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# Reactions of Lithiated *ortho*-Toluamides and Related Compounds with Vinylsilanes: Syntheses of 1-Tetralones and 1-Naphthols

Mutsuhiro DATE,[a] Mitsuaki WATANABE,*[,b] and Sunao FURUKAWA[a]

*Faculty of Pharmaceutical Sciences,[a] Center for Instrumental Analysis,[b] Nagasaki University, 1–14 Bunkyo-machi, Nagasaki 852, Japan.*
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**The reaction of lithiated *ortho*-toluamides and related species with vinylsilanes was examined in order to develop a new, convenient synthesis of 1-tetralones and 1-naphthols.**

**Keywords** lithiation; *ortho*-toluamide; vinylsilane; 1-tetralone; Michael addition; phthalide; 1-naphthol

Deprotonation of the toluene methyl position is difficult under the usual lithiation conditions. However, if a methyl group is located in an *ortho*-position with respect to a directed metalation group, deprotonation from the *ortho*-methyl group takes place in preference to deprotonation from the benzene ring.[1] The generated benzylic anions can be used for carbon chain extension reactions by treatment with carbon electrophiles. We have already demonstrated the usefulness of *ortho*-toluamide anions for the syntheses of natural products, such as hydrangenol,[2] phyllodulcin,[2] and WS-5995A.[3]

Recently, the potential of the lithiated *ortho*-toluamides,[2-4] *ortho*-toluates,[5] and phthalides[6] as 1,4-dipole equivalents for organic syntheses has been proposed by Swenton *et al.*[7] These synthons have mainly been used for the one-pot synthesis of naphthols by reaction with various Michael acceptors.[5,6] In addition, *ortho*-toluamide anions have been used for the syntheses of isoquinolines by addition–cyclization with nitriles[4b] or Schiff bases.[4c]

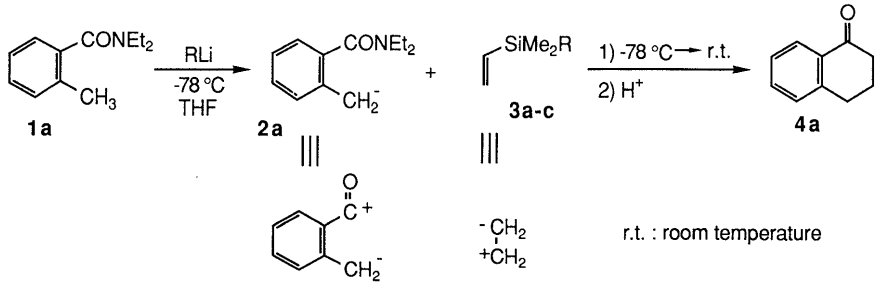
Stereoselective displacement of the silyl group of vinylsilanes with electrophiles is a well-known process.[8] Furthermore, nucleophilic addition of alkyl lithium reagents to vinylsilanes was reported by Cason and Brooks in 1952.[9] Recently, useful reactions such as conjugate addition of enolate anions to α-acetyl-substituted vinylsilanes and heteroconjugate addition to vinylsilanes activated by a phenylsulfonyl group on the α-position have been developed by Boeckman Jr., *et al.*[10] Stork and Ganem,[11] and Isobe *et al.*,[12] respectively. In 1980, Ager reported[13] that nucleophilic addition reactions to vinylsilanes at the β-position gave α-anions which could be trapped by electrophiles such as alkyl halides to give α,β-disubstituted compounds. These observations suggested that vinylsilanes could function as the required 1,2-dipole synthons. Thus, we envisaged that an anion on the carbon atom adjacent to the silyl group, generated by nucleophilic addition of *ortho*-toluamide anion to vinylsilanes, could attack[14] the adjacent amide group to form cyclic compounds. This reaction would constitute a new route to 1-tetralone derivatives, which are usually prepared by multi-step reactions such as Friedel–Crafts reaction (Chart 1).

*N*,*N*-Diethyl *ortho*-toluamide (**1a**) was lithiated in tetrahydrofuran (THF) at −78 °C to generate the red-purple lithio species (**2a**) which was subsequently treated with vinylsilanes (**3**) at −78 °C. The mixture was stirred for 1 h at room temperature. Acidic work-up and chromatographic purification gave 1-tetralone (**4a**) (Chart 1). Suitable reaction conditions (lithiating reagents, equivalents of reagents, and solvent) and substituents on the silyl atom were investigated and the results are summarized in Table I. When trimethylvinylsilane (**3a**; R = Me) was treated with **2a**, generated by lithium diisopropylamide (LDA) deprotonation of **1a**, **4a** was obtained in only 9% yield (Table I: run 1). When dimethylphenylvinylsilane (**3b**; R = Ph) was employed in a similar reaction, the yield of **4a** was increased

TABLE I. Synthesis of 1-Tetralone (**4a**) by the Reaction of Vinylsilanes (**3**) with *ortho*-Toluamide (**1a**)

| Run | RLi | 3 | R | Molar ratio 1a : RLi : 3 | 4a Yield (%) |
|---|---|---|---|---|---|
| 1 | LDA | **3a** | Me | 1.0 : 1.1 : 1.1 | 9 |
| 2 | *sec*-BuLi/TMEDA | **3a** | Me | 2.0 : 2.1 : 1.0 | 12 |
| 3 | LDA | **3b** | Ph | 1.0 : 1.1 : 2.0 | 19 |
| 4 | LDA | **3c** | OEt | 1.0 : 1.1 : 1.1 | 44 |
| 5 | LDA | **3c** | OEt | 2.0 : 2.1 : 1.0 | 54 |
| 6 | LCI | **3c** | OEt | 1.0 : 1.1 : 1.1 | 38 |
| 7 | *sec*-BuLi/TMEDA | **3c** | OEt | 1.0 : 1.1 : 1.1 | 40 |
| 8 | *sec*-BuLi/TMEDA | **3c** | OEt | 2.0 : 2.1 : 1.0 | 56 (13)[a] |

*a*) Ether was used as the solvent.




1,4-dipole synthon 1,2-dipole synthon

Chart 1

to 19% (Table I: run 3). In contrast to the above reactions, **4a** was obtained in higher yield (44%) using ethoxydimethylvinylsilane (**3c**; R=OEt) (Table I: run 4). Thus, among various substituents on the silicon atom of vinylsilanes, the ethoxy substituent (**3c**) was preferred over the methyl (**3a**) and the phenyl substituents (**3b**). A similar tendency has been observed in the addition of Grignard reagents to vinylsilanes by Buell *et al.*[15] We also examined the effect of the kind of lithiating reagent, the ratio of the reagent, and the solvent on the course of the reaction. When lithium *N*-isopropylcyclohexylamide (LICA) or *sec*-BuLi/tetramethylethylenediamine (TMEDA) instead of LDA was used in this reaction, **4a** was obtained in 38% or 40% yield, respectively, as shown in runs 6 and 7 (Table I). However, when 2.0 eq of **1a** and 2.1 eq of LDA or *sec*-BuLi/TMEDA was employed in a similar reaction, the yield of **4a** was increased to 54% or 56% (Table I: runs 5 and 8), respectively. Thus, the yield of **4a** was increased by the use of 2 eq of the lithiated **1a** and not affected by the type of lithiating reagent. In addition, when ether was used as a solvent (run 8), the yield of **4a** was decreased to 13% and addition of hexamethylphosphoric triamide (HMPT) did not influence the yield of **4a** (27% yield).

Various methoxy substituted 1-tetralones were synthesized in Chart 2 in moderate yields from the corresponding methoxy substituted *ortho*-toluamides (**1b**—**f**)[16] and ethoxydimethylvinylsilane (**3c**) using LDA as a base (Table II: runs 1—5). In the reaction of *N*,*N*-diethyl 6-methoxytoluamide (**1d**) with **3c**, 8-methoxy-1-tetralone was obtained in low yield presumably due to steric hindrance effects in the cyclization step. When α-substituted vinylsilanes (**3d** and **3e**) were employed in the reaction, 2-substituted 1-tetralones (**4g**—**k**) were obtained (Table II: runs 6—12).

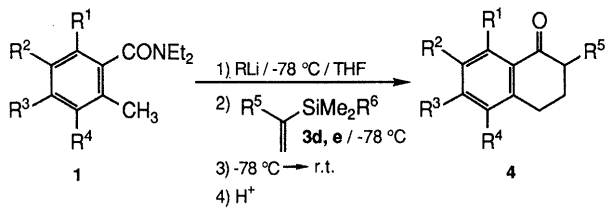



Chart 2

TABLE II. Synthesis of Substituted 1-Tetralones (**4**) by the Reaction of Vinylsilanes (**3**) with *ortho*-Toluamides (**1**)

| Run | *ortho*-Toluamide (**1**) | | | | | Vinylsilane (**3**) | | | RLi | 1-Tetralone (**4**) | | | | | | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $R^1$ | $R^2$ | $R^3$ | $R^4$ | | $R^5$ | $R^6$ | | | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | |
| 1 | **1b** | H | H | H | OMe | **3c** | H | OEt | LDA | **4b** | H | H | H | OMe | H | 62 |
| 2 | **1c** | H | H | OMe | H | **3c** | H | OEt | LDA | **4c** | H | H | OMe | H | H | 54 |
| 3 | **1d** | OMe | H | H | H | **3c** | H | OEt | LDA | **4d** | OMe | H | H | H | H | 8 |
| 4 | **1e** | H | H | OMe | OMe | **3c** | H | OEt | LDA | **4e** | H | H | OMe | OMe | H | 48 |
| 5 | **1f** | H | OMe | H | OMe | **3c** | H | OEt | LDA | **4f** | H | OMe | H | OMe | H | 45 |
| 6 | **1a** | H | H | H | H | **3d** | Ph | Me | LDA | **4g** | H | H | H | H | Ph | 35 |
| 7 | **1a** | H | H | H | H | **3d** | Ph | Me | *sec*-BuLi/TMEDA | **4g** | H | H | H | H | Ph | 70 |
| 8 | **1b** | H | H | H | OMe | **3d** | Ph | Me | LDA | **4h** | H | H | H | OMe | Ph | 50 |
| 9 | **1c** | H | H | OMe | H | **3d** | Ph | Me | LDA | **4i** | H | H | OMe | H | Ph | 25 |
| 10 | **1a** | H | H | H | H | **3e** | PhS | Me | LDA | **4j** | H | H | H | H | PhS | 43 |
| 11 | **1a** | H | H | H | H | **3e** | PhS | Me | *sec*-BuLi/TMEDA | **4j** | H | H | H | H | PhS | 54 |
| 12 | **1b** | H | H | H | OMe | **3e** | PhS | Me | LDA | **4k** | H | H | H | OMe | PhS | 35 |

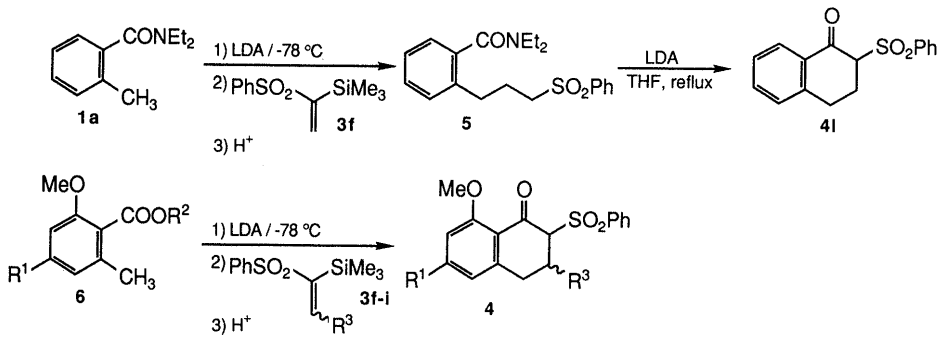



Chart 3

TABLE III. Synthesis of 2-Phenylsulfonyl-1-tetralones (**4**) by the Reaction of α-Phenylsulfonylvinylsilanes (**3**) with *ortho*-Toluates (**6**)

| Run | *ortho*-Toluate (**6**) | | | Vinylsilane (**3**) | | 1-Tetralone (**4**) | | | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | $R^1$ | $R^2$ | | $R^3$ | | $R^1$ | $R^2$ | |
| 1 | **6a** | H | Et | **3f** | H | **4m** | H | H | 91 |
| 2 | **6a** | H | Et | **3g** | Ph | **4n** | H | Ph | 93 |
| 3 | **6a** | H | Et | **3h** | *o*-MeO–$C_6H_4$ | **4o** | H | *o*-MeO–$C_6H_4$ | 65 |
| 4 | **6a** | H | Et | **3i** | *p*-MeO–$C_6H_4$ | **4p** | H | *p*-MeO–$C_6H_4$ | 98 |
| 5 | **6b** | MeO | Me | **3f** | H | **4g** | MeO | H | 96 |

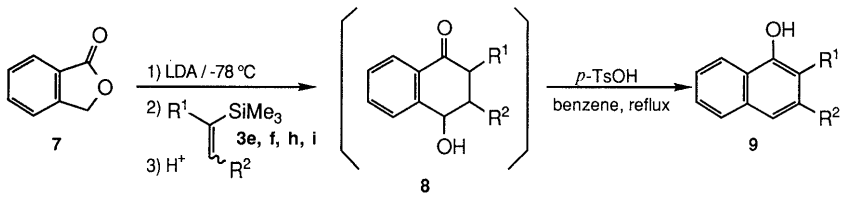



Chart 4

TABLE IV. Synthesis of 1-Naphthols (**9**) by the Reaction of Vinylsilanes (**3**) with Phthalide (**7**)

| Run | Vinylsilane (3) | | 1-Naphthol (9) | | Yield (%) |
|---|---|---|---|---|---|
| | | | $R^1$ | $R^2$ | |
| 1 | **3e** | **9a** | PhS | H | 75 |
| 2 | **3f** | **9b** | $PhSO_2$ | H | 96 |
| 3 | **3h** | **9c** | $PhSO_2$ | *o*-MeO-$C_6H_4$ | 60 |
| 4 | **3i** | **9d** | $PhSO_2$ | *p*-MeO-$C_6H_4$ | 93 |

Since the α-substituted vinylsilanes (**3d** and **3e**) were easily prepared starting from thioanisole or ketones according to the procedures of Gröbel and Seebach[17] or Chan *et al.*,[18] respectively, the above reaction represents a useful method for synthesis of substituted 1-tetralone derivatives.

1-Phenylsulfonyl-1-(trimethylsilyl)ethene (**3f**), readily prepared by the oxidation of **3e** using *m*-chloroperbenzoic acid (MCPBA), is a good Michael acceptor and has been utilized for a wide variety of synthetic processes such as the synthesis of sulfines by van der Leij and Zwanenburg,[19] and a total synthesis of maytansinol *via* heteroconjugate addition by Isobe *et al.*[12] The reaction of the lithio species (**2a**) with **3e** afforded a cyclic product (**4j**; 54% yield) as described in Table II. In contrast, the reaction of lithiated **1a** and **3f** afforded the Michael adduct (**5**) in 75% yield and none of the cyclic compound was detected. Although Michael reaction of lithiated **1a** with **3f** occurred smoothly, the nucleophilic reactivity of the generated α-carbanion is poorer than that of the α-carbanion generated from **2a** and **3e** owing to the electron-attracting effect of the phenylsulfonyl group. However, when the Michael adduct (**5**) was treated with LDA in refluxing THF for 3 h, 2-phenylsulfonyl-1-tetralone (**4l**) was obtained in 69% yield (Chart 3).

On the other hand, when the lithio species of ethyl *ortho*-toluate (**6a**) was used as the 1,4-dipole synthon, 8-methoxy-2-phenylsulfonyl-1-tetralone (**4m**) was directly obtained in high yield. In a similar manner, highly substituted 1-tetralones (**4n—q**) were synthesized starting from **6** and **3f—i** in a one-pot process (Chart 3 and Table III). Although this procedure is useful for the synthesis of 8-methoxy-substituted 1-tetralones, 1-tetralones lacking the 8-methoxy group can not be obtained by this method because of the instability of the toluate anions lacking the 6-methoxy group.[5b]

Finally, we briefly examined the reaction of phthalide (**7**) with vinylsilanes (**3**) as shown in Chart 4. The yellow phthalide anion, prepared from **7** and LDA at −78 °C, was condensed with **3e** to give 2-phenylthio-4-hydroxy-1-tetralone (**8**) which, without purification, was treated with *p*-toluenesulfonic acid in refluxing benzene to afford 2-phenylthio-1-naphthol (**9a**) in 75% overall yield. When **3f** or **3i** was employed in the reaction, 2-phenylsulfonyl-1-naphthols were synthesized in 96% or 93% yields (Table IV: runs 2 and 4), respectively.

In conclusion, we have shown that lithiated *ortho*-toluamides and related compounds behave as 1,4-dipole synthons in the reaction with vinylsilanes to give various 1-tetralone derivatives in a one-pot tandem Michael addition–cyclization process. The vinylsilanes were also useful building blocks in the reaction with phthalide anions to give 1-naphthol derivatives.

## Experimental

All melting points are uncorrected. The infrared (IR) spectra were obtained in KBr disk using a JASCO 810 spectrophotometer. The ultraviolet (UV) spectra were recorded in 95% ethanol on a Hitachi 323 spectrophotometer. The proton nuclear magnetic resonance ($^1$H-NMR) spectra were obtained with JEOL 90Q, JEOL JNM-PMX 60, and Hitachi R-600 spectrometers using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. The mass spectra (MS) were determined on a JEOL-DX 303 mass spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of the Center for Instrumental Analysis in Nagasaki University. All solvents used for lithiation reactions were freshly distilled from sodium benzophenone ketyl before use. Chromatography was carried out by flash chromatography on a column of Kieselgel 60 (230—400 mesh).

**Vinylsilane Derivatives** Trimethylvinylsilane (**3a**), dimethylphenylvinylsilane (**3b**), and ethoxydimethylvinylsilane (**3c**) were purchased from Shin-Etsu Chemical Co. Other vinylsilanes were prepared according to literature procedures or applications thereof.

**1-Phenyl-1-(trimethylsilyl)ethene (3d)** This was prepared in 52% yield according to a literature procedure.[18] bp 74 °C/7 mmHg (lit.[18] bp 73—77 °C/8 mmHg).

**1-Phenylthio-1-(trimethylsilyl)ethene (3e)** This was prepared in 95% yield according to a literature procedure.[13] bp 130 °C/18 mmHg (lit.[13] bp 122—123 °/15 mmHg).

**1-Phenylsulfonyl-1-(trimethylsilyl)ethene (3f)**[19] This was obtained in 96% yield by the oxidation of **3e** with MCPBA. bp 133 °C/2 mmHg. IR cm$^{-1}$: 1585, 1305, 1255, 1155. UV nm (log ε): 267 (2.98), 273 (2.99). $^1$H-NMR δ: 0.15 (s, 9H), 6.21 (s, 1H), 6.52 (s, 1H), 7.40—7.59 (m, 3H), 7.71—7.85 (m, 2H).

**2-Phenyl-1-phenylsulfonyl-1-(trimethylsilyl)ethene (3g)** This was prepared in 93% yield by the oxidation of 2-phenyl-1-phenylthio-1-(trimethylsilyl)ethene[17] with MCPBA. mp 72 °C (ether) (lit.[12] mp 89.2 °C for *Z* isomer and mp 85 °C for *E* isomer).

**2-(2′-Methoxyphenyl)-1-phenylsulfonyl-1-(trimethylsilyl)ethene (3h)** This was prepared in 93% yield from 2-(2′-methoxyphenyl)-1-phenylthio-1-(trimethylsilyl)ethene, which was obtained by applying a literature procedure,[17] by oxidation with MCPBA. mp 87 °C (ether/pentane). MS *m/z*: 346 ($M^+$). IR cm$^{-1}$: 1605, 1590, 1295, 1255, 1150. UV nm (log ε): 273 (3.89), 311 (sh) (3.60). $^1$H-NMR δ: 0.45 (s, 9H), 3.45 (s, 3H), 6.34—7.59 (m, 10H). *Anal.* Calcd for $C_{18}H_{22}O_3SSi$: C, 62.39; H, 6.40. Found: C, 62.85; H, 6.16.

**2-(4′-Methoxyphenyl)-1-phenylsulfonyl-1-(trimethylsilyl)ethene (3i)** This was prepared in 91% yield from 2-(4′-methoxyphenyl)-1-phenylthio-1-(trimethylsilyl)ethene, which was obtained by applying a literature method,[17] by oxidation with MCPBA. mp 116 °C (ether). MS *m/z*: 346 ($M^+$). IR cm$^{-1}$: 1605, 1585, 1305, 1255, 1175. UV nm (log ε): 299 (4.37). $^1$H-NMR δ: 0.39 (s, 9H), 3.72 (s, 3H), 6.61 (d, *J*=9.6 Hz, 2H), 7.12—7.63 (m, 5H), 7.75—8.08 (m, 3H). *Anal.* Calcd for $C_{18}H_{22}O_3SSi$: C, 62.39; H, 6.40. Found: C, 62.24; H, 6.43.

**Typical Procedure for the Syntheses of 1-Tetralones (4)** The following

procedure for the synthesis of 1-tetralone (**4a**) is representative; the other 1-tetralones were obtained similarly.

**1-Tetralone (4a) i) Using *sec*-BuLi/TMEDA** A solution of *sec*-BuLi (1.0 M in hexane, 6.3 ml, 6.3 mmol) was injected into a stirred solution of *N,N*-diethyl *ortho*-toluamide (**1a**, 1.15 g, 6 mmol) and TMEDA (0.95 ml, 6.3 mmol) in THF (50 ml) at −78 °C under a nitrogen atmosphere. The mixture was stirred at −78 °C for 1 h. A solution of ethoxydimethylvinylsilane (**3c**, 0.39 g, 3 mmol) in THF (20 ml) was injected into the mixture at −78 °C and the cooling bath was removed. After being stirred for a further 1 h, the reaction mixture was quenched with saturated $NH_4Cl$ solution, acidified with 10% HCl, and then evaporated to give a residue. The residue was extracted with ether and the extract was dried ($Na_2SO_4$) and evaporated to give crude **4a**, which was chromatographed over silica gel using $CH_2Cl_2$ as an eluent. Further purification by distillation gave pure **4a** (0.25 g, 56%). bp 115 °C/7 mmHg. MS *m/z*: 146 ($M^+$). IR $cm^{-1}$: 1680 (C=O). UV nm (log ε): 249 (4.07), 295 (3.27). $^1$H-NMR δ: 1.95—2.28 (m, 2H), 2.43—2.67 (m, 2H), 2.90 (t, *J*=5.0 Hz, 2H), 6.98—7.35 (m, 3H), 7.83—7.93 (m, 1H).

**ii) Using LDA or LICA** A hexane solution of *n*-BuLi (1.20 M, 5.25 ml, 6.3 mmol) was injected into a stirred solution of diisopropylamine (0.88 ml, 6.3 mmol) or *N*-isopropylcyclohexylamine (1.0 ml, 6.3 mmol) in THF (30 ml) at 0 °C under a nitrogen atmosphere for generation of LDA or LICA, respectively. The mixture was stirred for 30 min at the same temperature and then cooled to −78 °C. A solution of **1a** (1.15 g, 6 mmol) in THF (20 ml) was injected into the solution of LDA or LICA and stirred for 1 h at −78 °C. Then a solution of **3c** (0.39 g, 3 mmol) was injected into the above red-purple solution. After removal of the cooling bath, the mixture was allowd to warm to room temperature over 1 h. Standard work-up afforded crude **4a**, which was purified by chromatography ($CH_2Cl_2$ as eluent) and distillation to give pure **4a** (0.24 g, 54% using LDA; 0.17 g, 38% using LICA).

**5-Methoxy-1-tetralone (4b)** mp 86—87 °C (hexane) (lit.[20a] mp 89—89.5 °C, lit.[20b] mp 92—93 °C, lit.[20c] mp 87—88 °C). MS *m/z*: 176 ($M^+$). IR $cm^{-1}$: 1685 (C=O). UV nm (log ε): 225 (4.36), 257 (3.93), 317 (3.38). $^1$H-NMR δ: 1.90—2.22 (m, 2H), 2.47—2.92 (m, 4H), 3.87 (s, 3H), 6.80 (dd, *J*=8.0, 2.0 Hz, 1H), 7.15 (t, *J*=8.0 Hz, 1H), 7.57 (dd, *J*=8.0, 2.0 Hz, 1H). *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.06; H, 6.96.

**6-Methoxy-1-tetralone (4c)** mp 78 °C (ether/pentane) (lit.[21a] mp 80 °C. lit.[21b] mp 76—78 °C, lit.[21c] mp 77—78.5 °C, lit.[21d] mp 75—77 °C). MS *m/z*: 176 ($M^+$). IR $cm^{-1}$: 1680 (C=O). UV nm (log ε): 225 (3.45), 230 (sh) (3.42), 276 (3.54). $^1$H-NMR δ: 1.95—2.23 (m, 2H), 2.38—2.58 (m, 2H), 2.87 (t, *J*=6.0 Hz, 2H), 3.82 (s, 3H), 6.63 (d, *J*=2.0 Hz, 1H), 6.73 (dd, *J*=8.0, 2.0 Hz, 1H), 7.87 (d, *J*=8.0 Hz, 1H).

**8-Methoxy-1-tetralone (4d)** bp 140 °C/0.9 mmHg (lit.[5e] bp 94—96 °C/0.02 mmHg). MS *m/z*: 176 ($M^+$). IR $cm^{-1}$: 1675 (C=O). UV nm (log ε): 257 (3.23), 319 (2.89). $^1$H-NMR δ: 1.66—2.15 (m, 2H), 2.38—2.54 (m, 2H), 2.70—2.97 (m, 2H), 3.72 (s, 3H), 6.61—6.74 (m, 2H), 7.20 (t, *J*=6.0 Hz, 1H).

**5,6-Dimethoxy-1-tetralone (4e)** mp 84 °C (ether/pentane). MS *m/z*: 206 ($M^+$). IR $cm^{-1}$: 1675 (C=O). UV nm (log ε): 230 (4.21), 280 (4.13). $^1$H-NMR δ: 1.93—2.23 (m, 2H), 2.37—2.56 (m, 2H), 2.79—2.97 (m, 2H), 3.72 (s, 3H), 3.86 (s, 3H), 6.73 (d, *J*=8.0 Hz, 1H), 7.66 (d, *J*=8.0 Hz, 1H). *Anal.* Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.84; H, 6.69.

**5,7-Dimethoxy-1-tetralone (4f)**[22] mp 150 °C (ether/pentane). MS *m/z*: 206 ($M^+$). IR $cm^{-1}$: 1675 (C=O). UV nm (log ε): 250 (3.68), 310 (3.55). $^1$H-NMR δ: 1.92—2.21 (m, 2H), 2.42—2.83 (m, 4H), 3.77 (s, 6H), 6.43 (d, *J*=2.0 Hz, 1H), 6.95 (d, *J*=2.0 Hz, 1H). *Anal.* Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.88; H, 6.89.

**2-Phenyl-1-tetralone (4g)** mp 75—76 °C (hexane/ether). MS *m/z*: 222 ($M^+$). IR $cm^{-1}$: 1680 (C=O). UV nm (log ε): 250 (3.66), 295 (2.83). $^1$H-NMR δ: 2.18—2.53 (m, 2H), 2.94—3.14 (m, 2H), 3.57 (t, *J*=7.0 Hz, 1H), 7.03—7.57 (m, 8H), 7.95—8.16 (m, 1H). *Anal.* Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.80; H, 6.34.

**5-Methoxy-2-phenyl-1-tetralone (4h)** mp 153 °C (ether). MS *m/z*: 252 ($M^+$). IR $cm^{-1}$: 1690 (C=O). UV nm (log ε): 242 (4.14), 283 (3.48). $^1$H-NMR δ: 2.36 (dd, *J*=8.0, 5.0 Hz, 2H), 2.90 (t, *J*=5.0 Hz, 1H), 2.99 (t, *J*=5.0 Hz, 1H), 3.63 (d, *J*=8.0 Hz, 1H), 3.76 (s, 3H), 6.93 (dd, *J*=7.2, 1.8 Hz, 1H), 7.07—7.40 (m, 6H), 7.68 (dd, *J*=7.2, 1.8 Hz, 1H). *Anal.* Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.93. Found: C, 80.82; H, 6.99.

**6-Methoxy-2-phenyl-1-tetralone (4i)** mp 108 °C (ether/pentane). MS *m/z*: 252 ($M^+$). IR $cm^{-1}$: 1675 (C=O). UV nm (log ε): 226 (4.08), 278 (4.22). $^1$H-NMR δ: 2.00—2.51 (m, 2H), 2.73—2.93 (m, 2H), 3.55 (d, *J*=8.0 Hz, 1H), 3.70 (s, 3H), 6.72—6.82 (m, 2H), 6.87—7.42 (m, 5H), 7.95 (dd, *J*=7.2, 1.8 Hz, 1H). *Anal* Calcd for $C_{17}H_{16}O_2$ 1/4$H_2O$: C, 79.50; H, 6.28. Found: C, 79.34; H, 6.50.

**2-Phenylthio-1-tetralone (4j)** Oil. MS *m/z*: 254 ($M^+$). IR $cm^{-1}$: 1680 (C=O). UV nm (log ε): 252 (4.20), 2.91 (sh) (3.52). $^1$H-NMR δ: 2.13—2.36 (m, 2H), 2.70—3.50 (m, 2H), 3.91 (t, *J*=6.0 Hz, 1H), 6.93—7.44 (m, 8H), 7.77—8.02 (m, 1H). *Anal.* Calcd for $C_{16}H_{14}OS$: C, 75.55; H, 5.55; S, 12.61. Found: C, 75.74; H, 5.57; S, 12.50.

**5-Methoxy-2-phenylthio-1-tetralone (4k)** mp 126 °C (ether/pentane). MS *m/z*: 284 ($M^+$). IR $cm^{-1}$: 1680 (C=O). UV nm (log ε): 225.5 (4.38), 258 (4.12), 320 (3.46). $^1$H-NMR δ: 2.33—2.66 (m, 2H), 2.97—3.28 (m, 2H), 3.97 (s, 3H), 4.21 (t, *J*=6.0 Hz, 1H), 7.07—7.89 (m, 8H). *Anal.* Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67; S, 11.28. Found: C, 71.55; H, 5.72; S, 11.17.

**8-Methoxy-2-phenylsulfonyl-1-tetralone (4m)** mp 162 °C ($CH_2Cl_2$/ether). MS *m/z*: 316 ($M^+$). IR $cm^{-1}$: 1675 (C=O). UV nm (log ε): 268 (4.14), 329 (3.62). $^1$H-NMR δ: 2.50—2.79 (m, 2H), 2.87—3.05 (m, 1H), 3.19—3.39 (m, 1H), 3.84 (s, 3H), 4.10 (dd, *J*=6.4, 5.9 Hz, 1H), 6.81 (d, *J*=7.5 Hz, 1H), 6.84 (d, *J*=7.5 Hz, 1H), 7.27—7.65 (m, 4H), 7.88—7.99 (m, 2H). *Anal.* Calcd for $C_{17}H_{16}O_4S$: C, 64.54; H, 5.10; S, 10.14. Found: C, 64.45; H, 5.15; S, 10.06.

**8-Methoxy-3-phenyl-2-phenylsulfonyl-1-tetralone (4n)** mp 160 °C (ether). MS *m/z*: 392 ($M^+$). IR $cm^{-1}$: 1665 (C=O). UV nm (log ε): 268 (3.99), 274 (3.98), 332 (3.63). $^1$H-NMR δ: 2.98—3.25 (m, 2H), 3.60—3.66 (m, 1H), 3.89 (s, 3H), 4.31 (d, *J*=3.0 Hz, 1H), 6.78—6.88 (m, 2H), 7.16—7.63 (m, 9H), 7.76—7.87 (m, 2H). *Anal.* Calcd for $C_{23}H_{20}O_4S$: C, 70.40; H, 5.14; S, 8.16. Found: C, 70.13; H, 5.18; S, 8.20.

**8-Methoxy-3-(2′-methoxyphenyl)-2-phenylsulfonyl-1-tetralone (4o)** mp 201 °C (ether). MS *m/z*: 422 ($M^+$). IR $cm^{-1}$: 1670 (C=O). UV nm (log ε): 272 (4.07), 304 (3.60). $^1$H-NMR δ: 3.09—3.33 (m, 2H), 3.60—3.67 (m, 1H), 3.74 (s, 3H), 3.87 (s, 3H), 4.44 (d, *J*=3.0 Hz, 1H), 6.63—7.64 (m, 10H), 7.81—7.92 (m, 2H). *Anal* Calcd for $C_{24}H_{22}O_5S \cdot 1/4H_2O$: C, 67.50; H, 5.31; S, 7.51. Found: C, 67.36; H, 5.31; S, 7.44.

**8-Methoxy-3-(4′-methoxyphenyl)-2-phenylsulfonyl-1-tetralone (4p)** mp 166 °C (ether). MS *m/z*: 422 ($M^+$). IR $cm^{-1}$: 1675 (C=O). UV nm (log ε): 268 (4.06), 274 (4.04), 304 (3.62). $^1$H-NMR δ: 2.96—3.22 (m, 2H), 3.56—3.64 (m, 1H), 3.73 (s, 3H), 3.88 (s, 3H), 4.26 (d, *J*=3.0 Hz, 1H), 6.70—7.63 (m, 10H), 7.76—7.87 (m, 2H). *Anal.* Calcd for $C_{24}H_{22}O_5S$: C, 68.24; H, 5.25; S, 7.57. Found: C, 68.42; H, 5.29; S, 7.46.

**6,8-Dimethoxy-2-phenylsulfonyl-1-tetralone (4q)** mp 173 °C (MeOH). MS *m/z*: 346 ($M^+$). IR $cm^{-1}$: 1675 (C=O). UV nm (log ε): 285 (4.23), 314 (3.96). $^1$H-NMR δ: 2.44—2.70 (m, 2H), 2.81—2.93 (m, 1H), 3.19—3.39 (m, 1H), 3.78 (s, 6H), 4.03 (br s, 1H), 6.28 (s, 2H), 7.44—7.65 (m, 3H), 7.77—8.00 (m, 2H). *Anal.* Calcd for $C_{18}H_{18}O_5S$: C, 62.41; H, 5.24; S, 9.24. Found: C, 62.40; H, 5.36; S, 9.01.

**Reaction of *N,N*-Diethyl *ortho*-Toluamide (1a) with 1-Phenylsulfonyl-1-trimethylsilylethene (3f)** A solution of **3f** (0.79 g, 3.3 mmol) in THF (20 ml) was injected into a solution of lithiated *N,N*-diethyl *ortho*-toluamide (**2a**), generated from **1a** (0.57 g, 3 mmol) in THF (50 ml) with LDA (3.3 mmol), at −78 °C under a nitrogen atmosphere. The mixture was allowed to warm to room temperature and stirred for 2 h. Standard work-up afforded the crude Michael adduct (**5**), which was purified by chromatography ($CH_2Cl_2$) to give pure **5** (0.81 g, 75%). Viscose oil. MS *m/z*: 359 ($M^+$). IR $cm^{-1}$: 1635 (C=O). UV nm (log ε): 252 (sh) (3.35), 259 (sh) (3.31), 265 (3.31), 276 (3.21), $^1$H-NMR δ: 1.02 (t, *J*=7.1 Hz, 3H), 1.21 (t, *J*=7.3 Hz, 3H), 1.96—2.21 (m, 2H), 2.61—2.82 (m, 2H), 2.93—3.18 (m, 4H), 3.30—3.80 (m, 2H), 7.07—7.26 (m, 4H), 7.52—7.66 (m, 3H), 7.81—7.97 (m, 2H). *Anal.* Calcd for $C_{20}H_{25}NO_3S$: C, 66.82; H, 7.01; N, 3.90; S, 8.92. Found: C, 66.92; H, 6.98; N, 3.95; S, 8.73.

**Cyclization of the Michael Adduct (5); 2-Phenylsulfonyl-1-tetralone (4l)** A solution of **5** (0.99 g, 1.3 mmol) in THF (20 ml) was injected into a solution of LDA (2.6 mmol) at 0 °C under a nitrogen atmosphere. The mixture was refluxed for 3 h, then allowed to cool. The standard work-up afforded crude **4l**, which was purified by chromatography and recrystallization to give pure **4l** (0.26 g, 69%), mp 100 °C (ether). MS *m/z*: 286 ($M^+$). IR $cm^{-1}$: 1685 (C=O). UV nm (log ε): 248 (4.16), 391 (3.33). $^1$H-NMR δ: 2.33—3.52 (m, 4H), 4.10 (t, *J*=6.0 Hz, 1H), 7.10—7.66 (m, 6H), 7.82—8.01 (m, 3H). *Anal.* Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93; S, 11.20. Found: C, 66.90; H, 4.95; S, 11.31.

**Typical Procedure for the Syntheses of 1-Naphthols (9)** The following procedure for the synthesis of 1-naphthol (**9a**) is representative; the other 1-naphthols were obtained similarly.

**2-Phenylthio-1-naphthol (9a)** A solution of phthalide (**7**, 0.4 g, 3 mmol) in THF (20 ml) was injected into a solution of LDA (3.3 mmol) at −78 °C under a nitrogen atmosphere. The mixture was stirred for 1 h at −78 °C. A solution of **3e** (0.69 g, 3.3 mmol) in THF (20 ml) was injected into the mixture at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h at room temperature. Standard work-up

afforded crude **8**, which (without further purification) was used for the next dehydrative aromatization reaction. A solution of **8** and *p*-toluenesulfonic acid (0.01 g) in benzene (50 ml) was refluxed for 8 h. The reaction mixture was cooled to room temperature and washed with 5% $NaHCO_3$ and saturated NaCl. The organic layer was dried over $Na_2SO_4$ and evaporated to dryness. The residue was purified by chromatography ($CH_2Cl_2$ as eluent) to give **9a** (0.57 g, 75%), oil (lit.[23] oil). MS *m/z*: 252 ($M^+$). IR $cm^{-1}$: 3420 (OH). UV nm (log ε): 246 (4.25), 276 (sh) (3.48), 304 (sh) (3.81), 318 (3.21), 333 (3.14). $^1$H-NMR δ: 7.10 (s, 5H), 7.16 (s, 1H), 7.36—7.86 (m, 5H), 8.16—8.37 (m, 1H). *Anal* Calcd for $C_{16}H_{12}OS$: C, 76.16; H, 4.79; S, 12.71. Found: C, 76.35; H, 4.63; S, 12.59.

**2-Phenylsulfonyl-1-naphthol (9b)** mp 125 °C (MeOH). MS *m/z*: 284 ($M^+$). IR $cm^{-1}$: 3300 (OH). UV nm (log ε): 219 (3.96), 242 (3.96), 276 (sh) (3.20), 287 (sh) (3.09), 300 (sh) (2.94), 330 (3.11), 342 (3.12). $^1$H-NMR δ: 7.13—7.62 (m, 8H), 7.68—8.01 (m, 2H), 8.21—8.42 (m, 1H), 10.36 (br s, 1H). *Anal.* Calcd for $C_{16}H_{12}O_3S$: C, 67.60; H, 4.26; S, 11.26. Found: C, 67.38; H, 4.43; S, 11.10.

**3-(2′-Methoxyphenyl)-2-phenylfulfonyl-1-naphthol (9c)** Viscose oil. MS *m/z*: 390 ($M^+$). IR $cm^{-1}$: 3280 (OH). UV nm (log ε): 243 (4.43), 339 (3.67). $^1$H-NMR δ: 3.59 (s, 3H), 6.68—7.66 (m, 10H), 7.88—8.08 (m, 3H), 8.35—8.57 (m, 2H). *Anal.* Calcd for $C_{23}H_{18}O_4S$: C, 70.76; H, 4.65; S, 8.20. Found: C, 70.63; H, 4.54; S, 8.41.

**3-(4′-Methoxyphenyl)-2-phenylsulfonyl-1-naphthol (9d)** mp 120 °C (ether). MS *m/z*: 390 ($M^+$). IR $cm^{-1}$: 3350 (OH). UV nm (log ε); 221 (4.60), 240 (4.58), 315 (3.80), 345 (3.88). $^1$H-NMR δ: 3.84 (s, 3H), 7.23 (d, $J$=1.2 Hz, 2H), 7.36—7.73 (m, 5H), 7.91—8.06 (m, 3H), 8.37—8.59 (m, 2H), 8.97 (d, $J$=9.6 Hz, 2H), 9.88 (br s, 1H). *Anal.* Calcd for $C_{23}H_{18}O_4S$: C, 70.76; H, 4.65; S, 8.20. Found: C, 70.51; H, 4.77; S, 8.31.

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