# A Facile Solvent-Free Synthesis of 1-Alkyl/Aralkyl-2-(1-arylsulfonyl alkyl) Benzimidazoles Using ''TBAB'' as Surface Catalyst



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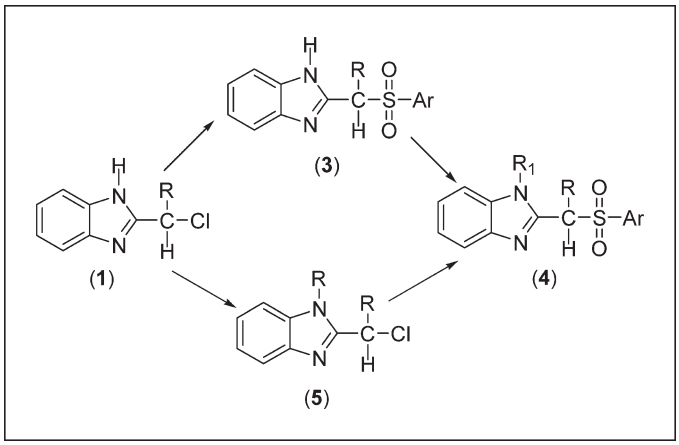


Reaction 2-(α-chloroalkyl)benzimidazoles **1** with aryl sulphinate sodium salt **2** under solvent-free conditions in the presence of tetrabutylammonium bromide as surface catalyst, by simple physical grinding using mortar and pestle, gives 1*H*-2-(α-arylsulfonylalkyl)benzimidazoles **3**. The latter on treatment with alkylating agents under solvent-free conditions results in 1-alkyl/aralkyl-2-(α-arylsulfonylalkyl)benzimidazoles **4**. Alternatively, **4** can also be prepared directly from 1-alkyl/aralkyl-2-(α-chloroalkyl)benzimidazoles **5** by reaction with **2**, which in turn could be prepared by reaction of **1** with alkylating agents under solvent-free conditions and all these reactions are free from organic solvents including experimental procedures.

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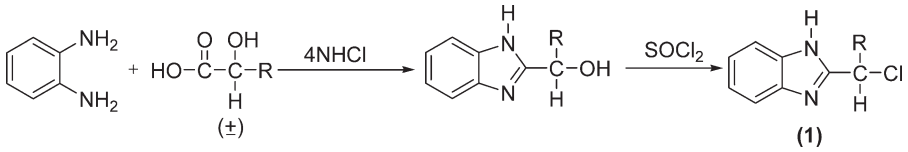
## BACKGROUND

Benzimidazoles are an important class of heterocyclic compounds, several derivatives of which have been found to be useful as intermediates/subunits for the development of molecules of pharmaceutical or biological interest. Substituted benzimidazole derivatives have applications in diverse therapeutic areas including antiulcers, antihypertensive, antiviral, antifungal, anticancer, and antihistaminics to name just a few [1–3]. Sulphones exhibit noteworthy antibacterial, antimalarial, antifungal, and antitubercular properties [4–10]. In recent years, considerable attention has been paid to the reactions done under solvent-free conditions [11,12]. One of the areas of central attention in this field includes reaction between solids [13,14]. These reactions are not only of interest from an economical point of view, in many cases, but also they offer considerable synthetic advantages in terms of yield, selectivity, and simplicity of the reaction procedure. Another important goal in green chemistry is represented by the elimination of volatile organic solvents, in fact, solvent-free conditions that makes synthesis simpler, saves energy, and prevents solvent waste, hazards, and toxicity [15]. Tetrabutylammonium bromide (TBAB) is widely used as phase transfer catalyst (PTC) in many organic reactions [16–22], such as coupling reactions, Heck reaction, Suzuki-coupling of O, O-acetals to S, S-acetals and so forth. Quite a few organic reactions proceed well in solid state [23–27]. All these merits are in accord with the ''green'' requirements of energy saving and high efficiency.

## RESULTS

In continuation of our earlier work [28–31] on synthesis of new benzimidazole derivatives with potential biological activity, we now wish to report the preparation of the title compounds under solvent-free conditions, that is, without using any organic solvent, in the presence of TBAB as surface catalyst (SC) at room temperature, followed by alkylations on various types of these

**Scheme 1**




derivatives and the work up was carried out with water, without using of any organic solvent, such as ethyl acetate, $CHCl_3$, DCM, and so forth. This is totally free from organic solvent. Among alternatives, water is very benign. The use of water for organic reactions offers ''green'' chemistry benefits [32]. The results of these studies are presented in this communication.

## RESULTS AND DISCUSSION

2-(α-Chloromethyl)benzimidazole **1a** (*i.e.*, **1**, R = H) [33] (Scheme 1) on reaction with *p*-tolylsulphinate sodium salt **2a** [*i.e.*, **2**, Ar = $C_6H_4$—$CH_3$(*p*)] in solid phase by simple physical mixing/grinding in a mortar and pestle in the presence of TBAB as SC yielded a neat product on simple aqueous work up. The product has been characterized as 1*H*-2-(*p*-tolylsulfonylmethyl)benzimidazole **3a** [*i.e.*, **3**, R = H, Ar = $C_6H_4$—$CH_3$(*p*)], based on spectral and analytical data and also it was found to be identical with product reported in solution phase [34].

Previously [34], alkylations were carried out under solution phase, that is, using acetonitrile/acetone as solvent, $K_2CO_3$ as base, and TEBAC as PTC. In this work, reaction of **3a** [R = H, Ar = $C_6H_4$—$CH_3$(*p*)] with dimethylsulphate (DMS) as alkylating agent, $K_2CO_3$ as base in the presence of TBAB as SC in solid phase, that is, by simple grinding of reaction mixture in a mortar and pestle, gave the corresponding N-methylated product **4a** (Scheme 2, Table 1).

The above reaction has been found to be a general one and has been extended to other **1a** and **2a** and followed by reaction of **3a** with DMS was extended to DES and benzyl chloride to obtain N-alkyl/aralkyl-substituted derivatives of **4**, the products thus obtained were assigned structure **3**/**4** based on spectral data and analytical data (Scheme 2, Table 1), and also that were found to be identical with those reported earlier in literature [34] from solution-phase reactions. Similarly, reaction of **1a** (*i.e.*, **1**, R = H) with DMS as alkylating agent using $K_2CO_3$ as base in the presence of TBAB as catalyst in solid-phase resulted in the formation of **5a** (*i.e.*, **5**, R = H, $R^1 = CH_3$).

This reaction of **1a** with DMS was extended to DES and benzyl chloride to obtain N-alkyl/aralkyl-substituted derivatives of **5**. Alternatively, **4a** could also be obtained directly from reaction of **5a** with **2a** [*i.e.*, **2**, Ar = $C_6H_4$—$CH_3$(*p*)], under solvent-free conditions in the presence of TBAB, as a catalyst in solid phase by simple physical mixing/grinding in a mortar and pestle, yielded a neat product on simple aqueous work up. The product has been characterized as 1*H*-2-(*p*-tolylsulfonylmethyl)benzimidazole **3a**, which is identical with the product obtained from **3a** with DMS under solvent-free conditions (Scheme 3) with all respects (*i.e.*, TLC, M.P., mmp). Further, it has been extended to its other derivatives in the similar manner; the structure of the compound structure was assigned based on spectral and analytical data. (Scheme 3, Table 2).

It was found that above reactions between **1** and sodium benzenesulphinate did not occur in the absence of TBAB even after grinding the mixture of solids for 2–3 h (Scheme 4). Thus, it appears that TBAB acts like SC and that is why the addition of sodium benzenesulphinate makes the reaction much faster, because TBAB enhances the neucleophilicity of the sulphinate ion and facilitating reaction between **1** and sodium benzenesulphinate (Scheme 5). Similarly in the alkylation reactions, reaction between **1** and alkylating agent did not occur in the absence of TBAB even after grinding the mixture of solids for 2 h. But in the presence of TBAB reaction completes smoothly in short times.

As per literature search, there are number of reports for various organic transformations/methodologies under solvent-free conditions, but they were using organic solvents, such as ethyl acetate, dichloromethane, chloroform, ether, and so forth, in the work up procedure. But, in our present method, we have not used any organic solvents in the work up procedure; we have isolated the

**Scheme 2**

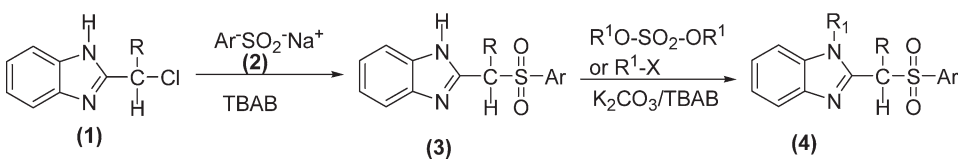


**Table 1**

Physical characterization data for **3** and **4**[a] compounds.

| SM | R | $R^1$ | Reagent (Ar)/ Alkylating agent | Product | Solution phase | | Solvent-free | | M.P. (°C) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Time (h) | Yield (%) | Time (min) | Yield (%) | |
| **1a** | H | – | —$C_6H_4$—$CH_3$—*p* | **3a** | 3.5 | 79 | 4 | 90 | 202 (202) [34] |
| **1b** | H | – | —$C_6H_5$ | **3b** | 3.5 | 78 | 5 | 88 | 198–200 (198–200) [34] |
| **1c** | Me | – | —$C_6H_4$—$CH_3$—*p* | **3c** | 4 | 85 | 5 | 94 | 154–56 (154–56) [34] |
| **1d** | Me | – | —$C_6H_5$ | **3d** | 4 | 82 | 5 | 93 | 180–82 (180) [34] |
| **3a** | H | Me | DMS | **4a** | 3 | 74 | 4 | 90 | 206 (206) [34] |
| **3a** | H | Et | DES | **4b** | 3.5 | 69 | 5 | 89 | 168–70 (168) [34] |
| **3a** | H | Bn | Bn—Cl | **4c** | 3.5 | 70 | 4 | 90 | 182–84 (182) [34] |
| **3c** | Me | Me | DMS | **4d** | 3 | 73 | 5 | 89 | 172 |
| **3c** | Me | Et | DES | **4e** | 3 | 69 | 5 | 90 | 160–62 |
| **3c** | Me | Bn | Bn—Cl | **4f** | 3.5 | 71 | 5 | 92 | 170 |
| **3d** | Me | Me | DMS | **4g** | 3 | 72 | 5 | 88 | 182–84 |
| **3d** | Me | Bn | Bn—Cl | **4h** | 4 | 69 | 5 | 90 | 130–32 |

[a] Yields refers to products isolated from water without any purification.

**Scheme 3**

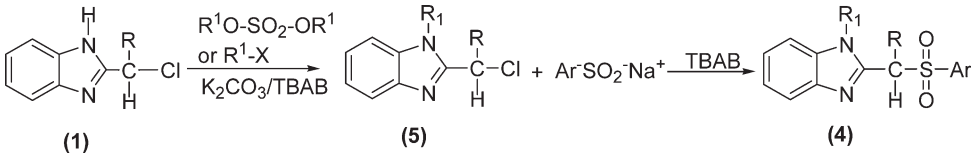


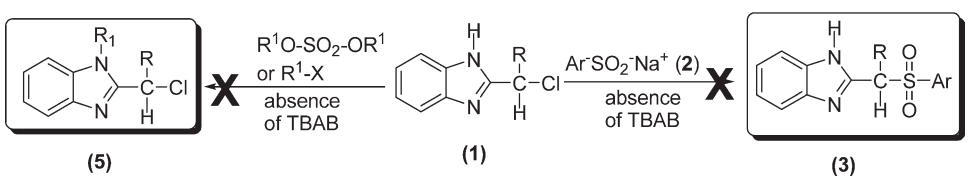

**Table 2**

Physical characterization data for **5** and **4**[a] compounds.

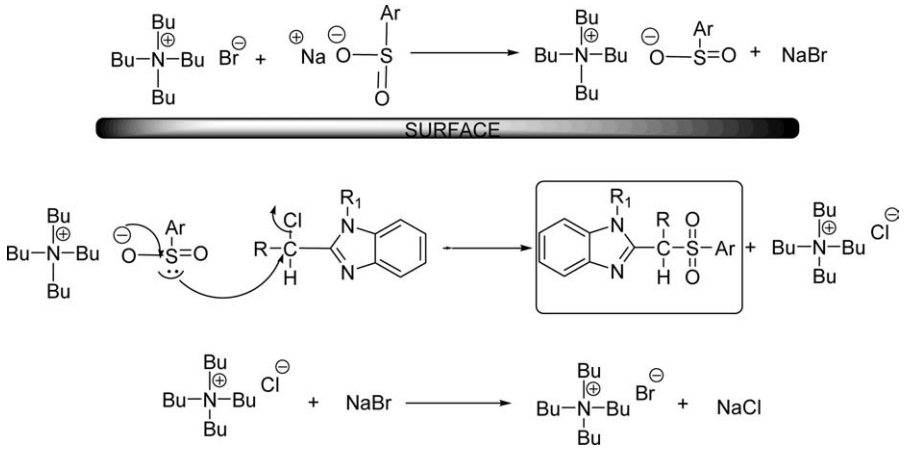
| SM | R | $R^1$ | Reagent (Ar)/Alkylating agent | Product | Solution phase | | Solvent-free | | M.P. (°C) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Time (h) | Yield (%) | Time (min) | Yield (%) | |
| **1a** | H | – | DMS | **5a** | 4.0 | 62 | 8 | 92 | 94–96 (94) [34] |
| **1a** | H | – | Bn—Cl | **5b** | 4.0 | 64 | 8 | 90 | 100–02 (100) [34] |
| **1c** | Me | – | DMS | **5c** | 3.5 | 68 | 7 | 94 | 60 (60) [34] |
| **1d** | Me | – | Bn—Cl | **5d** | 3.5 | 69 | 7 | 92 | 74–76 (72–76) [34] |
| **5a** | H | Me | —$C_6H_4$—$CH_3$—*p* | **4a** | 3 | 76 | 5 | 94 | 206 |
| **5b** | H | Bn | —$C_6H_4$—$CH_3$—*p* | **4c** | 3.5 | 74 | 4 | 93 | 182–84 |
| **5c** | Me | Me | —$C_6H_4$—$CH_3$—*p* | **4d** | 3 | 76 | 5 | 96 | 172 |
| **5d** | Me | Bn | —$C_6H_4$—$CH_3$—*p* | **4f** | 3.5 | 74 | 5 | 96 | 170 |
| **5c** | Me | Me | —$C_6H_5$ | **4g** | 3 | 75 | 5 | 94 | 182–84 |
| **5d** | Me | Bn | —$C_6H_5$ | **4h** | 4 | 72 | 5 | 94 | 130–32 |

[a] Yields refers to products isolated from water without any purification.

**Scheme 4**



**Scheme 5.** The plausible mechanism: (for formation of **3**).




solid products by simple aqueous procedure using only water, which is totally free from organic solvents.

## CONCLUSIONS

In summary, we have developed a simple and efficient method for the preparation of 1-alkyl/aralkyl-2-(α-chloroalkyl)benzimidazole and 1-alkyl/aralkyl-2-(1-arylsulfonylalkyl)benzimidazoles using TBAB as SC under solvent-free conditions by simple physical grinding in mortar and pestle at room temperature. The present protocol has several advantages, completely free from organic solvents, in work up procedure water was used, which is free from organic solvent usage, fast reaction times, high yields, eco-friendly operational and experimental simplicity, readily available catalyst, and with high generality.

## EXPERIMENTAL

Melting points were determined in open glass capillaries using Buchi melting point apparatus and are uncorrected. IR spectra were recorded using potassium bromide pellets with a Perkin IR spectrometer. All $^1$H NMR spectra were recorded on a VARIAN 200-MHz instrument with an internal standard of tetramethylsilane. Mass spectra were recorded on Agilent-LC-MS instrument giving only $M^+$ values using ($M^+ + 1$) mode. Analytical TLC was performed with Silica gel GF-254 from Merck (Germany) containing fluorescent indicator. Spots were detected with UV-light or iodine. The following experimental procedures are representative of the general procedures used to synthesize all compounds.

**Typical procedure for 3.** A mixture of **1** (10 mmol), **2** (10.1 mmol), and TBAB catalytic amount (10 mol %) were ground together in a mortar with pestle at RT till the reaction was complete, as shown by TLC. The solid mixture was then suspended in water to remove inorganic impurities and the insoluble product was filtered, washed with water, and dried, gave pure product **3** (Table 1).

***3a.*** IR (KBr) cm$^{-1}$: 3000, 1308; $^1$H NMR (DMSO-$d_6$): δ 2.40 (s, 3H, —$CH_3$), 4.95 (s, 2H, —$CH_2$), 7.20–7.70 (m, 8H, Ar-H), 12.60 (bs, 1H, —NH, $D_2O$ exchangeable); $M^+ + 1$: 287; Anal. Calcd. for ($C_{15}H_{14}N_2O_2S$) requires: C, 62.92; H, 4.93; N, 9.78%; Found: C, 62.86; H, 4.87; N, 9.74%.

***3b.*** IR (KBr) cm$^{-1}$: 3000, 1300; $^1$H NMR (DMSO-$d_6$): δ 4.85 (s, 2H, —$CH_2$), 7.15–7.80 (m, 9H, Ar-H), 12.65 (bs, 1H, —NH, $D_2O$ exchangeable); $M^+ + 1$: 273; Anal. Calcd. for ($C_{14}H_{12}N_2O_2S$) requires: C, 61.75; H, 4.44; N, 10.29%; Found: C, 61.70; H, 4.40; N, 10.26%.

***3c.*** IR (KBr) cm$^{-1}$: 3000, 1298; $^1$H NMR (DMSO-$d_6$): δ 1.84 (d, $J$ = 7.16 Hz, 3H, —CH—C**H**$_3$), 2.36 (s, 3H, —$C_6H_4$—C**H**$_3$—(*p*)), 4.68 (q, $J$ = 7.14 Hz, 1H, —C**H**—$CH_3$), 7.20–7.70 (m, 8H, Ar-H), 10.30 (bs, 1H, —N**H**—, $D_2O$ exchangeable); $M^+ + 1$: 301; Anal. Calcd. for ($C_{16}H_{16}N_2O_2S$) requires: C, 63.98; H, 5.37; N, 9.33%; Found: C, 63.94; H, 5.35; N, 9.30%.

***3d.*** IR (KBr) cm$^{-1}$: 3000, 1308; $^1$H NMR (DMSO-$d_6$): δ 1.90 (d, $J$ = 7.16 Hz, 3H, —CH—C**H**$_3$), 4.70 (q, $J$ = 7.12Hz, 1H, —C**H**—$CH_3$), 7.20–7.70 (m, 9H, Ar-H), 10.30 (bs, 1H, —NH, $D_2O$ exchangeable); $M^+$+1: 287; Anal. Calcd. for ($C_{15}H_{14}N_2O_2S$) requires: C, 62.92; H, 4.93; N, 9.78%; Found: C, 62.86; H, 4.91; N, 9.74%

**Typical procedure for 4 from 3.** A mixture of **3** (10 mmol), alkylating agent (10.1 mmol), $K_2CO_3$ (11 mmol), and TBAB catalytic amount (10 mol %) were ground together in a mortar and pestle at RT till the reaction was complete, as shown by TLC. The solid mixture was then suspended in water to remove inorganic materials and water solubles. The insoluble product was filtered, washed with water, and dried, to obtain **4** (Table 1).

***4a.*** IR (KBr) cm$^{-1}$: showed the absence of a strong broad band at ~3000 cm$^{-1}$ assigned to benzimidazole, 1300; $^1$H NMR ($CDCl_3$): δ 2.45 (s, 3H, —$CH_3$), 3.95 (s, 3H, —$NCH_3$), 4.75 (s, 2H, —$CH_2$), 7.20–7.70 (m, 8H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 301; Anal. Calcd. for ($C_{16}H_{16}N_2O_2S$) requires: C, 63.98; H, 5.37; N, 9.33%; Found: C, 63.94; H, 5.32; N, 9.28%.

***4b.*** IR (KBr): showed the absence of a strong broad band at ~3000 cm$^{-1}$ assigned to benzimidazole (—NH); $^1$H NMR ($CDCl_3$): δ 1.45 (t, $J$ = 18 Hz, 3H, —$CH_2$—C**H**$_3$), 2.45 (s, 3H,

—$CH_3$), 4.45 (q, $J$ = 16 Hz, 2H, —C**H**$_2$—$CH_3$), 4.85 (s, 2H,—$CH_2$), 7.15–7.70 (m, 8H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 315; Anal. Calcd. for ($C_{17}H_{18}N_2O_2S$) requires: C, 64.94; H, 5.77; N, 8.91%; Found: C, 64.90; H, 5.72; N, 8.86%.

***4c.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole (—NH); $^1$H NMR ($CDCl_3$): δ 2.45 (s, 3H, —$CH_3$), 4.72 (s, 2H, —$CH_2$), 5.65 (s, 2H, —N—C**H**$_2$—Ph), 7.10–7.80 (m, 13H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 377; Anal. Calcd. for ($C_{22}H_{20}N_2O_2S$) requires: C, 70.19; H, 5.35; N, 7.44%; Found: C, 70.15; H, 5.30; N, 7.42%.

***4d.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole (—NH); $^1$H NMR ($CDCl_3$): δ 1.85 (d, $J$ = 7.18 Hz, 3H, —$CH_2$—C**H**$_3$), 2.40 (s, 3H, —$C_6H_4$—C**H**$_3$—(*p*)), 3.95 (s, 3H, —$NCH_3$), 4.70 (q, $J$ = 7.0 Hz, 1H, —C**H**—$CH_3$), 7.20–7.70 (m, 8H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 315; Anal. Calcd. for ($C_{17}H_{18}N_2O_2S$) requires: C, 64.94; H, 5.77; N, 8.91%; Found: C, 64.90; H, 5.75; N, 8.86%.

***4e.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole (—NH); $^1$H NMR ($CDCl_3$): δ 1.50 (t, $J$ = 18.0 Hz, 3H, —$CH_2$—C**H**$_3$), 1.75 (d, $J$ = 12 Hz, 3H, —CH—C**H**$_3$), 2.45 (s, 3H, —$CH_3$) 4.35 (q, $J$ = 14.6 Hz, 1H, —C**H**—$CH_3$), 4.65 (q, $J$ = 16.0 Hz, 2H, —C**H**$_2$—$CH_3$), 7.15–7.65 (m, 8H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 329; Anal. Calcd. for ($C_{18}H_{20}N_2O_2S$) requires: C, 65.83; H, 6.14; N, 8.53%; Found: C, 65.78; H, 6.10; N,8.50%.

***4f.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole (—NH); $^1$H NMR ($CDCl_3$): δ 1.68 (d, $J$ = 14.2 Hz, 3H, —CH—C**H**$_3$), 2.45 (s, 3H, —$CH_3$), 4.45 (q, $J$ = 14.4 Hz, 1H, —C**H**—$CH_3$), 5.55–5.90 (dd, 2H, —N—C**H**$_2$—Ph), 7.0–7.65 (m, 13H, Ar-H); $M^+$ + 1: 391; Anal. Calcd. for ($C_{23}H_{22}N_2O_2S$) requires: C, 70.74; H, 5.68; N, 7.17%; Found: C, 70.72; H, 5.64; N, 7.13%.

***4g.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole (—NH); $^1$H NMR ($CDCl_3$): δ 1.70 (d, $J$ = 7.18 Hz, 3H, —CH—C**H**$_3$), 3.85 (s, 3H, —$NCH_3$), 5.10 (q, $J$ = 7.0 Hz, 1H, —C**H**—$CH_3$), 7.2–7.87 (m, 9H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 301; Anal. Calcd. for ($C_{16}H_{16}N_2O_2S$) requires: C, 63.98; H, 5.37; N, 9.33%; Found: C, 63.95; H, 5.33; N, 9.29%.

***4h.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole (—NH); $^1$H NMR ($CDCl_3$): δ 1.65 (d, $J$ = 7.12 Hz, 3H, —CH—C**H**$_3$), 4.60 (q, $J$ = 7.16 Hz, 1H, —C**H**—$CH_3$), 5.50–5.70 (dd, 2H, —C**H**$_2$—Ph), 6.95–7.65 (m, 14H, Ar-H); $M^+$ + 1: 377; Anal. Calcd. for ($C_{22}H_{20}N_2O_2S$) requires: C, 70.19; H, 5.35; N, 7.44%; Found: C, 70.15; H, 5.31; N, 7.42%.

**Typical procedure for 4 from 5.** A mixture of **5** (10 mmol), **2** (10.1 mmol), and TBAB catalytic amount 10 mol % were ground together in a mortar at RT till the reaction was complete, as shown by TLC. The solid mixture was then suspended in water to remove inorganic impurities and the insoluble product was filtered, washed with water, and dried. The crude product was recrystallized from hot benzene to get the pure product **4** (Table 2).

**Typical procedure for 5.** A mixture of **1** (10 mmol), alkylating agent (10.2 mmol), $K_2CO_3$ (11 mmol), and TBAB catalytic amount 10 mol % were ground together in a mortar and pestle at RT till the completion of reaction, as shown by TLC. The solid mixture was then suspended in water to remove inorganic impurities and the insoluble product was filtered, washed with water, and dried, gave a pure **5** (Table 2).

***5a.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole; $^1$H NMR ($CDCl_3$): δ 3.95 (s, 3H, —NC**H**$_3$), 4.95 (s, 2H, —C**H**$_2$), 7.15–7.80 (m, 4H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 181; Anal. Calcd. for ($C_9H_{9Cl}N_2$) requires: C, 59.84; H, 5.02; N, 15.51%; Found: C, 59.82; H, 5.0; N, 15.47%.

***5b.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole; $^1$H NMR ($CDCl_3$): δ 4.96 (s, 2H, —$CH_2$), 5.60 (s, 2H, —C**H**$_2$—ph), 7.15–7.80 (m, 9H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 257; Anal. Calcd. for ($C_{15}H_{13}ClN_2$) requires: C, 70.18; H, 5.10; N, 10.91%; Found: C, 70.15; H, 5.07; N, 10.89%.

***5c.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole; $^1$H NMR ($CDCl_3$): δ 2.15 (d, $J$ = 7.16Hz, 3H, —CH—C**H**$_3$), 3.90 (s, 3H, —$NCH_3$), 5.30 (q, $J$ = 7.12 Hz, 1H, —C**H**—$CH_3$), 7.10–7.80 (m, 4H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 195; Anal. Calcd. for ($C_{10}H_{11}ClN_2$) requires: C, 61.70; H, 5.70; N, 14.39%; Found: C, 61.68; H, 5.66; N, 14.36%.

***5d.*** IR (KBr): showed the absence of a strong broad band at ~3000 $cm^{-1}$ assigned to benzimidazole; $^1$H NMR ($CDCl_3$): δ 2.10 (d, $J$ = 7.12Hz, 3H, —CH—C**H**$_3$), 5.10 (q, $J$ = 7.0 Hz, 1H, —C**H**—$CH_3$), 5.55 (s, 2H, —C**H**$_2$—Ph), 7.05–7.80 (m, 9H, Ar-H); $\mathbf{M}^+ + \mathbf{1}$: 271; Anal. Calcd. for ($C_{16}H_{15}ClN_2$) requires: C, 70.98; H, 5.58; N, 10.35%; Found: C, 70.94; H, 5.56; N, 10.33%.

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