-4010.
- Firouzabadi, H.; Iranpoor, N.; Nowrouzi, F. *Tetrahedron* **2004**, *60*, 10843-10850.
- Cui, D. M.; Zhang, C.; Kawamura, M.; Shimada, S. *Tetrahedron Lett.* **2004**, *45*, 1741-1745.
- Hosseini Sarvari, M.; Sharghi, H. *Synthesis* **2004**, 2165-2168.
- Kawamura, M.; Cui, D. M.; Shimada, S. *Tetrahedron* **2006**, *62*, 9201-9209.
- Wagholikar, S. G.; Niphadkar, P. S.; Mayadevi, S.; Sivasanker, S. *Appl. Catal. A: General* **2007**, *317*, 250-257.
- Khodaei, M. M.; Alizadeh, A.; Nazari E. *Tetrahedron Lett.* **2007**, *48*, 4199-4202.
- Shimizu, K. I.; Niimi, K.; Satsuma, A. *Catal. Commun.* **2008**, *9*, 980-983.
- Hajipour, A. R.; Zarei, A.; Khazdooz, L.; Ruoho, A. E. *Synth. Commun.* **2009**, *39*, 2702-2722.
- Parvanak Borujeni, K.; Tamami, B. *Catal. Commun.* **2007**, *8*, 1191-1196.
- In the preparation, 1.0 g of solid catalyst was fused with Na metal, extracted with 10 mL of water, and filtered. The aluminium and chloride content of the filtrate was determined by the Mohr titration method. For the procedure, refer to: I. M. Kolthoff, E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 3rd ed., Macmillan Company, New York, 1965, pp. 451 and 542.
- Paul, S.; Nanda, P.; Gupta, R.; Loupy, A. *Synthesis* **2003**, 2877-2881.

29. Gopalakrishnan, M.; Sureshkumar, P.; Kanagarajan, V.; Thanusu, J. *Catal. Commun.* **2005**, *6*, 753-756.
30. Desmurs, J. R.; Labrouillere, M.; Roux, C. L.; Gaspard, H.; Laporterie, A.; Dubac, J. *Tetrahedron Lett.* **1997**, *38*, 8871-8874.
31. Kobayashi, S.; Iwamoto, S. *Tetrahedron Lett.* **1998**, *39*, 4697-4700.
32. Chen, X.; Yu, M.; Wang, M. *J. Chem. Res.* **2005**, 80-81.
33. Chapman, C. J.; Frost, C. G.; Hartley, J. P.; Whittle, A. J. *Tetrahedron Lett.* **2001**, *42*, 773-775.
34. Sasse, A.; Ligneau, X.; Sadek, B.; Elz, S.; Pertz, H. H.; Ganellin, C. R.; Arrang, J. M.; Schwartz, J. C.; Schunack, W.; Stark, H. *Arch. Pharm. (Weinheim, Ger.)* **2001**, *334*, 45-52.
35. Kawada, A.; Mitamura, S.; Kobayashi, S. *Synlett* **1994**, 545-546.
36. Gatti, N. *Tetrahedron Lett.* **1990**, *31*, 3933-3935.
37. Pivsa-Art, S.; Okura, K.; Miura, M.; Murata, S.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1994**, *13*, 1703-1706.
38. Strekowski, L.; Wydra, R. L.; Cegła, M. T.; Czarny, A.; Patterson, S. *J. Org. Chem.* **1989**, *54*, 6120-6123.
39. Kawada, A.; Mitamura, S.; Kobayashi, S. *J. Chem. Soc., Chem. Commun.* **1996**, 183-184.
40. Nomiya, K.; Sugaya, Y.; Sasa, S.; Miwa, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2089-2090.
41. Cadamuro, S.; Degani, I.; Dughera, S.; Fochi, R.; Gatti, A.; Prandi, C. *Gazz. Chim. Ital.* **1990**, *120*, 619-627.
42. Akgün, E.; Pindur, U.; Müller, J.;. *Heterocycl. Chem.* **1983**, *20*, 1303-1306.
43. *Dictionary of Organic Compounds*; 6th Ed., Vol. 9; Chapman and Hall, London, 1996, p. 566.
44. Miki, Y.; Tsuzaki, Y.; Kai, C.; Hachiken, H. *Heterocycles* **2002**, *57*, 1635-1643.