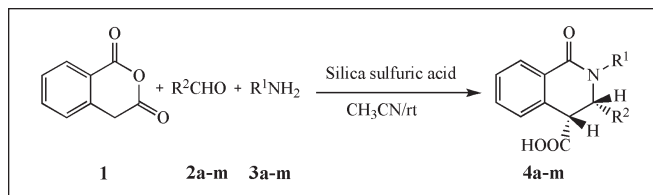


Javad Azizian,* Ali A. Mohammadi, Ebrahim Soleimani, Ali R. Karimi,
and Mohammad R. Mohammadzadeh

Department of Chemistry, Faculty of Science, Shahid Beheshti University, P. O. Box 19395-4716, Tehran, Iran

E-mail: j-azizian@cc.sbu.ac.ir

Received April 18, 2005



A mild and stereoselective three-component one-step synthesis of *cis*-isoquinolonic acid using silica sulfuric acid as a heterogeneous catalyst from an aldehyde, amine and homophthalic anhydride in acetonitrile is described. This new method produces pure products in high yields (81-91%).

J. Heterocyclic Chem., **43**, 187 (2006).

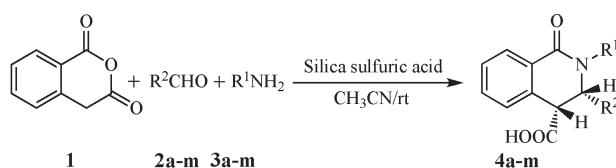
During recent years, the use of silica sulfuric acid as catalysts or promoters in organic synthesis has attracted great interest from many chemists [1]. Silica sulfuric acid can enhance the reactivity and selectivity of many types of reaction, such as oxidation, reduction, carbon-carbon bond formation, cycloaddition and protection.

Isoquinolonic acid and the derivatives are pharmacologically important and have biological activities [2] including anti-inflammatory and psychotropic behaviour. In addition, isoquinolonic acids have been reported as starting materials for the total synthesis of natural compounds such as nitidine chloride [3], 4-epicorynoline, corynoline, 6-oxocorynoline [4], decumbenine **B** [5]. Therefore, many synthetic methods for preparing such compounds have been developed [6]. The cycloaddition of homophthalic anhydride with imines has been reported in the presence of a catalytic amount of Lewis acids (such as $ZnCl_2$, $FeCl_3$, $AlCl_3$) bases (TEA, DIEA) *etc.*, protic acids (CH_3COOH , HCl), or absence catalyst, which often produce a mixture of *cis*- and *trans*-isomers. Recently, $BF_3 \cdot Et_2O$ [7] has been employed for the preparation of *trans*-isoquinolonic acids, and trimethyl orthoformate [8], ionic liquids [9a] and ytterbium (III) triflate [9b] have been employed for the synthesis of *cis*-isomers.

In connection with our ongoing work on multi-component condensations (MCCs) [10], we now wish to report a facile, rapid and stereoselective one-pot three-component procedure for the preparation of *cis*-isoquinolonic acids derivatives with silica sulfuric acid as a heterogeneous, non-toxic, reusable, inexpensive and easily available reagent, at room temperature. Very recently, we have reported the preparation of *cis*-isoquinolonic acids by the reaction of homophthalic anhydride with imines in the presence of $KAl(SO_4)_2 \cdot 12H_2O$ [11]. In this paper, we

describe a general and practical route for the cyclocondensation reaction using silica sulfuric acid as the catalyst [12]. This is a novel, one-pot combination that not only preserves the simplicity of cycloaddition's multi-component reaction but also consistently produces excellent yields of the *cis*-isoquinolonic acids. In the presence of the silica sulfuric acid (0.23 g, equal to 0.6 mmol), the reaction of homophthalic anhydride **1** (1 mmol), aldehyde **2a-m** (1 mmol), and amine **3a-m** (1 mmol) in acetonitrile was carried out in a one-pot condensation at room temperature (Scheme 1).

Scheme 1



The results (Table 1) show a series of aromatic aldehydes and amines that undergo the cyclocondensation to give excellent yields (81-91%) of the products. The all *cis*-stereochemistry of cycloadducts **4** was attributed from the two doublets ($J=4.6-6.9$ Hz) observed close to 4.52-4.99 ppm and 4.96-5.97 ppm, for the H-3 and H-4 hydrogen atoms, respectively.

This new procedure is also simple to operate. The work-up consists of simple filtration and the catalyst is reusable and can be applied several times without any decrease in the yield of the reactions. All the products were characterized by IR, 1H NMR, ^{13}C NMR, MS, and elemental analyses [13]. After the reaction was completed, the *cis*-isoquinolonic acids **4a-m** precipitated from the reaction mixture.

Table 1
The Reaction of Homophthalic Anhydride, Amines and Aldehydes

Product 4	R ²	R ¹	Time (h)	Yield ^a (%)	M.P (°C)	Lit. M.P (°C)
a	Ph	Ph	7	88	201-3	198 [8]
b	Ph	4-ClC ₆ H ₄	6.5	90	200-1	182 [8]
c	Ph	4-MeC ₆ H ₄	6	91	187-8	178 [8]
d	Ph	PhCH ₂	7.5	88	179-80	-
e	4-ClC ₆ H ₄	PhCH ₂	8	87	180-1	-
f	Ph	PhCH ₂ CH ₂	8.5	84	168-70	-
g	Ph	Benzimidazol	9	85	222-4 dec.	-
h	4-NO ₂ C ₆ H ₄	4-MeC ₆ H ₄	7.5	86	246-8 dec.	-
i	4-BrC ₆ H ₄	4-ClC ₆ H ₄	7	89	225-6 dec.	-
l	3-ClC ₆ H ₄	4-ClC ₆ H ₄	8	87	210-1 dec.	-
m	2-BrC ₆ H ₄	PhCH ₂	8.5	81	216-8	-

^aYields of pure isolated product based on homophthalic anhydride.

In summary, we have described a successful strategy, efficient and convenient green synthesis for the preparation of tetrahydroisoquinolonic acids in a valuable three-component cyclocondensation reaction of homophthalic anhydride, aldehydes and amines using the inexpensive, non-toxic and easily available silica sulfuric acid catalyst. The method offers several advantages including high yield of products, a recyclable catalyst and easy experimental work-up procedure. Surprisingly, this reaction is stereoselective in the preparation of *cis*-isoquinolonic acids, since no detectable amount of *trans*-isomers, which makes it a useful process for the synthesis of *cis*-isoquinolonic acids.

EXPERIMENTAL

Melting points were measured on the Electro thermal 9100 apparatus and are uncorrected. IR spectra were measured on a Shimadzu IR-470 Spectrophotometer. ¹H NMR and ¹³C NMR spectra were determined on Bruker 500 DRX AVNCE instrument at 500 and 125 MHz, respectively. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer.

General Procedure for the Preparation of *cis*-Isoquinolonic Acids.

A mixture of homophthalic anhydride (1 mmol, 162 mg), aldehydes (1.2 mmol), amine (1 mmol), silica sulfuric acid (0.23 g) and acetonitrile (8-10 ml) in a 25 ml flask was stirred at room temperature for the time period as indicated in Table 1. After completion the reaction (monitored by TLC, ethyl acetate/*n*-hexane 1/1), the solvent was evaporated under reduced pressure, then water (25 ml) was added to the reaction mixture and the resulting solid was separated by filtration. The crude product was washed with ether to afford pure *cis*-isoquinolonic acids in 81-91% yields.

Spectral Data for Products.

1-Oxo-2,3-diphenyl-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4a**).

White powder, yield 88%, mp 201-3 °C, IR(KBr), (ν_{\max} /cm⁻¹): 3020, 2915, 1723, 1633. ¹H NMR (DMSO) δ_{H} : 4.94(d, 1H, *J*=6.9

Hz, H₃), 5.49(d, 1H, *J*=6.9 Hz, H₄), 7.01-7.30(m, 10H), 7.57-7.60(m, 3H), 8.07(d, 1H, *J*=8.7 Hz), 12.04(broad, 1H). ¹³C NMR (DMSO) δ_{C} : 49.54, 65.12, 126.60, 128.10, 128.24, 128.36, 128.39, 128.44, 128.67, 129.47, 129.60, 132.64, 135.90, 136.15, 137.35, 139.55, 163.20, 171.10. MS (*m/z*, %): 343 (M⁺, 75), 298 (30), 207 (25), 181 (100), 134 (45), 118 (35), 105 (35), 90 (25), 77 (80), 63 (35), 51 (50), 39(35).

Anal. Calcd. for C₂₂H₁₇NO₃: C, 76.95; H, 4.99; N, 4.08. Found: C, 76.78; H, 4.90; N, 4.00.

2-(4-Chlorophenyl)-1-oxo-3-phenyl-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4b**).

White powder, yield 90%, mp 200-1 °C, IR(KBr), (ν_{\max} /cm⁻¹): 3070, 2913, 1723, 1630. ¹H NMR (DMSO) δ_{H} : 4.86(d, 1H, *J*=4.6 Hz, H₃), 5.52(d, 1H, *J*=4.6 Hz, H₄), 7.04-7.57(m, 12H), 8.06(d, 1H, *J*=7.3 Hz), 12.91(broad, 1H). ¹³C NMR (DMSO) δ_{C} : 49.62, 64.57, 128.19, 128.22, 128.37, 128.43, 128.53, 128.67, 129.00, 129.38, 129.75, 131.30, 132.94, 134.94, 137.51, 140.86, 163.52, 170.93. MS (*m/z*, %): 377 (M⁺, 30), 358 (20), 333 (60), 250 (20), 214 (100), 178 (50), 138 (30), 118 (95), 111 (80), 90 (95), 75 (80), 63 (85), 51 (70), 39(55).

Anal. Calcd. for C₂₂H₁₆NO₃Cl: C, 69.94; H, 4.27; N, 3.71. Found: C, 69.87; H, 4.18; N, 3.60.

1-Oxo-3-phenyl-2-*p*-tolyl-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4c**).

White powder, yield 91%, mp 187-8 °C, IR(KBr), (ν_{\max} /cm⁻¹): 3010, 2910, 1723, 1614. ¹H NMR (DMSO) δ_{H} : 2.23(s, 3H, CH₃), 4.93(d, 1H, *J*=5.7 Hz, H₃), 5.43(d, 1H, *J*=5.7 Hz, H₄), 6.99-7.15(m, 9H), 7.45-7.60(m, 3H), 8.05(d, 1H, *J*=7.6 Hz), 12.90(broad, 1H). ¹³C NMR (DMSO) δ_{C} : 21.03, 49.44, 65.02, 127.64, 128.02, 128.22, 128.26, 128.33, 128.41, 128.57, 129.57, 129.69, 132.68, 134.70, 136.35, 137.76, 139.64, 163.31, 170.88. MS (*m/z*, %): 357 (M⁺, 30), 313 (35), 236 (25), 208 (45), 195 (100), 178 (70), 134 (30), 118 (75), 91 (85), 77 (95), 63 (50), 51 (70), 39(55).

Anal. Calcd. for C₂₃H₁₉NO₃: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.17; H, 5.29; N, 3.85.

2-Benzyl-1-oxo-3-phenyl-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4d**).

White powder, yield 88%, mp 179-80 °C, IR(KBr), (ν_{\max} /cm⁻¹): 3025, 2910, 1742, 1613. ¹H NMR (DMSO) δ_{H} : 3.75(d, 1H, *J*=15.3

Hz, CH₂), 4.69(d, 1H, *J*=6.0 Hz, H₃), 4.96(d, 1H, *J*=6.0 Hz, H₄), 5.31(d, 1H, *J*=15.3 Hz, CH₂), 6.96-7.57(m, 13H), 8.08(d, 1H, *J*=7.5 Hz), 12.99(broad, 1H). ¹³C NMR (DMSO) δ_C: 48.55, 48.57, 61.18, 127.69, 127.93, 127.97, 128.03, 128.25, 128.50, 128.75, 129.01, 129.18, 132.52, 134.15, 137.79, 163.59, 170.72. MS (*m/z*, %): 358 (M⁺, 25), 357 (35), 269 (30), 207 (25), 136 (30), 118 (80), 116 (75), 91 (100), 77 (35), 62 (30), 51 (35), 39(30).

Anal. Calcd. for C₂₃H₁₉NO₃: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.20; H, 5.27; N, 3.83.

2-Benzyl-3-(4-chlorophenyl)-1-oxo-3-phenyl-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4e**).

White powder, yield 87%, mp 180-1 °C, IR(KBr), (ν_{max}/cm⁻¹): 3050, 2905, 1737, 1608. ¹H NMR (DMSO) δ_H: 3.83(d, 1H, *J*=15.3 Hz, CH₂), 4.70(d, 1H, *J*=6.2 Hz, H₃), 4.99(d, 1H, *J*=6.2 Hz, H₄), 5.24(d, 1H, *J*=15.3 Hz, CH₂), 6.94-7.55(m, 13H), 8.07(d, 1H, *J*=7.5 Hz), 13.02(broad, 1H). ¹³C NMR (DMSO) δ_C: 48.52, 48.72, 60.55, 127.69, 128.03, 128.10, 128.49, 128.71, 128.97, 129.03, 130.08, 132.65, 133.39, 133.91, 136.24, 137.67, 163.46, 170.69. MS (*m/z*, %): 391 (M⁺, 15), 347 (40), 242 (40), 207 (30), 178 (35), 118 (45), 106 (45), 91 (100), 65 (50), 51 (30), 39(30).

Anal. Calcd. for C₂₃H₁₈NO₃Cl: C, 70.50; H, 4.63; N, 3.57. Found: C, 70.43; H, 4.54; N, 3.51.

1-Oxo-2-ethylphenyl-3-phenyl-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4f**).

White powder, yield 84%, mp 168-70 °C, IR(KBr), (ν_{max}/cm⁻¹): 3025, 2910, 1738, 1614. ¹H NMR (DMSO) δ_H: 2.67(m, 1H, CH₂), 2.86-2.92(m, 1H, CH₂), 2.98-3.04(m, 1H, CH₂), 4.01-4.06(m, 1H, CH₂), 4.52(d, 1H, *J*=6.2 Hz, H₃), 4.98(d, 1H, *J*=6.2 Hz, H₄), 6.97(d, 2H, *J*=6.2 Hz), 7.16-7.19(m, 6H), 7.25-7.28(m, 2H), 7.41-7.44(m, 1H), 7.49(m, 2H), 8.02(d, 1H, *J*=6.8 Hz), 12.91(broad, 1H). ¹³C NMR (DMSO) δ_C: 34.05, 48.14, 48.45, 62.00, 126.73, 127.70, 127.84, 128.24, 128.34, 128.63, 128.67, 128.89, 129.08, 129.40, 132.31, 134.06, 137.74, 139.54, 163.13, 170.79. MS (*m/z*, %): 371 (M⁺, 10), 353 (15), 327 (25), 280 (35), 236 (80), 221 (30), 207 (60), 174 (40), 146 (25), 118 (40), 91 (100), 92 (30), 65 (30), 51 (30), 44 (30), 39(25).

Anal. Calcd. for C₂₅H₂₅NO₃: C, 77.49; H, 6.50; N, 3.61. Found: C, 77.41; H, 6.43; N, 3.57.

2-(1*H*-Benzoimidazol-yl)-1-oxo-3-phenyl-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4g**).

White powder, yield 85%, mp 222-4 dec. °C, IR(KBr), (ν_{max}/cm⁻¹): 3060, 2915, 1700, 1657. ¹H NMR (DMSO) δ_H: 4.61(d, 1H, *J*=6.5 Hz, H₃), 5.96(d, 1H, *J*=6.5 Hz, H₄), 7.29-7.43(m, 7H), 7.47-7.57(m, 3H), 7.65(m, 1H), 7.95(d, 1H, *J*=7.7 Hz), 8.03(d, 1H, *J*=7.6 Hz), 12.53(broad, 1H). ¹³C NMR (DMSO) δ_C: 49.19, 79.08, 80.35, 124.91, 126.27, 127.28, 128.08, 128.21, 128.72, 128.93, 128.98, 129.02, 129.23, 129.83, 130.22, 134.40, 134.85, 137.26, 137.97, 163.97, 171.58. MS (*m/z*, %): 383 (M⁺, 10), 368 (20), 313 (15), 250 (35), 178 (35), 118 (100), 105 (60), 90 (95), 77 (75), 63 (55), 51 (65), 39(45).

Anal. Calcd. for C₂₃H₁₇N₃O₃: C, 72.05; H, 4.47; N, 10.96. Found: C, 71.91; H, 4.40; N, 10.87.

3-(4-Nitrophenyl)-1-oxo-2-*p*-tolyl-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic acid (**4h**).

White powder, yield 86%, mp 246-8 dec. °C, IR(KBr), (ν_{max}/cm⁻¹): 3065, 2915, 1723, 1630, 1598. ¹H NMR (DMSO) δ_H: 2.23(s, 3H, CH₃), 4.99(d, 1H, *J*=5.1 Hz, H₃), 5.97(d, 1H, *J*=5.1

Hz, H₄), 7.09(m, 4H), 7.31(d, 2H, *J*=8.2), 7.49-7.61(m, 3H), 8.03(d, 2H, *J*=8.2 Hz), 8.08(d, 1H, *J*=7.2 Hz), 12.52(broad, 1H). ¹³C NMR (DMSO) δ_C: 48.74, 63.40, 123.04, 127.15, 127.43, 127.73, 127.83, 129.10, 129.27, 132.38, 136.01, 138.59, 144.92, 146.95, 162.68, 170.20. MS (*m/z*, %): 402 (M⁺, 10), 383 (15), 356 (50), 295 (40), 252 (25), 240 (50), 193 (30), 165 (20), 118 (70), 106 (100), 90 (60), 77 (30), 63 (35), 51 (30), 39 (50).

Anal. Calcd. for C₂₃H₁₈N₂O₅: C, 68.65; H, 4.51; N, 6.96. Found: C, 68.59; H, 4.47; N, 6.87.

3-(4-Bromophenyl)-2-(4-chlorophenyl)-1-oxo-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4i**).

White powder, yield 89%, mp 225-6 dec. °C, IR(KBr), (ν_{max}/cm⁻¹): 3065, 2920, 1723, 1630. ¹H NMR (DMSO) δ_H: 4.86(d, 1H, *J*=4.9 Hz, H₃), 5.54(d, 1H, *J*=4.9 Hz, H₄), 6.94-6.99(m, 4H), 7.20-7.28(m, 4H), 7.36-7.59(m, 5H), 8.05(d, 1H, *J*=7.5 Hz), 2.43(broad, 1H). ¹³C NMR (DMSO) δ_C: 48.87, 63.17, 127.57, 127.68, 127.81, 128.48, 128.57, 128.96, 129.21, 129.99, 130.81, 131.00, 132.45, 134.11, 136.40, 139.38, 162.80, 170.24. MS (*m/z*, %): 456 (M⁺, 15), 412 (55), 345 (50), 301 (60), 267 (45), 257 (35), 223 (25), 193 (30), 178 (20), 118 (60), 106 (100), 90 (50), 77 (35), 63 (30), 51 (30), 39 (55).

Anal. Calcd. for C₂₂H₁₅NO₃BrCl: C, 57.86; H, 3.31; N, 3.07. Found: C, 57.78; H, 3.22; N, 2.98.

3-(3-Chlorophenyl)-2-(4-chlorophenyl)-1-oxo-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4l**).

White powder, yield 87%, mp 210-1 dec. °C, IR(KBr), (ν_{max}/cm⁻¹): 3040, 2915, 1722, 1630. ¹H NMR (DMSO) δ_H: 4.83(d, 1H, *J*=5.3 Hz, H₃), 5.60(d, 1H, *J*=5.3 Hz, H₄), 7.01(d, 1H, *J*=7.2 Hz), 7.10(s, 1H), 7.20-7.26(m, 4H), 7.36-7.38(m, 2H), 7.49-7.62(m, 3H), 8.05(d, 1H, *J*=7.7), 12.53(broad, 1H). ¹³C NMR (DMSO) δ_C: 49.09, 62.99, 126.53, 127.53, 127.75, 127.81, 127.86, 127.91, 128.43, 128.58, 129.18, 129.92, 130.76, 132.50, 134.27, 139.50, 139.90, 162.92, 170.32. MS (*m/z*, %): 411 (M⁺, 15), 367 (25), 333 (40), 299 (45), 257 (45), 244 (50), 223 (35), 178 (35), 165 (25), 118 (100), 111 (25), 90 (45), 77 (30), 63 (30), 51 (35), 39 (50).

Anal. Calcd. for C₂₂H₁₅NO₃Cl₂: C, 64.09; H, 3.67; N, 3.40. Found: C, 64.00; H, 3.57; N, 3.32.

2-Benzyl-3-(2-bromophenyl)-1-oxo-1,2,3,4-tetrahydro-isoquinoline-4-carboxylic Acid (**4m**).

White powder, yield 81%, mp 216-8 °C, IR(KBr), (ν_{max}/cm⁻¹): 3060, 2925, 1735, 1610. ¹H NMR (DMSO) δ_H: 3.71(d, 1H, *J*=15.2 Hz, CH₂), 4.61(d, 1H, *J*=6.5 Hz, H₃), 5.32(d, 1H, *J*=15.2 Hz, CH₂), 5.43(d, 1H, *J*=6.5 Hz, H₄), 6.95(m, 1H), 7.14-7.34(m, 8H), 7.50-7.60(m, 3H), 8.08(d, 1H, *J*=7.6 Hz), 12.50(broad, 1H). ¹³C NMR (DMSO) δ_C: 47.67, 47.78, 58.09, 124.32, 127.18, 127.37, 127.48, 127.57, 127.70, 128.02, 128.24, 128.38, 128.60, 130.01, 132.30, 132.56, 133.68, 135.96, 136.72, 162.91, 169.98. MS (*m/z*, %): 435 (M⁺, 15), 391 (15), 356 (50), 345 (10), 312 (35), 302 (10), 278 (35), 261 (10), 234 (40), 206 (45), 178 (55), 118 (20), 106 (35), 91 (100), 65 (45), 51 (35), 39 (30).

Anal. Calcd. for C₂₃H₁₈NO₃Br: C, 63.32; H, 4.16; N, 3.21. Found: C, 63.23; H, 4.10; N, 3.13.

REFERENCES AND NOTES

- [1a] M. A. Zolfigol and M. Safaiee, *Synlett*, **5**, 827 (2004); [b] F. Shirini, M. A. Zolfigol and M. Khaleghi, *Mendeleev Communications*, **34**

- (2004); [c] M. M. Khodaei, P. Salehi, M. A. Zolfigol and S. Sirouszadeh *Polish J. Cehm.*, **3**, 387 (2004); [d] F. Shirini, M. A. Zolfigol and K. Mohammadi, *Bull. Kore. Chem. Soc.*, **25**, 325 (2004); [e] P. Salehi, M. Dabiri and M. A. Zolfigol, *Heterocycles*, **60**, 2435 (2003); [f] M. A. Zolfigol, I. Mohammadpoor-Baltork, B. F. Mirjalili and A. Bamoniri, *Synlett.*, **12**, 1877 (2003).
- [2a] J. V. Johnson, S. Rauckman, P. D. Baccanari and B. Roth, *J. Med. Chem.*, **32**, 1942 (1989); [b] E. Stanoeva and M. Haimova, *Khim. Geterotsikl. Soedin.*, 1587 (1984); [c] M. A. Haimova, N. M. Mollov, S. C. Ivanova, A. I. Dimitrova and V. I. Ognyanov, *Tetrahedron*, **33**, 331 (1977); [d] N. Yamada, S. Kadowaki, K. Takahashi and K. Umeu, *Biochem. Pharmacol.*, **44**, 1211 (1992).
- [3] M. Cushman and L. Cheng, *J. Org. Chem.*, **43**, 286 (1978).
- [4] M. Cushman, A. Abbaspour and Y. P. Gupta, *J. Am. Chem. Soc.*, **105**, 2873 (1983).
- [5] X. Y. Xu, G. W. Qin, R. S. Xu and X. Z. Zhu, *Tetrahedron*, **54**, 14179 (1998).
- [6a] M. Cushman and E. J. Madaj, *J. Org. Chem.*, **52**, 907 (1987); [b] M. Cushman, J. Gentry and F. W. Dekow, *J. Org. Chem.*, **42**, 1111 (1977); [c] B. Bonnaud, A. Carlessi and D. C. H. Bigg, *J. Heterocyclic Chem.*, **30**, 257 (1993); [d] M. A. Haimova, N. M. Mollov, S. C. Ivanova, A. I. Dimitrova and V. I. Ognyanov, *Tetrahedron*, **33**, 331 (1977); [e] M. P. Stoyanova, I. D. Kozekov and M. D. Palamareva, *J. Heterocyclic Chem.*, **40**, 795 (2003).
- [7] N. Yu, L. Bourel, B. Deprez, and J. C. Gesquiere, *Tetrahedron Lett.*, **39**, 829 (1998).
- [8] N. Yu R., Poulain and J. C. Gesquiere, *Synlett*, 355 (2000).
- [9a] J. S. Yadav, B. V. S. Reddy, K. Saritha Raj and A. R. Prasad, *Tetrahedron*, **59**, 1805 (2003); [b] L. Wang, J. Liu, H. Tian, C. Qian and J. Sun, *Adv. Synth. Catal.*, **347**, 689 (2005).
- [10a] J. Azizian, A. R. Karimi, Z. Kazemizadeh, A. A. Mohammadi and M. R. Mohammadzadeh, *Tetrahedron Lett.* In press; [b] J. Azizian, A. R. Karimi, A. A. Mohammadi and M. R. Mohammadzadeh, *Synthesis*, **14**, 2263 (2004); [d] J. Azizian, A. A. Mohammadi and A. R. Karimi, *Synth. Commun.*, **33**, 415 (2003); [e] J. Azizian, A. R. Karimi and A. A. Mohammadi, *Synth. Commun.*, **33**, 387 (2003); [f] J. Azizian, A. R. Karimi, H. Arefrad, A. A. Mohammadi, and M. R. Mohammadzadeh, *Molecular Diversity*, **6**, 223 (2003).
- [11] J. Azizian, A. A. Mohammadi, A. R. Karimi, M. R. Mohammadzadeh and M. Koohshri, *Heterocycles*, **63**, 2013 (2003).
- [12] For the preparation of silica sulfuric acid see: M. A. Zolfigol, *Tetrahedron*, **57**, 9509 (2001).