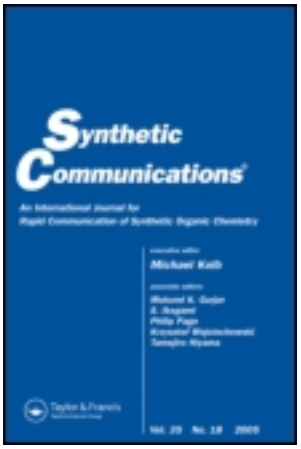

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Zinc-Mediated Tandem-One-Pot Facile Synthesis of 1-(Arylsulfonyl) Aryl/Heteryl Methanes: A Case of C—S Bond Formation

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ZINC-MEDIATED TANDEM-ONE-POT FACILE SYNTHESIS OF 1-(ARYLSULFONYL) ARYL/HETERYL METHANES: A CASE OF C–S BOND FORMATION

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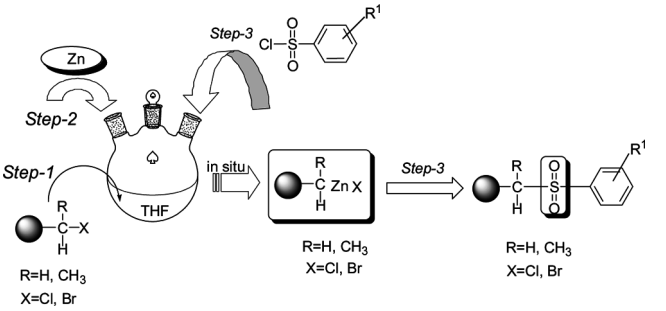
GRAPHICAL ABSTRACT



Abstract *Reaction of arylmethyl/heteryl methyl zinc chloride (generated in situ from aryl methyl and heteryl methyl chloride and zinc metal) with aryl sulfonyl chlorides in tetrahydrofuran (THF) under mild conditions (i.e., at room temperature) furnishes the corresponding 1-(aryl sulfonyl)aryl/heteryl methanes in good yields.*

Keywords Aryl sulfonyl chloride; 2-(α-chloroalkyl)benzimidazoles; KI; one pot; zinc

INTRODUCTION

The aryl sulfones are common structures in valuable molecules in fields such as pharmaceuticals, agrochemicals, and polymer sciences.[1] In particular, their immense utilities in medicinal chemistry and their unique bioactivities have attracted considerable attention. For example, diaryl sulfones have been reported to inhibit HIV-1[2] reverse transcriptase, and diphenyl sulfone[3] is used as an intermediate for the synthesis of 4,4′-diamino-diphenyl sulfone (DAPSONE), which is effective for leprosy treatment.[4] The aryl sulfones can be prepared from the transition metal–catalyzed reactions using sulfonic acids or sulfonyl chloride,[5] but the

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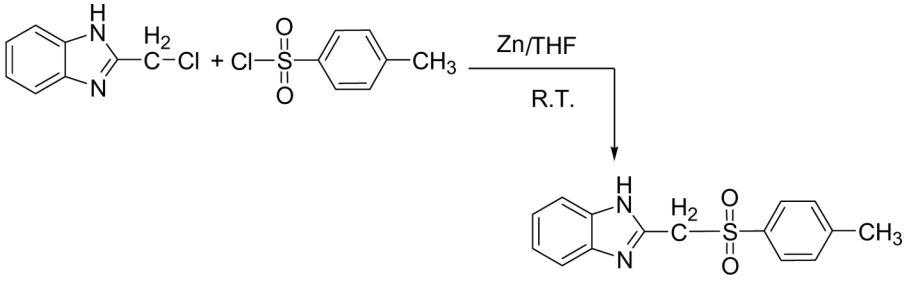
prefunctionalizing such as metallization or halogenations of arenas are required. A well-known process involving the formation of new C–S bonds from aromatic C–H bonds is the Friedel–Crafts (FC) sulfonylation of various arenes, especially electron-rich arenas.[6,7] Sulfonchlorides or sulfoanhydride are general substrates employed in the FC sulfonylation. Organozinc reagents are some of the most useful organometallic reagents for organic synthesis.[8] However, their applications in organic synthesis were limited to very specific reactions because of their moderate reactivity. These reagents were soon replaced by the more reactive organo magnesium and organo lithium reagents, which found broad applications in organic synthesis. However, it became clear that this high reactivity had some drawbacks, such as low chemoselectivity, and only allowed R groups bearing relatively little functionality. When one looks at the reductive potential of various metals, zinc stands out as a promising candidate. While zinc has a much more negative reductive potential ($E^\circ = -1.216$ ev), pure zinc is not sensitive to air and water. It was noticed that organozinc reagents could be easily prepared and have higher functional group compatibility in comparison with organo lithium and Grignard reagents. The easy of preparation and high functional group compatibility of organozincs allow numerous applications in synthetic chemistry. It is already used in the Reformatsky reaction,[9] Negishi coupling,[10] Barbier-type reactions,[11] transformation of acid chloride or chloroformates to a wide range of functional groups, such as amides,[12] FC acylation,[13] and recently in the synthesis of diarylmethanes.[14]

In continuation of our earlier work[15–17] on synthesis of new derivatives with potential biological activity, we now report a simple, one-pot preparation of the title compounds using zinc metal without isolating the sodium or potassium salts of substituted benzenesulphonyl chlorides.

At first, we prepared activated zinc by treating commercially available zinc with 2% hydrochloric acid and then with water, alcohol, acetone, and absolute ether. The zinc was then warmed in a hot air oven at 100 °C for a short time and used immediately.

2-Chloromethyl benzimidazole was reacted with activated zinc in tetrahydrofuran (THF) at room temperature (25–30 °C) (slowly the temperature of reaction mixture rose up to 40–45 °C) and kept for about 1.5–2.0 h (allowing in situ generation of the chloromethyl zinc benzimidazole), followed by the addition of *p*-methylbenzene sulfonyl chloride slowly under stirring conditions for about 0.5 h. The formation



Scheme 1. 2-Chloromethyl benzimidazole with activated zinc followed by addition of *p*-methylbenzene sulfonyl chloride.

Table 1. Comparison of yields at different temperatures

Temperature (°C)	Time (h)	Zn (eq.)[a]	Yield (%)
28–30	3.0	1.2	72
10	8.0–8.5	1.2	56
65	3.0	1.2	63

[a]All the reactions were performed in THF at the indicated temperature for the indicated time.

of the product was indicated by thin-layer chromatography (TLC), and later simple workup resulted in the formation of the compound. The structure of the compound was established by comparison of its spectral and analytical data with those of the authentic sample[18] (Scheme 1).

To ascertain the optimum temperature, several reactions were carried out on chloromethyl benzimidazole and *p*-methyl benzene sulfonyl chloride mediated by zinc, and finally the best result was obtained at 30 °C (room temperature only) (Table 1).

Having established the reaction temperature, various halo compounds and sulfonyl chlorides were subjected to reactions that resulted in the formation of a C−S bond in one pot.

In the presence of zinc powder, we observed a smooth insertion reaction in which complete consumption of the starting materials was observed in 1.5–2.0 h at ambient temperature (30 °C), followed by reaction with sulfonyl chlorides, which provided aryl/heteryl sulfone derivatives in average to good yields (Table 2).

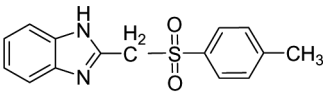
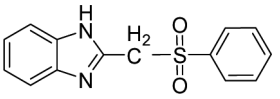
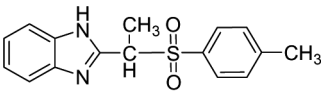
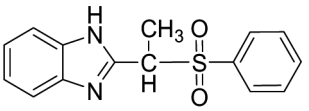
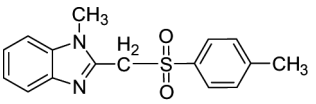
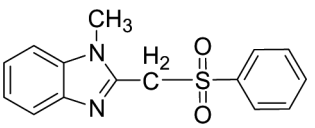
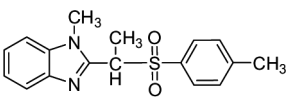
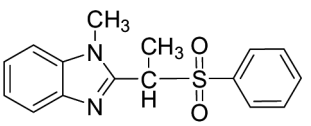
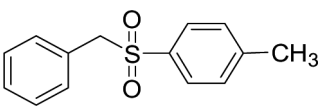
Similarly, for all the entries except for **1e** and **1f**, the procedure is the same as described. For reactions with **1e** and **1f**, halomethyl derivatives (10 mmol), zinc (12 mmol), and a catalytic amount of KI were stirred for about 1.5 h and followed by the addition of required sulfonyl chloride slowly under stirring. The formation of the product was indicated by TLC. Later the reaction mixture filtered, and the filtrate poured into ice cold water. A few drops of sulfuric acid were added and extracted with ethyl acetate, resulting in the formation of the compound (Schemes 3 and 4 respectively).

EXPERIMENTAL

General Procedure for Compounds 3a–3h

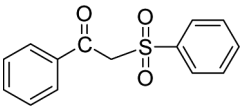
2-Chloromethyl benzimidazole (1.6 g, 10 mmol) was reacted with activated zinc (0.78 g, 12 mmol) in tetrahydrofuran (THF) at room temperature (25–30 °C) (slowly the temperature of reaction mixture rose up to 40–45 °C within 45–60 min) and kept for about 1.5–2.0 h (allowing for generation of the in situ chloromethyl zinc benzimidazole), followed by the addition of *p*-methylbenzene sulfonyl chloride (2.0 g, 10.5 mmol) slowly under stirring conditions for about 0.5 h. The formation of the product was indicated by TLC. Later the reaction mixture was filtered, and the filtrate was poured into ice cold water. A few drops of sulfuric acid were added and extracted with ethyl acetate, resulting in the formation of the compound. The structure of the compound was established as **3a** by comparison of its spectral and analytical data with those of the authentic sample.

Table 2. Synthesis of compound **3** from **1** and **2**

Entry	Reagent	Product **(3)**	Time (h)	Yield (%)
1a	**2a**	 **(3a)**	3.0	72
1a	**2b**	 **(3b)**	4.5	71
1b	**2a**	 **(3c)**	4.5	68
1b	**2b**	 **(3d)**	4.5	70
1c	**2a**	 **(3e)**	4.5	70
1c	**2b**	 **(3f)**	4.0	71
1d	**2a**	 **(3g)**	4.5	72
1d	**2b**	 **(3h)**	4.0	69
1e[#]	**2a**	 **(3i)**	5.0	68

(*Continued*)

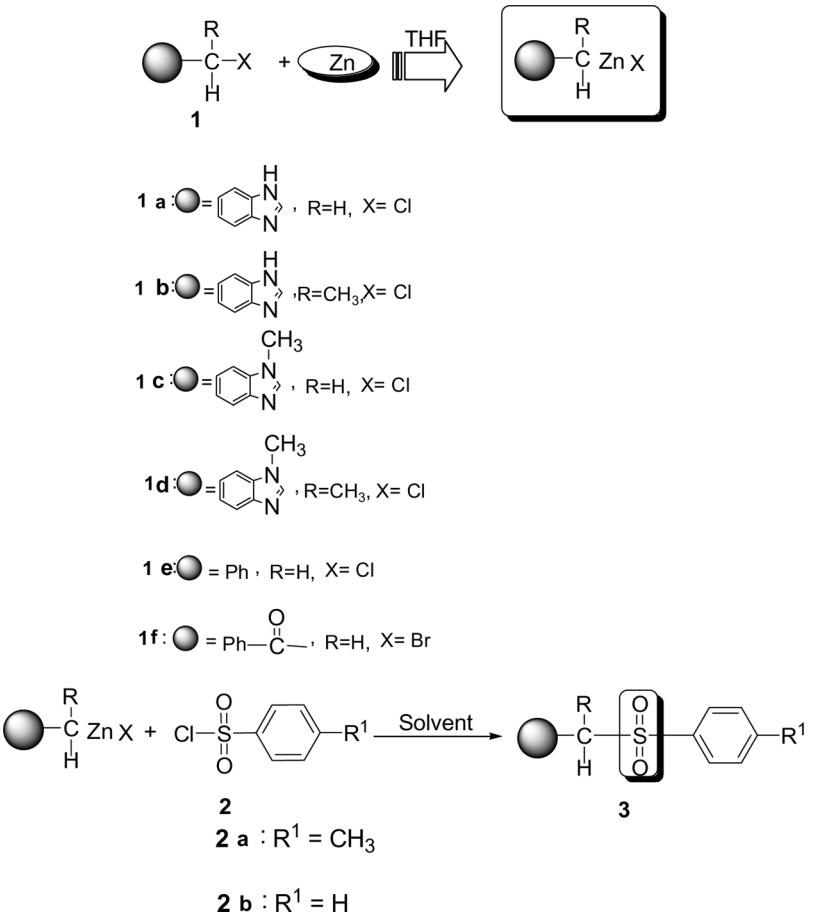
Table 2. Continued

Entry	Reagent	Product (3)	Time (h)	Yield (%)
1f[#]	**2b**	 **(3j)**	4.0	69

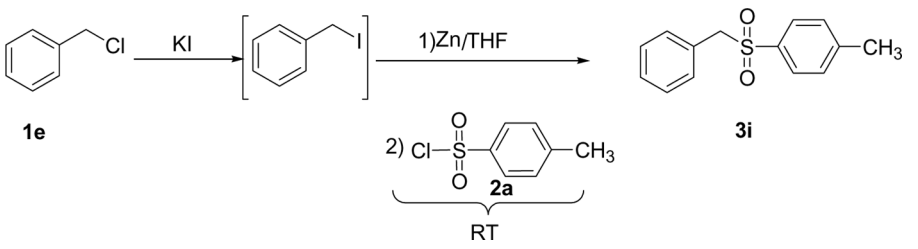
[#]We observed the formation of product in this case taking place in 3.0 h when KI is used during the formation of zinc complex.

Data for Compounds 3a–3h

2-(Toluene-4-sulfonylmethyl)-1H-benzimidazole **(3a):** IR (KBr) cm^{-1}: 3000 (NH), 1308 (SO_2); ^1H NMR (DMSO-d_6): δ 2.4 (s, 3H, $-CH_3$), 4.95 (s, 2H, $-CH_2$),



Scheme 2. Scope of the reaction conditions.



Scheme 3. Synthesis of **3i** using KI in catalytic amounts.

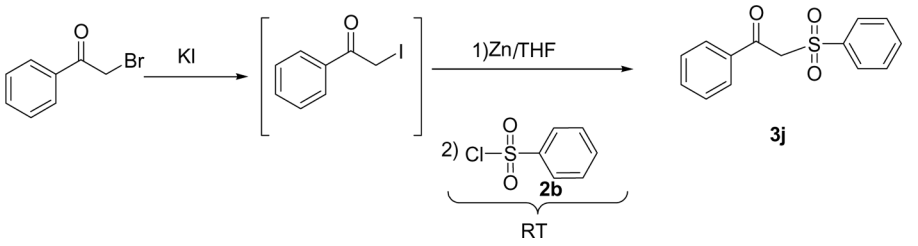
7.2–7.7 (m, 8H, Ar-H), 12.6 (bs, 1H, −NH, D_2O exchangeable); $M^{+\cdot}+1$: 287. Anal. calcd. for $C_{15}H_{14}N_2O_2S$ requires C, 62.92; H, 4.93; N, 9.78%. Found: C, 62.86; H, 4.87; N, 9.74%.

2-Benzenesulfonylmethyl-1H-benzimidazole (3b). IR (KBr) cm^{-1}: 3000 (NH), 1300 (SO_2); ^1H 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); $M^{+\cdot}+1$: 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%.

2-[1-(Toluene-4-sulfonyl)-ethyl]-1H-benzimidazole (3c). IR (KBr) cm^{-1}: 3000 (NH), 1298 (SO_2); ^1H NMR (DMSO-d_6): δ 1.84 (d, $J=7.16$ Hz, 3H, $-CH-CH_3$), 2.36 [s, 3H, $-C_6H_4-CH_3$-(*p*)], 4.68 (q, $J=7.14$ Hz, 1H, $-CH-CH_3$), 7.2–7.7 (m, 8H, Ar-H), 10.3 (bs, 1H, -N**H**-, D_2O exchangeable); $M^{+\cdot}+1$: 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%.

2-(1-Benzenesulfonyl-ethyl)-1H-benzimdazole (3d). IR (KBr) cm^{-1}: 3000, 1308 (SO_2); ^1H NMR (DMSO-d_6): δ 1.9 (d, $J=7.16$ Hz, 3H, $-CH-CH_3$), 4.7 (q, $J=7.12$ Hz, 1H, $-CH-CH_3$), 7.2–7.7 (m, 9H, Ar-H), 10.3 (bs, 1H, −NH, D_2O exchangeable); $M^{+\cdot}+1$: 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%.

1-Methyl-2-(toluene-4-sulfonylmethyl)-1H-benzimidazole (3e). IR (KBr) cm^{-1}: 1300 (SO_2); ^1H NMR ($CDCl_3$): δ 2.45 (s, 3H, $-CH_3$), 3.95 (s, 3H, $-NCH_3$), 4.75 (s, 2H, $-CH_2$), 7.2–7.7 (m, 8H, Ar-H); $M^{+\cdot}+1$: 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%.



Scheme 4. Synthesis of **3j** using KI in catalytic amounts.

2-Benzenesulfonylmethyl-1-methyl-1H-benzimidazole (3g). ^{1}H NMR ($CDCl_3$): δ 1.85 (d, $J = 7.18$ Hz, 3H, $-CH_2-CH_3$), 2.40 [s, 3H, $-C_6H_4-CH_3$-(*p*)], 3.95 (s, 3H, $-NCH_3$), 4.70 (q, $J = 7.0$ Hz, 1H, $-CH-CH_3$), 7.2–7.7 (m, 8H, Ar-H); $M^{+\cdot} + 1$: 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%.

1-Methyl-2-[1-toluene-4-sulfonyl)-ethyl]-1H-benzimidazole (3h). IR (KBr): ^{1}H NMR ($CDCl_3$): δ 1.70 (d, $J = 7.18$ Hz, 3H, $-CH-CH_3$), 3.85 (s, 3H, $-NCH_3$), 5.10 (q, $J = 7.0$ Hz, 1H, $-CH-CH_3$), 7.2–7.87 (m, 9H, Ar-H); $M^{+\cdot} + 1$: 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%.

General Procedure for Reactions with Entries 1e and 1f

Halo methyl derivatives **1e** and **1f** (10 mmol), zinc (12 mmol), and a catalytic amount of KI were stirring for about 1.5 h followed by the addition of required sulfonyl chloride slowly under stirring. The formation of the product was indicated by TLC. Later the reaction mixture was filtered, and the filtrate was poured into ice-cold water. A few drops of sulfuric acid were added and extracted with ethyl acetate, resulting in the formation of the compound.

1-Methyl-4-phenylmethanesulfonyl-benzene (3i). IR (KBr) cm^{-1}: 1312 (SO_2); ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 3H, $-CH_3$), 4.61 (s, 2H, $-CH_2$), 7.11–7.57 (m, 9H, aromatic protons); $M^{+\cdot} + 1$: 247.

CONCLUSION

These reactions are not only of interest from an economical point of view; in many cases, they also offer considerable synthetic advantages in terms of yield, selectivity, and simplicity of the reaction procedure. To our delight, a complete switchover of expedient outcome was realized in this reaction.

ACKNOWLEDGMENTS

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