*Chemistry of Heterocyclic Compounds, Vol. 48, No. 6, September, 2012 (Russian Original Vol. 48, No. 6, June, 2012)*

# NANO-$SnCl_4 \cdot SiO_2$ – A VERSATILE AND EFFICIENT CATALYST FOR SYNTHESIS OF 14-ARYL- OR 14-ALKYL-14*H*-DIBENZO[*a*,*j*]XANTHENES

**B. F. Mirjalili[1]*, A. Bamoniri[2], and M. A. Mirhoseini[1]**

*2-Naphthol and various aldehydes were used for the synthesis of 14-aryl- or 14-alkyl-14H-dibenzo[a,j]xanthene in the presence of nano-$SnCl_4 \cdot SiO_2$ under solvent-free condition. Nano-$SnCl_4 \cdot SiO_2$ is an efficient, readily available, and reusable catalyst for this reaction resulting in good to excellent yields.*

**Keywords:** 14-aryl- or 14-alkyl-14*H*-dibenzo[*a*,*j*]xanthenes, nano-$SnCl_4 \cdot SiO_2$, 2-naphthol, reusable catalyst, solvent-free conditions.

Tin tetrachloride is a powerful Lewis acid which is, however, a highly volatile, corrosive liquid that is difficult to handle. In the presence of moisture it is readily hydrolyzed to produce HCl. Silica-supported $SnCl_4$ [1-2] is a mild solid Lewis acid, which could promote acid-catalyzed organic reactions. It does not need special precautions for preparation, handling, or storage. It can be stored at ambient temperatures for months without losing its catalytic activity. This catalyst was previously applied for the one-pot synthesis of β-acetamido ketones [3], acylals [4], and silylation of hydroxyl group [5].

Benzoxanthenes possessing therapeutic and pharmacological properties, such as antibacterial [6], anti-inflammatory [7], and antiviral [8] activities, are important compounds in organic synthesis. Furthermore, these heterocyclic derivatives are used as sensitizers in photodynamic therapy [9], as leuco-dyes in laser technology [10], as antagonists of the paralyzing action of zoxazolamine [11], and in fluorescent materials for visualization of biomolecules [12]. 14-Aryl- or 14-alkyl-14*H*-dibenzo[*a*,*j*]xanthenes are prepared *via* condensation of 2-naphthol with various aldehydes. Previously, catalysts such as $Mg(HSO_4)_2$ [13], silica chloride [14], $TaCl_5$ [15], $SiO_2$–$PrSO_3H$ [16], $Sc[N(SO_2C_8F_{17})_2]_3$ [17], 1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate (MIMPS)$HSO_4$ [18], $Fe(HSO_4)_3$ [19], and $BiCl_3$ [20] were applied for the above-mentioned reaction.

In continuation of our investigations on the application of solid acids in organic synthesis [3, 21–27], we have studied the synthesis of these compounds in the presence of nano-silica-supported tin chloride as an acidic catalyst. Nano-$SnCl_4 \cdot SiO_2$ was prepared *via* the reaction of nano-$SiO_2$ with $SnCl_4$. The morphology of nanoparticles was observed with SEM. The particle sizes of the commercial nano-silica gel and synthesized 35% nano-$SnCl_4 \cdot SiO_2$ (**1**) were about 24 nm and 42 nm, respectively (Fig. 1).

---

*To whom correspondence should be addressed, e-mail: fmirjalili@yazduni.ac.ir.

[1]College of Science, Yazd University, P.O. Box 8915813149, Yazd, Iran.
[2]University of Kashan, P.O. Box 87317-51167, Kashan, Iran; e-mail: bamoniri@kashanu.ac.ir.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 923-927, May, 2012. Original article submitted July 27, 2011.

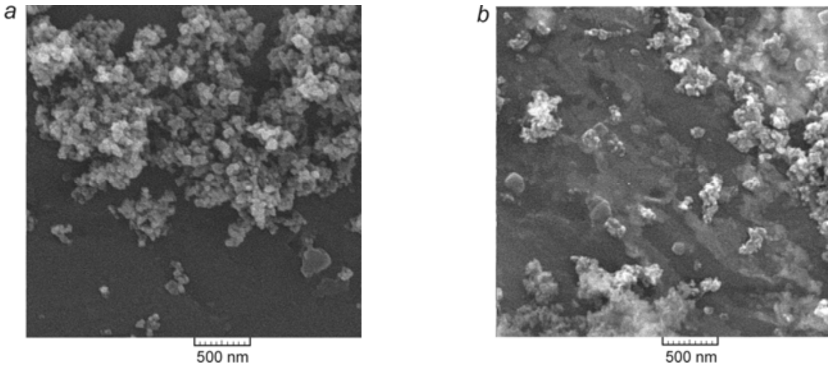
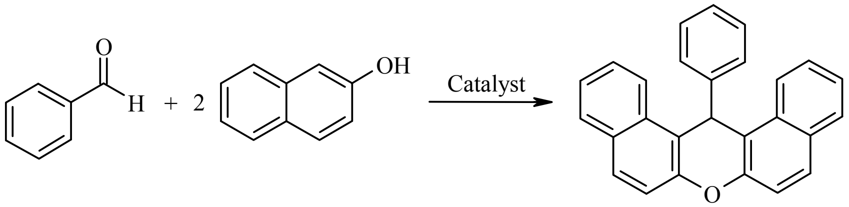


Fig. 1. SEM photograph of (*a*) nano-$SiO_2$ and (*b*) 35% nano-$SnCl_4 \cdot SiO_2$ (**1**).

Because the catalyst **1** produces HCl in water, we determined its acidic capacity by titration. We have found that 1 g of catalyst produced 4.95 mmol of $H^+$. Also, the loading amount of Sn on 1 g of 50% $SnCl_4 \cdot SiO_2$ (**2**) was determined by the addition of hot water and separation of the obtained $Sn(OH)_4$ as a floating solid. The calculated loading amount of Sn in the catalyst is 65.6 $mg \cdot g^{-1}$. The percent of $SnCl_4 \cdot SiO_2$ was calculated

TABLE 1. Preparation of 14-(4-Bromophenyl)-14*H*-dibenzo[*a,j*]xanthene under Various Conditions*



| Entry | Ref. | T, °C | Time, h | Solvent | Catalyst (g) | Yield, % |
|---|---|---|---|---|---|---|
| 1 | — | 90 | 1 | — | $SiO_2$ (0.1) | 10 |
| 2 | — | 70 | 1 | — | 30% $SnCl_4 \cdot SiO_2$ (0.05) | 65 |
| 3 | — | 70 | 1 | — | 50% $SnCl_4 \cdot SiO_2$ (0.05) | 74 |
| 4 | — | 90 | 1 | — | 50% $SnCl_4 \cdot SiO_2$ (0.05) | 93 |
| 5 | — | reflux | 2 | $CHCl_3$ | 50% $SnCl_4 \cdot SiO_2$ (0.05) | 20 |
| 6 | — | reflux | 1.5 | EtOAc | 50% $SnCl_4 \cdot SiO_2$ (0.05) | 30 |
| 7 | — | reflux | 2 | $H_2O$ | 50% $SnCl_4 \cdot SiO_2$ (0.05) | 35 |
| 8 | — | reflux | 2 | EtOH | 50% $SnCl_4 \cdot SiO_2$ (0.05) | — |
| 9 | — | 90 | 1 | — | $SnCl_4$ (0.5 ml) | 80 |
| 10 | — | 90 | 0.7 | — | 20% nano-$SnCl_4 \cdot SiO_2$ (0.015) | 70 |
| 11 | — | 90 | 0.7 | — | 35% nano-$SnCl_4 \cdot SiO_2$ (0.01) | 72 |
| 12 | — | 90 | 0.2 | — | 35% nano-$SnCl_4 \cdot SiO_2$ (0.015) | 92 |
| 13 | — | 90 | 1 | — | 35% nano-$SnCl_4 \cdot SiO_2$ (0.015), 2nd run | 82 |
| 14 | — | 90 | 1 | — | 35% nano-$SnCl_4 \cdot SiO_2$ (0.015), 3rd run | 70 |
| 15 | [13] | 60 | 0.3 | — | $Mg(HSO_4)_2$ | 97 |
| 16 | [15] | 100 | 1 | — | $TaCl_5$ | 95 |
| 17 | [16] | 125 | 0.3 | — | $SiO_2$–$PrSO_3H$ | 98 |
| 18 | [17] | 110 | 5 | perfluoro-decalin | $Sc[N(SO_2C_8F_{17})_2]_3$ | 93 |
| 19 | [18] | 100 | 0.1 | — | (MIMPS)$HSO_4$ | 93 |
| 20 | [19] | reflux | 4 | $(ClCH_2)_2$ | $Fe(HSO_4)_3$ | 85 |
| 21 | [20] | 110 | 0.1 | — | $BiCl_3$ | 96 |

---

* The ratio of 2-naphthol (mmol) : aldehyde (mmol) : 35% nano-$SnCl_4 \cdot SiO_2$ (g) is 2:1:0.015.

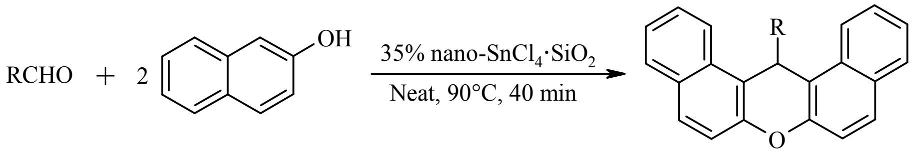
according to the assumed silica gel-bonded $SnCl_3$. The chemical absorption of $SnCl_4$ to silica gel is partial, and the number of bonded chlorine atom to any Sn is unknown. Therefore, the calculated amounts of Sn and HCl are not equivalent.

In this research, we have applied various $SnCl_4 \cdot SiO_2$ and nano-$SnCl_4 \cdot SiO_2$ catalysts for the synthesis of 14-aryl- or 14-alkyl-14*H*-dibenzo[*a,j*]xanthenes. The reaction of benzaldehyde with 2 equivalents of 2-naphthol was examined to optimize the reaction conditions (Table 1). The best run in the presence of 50% $SnCl_4 \cdot SiO_2$ (**2**) was achieved in a solvent-free regime at 90°C (Entry 4).

We have repeated the above-mentioned reactions with 35% nano-$SnCl_4 \cdot SiO_2$ and found that the activity of the catalyst **1** is 3.3 times higher compared to bulk $SnCl_4 \cdot SiO_2$, requiring only 0.015 g. Moreover, the reactions in the presence of 35% nano-$SnCl_4 \cdot SiO_2$ were completed in a shorter time (Entry 12). The reactions were done in an open vessel without any $N_2$ protection. The reaction when conducted with 1-naphthol instead of 2-naphthol did not afford any product. To examine the reusability of 35% nano-$SnCl_4 \cdot SiO_2$ (**1**) in a solvent-free condition after each consequent run, the product was dissolved in $CHCl_3$ and filtered through Whatman paper. The catalyst residue was washed with acetone, dried at 100°C, and used once again. Treatment with acetone removes the tar from the catalyst surface more efficiently (Entries 13 and 14). The catalyst **1** was found to be reusable, although a gradual decline was observed in its activity. All of the obtained products were known substances characterized by their IR and $^1H$ NMR spectra and physical properties in the literature.

According to the obtained best conditions, we have applied 2-naphthol and various aldehydes for the synthesis of 14-aryl- or 14-alkyl-14*H*-dibenzo[*a,j*]xanthene derivatives (Table 2).

TABLE 2. Synthesis of 14-Aryl- or 14-Alkyl-14*H*-dibenzo[*a,j*]xanthenes in the Presence of 35% nano-$SnCl_4 \cdot SiO_2$ at 90°C for 40 min*



| R | Mp, °C | | Yield, % |
|---|---|---|---|
| | Measured | Reported [Ref.] | |
| Et | 151-150 | 150-152 [13] | 81 |
| 3-$O_2NC_6H_4$ | 210-211 | 210-211 [13] | 93 |
| 4-$BrC_6H_4$ | 297-298 | 297 [13] | 92 |
| 4-$MeC_6H_4$ | 227-229 | 227-229 [13] | 89 |
| 4-$ClC_6H_4$ | 288-289 | 290 [20] | 90 |
| 4-$O_2NC_6H_4$ | 311-312 | 311-312 [13] | 95 |
| 4-$MeOC_6H_4$ | 202-204 | 203-205 [13] | 85 |
| 2-$ClC_6H_4$ | 214-215 | 214-216 [13] | 90 |
| Ph | 184-185 | 184 [20] | 80 |
| *i*-Bu | 155-156 | 155-157 [13] | 73 |
| *n*-Bu | 152-153 | 151-153 [17] | 75 |
| 4-$HOC_6H_4$ | 136-137 | 139-141 [16] | 85 |
| 2,4-$ClC_6H_3$ | 267-269 | 269-270 [16] | 89 |

---

* The ratio of 2-naphthol (mmol) : aldehyde (mmol) : 35% nano-$SnCl_4 \cdot SiO_2$ (g) is 2:1:0.015.

The applicability of the present method to a large-scale process was examined with 20 mmol of 2-naphthol and 10 mmol of benzaldehyde under thermal conditions, which gave 14-phenyldibenzo[*a,j*]xanthene in 79% yield.

Thus, 35% nano-$SnCl_4 \cdot SiO_2$ was applied for the preparation of 14-aryl- or 14-alkyl-14*H*-dibenzo-[*a,j*]xanthene derivatives in a simple and straightforward protocol. Short reaction time, high yields, simplicity of operation, easy work-up, and catalyst reusability are advantages of this method.

## EXPERIMENTAL

Melting points were determined on a Buchi melting point B-540 B.V.CHI apparatus and were uncorrected. SEM of nano particles was performed with a VEGA/TESCAN scanning electron microscope. The progress of the reactions of 2-naphthol and aldehydes was monitored by TLC using silica gel F 254 80 TLC plates, with EtOAc–hexane 1:4 as eluent. The commercial nano-silica gel was purchased from Aldrich company. All other chemicals were purchased from Sigma–Aldrich and Merck and were used without any additional purification.

**Preparation of 35% Nano-$SnCl_4 \cdot SiO_2$ (1)**. To a mixture of nano-silica gel (0.65 g) and $CHCl_3$ (5 ml), $SnCl_4$ (0.35 g, 0.16 ml, 1.34 mmol) was added dropwise. The resulting suspension was stirred for 1 h at room temperature, filtered, washed with chloroform, and dried at room temperature.

The synthesis of 20% nano-$SnCl_4 \cdot SiO_2$ was performed in a similar manner by mixing $SnCl_4$ (0.2 g, 0.77 mmol) and nano-silica gel (0.8 g) in $CHCl_3$ (5 ml).

**Preparation of 50% $SnCl_4 \cdot SiO_2$ (2)**. To a mixture of silica gel (0.5 g) and $CHCl_3$ (5 ml), $SnCl_4$ (0.5 g, 0.22 ml, 1.92 mmol) was added dropwise. The resulting suspension was stirred for 1 h at room temperature, filtered, washed with chloroform, and dried at room temperature.

The synthesis of 30% $SnCl_4 \cdot SiO_2$ was performed in a similar manner by mixing $SnCl_4$ (0.3 g, 1.15 mmol) and silica gel (0.7 g) in $CHCl_3$ (5 ml).

**14-Aryl or 14-Alkyl-14*H*-dibenzo[*a,j*]xanthenes (General Method)**. A mixture of 2-naphthol (0.288 g, 2 mmol), aldehyde (1 mmol), and 35% nano-$SnCl_4 \cdot SiO_2$ (0.015 g) was heated at 90°C. After completion of the reaction, the product was dissolved in $CHCl_3$ and filtered to recover the catalyst, which was then washed with hot EtOH. The filtrate was cooled to obtain crude 14-aryl- or 14-alkyl-14*H*-dibenzo[*a,j*]xanthene derivatives, which were recrystallized from 2-PrOH–$CHCl_3$, 8:2.

## REFERENCES

1. M. J. Pilling, P. Gardner, M. E. Pemble, and M. Surman, *Surf. Sci.*, **418**, L1 (1998).
2. M. J. Pilling, P. Gardner, R. Kausar, M. E. Pemble, and M. Surman, *Surf. Sci.*, **433**, 22 (1999).
3. B. B. F. Mirjalili, M. M. Hashemi, B. Sadeghi, and H. Emtiazi, *J. Chin. Chem. Soc.*, **56**, 386 (2009).
4. H. C. Li and Y. Q. Li, *Chin. Chem. Lett.*, **12**, 565 (2001).
5. K. Niknam, M. A. Zolfigol, D. Saberi, and H. Molaee, *J. Chin. Chem. Soc.*, **56**, 1257 (2009).
6. T. Hideo, JP Pat. Appl. 56005480; *Chem. Abstr.*, **95**, 80922b (1981).
7. J.-P. Poupelin. G. Saint-Ruf, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Ernouf, and R. Lacroix, *Eur. J. Med. Chem.*, **13**, 67 (1978).
8. R. W. Lambert, J. A. Martin, J. H. Merrett, K. E. B. Parkes, and G. J. Thomas, WO Pat. Appl. 9706178; *Chem. Abstr.*, **126**, p212377y (1997).
9. R.-M. Ion, A. Planner, K. Wiktorowicz, and D. Frackowiak, *Acta Biochim. Pol.*, **45**, 833 (1998).
10. S. M. Menchen, S. C. Benson, J. Y. L. Lam, W. Zhen, D. Sun, B. B. Rosenblum, S. H. Khan, and M. Taing, US Pat. Appl. 6583168; *Chem. Abstr.*, **139**, 54287f (2003).

11. G. Saint-Ruf, A. De, and H. T. Hieu, *Bull. Chim. Ther.*, **7**, 83 (1972).
12. A. Bekaert, J. Andrieux, and M. Plat, *Tetrahedron Lett.*, **33**, 2805 (1992).
13. B. F. Mirjalili, A. Bamoniri, and A. Akbari, *Chin. Chem. Lett.*, **22**, 4548 (2011).
14. L. Q. Wu, C. G. Yang, L. M. Yang, and L. J. Yang, *Phosphorus, Sulfur Silicon Relat. Elem.*, **185**, 903 (2010).
15. A. K. Bhattacharya, K. C. Rana, M. Mujahid, I. Sehar, and A. K. Saxena, *Bioorg. Med. Chem. Lett.*, **19**, 5590 (2009).
16. G. M. Ziarani, A. R. Badiei, and M. Azizi, *Sci. Iran.*, **18**, 453 (2011).
17. M. Hong and C. Cai, *J. Fluorine Chem.*, **130**, 989 (2009).
18. K. Gong, D. Fang, H.-L. Wang, X.-L. Zhou, and Z.-L. Liu, *Dyes Pigm.*, **80**, 30 (2009).
19. H. Eshghi, M. Bakavoli, and H. Moradi, *Chin. Chem. Lett.*, **19**, 1423 (2008).
20. E. Soleimani, M. M. Khodaei, and A. T. K. Koshvandi, *Chin. Chem. Lett.*, **22**, 927 (2011).
21. B. Sadeghi, B. B. F. Mirjalili, and M. M. Hashemi, *Tetrahedron Lett.*, **49**, 2575 (2008).
22. B. B. F. Mirjalili, A. Bamoniri, and A. Akbari, *Tetrahedron Lett.*, **49**, 6454 (2008).
23. B. Sadeghi, B. B. F. Mirjalili, and M. M. Hashemi, *J. Iran. Chem. Soc.*, **5**, 694 (2008).
24. B. B. F. Mirjalili, A. Bamoniri, and A. Akbari, *Khim. Geterotsikl. Soedin.*, 591 (2011). [*Chem. Heterocycl. Compd.*, **47**, 487 (2011).]
25. B. B. F. Mirjalili, and A. Akbari, *Chin. Chem. Lett.*, **22**, 753 (2011).
26. B. F. Mirjalili, A. Bamoniri, A. Akbari, and N. Taghavinia, *J. Iran. Chem. Soc.*, **8**, S129 (2011).
27. B. F. Mirjalili, A. Bamoniri, and A. Akbari, *J. Iran. Chem. Soc.*, **8**, S135 (2011).