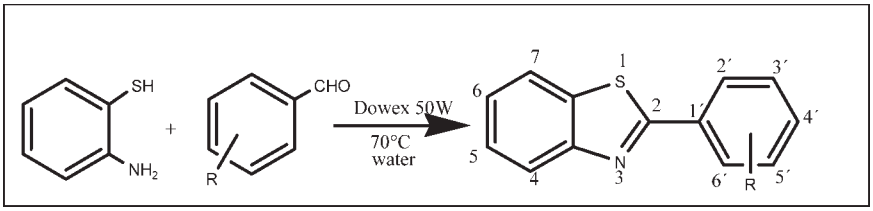
Water-Promoted Dowex 50W Catalyzed Highly Efficient Green Protocol for 2-Arylbenzothiazole Formation

Chhanda Mukhopadhyay* and Arup Datta

Department of Chemistry, University of Calcutta, Kolkata 700009, India
*E-mail: csm@vsnl.net or cmukhop@yahoo.co.in

Received December 18, 2007
DOI 10.1002/jhet.9
Published online 5 February 2009 in Wiley InterScience (www.interscience.wiley.com).



2-Aminothiophenol and a variety of aryl aldehydes were allowed to react in one-pot operation to give 2-aryl-benzothiazoles in excellent yields in the presence of Dowex 50W in water. Very high yields coupled with the ease of work-up procedure, formation of no side products, employment of ''reusable'' catalyst, and ''green'' synthesis in aqueous medium without maintaining anhydrous reaction conditions are the most important aspects of this methodology.

J. Heterocyclic Chem., **46**, 91 (2009).

INTRODUCTION

The 2-substituted benzothiazole moiety is particularly very interesting in the area of medicinal and organic chemistry. The benzothiazolyl system possesses highly selective and potent antitumor activity. An example is that of substituted 2-(4-aminophenyl)-benzothiazoles, which show nanomolar inhibitory *in vitro* activity against a wide range of human breast, ovarian, colon, and renal cell lines [1]. Another such compound that shows potent and selective inhibitory activity against lung, colon, and breast cancer cell lines is 2-(3,4-dimethoxyphenyl)-5-fluorobenzothiazole [2]. Also, the 2-(4-dimethylaminophenyl)-benzothiazole is an integral component used for the treatment of Alzheimer's disease [3]. The presence of the benzothiazole nucleus is essential in the thermally stable rigid-rod polymers with high tensile strength and modulus [4]. Thus, the synthesis of this benzothiazole moiety is always a great challenge.

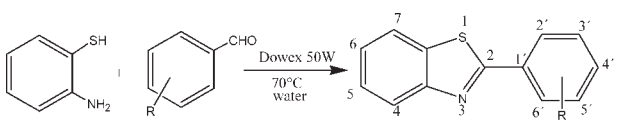
A number of synthetic routes are available for the construction of the benzothiazole nucleus. Among them, the most common ones being the condensation of 2-aminothiophenols with substituted carboxylic acids, acyl chlorides, aldehydes, and nitriles [5]. An alternate method includes potassium ferricyanide cyclization of thiobenzanilides (Jacobson's method [6]). Solvent-free synthesis of benzothiazoles under microwave irradiation in the presence of silica gel is also known [7a]. Very recently, the synthesis of this moiety under microwaves in absence of any catalyst has been reported by us [7b]. Most of these methods employ costly reagents and perfectly dry reaction conditions or the use of microwaves. Thus, a truly efficient diverse green synthetic scheme of such an important organic moiety in aqueous medium still needs to be explored.

RESULTS AND DISCUSSION

It has been recently reported from our laboratory [8] that Dowex 50W has proved to be a very effective and efficient catalyst for the construction of the 4-aryl-dihydropyrimidone nucleus. On the basis of such observation, we chose the sulfonic acid resin Dowex 50W in aqueous medium for the construction of the benzothiazole ring. Thus, a variety of aromatic aldehydes (**1**) were coupled with 2-aminothiophenol (**2**) in the presence of 10 mol % of Dowex 50W in water in a one-pot operation for the first time to synthesize the 2-substituted benzothiazoles (**3**) (Scheme 1, Table 1) in excellent yields. Water proved to be the best medium for this reaction. The yields of the products decreased on performing the reaction in water-methanol, water-ethanol, or water-tetrahydrofuran mixed solvents (all 50:50 by volume).

The advantages of using Dowex 50W are as follows: (a) it can be reused at least three times without

Scheme 1



2 **1** **3**

Table 1

Synthesis of 2-arylbenzothiazoles by Dowex 50W in water under aerial oxygen.

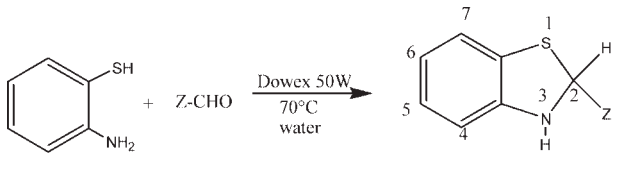
Entry	R (1)	Time (h)	Yield (%) (3)	Observed mp (°C)	Reported mp (°C)	References
1	a: H	12	a: 85	112–114	114–115	[5a,10]
2	b: 4-OMe	10	b: 89	120–121	121–122	[5a,10]
3	c: 2-OMe	08	c: 83	101–103	101–102	[7]
4	d: 3-NO_2	08	d: 88	181–182	183–185	[5b]
5	e: 4-Cl	12	e: 90	115–117	117–118	[5a,11]
6	f: 4-NO_2	06	f: 87	228–230	229–230	[5a,7]
7	g: 4-OH	10	g: 92	225–226	227–228	[7]
8	h: 3-OH	12	h: 86	161–163	160–162	[12]
9	i: 3-OMe- 4-OH	10	i: 90	162–164	161–163	[12]
10	j: 3-Br	08	j: 92	84–86	83–84	[13]
11	k: 4-$N(CH_3)_2$	10	k: 88	160–162	160–161	[3]
12	l: 2-furanyl	09	l: 85	103–104	103–104	[5a,7,11]
13	m: 2-NO_2	05	m: 83	135–136	138–140	[7]
14	n: 2-Cl	10	n: 85	84–85	82	[7]
15	o: 2-cinnamyl	07	o: 82	110–111	112	[5b]
16	p: 4- Br	08	p: 84	132	130	[14]
17	q: 3,4- $(OMe)_2$	07	q: 87	141–143	142–144	[15]
18	r: 2.5-$(OMe)_2$	07	r: 85	147–149	Not reported	[16]

substantial loss of activity (b) dry conditions are not required (c) the reaction takes place very smoothly (d) no side products are obtained (e) the purification of the final product is very simple (f) no hazardous wastes from solvents or chemicals take place (g) the reaction conditions are very mild employing temperature of only 70°C, thus being able to sustain quite a large number of functional groups. Therefore, Dowex 50W is a ''green catalyst'' for the 2-aryl-benzothiazole formation in aqueous medium.

With salicaldehyde (**1s**), the reaction stopped at the benzothiazoline [**4**(**i**)(**s**)] stage (Scheme 2, Table 2, entry 1), and the stability of this intermediate by six-membered hydrogen bond (intramolecular) (Fig. 1) prevents it to react further to produce the benzothiazole. The isolation of this intermediate [**4**(**i**)(**s**)] confirms our earlier proposed mechanism [7b].

The fact that the reaction of salicaldehyde (**1s**) and 2-aminothiophenol (**2**) stops at the benzothiazoline stage is further proved by the work of Charles and Freiser [9]. The intermediate benzothiazoline [**4**(**i**)(**s**)] from salicaldehyde (**1s**) is converted to 2-hydroxyphenyl benzothiazole (**3s**) in good yield but under very drastic conditions (Scheme 3, Table 3, entry 1). The isolation of 2-hydroxyphenyl benzothiazoline [**4**(**i**)(**s**)] surely proves that the reaction passes through this intermediate. Following the same mechanistic pathway cited in our earlier reference [7b], benzothiazoles (**3**) are the final products for all the cases cited in Table 1.

Scheme 2



2 [Z=(R substituted aryl)(**1**) Z=alkyl] **4**(i) Z=R-substituted aryl (ii) Z=alkyl

The reaction therefore proceeds *via* the intermediate formation of benzothiazoline [7b]. This is further proved by the actual isolation of such intermediates from 2-chloro and 4-nitrobenzaldehydes by carrying out the reaction for a shorter time (entries 2 and 3, Table 2), which then proceed to completion (entries 2 and 3, Table 3). When the same reaction with Dowex 50W was carried out under argon atmosphere (in absence of oxygen) (carried out with 2-chloro, 4-nitro- and 2-hydroxy benzaldehydes), the reactions stopped at the benzothiazoline stage, which never proceeded to benzothiazoles. This surely proves that aerial oxygen is not essential for benzothiazoline formation, though it is absolutely essential for the oxidation step leading to the formation of benzothiazoles. The overall yield of the stepwise reaction was more or less the same as that of the one-step reaction, although the total time required for the stepwise reaction was slightly greater. It was not possible to isolate the intermediate benzothiazoline for all the other substrates as the next steps of oxidation and dehydration were very fast leading to the formation of benzothiazoles (the ultimate products in all cases). Stopping the reaction at various stages resulted in the formation of a mixture of benzothiazoline and benzothiazole of varied percentage compositions (done for 4-methoxy

Table 2

Synthesis of 2-aryl and 2-alkyl-benzothiazolines by Dowex 50W in water both under aerobic and anaerobic conditions.

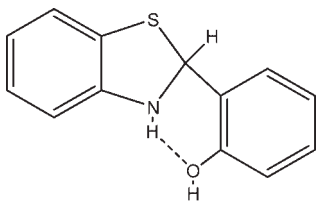
Entry	*Z* (Scheme 2)	Time (h)	Yield (%)(4)	Observed mp (°C)	Literature mp (°C)	References
1	1s: (2-OH)C_6H_4	06	(i) s: 90	141–142	141–144	[9,17]
2	1n: (2-Cl)C_6H_4	02	(i) n: 85	76	Not reported	[18]
3	1f: (4-NO_2)C_6H_4	01	(i) f: 87	115–117	117–118	[19]
4	t: —$(CH_2)_2CH_3$	06	(ii) t: 50			[20]
5	u: —CH_2CH_3	07	(ii) u: 55			[20]

benzaldehyde) [benzothiazoline: benzothiazole = 43:57 (obtained by the ^{1}H NMR integration of the methoxy peaks after 2 h and benzothiazoline: benzothiazole = 26:74 after 6 h].

Thus, Dowex 50W catalyses both the steps; the formation of the benzothiazoline ring and the formation of benzothiazole from benzothiazoline. Carrying out the reaction in argon (truly oxygen free) atmosphere, results in the isolation of benzothiazolines (for 2-chloro and 4-nitro benzaldehydes). Thus, the presence of the aerial oxygen is essential for the benzylic oxidation (C—H to C—OH) step, which is the penultimate one for benzothiazole formation. Without Dowex 50W, the reaction just initializes to 20% formation of the benzothiazoline along with unreacted aldehyde, which then never proceeds further. Thus, Dowex 50W has a definitive catalytic role toward benzothiazole formation. The reaction is widely applicable to a variety of substrates; nitro, methoxy, chloro, bromo, and hydroxy groups on the aryl nucleus perform smooth reactions (Table 1). With aliphatic aldehydes, the reaction stops at the benzothiazoline stage (done with *n*-propanal and *n*-butanal, Table 2), probably because of lower stability of the resultant benzothiazole (absence of conjugation with the aromatic ring).

CONCLUSIONS

This procedure of the synthesis of 2-aryl-benzothiazoles by Dowex 50W in aqueous medium in one-pot operation is a green, highly efficient, and cost effective method than the existing procedures. We hope that our method will be highly beneficial to both academic and industrial processes, being a highly general one with varied substituents in the aromatic aldehydes.



(the dotted lines indicating H-bond formation)

Figure 1. Intramolecular six-membered H-bond formation in 2-phenylbenzothiazoline.

EXPERIMENTAL

A typical experimental procedure is as follows: A mixture of 2-aminothiophenol (5 mmol), aromatic aldehyde (5 mmol), and Dowex 50W (10 mol %) were stirred in water (4 mL) at 70°C for the specified time period (Table 1), till the TLC showed the absence of the starting aldehyde. The reaction mixture was cooled, diluted with ethyl acetate (20 mL), filtered to remove Dowex 50W and extracted the aqueous part with ethyl acetate (2 × 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The crude products were purified by crystallization from ethyl acetate and petroleum ether (60–80°C) to afford the 2-aryl-benzothiazoles (or 2-aryl-benzothiazolines) in excellent yields. All the products were characterized by their melting points, IR, ^{1}H NMR, and ^{13}C NMR spectral analyses. The data for a few selected compounds are given below:

2-(2′-Methoxyphenyl)-benzothiazole. (Table 1, entry 3): IR (KBr): 3435, 2932, 2372, 1586, 1458, 1427, 1286, 1246, 1013, and 754 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.51 (dd, J = 7.9 Hz and 1.7 Hz, 1H, C_4-H), 8.07 (dt, J = 7.8 Hz and 1.0 Hz, 1H, C_7-H), 7.89 (dt, J = 7.4 Hz and 0.6 Hz, 1H, $C_{6'}$-H), 7.48–7.38 (m, 2H, C_5-H and C_6-H), 7.33 (dt, J = 7.5 Hz and 1.1 Hz, 1H, $C_{4'}$-H), 7.10 (dt, J = 7.8 Hz and 1.1 Hz, 1H, $C_{5'}$-H), 7.02 (dd, J = 8.0 Hz and 0.7 Hz, 1H, $C_{3'}$-H), 4.00 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 163.1, 157.2, 152.2, 136.1, 131.7, 129.5, 125.8, 124.5, 122.8, 122.3, 121.1, 121.1, 111.7, 55.7.

2-(4′-Hydroxyphenyl)-benzothiazole. (Table 1, entry 7): IR (KBr): 3436, 2366, 1601, 1479, 1308, 1256, 1171, 1025, 832, and 760 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 10.23 (brs, 1H, OH), 8.07 (brd, J = 7.9 Hz, 1H, C_4-H), 7.98 (brd, J = 8.1

Scheme 3

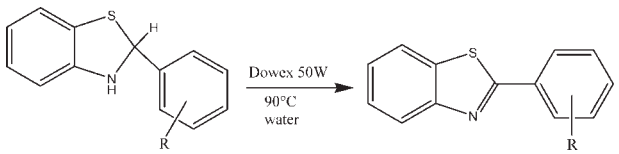


Table 3

Conversion of 2-arylbenzothiazolines to 2-arylbenzothiazoles under aerobic conditions (does not take place without oxygen).

Entry	R [4(i)] (Scheme 3)	Time (h)	Yield (%) (overall) (w.r.t. starting aldehyde) (3)	Observed mp (°C)	Literature [7b] mp (°C)
1	s: 2-OH	25	s: 70	124–126	127–128
2	n: 2-Cl	10	n: 85	84–85	82
3	f: 4-NO_2	05	f: 88	228–230	229–230

Hz, 1H. C_7-H), 7.94 (d, J = 8.6 Hz, 2H, $C_{2'}$-H and $C_{6'}$-H), 7.50 (brt, J = 7.1 Hz, 1H, C_5-H), 7.40 (brt, J = 7.6 Hz, 1H, C_6-H), 6.94 (d, J = 8.6 Hz, 2H, $C_{3'}$-H and $C_{5'}$-H); ^{13}C NMR (DMSO-d_6, 75 MHz), δ: 167.9, 161.0, 154.2, 134.6, 129.5, 126.9, 125.4, 124.5, 122.8, 122.6, 116.6.

2-(2′-Hydroxyphenyl)-benzothiazoline. (Table 2, entry 1): IR(KBr): 3256, 1585, 1484, 1460, 1232, 755 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 9.87 (s, 1H. OH), 7.39 (dd, J = 7.6 Hz and 1.5 Hz, 1H, $C_{6'}$-H), 7.11 (dt, J = 7.6 Hz and 1.2 Hz, 1H, $C_{4'}$-H), 6.94 (brd, J = 7.3 Hz,1H, C_7-H), 6.89–6.76 (m, 3H, C_4-H, C_5-H and C_6-H), 6.67 (dd, J = 7.8 Hz and 0.7 Hz, 1H, $C_{3'}$-H), 6.57 (dt, J = 7.5 Hz and 1.1 Hz, 1H, $C_{5'}$-H), 6.48 (d, J = 1.4 Hz, 1H, C_2-H), [the absence of the NH proton around δ (4–4.5) indicates that it is H-bonded to the more electronegative O-atom]; ^{13}C NMR (DMSO-d_6, 75 MHz), δ: 154.0, 148.3, 130.1, 129.1, 126.4, 125.7, 125.6, 121.7, 119.3, 119.0, 115.4, 109.1, 63.5.

2-(2′-Hydroxyphenyl)-benzothiazole. (Table 3, entry 1): IR (KBr): 3437, 2923, 2372, 1580, 1477, 1210, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 12.52 (brs, 1H, OH), 8.00 (brd, J = 8.1 Hz, 1H, C_4-H), 7.91 (brd, J = 7.7 Hz, 1H, C_7-H), 7.71 (dd, J = 7.9 Hz and 1.5 Hz, 1H, $C_{6'}$-H), 7.51 (dt, J = 7.2 Hz and 1.2 Hz, 1H, C_5-H), 7.40 (dt, J = 7.4 Hz and 1.1 Hz, 2H, C_6-H and $C_{4'}$-H), 7.11 (dd, J = 8.4 Hz and 1.1 Hz, 1H, $C_{3'}$-H), 6.97 (dt, J = 7.5 Hz and 1.0 Hz, 1H, $C_{5'}$-H); ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 169.4, 158.0, 151.9, 132.8, 132.6, 128.4, 126.7, 125.6, 122.2, 121.5, 119.5, 117.9, 116.8.

2-(2′-Chlorophenyl)-benzothiazoline. (Table 2, entry 2): IR(KBr): 3344, 3063, 2371, 1573, 1462, 1240, 1033 and 734 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.77–7.71(m, 1H, $C_{3'}$-H), 7.40–7.31(m, 1H, C_4-H), 7.28–7.18 (m, 2H, $C_{4'}$-H and $C_{6'}$-H), 7.04 (dd, J = 7.5 Hz and 0.9 Hz, 1H, C_7-H), 6.95 (dt, J = 9.0 Hz and 1.3 Hz, 1H, C_5-H), 6.79–6.71 (m, 2H, C_6-H and $C_{5'}$-H), 6.66 (s, 1H, C_2-H), 4.43 (brs, 1H, NH) ; ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 146.1, 140.0, 131.6. 129.6, 129.3, 127.4, 127.3, 126.3, 125.5, 122.0, 121.1, 110.4, 65.6.

2-(2′-Chlorophenyl)-benzothiazole. (Table 3, entry 2): IR (KBr): 3435, 2363, 1423, 1266, 1053 and 755 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.21–8.18 (m, 1H, $C_{3'}$-H), 8.12 (dd, J = 9.0 Hz and 0.6 Hz, 1H, C_4-H), 7.94 (dd, J = 7.8 Hz and 0.6 Hz, 1H, C_7-H), 7.54–7.49 (m, 2H, $C_{4'}$-H and $C_{6'}$-H), 7.44–7.38 (m, 3H, C_5-H, C_6-H and $C_{5'}$-H); ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 164.2, 152.5, 136.1, 132.7, 132.3, 131.7, 131.1, 130.8, 127.1, 126.3, 125.4, 123.5 and 121.4.

2-(4′-Nitrophenyl)-benzothiazoline. (Table 2, entry 3): IR (KBr): 3333, 2371, 1595, 1515, 1340, 853 and 756 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.22 (dt, J = 8.8 Hz and 1.9 Hz, 2H, $C_{3'}$-H and $C_{5'}$-H), 7.68 (dt, J = 8.5 Hz and 2.3 Hz, 2H, $C_{2'}$-H and $C_{6'}$-H), 7.06 (dd, J = 6.5 Hz and 1.0 Hz, 1H, C_4-H), 7.00 (dt, J = 6.4 Hz, and 1.3 Hz, 1H, C_5-H), 6.81(dt, J = 6.4 Hz and 1.1 Hz, 1H, C_6-H), 6.75 (dd, J = 6.7 Hz and 0.8 Hz, 1H, C_7-H), 6.43 (d, J = 3.7 Hz, 1H, C_2-H), 4.52 (s, 1H, NH) ; ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 149.3, 147.9, 145.8, 127.2, 126.0, 125.9, 124.1, 121.8, 121.5, 110.5, 68.3.

2-(4′-Nitrophenyl)-benzothiazole. (Table 3, entry 3): IR (KBr): 3436, 2372, 1520, 1343, 852 and 764 cm^{-1}; ^{1}H NMR, $CDCl_3$, 300 MHz) δ: 8.43–8.35 (m, 4H, $C_{3'}$-H, $C_{5'}$-H, $C_{2'}$-H and $C_{6'}$-H), 8.24 (dd, J = 7.7 Hz and 1.0 Hz, 1H, C_4-H), 8.16 (dd, J = 7.7 Hz and 0.9 Hz, 1H, C_7-H), 7.63 (dt, J = 6.0 Hz and 1.3 Hz, 1H, C_5-H), 7.55 (dt, J = 6.9 Hz and 1.4 Hz, 1H, C_6-H) ; ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 165.4, 154.0, 149.3, 138.8, 135.6 128.9, 127.6, 126.9, 125.1, 124.0, 123.1.

2-(*n*-Propyl)-benzothiazoline. (Table 2, entry 4): IR (KBr): 3355, 2958, 2930, 2872, 2360, 1583, 1468, 1402, 1119 and 741 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.04 (dd, J = 7.5 Hz and 1.2 Hz, 1H, C_4-H), 6.88 (dt, J = 6.0 Hz and 1.3 Hz, 1H, C_5-H), 6.71 (dt, J = 6.0 Hz and 1.2 Hz, 1H, C_6-H), 6.61 (dd, J = 6.0 Hz and 1.1 Hz, 1H, C_7-H), 5.24 (t, J = 6.6 Hz, 1H, C_2-H), 1.87–1.77 (m, 2H, -CH_2-CH_2-CH_3), 1.49–1.36 (m, 2H, -CH_2-CH_2-CH_3), 0.94 (t, J = 7.3 Hz, 3H, -CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 146.6, 127.5, 125.0, 121.9, 120.7, 110.7, 68.5, 40.6, 19.3, 13.7.

Acknowledgments. One of the authors (A.D.) thanks the Council of Scientific and Industrial Research (New Delhi) for his fellowship (J.R.F.). The authors also thank CAS Instrumentation facility, University of Calcutta, for providing spectral data.

REFERENCES AND NOTES

[1] Bradshaw, T. D.; Wrigley, S.; Shi, D-F.; Schulz, R. J.; Paull, K. D.; Stevens, M. F. G. Br J Cancer 1998, 77, 745.

[2] Mortimer, C. G.; Wells, G.; Crochard, J-P.; Stone, E. L.; Bradshaw, T. D.; Stevens, M. F. G.; Westwell, A. D. J Med Chem 2006, 49, 179.

[3] Mathis, C. A.; Wang, Y.; Holt, D. P.; Huang, G-F.; Debnath, M. L.; Klunk, W. E. J Med Chem 2003, 46, 2740.

[4] Cassidy, P. E. Thermally Stable Polymer, Marcel Dekker: New York, 1980.

[5] [a] Ben-Alloum, A.; Bakkas, S.; Soufiaoui, M. Tetrahedron Lett 1997, 38, 6395; [b] Li, Y.; Wang, Y-L.; Wang, J-Y. Chem Lett 2006, 35, 460.

[6] Shi, D. F.; Bradshaw, T. D.; Wrigley, S.; McCall, C. J.; Lelieveld, P.; Fichtner, I.; Stevens, M. F. G. J Med Chem 1996, 39, 3375.

[7] [a] Kodamari, M.; Tamaru, Y.; Aoyama, T. Synth Commun 2004, 34, 3029; [b] Mukhopadhyay, C.; Datta, A. Heterocycles 2007, 71, 1837.

[8] Mukhopadhyay, C.; Datta, A.; Banik, B. K. Heterocycles 2007, 71, 181.

[9] Charles, R. G.; Freiser, H. J Org Chem 1953, 18, 422.
[10] Tale, R. H. Org Lett 2002, 4, 1641.
[11] Boger, D. L. J Org Chem 1978, 43, 2296.
[12] Ranu, B. C.; Ranjan, D.; Suvendu, S. Chem Lett 2004, 33, 274.
[13] Wattenburg, L. W.; Page, M. A.; Leong, J. L. Cancer Res 1968, 28, 2539.
[14] Moghaddam, F. M.; Bardajee, G.; Rezanejade, I. H.; Taimoory, S.; Maryam, D. Synth Commun 2006, 36, 2543.
[15] Seijas, J. A.; Vazquez, T.; Pilar, M.; Carballido, R.; Raquel, M.; Crecente, C. J.; Romar-Lopez, L. Synlett 2007, 2, 313.
[16] Hubbard, W. L.; Grahame, R. E.; Corey, R. A.; Jancis, E. H. US (1977), 8 pp., Division of US3, 974, 287.
[17] Yamamoto, K.; Fujita, H.; Tabashi, K.; Kawashima, Y.; Kato, E.; Oya, M.; Iso, T.; Iwao, J. J Med Chem 1988, 31, 919.
[18] Tatsuya, K. Inorg Chim Acta 2000, 300–302, 512.
[19] Chikashita, H.; Miyazaki, M.; Ito, K. J Chem Soc Perkin Trans I Org Bioorg Chem 1987, 4, 699.
[20] Larive, H.; Chambonnet, A. J.; Metzger. J Bull Soc Chim France 1963, 8–9, 675.