# Synthesis and Application of Silica Phenyl Sulfonic Acid as a Solid Acid Heterogeneous Catalyst for One-Pot Synthesis of 2-Aryl-1-arylmethyl-1H-1,3-benzimidazoles and Bis(indolyl)methanes in Water



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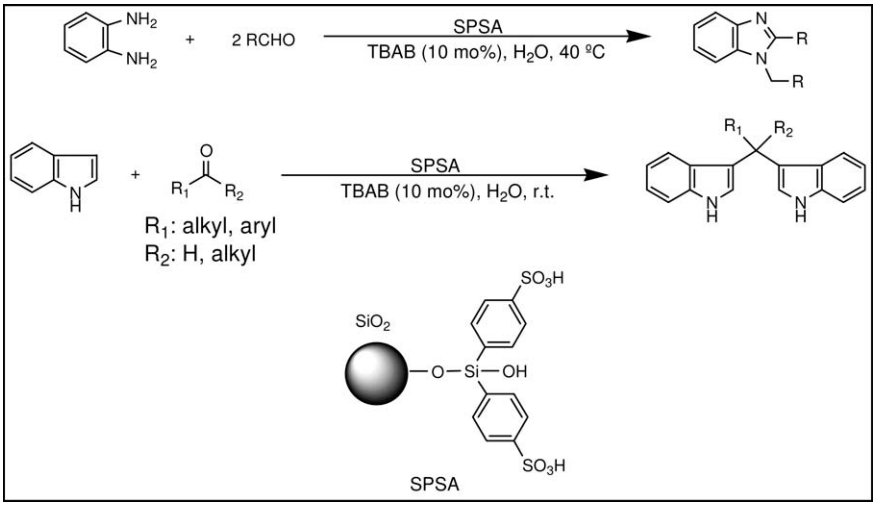
Received August 30, 2010
DOI 10.1002/jhet.765
Published online 23 August 2011 in Wiley Online Library (wileyonlinelibrary.com).




Silica phenyl sulfonic acid (SPSA) was prepared and effectively used in the one-pot synthesis of 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles from *o*-phenylenediamine with aldehydes in water in the presence of tetrabutyl ammonium bromide with good to high yield. Also, SPSA was used as a catalyst for the synthesis of bis(indolyl)methanes in water.

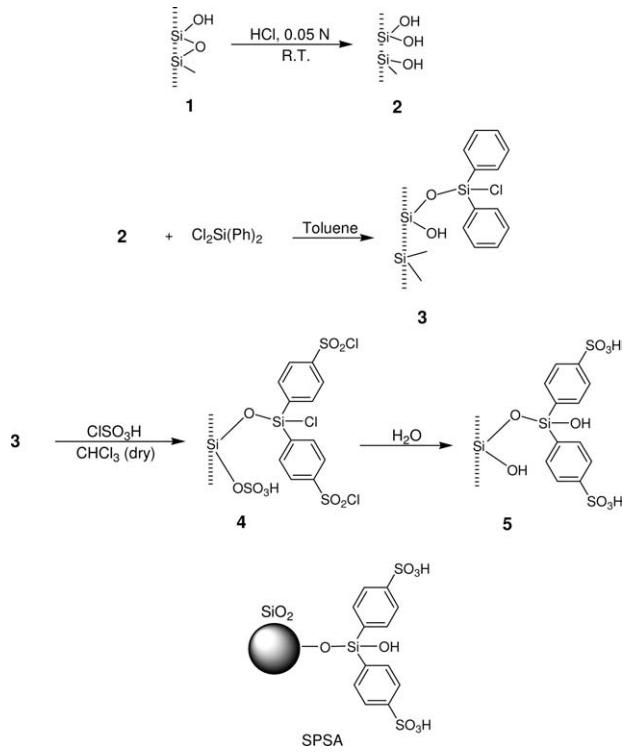
*J. Heterocyclic Chem.*, **48**, 1448 (2011).

## INTRODUCTION

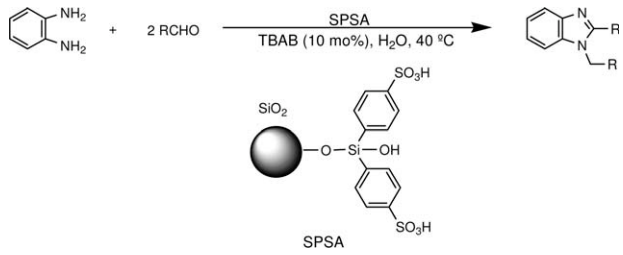
Benzimidazole derivatives have versatile pharmacological properties [1] based on their presence in both clinical medicines [2] and compounds with broad ranges of biological functions [3]. The most prominent benzimidazole compound in nature is *N*-ribosyl-dimethylbenzimidazole, which serves as an axial ligand for cobalt in vitamin $B_{12}$[4]. Thus, synthesis of this heterocyclic nucleus is, therefore, of continuing interest, but few methods are available for the synthesis of 1,2-disubstituted benzimidazoles. The more important ones include: *N*-alkylation of 2-substituted benzimidazole in the presence of a strong base [5], *N*-alkylation of *o*-nitroanilides followed by reductive cyclization [6], cyclocondensation of *N*-substituted *o*-aminoanilides [7], and condensation of *N*-substituted phenylenediamines with the sodium salt of α-hydroxybenzylsulfonic acid [8]. In addition, 1,2-disubstituted benzimidazoles can also be accessed by direct one-step condensation of 1,2-phenylenediamines with aryl aldehydes under the influence of a variety of acid catalysts [9]. However, the last protocol is currently most popular, probably because of the ease of accessibility of substituted aryl aldehydes.

The development of bis(indolyl)alkane synthesis has been of considerable interest in organic synthesis because of their wide occurrence in various natural products possessing biological activity and usefulness for drug design [10]. Bis(indolyl)methanes are found in cruciferous plants and are known to promote beneficial estrogen metabolism [11] and induce apoptosis in human cancer cell. Thus, the development of facile and environmentally friendly synthetic methods for the preparation of these compounds constitutes an active area of investigation in pharmaceutical and organic synthesis

**Scheme 1**




**Scheme 2**




[12–14]. Very recently, we have published a comprehensive review related to the synthesis and applications of bisindolylmethanes and trisindolylmethanes [15a].

Synthetically, the reaction of 1H-indole with aldehydes or ketones produces azafulvenium salts that react further with a second 1H-indole molecule to form bis(indol-3-yl)methanes [15b]. In recent years, synthesis of this class of molecules under mild conditions have been reported, with promoters such as montmorillonite clay K-10 [16], trichloro-1,3,5-triazine [17], $AlPW_{12}O_{40}$ [18], sodium dodecyl sulfate (SDS) [19], $ZrCl_4$ [20], $H_2NSO_3H$ [21], $I_2$ [22], zeolites [23], bentonite [24], $In(OTf)_3$/ionic liquid [25], $CuBr_2$ [26], $Dy(OTf)_3$/ionic liquid [27], $HClO_4$-$SiO_2$ [28], $InCl_3$ [29], MW/Lewis acids ($FeCl_3$, $BiCl_3$, $InCl_3$, $ZnCl_2$, and $CoCl_2$) [30], $NaHSO_4$ and Amberlyst-15 [31], sulfated zirconia [32], $ZrOCl_2/SiO_2$ [33], silica sulfuric acid (SSA) [34], $TiO_2$ [35], $(NH_4)_2HPO_4$ [36], acidic ionic liquid [37], $NaBF_4$ [38], metal hydrogen sulfates [39], tetrabutylammonium tribromide [40], superacid $SO_4^{2-}/TiO_2$ [41], $NaHSO_4$/ionic liquid [42], NBS [43], $Ph_3CCl$ [44], $H_3PW_{12}O_{40}$ [45], $LiClO_4$ [46], $Zr(DS)_4$ [47] and $Bi(NO_3)_3.5H_2O$ [48], $(CO_2H)_2.2H_2O$ [49], and *N*-chloro sulfonamides [50]. However, most of the existing methods involve toxic metal ions and solvent, high cost, and cumbersome work-up procedures. Consequently, new procedures that address these drawbacks are desirable.

Developing environmentally benign and economical syntheses are an area of research that is being vigorously pursued and avoiding the use of harmful organic solvents is a fundamental strategy to achieving this. One of the most attractive alternatives to organic solvents is water, which has witnessed increasing popularity due to being inexpensive, readily available, and environmentally benign. In addition, reactions in aqueous media illustrate unique reactivities and selectivities that are not usually observed in organic media [51].

## RESULTS AND DISCUSSION

In continuation of our studies on the synthesis [52] and application of SSA [52] as a solid acid heterogeneous

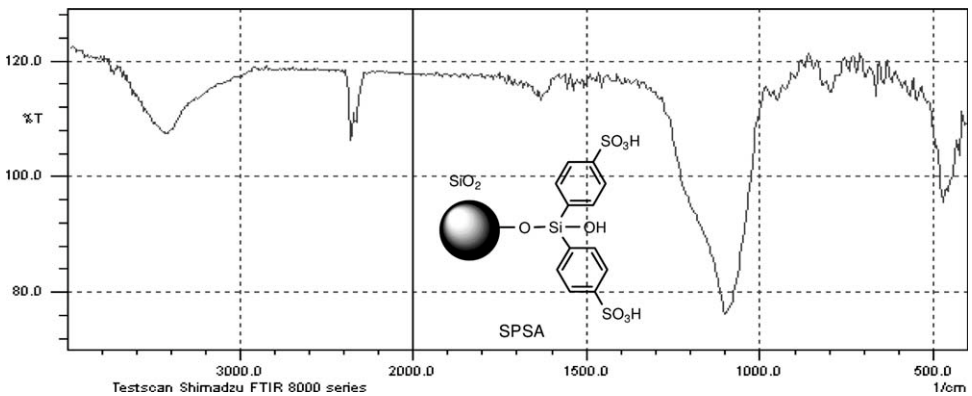



**Figure 1.** FTIR spectrum silica phenyl sulfonic acid (SPSA).

**Table 1**

Synthesis of 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles catalyzed by SPSA in the presence of TBAB in water.

| Entries | R | Time (min) | Yield (%)[a] | Mp (°C) (lit.) | Refs. |
|---|---|---|---|---|---|
| 1 | $C_6H_5$ | 10 | 98 | 131–132 (132) | [9d] |
| 2 | 4-$MeC_6H_5$ | 12 | 95 | 127–129 (128–130) | [9i] |
| 3 | 4-$MeOC_6H_5$ | 15 | 90 | 128–130 (129–130) | [9d] |
| 4 | 2-$MeOC_6H_5$ | 12 | 95 | 124–125 (125–126) | [9d] |
| 5 | 4-$ClC_6H_5$ | 15 | 96 | 134–136 (136) | [9g] |
| 6 | 2-$ClC_6H_5$ | 15 | 95 | 157–158 (158–159) | [53c] |
| 7 | 4-$OHC_6H_5$ | 10 | 90 | 222–223 (222) | [53b] |
| 8 | 4-$NO_2C_6H_5$ | 15 | 90 | 303–305 (306–308) | [54] |
| 9 | 4-$(Me_2N)C_6H_5$ | 10 | 88 | 253–255 (255) | [9i] |
| 10 | $C_6H_5$—CH=CH | 10 | 90 | 210–212 (212–213) | [9d] |
| 11 | 2-Furyl | 12 | 85 | 94–95 (94) | [9d] |
| 12 | $CH_3(CH_2)_2$ | 300 | 0 | – | – |
| 13 | $CH_3(CH_2)_8$ | 300 | 0 | – | – |

[a] Products were characterized from their physical properties, comparison with authentic samples, and by spectroscopic methods.

catalyst, we reported the synthesis of silica phenyl sulfonic acid (SPSA) as a new type of silica in organic reaction. Although our first report of SSA has been widely used [52a] but also we think that SPSA is superior due to its more stability in the presence of moisture. SPSA is easily prepared from the silanization of activated silica gel with diphenyldichlorosilane (DPCS) followed by adding chlorosulfonic acid at room temperature, and washed with water (Scheme 1). FTIR spectrum SPSA was shown in Figure 1.

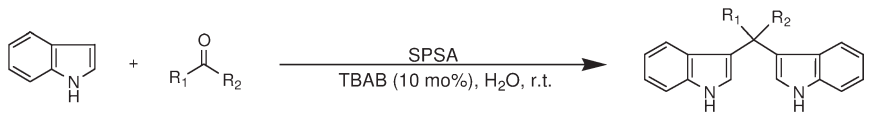
The first synthesis of sulfobenzylsilicas has reported by Saunders et al. [53a] in 1974. The preparation involved the chlorination of reactive silanol groups, the reaction of this product with benzyllithium, and finally sulfonation. We believe that this method is not very easy, and they have to use organolithium reagent to achieved sulfobenzylsilicas. But our method is a shortcut way to synthesis of these types of compounds without using of any organolithium reagent.

In continuation of our recent interest in the synthesis of heterocyclic compounds [52], we, herein, developed a green and selective reaction to synthesis of 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles through the reactions of 1,2-phenylenediamine with aryl aldehydes in aqueous media, in the presence of SPSA as a solid acid heterogeneous catalyst, and tetrabutyl ammonium bromide (TBAB) as a surfactant to assist in solubilizing the organic substrates (Scheme 2). However, this process is green, environmentally friendly, clean, and could be carried out easily at room temperature without undesirable side reactions.

We started this synthesis by examining the reaction of 1,2-phenylenediamine (1 mmol) with benzaldehyde (2 mmol) as a model reaction. We found that the use of SPSA (50 mg) and 10 mol % TBAB allowed the direct conversion of 1,2-phenylenediamine into the corresponding 1,2-disubstituted benzimidazole in a yield of 98% in water (5 mL) at 40°C (Table 1, entry 4). The use of more than 50 mg of SPSA did not enhance chemical yield.

To test the generality of this reaction, a series of aromatic aldehydes was subjected to the optimal reaction conditions (Table 1). By using water as solvent at 40°C, 1,2-disubstituted benzimidazoles with various functional groups were obtained in excellent yields. Among the reactions of different aromatic aldehydes, no significant distinction on the yields of target products was observed. Even the sensitive substrate furfuraldehyde (Table 1, entry 11) produced the corresponding 1,2-disubstituted benzimidazole without any difficulty. All substrates gave their corresponding 1,2-disubstituted benzimidazoles exclusively as a single product. However, butyraldehyde and octanal (Table 1, entries 12, 13) failed to react under the present reaction conditions.

**Scheme 3**




$R_1$: alkyl, aryl
$R_2$: H, alkyl

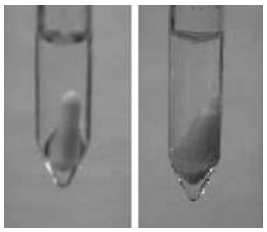


**Figure 2.** Photographs of the reaction of indole with benzaldehyde in the presence of SPSA and TBAB in $H_2O$ at 25°C: (left side) at the start of the reaction; and (right side) at the end of the reaction.

A possible mechanism for the reaction consists of a two-step sequence involving the acid catalyst-promoted formation of the *N*,*N*-dibenzylidene-1,2-phenylenediamine derivative followed by ring closure. Aromatization then takes place by a deprotonation–reprotonation process [9j].

The scope of this system has been successfully extended to the synthesis of bis(indolyl)methanes in water (Scheme 3). The optimum conditions were indole (2 mmol) and aldehyde (1 mmol), in the presence of SPSA (200 mg) and TBAB (10 mol %) in water at 25°C (Fig. 2).

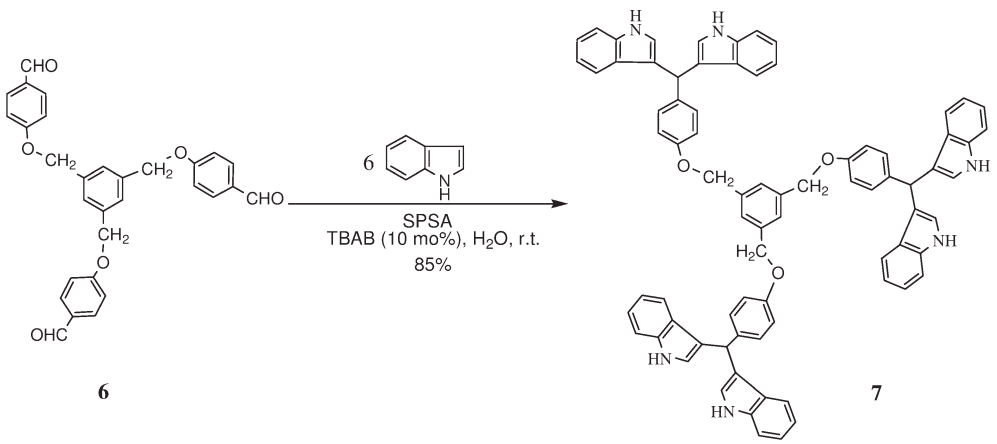
**Table 2**

Synthesis of Bis(indolyl)methanes catalyzed by SPSA in the presence of TBAB in water.

| Entries | $R_1$ | $R_2$ | Time (min) | Yield (%)[a] | Mp (°C) (lit.) | Refs. |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | H | 10 | 96 | 124–125 (124–125) | [55] |
| 2 | 4-Me$C_6H_5$ | H | 12 | 95 | 94–95 (93–94) | [19] |
| 3 | 4-MeO$C_6H_5$ | H | 5 | 98 | 190–192 (192–193) | [55] |
| 4 | 2-MeO$C_6H_5$ | H | 5 | 98 | 134–136 (133–135) | [48] |
| 5 | 4-Cl$C_6H_5$ | H | 5 | 96 | 76–78 (78–80) | [55] |
| 6 | 2-Cl$C_6H_5$ | H | 5 | 98 | 70–72 (70–71) | [19] |
| 7 | 4-Br$C_6H_5$ | H | 10 | 90 | 110–112 (112–113) | [47] |
| 8 | 4-OH$C_6H_5$ | H | 15 | 92 | 123–125 (123–125) | [56] |
| 9 | 4-$NO_2C_6H_5$ | H | 25 | 80 | 218–220 (217–220) | [19] |
| 10 | 3-$NO_2C_6H_5$ | H | 25 | 85 | 258–260 (260–261) | [57] |
| 11 | 4-($Me_2N$)$C_6H_5$ | H | 20 | 90 | 224–226 (225–226) | [48] |
| 12 | $C_6H_5$—CH=CH | H | 25 | 90 | 98–100 (98–99) | [19] |
| 13 | 2-Furyl | H | 15 | 92 | >300 (>300) | [19] |
| 14 | 2-Thienyl | H | 12 | 95 | 151–154 (150–153) | [19] |
| 15 | $CH_3(CH_2)_2$ | H | 30 | 80 | 121–123 (122–124) | [47] |
| 16 | $CH_3(CH_2)_8$ | H | 30 | 75 | 190–182 (181–182) | [47] |
| 17 | Indol-3-carbaldehyde | – | 30 | 80 | 255–257 (256–258) | [58a] |
| 18 | Terephthaldialdehyde | – | 20 | 85 | 194–195 (194–195) | [50] |
| 19 | Isatin | – | 30 | 70 | >300 (>300) | [58b] |
| 20 | $C_6H_5$ | $CH_3$ | 20 | 90 | 165–167 (166–168) | [47] |
| 21 | 4-$NO_2C_6H_5$ | $CH_3$ | 25 | 85 | 190–192 (190–191) | [47] |
| 22 | Cyclohexanone | – | 20 | 85 | 115–116 (114–116) | [48] |

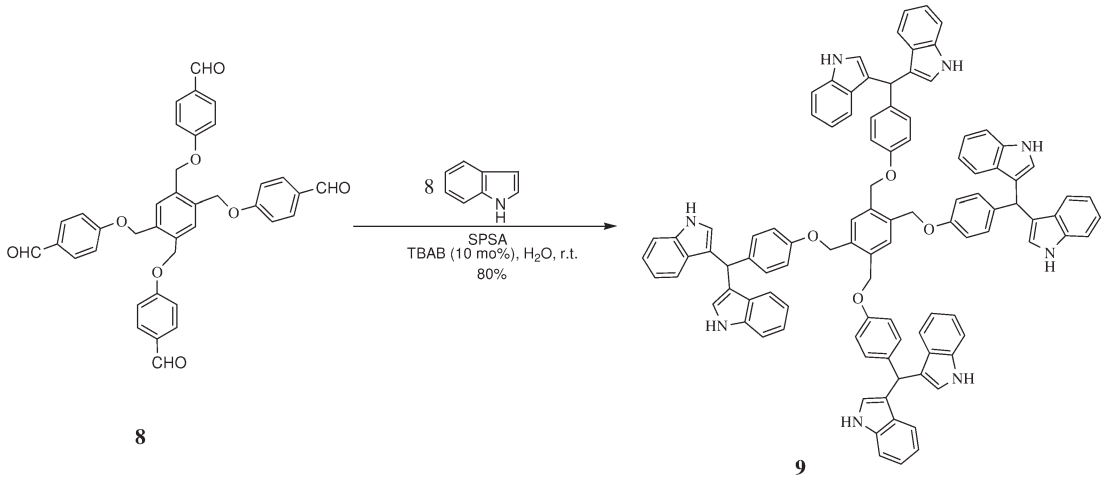
[a] Products were characterized from their physical properties, comparison with authentic samples and by spectroscopic methods.

**Scheme 4**




**6** **7**

**Scheme 5**




**8** **9**

These results promoted us to investigate the scope, and the generality of this new protocol for various aldehydes and ketones under optimized conditions. As shown in Table 2, a series of aromatic, aliphatic, and heterocyclic aldehydes underwent electrophilic substitution reaction with indole smoothly to afford a wide range of substituted bis(indolyl)methanes in good to excellent yields (Table 2, entries 1–22). Ketones required longer reaction times, which is most probably due to the electron-donating and steric effects of the methyl group.

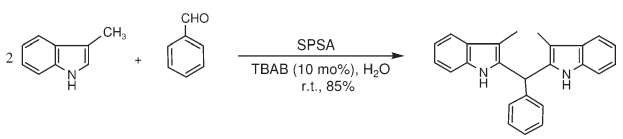
This reaction was further explored for the synthesis of tri(bisindolyl)methane (**7**) and tetra(bisindolyl)methanes (**9**) as new triarylmethanes and tetraarylmethanes, by the condensation of aldehyde (**6**) with six equivalents indole and aldehydes (**8**) with eight equivalents indole under similar condition in high yields (Schemes 4 and 5).

3-Substituted indole was examined for this reaction under the above reaction conditions with aldehydes (Scheme 6). Because the more active site (C-3) in indole was blocked in this case, electrophilic substitution took place at C-2 in indole giving the corresponding bis(indolyl)methane in high yield under same conditions.

## CONCLUSION

In summary, a practical and convenient synthetic method in aqueous media using SPSA as a solid acid heterogeneous catalyst, and TBAB as a surfactant has been developed for the facile synthesis of 1,2-disubstituted benzimidazoles and bis(indolyl)methanes. In addition, efficiency, mild reaction conditions, easy work up, simplicity, and chemoselectivity of this protocol provide a fast, green, and low-cost procedure for the synthesis of these compounds.

**Scheme 6**




## EXPERIMENTAL

**Preparation of modified silica sulfuric acid.** Fifty grams of silica gel **1** ($SiO_2$, mesh 35–70, 675 $m^2$/gr, Merk) was added to 200 mL HCl (0.1*M*) in a suitable vessel and stirred for 60 min at room temperature. After 60 min, the solid was filtrated and washed with deionized water for several times to get the activated silica gel (**2**). The activated $SiO_2$ (**2**) was dried under vacuum (60 mm/Hg) in 70°C for 3 h.

Activated $SiO_2$ (50 g) was dispersed in dry toluene (70 mL) under nitrogen condition and then DPCS (25 mL) was added to the dispersion for 30 min at room temperature and stirred for 15 h in reflux conditions. After that, filterated and washed with dry toluene (100 mL) and dry $CHCl_3$ (200 mL) and dried under vacuum (60 mm/Hg) in 70°C to get the chlorodiphenylsilylated silica (**3**). In the next step, 25 g dry phenyl silica (**3**) was suspended in 50 mL of dry chloroform in a three-neck flask fitted with a motor-driven glass stirrer, gas inlet tube, and dropping funnel. A solution of 30 g of chlorosulfonic acid in 50 mL of dry chloroform was added dropwise in 10 min. The sulfonating mixture was stirred 20 h at room temperature. After filtering off the sulfonating mixture, the product was washed with small portions of chloroform totaling 250 mL. The washing was continued using a total of 200 mL of acetone. Residual acid, color, and chloride ion were removed by suspending the product in five successive 100-mL portions of distilled water and allowing water to filter through by gravity percolation.

The product was washed with acetone and chloroform and dried under vacuum (60 mm/Hg) in 70°C. Final weight recovered was 26.3 g (**5**).

**General procedure for the synthesis of 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles.** The aryl aldehyde (2 mmol) and 1,2-phenylenediamine (1 mmol) were added to a solution of TBAB (10 mol %, 0.032 g) and SPSA (50 mg) in $H_2O$

(5 mL), and the mixture stirred at 40°C for the time given (Table 1). The progress of the reaction was monitored by TLC (eluent: 4:1 *n*-hexane-acetone). After completion of the reaction, the resulting precipitate of product filtered off. Then ethanol (10 mL) was added to the solid, and the catalyst was removed by filtration. Evaporation of the solvent under reduced pressure gave the crude products. Finally, the crude product was recrystallized in ethanol (85–98%).

**Synthesis of bis(indolyl)methanes.** The aldehyde or ketone (1 mmol) and indole (2 mmol) were added to a solution of TBAB (10 mol %, 0.032 g) and SPSA (200 mg) in $H_2O$ (5 mL), and the mixture stirred at room temperature for the time given (Table 1). The progress of the reaction was monitored by TLC (eluent: 4:1 *n*-hexane-acetone). After completion of the reaction, the resulting precipitate of product filtered off. Then ethanol (10 mL) was added to the solid, and the catalyst was removed by filtration. Evaporation of the solvent under reduced pressure gave the crude products. Finally, the crude product was recrystallized in ethanol–water (70–98%).

**Acknowledgments.** The authors are thankful to Bu-Ali Sina University, Center of Excellence and Development of Chemical Methods (CEDCM) for financial support and Payame Noor University (PNU).

## REFERENCES AND NOTES

[1] For recent reviews, see: (a) Bhattacharya, S.; Chaudhuri, P. Curr Med Chem 2008, 15, 1762; (b) Horton, D. A.; Bourne, G. T.; Smythe, M. L. Chem Rev 2003, 103, 893; (c) Boiani, M.; Gonz'alez, M. Mini-Rev Med Chem 2005, 5, 409.

[2] (a) Preston, P. N. Chem Rev 1974, 74, 279; (b) Muhaimeed, H. A. J Int Med Res 1997, 25, 175; (c) Scott, L. J.; Dunn, C. J.; Mallarkey, G.; Sharp, M. Drugs 2002, 62, 1503; (d) Venkatesan, P. J Antimicrob Chemother 1998, 41, 145; (e) Shah, D. I.; Sharma, M.; Bansal, Y.; Bansal, G.; Singh, M. Eur J Med Chem 2008, 43, 1808.

[3] (a) Denny, W. A.; Rewcastle, G. W.; Baguley, B. C. J Med Chem 1990, 33, 814; (b) Labanauskas, L. K.; Brukstus, A. B.; Gaidelis, P. G.; Buchinskaite, V. A.; Udrenaite, E. B.; Dauksas, V. K. Pharm Chem J 2000, 34, 353; (c) Sevak, R.; Paul, A.; Goswami, S.; Santini, D. Pharmacol Res 2002, 46, 351.

[4] Barker, H. A.; Smyth, R. D.; Weissbach, H.; Toohey, J. I.; Ladd, J. N.; Volcani, B. E. J Biolog Chem 1960, 235, 480.

[5] (a) Porcari, A. R.; Devivar, R. V.; Kucera, L. S.; Drach, J. C.; Townsend, L. B. J. J Med Chem 1998, 41, 1252; (b) Ries, U. J.; Mihm, G.; Narr, B.; Hasselbach, K. M.; Wittneben, H.; Entzeroth, M.; Van Meel, J. C. A.; Wienen, W.; Hauel, N. H. J Med Chem 1993, 36, 4040.

[6] (a) Roth, T.; Morningstar, M. L.; Boyer, P. L.; Hughes, S. H.; Buckheit, R. W., Jr.; Michejda, C. J. J Med Chem 1997, 40, 4199; (b) Morningstar, M. L.; Roth, T.; Farnsworth, D. W.; Smith, M. K.; Watson, K.; Buckheit, R. W., Jr.; Das, K.; Zhang, W.; Arnold, E.; Julias, J. G.; Hughes, S. H.; Michejda, C. J. J Med Chem 2007, 50, 4003.

[7] Takeuchi, K.; Bastian, J. A.; Gifford-Moore, D. S.; Harper, R. W.; Miller, S. C.; Mullaney, J. T.; Sall, D. J.; Smith, G. F.; Zhang, M.; Fisher, M. Bioorg Med Chem Lett 2000, 10, 2347.

[8] Göker, H.; Özden, S.; Yildiz, S.; Boykin, D. W. Eur J. Med Chem 2005, 40, 1062.

[9] (a) Smith, J. G.; Ho, I. Tetrahedron Lett 1971, 12, 3541; (b) Nagata, K.; Itoh, T.; Ishikawa, H.; Ohsawa, A. Heterocycles 2003, 61, 93; (c) Itoh, T.; Nagata, K.; Ishikawa, H.; Ohsawa, A. Heterocycles 2004, 63, 2769; (d) Perumal, S.; Mariappan, S.; Selvaraj, S. Arkivoc 2004, 8, 46; (e) Chakrabarty, M.; Karmakar, S.; Mukherji, A.; Arima, S.; Harigaya, Y. Heterocycles 2006, 68, 967; (f) Sun, P.; Hu, Z. J Heterocycl Chem 2006, 43, 773; (g) Salehi, P.; Dabiri, M.; Zolfigol, M. A.; Otokesh, S.; Baghbanzadeh, M. Tetrahedron Lett 2006, 47, 2557; (h) Varala, R.; Nasreen, A.; Enugala, R.; Adapa, S. R. Tetrahedron Lett 2007, 48, 69; (i) Kim, B. H.; Han, R.; Kim, J. S.; Jun, Y. M.; Baik, W.; Lee, B. M. Heterocycles 2004, 63, 41; (j) Ghorbani-Vaghei, R.; Veisi, H. Mol Divers 2010, 14, 249; (k) Bahrami, K.; Khodaei, M. M.; Nejati, A. Green Chem, to appear.

[10] Sundberg, R. J. The Chemistry of Indoles; Academic Press: New York, 1996.

[11] Zeligs, M. A. J Med Food 1998, 1, 67.

[12] Chakrabarty, M.; Ghosh, N.; Basak, R.; Harigaya, Y. Tetrahedron Lett 2002, 43, 4075.

[13] (a) Bandgar, B. P.; Shaikh, K. A. Tetrahedron Lett 2003, 44, 1959; (b) Ramanatham, V. K.; Kotha, V. S. R. S. K.; Kotarkonda, R. G. J Heterocycl Chem 2005, 42, 153.

[14] Reddy, A. V.; Ravinder, K.; Reddy, V. L. N.; Venkateshwer Goud, T.; Ravikanth, V.; Venkateswarlu, Y. Synth Commun 2003, 33, 3687.

[15] (a) Shiri, M.; Zolfigol, M. A.; Kruger, H. G.; Tanbakouchian, Z. Chem Rev 2010, 110, 2250; (b) Remers, W. A. In Heterocyclic Compounds; Houlihan, W. J., Ed.; Interscience Publishers: New York, 1972, p 1.

[16] Maiti, A. K.; Bhattacharyya, P. J Chem Res 1997, 424.

[17] Sharma, G. V. M.; Reddy, J. J.; Lakshmi, P. S.; Krishna, P. R. Tetrahedron Lett 2004, 45, 7729.

[18] Firouzabadi, H.; Iranpoor, N.; Jafari, A. A. J Mol Catal A Chem 2005, 244, 168.

[19] Deb, M. L.; Bhuyan, P. J. Tetrahedron Lett 2006, 47, 1441.

[20] Zhang, Z.-H.; Yin, L.; Wang, Y.-M. Synthesis 2005, 1949.

[21] Li, J.-T.; Dai, H.-G.; Xu, W.-Z.; Li, T.-S. Ultrason Sonochem 2006, 13, 24.

[22] Bandgar, B. P.; Shaikh, K. A. Tetrahedron Lett 2003, 44, 1959.

[23] Karthik, M.; Tripathi, A. K.; Gupta, N. M.; Palanichamy, M.; Murugesan, V. Catal Commun 2004, 5, 371.

[24] Penieres-Carrillo, G.; García-Estrada, J. G.; Gutiérrez-Ramírez, J. L.; Alvarez-Toledano, C. Green Chem 2003, 5, 337.

[25] Ji, S.-J.; Zhou, M.-F.; Gu, D.-G.; Wang, S.-Y.; Loh, T.-P. Synlett 2003, 2077.

[26] Mo, L.-P.; Ma, Z.-C.; Zhang, Z.-H. Synth Commun 2005, 35, 1997.

[27] Mi, X.; Luo, S.; He, J.; Cheng, J.-P. Tetrahedron Lett 2004, 45, 4567.

[28] Kamble, V. T.; Kadam, K. R.; Joshi, N. S.; Muley, D. B. Catal Commun 2007, 8, 498.

[29] Pradhan, P. K.; Dey, S.; Giri, V. S.; Jaisankar, P. Synthesis 2005, 1779.

[30] Xia, M.; Wang, S. H.; Yuan, W. B. Synth Commun 2004, 34, 3175.

[31] Ramesh, C.; Banerjee, J.; Pal, R.; Das, B. Adv Synth Catal 2003, 345, 557.

[32] Reddy, B. M.; Sreekanth, P. M.; Lakshmanan, P. J Mol Catal A Chem 2005, 237, 93.

[33] Firouzabadi, H.; Iranpoor, N.; Jafarpour, M.; Ghaderi, A. J Mol Catal A Chem 2006, 253, 249.

[34] (a) Pore, D. M.; Desai, U. V.; Thopate, T. S.; Wadgaonkar, P. P. Arkivoc 2006, 12, 75; (b) Zolfigol, M. A.; Salehi, P.; Shiri, M.; Sayadi, A.; Abdoli, A.; Keypour, H.; Rezaeivala, M.; Niknam, K.; Kolvari, E. Mol Divers 2008, 12, 203.

[35] Hosseini-Sarvari, M. Acta Chim Slovenica 2007, 54, 354.

[36] Dabiri, M.; Salehi, P.; Baghbanzadeh, M.; Vakilzadeh, Y.; Kiani, S. Monatshefte for Chemie 2007, 138, 595.

[37] Hagiwara, H.; Sekifuji, M.; Hoshi, T.; Qiao, K.; Yokoyama, C. Synlett 2007, 1320.

[38] Kamble, V. T.; Bandgar, B. P.; Bavikar, S. N. Chin J Chem 2007, 25, 13.

[39] Niknam, K.; Zolfigol, M. A.; Sadabadi, T.; Nejati, A. J Iran Chem Soc 2006, 3, 318.

[40] Lin, X. F.; Cui, S. L.; Wang, Y. G. Synth Commun 2006, 36, 3153.

[41] Zeng, X. F.; Ji, S. J. Lett Org Chem 2006, 3, 374.

[42] Zhang, L. P.; Li, Y. Q.; Zhou, M. Y. Chin Chem Lett 2006, 17, 723.

[43] Koshima, H.; Matsuaka, W. J Heterocycl Chem 2002, 1089.

[44] Khalafi-Nezhad, A.; Parhami, A.; Zare, A.; Moosavi Zare, A. R.; Hasaninejad, A.; Panahi, F. Synthesis 2008, 617.

[45] Azizi, N.; Torkian, L.; Saidi, M. R. J Mol Catal A Chem 2007, 275, 109.

[46] Mehrazma, S.; Azizi, N.; Saidi, M. R. Lett Org Chem 2006, 3, 161.

[47] Zolfigol, M. A.; Salehi, P.; Shiri, M.; Tanbakouchian, Z. Catal Commun 2007, 8, 173.

[48] Khodaei, M. M.; Mohammadpoor-Baltork, I.; Memarian, H. R.; Khosropour, A. R.; Nikofar, K.; Ghanbary, P. J Heterocyclic Chem 2008, 45, 1.

[49] Ghorbani-Vaghei, R.; Veisi, H.; Keypour, H.; Dehghani-Firouzabadi, A. A. Mol Divers 2010, 14, 87.

[50] Ghorbani-Vaghei, R.; Veisi, H. J Braz Chem Soc 2010, 21, 193.

[51] (a) Kobayashi, S.; Mori, Y.; Nogayama, S.; Manabe, K. Green Chem 1999, 1, 175; (b) Cornils, B. Angew Chem Int Ed Engl 1995, 34, 1575.

[52] (a) Zolfigol, M. A. Tetrahedron 2001, 57, 9509; (b) Shirini, F.; Zolfigol, M. A.; Salehi, P. Curr Org Chem 2006, 10, 2171; (c) Zolfigol, M. A.; Salehi, P.; Shiri, M.; Faal Rastegar, T.; Ghaderi, A. J Iran Chem Soc 2008, 5, 490; (d) Zolfigol, M. A.; Hojati, S. F. J Iran Chem Soc 2008, 5, 65; (e) Veisi, H. Tetrahedron Lett 2010, 51, 2109.

[53] (a) Saunders, D. H.; Barford, R. A.; Magidman, P.; Olszewski, L. T.; Rothbart, H. L. Anal Chem 1974, 46, 834; (b) Sharma, S. D.; Konwar, D. Synth Commun 2009, 39, 980; (c) Wan, J. -P.; Gan, S. -F.; Wu, J. -M.; Pan, Y. Green Chem 2009, 11, 1633.

[54] Bellina, F.; Calanderi, C.; Cauteruccio, S.; Rossi, R. Tetrahedron 2007, 63, 1970.

[55] Srinivasa, A. B.; Nandeshwarappa, P.; Kiran, B. M.; Mahadevan, K. M. Phosphorus Sulfur Silicon 2007, 182, 2243.

[56] Sadaphal, S. A.; Shelke, K. F.; Sonar, S. S.; Shingare, M. S. Cent Eur J Chem 2008, 6, 622.

[57] Waterng, S. -R.; Wang, Q. -Y.; Ding, Y.; Liu, X. -L.; Cai, M. -Z. Catal Lett 2009, 128, 418.

[58] (a) Sekiya, M.; Yanaihara, C.; Suzuki, J. Chem Pharm Bull 1969, 17, 752; (b) Wang, S. -Y.; Ji, S. -J. Tetrahedron 2006, 62, 1527.