Silica-supported Perchloric Acid Catalyzed One-pot Synthesis of 1,4-Dihydropyridines

Ramesh, Dasari Rajaram, Singanaboina Narasimhulu, Manchala
Reddy, Thummalpally Srikanth Mahesh, Kondempudi Chinni
Manasa, Gajji Venkateswarlu, Yenamandra*

Natural Products Laboratory, Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad-500 007, India

An environmentally friendly and highly efficient procedure for the preparation of 1,4-dihydropyridines by the reaction between α,β-unsaturated aldehydes, aromatic amines and β-keto esters in the presence of silica supported perchloric acid is described.

Keywords 1,4-dihydropyridines, silica supported perchloric acid, Hantzsch reaction, β-keto esters

Introduction

Multi component reactions (MCRs) constitute an important group of transformations that combine three or more substrates for an ideal synthesis, which gives operational simplicity, atom economy, bond-forming efficiency, the access to molecular complexity from simple starting materials and so on. The modular character of this approach is extremely suitable for drug discovery and therefore it is widely used for the fast generation of bioactive compounds.[1]

1,4-Dihydropyridines are important class of heterocycles with a wide range of biological activities such as radio protective effect,[2] HIV protease inhibitors,[3] in the management of cardiovascular diseases[4] and some other pharmacological activities.[5] Further 1,4-dihydropyridines are also very important synthetic intermediates for the synthesis of various nitrogen containing heterocycles.[6] The best-known procedure for the preparation of 1,4-dihydropyridines is the classical Hantzsch synthesis which involves the condensation of two molecules of a β-ketoester, one molecule of an aldehyde, and one molecule of ammonia.[7] But some important types of derivatives, including *N*-aryl-1,4-dihydropyridines[8] and C_5-C_6-unsubstituted 1,4-dihydropyridines are not allowed to synthesis by this method. Because of their biological activities and synthetic point of view few efficient routes have been developed, these are the reaction between α,β-unsaturated imines and β-dicarbonyl compounds in the presence of sodium ethoxide[9] at 150 ℃, Michael reaction followed by cyclization between a β-dicarbonyl compound and α,β-unsaturated imine in the presence of lithium iodide[10] and hetero Diels-Alder reactions of 1-azadienes and allenic esters[11] to generate the *N*-aryl and C^5-C^6-unsubstituted systems. However many of these procedures have one or more disadvantages such as refluxing at high temperature, long reaction times (55—85 h), requiring unusual starting materials, using toxic solvents, forming side products, low yields, and difficulties in workup. In order to circumvent these associated problems with these procedures, for the first time a multi component procedure has been developed using CAN for the synthesis of 1,4-dihydropyridines.[12] Since, 1,4-dihydropyridine derivatives are useful and important intermediates in synthesis and pharmaceuticals, the development of simple, convenient and high yielding protocols is desirable.

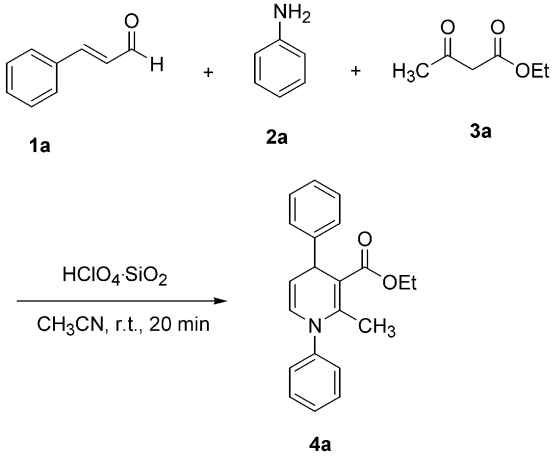
Results and discussion

Recently silica supported catalysts[13] as well as perchloric acid impregnated on silica gel has gained considerable attention in current organic synthesis due to its ease of preparation, high efficiency, environmental benignity, reusability of the catalyst and its economic viability. Because of its versatility of the catalyst in organic transformations[14] we investigated employing $HClO_4$•SiO_2 as a catalyst for the synthesis of 1,4-dihydropyridines. The catalyst $HClO_4$•SiO_2 was prepared by the following reported procedure[15] in which 1 g of silica gel contains 0.37 mmol of $HClO_4$.

Initially, a reaction was performed between cinnamaldehyde (**1a**), aniline (**2a**), and ethylacetoacetate (**3a**) in acetonitrile in the presence of $HClO_4$•SiO_2 at room temperature to afford the corresponding 1,4-dihydropyridine (**4a**) (Entry 1) (Scheme 1) in 96% yield in 20 min.[16]

* E-mail: luchem@iict.res.in; Fax: +0091(40)27160512
Received June 20, 2011; revised July 13, 2011; accepted July 21, 2011.

Scheme 1



The reaction proceeded very efficiently at room temperature with excellent yields and without formation of any side products. This is due to the rapid formation and activation of the imines by solid $HClO_4$•SiO_2. Similarly several types of anilines containing electron releasing and electron withdrawing groups at *ortho*, *para*, and *meta* positions such as alkyl, alkoxy, bromo, chloro and fluoro were reacted with various *β*-keto esters such as ethyl, methyl, allyl, and tertiary butyl acetoacetates and cinnamaldehyde in a one-pot operation by using catalytic amount (5 mol%) of $HClO_4$•SiO_2 to give 1,4-dihydropyridines in 74%—96% yields (Table 1).

The reaction with aliphatic amines (*eg*. Benzyl amine and phenylethylamine) gave complex reaction mixtures containing only small amounts of the desired products and the reactions with substituted cinnamaldehydes were also unsuccessful.

Moreover, it is noteworthy that this reaction does not require any inert conditions to get good to excellent yields without loss of efficiency of the catalyst. After the completion of reaction, the catalyst was recovered by filtration, washed with acetonitrile and recycled (after activation at 120 ℃ for 4—5 h) for four times in subsequent reactions without substantial loss of its catalytic activity. The recyclability of the catalyst was verified on the reaction of cinnamaldehyde, ethylacetoacetate and aniline (Entry 1, Table 1) to afford dihydropyridines in 96%, 92%, 85% and 79% yields over four cycles.

In conclusion, we described a simple, efficient and practical method for the synthesis of dihydropyridines through a one-pot three-component coupling of cinnamaldehyde, *β*-keto ester and aromatic amines by using heterogeneous catalyst, silica supported perchloric acid. This simple method combined with ease of recovery and reusability of the catalyst is expected to contribute to the development of clean, cost effective, and environmentally friendly procedure for the synthesis of 1,4-dihydropyridines.

Experimental

Solvents were dried over standard drying agents and freshly distilled prior to use. The reagents were purchased from Aldrich and Acros and were used without further purification unless otherwise stated. Organic solvents were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* below 40 ℃. All column chromatographic (CC) separations were performed using silica gel (Acme's 60—120 mesh). ^{1}H NMR (200 and 300 MHz) spectra were measured with a Varian Gemini FT-200 and Bruker Avance 300 instrument with tetramethylsilane as an internal standard in $CDCl_3$; *J* values are given in Hz. Mass spectra were recorded on Agilent Technologies 1100 Series (Agilent Chemistation Software).

General procedure for preparation of compounds 4a—4w

To a stirred solution of cinnamaldehyde (0.132 g, 1 mmol), aniline (0.094 g, 1 mmol) and ethylacetoacetate (0.130 g, 1 mmol) in acetonitrile (5 mL), $HClO_4$•SiO_2 (5 mol%) was added. The reaction mixture was stirred at r.t. for 20 min and the reaction was monitored by TLC. After the completion of reaction mixture, the contents were filtered (to remove the catalyst). The filtrate was concentrated by vacuum. The residue was purified by silica-gel column chromatography by eluting with AcOEt/PE (1∶9) to afford the pure product in 96% yield (0.306 g).

Ethyl-2-methyl-1,4-diphenyl-1,4-dihydropyridine (4a) Yield 0.306 g (96%), gummy syrup; ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 1.19 (t, *J*=7.1 Hz, 3H), 2.21 (s, 3H), 4.08 (q, *J*=7.1 Hz, 2H), 4.75 (d, *J*=5.5 Hz, 1H), 5.07 (dd, *J*=5.5, 7.6 Hz, 1H), 6.23 (d, *J*=7.6 Hz, 1H), 7.24—7.47 (m, 10H); IR (KBr) *v*: 1690, 1568, 1221 cm^{-1}; ESI-MS *m/z*: 319 (M^+).

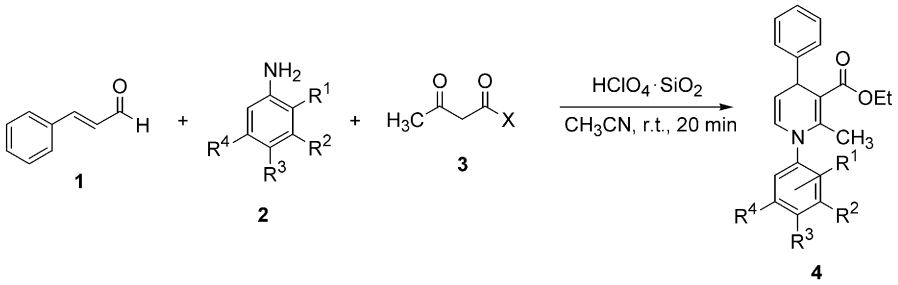
Ethy-2-methyl-1-(2-methylphenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4b) Yield 0.313 g (94%), gummy syrup; ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 1.1 (t, *J*=6.5 Hz, 3H), 2.08 (s, 3H), 2.30 (s, 3H), 4.02 (q, *J*=6.68 Hz, 2H), 4.70 (d, *J*=5.28 Hz, 1H), 4.95 (dd, *J*=5.28 Hz, 7.45, 1H), 5.85 (d, *J*=7.45 Hz, 1H), 7.10—7.38 (m, 9H); IR (Neat) *v*: 3025, 2980, 1689, 1568, 1225 cm^{-1}; ESI-MS *m/z*: 334 $(M+H)^+$.

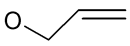
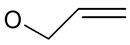
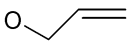
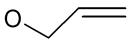
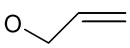
Ethyl-1,4-dihydro-1-(4-isopropylphenyl)-2-methyl-4-phenylpyridine-3-carboxylate (4d) Yield 0.346 g (96%), gummy syrup; ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 1.12 (t, *J*=6.7 Hz, 3H), 1.28 (d, *J*=6.79 Hz, 6H), 2.12 (s, 3H), 2.90—2.92 (m, 1H), 3.98—4.02 (m, 2H), 4.62 (d, *J*=5.28 Hz, 1H), 4.90 (dd, *J*=7.55, 6.04 Hz, 1H), 6.95 (d, *J*=7.54 Hz, 1H), 7.09—7.13 (m, 3H), 7.20—7.31 (m, 6H); IR (Neat) *v*: 3024, 2960, 1682, 1564, 1510, 1220 cm^{-1}; ESI-MS *m/z*: 361 (M^+).

Ethyl-2-methyl-1-(4-bromophenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4e) Yield 0.357 g (90%), gummy syrup; ^{1}H NMR ($CDCl_3$, 200 MHz) *δ*: 1.12 (t, *J*=7.5 Hz, 3H), 2.12 (s, 3H), 4.02 (q, *J*=6.0 Hz, 2H), 4.66 (d, *J*=5.2 Hz, 1H), 4.98 (dd, *J*=6.04, 7.55

CHINESE JOURNAL OF CHEMISTRY

Table 1 $HClO_4$•SiO_2 catalyzed synthesis of 1,4-dihydropyridinesa



Entry	R^1	R^2	R^3	R^4	X	Product	Time/min	Yield/%
1	H	H	H	H	OC_2H_5	**4a**	20	96
2	CH_3	H	H	H	OC_2H_5	**4b**	20	94
3	H	CH_3	H	H	OC_2H_5	**4c**	20	88
4	H	H	$CH(CH_3)_2$	H	OC_2H_5	**4d**	20	96
5	H	H	Br	H	OC_2H_5	**4e**	15	90
6	H	H	Cl	H	OC_2H_5	**4f**	20	92
7	H	H	F	H	OC_2H_5	**4g**	20	93
8	H	H	OCH_3	H	OC_2H_5	**4h**	20	90
9	H	H	H	H	OCH_3	**4i**	20	95
10	CH_3	H	H	H	OCH_3	**4j**	20	96
11	H	H	$CH(CH_3)_2$	H	OCH_3	**4k**	20	92
12	H	H	OCH_3	H	OCH_3	**4l**	20	90
13	H	H	Cl	H	OCH_3	**4m**	20	94
14	H	H	F	H	OCH_3	**4n**	20	94
15	H	H	H	H		**4o**	20	94
16	CH_3	H	H	H		**4p**	20	92
17	H	H	$CH(CH_3)_2$	H		**4q**	20	94
18	H	H	Cl	H		**4r**	20	96
19	H	H	F	H		**4s**	20	94
20	H	H	H	H	$OC(CH_3)_3$	**4t**	45	78
21	H	H	CH_3	H	$OC(CH_3)_3$	**4u**	45	74
22	H	H	H	H	$SC(CH_3)_3$	**4v**	45	75
23	H	H	CH_3	H	$SC(CH_3)_3$	**4w**	20	96

[a] All products were characterized by ^{1}H NMR and mass spectral data and spectral data of known compounds compared with reported compounds.

Hz, 1H), 6.09 (d, J=7.5 Hz, 1H), 7.06 (d, J=8.3 Hz, 2H), 7.24—7.28 (m, 5H), 7.53 (d, J=8.3 Hz, 2H); IR (Neat) ν: 3061, 2943, 1667, 1567, 1510, 1221 cm^{-1}; ESI-MS: *m/z* 397 $(M)^+$.

Ethyl-2-methyl-1-(4-chlorophenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4f) Yield 0.324 g (92%), gummy syrup; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 2.01 (t, J=6.5 Hz, 3H), 2.08 (s, 3H), 4.05 (q, J=6.6 Hz,

2H), 4.68 (d, J=5.2 Hz 1H), 4.98 (dd, J=5.15, 7.48 Hz, 1H), 6.10 (d, J=7.4 Hz, 1H), 7.15 (d, J=8.2 Hz, 2H), 7.22—7.34 (m, 5H), 7.38 (d, J=8.2 Hz, 2H); IR (Neat) v: 3026, 2980, 1690, 1567, 1223 cm^{-1}; ESI-MS *m/z*: 354 $(M+H)^+$.

Ethyl-2-methyl-1-(4-methoxyphenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4h) Yield 0.314 g (90%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.1 (t, J=6.5 Hz, 3H), 2.10 (s, 3H), 3.80 (s, 3H), 3.94 (q, J=6.5 Hz, 2H), 4.62 (d, J=1.5 Hz, 1H), 4.88 (dd, J=5.12, 7.3 Hz, 1H), 6.05 (d, J=7.3 Hz, 1H), 6.88 (d, J=8.77 Hz, 2H), 7.12 (d, J=8.77 Hz, 2H), 7.21—7.29 (m, 5H); IR (Neat) v: 3059, 2978, 1687, 1567, 1510, 1221 cm^{-1}; ESI-MS *m/z*: 349 $(M)^+$.

Methyl-2-methyl-1,4-diphenyl-1,4-dihydropyridine-3-carboxylate (4i) Yield 0.289 g (95%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.15 (s, 3H), 3.57 (s, 3H), 4.66 (d, J=5.8 Hz, 1H), 4.99 (dd, J=5.8 Hz, 7.3 Hz, 1H), 6.13 (d, J=7.3 Hz, 1H), 7.14—7.45 (m, 10H); IR (Neat) v: 1693, 1569, 1224 cm^{-1}; ESI-MS *m/z*: 306 $(M+H)^+$.

Methyl-2-methyl-1-(2-methylphenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4j) Yield 0.306 g (96%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.05 (s, 3H), 2.25 (s, 3H), 3.52 (s, 3H), 4.65 (d, J=5.26 Hz, 1H), 4.95 (dd, J=5.26, 7.54 Hz, 1H), 5.85 (d, J=7.54 Hz, 1H), 7.10—7.30 (m, 9H); IR (Neat) v: 3076, 2874, 2753, 1610, 1497, 1227 cm^{-1}; ESI-MS *m/z*: 320 $(M+H)^+$.

Methyl-2-methyl-1-(4-isopropylphenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4k) Yield 0.319 g (92%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.25 (d, J=6.6 Hz, 6H); 2.15 (s, 3H), 2.9—3.01 (m, 1H), 3.55 (s, 3H), 4.7 (d, J=5.1 Hz, 1H), 4.96 (dd, J=5.8, 8.0 Hz, 1H), 6.12 (d, J=8.08 Hz, 1H), 7.04—7.32 (m, 9H); IR (Neat) v: 3028, 2959, 2926, 1695, 1566, 1513, 1225 cm^{-1}; ESI-MS *m/z*: 347 $(M)^+$.

Methyl-2-methyl-1-(4-methoxyphenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4l) Yield 0.301 g (90%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.17 (s, 3H), 4.48 (d, J=5.2 Hz, 2H), 4.68 (d, J=5.2 Hz, 1H), 5.0 (dd, J=5.2, 7.5 Hz, 1H), 5.09—5.11 (m, 2H), 5.74—5.76 (m, 1H), 6.08 (d, J=7.5 Hz, 1H), 7.12 (d, J=8.3 Hz, 2H), 7.24—7.32 (m, 5H), 7.38 (d, J=8.3 Hz, 2H); IR (Neat) v: 3038, 2969, 2935, 1685, 1566, 1513, 1225 cm^{-1}; ESI-MS *m/z*: 335 $(M)^+$.

Methyl 2-methyl-1-(4-chlorophenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4m) Yield 0.318 g (94%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.12 (s, 3H), 3.56 (s, 3H), 4.66 (d, J=6.04 Hz, 1H), 5.04 (dd, J=5.2, 7.54 Hz, 1H), 6.12 (d, J=7.54 Hz, 1H), 7.15 (d, J=8.30 Hz, 2H), 7.26—7.32 (m, 5H), 7.38 (d, J=8.3 Hz, 2H); IR (Neat) v: 3026, 2924, 2853, 1690, 1597, 1492, 1227 cm^{-1}; ESI-MS *m/z*: 339 $(M)^+$.

Allyl-2-methyl-1,4-diphenyl-1,4-dihydropyridine-3-carboxylate (4o) Yield 0.311 g (94%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.15 (s, 3H), 4.45 (d, J=5.2 Hz, 2H), 4.67 (d, J=5.2 Hz, 1H), 4.97 (dd, J=5.2, 7.5 Hz, 1H), 5.04—5.08 (m, 2H), 5.76 (m, 1H), 6.12 (d, J=7.5 Hz, 1H), 7.10—7.42 (m, 10H); IR (Neat) v: 1698, 1597, 1495, 1222 cm^{-1}; ESI-MS *m/z*: 331 $(M)^+$.

Allyl-2-methyl-1-(2-methylphenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4p) Yield 0.317 g (92%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.10 (s, 3H), 2.30 (s, 3H), 4.44 (d, J=5.2 Hz, 2H), 4.69 (d, J=5.2 Hz, 1H), 4.98—5.01 (m, 3H), 5.69—5.72 (m, 1H), 5.83—5.85 (m, 1H), 7.04—7.38 (m, 9H); IR (Neat) v: 3019, 2929, 1688, 1565, 1492, 1223 cm^{-1}; ESI-MS *m/z*: 346 $(M+H)^+$.

Allyl-2-methyl-4-phenyl-1-(4-isopropylphenyl)-1,4-dihydropyridine-3-carboxylate (4q) Yield 0.352 g (94%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.24 (d, J=6.7 Hz, 6H), 2.16 (s, 3H), 2.88—2.91 (m, 1H), 4.46 (d, J=6.0 Hz, 1H), 4.69 (d, J=5.2 Hz, 1H), 4.98 (t, J=6.04 Hz, 1H), 5.13—5.05 (m, 3H), 5.76—5.78 (m, 1H), 6.12 (d, J=7.5 Hz, 1H), 7.20—7.36 (m, 9H); IR (Neat) v: 1692, 1568, 1226 cm^{-1}; ESI-MS *m/z*: 375 $(M)^+$.

Allyl-2-methyl-1-(4-chlorophenyl)-4-phenyl-1,4-dihydropyridine-3-carboxylate (4r) Yield 0.350 g (96%), gummy syrup; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.17 (s, 3H), 4.48 (d, J=5.2 Hz, 2H), 4.68 (d, J=5.2 Hz, 1H), 5.0 (dd, J=5.2, 7.5 Hz, 1H), 5.08—5.11 (m, 2H), 5.74—5.77 (m, 1H), 6.08 (d, J=7.5 Hz, 1H), 7.12 (d, J=8.3 Hz, 2H), 7.24—7.32 (m, 5H), 7.38 (d, J=8.3 Hz, 2H); IR (Neat) v: 3026, 1693, 1565, 1491, 1220 cm^{-1}; M/S *m/z*: 365 $(M)^+$.

Acknowledgements

The authors thank to Council of Scientific and Industrial Research New Delhi, India, for financial assistance.

References

1 Review of MCRs, see:
(a) Domling, A.; Ugi, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3168.
(b) Bienayme, H.; Hulme, C.; Oddon, G.; Schmitt, P. *Chem. Eur. J.* **2000**, *6*, 3321.
(c) Zhu, J. *Eur. J. Org. Chem.* **2003**, 1133.
(d) Orru, R. V. A.; de Greef, M. *Synthesis* **2003**, *10*, 1471.
(e) Simon, C.; Constantieux, T.; Rodriguez, J. *Eur. J. Org. Chem.* **2004**, 4957.
(f) Ramon, D. J.; Yus, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1602.
(g) *Multicomponent Reactions*, Eds.: Zhu, J.; Bienayme, H., Wiley-VCH, Weinheim, **2005**.
2 Donkor, I. O.; Zhou, X.; Schmidt, J.; Agarwal, K. C.; Kishore, V. *Bioorg. Med. Chem.* **1998**, *6*, 563.
3 (a) Hilgeroth, A. *Mini Rev. Med. Chem.* **2002**, *2*, 235.
(b) Hilgeroth, A.; Wiese, M.; Billich, A. *J. Med. Chem.* **1999**, *42*, 4729.
4 Aouam, K.; Berdeaux, A. *Therapie* **2003**, *58*, 333.

5 (a) Straub, T.; Boesenberg, C.; Gekeler, V.; Boege, F. *Biochemistry* **1997**, *36*, 10777.
(b) Kuzmin, A.; Semenova, S.; Ramsey, N. F.; Zvartau, E. E.; Van Ree, J. M. *Eur*. *J*. *Pharmacol*. **1996**, *295*, 19.
(c) Advendano, C.; Menendez, J. C. *Curr*. *Med*. *Chem*. **2002**, *9*, 159.
(d) Advendano, C.; Menendez, J. C. *Med*. *Chem*. *Rev*. **2004**, *1*, 419.
(e) Boumendjel, A.; Baubichon-Cortay, H.; Trompier, D.; Perrotton, T.; Di Pietro, A. *Med*. *Res*. *Rev*. **2005**, *25*, 453.

6 (a) Comins, D. L.; O'Connor, S. *Adv*. *Heterocycl*. *Chem*. **1998**, *44*, 199.
(b) Kumar, R.; Chandra, R. *Adv*. *Heterocycl*. *Chem*. **2001**, *78*, 269.
(c) Lavilla, R. *J*. *Chem*. *Soc*., *Perkin Trans*. *1* **2002**, 1141.

7 (a) Hantzsch, A. *Ann*. *Chem*. **1882**, *215*, 72.
(b) Stout, D. M.; Meyers, A. *J*. *Chem*. *Rev*. **1982**, *82*, 223.
(c) Balogh, M.; Hermecz, I.; Szabo, G. N.; Simon, K.; Meszaros, Z. *J*. *Chem*. *Soc*., *Perkin Trans*. *1* **1986**, 753.
(d) Katritzky, A. R.; Ostercamp, D. L.; Yousaf, T. I. *Tetrahedron* **1986**, *42*, 5729.
(e) Mencon, I.; Angeles, E.; Martinez, L.; Posada, M. E.; Toscano, R. A.; Martinez, R. *J*. *Heterocycl*. *Chem*. **1995**, *32*, 831.

8 (a) Kidwai, M.; Mohan, R. *Can*. *J*. *Chem*. **2004**, *82*, 427.
(b) Vanden Eynde, J. J.; Mayence, A. *Molecules* **2003**, *8*, 381.

9 Sammour, A.; Selim, M. I. B.; Elseen, M. M. N. *J*. *Prakt*. *Chem*. **1972**, *314*, 139.

10 Geirsson, J. K. F.; Johannesdotir, J. F. *J*. *Org*. *Chem*. **1996**, *61*, 7320.

11 Ishar, M. P. S.; Kumar, K.; Kaur, S.; Kumar, S.; Girdhar, N. K.; Sachar, S.; Markawa, A.; Kapoor, A. *Org*. *Lett*. **2001**, *3*, 2133.

12 Sridharan, V.; Perumal, P. T.; Avendano, C.; Menendez, J. C. *Tetrahedron* **2007**, *63*, 4407.

13 (a) Khadilkar, B. M.; Borkar, S. D. *Tetrahedron Lett*. **1997**, *38*, 1641.
(b) Hajipur, A. R.; Abidi, H.; Ruoho, A. E. *J*. *Org*. *Chem*. **2003**, *68*, 4553.
(c) Lamber, A.; Carr, G.; Clark, J. H.; Macquarrie, D. J. *New J*. *Chem*. **2000**, *24*, 485.
(d) Clark, J. H.; Macquarrie, D. J.; Mubofu, E. B. *Green Chem*. **2000**, *2*, 53.
(e) Gonzalez-Nunez, M. E.; Mello, R.; Olmos, A.; Asensio, G. *J*. *Org*. *Chem*. **2005**, *70*, 10879.

14 (a) Agarwal, A.; Rani, S.; Vankar, Y. D. *J*. *Org*. *Chem*. **2004**, *69*, 6137
(b) Khan, A. T.; Pravin, T.; Choudhury, L. H. *Synthesis* **2006**, 2497.
(c) Kamble, V. T.; Jamode, V. S.; Joshi, N. S.; Biradar, A. V.; Deshmukh, R. Y. *Tetrahedron Lett*. **2006**, *47*, 7655.
(d) Narasimhulu, M.; Srikanth Reddy, T.; Chinni Mahesh, K.; Prabhakar, P.; Bhujangarao, C.;Venkateswarlu, Y. *J*. *Mol*. *Cat*. *A*: *Chem*. **2007**, *266*, 114.
(e) Meshram, H. M.; Reddy, P. N.; Murthy, P. V.; Yadav, J. S. *Synth*. *Commun*. **2007**, *37*, 4117.
(f) Mukharjee, C.; Mishra, A. K. *Synthesis* **2007**, 683.
(g) Shaterian, H. R.; Yarahmadi, H.; Ghashang, M. *Tetrahedron* **2008**, *64*, 1263.

15 Du, Y.; Wei, G. S.; Cheng, Y.; Hua, R.; Linhardt, J. *Tetrahedron Lett*. **2006**, *47*, 307.

(CJOC201100032 Lu, Y.)

