Directed Lithiation of Chlorobenzenes. Regioselectivity and Application to a Short Synthesis of Benzocyclobutenes

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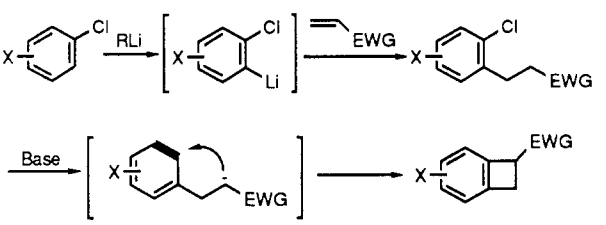
Chlorobenzene and its OMe, $OSiMe_2$-*t*-Bu, and Cl derivatives **1** were lithiated with high regioselectivity ortho to chlorine by treatment with *sec*-BuLi in THF at −105 °C without complications due to benzyne formation. The lithio species thus generated underwent smooth Michael addition on treatment with 1-(phenylsulfonyl)-1-(trimethylsilyl)ethene (**2**). The desilylated Michael adducts **3** or **6** were converted in good yields to 1-(phenylsulfonyl)benzocyclobutenes **7** via benzyne intermediates.

Introduction

Heteroatom-directed ortho-lithiation is a useful method for the regioselective construction of substituted aromatic systems that are difficult to prepare by electrophilic substitution methodology.[1] Many common functional groups are known to promote ortho-lithiation.[1a] In addition, new ortho-directing groups have been devised in recent years, and on the basis of these, many unique synthetic methodologies have been developed.[1b-h] The directing ability of chlorine has been well established in the base-catalyzed generation of benzynes from chlorobenzenes.[2] However, the utility of chlorobenzenes for the electrophilic functionalization of aromatic rings via ortho-lithiated species has been limited to substrates such as polychlorinated benzenes,[3] chlorobenzenes possessing another strong directing group at the meta position,[4] the chromium tricarbonyl complex of chlorobenzene,[5] and chlorinated heteroaromatics.[6] In these substrates, other anion-stabilizing effects are operating to prevent the elimination of LiCl from the lithiated species. It has been assumed that ortho-lithiation of simple chlorobenzenes without such effects is not practical due to rapid formation of benzynes.[7] For this reason, for example, *o*-lithiochlorobenzene has been generated from *o*-bromochlorobenzene by rapid Br–Li exchange at −100 °C and used for electrophilic substitution at that temperature.[8] An attempt to metalate chlorobenzene directly by using a superbasic BuLi/*t*-BuOK system has been reported to fail.[9] We propose, however, that the ortho-acidifying effect of chlorine is fairly strong due to its inductive electron-withdrawing capacity. Therefore, if lithiation was conducted at temperatures low enough to prevent benzyne formation, the *o*-lithio species would accumulate to allow practical electrophilic substitutions. If this is the case, the utility of chlorobenzene would be enhanced by combination of its use for ortho functionalization and benzyne generation.

Scheme I[a]



[a] EWG = electron-withdrawing group.

In this paper, we describe the successful ortho-lithiation of chlorobenzenes and the application of this methodology to a short synthesis of benzocyclobutenes.[10] The significance of benzocyclobutenes as *o*-quinodimethane precursors in Diels–Alder syntheses of polycyclic compounds including complex natural products has been well established.[11] Our synthetic design is shown in Scheme I. *o*-Lithiochlorobenzene is added to an appropriate Michael acceptor, and the adduct thus obtained is cyclized to benzocyclobutene under benzyne-mediated Bunnett cyclization conditions.[12] Chlorine, therefore, serves the dual function of ortho director for the initial lithiation and leaving group for the subsequent benzyne formation.

Results and Discussion

Directed Lithiation of Chlorobenzenes. We examined the lithiation of chlorobenzenes by employing 1-(phenylsulfonyl)-1-(trimethylsilyl)ethene[13] (**2**) as the electrophile because this type of vinyl sulfone exhibits excellent reactivity as a Michael acceptor for a wide range

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(8) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1956**, *78*, 2217.

(9) Reference 1j, p 214.

(10) For general reviews of benzocyclobutene chemistry, see: (a) Klundt, I. L. *Chem. Rev.* **1970**, *70*, 471. (b) Thummel, R. P. *Acc. Chem. Res.* **1980**, *13*, 70.

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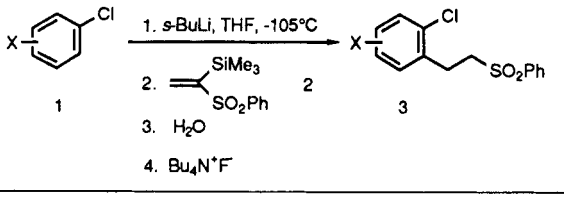
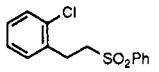
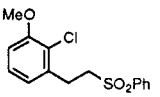
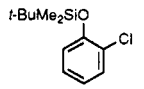
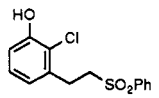
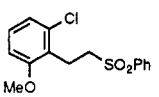
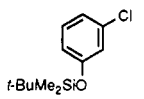
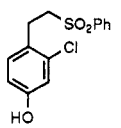
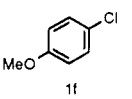
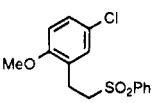
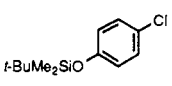
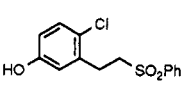
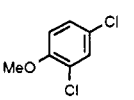
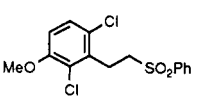
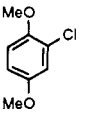
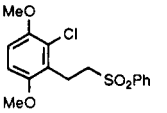
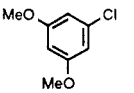
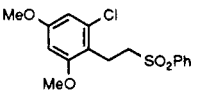
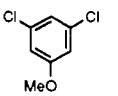
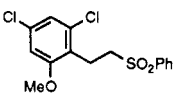
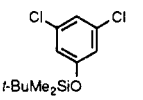
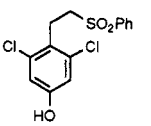
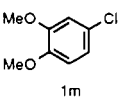
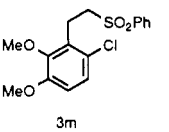
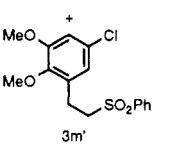
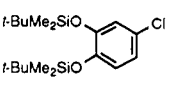
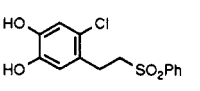
Table I. Directed Lithiation of Chlorobenzenes and Subsequent Reaction with 1-(Phenylsulfonyl)-1-(trimethylsilyl)ethene



entry	chlorobenzene	lithiation time, h	product(s)	yield, %
1	 1a	2	 3a	79
2	1a	2	3a	80[a]
3	1a	3	3a	88
4	 1b	2	 3b	48[b]
5	 1c	2	 3c	61[b]
6	 1d	1	 3d	83
7	 1e	3	 3e	69
8	 1f	1	 3f	83[c]
9	 1g	2	 3g	86
10	 1h	1	 3h	87[c]
11	 1i	1	 3i	94
12	 1j	1	 3j	86[c]
13	 1k	1	 3k	86
14	 1l	1	 3l	77
15	 1m	1	 3m	75
			 3m'	8
16	 1n	3	 3n	78[d]

[a] Yield in the presence of TMEDA. [b] A considerable amount (~30%) of 3-methyl-1-(phenylsulfonyl)pentane (4) was isolated as a by-product. [c] A trace amount (2–3%) of a regioisomer was formed. [d] Yield after methylation.

of organolithium compounds.[13,14]

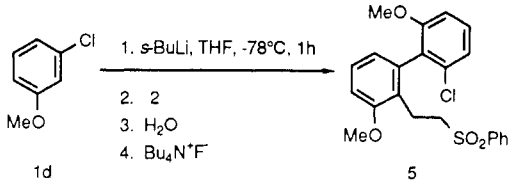
Chlorobenzene (**1a**) was lithiated by *sec*-BuLi in THF at −105 °C for 2 h and subsequently treated with **2**. After being allowed to warm to ca. −50 °C, the reaction mixture was quenched with water and treated with tetrabutylammonium fluoride (TBAF). After the usual workup and chromatographic purification, the anticipated desilylated Michael adduct **3a** was obtained in 79% yield accompanied by 3-methyl-1-(phenylsulfonyl)pentane (**4**) (18%), which was formed by the Michael addition of unreacted *sec*-BuLi to **2** (Table I, entry 1). Addition of TMEDA did not improve the yield of **3a** (entry 2). Elongation of the reaction time to 3 h improved the yield of **3a** to 88% (entry 3). These results indicate that the ortho-lithiation of chlorobenzene (**1a**) is slow at −105 °C, but the lithiated species is stable at this temperature at least for 2–3 h and may be trapped by reactive electrophiles such as **2**. The ortho regioselectivity of this reaction was established by comparison of **3a** with an authentic material prepared by the Michael reaction of *o*-lithiochlorobenzene unequivocally

(14) Isobe, M.; Kitamura, M.; Goto, T. *Tetrahedron Lett.* **1979**, 3465; *Chem. Lett.* **1980**, 331. Isobe, M.; Ichikawa, Y.; Funabashi, Y.; Mio, S.; Goto, T. *Tetrahedron* **1986**, *42*, 2863.

generated from *o*-bromochlorobenzene.[8] The trimethylsilyl group in the Michael acceptor **2** was found to be indispensable for the success of this reaction. When commercially available phenyl vinyl sulfone was treated with *o*-lithiochlorobenzene, none of the Michael adduct **3a** was obtained.

Next, we examined the lithiation of substituted chlorobenzenes under similar conditions. The results are summarized in Table I. The regioselectivity was determined by 400-MHz ^{1}H NMR studies, including NOE experiments, of the isolated Michael adducts. First, lithiation of monomethoxy or monosilyloxy chlorobenzenes **1b–g** was conducted (entries 4–9). 2-Chloroanisole (**1b**) was lithiated exclusively at the 3-position (entry 4). This result is in sharp contrast to the lithiation of 4-chloroanisole (**1f**), in which lithiation occurred almost exclusively at the position ortho to the methoxy group (entry 8). This inconsistency may be explained as follows. Under kinetically controlled conditions, the methoxy group should be a more effective ortho director than chlorine due to its ability to coordinate the lithiating agent. However, in the lithiation of 2-chloroanisole (**1b**), precoordination[15] of the oxygen lone-pair electrons to the lithiating agent for subsequent C-6 deprotonation may be prohibited by steric repulsion between chlorine and the methoxy group.[16] Therefore, lithiation is expected to occur at the most acidic position, ortho to the chlorine.[17]

3-Chloroanisole (**1d**) was smoothly lithiated at −105 °C within 1 h at the 2-position, to give adduct **3d** in good yield (entry 6). We thought that the lithio species derived from 3-chloroanisole (**1d**) may have some thermal stability due to the additional coordinating effect of the methoxy group. However, when lithiation was carried out at −78 °C for 1 h, only biphenyl derivative **5** was obtained. This compound was presumably derived by addition of 3-chloro-2-lithioanisole to the methoxybenzyne generated from this lithio species, followed by Michael addition of **2** to the resulting lithiobiphenyl.[18] Thus, the low temperature (−105 °C) is essential to prevent benzyne formation.



1d 5

It has been reported that bulky silyl protecting groups, such as the *tert*-butyldimethylsilyl (TBDMS) group, of phenols prevent ortho-lithiation due to steric hindrance.[19] The utility of TBDMS as a protecting group for regiochemical control in the lithiation of chlorophenols was examined. Thus, lithiation of the TBDMS ether (**1e**) of 3-chlorophenol, in contrast to the lithiation of 3-chloroanisole (**1d**), occurred exclusively at the 4-position, and the Michael adduct **3e** was obtained in a moderate yield (entry 7). A similar change of lithiation site was observed for 4-chloroanisole (**1f**) and the TBDMS ether (**1g**) of 4-chlorophenol (entry 8 vs 9). The phenolic Michael adducts **3e** and **3g** were cleanly converted into their *O*-methyl derivatives **6e** and **6g** (Me_2SO_4/K_2CO_3/acetone). These results indicate that regioisomers of chlorophenol derivatives are available by proper selection of the protecting group for phenolic oxygen via the lithiation route.

Next, the lithiation of trisubstituted compounds **1h–n** were examined (entries 10–16). The lithiations of 2,4-dichloroanisole (**1h**) and 2-chloro-1,4-dimethoxybenzene (**1i**) occurred with high regioselectivity and in high yields at the expected position between the two directing groups (entries 10 and 11). On the other hand, of the two similar alternatives in 5-chloro-1,3-dimethoxybenzene (**1j**) and 3,5-dichloroanisole (**1k**), lithiation occurred regioselectively at the position between the methoxy and chlorine groups (entries 12 and 13). In these cases, the alkyllithium may initially coordinate to the methoxy group and then abstract the most acidic ortho proton adjacent to the chlorine.

The regiochemical control of lithiation by using a bulky TBDMS group is also quite effective in trisubstituted systems. In contrast to the lithiation of 3,5-dichloroanisole (**1k**), the TBDMS ether (**1l**) of 3,5-dichlorophenol underwent lithiation exclusively at the position between two chlorines (entry 14). The Michael adduct **3l** was converted into its *O*-methyl derivative **6l**. The lithiation of 4-chloroveratrol (**1m**) occurred selectively at the 3-position, to give the Michael adduct **3m** as the major product (entry 15). On the other hand, the bis-TBDMS ether (**1n**) of 4-chlorocatechol was lithiated at the 5-position exclusively and the Michael adduct **3n**, which was purified as dimethyl derivative **6n**, was obtained in good yield (entry 16).

In summary, the regioselectivities of lithiations of substituted chlorobenzenes are quite high due to the combined influence of the electron-withdrawing capacity of chlorine, the coordinating ability of the methoxy oxygen, and the steric hindrance of the TBDMS protecting group.

Synthesis of Benzocyclobutenes. The benzyne-mediated synthesis of benzocyclobutenes developed by Bunnett and Scorkz[12] constitutes a general method for the preparation of 1-substituted benzocyclobutenes. A number of 1-cyanobenzocyclobutenes have been synthesized via this method and employed for the syntheses of a wide range of natural products.[11] By comparison, only one example[12] of a 1-(phenylsulfonyl)benzocyclobutene has been reported. The readily obtainable Michael adducts **3** should serve as ideal starting materials for ring-substituted 1-(phenylsulfonyl)benzocyclobutenes. Thus, the cyclizations of methoxy-substituted compounds **3** and **6** to the benzocyclobutenes **7** under benzyne-generating conditions were conducted. The results are summarized in Table II.

Cyclization studies showed that yields depend on the substitution pattern of the benzene ring of the starting material and on the reaction conditions. Thus, under Bunnett's conditions[12] (KNH_2/liquid NH_3/−33 °C/15 min), compound **3a** was cyclized to the benzocyclobutene **7a** in 55% yield accompanied by a few unidentified polar byproducts, which may consist of aniline derivatives (entry 1). The use of $NaNH_2$ for cyclization of **3a** (liquid NH_3/−33 °C/2 h) gave incomplete reaction. On the other hand, compound **6e** was cleanly cyclized to the corresponding benzocyclobutene **7e** by using $NaNH_2$, possibly

(15) The significance of the precoordination of the substrate electron pair to the lithiating agent for stereo- and regioselective lithiations has been reviewed. See: Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.

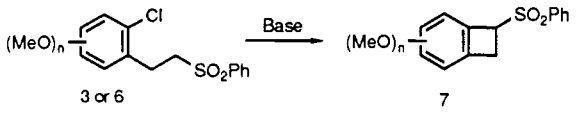
(16) For a similar example of this steric inhibition of the methoxy coordination, see: Slocum, D. W.; Koonsvitsky, D. W. *J. Org. Chem.* **1973**, *38*, 1675.

(17) Lithiation of 2-fluoroanisole occurs preferentially at the 6-position although fluorine is more electronegative than chlorine. In this case, small fluorine may not interefere with the methoxy coordination. See ref 19f.

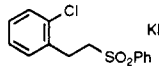
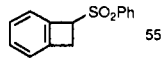
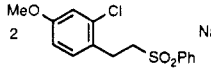
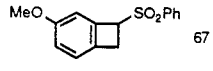
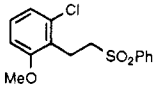
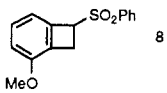
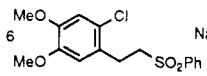
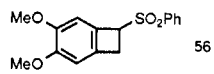
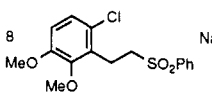
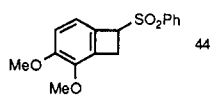
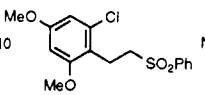
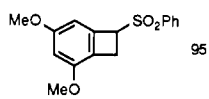
(18) Similar biphenyl formation from 3-fluoro-2-lithioanisole has been reported. See: Adejare, A.; Miller, D. D. *Tetrahedron Lett.* **1984**, *25*, 5597.

(19) (a) Fukui, M.; Ikeda, T.; Oishi, T. *Chem. Pharm. Bull.* **1983**, *31*, 466. (b) Masters, N. F.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 955. (c) Trost, B. M.; Saulnier, M. G. *Tetrahedron Lett.* **1985**, *26*, 123. (d) Kirk, K. L.; Olubajo, O.; Buchhold, K.; Lewandowski, G. A.; Gusovsky, F.; McCulloh, D.; Daly, J. W.; Creveling, C. R. *J. Med. Chem.* **1986**, *29*, 1982. (e) Sinhababu, A. K.; Kawase, M.; Borchard, R. T. *Tetrahedron Lett.* **1987**, *28*, 4139. (f) Furlano, D. C.; Calderon, S. N.; Chen, G.; Kirk, K. L. *J. Org. Chem.* **1988**, *53*, 3145.

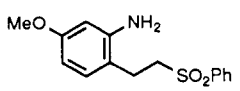
Table II. Synthesis of 1-(Phenylsulfonyl)benzocyclobutenes



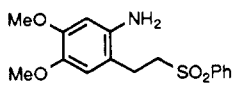
3 or 6 7

entry	substrate	conditn	benzocyclobutene	yield, %
1	 3a	KNH_2, 15 min	 7a	55
2	 6e	$NaNH_2$, 2h	 7e	67
3	6e	LDA	7e	68
4	 3d	$NaNH_2$, 5h	 7d	8
5	3d	KNH_2, 3h	7d	94
6	 6n	$NaNH_2$, 2h	 7n	56
7	6n	LDA	7n	66
8	 3m	$NaNH_2$, 5h	 7m	44
9	3m	KNH_2, 3h	7m	95
10	 3j	$NaNH_2$, 2h	 7j	95

because the initial metalation was facilitated by the methoxy group (entry 2). The LDA/THF system[20] was also useful to effect cyclization of **6e** (entry 3). Similarly facile cyclizations were observed for the dimethoxy compound **6n** (entries 6 and 7). In entries 2 and 6, the amine byproducts **8** (32%) and **9** (47%), respectively, were isolated.



8



9

The cyclization of compound **3d** was extremely sluggish when $NaNH_2$ was used as a base (8% of the benzocyclobutene **7d** and 91% of the starting material **3d** were obtained after 5 h of reaction) (entry 4). However, when the kinetically more basic KNH_2 was used, the benzocyclobutene **7d** was obtained in excellent yield (entry 5). In this reaction, the formation of the amine byproducts was negligible, possibly owing to the steric effect of the methoxy group, which forced rapid intramolecular addition of the side-chain carbanion to the benzyne, thus precluding intermolecular addition of ammonia or amide ion.[21] Similar reactivities were observed in the cyclizations of dimethoxy compound **3m** (entries 8 and 9). The cyclization of **3j** occurred rapidly and in high yield when $NaNH_2$ was used as a base (entry 10). In this case, one methoxy group may facilitate metalation, while the other methoxy group may promote the intramolecular cyclization by its steric effect.

(20) Jung, M. E.; Lowen, G. T. *Tetrahedron Lett.* **1986**, *27*, 5319.

Conclusion

Herein, we have demonstrated that the ortho-lithiation of chlorobenzenes **1** proceeds with high regioselectivity at −105 °C without complications due to benzyne formation. The TBDMS protecting group in the chlorophenol series effectively prohibits lithiation ortho to the TBDMSO group. The Michael adducts **3** and **6** undergo cyclization to 1-(phenylsulfonyl)benzocyclobutenes **7** in good to excellent yields under appropriate benzyne-generating conditions. These results provide a short and regioselective synthesis of aryl-ring-substituted 1-(phenylsulfonyl)-benzocyclobutenes **7** from commercially available or easily synthesized chlorobenzenes **1**. The benzocyclobutenes **7** may be useful building blocks for the Diels–Alder-based synthesis of polycyclic compounds. Application of this approach for the syntheses of complex natural products via intramolecular Diels–Alder reactions may be particularly fruitful in view of ease of functionalization of these benzocyclobutenes via sulfonyl-stabilized carbanions.

Experimental Section

General. All melting points and boiling points are uncorrected. IR spectra were recorded on a JASCO A-100 spectrometer. ^1H NMR spectra (400 MHz) were determined on a JEOL JNM-GX 400 spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard. Mass spectra were obtained on a JEOL JMS-DX 303 spectrometer. Elemental analyses were performed at the microanalytical laboratory in Nagasaki University.

Column chromatography was peformed on Merck silica gel 60 (230–400 mesh). *sec*-BuLi was purchased from Aldrich Chemical Company and used after titration with 2,5-dimethoxybenzyl alcohol.[22] THF used for lithiations was distilled from Na–benzophenone ketyl under N_2. Commercially available chlorobenzenes were distilled before use.

Synthesis of TBDMS Ethers 1c, 1e, 1g, 1l, and 1n. The following procedures are representative.

1-[(*tert*-Butyldimethylsilyl)oxy]-2-chlorobenzene (1c). With ice cooling, imidazole (7.49 g, 0.11 mol) was added all at once to a stirred solution of 2-chlorophenol (12.86 g, 0.10 mol) and *tert*-butyldimethylchlorosilane (15.07 g, 0.10 mol) in DMF (50 mL). After 10 min, the cooling bath was removed, and the mixture was stirred overnight. The reaction mixture was diluted with water, and the product was extracted with hexane. The combined extract was washed sequentially with water, aqueous K_2CO_3, and water. The dried (Na_2SO_4) extract was evaporated, and the residual oil was distilled under reduced pressure, to give **1c** (21.66 g, 89%): bp 66–68 °C/0.4 mm; ^1H NMR δ 0.23 (s, 6 H, $SiMe_2$), 1.04 (s, 9 H, *t*-Bu), 6.85–6.89 (m, 2 H, H-4 and H-6), 7.10 (m, 1 H, H-5), 7.33 (m, 1 H, H-3).

1-[(*tert*-Butyldimethylsilyl)oxy]-3-chlorobenzene (1e). This compound was prepared from 3-chlorophenol in 81% yield: bp 60 °C/0.3 mm; ^1H NMR δ 0.20 (s, 6 H, $SiMe_2$), 0.98 (s, 9 H, *t*-Bu), 6.71 (m, 1 H, H-6), 6.84 (t, 1 H, H-2, J = 2.2 Hz), 6.93 (m, 1 H, H-4), 7.13 (t, 1 H, H-5, J = 8.1 Hz).

1-[(*tert*-Butyldimethylsilyl)oxy]-4-chlorobenzene (1g). This compound was prepared from 4-chlorophenol in 87% yield:

(21) For a similar discussion, see: Kessar, V.; Gupta, Y. P.; Balakrishnan, P.; Sawal, K. K.; Mohammad, T.; Dutt, M. *J. Org. Chem.* **1988**, *53*, 1708.

(22) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.

bp 59 °C/0.25 mm; ^{1}H NMR δ 0.18 (s, 6 H, $SiMe_2$), 0.97 (s, 9 H, *t*-Bu), 6.76 (m, 2 H, H-2 and H-6), 7.17 (m, 2 H, H-3 and H-5).

1-[(*tert*-Butyldimethylsilyl)oxy]-3,5-dichlorobenzene (1l). This compound was prepared from 3,5-dichlorophenol in 91% yield: bp 84–85 °C/0.4 mm; ^{1}H NMR δ 0.21 (s, 6 H, $SiMe_2$), 0.97 (s, 9 H, *t*-Bu), 6.73 (d, 2 H, H-2 and H-6, J = 1.8 Hz), 6.96 (t, 1 H, H-4, J = 1.8 Hz).

1,2-Bis[(*tert*-butyldimethylsilyl)oxy]-4-chlorobenzene (1n). This compound was prepared from 4-chlorocatechol in a similar manner as described above except for the reagent ratio [4-chlorocatechol (1.0 equiv), TBDMSCl (2.0 equiv), imidazole (2.1 equiv)] and purified by Kugelrohr distillation (95% yield): bp 140 °C (oven temperature)/0.2 mm; ^{1}H NMR δ 0.18 (s, 6 H, $SiMe_2$), 0.20 (s, 6 H, $SiMe_2$), 0.97 (s, 9 H, *t*-Bu), 0.98 (s, 9 H, *t*-Bu), 6.72–6.81 (m, 3 H, Ar H).

1-(Phenylsulfonyl)-1-(trimethylsilyl)ethene (2). With ice cooling, 80% *m*-chloroperbenzoic acid (37.10 g, 172 mmol) was added portionwise to a mechanically stirred solution of 1-(phenylthio)-1-(trimethylsilyl)ethene[23] (17.95 g, 86 mmol) in CH_2Cl_2 (300 mL). After being stirred for 5 h, the reaction mixture was washed sequentially with $NaHCO_3$, $Na_2S_2O_3$, and $NaHCO_3$ solutions and then with water. After drying over Na_2SO_4, the solution was evaporated. The residual oil was purified by Kugelrohr distillation, to give **2** (19.60 g, 95%): bp 130 °C (oven temperature)/0.1 mm; IR (neat) 1305, 1150 (SO_2) cm^{-1}; ^{1}H NMR δ 0.15 (s, 9 H, $SiMe_3$), 6.25 (s, 1 H, vinylic H), 6.72 (s, 1 H, vinylic H), 7.53 (m, 2 H, SO_2Ph), 7.60 (m, 1 H, SO_2Ph), 7.85 (m, 2 H, SO_2Ph).

Ortho-Lithiation of Chlorobenzenes 1 and Subsequent Reaction with 1-(Phenylsulfonyl)-1-(trimethylsilyl)ethene (2). General Procedure. A dried 50-mL, two-necked, round-bottomed flask fitted with a gas inlet, septum, and magnetic stirring bar was flashed with N_2 and charged with the chlorobenzene (2.0 mmol) and dry THF (10 mL). The flask was immersed in a Dewar cooling bath filled with a 1:1 mixture of MeOH and acetone which was cooled to −110 °C with liquid N_2. *sec*-BuLi (1.75 mL, 2.1 mmol, 1.2 M in cyclohexane) was added slowly via syringe, and the mixture was stirred for 1–3 h (see Table I), the bath temperature being kept at −105 (±5) °C [internal temperature −95 (±5) °C] with occasional addition of liquid N_2. After the bath was cooled to −110 °C, a solution of **2** (505 mg, 2.1 mmol) in THF (2 mL) was added via syringe. The reaction mixture was allowed to warm to ca. −50 °C and quenched with water. TBAF (2.1 mL, 2.1 mmol, 1.0 M in THF) was added to the mixture, and the whole was evaporated. When the starting chlorobenzene had a TBDMSO group, an additional 2 or 4 mL, depending on the number of protecting groups, of TBAF solution was added. Water was added to the residue, and the products were extracted with ether or AcOEt. In cases where the product possessed a phenolic hydroxyl group, the residue was acidified with 10% HCl before extraction. The extract was washed with water and brine solution, dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography, to give the Michael adduct **3**. The solvent systems for the chromatography were as follows: 3:1 hexane–AcOEt for **3a**, **3b**, **3d**; 2:1 hexane–AcOEt for **3m**, **3m′**; 1:1 hexane–AcOEt for **3i**; 10:1 toluene–AcOEt for **3h**, **3j**, **3k**; CH_2Cl_2 for **3c**, **3f**; 30:1 CH_2Cl_2–acetone for **3e**; and 10:1 CH_2Cl_2–acetone for **3g**.

1-Chloro-2-[2-(phenylsulfonyl)ethyl]benzene (3a): mp 44–45 °C (lit.[12] mp 45–47 °C); IR (KBr) 1295, 1155, 1140 (SO_2) cm^{-1}; ^{1}H NMR δ 3.11 (m, 2 H, CH_2), 3.37 (m, 2 H, CH_2), 7.15 (m, 3 H, Ar H), 7.26 (m, 1 H, Ar H), 7.56 (m, 2 H, SO_2Ph), 7.66 (m, 1 H, SO_2Ph), 7.94 (m, 2 H, SO_2Ph).

2-Chloro-1-methoxy-3-[2-(phenylsulfonyl)ethyl]benzene (3b): mp 118.5–119 °C (ether); IR (KBr) 1305, 1155 (SO_2) cm^{-1}; ^{1}H NMR δ 3.13 (m, 2 H, CH_2), 3.38 (m, 2 H, CH_2), 3.85 (s, 3 H, OMe), 6.80 (m, 2 H, H-4 and H-6), 7.13 (t, 1 H, H-5, $J \simeq 8$ Hz), 7.57 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.95 (m, 2 H, SO_2Ph). Irradiation of OMe protons enhanced the intensity (5.4%) of the peak assignable to H-6 due to ^{1}H{^{1}H} NOE.

2-Chloro-3-[2-(phenylsulfonyl)ethyl]phenol (3c): mp 136–139 °C (AcOEt–hexane); IR (KBr) 3330 (OH), 1305, 1290, 1150 (SO_2) cm^{-1}; ^{1}H NMR δ 3.11 (m, 2 H, CH_2), 3.36 (m, 2 H, CH_2), 6.01 (s, 1 H, OH), 6.73 (dd, 1 H, H-6, J = 7.7 and 1.5 Hz), 6.88 (dd, 1 H, H-4, J = 8.1 and 1.5 Hz), 7.06 (t, 1 H, H-5, $J \simeq 8$ Hz), 7.58 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.94 (m, 2 H, SO_2Ph).

1-Chloro-3-methoxy-2-[2-(phenylsulfonyl)ethyl]benzene (3d): mp 118.5–119.5 °C (AcOEt–hexane); IR (KBr) 1295, 1150 (SO_2) cm^{-1}; ^{1}H NMR δ 3.15 (m, 2 H, CH_2), 3.29 (m, 2 H, CH_2), 3.74 (s, 3 H, OMe), 6.70 (dd, 1 H, H-4, J = 8.4 and 1 Hz), 6.91 (dd, 1 H, H-6, J = 8.1 and 1 Hz), 7.10 (t, 1 H, H-5, $J \simeq 8$ Hz), 7.59 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.98 (m, 2 H, SO_2Ph).

3-Chloro-4-[2-(phenylsulfonyl)ethyl]phenol (3e): mp 69–70 °C; IR (KBr) 3390 (OH), 1305, 1155, 1140 (SO_2) cm^{-1}; ^{1}H NMR δ 3.01 (m, 2 H, CH_2), 3.35 (m, 2 H, CH_2), 6.66 (dd, 1 H, H-6, J = 8.4 and 2.6 Hz), 6.82 (d, 1 H, H-2, J = 2.6 Hz), 6.96 (d, 1 H, H-5, J = 8.4 Hz), 7.57 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.91 (m, 2 H, SO_2Ph).

4-Chloro-1-methoxy-2-[2-(phenylsulfonyl)ethyl]benzene (3f): mp 128–130 °C (AcOEt–hexane); IR (KBr) 1300, 1285, 1150 (SO_2) cm^{-1}; ^{1}H NMR δ 2.96 (m, 2 H, CH_2), 3.36 (m, 2 H, CH_2), 3.72 (s, 3 H, OMe), 6.68 (d, 1 H, H-6, J = 8.8 Hz), 7.01 (d, 1 H, H-3, J = 2.6 Hz), 7.12 (dd, 1 H, H-5, J = 8.8 and 2.6 Hz), 7.56 (m, 2 H, SO_2Ph), 7.65 (m, 1 H, SO_2Ph), 7.91 (m, 2 H, SO_2Ph). Irradiation of OMe protons enhanced the intensity (6.2%) of the doublet assignable to H-6 due to ^{1}H{^{1}H} NOE.

4-Chloro-3-[2-(phenylsulfonyl)ethyl]phenol (3g): mp 97–98.5 °C (AcOEt–hexane); IR (KBr) 3420, 3380 (OH), 1290, 1150 (SO_2) cm^{-1}; ^{1}H NMR δ 3.05 (m, 2 H, CH_2), 3.38 (m, 2 H, CH_2), 5.47 (br s, 1 H, OH), 6.65 (dd, 1 H, H-6, J = 8.8 and 2.9 Hz), 6.70 (d, 1 H, H-2, J = 2.9 Hz), 7.12 (d, 1 H, H-5, J = 8.8 Hz), 7.58 (m, 2 H, SO_2Ph), 7.68 (m, 1 H, SO_2Ph), 7.94 (m, 2 H, SO_2Ph).

1,3-Dichloro-4-methoxy-2-[2-(phenylsulfonyl)ethyl]benzene (3h): mp 115–116 °C (AcOEt–hexane); IR (KBr) 1295, 1155, 1135 (SO_2) cm^{-1}; ^{1}H NMR δ 3.30 (s, 4 H, CH_2CH_2), 3.85 (s, 3 H, OMe), 6.76 (d, 1 H, H-5, J = 8.8 Hz), 7.20 (d, 1 H, H-6, J = 8.8 Hz), 7.60 (m, 2 H, SO_2Ph), 7.69 (m, 1 H, SO_2Ph), 7.99 (m, 2 H, SO_2Ph).

2-Chloro-1,4-dimethoxy-3-[2-(phenylsulfonyl)ethyl]benzene (3i): mp 90.5–91 °C (ether); IR (KBr) 1305, 1165, 1145 (SO_2) cm^{-1}; ^{1}H NMR δ 3.18 (m, 2 H, CH_2), 3.27 (m, 2 H, CH_2), 3.70 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 6.67 (d, 1 H, H-5 or H-6, J = 8.8 Hz), 6.75 (d, 1 H, H-5 or H-6, J = 8.8 Hz), 7.59 (m, 2 H, SO_2Ph), 7.68 (m, SO_2Ph), 7.98 (m, 2 H, SO_2Ph).

1-Chloro-3,5-dimethoxy-2-[2-(phenylsulfonyl)ethyl]benzene (3j): mp 93–94.5 °C (AcOEt–hexane); IR (KBr) 1310, 1155 (SO_2) cm^{-1}; ^{1}H NMR δ 3.05 (m, 2 H, CH_2), 3.24 (m, 2 H, CH_2), 3.68 (s, 3 H, OMe), 3.73 (s, 3 H, OMe), 6.28 (d, 1 H, H-4, J = 2.2 Hz), 6.44 (d, 1 H, H-6, J = 2.2 Hz), 7.58 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.96 (m, 2 H, SO_2Ph).

1,5-Dichloro-3-methoxy-2-[2-(phenylsulfonyl)ethyl]benzene (3k): mp 120–121 °C (AcOEt–hexane); IR (KBr) 1295, 1150 (SO_2) cm^{-1}; ^{1}H NMR δ 3.10 (m, 2 H, CH_2), 3.25 (m, 2 H, CH_2), 3.74 (s, 3 H, OMe), 6.70 (d, 1 H, H-4, J = 2.2 Hz), 6.94 (d, 1 H, H-6, J = 2.2 Hz), 7.59 (m, 2 H, SO_2Ph), 7.68 (m, 1 H, SO_2Ph), 7.96 (m, 2 H, SO_2Ph).

3,5-Dichloro-4-[2-(phenylsulfonyl)ethyl]phenol (3l). The crude product was purified by recrystallization from AcOEt–hexane: mp 168.5–169.5 °C; IR (KBr) 3340 (OH), 1290, 1145 (SO_2) cm^{-1}; ^{1}H NMR δ 3.20 (m, 2 H, CH_2), 3.27 (m, 2 H, CH_2), 5.76 (s, 1 H, OH), 6.78 (s, 2 H, H-2 and H-6), 7.60 (m, 2 H, SO_2Ph), 7.69 (m, 1 H, SO_2Ph), 7.98 (m, 2 H, SO_2Ph).

1-Chloro-3,4-dimethoxy-2-[2-(phenylsulfonyl)ethyl]benzene (3m): mp 122.5–123.5 °C (AcOEt–hexane); IR (KBr) 1300, 1145 (SO_2) cm^{-1}; ^{1}H NMR δ 3.11 (m, 2 H, CH_2), 3.30 (m, 2 H, CH_2), 3.68 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 6.72 (d, 1 H, H-5, J = 8.8 Hz), 7.01 (d, 1 H, H-6, J = 8.8 Hz), 7.60 (m, 2 H, SO_2Ph), 7.68 (m, 1 H, SO_2Ph), 7.99 (m, 2 H, SO_2Ph).

5-Chloro-1,2-dimethoxy-3-[2-(phenylsulfonyl)ethyl]benzene (3m′): mp 114–114.5 °C (ether); IR (KBr) 1320, 1310, 1140 (SO_2) cm^{-1}; ^{1}H NMR δ 2.95 (m, 2 H, CH_2), 3.34 (m, 2 H, CH_2), 3.65 (s, 3 H, OMe), 3.81 (s, 3 H, OMe), 6.67 (d, 1 H, H-6, J = 2.2 Hz), 6.75 (d, 1 H, H-4, J = 2.2 Hz), 7.58 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.94 (m, 2 H, SO_2Ph).

3-Methyl-1-(phenylsulfonyl)pentane (4): bp 140–150 °C (Kugelrohr distillation)/0.2 mm; IR (neat) 1310, 1150 (SO_2) cm^{-1}; ^{1}H NMR δ 0.82 (t, 3 H, CH_3, J = 7.2 Hz), 0.84 (d, 3 H, CH_3, J = 6.6 Hz), 1.08–1.78 (m, 5 H, CH_2 and CH), 3.02–3.16 (m, 2 H, CH_2), 7.57 (m, 2 H, SO_2Ph), 7.66 (m, 1 H, SO_2Ph), 7.92 (m, 2 H,

(23) Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852.

SO_2Ph).

2'-Chloro-3,6'-dimethoxy-2-[2-(phenylsulfonyl)ethyl]biphenyl (5). *sec*-BuLi (4.6 mL, 5.3 mmol, 1.15 M in cyclohexane) was added to a stirred solution of 3-chloroanisole (**1d**) (713 mg, 5.0 mmol) in dry THF (20 mL) under N_2 at −78 °C. After 1 h, a solution of 1-(phenylsulfonyl)-1-(trimethylsilyl)ethene (**2**) (1202 mg, 5.0 mmol) in THF (3 mL) was added. The reaction mixture was stirred overnight at −78 °C and warmed to ambient temperature. After quenching with water, TBAF (6.0 mL, 6.0 mmol, 1.0 M in THF) was added, and the whole was evaporated. Water was added to the residue, and the product was extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography (CH_2Cl_2), to give the biphenyl **5** (752 mg, 72%): mp 141–143 °C (AcOEt–hexane); IR (KBr) 1305, 1150 (SO_2) cm^{-1}; ^1H NMR δ 2.57–2.72 (m, 2 H, CH_2), 3.17–3.34 (m, 2 H, CH_2), 3.63 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 6.65 (dd, 1 H, Ar H, J = 7.7 and 0.7 Hz), 6.72 (d, 1 H, Ar H, J = 8.4 Hz), 6.84 (d, 1 H, Ar H, J = 7.7 Hz), 6.96 (dd, 1 H, Ar H, J = 8.1 and 0.7 Hz), 7.18 (t, 1 H, Ar H, $J \simeq 8$ Hz), 7.25 (t, 1 H, Ar H, $J \simeq 8$ Hz), 7.46 (m, 2 H, SO_2Ph), 7.59 (m, 1 H, SO_2Ph), 7.75 (m, 2 H, SO_2Ph); MS m/e 416 (M^+).

Methylation of the Phenolic Michael Adducts 3e, 3g, 3l, and 3n. The following procedures are representative.

2-Chloro-4-methoxy-1-[2-(phenylsulfonyl)ethyl]benzene (6e). A mixture of compound **3e** (2.03 g, 6.84 mmol), Me_2SO_4 (1.04 g, 8.25 mmol), K_2CO_3 (5.70 g, 41 mmol), and acetone (100 mL) was refluxed with stirring for 2 h. After cooling, NH_4OH was added to decompose excess Me_2SO_4, and the mixture was stirred for 2 h. After evaporation, water was added to the residue and the product was extracted with CH_2Cl_2. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by passage through a column of silica gel using CH_2Cl_2 as an eluent, to give 1.99 g (93%) of **6e**: mp 53–54 °C (ether); IR (KBr) 1305, 1145 (SO_2) cm^{-1}; ^1H NMR δ 3.06 (m, 2 H, CH_2), 3.35 (m, 2 H, CH_2), 3.76 (s, 3 H, OMe), 6.72 (dd, 1 H, H-5, J = 8.4 and 2.6 Hz), 6.84 (d, 1 H, H-3, J = 2.6 Hz), 7.08 (d, 1 H, H-6, J = 8.4 Hz), 7.58 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.94 (m, 2 H, SO_2Ph).

1-Chloro-4-methoxy-2-[2-(phenylsulfonyl)ethyl]benzene (6g). This compound was prepared from **3g** in 99% yield: mp 101–102 °C (AcOEt–hexane); IR (KBr) 1295, 1155, 1135 (SO_2) cm^{-1}; ^1H NMR δ 3.09 (m, 2 H, CH_2), 3.39 (m, 2 H, CH_2), 3.77 (s, 3 H, OMe), 6.69–6.74 (m, 2 H, H-3 and H-5), 7.19 (d, 1 H, H-6, J = 8.4 Hz), 7.60 (m, 2 H, SO_2Ph), 7.68 (m, 1 H, SO_2Ph), 7.96 (m, 2 H, SO_2Ph).

1,3-Dichloro-5-methoxy-2-[2-(phenylsulfonyl)ethyl]benzene (6l). This compound was prepared from **3l** in ca. 100% yield: mp 136–136.5 °C (AcOEt); IR (KBr) 1320, 1140 (SO_2) cm^{-1}; ^1H NMR δ 3.21 (m, 2 H, CH_2), 3.28 (m, 2 H, CH_2), 3.75 (s, 3 H, OMe), 6.81 (s, 2 H, H-4 and H-6), 7.60 (m, 2 H, SO_2Ph), 7.69 (m, 1 H, SO_2Ph), 7.99 (m, 2 H, SO_2Ph).

1-Chloro-4,5-dimethoxy-2-[2-(phenylsulfonyl)ethyl]benzene (6n). This compound was prepared from crude **3n**, which was not purified due to instability to atmospheric oxygen, and purified by column chromatography (hexane–AcOEt, 1:1): 78% overall yield from **1n**; mp 125.5–126.5 °C (AcOEt–hexane); IR (KBr) 1305, 1150 (SO_2) cm^{-1}; ^1H NMR δ 3.06 (m, 2 H, CH_2), 3.36 (m, 2 H, CH_2), 3.82 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 6.68 (s, 1 H, H-3), 6.77 (s, 1 H, H-6), 7.59 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.95 (m, 2 H, SO_2Ph).

Synthesis of Benzocyclobutenes 7. A General Procedure Using KNH_2 or $NaNH_2$ as a Base. A dried 100-mL, three-necked, round-bottomed flask equipped with a dry ice condenser, NH_3 gas inlet, septum, and magnetic stirring bar was flushed with N_2. The flask was immersed in a dry ice–acetone bath and filled with liquid NH_3 (ca. 100 mL). The cooling bath was removed. A small piece of K (or Na) was added to confirm that the liquid NH_3 was dry (blue color). Then, K (or Na) (10–12 mmol) was added to the flask. After 30 min of stirring, a trace amount of powdered $Fe(NO_3)_3 \cdot 9H_2O$ was added. When the blue color had disappeared, a solution of sulfone **3** or **6** (2 mmol) in dry THF (5 mL) was added. After being stirred for an appropriate period (see Table II), the reaction mixture was quenched by the careful addition of powdered NH_4Cl. When NH_3 had evaporated, water was added to the residue and the whole was extracted with CH_2Cl_2. The extract was washed with water, dried (Na_2SO_4), and evaporated. The residue was purified by column chromatography, to give the benzocyclobutene **7**. The solvent systems for the chromatography were as follows: CH_2Cl_2 for **7a**, **7d**, **7e**, **7j**; 2:1 hexane–AcOEt for **7m**; and 1:1 hexane–AcOEt for **7n**.

A Procedure Using LDA as a Base. *n*-BuLi (2.05 mL, 3.0 mmol, 1.46 M in hexanes) was added to a solution of diisopropylamine (0.42 mL, 3.0 mmol) in dry THF (30 mL) under N_2 at −78 °C with stirring. After 30 min, a solution of **6e** (or **6n**) (1.0 mmol) in THF (3 mL) was added. The reaction mixture was gradually warmed to ambient temperature (overnight) and stirred for an additional 3 h. After quenching with saturated NH_4Cl, the solvents were evaporated. The residue was extracted with AcOEt. The extract was washed with water, dried (Na_2SO_4), and evaporated. The crude product was purified by column chromatography (AcOEt–hexane, 2:1 or 1:1), to give benzocyclobutene **7e** (or **7n**).

1-(Phenylsulfonyl)benzocyclobutene (7a): mp 104–104.5 °C (ether) (lit.[12] mp 103.5–104.5 °C); IR (KBr) 1295, 1145 (SO_2) cm^{-1}; ^1H NMR δ 3.51 (m, 2 H, H-2), 4.93 (m, 1 H, H-1), 6.99 (d, 1 H, H-3 or H-6, J = 7.3 Hz), 7.06 (d, 1 H, H-3 or H-6, J = 7.0 Hz), 7.21–7.31 (m, 2 H, H-4 and H-5), 7.53 (m, 2 H, SO_2Ph), 7.65 (m, 1 H, SO_2Ph), 7.88 (m, 2 H, SO_2Ph); MS m/e 244 (M^+).

5-Methoxy-1-(phenylsulfonyl)benzocyclobutene (7e): mp 98–98.5 °C (AcOEt–ether–hexane); IR (KBr) 1295, 1145 (SO_2Ph) cm^{-1}; ^1H NMR δ 3.39 (dd, 1 H, H-2, J = 14 and 2.6 Hz), 3.41 (dd, 1 H, H-2, J = 14 and 4.4 Hz), 3.76 (s, 3 H, OMe), 4.87 (m, 1 H, H-1), 6.62 (d, 1 H, H-6, J = 2.2 Hz), 6.85 (dd, 1 H, H-4, J = 8.4 and 2.2 Hz), 6.96 (d, 1 H, H-3, J = 8.4 Hz), 7.54 (m, 2 H, SO_2Ph), 7.65 (m, 1 H, SO_2Ph), 7.89 (m, 2 H, SO_2Ph); MS m/e 274 (M^+).

3-Methoxy-1-(phenylsulfonyl)benzocyclobutene (7d): mp 75–76 °C (ether–hexane); IR (KBr) 1305, 1145 cm^{-1}; ^1H NMR δ 3.62 (dd, 1 H, H-2, J = 14 and 4.8 Hz), 3.63 (dd, 1 H, H-2, J = 14 and 2.9 Hz), 3.80 (s, 3 H, OMe), 4.89 (m, 1 H, H-1), 6.57 (d, 1 H, H-4, J = 7.3 Hz), 6.75 (d, 1 H, H-6, J = 8.4 Hz), 7.16 (dd, 1 H, H-5, J = 8.4 and 7.3 Hz), 7.54 (m, 2 H, SO_2Ph), 7.66 (m, 1 H, SO_2Ph), 7.89 (m, 2 H, SO_2Ph); MS m/e 274 (M^+).

4,5-Dimethoxy-1-(phenylsulfonyl)benzocyclobutene (7n): mp 132–132.5 °C (AcOEt–hexane); IR (KBr) 1300, 1145 (SO_2) cm^{-1}; ^1H NMR δ 3.34 (dd, 1 H, H-2, J = 14 and 2.5 Hz), 3.39 (dd, 1 H, H-2, J = 14 and 4.4 Hz), 3.81 (s, 3 H, OMe), 3.82 (s, 3 H, OMe), 4.83 (dd, 1 H, H-1, J = 4.4 and 2.5 Hz), 6.62 (s, 1 H, H-3 or H-6), 6.63 (s, 1 H, H-3 or H-6), 7.53 (m, 2 H, SO_2Ph), 7.65 (m, 1 H, SO_2Ph), 7.87 (m, 2 H, SO_2Ph); MS m/e 304 (M^+).

3,4-Dimethoxy-1-(phenylsulfonyl)benzocyclobutene (7m): mp 154–154.5 °C (AcOEt); IR (KBr) 1305, 1295, 1140 (SO_2) cm^{-1}; ^1H NMR δ 3.71 (m, 2 H, H-2), 3.82 (s, 3 H, OMe), 3.89 (s, 3 H, OMe), 4.85 (m, 1 H, H-1), 6.53 (d, 1 H, H-5, J = 7.7 Hz), 6.76 (d, 1 H, H-6, J = 7.7 Hz), 7.55 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.89 (m, 2 H, SO_2Ph); MS m/e 304 (M^+).

3,5-Dimethoxy-1-(phenylsulfonyl)benzocyclobutene (7j): mp 112–113.5 °C (ether); IR (KBr) 1305, 1290, 1145 (SO_2) cm^{-1}; ^1H NMR δ 3.51 (m, 2 H, H-2), 3.73 (s, 3 H, OMe), 3.77 (s, 3 H, OMe), 4.83 (m, 1 H, H-1), 6.23 (d, 1 H, H-4, J = 1.5 Hz), 6.32 (d, 1 H, H-6, J = 1.5 Hz), 7.55 (m, 2 H, SO_2Ph), 7.66 (m, 1 H, SO_2Ph), 7.90 (m, 2 H, SO_2Ph); MS m/e 304 (M^+).

5-Methoxy-2-[2-(phenylsulfonyl)ethyl]aniline (8): mp 135.5–136 °C (AcOEt–hexane); IR (KBr) 3370, 3325, 3230 (NH_2), 1290, 1140 (SO_2) cm^{-1}; ^1H NMR δ 2.89 (m, 2 H, CH_2), 3.33 (m, 2 H, CH_2), 3.72 (s, 3 H, OMe), 6.21 (d, 1 H, H-3, J = 2.6 Hz), 6.24 (dd, 1 H, H-5, J = 8.4 and 2.6 Hz), 6.83 (d, 1 H, H-6, J = 8.4 Hz), 7.58 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.94 (m, 2 H, SO_2Ph).

4,5-Dimethoxy-2-[2-(phenylsulfonyl)ethyl]aniline (9): mp 134–136 °C (AcOEt–hexane); IR (KBr) 3420, 3350 (NH_2), 1290, 1145, 1135 (SO_2) cm^{-1}; ^1H NMR δ 2.91 (m, 2 H, CH_2), 3.35 (m, 2 H, CH_2), 3.75 (s, 3 H, OMe), 3.79 (s, 3 H, OMe), 6.25 (s, 1 H, H-6), 6.48 (s, 1 H, H-3), 7.58 (m, 2 H, SO_2Ph), 7.67 (m, 1 H, SO_2Ph), 7.94 (m, 2 H, SO_2Ph).

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Supplementary Material Available: Analytical data of new compounds (2 pages). Ordering information is given on any current masthead page.