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Tetrahedron 64 (2008) 2071–2079
Tetrahedron
www.elsevier.com/locate/tet

Unusual dimerization of *N*-protected bromomethylindoles/benzyl bromide with arylmetal halides: generation of indolylmethyl/benzyl radical

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Received 30 April 2007; received in revised form 4 December 2007; accepted 20 December 2007
Available online 24 December 2007

Abstract

A detailed study on the interaction of *N*-protected bromomethylindoles with various types of aryl/alkyl Grignard is reported. Full experimental details on the mechanism of the unusual dimerization reaction are presented.

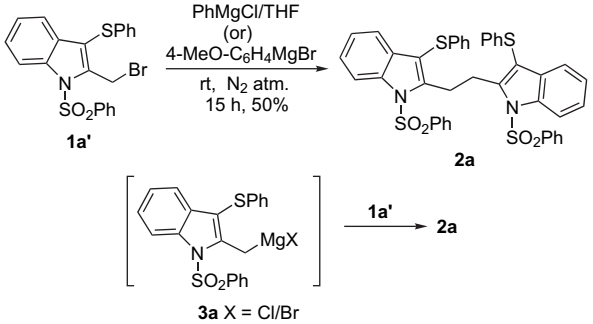
Keywords: Bromomethylindole; Benzylbromide; Alkyl/aryl Grignard; Indolylmethyl/benzyl radical

1. Introduction

Indole and its myriad of derivatives are important segments of a large number of natural products of both marine and terrestrial origin, and hence it continues to capture the attention of the synthetic organic chemist. Over the years, synthetic elaboration of *N*-protected bromomethylindoles has been thoroughly exploited to effect the syntheses of different types of indole based natural products.[1] In continuation of our interest in the synthesis of carbazole-based alkaloids,[2] we wanted to develop a viable procedure for the arylation of *N*-protected bromomethylindoles, as the existing procedure is applicable only to electron rich arenes.[3] In the course of this investigation, we discovered an unusual dimerization of *N*-protected bromomethylindoles with the interaction of arylmagnesium halides.

2. Results and discussion

In continuation of our synthetic studies on indole derivatives, recently, we have reported[4] an unusual dimerization of *N*-protected 2-bromomethylindoles **1a′** via interaction with phenylmagnesium chloride or 4-methoxyphenylmagnesium bromide at room temperature. In that report, we proposed the formation of dimer **2a** via the intermediacy of an indolylmethyl Grignard **3**, Scheme 1. In both the conditions, i.e., a slow addition of phenylmagnesium chloride to the solution of bromo compound **1a′** in THF or reverse addition of bromo compound to the Grignard, the dimer **2a** was obtained in almost comparable yield.



Scheme 1.

The unusual dimerization reaction was then tested with a variety of bromomethylindoles **1a′**–**j** and the results obtained are presented in Table 1. In general, the phenylmagnesium

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doi:10.1016/j.tet.2007.12.047

Table 1
Dimerization of *N*-protected bromomethyl indoles using PhMgCl

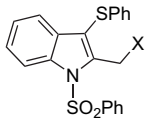
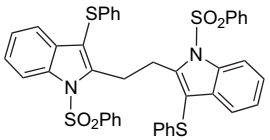
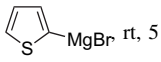
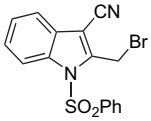
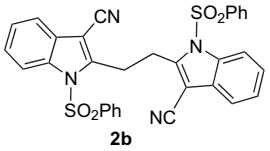
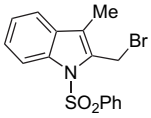
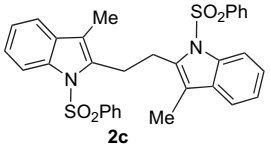
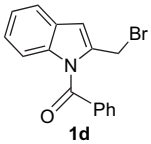
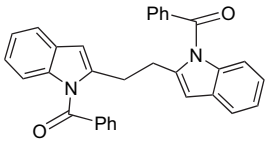
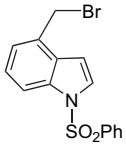
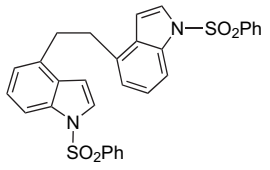
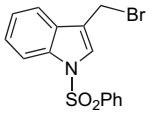
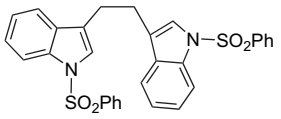
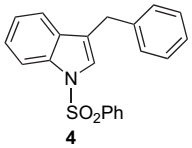
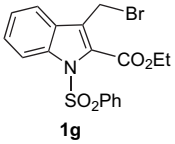
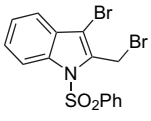
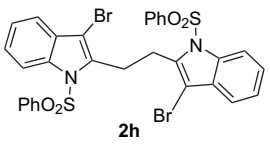
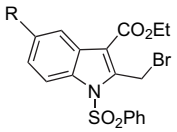
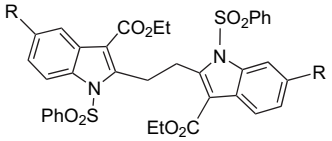
Entry	Bromo/chloro indole[5]	Conditions	Dimerized product	Yield[a] (%)
1		1.2 equiv PhMgCl, rt, 3 h	 **2a**	60
		1.2 equiv $MeOC_6H_4MgBr$, rt, 5 h		52
		1.2 equiv  rt, 5 h		48
	1a' X = Br	1.2 equiv $MeSC_6H_4MgBr$, rt, 4 h		51
	1a″ X=Cl	1.2 equiv PhMgCl, rt, 5 h		48
2	 **1b**	1.2 equiv PhMgCl, rt, 8 h	 **2b**	20
3	 **1c'** X = Br	1.2 equiv PhMgCl, rt, 5 h	 **2c**	48
	1c″ X=Cl	1.2 equiv PhMgCl, rt, 7 h		43
4	 **1d**	1.2 equiv PhMgCl, rt, 5 h	 **2d**	42
5	 **1e**	1.2 equiv PhMgCl, rt, 10 h	 **2e**	45
6	 **1f**	1.2 equiv PhMgCl, rt, 5 h	 **2f**	0
			 **4**	50
7	 **1g**	2 equiv PhMgCl, rt, 6 h	No reaction	
8	 **1h**	1.2 equiv PhMgCl, rt, 10 h	 **2h**	71

Table 1 (*continued*)

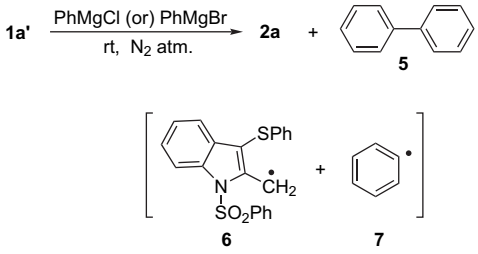
Entry	Bromo/chloro indole[5]	Conditions	Dimerized product	Yield[a] (%)
9	 **1i** R = H	1.2 equiv PhMgCl, rt, 6 h	 **2i** R = H	48
	1j R=OMe	1.2 equiv PhMgCl, rt, 6 h	**2j** R=OMe	55

[a] Isolated yield after column chromatography.

chloride induced dimerization was found to occur with a wide variety of bromomethylindoles with the exception of 3-bromomethylindoles **1f** and **1g** (entries 6 and 7). The dimerization of bromo compound **1a′** proceeded in reasonable yields with aryl/heteroaryl Grignards (entry 1). The rate and yield of the dimerization were found to be somewhat less with the corresponding *N*-protected chloromethylindoles (entries 1 and 3). The presence of cyano group at the 3-position significantly lowers the yield of the dimerization process (entry 2). On the other hand, the bromo compounds **1i** and **1j** containing an ethyl ester at the indole-3-position smoothly proceeded with the dimerization process to afford the respective products **2i** and **2j** in 48 and 55% yields (entry 9). The observed dimerization was found to be successful with 1-phenylsulfonyl-4-bromomethylindole **1e** (entry 5). However, contrary to our earlier observation,[4] the interaction of 1-phenylsulfonyl-3-bromomethylindole with phenylmagnesium chloride did not produce the dimer **2f**, instead column chromatographic purification led to isolation of the corresponding phenylated indole **4** in 50% yield (entry 6).

To our surprise, interaction of *N*-phenylsulfonyl-2-carbethoxy-3-bromomethylindole **1g** with phenylmagnesium chloride produced neither dimer nor phenylated product, only the starting bromo compound was recovered unchanged (entry 7).

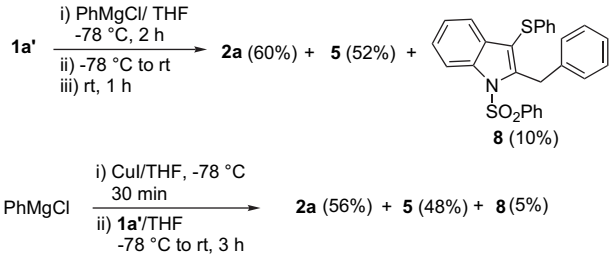
Even though the formation of the dimer **2a** was proposed through the intermediacy of indolylmethylmagnesium halide,[4] there is no literature precedence for this type of Grignard exchange between benzylic halides and aryl Grignards. To our delight, the interaction of bromo compound **1a′** with phenylmagnesium chloride followed by a careful column chromatographic separation led to the isolation of biphenyl **5** in 63% yield in addition to the dimer **2a**, Scheme 2. Similarly, the interaction of the bromo compound **1a′** with freshly prepared phenylmagnesium bromide led to the isolation of dimer **2a** and biphenyl **5** in 65 and 67% yields, respectively. The



Scheme 2.

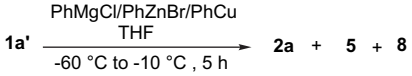
formation of biphenyl **5** is possible only when radical intermediate is involved. Obviously, the interaction of bromo compounds with aryl Grignards produced the indolylmethyl radical **6** and phenyl radical **7**. Self-dimerization of these radicals must lead to the dimer **2a** and biphenyl **5**, Scheme 2.

In order to understand the mechanistic rational behind this dimerization process, as a representative case the dimerization of bromo compound **1a′** was planned at low temperature. Accordingly, a solution of bromo compound **1a′** was interacted with phenylmagnesium chloride in dry THF at −78 °C for 2 h followed by quenching of the reaction mixture with aq NH_4Cl led to the quantitative recovery of the bromo compound **1a′**. However, when the mixture of bromo compound **1a′** with phenylmagnesium chloride in dry THF was slowly raised from −78 °C to room temperature followed by usual workup, dimer **2a**, biphenyl **5**, and phenylated product **8**[6] were isolated in 60, 52, and 10% yields, respectively. Under the identical conditions, interaction of the bromo compound **1a′** with in situ generated PhCu also afforded the products **2a** and **5** along with minor amount of the 2-benzylindole **8**, Scheme 3. The formation of benzylindole **8** in minor portions might be due to the cross-coupling between indolylmethyl radical **6** and phenyl radical **7**.



Scheme 3.

Finally, the reaction of bromo compound **1a′** with PhMgCl and in situ generated PhZnBr or PhCu were carried out at different temperatures. The results obtained under these conditions are outlined in Scheme 4. In all the cases, the biphenyl **8** was isolated around 40–55% yields.



Scheme 4.

Table 2

Temperature (°C)	Yield of **2a** (%)	Yield of **8** (%)
−60	No reaction	No reaction
−30	40, 40, 42	20, 18, 15
−10	54, 45, 40	08, 10, 12

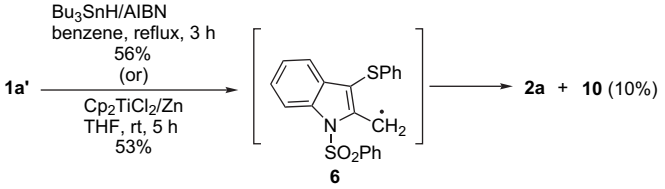
Interaction of bromo compound **1a′** with PhMgCl or in situ generated PhZnBr/PhCu at −60 °C for 5 h led to the recovery of starting material. The yield of dimerization/addition products obtained at −30, −20, and at −10 °C using respective aryl nucleophiles are presented in Table 2. Now it is clear that at low temperature, the self-dimerization of indolylmethyl radical **6** led to the formation of dimer **2a**. The cross-coupling of indolylmethyl radical **6** with phenyl radical **7** produced the 2-benzylindole **8**. This could be the reason why 2-benzylindole **8** was always formed in minor amounts irrespective of the nature of the aryl nucleophiles employed, i.e., PhMgCl or PhZnBr or PhCu.

It should be mentioned that Negishi and Qian observed[7] a small amount of similar dimerization process during a Pd-mediated coupling of benzyl bromide with phenylethynylzinc bromide. Okamoto and co-workers also observed (in minor amount) the dimerization of benzyl bromide during a cobalt-catalyzed benzyl-alkynyl coupling.[8] There are plenty of reports of the formation of radical intermediates using Grignard reagents in the presence of transition metal catalyst.[9] However, there have been only a few reports[10] for involvement of radical intermediates during the interaction of halo compounds and Grignards reagents. Recently, Oshima and co-workers[11] reported an ethylmagnesium bromide-mediated radical cyclization of allyl β-iodoacetals.

In order to get further insight into the mechanism of the observed dimerization process, the interaction of bromo compound **1a′** with alkylmagnesium halides such as isopropylmagnesium bromide, BuMgBr, Bu_2Mg, and $TMSCH_2MgCl$ was planned, Scheme 5. The reaction of bromo compound **1a′** with isopropylmagnesium bromide yielded the corresponding alkylated products **9** along with 1-phenylsulfonyl-3-phenylthio-2-methylindole **10**.[12] It should be mentioned that in the case of isopropylmagnesium bromide not even a trace of dimeric product **2a** was observed. However, the reaction of bromo compound **1a′** with BuMgBr/Bu_2Mg furnished the dimer **2a** along with butylated product **11**. When the bromo compound **1a′** was reacted with freshly prepared $TMSCH_2MgCl$, *N*-phenylsulfonyl cleaved dimer **12** and *N*-protected dimer **2a** were isolated in 35 and 18% yields, respectively. The observed cleavage of phenylsulfonyl group of **2a** may be due to the nucleophilic character of $TMSCH_2MgCl$.

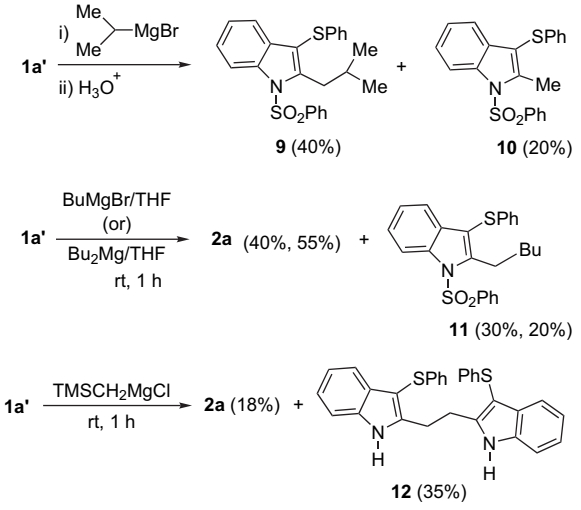
The isolation of compound **10** in the case of isopropylmagnesium bromide confirms the intermediacy of indolylmethylmagnesium chloride **3**. On the other hand, the absence of compound **10** in the case of BuMgBr/Bu_2Mg/$TMSCH_2MgCl$ effectively rules out the intermediacy of indolylmethyl Grignard and hence in these cases, the observed dimerization might proceed only through an indolylmethyl radical.

Alternatively, the dimer **2a** could also be prepared via the interaction of the bromo compound **1a′** with Bu_3SnH and AIBN or in situ generated Cp_2TiCl, Scheme 6.

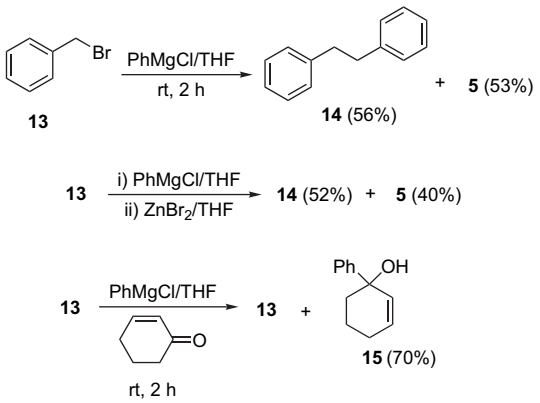


Scheme 6.

In order to generalize the dimerization process, the reaction has to be tested with benzylic systems. To our surprise, benzyl bromide **13** also underwent a smooth dimerization when interacted with phenylmagnesium chloride at room temperature to yield 1,2-diphenyl ethane **14**[13,14] and biphenyl **5** in 56 and 53% yields, Scheme 7. Since benzylmagnesium chloride is stable and commercially available, it is certain that the dimerization of **13** might proceed only through the intermediacy of benzyl radical.



Scheme 5.

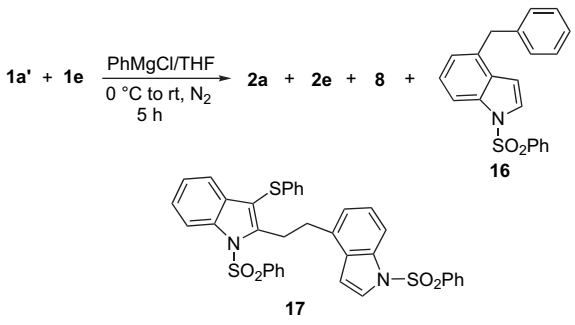


Scheme 7.

Similar to the case of bromomethylindole **1a′**, interaction of benzyl bromide **12** with in situ generated phenylzinc bromide

also furnished the dimer **14** and biphenyl **5**. An attempt was made to trap the intermediate benzyl radical as reported by Roy and co-workers[15] through the interaction of benzyl bromide **13** and phenylmagnesium chloride in the presence of cyclohexen-1-one. However, workup of the reaction afforded Grignard addition product **15** [M^+, 174.02 (87%)] and benzyl bromide **13** was recovered unchanged, Scheme 7.

Finally, a cross-coupling experiment was performed with mixture of bromo compounds **1a′** and **1e**, Scheme 8. The interaction of 1:1 mixture of these bromo compounds with excess of phenylmagnesium chloride followed by workup led to the formation of respective self-dimerization products **2a/2e** and arylated products **8/16**.[6] It should be mentioned that not even a trace of cross-coupled dimer **17** was observed.



Scheme 8.

Thus, the PhMgCl induced dimerization observed in the case of bromomethylindoles was found to be successful even with benzylbromide. Hence, it may be concluded that the observed dimerization of benzyl/indolylmethyl bromides occurs only through the intermediacy of the respective benzyl/indolylmethyl radical.

3. Summary

In summary, we have carried out the interaction of *N*-phenylsulfonyl-2/3/4-bromomethylindoles with alkyl Grignards and arylmetal halides. The observed dimerization was extended to the benzylic bromide as well. Through different set of reactions, an involvement of indolylmethyl/benzyl radical for the observed dimerization has been proved. An attempt to trap the benzylic radical with cyclohexen-1-one was unsuccessful. Further work is in progress to trap benzylic radical/indolylmethyl radical through an intramolecular pathway. Considering the enormous scope for tin free radical reaction, radical generation using arylmetal halides may find application in organic synthesis.

4. Experimental

4.1. General

All melting points are uncorrected. IR spectra were recorded on a SHIMADZU FT-IR 8300 instrument. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as an internal standard on a JEOL 400, 500 and Bruker-300 spectrometers, respectively. Mass spectra were recorded on a JEOL DX 303 HF spectrometer. Elemental analyses were carried out on a Perkin–Elmer 240 B instrument.

4.2. Representative procedure for dimerization

1-Phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.5 g, 1.09 mmol) dissolved in dry THF (10 mL) was stirred at 0–10 °C under nitrogen atmosphere. To this phenylmagnesium chloride (0.65 mL, 1.31 mmol, 2.0 M in THF) was added slowly. The reaction mixture was slowly raised to room temperature and stirred for 5 h. Then it was quenched with saturated ammonium chloride solution (10 mL), extracted with ethyl acetate (2×20 mL), and the extracts were combined and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (silica gel, hexane/EtOAc 9:1) afforded **2a** (0.25 g, 60%).

4.2.1. 1,2-Bis(1-phenylsulfonyl)-3-(phenylthio)-1H-indol-2-ylethane *2a*

Compound **2a** (0.25 g, 60%) was obtained as a colorless solid; mp 220 °C; [Found: C, 66.30; H, 4.40; N, 3.92; S, 16.81. $C_{42}H_{32}N_2O_4S_4$ requires C, 66.64; H, 4.26; N, 3.70; S, 16.94%]; R_f (10% EtOAc/hexane) 0.55; ν_{max} (KBr) 1365, 1172 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.22 (2H, d, *J* 8.3 Hz, ArH), 7.73 (4H, d, *J* 7.3 Hz, ArH), 7.53–7.51 (2H, m, ArH), 7.37 (4H, t, *J* 8.3 Hz, ArH), 7.32–7.27 (2H, m, ArH), 7.24 (2H, t, *J* 7.3 Hz, ArH), 7.16 (2H, t, *J* 7.8 Hz, ArH), 6.94–6.92 (6H, m, ArH), 6.68–6.65 (4H, m, ArH), 3.77 (4H, s, CH_2); δ_C (75.5 MHz, $CDCl_3$) 144.6, 138.8, 137.3, 136.6, 134.1, 130.9, 129.5, 128.7, 126.5, 126.3, 125.4, 125.2, 124.4, 120.3, 115.6, 113.7, 28.1; *m/z* (EI) 378 (M^+, 16%).

4.2.2. 1,2-Bis(1-phenylsulfonyl)-3-(cyano)-1H-indol-2-ylethane *2b*

Following the general procedure, compound **2b** (80 mg, 20%) was obtained as a colorless solid; mp 230 °C; [Found: C, 65.31; H, 3.91; N, 9.35; S, 10.67. $C_{32}H_{22}N_4O_4S_2$ requires C, 65.07; H, 3.75; N, 9.49; S, 10.86%]; R_f (10% EtOAc/hexane) 0.50; ν_{max} (KBr) 2221, 1366, 1187 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.25 (2H, d, *J* 8.8 Hz, ArH), 7.86 (4H, d, *J* 7.8 Hz, ArH), 7.61 (2H, t, *J* 7.4 Hz, ArH), 7.55 (2H, d, *J* 7.8 Hz, ArH), 7.49 (4H, t, *J* 8.1 Hz, ArH), 7.44–7.42 (2H, m, ArH), 7.37 (2H, t, *J* 7.1 Hz, ArH), 3.82 (4H, s, CH_2); δ_C (100.6 MHz, $CDCl_3$) 146.7, 137.6, 135.9, 134.8, 129.8, 127.1, 126.5 (2C), 125.1, 119.5, 115.1, 112.9, 96.5, 28.9.

4.2.3. 1,2-Bis(1-phenylsulfonyl)-3-(methyl)-1H-indol-2-ylethane *2c*

Following the general procedure, compound **2c** (0.19 g, 48%) was obtained as a colorless solid; mp 268 °C; [Found: C, 67.52; H, 5.02; N, 4.97; S, 11.23. $C_{32}H_{28}N_2O_4S_2$ requires C, 67.58; H, 4.96; N, 4.93; S, 11.28%]; R_f (10% EtOAc/hexane) 0.52; ν_{max} (KBr) 1369, 1167 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.22 (2H, d, *J* 8.1 Hz, ArH), 7.67 (4H, d, *J* 7.2 Hz, ArH), 7.47 (2H, t, *J* 7.5 Hz, ArH), 7.35 (4H, t, *J* 7.2 Hz, ArH),

7.29–7.21 (6H, m, ArH), 3.45 (4H, s, CH_2), 1.84 (6H, s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 138.7, 136.7, 135.2, 133.5, 131.7, 129.1, 126.2, 124.4, 123.6, 119.4, 118.7, 115.1, 29.7, 8.5.

4.2.4. 1,2-Bis(1-benzoyl)-1H-indol-2-ylethane **2d**

Following the general procedure, compound **2d** (0.16 g, 42%) was obtained as a colorless liquid; [Found: C, 82.11; H, 5.13; N, 5.91. $C_{32}H_{24}N_2O_2$ requires C, 82.03; H, 5.16; N, 5.98%]; ν_{max} (KBr) 1690 cm^{-1}; R_f (5% EtOAc/hexane) 0.57; δ_H (300 MHz, $CDCl_3$) 7.63 (4H, d, *J* 6.9 Hz, ArH), 7.52 (2H, t, *J* 7.5 Hz, ArH), 7.56 (6H, t, *J* 7.8 Hz, ArH), 7.34–7.28 (2H, m, ArH), 7.11 (4H, d, *J* 3.6 Hz, ArH), 6.32 (2H, s, ArH), 4.24 (4H, s, CH_2); δ_C (75.5 MHz, $CDCl_3$) 170.0, 138.5, 137.2, 135.6, 132.9, 130.2, 130.1, 128.5, 122.7, 122.6, 119.8, 114.3, 108.6, 30.2.

4.2.5. 1,2-Bis(1-phenylsulfonyl)1H-indol-4-ylethane **2e**

Following the general procedure, compound **2e** (0.17 g, 45%) was obtained as a colorless solid; mp 200 °C; [Found: C, 66.59; H, 4.51; N, 5.23; S, 11.92. $C_{30}H_{24}N_2O_4S_2$ requires C, 66.65; H, 4.47; N, 5.18; S, 11.86%]; R_f (10% EtOAc/hexane) 0.36; ν_{max} (KBr) 1375, 1181 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.86–7.80 (6H, m, ArH), 7.54–7.51 (2H, m, ArH), 7.46–7.41 (6H, m, ArH), 7.14 (2H, t, *J* 7.5 Hz, ArH), 6.92 (2H, d, *J* 7.2 Hz, ArH), 6.48 (2H, d, *J* 3.0 Hz, ArH), 3.20 (4H, s, CH_2); δ_C (75 MHz, $CDCl_3$) 138.3, 134.7, 134.5, 133.8, 129.9, 129.2, 126.8, 125.8, 124.7, 122.9, 111.4, 107.1, 34.1.

4.2.6. 3-Benzyl-1-(phenylsulfonyl)-1H-indole **4**

Interaction of bromo compound **1f** with 1.2 equiv of phenylmagnesium chloride using the above-mentioned procedure followed by workup and column chromatographic purification (silica gel, hexane/EtOAc 95:5) afforded **4** (0.25 g, 50%) as a colorless solid; mp 65 °C; [Found: C, 72.55; H, 4.89; N, 4.10; S, 9.25. $C_{21}H_{17}NO_2S$ requires C, 72.60; H, 4.93; N, 4.03; S, 9.23%]; R_f (5% EtOAc/hexane) 0.76; ν_{max} (KBr) 1369, 1182 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.98 (1H, d, *J* 8.4 Hz, ArH), 7.83 (2H, d, *J* 7.5 Hz, ArH), 7.49 (1H, t, *J* 7.2 Hz, ArH), 7.41–7.35 (3H, m, ArH), 7.31–7.14 (8H, m, ArH), 3.99 (2H, s, CH_2); δ_C (75.5 MHz, $CDCl_3$) 138.9, 138.2, 135.6, 133.7, 130.9, 129.2, 128.7, 128.6, 126.7, 126.5, 124.9, 123.9, 123.2, 122.8, 119.9, 113.8, 31.4.

4.2.7. 1,2-Bis(1-phenylsulfonyl)-3-(bromo)-1H-indol-2-ylethane **2h**

Following the general procedure, compound **2h** (0.29 g, 71%) was obtained as a colorless solid; mp 208 °C; [Found: C, 51.51; H, 3.41; N, 4.16; S, 8.98. $C_{30}H_{22}Br_2N_2O_4S_2$ requires C, 51.59; H, 3.17; N, 4.01; S, 9.18%]; R_f (20% EtOAc/hexane) 0.84; ν_{max} (KBr) 1373, 1184 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.22 (2H, d, *J* 8.3 Hz, ArH), 7.77 (4H, d, *J* 7.3 Hz, ArH), 7.53–7.51 (2H, m, ArH), 7.43–7.25 (10H, m, ArH), 3.65 (4H, s, CH_2); δ_C (100.6 MHz, $CDCl_3$) 139.1, 136.7, 134.7, 130.1, 129.9, 129.4, 127.9, 126.3, 124.9, 120.3, 115.6, 104.8, 28.2.

4.2.8. Diethyl-2,2′-(ethane-1,2-diyl)bis[1-(phenylsulfonyl)-1H-indole-3-carboxylate] **2i**

Following the general procedure, compound **2i** (0.19 g, 48%) was obtained as a colorless solid; mp 178 °C; [Found: C, 63.19; H, 4.63; N, 4.02; S, 9.42. $C_{36}H_{32}N_2O_8S_2$ requires C, 63.14; H, 4.71; N, 4.09; S, 9.37%]; R_f (20% EtOAc/hexane) 0.48; ν_{max} (KBr) 1707, 1377, 1175 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.28 (2H, d, *J* 8.1 Hz, ArH), 7.96 (2H, d, *J* 7.8 Hz, ArH), 7.83 (4H, d, *J* 7.8 Hz, ArH), 7.54 (2H, t, *J* 7.3 Hz, ArH), 7.43 (4H, t, *J* 7.5 Hz, ArH), 7.35–7.24 (4H, m, ArH), 4.09 (4H, s, CH_2), 3.57 (4H, q, *J* 7.2 Hz, $COOCH_2CH_3$), 1.02 (6H, t, *J* 6.9 Hz, $COOCH_2CH_3$); δ_C (75.5 MHz, $CDCl_3$) 163.8, 145.7, 139.1, 136.2, 134.2, 129.5, 127.5, 126.4, 124.9, 124.2, 121.9, 114.4, 113.8, 60.2, 26.9, 13.9.

4.2.9. Diethyl-2,2′-(ethane-1,2-diyl)bis[5-methoxy-1-(phenylsulfonyl)-1H-indole-3-carboxylate] **2j**

Following the general procedure, compound **2j** (0.23 g, 55%) was obtained as a colorless solid; mp 224 °C; [Found: C, 61.19; H, 4.79; N, 3.71; S, 8.68. $C_{38}H_{36}N_2O_{10}S_2$ requires C, 61.28; H, 4.87; N, 3.76; S, 8.61]; R_f (20% EtOAc/hexane) 0.46; ν_{max} (KBr) 1707, 1369, 1171 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.16 (2H, d, *J* 9.3 Hz, ArH), 7.80 (4H, d, *J* 7.8 Hz, ArH), 7.57–7.40 (8H, m, ArH), 6.94 (2H, dd, *J* 2.7 and 9.1 Hz, ArH), 4.04 (4H, s, CH_2), 3.81 (6H, s, OCH_3), 3.68 (4H, q, *J* 7.2 Hz, $COOCH_2CH_3$), 1.08 (6H, t, *J* 7.2 Hz, $COOCH_2CH_3$); δ_C (75.5 MHz, $CDCl_3$) 163.9, 156.9, 146.3, 138.9, 134.1, 130.7, 129.5, 128.7, 126.3, 115.3, 114.1, 113.6, 104.1, 60.3, 55.5, 27.2, 13.9.

4.2.10. Dimerization of bromo compound **1a′** using phenylmagnesium chloride at low temperature

Phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.55 g, 1.20 mmol) dissolved in dry THF (10 mL) was stirred at −78 °C under a N_2 atmosphere. To this phenylmagnesium chloride (1.5 mL, 3.0 mmol, 2.0 M in THF) was added and stirred for 3 h. Then the reaction mixture was slowly raised to room temperature (by discontinuing the cooling system of the low temperature bath), quenched with saturated NH_4Cl solution (5 mL), extracted with ethyl acetate (2×20 mL), and the combined organic extract was dried (Na_2SO_4). Removal of the solvent followed by column chromatographic purification (silica gel, hexane/EtOAc 95:5) afforded **2a** (0.28 g, 60%), **5** (0.10 g, 52%), and **8** (50 mg, 10%).

Data for ***5***: colorless solid; mp 71 °C [lit.[16] mp 70 °C]; R_f (hexane) 0.98; δ_H (300 MHz, $CDCl_3$) 7.58 (4H, d, *J* 7.5 Hz, ArH), 7.41 (4H, t, *J* 7.8 Hz, ArH), 7.31 (2H, t, *J* 7.5 Hz, ArH); δ_C (75.5 MHz, $CDCl_3$) 141.3, 128.9, 127.4, 127.3.

Data for ***8***: colorless solid; mp 122 °C; [Found: C, 71.24; H, 4.59; N, 3.13; S, 14.00. $C_{27}H_{21}NO_2S_2$ requires C, 71.18; H, 4.65; N, 3.07; S, 14.08%]; R_f (10% EtOAc/hexane) 0.60; ν_{max} (KBr) 1367, 1178 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.26 (1H, d, *J* 8.4 Hz, ArH), 7.52 (1H, d, *J* 7.8 Hz, ArH), 7.46–7.37 (4H, m, ArH), 7.31–7.12 (11H, m, ArH), 7.03 (2H, d, *J* 6.6 Hz, ArH), 4.79 (2H, s, CH_2); δ_C (75.5 MHz, $CDCl_3$) 144.2, 138.4, 138.1, 136.7, 136.2, 133.6, 130.5, 129.5,

129.0, 128.9, 128.8, 128.4, 126.6, 126.4, 125.6, 125.4, 124.3, 120.1, 115.2, 112.8, 32.2.

4.2.11. Dimerization of bromo compound *1a′* using in situ generated phenylcopper at low temperature

Phenylmagnesium chloride (1.5 mL, 3.0 mmol, 2.0 M in THF) was added to a stirred suspension of CuI (0.68 g, 3.59 mmol) in dry THF (20 mL) at −78 °C. After 30 min, 1-phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.55 g, 1.20 mmol) dissolved in dry THF (10 mL) was added and stirred for 2 h. Then, the reaction mixture was slowly raised to room temperature and quenched with saturated NH_4Cl solution (5 mL). It was then extracted with ethyl acetate (2× 20 mL) and the combined organic extract was dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (silica gel, hexane/EtOAc 95:5) afforded **2a** (0.26 g, 56%), **5** (90 mg, 48%), and **8** (30 mg, 5%).

4.2.12. 2-Benzyl-1-(phenylsulfonyl)-3-(phenylthio)-1H-indole *8*

Phenylmagnesium chloride (0.47 mL, 0.94 mmol) was added to a stirred solution of $B(OMe)_3$ (0.2 mL, 1.76 mmol) in THF (10 mL) at 0 °C under nitrogen atmosphere. After 20 min, $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol) and 1-phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.43 g, 0.94 mmol) were added, and the reaction mixture was stirred at room temperature for 12 h. It was then quenched with saturated ammonium chloride solution (10 mL), extracted with ethyl acetate (3×15 mL), and the combined organic extract was dried (Na_2SO_4). The solvent was completely removed under vacuo to afford **8** (0.27 g, 60%) as a colorless solid, mp 122 °C.

4.2.13. Interaction of bromo compound *1a′* with isopropylmagnesium bromide

1-Phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.5 g, 1.09 mmol) dissolved in dry THF (10 mL) was stirred at 0 °C under a N_2 atmosphere. To this isopropylmagnesium bromide (0.64 mL, 1.42 mmol, 1.0 M in THF) was added. The reaction mixture was stirred for 1 h, quenched with saturated NH_4Cl solution (5 mL), extracted with ethyl acetate (2×20 mL), and the combined organic extract was dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (silica gel, hexane/EtOAc 95:5) afforded **9** (0.18 g, 40%) and **10** (80 mg, 20%).

*Data for **9***: colorless solid; mp 90 °C; [Found: C, 68.32; H, 5.45; N, 3.23; S, 15.17. $C_{24}H_{23}NO_2S_2$ requires C, 68.38; H, 5.50; N, 3.32; S, 15.21%]; R_f (10% EtOAc/hexane) 0.80; ν_{max} (KBr) 1372, 1167 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.22 (1H, d, *J* 8.4 Hz, ArH), 7.73 (2H, d, *J* 7.5 Hz, ArH), 7.52 (1H, t, *J* 7.6 Hz, ArH), 7.36–7.12 (6H, m, ArH), 7.00–6.88 (2H, m, ArH), 6.66–6.63 (2H, m, ArH), 3.11 (2H, d, *J* 8.8 Hz, $CH_2CH(CH_3)_2$), 2.16 (1H, m, $CH_2CH(CH_3)_2$), 0.94 (6H, d, *J* 6.6 Hz, $CH_2CH(CH_3)_2$); δ_C (75.5 MHz, $CDCl_3$) 146.4, 138.4, 136.5, 135.8, 134.0, 133.8, 131.0, 129.4, 128.7, 127.1, 126.4, 125.3, 124.1, 119.6, 115.7, 114.6, 35.8, 22.3, 13.5.

*Data for **10***: colorless needles; mp 70 °C [lit.[13] mp 70 °C]; R_f (10% EtOAc/hexane) 0.70; ν_{max} (KBr) 1366, 1177 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.25 (1H, d, *J* 8.1 Hz, ArH), 7.79 (2H, d, *J* 7.5 Hz, ArH), 7.55 (1H, t, *J* 7.5 Hz, ArH), 7.44 (3H, t, *J* 6.2 Hz, ArH), 7.32 (1H, t, *J* 6.9 Hz, ArH), 7.21 (1H, t, *J* 6.9 Hz, ArH), 7.14–7.02 (3H, m, ArH), 6.93 (2H, d, *J* 6.9 Hz, ArH), 2.74 (3H, s, CH_3).

4.2.14. Interaction of bromo compound *1a′* with n-butylmagnesium bromide

1-Phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.6 g, 1.31 mmol) dissolved in dry THF (10 mL) was stirred at 0 °C under a N_2 atmosphere. To this freshly prepared *n*-butylmagnesium bromide [Mg, 0.21 g, 8.54 mmol; *n*-butyl bromide, 0.90 g, 0.7 mL, 6.57 mmol in dry THF (30 mL) reflux for 1 h] was added slowly. The reaction mixture was stirred for 3 h, quenched with saturated NH_4Cl solution (5 mL), extracted with ethyl acetate (2×20 mL), and the combined organic extract was dried (Na_2SO_4). Removal of the solvent followed by column chromatographic purification (silica gel, hexane/EtOAc 95:5) afforded **2a** (0.2 g, 40%) and **11** (0.17 g, 30%).

*Data for **11***: thick orange liquid; [Found: C, 68.89; H, 5.87; N, 3.19; S, 14.81. $C_{25}H_{25}NO_2S_2$ requires C, 68.93; H, 5.78; N, 3.22; S, 14.72%]; R_f (10% EtOAc/hexane) 0.80; ν_{max} (KBr) 1366, 1190 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.23 (1H, d, *J* 8.4 Hz, ArH), 7.73 (2H, d, *J* 7.8 Hz, ArH), 7.55 (1H, t, *J* 7.5 Hz, ArH), 7.44–7.34 (3H, m, ArH), 7.31 (1H, t, *J* 7.5 Hz, ArH), 7.20 (1H, t, *J* 7.2 Hz, ArH), 7.12–7.04 (3H, m, ArH), 6.88 (2H, d, *J* 8.1 Hz, ArH), 3.20 (2H, t, *J* 7.5 Hz, $CH_2(CH_2)_3CH_3$), 1.65 (2H, quintet, *J* 7.5 Hz, $CH_2CH_2(CH_2)_2CH_3$), 1.35–1.28 (4H, m, $CH_2CH_2(CH_2)_2CH_3$), 0.84 (3H, t, *J* 6.9 Hz, $CH_2(CH_2)_3CH_3$); δ_C (75.5 MHz, $CDCl_3$) 147.6, 138.8, 136.9, 136.7, 133.8, 130.9, 129.3, 128.8, 126.3, 126.1, 125.2, 125.1, 124.3, 119.7, 115.3, 111.1, 31.7, 30.6, 27.4, 22.3, 13.9.

4.2.15. Interaction of bromo compound *1a′* with dibutylmagnesium

1-Phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.6 g, 1.31 mmol) dissolved in dry THF (10 mL) was stirred at 0 °C under a N_2 atmosphere. To this dibutylmagnesium (2.6 mL, 2.61 mmol, 1.0 M in THF) was added. The reaction mixture was stirred for 1 h, quenched with saturated NH_4Cl solution (10 mL), extracted with ethyl acetate (2×20 mL), and the combined organic extract was dried (Na_2SO_4). Removal of the solvent followed by column chromatographic purification (silica gel, hexane/EtOAc 95:5) afforded **2a** (0.27 g, 55%) and **11** (0.11 g, 20%).

4.2.16. Interaction of bromo compound *1a′* with trimethylsilylmethylmagnesium chloride

1-Phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.5 g, 1.09 mmol) dissolved in dry THF (10 mL) was stirred at 0 °C under a N_2 atmosphere. To this freshly prepared trimethylsilylmethylmagnesium chloride [Mg, 70 mg, 2.92 mmol; $TMSCH_2Cl$, 0.27 g, 0.3 mL, 2.18 mmol in dry THF (20 mL)

reflux for 1 h] was added slowly. The reaction mixture was stirred for 1 h, quenched with saturated NH_4Cl solution (5 mL), extracted with ethyl acetate (2×20 mL), and the combined organic extract was dried (Na_2SO_4). Removal of the solvent followed by column chromatographic purification (silica gel, hexane/EtOAc 95:5) afforded **2a** (80 mg, 18%) and **12** (90 mg, 35%).

Data for ***12***: colorless solid; mp 216 °C; [Found: C, 75.63; H, 5.01; N, 5.83; S, 13.52. $C_{30}H_{24}N_2S_2$ requires C, 75.59; H, 5.08; N, 5.88; S, 13.45%]; R_f (10% EtOAc/hexane) 0.52; ν_{max} (KBr) 3379 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.01 (2H, s, NH), 7.52 (2H, d, *J* 7.8 Hz, ArH), 7.17–7.10 (16H, m, ArH), 3.27 (4H, s, CH_2); δ_C (100.6 MHz, $CDCl_3$) 142.9, 139.3, 135.4, 130.1, 128.9, 127.6, 125.7, 124.9, 122.5, 120.9, 119.0, 111.1, 99.6, 26.3; *m/z* (EI) 238 (M^+, 35%).

*4.2.17. Dimerization of bromo compound **1a′** using Bu_3SnH/AIBN*

To a stirred solution of bromo compound **1a′** (0.25 g, 1 mmol) in dry benzene (30 mL), Bu_3SnH (0.2 mL, 1.2 mmol) and a catalytic amount of AIBN (20 mg) were added under N_2. Then it was refluxed for 3 h. Benzene was removed in vacuo and the residue was dissolved in Et_2O (20 mL); a saturated KF solution (10 mL) was added. The resulting mixture was stirred at room temperature for 4 h. Then the organic layer was separated and washed with saturated $NaHCO_3$ solution (2×30 mL) followed by brine (2×20 mL) and dried ($MgSO_4$). Removal of the solvent followed by flash column chromatographic purification (silica gel, 10% EtOAc in hexane) afforded the dimerized compounds **2a** (0.12 g, 56%) and **10** (20 mg, 10%).

*4.2.18. Dimerization of bromo compound **1a′** using in situ generated Cp_2TiCl*

A solution of titanocene dichloride (0.54 g, 2.18 mmol) in dry THF (20 mL) was stirred with activated zinc dust (0.5 g, 7.63 mmol) for 1 h under N_2. The resulting green solution was then added dropwise to a stirred solution of bromo compound **1a′** (0.5 g, 1.09 mmol) in dry THF (10 mL) at room temperature over 30 min. The resulting mixture was stirred for additional 5 h and decomposed with saturated aqueous sodium dihydrogen phosphate (10 mL) and the product extracted using ethyl acetate (2×20 mL). The combined extracts were washed successively with water (2×15 mL) and brine (2×15 mL), and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatographic purification (silica gel, 10% EtOAc in hexane) afforded the dimerized compounds **2a** (0.22 g, 53%) and **10** (40 mg, 10%).

*4.2.19. Dimerization of benzyl bromide **13** using phenylmagnesium chloride*

Interaction of benzyl bromide **13** (0.5 mL, 4.21 mmol) with phenylmagnesium chloride (6.3 mL, 12.6 mmol, 2.0 M in THF) at room temperature for 8 h followed by the usual workup afforded inseparable mixture of diphenylethane **14** and biphenyl **5** in 56 and 53% yields (based on ^1H NMR spectral data[17]); δ_H (300 MHz, $CDCl_3$) 7.59 (4H, t, *J* 7.1 Hz, ArH), 7.43 (4H, t, *J* 7.8 Hz, ArH), 7.35 (2H, t, *J* 6.0 Hz, ArH), 7.26 (4H, t, *J* 7.5 Hz, ArH), 7.20–7.16 (6H, m, ArH), 2.92 (4H, s, CH_2); δ_C (75.5 MHz, $CDCl_3$) 141.8, 141.3, 129.7, 128.8, 128.4, 128.3, 127.3, 127.2, 37.9.

*4.2.20. Dimerization of benzyl bromide **13** using in situ generated phenylzinc bromide*

To a solution of phenylmagnesium chloride (5.3 mL, 10.51 mmol, 2.0 M in THF) in dry THF (20 mL), anhydrous $ZnBr_2$ (2.84 g, 12.61 mmol) was added and the mixture stirred for 15 min. To this bromo compound **13** (0.5 mL, 4.21 mmol) was added and the mixture stirred for 4 h. The usual workup yielded mixture of diphenylethane **14** and biphenyl **5** in 52 and 40% yields (based on ^1H NMR integration).

*4.2.21. 2-Phenylcyclohex-2-enol **15***

To a stirred solution of cyclohexen-1-one (0.5 g, 5.20 mmol) in dry THF (10 mL), benzyl bromide **13** (0.74 mL, 6.25 mmol) was added at 0 °C under N_2 atmosphere. To this phenylmagnesium chloride (5.2 mL, 10.42 mmol, 2.0 M in THF) was added. The reaction mixture was stirred for 2 h, quenched with saturated NH_4Cl solution (10 mL), extracted with ethyl acetate (2×20 mL), and the combined organic extract was dried (Na_2SO_4). Removal of the solvent followed by column chromatographic purification (silica gel, hexane/EtOAc 92:8) afforded **15** (0.63 g, 70%) as a pale yellow liquid; [Found: C, 82.67; H, 8.17. $C_{12}H_{14}O$ requires C, 82.72; H, 8.10]; R_f (10% EtOAc/hexane) 0.30; ν_{max} liquid (KBr) 3415, 2933 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.51–7.48 (2H, m, ArH), 7.36–7.33 (2H, m, ArH), 7.27–7.24 (1H, m, ArH), 6.05–6.02 (1H, m, CH=*CH*CH_2), 5.79 (1H, d, *J* 10.0 Hz, *CH*=CH), 2.17–2.12 (2H, m, CH_2), 1.99 (1H, s, OH), 1.89–1.62 (4H, m, CH_2CH_2); δ_C (125.7 MHz, $CDCl_3$) 147.9, 132.3, 130.8, 129.5, 128.2, 125.6, 72.3, 39.7, 25.1, 19.3.

*4.2.22. Attempted cross-coupling reaction of bromo compound **1a′** and bromo compound **1e** with phenylmagnesium chloride*

1-Phenylsulfonyl-3-phenylthio-2-bromomethylindole **1a′** (0.5 g, 1.09 mmol) and 1-phenylsulfonyl-4-bromomethylindole **1e** (0.38 g, 1.09 mmol) in dry THF (20 mL) were stirred at 0 °C under N_2 atmosphere. To this phenylmagnesium chloride (2.7 mL, 5.45 mmol, 2.0 M in THF) was added. The reaction mixture was stirred for 5 h, quenched with saturated NH_4Cl solution (10 mL), extracted with ethyl acetate (2×20 mL), and the combined organic extract was dried (Na_2SO_4). Removal of the solvent followed by ^1H NMR analysis showed the presence of compounds **2a**, **2e**, **8**, and **16**.

*4.2.23. 4-Benzyl-1-(phenylsulfonyl)-1H-indole **16***

Phenylmagnesium chloride (0.5 mL, 1.0 mmol) was added to a stirred solution of $B(OMe)_3$ (0.23 mL, 2.0 mmol) in THF (10 mL) at 0 °C under nitrogen atmosphere. After 20 min, $Pd(PPh_3)_4$ (0.12 g, 0.10 mmol) and 1-phenylsulfonyl-4-bromomethylindole **1e** (0.35 g, 1.0 mmol) were added and the reaction mixture was stirred at room temperature for 12 h. It was

then quenched with saturated ammonium chloride solution (10 mL), extracted with ethyl acetate (3×15 mL), and the combined organic extract was dried (Na_2SO_4). The solvent was completely removed under vacuo to yield **16** as a colorless thick liquid (0.24 g, 68%); [Found: C, 72.53; H, 4.89; N, 4.11; S, 9.28. $C_{21}H_{17}NO_2S$ requires C, 72.60; H, 4.93; N, 4.03; S, 9.23%]; R_f (10% EtOAc/hexane) 0.55; ν_{max} (KBr) 1369, 1171 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.77 (3H, d, *J* 7.5 Hz, ArH), 7.44–7.36 (2H, m, ArH), 7.29 (2H, t, *J* 7.7 Hz, ArH), 7.16–7.03 (6H, m, ArH), 6.91 (1H, t, *J* 7.2 Hz, ArH), 6.54 (1H, d, *J* 3.0 Hz, ArH), 4.04 (2H, s, CH_2); δ_C (75.5 MHz, $CDCl_3$) 139.1, 137.3, 133.8, 132.8, 132.7, 129.1, 128.2, 127.7, 127.4, 125.7, 125.1, 124.9, 123.8, 122.7, 110.6, 106.5, 28.7.

Acknowledgements

We thank CSIR, New Delhi (01(2071)/06/EMR-II) for the financial support. N.R. and C.P. thank CSIR for CSIR-SRF fellowship. R.S. and V.D. thank UGC for fellowship. Authors thank DST-FIST for 300 MHz NMR facility.

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