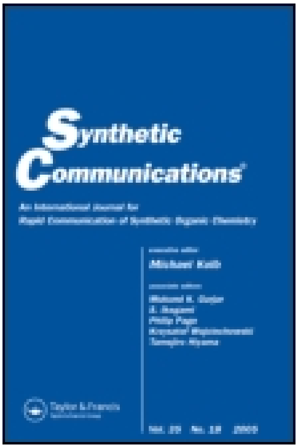


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Fluoroboric Acid Adsorbed on Silica-Gel-Catalyzed Synthesis of 14-Aryl-14H-dibenzo[a,j]xanthene Derivatives

Yu-Heng Liu [a], Xu-Ye Tao [a], Li-Qin Lei [a] & Zhan-Hui Zhang [a]

[a] College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang, China

To cite this article: Yu-Heng Liu , Xu-Ye Tao , Li-Qin Lei & Zhan-Hui Zhang (2009): Fluoroboric Acid Adsorbed on Silica-Gel-Catalyzed Synthesis of 14-Aryl-14H-dibenzo[a,j]xanthene Derivatives, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:4, 580-589

To link to this article: http://dx.doi.org/10.1080/00397910802412842

Synthetic Communications®, 39: 580–589, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802412842

Taylor & Francis
Taylor & Francis Group

Fluoroboric Acid Adsorbed on Silica-Gel–Catalyzed Synthesis of 14-Aryl-14*H*-dibenzo[*a,j*]xanthene Derivatives

Yu-Heng Liu, Xu-Ye Tao, Li-Qin Lei, and Zhan-Hui Zhang
College of Chemistry and Material Science, Hebei Normal University,
Shijiazhuang, China

Abstract: A simple and efficient procedure has been developed for the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives using fluoroboric acid adsorbed on silica gel as a heterogeneous catalyst. The methodology involves the one-pot condensation reaction of β-naphthol and aryl aldehydes under solvent-free conventional heating conditions. The present approach offers several advantages such as shorter reaction times, simple work-up, excellent yields, low cost, and mild reaction conditions. The catalyst is easily recoverable and reusable without loss of its catalytic activity.

Keywords: Aldehyde, HBF_4-SiO_2, heterogeneous catalyst, β-naphthol, solvent-free conditions, xanthene

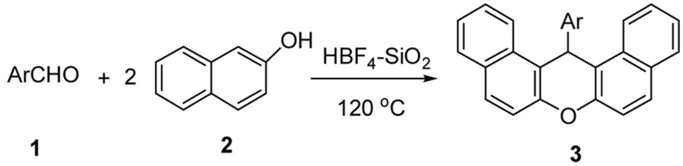
Xanthene and its derivatives are known as an important class of heterocyclic compounds. They have been widely used as leuco-dye,[1] in laser technology,[2] and fluorescent materials.[3] They have been reported to possess diverse biological and therapeutic properties such as antibacterial, antiviral, and anti-inflammatory activities.[4] These compounds are also utilized as antagonists for the paralyzing action of zoxazolamine and in photodynamic therapy.[5] As a result, various synthetic approaches have been developed for the preparation of such compounds including cyclohydration, trapping of benzynes by phenols, and cyclocondensation

Received June 1, 2008.

Address correspondence to Zhan-Hui Zhang, College of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050091, China. E-mail: zhahui@126.com

between 2-hydroxy aromatic aldehydes and 2-tetralone. In addition, 14-aryl-14*H*-dibenzo[*a,j*]xanthenes and related products are prepared by reaction of 2-naphthol and formamide, 2-naphthol-1-methanol, carbon monoxide, or aldehydeacetals.[6] In spite of potential utility of aforementioned routes for the synthesis of xanthene derivatives, many of these methods suffer from one or more disadvantages, such as low yields, prolonged reaction time, and lack of easy availability of the starting materials. Recently, several improved procedures were reported for the synthesis of 14*H*-dibenzo[*a,j*]xanthene by the reaction of 2-naphthol with aldehydes in the presence of protic acids such as toluenesulfonic acid[7] and methanedulfonic acid;[8] Lewis acids such as $KAl(SO_4)_2{\cdot}12H_2O$,[9] $Ce(SO_4)_2$,[10] LiBr[11] and iodine;[12] and heterogeneous catalysts such as sulfamic acid,[13] $NaHSO_4{\cdot}SiO_2$,[14] WO_3/ZrO_2,[14] Amberlyst-15,[15] perchloric acid–silica,[16] cation-exchange resin,[17] and Dowex-50W.[18] Other catalysts used for this transformation are potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40}{\cdot}3H_2O$),[19] sulfonyl-functionalized ionic liquid,[20] and wet cyanuric chloride.[21] However, some of these catalysts are toxic, difficult to prepare, and expensive. Thus, the quest for less expensive, environmentally benign, and easily handled catalyst and mild reaction conditions for the synthesis of xanthenes is a major challenge.

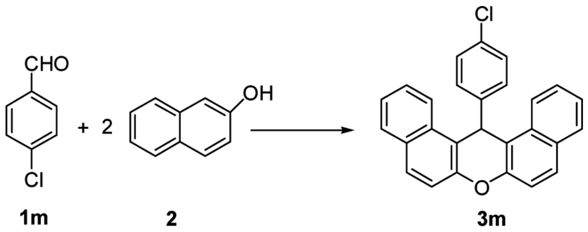
In recent years, solid-supported catalysts, in which the catalysts are absorbed onto an insoluble inorganic or organic support, have been applied widely in organic synthesis.[22] Silica-supported fluoroboric acid as a recyclable solid acid catalyst was prepared by adsorbing fluoroboric acid on silica gel.[23] It has been demonstrated to be an efficient catalyst for various useful chemical transformations, such as the ring opening of epoxides with nitrogen heterocycles,[24] conversion of aldehydes into acetals[25] or acylals,[26] chemoselective protection of carbonyl compounds, transthioacetalization of *O,O*- and *S,O*-acetals,[27] Mannich-type reaction,[28] thia-Michael addition,[29] and the synthesis of 1,5-benzodiazepines[30] and thiiranes.[31] In continuation of our work to develop new synthetic methodologies,[32] we report for the first time a facile and efficient synthetic strategy for the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives using HBF_4-SiO_2 as heterogeneous catalyst under solvent-free conditions (Scheme 1).



Scheme 1. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives.

To prove the catalytic activity of HBF_4-SiO_2 in the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives, we initially conducted a blank reaction, in which 4-chlorobenzaldehyde (**1q**) was reacted with β-naphthol (**2**) at room temperature and 120 °C without catalyst under solvent-free conditions (Table 1, entries 1 and 2). The results showed that the reactions were very sluggish, and no product formation was observed. However, addition of a catalytic amount of HBF_4-SiO_2 resulted in the product **3m**. The effect of amount of catalyst on the yield and rate was also investigated. It was found that 0.2 g (10 mmol%) of catalyst was enough for a fairly high yield. The lesser amounts gave a low yield even after long reaction time, and the more amounts could not cause the obvious increase in the yield of product. Meanwhile, we also tested the

Table 1. Reaction of 4-chlorobenzaldehyde (**1m**) and β-naphthol (**2**) under different reaction conditions



Entry	Catalyst	Temperature (°C)	Time (h)	Yield (%)[a]
1	No catalyst	25	12	0
2	No catalyst	120	5	0
3	SiO_2	120	5	5
4	HBF_4-SiO_2 (10 mol%)	80	2	85
5	HBF_4-SiO_2 (10 mol%)	100	1.5	90
6	HBF_4-SiO_2 (10 mol%)	120	1	95
7	HBF_4-SiO_2 (5 mol%)	120	3.5	85
8	HBF_4-SiO_2 (20 mol%)	120	1	95
9	HBF_4-SiO_2 (10 mol%)	111	1	0[b]
10	HBF_4-SiO_2 (10 mol%)	83	1	0[c]
11	HBF_4-SiO_2 (10 mol%)	78	1	0[d]

[a] Isolated yield.

[b] 5 mL toluene were added.

[c] 5 mL $ClCH_2CH_2Cl$ were added.

[d] 5 mL EtOH were used.

effect of reaction temperature on the catalyzed reaction. When the reaction was carried out at 120 °C, the maximum yield was obtained in a short reaction period (Table 1, entry 6). Some common organic solvent such as toluene, 1,2-dichloroethane, and ethanol were also tested for this reaction, and the results indicated that no product was observed. We chose to perform this reaction at 120 °C in the presence of 10 mmol% of catalyst under solvent-free conditions.

After optimizing the reaction conditions, we next examined the generality and substrate scope of this methodology, and the results are summarized in Table 2. The reaction was amenable to a wide variety

Table 2. HBF_4-SiO_2 catalyzed preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives under solvent-free conditions

				MP (°C)	
Entry	Aldehydes	Time (h)	Yield (%)[a]	Found	Reported
a	PhCHO	1.5	92	182–183	181–183[19]
b	3-MeC_6H_4CHO	3	93	198–200	198[12]
c	4-MeC_6H_4CHO	3	90	234–236	238–240[19]
d	4-$Me_2CHC_6H_4CHO$	3	93	240–241	239–240[20]
e	2-$MeOC_6H_4CHO$	3	92	258–260	260[7]
f	4-$MeOC_6H_4CHO$	2	93	212–213	213–215[19]
g	$^iPrC_6H_4CHO$	2	94	240–241	239–240[20]
h	4-OHC_6H_4CHO	4	87	201–202	200–202[10]
i	3-FC_6H_4CHO	2	95	261–263	259[13]
j	4-FC_6H_4CHO	1.5	92	229–230	238[9]
k	2-ClC_6H_4CHO	2	90	215–217	215[7]
l	3-ClC_6H_4CHO	1	94	210–212	209–211[19]
m	4-ClC_6H_4CHO	1	95	301–303	300–302[19]
n	2,4-$Cl_2C_6H_3CHO$	2	91	252–253	253–255[19]
o	2,6-$Cl_2C_6H_3CHO$	1.5	95	265–266	267–268[20]
p	2-BrC_6H_4CHO	3	88	190–192	192[7]
q	3-BrC_6H_4CHO	1	94	192–193	190[13]
r	4-BrC_6H_4CHO	1	95	296–298	297[7]
s	2-$NO_2C_6H_4CHO$	3.5	89	289–291	293[13]
t	3-$NO_2C_6H_4CHO$	1	90	215–216	211[7]
u	4-$NO_2C_6H_4CHO$	1	94	310–312	310[7]
v	3-NO_2-4-OHC_6H_3CHO	1	95	268–270	
w	4-CNC_6H_4CHO	2	90	336–338	
x	2-Naphthalene-carbaldehyde	1.5	93	199–201	198–200[10]
y	Anthracene-9-carbaldehyde	1.5	95	233–235	

[a] Isolated yield.

of substituents on aryl aldehydes. It is evident that substituents in the aromatic ring of aldehydes have a tremendous effect on the reaction process. Electron-withdrawing groups (such as halide, nitro, and cyano) in the aromatic ring of aldehydes accelerated the reaction, whereas electron-donating groups (such as methyl, methoxy, and hydroxyl) retarded the reaction. Generally, *ortho*-substituted benzaldehydes required longer reaction times, which were probably attributed to the steric hindrance (Table 2, entries **1k**, **1n**, **1o**, **1p**, and **1s**). 2-Naphthalenecarbaldehyde and anthracene-9-carbaldehyde (Table 2, entries **1x** and **1y**) were examined under the same condition to give the corresponding products in excellent yields. However, heterocyclic aldehydes such as furan-2-carbaldehyde and thiophene-2-carbaldehyde did not undergo the condensation reaction with β-naphthol in the presence of HBF_4-SiO_2 to produce the desired products. The reaction conducted with phenol instead of β-naphthol also did not afford any product.

The reusability of the catalyst was studied. After completing the model reaction, the catalyst was removed by simple filtration, washed with $CHCl_3$, and subjected to a second run of the reaction process with the same substrate. The results of the first experiment and subsequent ones were almost consistent in yields after three runs (95%, 92%, and 90%).

In conclusion, we have developed a simple and efficient method for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives by the one-pot condensation reaction of β-naphthol and aryl aldehydes using HBF_4-SiO_2 as a heterogeneous catalyst under solvent-free conditions. The short reaction times, simple workup, high yields, mild reaction conditions, and utilization of an inexpensive and reusable catalyst are feature of this new procedure. We believe that this procedure provides a valuable addition to current methodologies.

EXPERIMENTAL

Melting points were determined on an X-4 apparatus and are uncorrected. IR spectra were obtained using Shimadzu FTIR-8900 spectrometer. ^1H NMR spectra were recorded with a Varian Mercury Plus 400 spectrometer using TMS as internal standard. Elemental analyses were performed on Vario EL III CHNOS elemental analyzer.

Preparation of Tetrafluoroboric Acid Adsorbed on Silica Gel (HBF_4-SiO_2)

The catalyst system HBF_4-SiO_2 was prepared following the originally reported method.[23] A mixture of silica gel (26.7 g, 300–400 mesh) and

40% aq. HBF_4 (3.3 g, 8.25 mL, 15 mmol) in diethyl ether (75 ml) was stirred for 3 h. The mixture was concentrated, and the residue dried under vacuum at 100°C for 72 h to afford HBF_4-SiO_2 (0.5 mmol HBF_4/g) as a free-flowing power.

General Procedure for the Preparation of 14-Aryl-14*H*-dibenzo[*a,j*] xanthene Derivatives

To a mixture of aldehydes (1 mmol) and β-naphthol (2 mmol), HBF_4-SiO_2 (0.20 g, 0.1 mmol) was added, and the mixture was heated at 120 °C for an appropriate time (monitored by thin-layer chromatography, TLC). After completion of the reaction, the mixture was cooled to room temperature and washed with $CHCl_3$ (15 ml). The solvent was evaporated, and the crude product was recrystallized from EtOH to afford the pure product. The products were characterized by IR and ^{1}H NMR spectral data, and their melting points were compared with those of authentic samples and found to be identical.

Representative Spectral Data

14-(3-Nitro-4-hydroxyphenyl)-14*H*-dibenzo[*a,j*]xanthene (**3v**)

Yellow solid; mp 268–270 °C; IR (KBr): 3296, 3068, 1624, 1593, 1535, 1483, 1451, 1336, 1255, 1244, 1172, 968, 804 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.51$ (s, 1H), 6.89 (d, $J = 8.8$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.49 (d, $J = 8.8$ Hz, 2H), 7.60–7.66 (m, 3H), 7.82 (d, $J = 9.2$ Hz, 2H), 7.85 (d, $J = 8.4$ Hz, 2H), 8.27 (s, 1H), 8.29–8.30 (m, 2H), 10.35 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 37.03$, 116.05, 118.29, 120.66, 122.13, 122.31, 124.78, 127.44, 129.25, 129.32, 129.71, 131.19, 131.27, 133.17, 137.65, 148.99, 153.93 ppm. Anal. calcd. for $C_{27}H_{17}NO_4$: C, 77.32; H, 4.09; N, 3.34. Found: C, 77.50; H, 3.92; N, 3.20.

14-(4-Cyanophenyl)-14*H*-dibenzo[*a,j*]xanthene (**3w**)

Incarnadine needles; mp 336–338 °C; IR (KBr): 2873, 1635, 1591, 1558, 1506, 1458, 1398, 1245, 1179, 960, 810 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 6.54$ (s, 1H), 7.42–7.63 (m, 10H), 7.84 (t, $J = 8.8$ Hz, 4H), 8.27 (d, $J = 8.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 38.21$, 110.48, 116.13, 118.26, 122.21, 122.32, 124.77, 127.38, 123.10, 129.29, 129.75, 131.25, 132.62, 148.99, 150.24 ppm. Anal. calcd. for $C_{28}H_{17}NO$: C, 87.71; H, 4.47; N, 3.65. Found: C, 87.52; H, 4.28; N, 3.50.

14-Anthracen-9-yl-14*H*-dibenzo[*a,j*]xanthene (**3y**)

White solid, 233–235 °C; IR (KBr): 3082, 2898, 1635, 1529, 1458, 1402, 1348, 1255, 1141, 966, 825 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) $\delta = 6.60$ (s, 1H), 7.27–7.63 (m, 10H), 7.81–7.86 (m, 8H), 8.30 (d, $J = 8.8$ Hz, 2H), 8.42 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 37.88$, 116.08, 118.34, 118.80, 121.84, 121.96, 122.15, 122.33, 122.69, 124.82, 127.46, 129.33, 129.75, 129.81, 131.25, 134.53, 147.15, 148.42, 148.99 ppm. Anal. calcd. for $C_{35}H_{22}O$: C, 91.68; H, 4.84. Found: C, 91.82; H, 4.66.

ACKNOWLEDGMENTS

We are grateful for financial support from Hebei Normal University (L20061314), the Nature Science Foundation of Hebei Province (B2008000149), and the Natural Science Foundation of Hebei Education Department (2006318).

REFERENCES

1. Griffiths, J.; Lee, W. J. Synthesis, light absorption and fluorescence properties of new thiazole analogues of the xanthene dyes. *Dyes Pigments* **2003**, *57*, 107–114.
2. Ahmad, M.; King, T. A.; Ko, D.-K.; Cha, B. H.; Lee, J. Performance and photostability of xanthene and pyrromethene laser dyes in sol-gel phases. *J. Phys. D: Appl. Phys.* **2002**, *35*, 1473–1476.
3. Knight, C. G.; Stephens, T. Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH: Studies in phospholipid vesicles. *Biochem. J.* **1989**, *258*, 683–689.
4. Poupelin, J. P.; Saint-Rut, G.; Fussard-Blanpin, O.; Narcisse, G.; Uchida-Ernouf, G.; Lakroix, R. Synthesis and antiinflammatory properties of bis(2-hydroxy-1-naphthyl)methane derivatives, I: Monosubstituted derivatives. *Eur. J. Med. Chem.* **1978**, *13*, 67–71.
5. Ion, R. M.; Frackowiak, D.; Planner, A.; Wiktorowicz, K. The incorporation of various porphyrins into blood cells measured via flow cytometry, absorption, and emission spectroscopy. *Acta Biochim. Pol.* **1998**, *45*, 833–845.
6. Amini, M. M.; Seyyedhamzeh, M.; Bazgir, A. Heteropolyacid: An efficient and eco-friendly catalyst for the synthesis of 14-aryl-14*H*-dibenzo[a,j]-xanthene. *Appl. Catal. A: Gen.* **2007**, *323*, 242–245.
7. Khosropour, A. R.; Khodaei, M. M.; Moghannian, H. A facile, simple, and convenient method for the synthesis of 14-alkyl and aryl-14*H*-dibenzo[a,j] xanthenes catalyzed by *p*TSA in solution and solvent-free conditions. *Synlett* **2005**, 955–958.

8. Liu, D.; Yu, Y.; Shi, W.; Liu C.; Luo, G. A highly efficient solvent-free synthesis of benzoxanthenes catalyzed by methanesulfonic acid. *Prep. Biochem. Biotechnol.* **2007**, *37*, 77–81.
9. Dabiri, M.; Baghbanzadeh, M.; Nikcheh, M. S.; Arzroomchilar, E. Eco-friendly and efficient one-pot synthesis of alkyl- or aryl-14*H*-dibenzo [a,j]xanthenes in water. *Bioorg. Med. Chem.* **2008**, *18*, 436–438.
10. Selvam, N. P.; Shanthi, G.; Perumal, P. T. Ceric-sulfate-catalyzed synthesis of 14-aryl or alkyl-14H-dibenzo[aj]xanthenes under conventional heating and microwave irradiation. *Can. J. Chem.* **2007**, *85*, 989–995.
11. Saini, A.; Kumar, S.; Dandhu, J. S. A new LiBr-catalyzed, facile and efficient method for the synthesis of 14-alkyl or aryl-14*H*-dibenzo[a,j]xanthenes and tetrahydrobenzo[b]pyrans under solvent-free conventional and microwave heating. *Synlett* **2006**, 1928–1932.
12. Pasha, M. A.; Jayashankara, V. P. Molecular iodine catalyzed synthesis of aryl-14H-dibenzo[a,j]xanthenes under solvent-free condition. *Bioorg. Med. Chem.* **2007**, *17*, 621–623.
13. Rajitha, B.; Kumar B. S.; Reddy, Y. T.; Reddy, P. N.; Sreenivasulu, N. Sulfamic acid: A novel and efficient catalyst for the synthesis of aryl-14*H*-dibenzo[a.j]xanthenes under conventional heating and microwave irradiation. *Tetrahedron Lett.* **2005**, *46*, 8691–8693.
14. Nagarapu, L.; Baseeruddin, M. B.; Kumari, N. V.; Kantevari, S.; Rudradas, A. P. Efficient synthesis of aryl-14*H*-dibenzo[a.j]xanthenes using $NaHSO_4$-SiO_2 or 5%WO_3/ZrO_2 as heterogeneous catalysts under conventional heating in a solvent-free media. *Synth. Commun.* **2007**, *37*, 2519–2525.
15. Ko, S.; Yao, C.-F. Heterogeneous catalyst: Amberlyst-15 catalyzes the synthesis of 14-substituted-14H-dibenzo[a,j]xanthenes under solvent-free conditions. *Tetrahedron Lett.* **2006**, *47*, 8827–8829.
16. Bigdeli, M. A.; Heravi, M. M.; Mahdavinia, G. H. M. Silica supported perchloric acid ($HClO_4$-SiO_2): A mild, reusable and highly efficient heterogeneous catalyst for the synthesis of 14-aryl or alkyl-14-H-dibenzo[a,j] xanthenes. *J. Mol. Catal. A: Chem.* **2007**, *275*, 25–29.
17. Patil, S. B.; Bhat, R. P.; Samant, S. D. Cation-exchange resins: Efficient heterogeneous catalysts for facile synthesis of dibenzoxanthene from β-naphthol and aldehydes. *Synth. Commun.* **2006**, *36*, 2163–2168.
18. Shakibaei, G. I.; Mirzaei, P.; Bazgir, A. Dowex-50W promoted synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthene and 1,8-dioxo-octahydroxanthene derivatives under solvent-free conditions. *Appl. Catal. A: Gen.* **2007**, *325*, 188–192.
19. Nagarapu, L.; Kantevari, S.; Mahankhali, V. C.; Apuri, S. Potassium dodecatungstocobaltate trihydrate ($K_5CoW_{12}O_{40} \cdot 3H_2O$): A mild and efficient reusable catalyst for the synthesis of aryl-14*H*-dibenzo[a.j]xanthenes under conventional heating and microwave irradiation. *Catal. Commun.* **2007**, *8*, 1173–1177.
20. Kumari, P.; Yathindranath, V.; Chauan, S. M. S. Facile and efficient synthesis of 14-alkyl-oraryl-14-*H*-dibenzo[a,j]xanthenes using sulfonyl-functionalized ionic liquids. *Synth. Commun.* **2008**, *38*, 637–648.

21. Bigdeli, M. A.; Heravi, M. M.; Mahdavinia, G. H. Wet cyanuric chloride catalysed simple and efficient synthesis of 14-aryl or alkyl-14*H*-dibenzo[a,j]-xanthenes. *Catal. Commun.* **2007**, *8*, 1595–1598.
22. Solinas, A.; Taddei, M. Solid-supported reagents and catch-and-release techniques inorganic synthesis. *Synthesis* **2007**, 2409–2453.
23. Chakraborti, A. K.; Gulhane, R. Fluoroboric acid adsorbed on silica gel as a new and efficient catalyst for acylation of phenols, thiols, alcohols, and amines. *TetrahedronLett.* **2003**, *44*, 3521–3525.
24. Bandgar, B. P.; Patil, A. V. Fluoroboric acid adsorbed on silica gel catalysed regioselective ring opening of epoxides with nitrogen heterocycles. *Tetrahedron Lett.* **2007**, *48*, 173–176.
25. Kumar, D.; Kumar, R.; Chakraborti, A. K. Tetrafluoroboric acid adsorbed on silica gel as a reusable heterogeneous dual-purpose catalyst for conversion of aldehydes/ketones into acetals/ketals and back again. *Synthesis* **2008**, 1249–1256.
26. Kamble, V. T.; Bandgar, B. P.; Joshi, N. S.; Jamode, V. S. A remarkable HBF_4-SiO_2-catalyzed synthesis of acylals from aldehydes under solvent-free conditions. *Synlett* **2006**, 2719–2722.
27. Bandgar, B. P.; Patil, A. V.; Chavan, O. S. Silica supported fluoroboric acid as a novel, efficient, and reusable catalyst for the synthesis of 1,5-benzodiazepines under solvent-free conditions. *J. Mol. Catal. A: Chem.* **2006**, *256*, 99–105.
28. Chen, W. Y.; Li, X. S: Lu, J. Mannich-type reaction catalyzed by silica-supported fluoroboric acid under solvent-free conditions. *Synth. Commun.* **2008**, *38*, 546–552.
29. Sharma, G.; Kumar, R.; Chakraborti, A. K. Fluoroboric acid adsorbed on silica-gel (HBF_4-SiO_2) as a new, highly efficient, and reusable heterogeneous catalyst for thia-Michael addition to α,β-unsaturated carbonyl compounds. *Tetrahedron Lett.* **2008**, *49*, 4272–4275.
30. Kamble, V. T.; Bandgar, B. P.; Muley, D. B.; Joshi, N. S. An expedient and efficient chemoselective protection of carbonyl compounds and transthioacetalization of *O,O*- and *S,O*-acetals catalyzed by HBF_4-SiO_2. *J. Mol. Catal. A: Chem.* **2007**, *268*, 70–75.
31. Bandgar, B. P.; Patil, A. V.; Kamble, V. T.; Totre, J. V. An efficient synthesis of thiiranes from oxiranes using fluoroboric acid adsorbed on silica gel (HBF_4-SiO_2) as a catalyst under mild conditions in the absence of solvent. *J. Mol. Catal. A: Chem.* **2007**, *273*, 114–117.
32. (a) Zhang, Z.-H.; Tao, X.-Y. 2,4,6-Trichloro-1,3,5-triazine-promoted synthesis of 1,8-dioxo-octahydroxanthenes under solvent-free conditions. *Aust. J. Chem.* **2008**, *61*, 77–79; (b) Zhang, Z.-H. Sodium hydrogen sulfate in poly (ethylene glycol). An efficient recyclable system for the deprotection of 1,1-diacetates. *Monatsh. Chem.* **2005**, *136*, 1191–1195; (c) Mo, L.-P.; Ma, Z.-C.; Zhang, Z.-H. $CuBr_2$-catalyzed synthesis of bis(indolyl)methanes. *Synth. Commun.* **2005**, *35*, 1997–2004; (d) Zhang, Z.-H.; Hu, J.-Y. Cobalt(II) chloride–mediated synthesis of β-enamino compounds under solvent-free conditions. *J. Braz. Chem. Soc.* **2006**, *17*, 1447–1451; (e) Zhang, Z.-H.; Yang, S.-T.; Lin, J. Mild and effcient procedure for the synthesis of 1,5-benzodiazepines

catalyzed by magnesium perchlorate. *Synth. Commun.* **2006**, *36*, 1645–1654; (f) Zhang, Z.-H.; Lin, J. Effcient and convenient method for the synthesis of symmetrical triindolylmethanes catalyzed by iodine. *Synth. Commun.* **2007**, *37*, 209–215; (g) Zhang, Z.-H.; Li, T.-S.; Li, J.-J. Synthesis of enaminones and enamino esters catalysed by $ZrOCl_2 \cdot 8H_2O$. *Catal. Commun.* **2007**, *8*, 1615–1620; (h) Zhang, Z.-H.; Li, J.-J.; Gao, Y.-Z.; Liu, Y.-H. Synthesis of 2-substituted benzimidazoles by iodine-mediated condensation of orthoesters with 1,2-phenylenediamines. *J. Heterocycl. Chem.* **2007**, *44*, 1509–1512; (i) Zhang, Z.-H.; Li, T.-S.; Li, J.-J. A highly effective sulfamic acid/methanol catalytic system for the synthesis of benzimidazole derivatives at room temperature. *Monatsh. Chem.* **2007**, *138*, 89–94; (j) Zhang, Z.-H.; Liu, Y.-H. Antimony trichloride/SiO_2 promoted synthesis of 9-ary-3,4,5,6,7,9-hexahydroxanthene-1,8-diones. *Catal. Commun.* **2008**, *9*, 1715–1719; (k) Zhang, Z.-H.; Li, J.-J.; Li, T.-S. Ultrasound-assisted synthesis of pyrroles catalyzed by zirconium chloride under solvent-free conditions. *Ultrason. Sonochem.* **2008**, *15*, 673–676.