$FeCl_3$–SiO_2 AS HETEROGENEOUS CATALYSTS FOR THE PREPARATION OF DIHYDROPYRANO[3,2-*b*]CHROMENEDIONES

Wei-Lin LI[a1,*], Jin-Ying LIANG[a2], Tian-Bao WANG[b1] and Ya-Qin WANG[b2]

[a] *School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan 453003, P. R. China; e-mail: [1] linweilin1977@163.com, [2] weiwei525626@163.com*

[b] *The First Affiliated Hospital, Xinxiang Medical University, Henan 453003, P. R. China; e-mail: [1] tianbao1122@yahoo.com.cn, [2] wangyaqin1@yeah.net*

Received May 24, 2011
Accepted August 9, 2011
Published online January 19, 2012

$FeCl_3$–SiO_2 is environment-friendly heterogeneous catalyst for the condensation of kojic acid and aldehydes with dimedone to afford dihydropyrano[3,2-*b*]chromenediones. The solid acid catalyst is stable and can be easily recovered and reused without appreciable change in its efficiency.

Keywords: Dihydropyrano[3,2-*b*]chromenediones; Kojic acid; $FeCl_3$–SiO_2; Aldehydes; Heterogeneous catalysis; Synthetic methods.

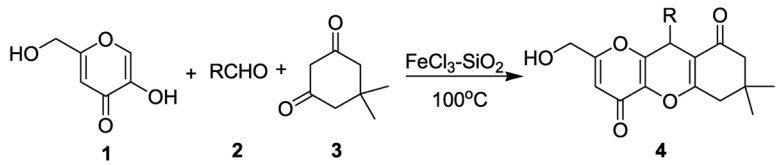
An important objective of chemistry is to adapt classical processes so that pollution effects are kept to a minimum, with both reduction in energy and consumption of raw materials. Solid acid catalysts play a prominent role in organic synthesis under heterogeneous conditions. In general, solid acid catalysts are mainly based on clay[1] or silica[2]. In terms of convenience, silica-based catalysts are inexpensive, easy to prepare, and insoluble in all organic solvents. Hence they can be recovered and recycled from reactions. Among various silica-based heterogeneous catalysts, silica-supported ferric chloride ($FeCl_3$–SiO_2) has advantages of low cost, ease of preparation and can be recycled[2e–2i].

Kojic acid derivatives have been identified as an important class of heterocyclic compounds in pharmacology[3]. Recently Reddy and co-workers reported synthesis of 2-(hydroxymethyl)-7,7-dimethyl-10-aryl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-diones using $InCl_3$ as a catalyst[4]. However, the method is associated with one or more disadvantages such as use of expensive, water-intolerant and non recyclable catalyst and harsh reaction conditions. Thus, there is still need of a simple and general procedure

doi:10.1135/cccc2011108

for one-pot synthesis of 2-(hydroxymethyl)-7,7-dimethyl-10-aryl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-diones under mild conditions.

In continuation of our interest in using silica-based catalysts in synthesis of heterocyclic compounds[5] we report herein a one-step synthesis of 2-(hydroxymethyl)-7,7-dimethyl-10-aryl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-diones from kojic acid, aromatic aldehydes, and dimedone in the presence of $FeCl_3$–SiO_2 as a solid catalyst, under solvent-free conditions. This method appeared to be efficient and economical, with a wide range of applications (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

In order to optimize the reaction conditions, we studied the synthesis of 2-(hydroxymethyl)-7,7-dimethyl-10-phenyl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-diones **4** from the condensation of kojic acid, benzaldehyde and dimedone, in the presence of a variety of catalysts (Table I). We examined this reaction in the absence and presence of several catalysts. It was found that when the reaction occurred without any catalysts or using catalysts such as I_2, *p*-TsOH, H_2SO_4, it resulted in poor yields (Table I, entries 1–4). However, catalysts such as $FeCl_3$, Ce_2SO_4, $ZnCl_2$, $Fe(HSO_4)_3$ could push the reaction forward with moderate yields (Table I, entries 5–8). But, when $FeCl_3$–SiO_2 was used in this reaction system, the yields of the products improved (Table I, entries 9–16).

We also evaluated the amount of $FeCl_3$–SiO_2 required for this transformation. It was found that when we increased the amount of the $FeCl_3$–SiO_2 from 1 to 5 mole %, the yields increased from 59 to 93%. Using 5 mole % $FeCl_3$–SiO_2 was sufficient to push the reaction forward. Extra amounts of the catalyst did not improve the yields.

Under the optimized reaction conditions, a series of dihydropyrano-[3,2-*b*]chromenedione derivatives **4** were synthesized (Table II). All the aforementioned reactions delivered excellent product yields and accommodated a wide range of aromatic aldehydes bearing both electro-donating and electro-withdrawing substituents.

TABLE I
Synthesis of 2-(hydroxymethyl)-7,7-dimethyl-10-phenyl-7,8-dihydropyrano[3,2-*b*]chromene-4,9(6*H*,10*H*)-dione (**4a**) in the presence of a variety of catalysts[a]

Entry	Catalyst	Time, min	Yield, %[b]
1	–	240	0
2	I_2 (5 mole %)	60	19
3	*p*-TsOH (5 mole %)	60	29
4	H_2SO_4 (5 mole %)	90	11
5	$FeCl_3$ (5 mole %)	60	79
6	Ce_2SO_4 (5 mole %)	60	82
7	$ZnCl_2$ (5 mole %)	60	80
8	$Fe(HSO_4)_3$ (5 mole %)	60	69
9	$FeCl_3$–SiO_2 (1 mole %)	90	59
10	$FeCl_3$–SiO_2 (2 mole %)	90	68
11	$FeCl_3$–SiO_2 (3 mole %)	60	76
12	$FeCl_3$–SiO_2 (4 mole %)	60	87
13	$FeCl_3$–SiO_2 (5 mole %)	60	93
14	$FeCl_3$–SiO_2 (6 mole %)	60	92
15	$FeCl_3$–SiO_2 (7 mole %)	60	90
16	$FeCl_3$–SiO_2 (8 mole %)	50	93

[a] Reaction conditions: kojic acid (1 mmol), benzaldehyde (1 mmol), dimedone (1 mmol); 100 °C; neat. [b] Isolated yield.

$FeCl_3$–SiO_2 as catalyst was isolated from the reaction mixture by simple filtration. The purified catalyst was achieved through washing the solid residue catalyst by water and ethanol followed by drying in an oven at 100 °C for 30 min. In every experiment, more than 98% of the $FeCl_3$–SiO_2 was easily recovered from the reaction mixture. Catalytic activity of the recovered catalyst was tested and showed to be the same as $FeCl_3$–SiO_2 used for the first time. The recovered catalyst was reused three times without any loss of activity (Table II, entry 1).

TABLE II
Preparation of dihydropyrano[3,2-*b*]chromenes using $FeCl_3$–SiO_2[a]

Entry	R	Time, min	Product	Yield, %[b]	m.p., °C (ref.[4])
1	C_6H_5	60	**4a**	93 (89, 85)[c]	184–185 (186–188)
2	4-Cl-C_6H_4	60	**4b**	91	205–206
3	4-F-C_6H_4	60	**4c**	93	161–162 (160–164)
4	4-NO_2-C_6H_4	40	**4d**	96	229–230
5	3-NO_2-C_6H_4	50	**4e**	92	212–213
6	2-Cl-C_6H_4	60	**4f**	92	216–217
7	2,4-Cl_2-C_6H_3	60	**4g**	90	166–167
8	3,4,5-MeO_3-C_6H_2	80	**4h**	87	174–175
9	2,5-MeO_2-C_6H_3	80	**4i**	89	192–193
10	4-Me-C_6H_4	70	**4j**	86	214–215
11	4-MeO-C_6H_4	70	**4k**	84	178–179 (180–182)

[a] Reaction conditions: kojic acid (1 mmol), aldehyde (1 mmol), dimedone (1 mmol), $FeCl_3$–SiO_2 (0.05 mmol); 100 °C; neat. [b] Isolated yield. [c] The catalyst was reused for three runs.

CONCLUSION

In conclusion, in this paper we have used $FeCl_3$–SiO_2 for the three-component coupling reaction of kojic acid, aldehydes and dimedone for the synthesis of dihydropyrano[3,2-*b*]chromenediones in good to excellent yields. The simplicity, easy workup, low cost, easy preparation and handling of the catalyst for the preparation of dihydropyrano[3,2-*b*]chromenediones are the highlights of this procedure. In addition, the use of $FeCl_3$–SiO_2 has resulted in a reduction in the unwanted and hazardous waste that is produced during conventional homogeneous processes.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were determined on Bruker AV-400 spectrometer (100 MHz for ^{13}C NMR) at room temperature using using tetramethylsilane (TMS) as an internal standard ($CDCl_3$ solution). Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. IR spectra (ν, cm^{-1}) were determined on FTS-40 infrared spectrometer. Elemental analyses were performed by a Vario-III elemental analyzer. Mass spectra were taken on a Macro mass spectrometer (Waters) by electro-spray method (ES). Melting points were determined on a XT-4 binocular microscope and were uncorrected. Commercially available reagents were used throughout without further purification unless otherwise stated.

Preparation of $FeCl_3$–SiO_2 Catalyst

In a 250 ml flask, chromatographic grade silica gel (50 g; 70–230 mesh) and anhydrous ferric chloride (4 g; 8% of the weight of SiO_2) were vigorously stirred under solvent-free conditions at room temperature for 24 h to achieve a homogeneous adsorption. A pale yellowish-green powder (2.0 g, equiv. to 2 mmol of $FeCl_3$) was obtained.

Preparation of **4**. General Procedure

A mixture of kojic acid (1 mmol), aldehyde (1 mmol), dimedone (1 mmol) and $FeCl_3$–SiO_2 (0.05 mmol) was heated at 100 °C for appropriate time (TLC). After completion, ethyl acetate (2 × 20 ml) was added, and the solid catalyst was removed by filtration. The solvent was evaporated and the crude product was puried by silica gel column chromatography using ethyl acetate–hexane (7:3) as an eluent.

2-(Hydroxymethyl)-7,7-dimethyl-10-phenyl-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4a**). IR (KBr): 3362, 3080, 2952, 2890, 1667, 1637, 1441, 1378, 1219, 1193, 1078, 990, 950, 712. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.32–7.21 (m, 5 H), 6.50 (s, 1 H), 4.87 (s, 1 H), 4.43–4.32 (m, 2 H), 2.71–2.59 (m, 2 H), 2.29–2.19 (m, 2 H), 1.11 (s, 3 H), 1.04 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.2, 171.3, 167.3, 163.9, 151.7, 140.5, 137.5, 128.8, 128.1, 127.8, 112.3, 112.2, 60.6, 50.4, 40.9, 38.4, 32.3, 29.0, 27.4. MS (ESI): *m/z* 353 $[M + H]^+$. For $C_{21}H_{20}O_5$ (352.13) calculated: 71.58% C, 5.72% H; found: 71.65% C, 5.68% H.

2-(Hydroxymethyl)-7,7-dimethyl-10-(4-chlorophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4b**). IR (KBr): 3325, 2961, 2930, 2870, 1672, 1640, 1600, 1490, 1442, 1377, 1218, 1190, 1076, 1014, 952, 850. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.28–7.18 (m, 4 H), 6.52 (s, 1 H), 4.87 (s, 1 H), 4.41–4.37 (m, 2 H), 2.66–2.60 (m, 2 H), 2.30–2.21 (m, 2 H), 1.11 (s, 3 H), 1.03 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.3, 171.4, 168.3, 164.1, 151.2, 138.9, 137.5, 133.6, 129.4, 129.0, 112.0, 111.9, 60.4, 50.3, 40.8, 37.8, 32.3, 28.9, 27.4. MS (ESI): *m/z* 387 $[M + H]^+$. For $C_{21}H_{19}ClO_5$ (386.09) calculated: 65.20% C, 4.95% H; found: 65.12% C, 4.88% H.

2-(Hydroxymethyl)-7,7-dimethyl-10-(4-florophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4c**). IR (KBr): 3363, 2953, 2930, 2853, 1675, 1638, 1601, 1509, 1443, 1378, 1219, 1192, 1157, 1075, 962, 845, 683. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.24–7.20 (m, 2 H), 6.99–6.95 (m, 2 H), 6.52 (s, 1 H), 4.87 (s, 1 H), 4.40–4.36 (m, 2 H), 2.65–2.61 (m, 2 H), 2.25–2.22 (m, 2 H), 1.10 (s, 3 H), 1.03 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.4, 171.5, 168.3, 164.0, 160.9, 151.5, 137.4, 136.2, 129.7, 129.6, 115.8, 115.6, 112.2, 112.0, 60.4, 50.3, 40.8, 37.7, 32.3, 28.9, 27.4. MS (ESI): *m/z* 371 $[M + H]^+$. For $C_{21}H_{19}FO_5$ (370.12) calculated: 68.10% C, 5.17% H; found: 68.20% C, 5.12% H.

2-(Hydroxymethyl)-7,7-dimethyl-10-(4-nitrophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4d**). IR (KBr): 3334, 2960, 2928, 2855, 1675, 1633, 1596, 1520, 1375, 1347, 1216, 1123, 1058, 1003, 946, 867, 622. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.18 (d, 2 H, J = 8.8), 7.47 (d, 2 H, J = 8.4), 6.53 (s, 1 H), 5.03 (s, 1 H), 4.42–4.37 (m, 2 H), 2.69–2.65 (m, 2 H), 2.27–2.23 (m, 2 H), 1.13 (s, 3 H), 1.04 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.0, 170.8, 167.0, 164.4, 150.0, 147.4, 137.9, 129.1, 124.1, 112.6, 111.5, 60.6, 50.3, 40.9, 38.4, 32.3, 28.9, 27.5. MS (ESI): *m/z* 398 $[M + H]^+$. For $C_{21}H_{19}NO_7$ (397.12) calculated: 63.47% C, 4.82% H, 3.52% N; found: 63.35% C, 4.85% H, 3.57% N.

2-(Hydroxymethyl)-7,7-dimethyl-10-(3-nitrophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4e**). IR (KBr): 3393, 2955, 2922, 2851, 1669, 1637, 1599, 1530, 1448, 1377, 1350, 1213, 1143, 1080, 678. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.11–8.09 (m, 2 H), 7.63 (d,

1 H, *J* = 8.0), 7.50 (t, 1 H, *J* = 8.0), 6.53 (s, 1 H), 5.03 (s, 1 H), 4.45–4.33 (m, 2 H), 274–2.61 (m, 2 H), 2.30–2.20 (m, 2 H), 1.12 (s, 3 H), 1.05 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.3, 171.3, 168.2, 164.7, 150.2, 148.4, 142.4, 137.7, 134.3, 129.8, 123.4, 122.9, 112.2, 111.3, 60.4, 50.3, 40.8, 38.3, 32.3, 28.9, 27.5. MS (ESI): *m/z* 398 $[M + H]^+$. For $C_{21}H_{19}NO_7$ (397.17) calculated: 63.47% C, 4.82% H, 3.52% N; found: 63.39% C, 4.80% H, 3.55% N.

2-(Hydroxymethyl)-7,7-dimethyl-10-(2-chlorophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4f**). IR (KBr): 3291, 2956, 2931, 2860, 1673, 1634, 1600, 1468, 1445, 1378, 1221, 1116, 1080, 758. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.36 (dd, 1 H, *J* = 0.8, 8.0), 7.20–7.16 (m, 3 H), 6.49 (s, 1 H), 5.44 (s, 1 H), 4.40–4.34 (m, 2 H), 2.67–2.64 (m, 2 H), 2.26–2.22 (m, 2 H), 1.12 (s, 3 H), 1.08 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.1, 171.3, 168.0, 164.7, 150.9, 137.8, 137.5, 133.7, 130.1, 129.0, 127.3, 112.0, 111.5, 60.4, 50.3, 40.8, 35.7, 32.2, 29.0, 27.5. MS (ESI): *m/z* 387 $[M + H]^+$. For $C_{21}H_{19}ClO_5$ (386.09) calculated: 65.20% C, 4.95% H; found: 65.30% C, 4.82% H.

2-(Hydroxymethyl)-7,7-dimethyl-10-(2,4-dichlorophenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4g**). IR (KBr): 3296, 2952, 2863, 1676, 1637, 1600, 1445, 1376, 1221, 1101, 1079, 854. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.39 (s, 1 H), 7.21–7.18 (m, 1 H), 7.14–7.12 (m, 1 H), 6.50 (s, 1 H), 5.39 (s, 1 H), 4.41–4.37 (m, 2 H), 2.71–2.65 (m, 2 H), 2.26–2.22 (m, 2 H), 1.13 (s, 3 H), 1.08 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.0, 171.1, 167.6, 164.8, 150.3, 137.7, 134.4, 134.2, 130.9, 129.9, 127.7, 112.2, 111.2, 60.5, 50.3, 40.8, 37.5, 32.2, 28.9, 27.6. MS (ESI): *m/z* 421 $[M + H]^+$. For $C_{21}H_{18}Cl_2O_5$ (420.05) calculated: 59.87% C, 4.31% H; found: 59.90% C, 4.28% H.

2-(Hydroxymethyl)-7,7-dimethyl-10-(3,4,5-trimethoxyphenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4h**). IR (KBr): 3296, 2960, 2923, 2869, 1673, 1637, 1598, 1508, 1422, 1375, 1329, 1220, 1126, 1076, 956. ^{1}H NMR ($CDCl_3$, 400 MHz): 6.50–6.44 (m, 3 H), 4.81 (s, 1 H), 4.45–4.37 (m, 2 H), 3.80 (s, 6 H), 3.79 (s, 3 H), 2.68–2.63 (m, 2 H), 2.28–2.27 (m, 2 H), 1.14 (s, 3 H), 1.11 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.3, 171.3, 167.7, 164.0, 153.4, 151.5, 137.3, 136.1, 112.1, 105.0, 60.8, 60.6, 56.1, 50.3, 40.9, 38.5, 32.2, 29.3, 27.1. MS (ESI): *m/z* 443 $[M + H]^+$. For $C_{24}H_{26}O_8$ (422.16) calculated: 65.15% C, 5.92% H; found: 65.20% C, 5.89% H.

2-(Hydroxymethyl)-7,7-dimethyl-10-(2,5-dimethoxyphenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4i**). IR (KBr): 3284, 2950, 2930, 2854, 1672, 1636, 1594, 1503, 1449, 1379, 1226, 1194, 1148, 1080, 1047, 819, 709. ^{1}H NMR ($CDCl_3$, 400 MHz): 6.77–6.74 (m, 3 H), 6.47 (s, 1 H), 5.17 (s, 1 H), 4.40–4.35 (m, 2 H), 3.78 (s, 3 H), 3.72 (s, 3 H), 2.63–2.61 (m, 2 H), 2.24–2.20 (m, 2 H), 1.11 (s, 3 H), 1.04 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.3, 171.3, 167.3, 164.6, 153.7, 151.7, 151.6, 137.8, 129.4, 116.1, 113.4, 112.7, 112.1, 111.4, 60.6, 56.6, 55.6, 50.4, 40.9, 33.8, 32.2, 29.2, 27.1. MS (ESI): *m/z* 413 $[M + H]^+$. For $C_{23}H_{24}O_7$ (412.15) calculated: 66.98% C, 5.87% H; found: 67.05% C, 5.80% H.

2-(Hydroxymethyl)-7,7-dimethyl-10-(4-methylphenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4j**). IR (KBr): 3368, 2953, 2931, 2847, 1668, 1636, 1442, 1376, 1219, 1189, 1120, 1076, 950, 862, 624. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.13 (d, 2 H, *J* = 8.0), 7.08 (d, 2 H, *J* = 8.0), 6.50 (s, 1 H), 4.83 (s, 1 H), 4.38–4.34 (m, 2 H), 2.64–2.61 (m, 2 H), 2.28 (s, 3 H), 2.23–2.20 (m, 2 H), 1.10 (s, 3 H), 1.03 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.4, 171.5, 168.2, 163.9, 152.0, 137.6, 137.5, 137.3, 129.5, 127.9, 112.4, 111.9, 60.4, 50.4, 40.8, 37.9, 32.2, 29.0, 27.4, 21.1. MS (ESI): *m/z* 367 $[M + H]^+$. For $C_{22}H_{22}O_5$ (366.15) calculated: 72.12% C, 6.05% H; found: 72.20% C, 6.00% H.

2-(Hydroxymethyl)-7,7-dimethyl-10-(4-methoxyphenyl)-7,8-dihydropyrano[3,2-b]chromene-4,9(6H,10H)-dione (**4k**). IR (KBr): 3355, 2958, 2922, 2836, 1672, 1637, 1511, 1443, 1377,

1219, 1193, 1120, 1029, 950, 860, 629. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.18–7.16 (m, 2 H), 6.83–6.80 (m, 2 H), 6.50 (s, 1 H), 4.83 (s, 1 H), 4.40–4.35 (m, 2 H), 3.75 (s, 3 H), 2.65–2.61 (m, 2 H), 2.23–2.22 (m, 2 H), 1.10 (s, 3 H), 1.04 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 196.4, 171.5, 168.0, 16.7, 159.0, 152.0, 137.3, 132.7, 129.1, 114.2, 112.5, 129.1, 60.5, 55.2, 50.4, 40.8, 37.5, 32.2, 29.0, 27.4. MS (ESI): *m/z* 383 $[M + H]^+$. For $C_{22}H_{22}O_6$ (382.14) calculated: 69.10% C, 5.80% H; found: 69.20% C, 5.72% H.

We are pleased to acknowledge the financial support from Xinxiang Medical University.

REFERENCES

1. a) Bahulayan D., Narayan G., Sreekumar V., Lalithambika M.: *Synth. Commun.* **2002**, *32*, 3565; b) Bahulayan D., Sukumar R., Sabu K. R., Lalithambika M.: *Green Chem.* **1999**, *1*, 191.
2. a) Modarresi-Alam A. R., Khamooshi F., Nasrollahzadeh M., Amirazizi H. A.: *Tetrahedron* **2007**, *63*, 8723; b) Das B., Laxminarayana K., Ravikanth B.: *J. Mol. Catal. A: Chem.* **2007**, *271*, 131; c) Bigdeli M. A., Heravi M. M., Mahdavinia G. H.: *J. Mol. Catal. A: Chem.* **2007**, *275*, 25; d) Polshettiwar V., Molnar A.: *Tetrahedron* **2007**, *63*, 6949; e) Dang Q., Brown B. S., Erion M. D.: *Tetrahedron Lett.* **2000**, *41*, 6559; f) Nasrollahzadeh M., Bayat Y., Habibi D., Moshaee S.: *Tetrahedron Lett.* **2009**, *50*, 4435; g) Chari M. A., Shobha D., Mukkanti K.: *Catal. Commun.* **2007**, *7*, 787; h) Morys P., Schlieper T.: *J. Mol. Catal. A: Chem.* **1995**, *95*, 27; i) Shaterian H. R., Yarahmadi H.: *Tetrahedron Lett.* **2008**, *49*, 1297.
3. a) Balaz S., Uher M., Brtko J., Veverka M., Bransova J., Dobias J., Podova M., Buchvald J.: *Folia Microbiol.* **1993**, 38, 387; b) Novotny L., Rauko P., Abdel-Hamid M., Vachalkova A.: *Neoplasma* **1999**, *46*, 89; c) Fickova M., Pravdova E., Rondhal L., Uher M., Brtko J.: *J. Appl. Toxicol.* **2008**, *28*, 554; d) Tanaka R., Tsujii H., Yamada T., Kajimoto T., Amano F., Hasegawa J., Hamashima Y., Node M., Katoh K., Takebe Y.: *Bioorg. Med. Chem.* **2009**, *17*, 52386; e) Aytemir M. D., Septioglu E., Calis U.: *Arzneim.–Forsch.* **2010**, *60*, 22.
4. Reddy B. V. S., Reddy M. R., Narasimhulu G., Yadav J. S.: *Tetrahedron Lett.* **2010**, *51*, 5677.
5. a) Wu L. Q., Wang X., Yang L. M., Yan F. L.: *Asian J. Chem.* **2010**, *22*, 6178; b) Wu L. Q., Wu Y. F., Yang C. G., Yang L. M., Yang L. J.: *J. Braz. Chem. Soc.* **2010**, *221*, 941; c) Wu L. Q., Yang C. G., Zhang C., Yang L. M.: *Bull. Korean Chem. Soc.* **2009**, *30*, 1665.