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A New Efficient Route to 2-Substituted Azulenes Based on Sulfonyl Group Directed Lithiation[§]

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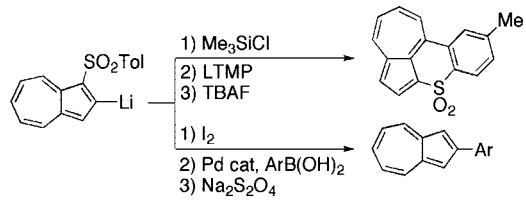

Directed lithiation of *p*-tolyl 1-azulenyl sulfone (**1**) at the 2-position of the azulenyl group was achieved by using lithium 2,2,6,6-tetramethylpiperidide (LTMP). The azulenyllithium thus generated could be efficiently trapped with various electrophiles to form 2-substituted derivatives **2** in moderate to good yields. *p*-Tolyl 2-trimethylsilyl-1-azulenyl sulfone (**2a**) was transformed into cyclic sulfone derivative **3a** through the directed lithiation in the *p*-tolyl group and subsequent intramolecular ring closure at the 8-position. 2-(Phenylsulfanyl)-1-azulenyl *p*-tolyl sulfone (**2b**) suffered from desulfonylation to form 2-phenylsulfanylazulene (**4**). The Suzuki coupling reaction of 2-iodo-1-azulenyl *p*-tolyl sulfone (**2d**) with arylboronic acids followed by desulfonylation efficiently gave 2-arylazulenes **10**.

Introduction

Azulene derivatives have attracted considerable attention in the design of biologically active molecules and advanced organic materials.[1,2] A practical method for the preparation of such compounds is therefore of great interest in synthetic organic chemistry. We have been interested in developing convenient synthetic methods for substituted azulenes.[3] Despite the excellent one-pot synthesis of azulene provided by Hafner,[4] chemical transformations to introduce a substituent into the ring skeleton of azulene have been very limited by its unique reactivity arising from the polarized π-electron system. In this regard, new azulene transformation techniques are highly desirable for the future development of this class of compounds.

Owing to the π-electron polarization, the five-membered ring of azulene suffers from electrophilic substitution exclusively at the 1- and 3-positions,[5] while the seven-membered ring undergoes preferential nucleophilic addition at the 4- and 8-positions, which competes with the addition at the 6-position, depending

[§] This paper is dedicated to Prof. Victor Snieckus.

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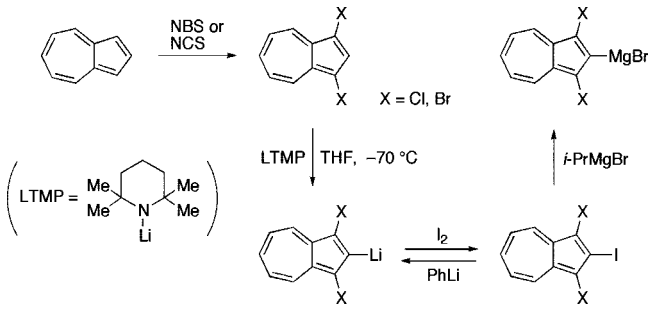
SCHEME 1



on the nature of the nucleophile.[6] It has been reported that the addition of methyl- and phenyllithiums takes place at the 4- and 8-positions in the normal fashion[6a] but bulky tritylsodium adds to the 6-position.[6b] Therefore, the introduction of substituents into positions that are less reactive or inert toward these reactions has always required multistep synthesis including the construction of the azulene skeleton.[7] As part of our efforts, we have recently reported convenient syntheses of 2- or 6-substituted azulenes.[8−10] In particular, it should be emphasized that azulenyllithium and azulenylmagnesium derivatives could be successfully generated,[8] since they had been considered for a long time to be incompatible with the highly electrophilic seven-membered ring of azulene (Scheme 1). This finding provided an important guide for generating σ-anions of azulene. Thus, an electron-withdrawing group effectively stabilizes these anionic species and facilitates the deprotonation or halogen−metal exchange.[11]

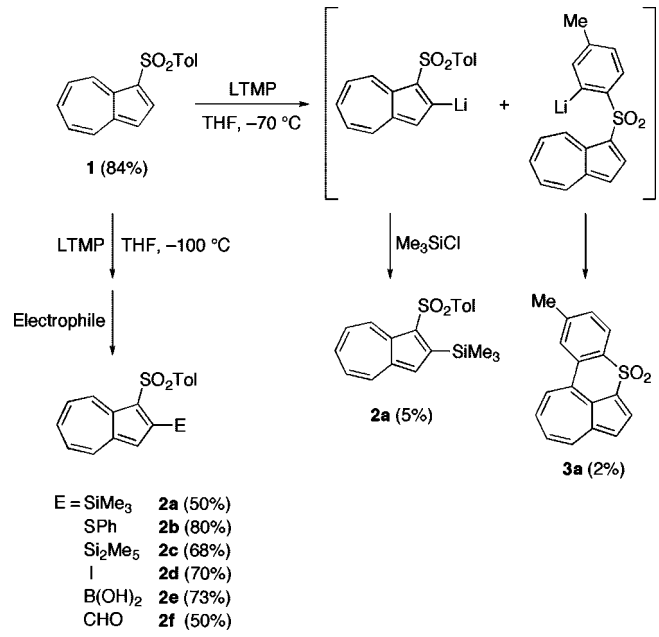
The sulfonyl group is a powerful directed metalation group (DMG) featuring strong electron-withdrawing properties. It has been utilized in the directed ortho lithiation of arenes for the elaboration of aromatic compounds.[12] Furthermore, sulfonylazulenes have attracted much attention in medicines.[1] The versatile application of the sulfonyl group prompted us to apply this metalation methodology to azulene systems. Herein, we report a convenient synthetic method of 2-substituted azulenes based on sulfonyl group directed lithiation.

Results and Discussion

As a substrate for the directed lithiation, we chose 1-azulenyl aryl sulfone **1**, which is easily prepared through a coupling reaction of azulene with sodium *p*-toluenesulfinate in the presence of copper salts (Scheme 2).[13] In addition to the proton at the 2-position of the five-membered ring, **1** possesses the acidic protons which are in close proximity to the sulfonyl oxygen atoms at the ortho-position of the tolyl ring and at the 8-position of the positively polarized seven-membered ring. To understand the site selectivity tendencies in the lithiation of **1**, we initially examined the reaction conditions used for 1,3-dihaloazulene. When a violet solution of **1** in THF was treated with LTMP (1.5 equiv) at −70 °C in the same solvent, the color of the reaction mixture immediately became reddish violet. Addition of chlorotrimethylsilane after 1 h at this temperature gave the desired product **2a** (5%) and cyclic azulenyl sulfone **3a** (2%), together with a 10% recovery of **1** (Scheme 2). The poor yield of **2a** suggests that the lithiated azulene is very reactive, while the formation of **3a** is an indication of the concomitant ortho-lithiation of the *p*-tolyl group. A competition experiment involving **1** and 1,3-dichloroazulene carried out at −100 °C revealed that trapping with D_2O gives deuterated products of **1** and 1,3-dichloroazulene in 52% and 18% yields, respectively (Scheme 3). This manifests that the sulfonyl group acts as a powerful lithiation group toward azulene systems. Next, to achieve efficient generation of azulenyllithium from **1**, we optimized the reaction conditions. Thus, by carrying out the lithiation at a lower temperature (−100 °C) and by adding a diluted solution of chlorotrimethylsilane dropwise at this temperature, the yield of **2a** increased dramatically to 50%, while at the same time only small quantities of **3a** were detected (Scheme 2). The azulenyllithium could be trapped with various electrophiles to give the corresponding 2-substituted products **2b**−**e** in moderate to good yields. An attempted trapping with DMF resulted in poor yield of **2f** (15%); however, the yield was improved to 50% by using more electrophilic ethyl formate. Through these trapping experiments, the 8-position did not suffer from any substitution reaction, which rules out the possibility of lithiation in the positively polarized seven-membered ring.

For comparison with the sulfonyl group directed lithiation at the 2-position, we tried the synthesis of sulfone **5a** from **2b**

SCHEME 2



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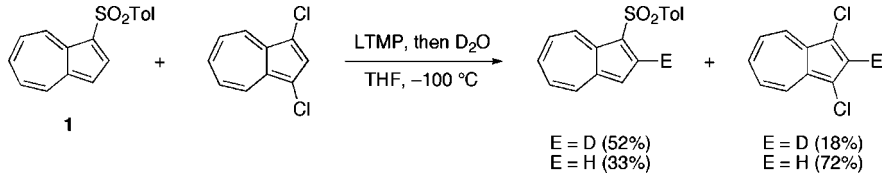
SCHEME 3



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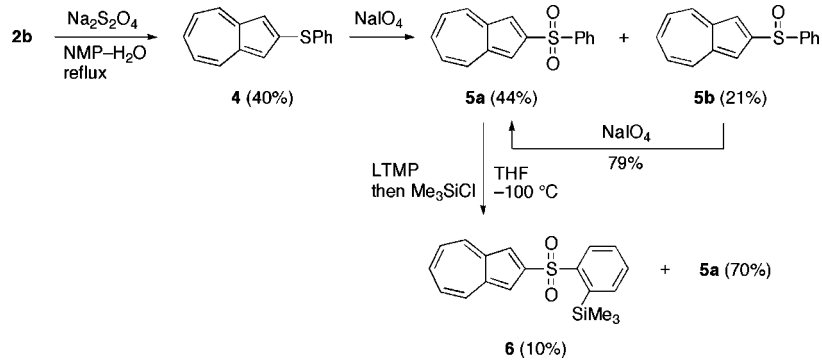
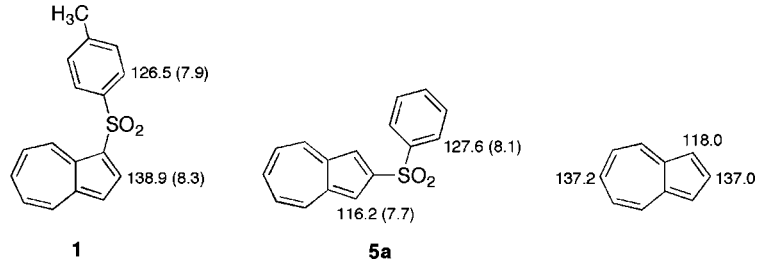


CHART 1. Assignment of ^{13}C and ^{1}H Chemical Shifts in $CDCl_3$[a]



[a] Proton shifts are in parentheses.

and attempted the lithiation at the 1-position (Scheme 4). Thus, **2b** was found to undergo desulfonylation[14] to give **4** when treated with $Na_2S_2O_4$ in the presence of $NaHCO_3$. Oxidation of **4** afforded a mixture of **5a** and **5b**. The reaction of **5a** with LTMP at −100 °C followed by addition of chlorotrimethylsilane, however, resulted in the formation of **6** along with recovery of **5a**. This result indicates that the ortho-lithiation in the phenyl group proceeds in preference to the lithiation at the 1-position. Hence, it can be concluded that the acidity of the ring protons decreases in the following order: 2-position > ortho-position >1-position.

Theoretical studies of the deprotonation enthalpies of azulene have shown that the protons at the 1- and 2-positions are less acidic than that at the 8-position, their acidities being comparable to that of the protons in benzene.[15] Although our experimental results with respect to the lithiation of **1** and **5a** are not in agreement with this previous study, the discrepancy may be accounted for by the following reasons. Thus, the 2-lithiated species from **1** forms the five-membered chelate ring through intramolecular oxygen−lithium interaction, which is geometrically more favorable than the six-membered ring[16] expected from the 8-lithiated species. Furthermore, the azulene nucleus is more sensitive to the substituent effects of the electron-withdrawing sulfonyl group than the benzene nucleus owing to the low aromatic resonance energy[17] of the former conjugation system, which lowers the π-electron density on the carbon at the 2-position to enhance the acidity of the attached proton. The difference in the reactivity toward lithiation between **1** and **5a** is attributed to the higher π-electron density of the ring carbon at the 1-position than at the 2-position owing to the π-polarization of the azulene nucleus.

The ^{13}C NMR studies of **1** and **5a** revealed that the tendency of the lithiation at the ring carbons corresponds with the order of their chemical shifts, as the 2-position (δ 138.9) > ortho-positions (δ 126.5 and 127.6) > 1-position (δ 116.2) (Chart 1). It is known that the ^{13}C chemical shifts of nonbenzenoid aromatic ions correlate linearly with the π-electron density relative to benzene.[18] If this empirical rule is applied, the 2-position is more electron-deficient than the ortho-positions and the 1-position is the most electron-rich. The electron deficiency at the 2-position may be clearly shown in azulene; the chemical shift of the carbon signal due to the 2-position (δ 137.0) is comparable to that due to its electron-deficient 6-position (δ 137.2) and is considerably deshielded compared

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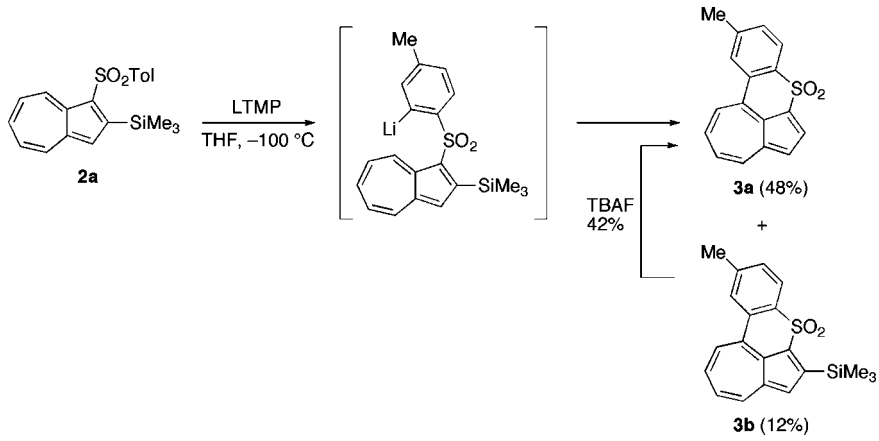

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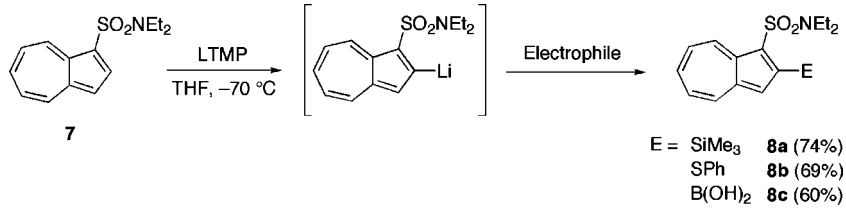

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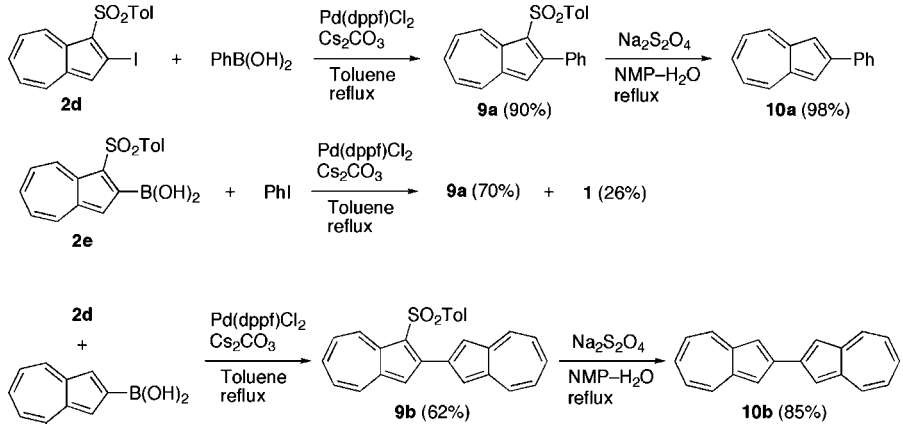

to that due to the electron-rich 1-position (δ 118.0). The ^{1}H NMR spectra of **1** and **5a** showed that a similar tendency is observed in the chemical shifts, as the 2-position (δ 8.3) > ortho-positions (δ 7.9 and 8.1) > 1-position (δ 7.7) (Chart 1). These spectroscopic findings seem to provide a measure about the acidity of the ring proton.

Recently, much attention has been focused on derivatives bearing an electron-deficient dibenzothiophene-*S*,*S*-dioxide moiety, owing to their electroluminescent,[19a] photoluminescent,[19b] and nonlinear optical properties.[19c] Although many examples have been reported for the synthesis of this class of compounds, analogous derivatives bearing an azulene skeleton, such as **3a**, have not appeared due to the lack of synthetic methods. Furthermore, azulene-fused heterocycles have attracted much attention from the viewpoint of their reactivity and structural characteristics.[3g,h] The unique electronic structure of nonalternant azulene, whose conjugation provides molecules with some useful physical properties,[2] led us to try the preferential synthesis of **3a**. Thus, the lithiation of **2a** with LTMP proceeds in the *p*-tolyl group to give **3a** directly as the main product (Scheme 5). Compound **3b** was easily converted to **3a** by deprotection of the silyl group with TBAF.

Sulfonamide **7** underwent sulfonyl group directed lithiation with LTMP at −70 °C to give the corresponding 2-substituted products **8** after trapping with electrophiles (Scheme 6). Unlike the lithiated derivative of **1**, that of **7** was stable even at −70 °C, suggesting that the stabilizing effect of the sulfonylamide group is stronger than that of the sulfonyl group.

Next, the synthetic utility of **2d** and **2e** was examined by Suzuki coupling (Scheme 7).[20] Recently, aryl-substituted azulenes have attracted much attention from the viewpoint of organic light-emitting devices such as hole-injecting materials.[2b] When **2d** was allowed to react with phenylboronic acid in the presence of Pd(dppf)Cl_2, BINAP, and Cs_2CO_3, **9a** was obtained in high yield. On the other hand, a similar coupling reaction of **2e** with iodobenzene also gave **9a**, but the yield was lower than that in the reaction of **2d** owing to the concomitant formation of **1**. Comparison of the reactivity between **2d** and **2e** reveals

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that the sulfonyl group facilitates the cross-coupling reaction in **2d**; however, it brings about the unfavorable deborylation in **2e**. Desulfonylation[14] of **9a** under reduction conditions proceeded smoothly to give the corresponding 2-substituted azulene **10a** in high yield. Encouraged by this result, we applied the efficient transformation of **2d** to the synthesis of biazulene **10b**. The importance of biaryls as components in liquid crystals and other novel materials is well established.[21] Furthermore, oligoazulenes have attracted enormous attention in recent years due to their utility as advanced materials.[22] Thus, the coupling reaction of **2d** with azulene-2-boronic acid[23] afforded **9b**, which was successfully converted into **10b**.

In summary, we have established a new method to introduce a substituent into the 2-position of an azulene skeleton based on sulfonyl group directed lithiation. Contrary to the previous theoretical study, the lithiation of **1** reveals that the ring proton at the 2-position is easily deprotonated compared to those at the 1-, 8-, and ortho-positions to afford substituted products **2**. The azulene analogue of dibenzothiophene-*S*,*S*-dioxide **3a** is selectively synthesized from **2a** by protection of the reactive 2-position with a trimethylsilyl group. Furthermore, the syntheses of 2-substituted azulenes **4** and **10** are achieved via desulfonylation. The present methods tolerate easy access to these useful derivatives that are difficult or impossible for their syntheses by conventional methods.

Experimental Section

Sulfonylation of Azulene. To a suspension of copper hydroxide (10 mmol) in water (20 mL) prepared from copper sulfate pentahydrate (10 mmol) and sodium hydroxide (20 mmol) was added at room temperature azulene (20 mmol) in CH_3CN (30 mL), *p*-toluenesulfinic acid sodium salt (20 mmol) (commercially available from Tokyo Chemical Industry Co., Ltd.) in water (20 mL), and copper sulfate pentahydrate (40 mmol) in water. The resulting mixture was stirred at 40 °C for 4 h. The reaction mixture was extracted with ether (3 × 10 mL) and the solvent was evaporated to leave a residue, which was purified by column chromatography on silica gel with hexane−AcOEt (5:1) to give **1**.

1-Azulenyl *p*-tolyl sulfone (1): 84%; reddish violet powder; mp 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (3H, s), 7.22 (2H, d, J = 8.2 Hz), 7.33 (1H, d, J = 4.2 Hz), 7.50 (1H, t, J = 10.0 Hz), 7.59 (1H, t, J = 10.0 Hz), 7.86 (1H, t, J = 10.0 Hz), 7.87 (2H, d, J = 8.2 Hz), 8.32 (1H, d, J = 4.2 Hz), 8.49 (1H, d, J = 10.0 Hz), 9.33 (1H, d, J = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 117.4, 124.1, 126.5, 127.5, 127.7, 129.6, 136.6, 137.2, 138.9, 139.5, 139.9, 141.3, 143.0, 144.2; IR (KBr) 1579, 1395, 1290, 1136, 740 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00. Found: C, 72.35; H, 5.07.

General Procedure for Directed Lithiation of 1 or 4 and Trapping with Electrophiles. A typical example is exemplified by the reaction with chlorotrimethylsilane. To a solution of **1** (1 mmol) in THF (5 mL) at −100 °C was added a solution of lithium 2,2,6,6-tetramethylpiperidide (1.2 mmol) prepared from 2,2,6,6-tetramethylpiperidine (1.2 mmol) and BuLi (1.2 mmol) in THF (5 mL) at −70 °C. The color of the solution immediately turned from violet to reddish violet showing the generation of an intermediate. To this solution thus obtained was added a solution of chlorotrimethylsilane (1 mmol) in THF (5 mL) and the resulting solution was stirred for 5 h during which time the temperature was gradually raised to ambient. The reaction was quenched with brine (10 mL) and the mixture was extracted with ether (3 × 7 mL). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−AcOEt (3:1) to give **2a**.

***p*-Tolyl 2-(trimethylsilyl)-1-azulenyl sulfone (2a):** 50%; violet powder; mp 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.50 (9H, s), 2.33 (3H, s), 7.18 (2H, d, J = 8.2 Hz), 7.48 (1H, t, J = 10.0 Hz), 7.49 (1H, t, J = 10.0 Hz), 7.54 (1H, s), 7.69 (2H, d, J = 8.2 Hz), 7.82 (1H, t, J = 10.0 Hz), 8.46 (1H, d, J = 10.0 Hz), 9.18 (1H, d, J = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 21.4, 126.0, 126.4, 127.3, 127.6 (2×), 129.3, 136.3, 138.8, 139.9, 140.0, 142.2, 142.5, 143.8, 155.8; IR (KBr) 1407, 1315, 1294, 1247, 1185, 1138, 1082, 842, 670, 539 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_2SSi$: C, 67.75; H, 6.25. Found: C, 67.45; H, 6.24.

2-(Phenylsulfanyl)-1-azulenyl *p*-tolyl sulfone (2b): 80%; red powder; mp 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 6.42 (1H, s), 7.26 (2H, d, J = 8.0 Hz), 7.32 (1H, t, J = 9.8 Hz), 7.50 (4H, m), 7.62 (3H, m), 7.91 (1H, d, J = 9.8 Hz), 8.04 (2H, d, J = 8.0 Hz), 9.29 (1H, d, J = 9.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 115.2, 118.0, 126.4, 128.5, 129.1, 129.5, 129.6, 129.8, 131.5, 132.9, 135.1, 135.3, 137.1, 140.0, 141.0, 142.3, 143.3, 153.3; IR (KBr) 1403, 1346, 1284, 1144, 1084, 795, 671, 539 cm^{-1}. Anal. Calcd for $C_{23}H_{18}O_2S_2$: C, 70.74; H, 4.65. Found: C, 70.64; H, 4.61.

2-(Pentamethyldisilyl)-1-azulenyl *p*-tolyl sulfone (2c): 68%; violet powder; mp 140−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (9H, s), 0.53 (6H, s), 2.33 (3H, s), 7.18 (2H, d, J = 8.3 Hz), 7.46 (3H, m), 7.68 (2H, d, J = 8.3 Hz), 7.79 (1H, t, J = 9.8 Hz), 8.43 (1H, d, J = 9.5 Hz), 9.05 (1H, d, J = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.6, −1.2, 21.3, 126.0 (2×), 127.1, 127.5, 127.6, 129.3, 135.5, 138.1, 139.5, 139.6, 142.2, 142.5, 143.8, 156.7; IR (KBr) 1406, 1285, 1242, 1133, 1084, 834, 672, 537 cm^{-1}.

2-Iodo-1-azulenyl *p*-tolyl sulfone (2d): 70%; dark red powder; mp 159−160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 7.23 (2H, d, J = 8.5 Hz), 7.53 (1H, t, J = 9.8 Hz), 7.60 (1H, s), 7.64 (1H, t, J = 10.1 Hz), 7.92 (2H, d, J = 8.5 Hz), 7.92 (1H, t, J = 9.3 Hz), 8.35 (1H, d, J = 9.7 Hz), 9.77 (1H, d, J = 10.2 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.9, 122.6, 126.3, 128.4, 129.6, 129.7, 129.8, 135.8, 138.3, 138.4, 139.2, 140.3, 141.4, 143.3, 143.4; IR (KBr) 1390, 1344, 1298, 1144, 1085, 668, 601, 536 cm^{-1}. Anal. Calcd for $C_{17}H_{13}IO_2S$: C, 50.01; H, 3.21. Found: C, 49.55; H, 2.92.

1-(*p*-Tolylsulfonyl)azulene-2-boronic acid (2e): 73%; violet powder; mp 170−172 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 2.31 (3H, s), 7.31 (2H, d, J = 8.0 Hz), 7.65 (1H, t, J = 9.6 Hz), 7.74 (1H, t, J = 10.2 Hz), 7.79 (1H, s), 7.88 (2H, s), 7.92 (2H, d, J = 8.4 Hz), 8.04 (1H, t, J = 9.6 Hz), 8.69 (1H, d, J = 9.6 Hz), 9.48 (1H, d, J = 10.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 121.5, 126.2, 126.9, 128.0, 128.3, 129.8, 135.6, 137.3, 139.4, 140.4, 141.4, 143.1, 144.2; one carbon signal was too weak to be assigned; IR (KBr) 1453, 1416, 1348, 1328, 1275, 1129, 1080, 744, 665, 562 cm^{-1}. Anal. Calcd for $C_{17}H_{15}BO_4S$: C, 62.60; H, 4.64. Found: C, 63.03; H, 4.83.

2-Formyl-1-azulenyl *p*-tolyl sulfone (2f): 50%; green powder; mp 211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 7.24 (2H, d, J = 8.1 Hz), 7.57 (1H, t, J = 9.7 Hz), 7.70 (1H, t, J = 10.1 Hz), 7.81 (1H, s), 7.83 (2H, d, J = 8.1 Hz), 8.00 (1H, t, J = 9.9 Hz), 8.64 (1H, d, J = 9.8 Hz), 9.75 (1H, d, J = 9.8 Hz), 11.05 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4. 118.9, 122.6, 126.2, 128.7, 129.3, 129.9, 139.4, 140.7, 141.2, 142.1, 142.7, 143.3, 143.7, 144.1, 190.4; IR (KBr) 1664, 1592, 1574, 1412, 1385, 1314, 1288, 1139, 1051 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55. Found: C, 69.91; H, 4.97.

10-Methyl-7-thianaphtho[3,2,1-*cd*]azulene-7,7-dioxide (3a): 48%; blue powder; mp 250−251 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (3H, s), 7.46 (1H, d, J = 4.4 Hz), 7.54 (1H, d, J = 8.0 Hz), 7.61 (1H, t, J = 10.0 Hz), 8.00 (1H, t, J = 10.0 Hz), 8.17 (1H, s), 8.30 (1H, d, J = 8.0 Hz), 8.40 (1H, d, J = 4.4 Hz), 8.45 (1H, d,

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(22) (a) Wang, F.; Lai, Y.-H.; Kocherginsky, N. M.; Kosteski, Y. Y. *Org. Lett.* **2003**, *5*, 995. (b) Dias, J. R. *J. Phys. Org. Chem.* **2007**, *20*, 395.

(23) Azulene-2-boronic acid was newly synthesized from its pinacol ester[9] by transesterification with phenylboronic acid. To read about the transesterification method, see: (a) Belfaitah, A.; Isly, M.; Carboni, B. *Tetrahedron Lett.* **2004**, *45*, 1969.

J = 10.0 Hz), 8.58 (1H, d, J = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 120.4, 124.6, 124.7, 127.9, 128.2, 130.6, 131.8, 132.9, 133.0, 136.1, 137.7, 138.4, 139.7, 142.2, 145.0; one carbon signal was too weak to be assigned; IR (KBr) 1385, 1270, 1258, 1202, 1132, 797, 610, 540 cm^{-1}. Anal. Calcd for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.31. Found: C, 72.99; H, 4.39.

2-Trimethylsilyl-10-methyl-7-thianaphtho[3,2,1-*cd*]azulene-7,7-dioxide (3b): 12%; dark blue powder; mp 253−255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 (9H, s), 2.56 (3H, s), 7.55 (1H, d, J = 7.8 Hz), 7.60 (1H, s), 7.61 (1H, t, J = 9.6 Hz), 7.98 (1H, t, J = 10.3 Hz), 8.14 (1H, s), 8.31 (1H, d, J = 8.0 Hz), 8.43 (1H, d, J = 10.7 Hz), 8.54 (1H, d, J = 8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0, 21.9, 124.5, 124.6, 125.4, 127.9, 128.2, 128.6, 131.7, 132.3, 133.3, 135.9, 137.5, 138.6, 139.0, 141.9, 145.0, 152.1. Anal. Calcd for $C_{20}H_{20}O_2SSi$: C, 68.14; H, 5.72. Found: C, 68.29; H, 5.99.

2-Phenylsulfanylazulene (4): 40%; violet crystals; mp 50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (2H, s), 7.14 (2H, t, J = 9.9 Hz), 7.44 (4H, m), 7.65 (2H, m), 8.04 (2H, t, J = 10.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.0, 124.2, 128.5, 129.4, 133.0, 133.3, 133.6, 135.1, 140.5, 148.1.

2-Azulenyl phenyl sulfone (5a): 44%; blue powder; mp 167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, t, J = 9.9 Hz), 7.52 (3H, m), 7.66 (2H, s), 7.76 (1H, t, J = 10.0 Hz), 8.06 (2H, d, J = 7.5 Hz), 8.45 (2H, d, J = 9.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.3, 125.2, 127.7, 129.2, 133.1, 139.7, 141.7, 141.9, 142.3, 146.4; IR (KBr) 1580, 1475, 1313, 1148, 802, 726, 636, 599 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2S$: C, 71.62; H, 4.51. Found: 71.64; H, 4.80.

2-Azulenyl phenyl sulfoxide (5b): 21%; blue solid; mp 92−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (2H, t, J = 9.8 Hz), 7.47 (3H, m), 7.49 (2H, s), 7.67 (1H, t, J = 9.8 Hz), 7.76 (2H, d, J = 7.4 Hz), 8.36 (2H, d, J = 9.7 Hz); ^{13}C NMR ($CDCl_3$) δ 113.9, 124.5, 124.8, 129.1, 130.8, 139.1, 139.5, 139.8, 145.4, 152.4; IR (KBr) 1578, 1392, 1086, 1045, 807, 748, 688, 489 cm^{-1}. Anal. Calcd for $C_{16}H_{12}OS$: C, 76.16; H, 4.79. Found: C, 75.90; H, 4.71.

2-Azulenyl 2-trimethylsilylphenyl sulfone (6): 10%, blue oil; ^{1}H NMR ($CDCl_3$) δ 0.43 (9H, s), 7.28 (2H, t, J = 9.9 Hz), 7.49 (1H, t, J = 7.5 Hz), 7.54 (2H, s), 7.55 (1H, t, J = 7.4 Hz), 7.74 (1H, t, J = 9.9 Hz), 7.81 (1H, d, J = 7.4 Hz), 8.02 (1H, d, J = 7.8 Hz), 8.42 (2H, d, J = 9.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.41, 116.0, 125.0, 129.4, 130.5, 132.0, 136.5, 139.5, 140.6, 141.3, 141.6, 146.5, 147.7. Anal. Calcd for $C_{19}H_{20}O_2SSi$: C, 67.02; H, 5.92. Found: C, 67.44; H, 6.08.

Preparation of *N*,*N*-Diethyl 1-Azulenylsulfonamide (7). To a solution of azulene (5 mmol) in dioxane (20 mL) was added SO_3·pyridine complex (3 mmol) and the mixture was stirred for 12 h at room temperature. After addition of triethylamine (3 mmol) and 2,4,6-trichloro-1,3,5-triazine (3 mmol) at 0 °C, the resulting solution was stirred for 10 min at this temperature. Then, diethylamine (10 mmol) was added at 0 °C and the mixture was stirred for 10 min at this temperature. The reaction mixture was evaporated to leave a residue, which was purified by column chromatography on silica gel with hexane−AcOEt (3:1) to give **7**.

***N*,*N*-Diethyl 1-azulenylsulfonamide (7):** 40%; dark violet powder; mp 54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (6H, t, J = 7.0 Hz), 3.27 (4H, q, J = 7.0 Hz), 7.33 (1H, d, J = 4.2 Hz), 7.49 (1H, t, J = 10.0 Hz), 7.55 (1H, t, J = 10.0 Hz), 7.85 (1H, t, J = 10.0 Hz), 8.17 (1H, d, J = 4.2 Hz), 8.50 (1H, d, J = 10.0 Hz), 9.29 (1H, d, J = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 41.5, 116.7, 122.8, 126.6, 126.8, 136.5, 136.6, 138.0, 139.1, 139.6, 143.0; IR (KBr) 1399, 1330, 1299, 1200, 1017, 943, 780, 697, 524 cm^{-1}. Anal. Calcd for $C_{14}H_{17}NO_2S$: C, 63.85; H, 6.51; N, 5.32. Found: C, 63.96; H, 6.51; N, 5.19.

1-(*N*,*N*-Diethylaminosulfonyl)-2-trimethylsilylazulene (8a): 74%; dark violet powder; mp 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.47 (9H, s), 1.04 (6H, t, J = 7.1 Hz), 3.30 (4H, q, J = 7.1 Hz), 7.46 (1H, t, J = 7.2 Hz), 7.48 (1H, s), 7.50 (1H, t, J = 7.7 Hz), 7.82 (1H, t, J = 9.9 Hz), 8.44 (1H, d, J = 9.5 Hz), 9.00 (1H, d, J = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.2, 13.1, 40.1, 125.5, 126.6, 127.0, 127.2, 136.1, 138.3, 138.5, 139.7, 143.2, 155.8; IR (KBr) 1577, 1463, 1404, 1346, 1241, 1181, 834, 693, 530 cm^{-1}. Anal. Calcd for $C_{17}H_{25}NO_2SSi$: C, 60.85; H, 7.51; N, 4.17. Found: C, 60.49; H, 7.50; N, 4.05.

1-(*N*,*N*-Diethylaminosulfonyl)-2-phenylsulfanylazulene (8b): 69%; reddish violet powder; mp 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (6H, t, J = 7.1 Hz), 3.43 (4H, q, J = 7.1 Hz), 6.44 (1H, s), 7.29 (1H, t, J = 10.3 Hz), 7.43 (4H, m), 7.59 (1H, t, J = 9.7 Hz), 7.66 (2H, m), 7.93 (1H, d, J = 9.9 Hz), 9.11 (1H, d, J = 10.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 41.0, 114.6, 117.9, 127.8, 128.2, 129.5, 129.7, 131.6, 133.1, 134.8, 135.2, 136.8, 139.5, 141.3, 152.5; IR (KBr) 1405, 1320, 1291, 1137, 694, 618 cm^{-1}. Anal. Calcd for $C_{20}H_{21}NO_2S_2$: C, 64.66; H, 5.70; N, 3.77. Found: C, 64.66; H, 5.56; N, 3.66.

1-(*N*,*N*-Diethylaminosulfonyl)azulene-2-boronic acid (8c): 60%; dark violet powder; mp 134−135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (6H, t, J = 7.2 Hz), 3.23 (4H, q, J = 7.2 Hz), 7.14 (2H, s), 7.49 (1H, t, J = 9.7 Hz), 7.56 (1H, t, J = 10.1 Hz), 7.89 (1H, t, J = 9.9 Hz), 7.92 (1H, s), 8.53 (1H, t, J = 9.1 Hz), 9.47 (1H, d, J = 10.2 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 14.0, 41.8, 125.8, 127.4, 128.3, 128.4, 138.4, 140.0, 141.1, 141.9, 143.8; one carbon signal was too weak to be assigned; IR (KBr) 1577, 1450, 1392, 1322, 1260, 1121, 1063, 730, 688, 555 cm^{-1}. Anal. Calcd for $C_{14}H_{18}BNO_4S$: C, 54.74; H, 5.91; N, 4.56. Found: C, 54.95; H, 6.20; N, 4.32.

General Procedure of the Coupling Reaction. Phenylboronic acid (0.2 mmol), **2d** (0.1mmol), Pd(dppf)Cl_2 (0.01mmol), cesium carbonate (1 mmol), and (*R*)-BINAP (0.01 mmol) were dissolved in toluene (7 mL) and the resulting mixture was refluxed for 1 h. The reaction was quenched at room temperature with brine (10 mL) and the mixture was extracted with ether (3 × 7 mL). The combined extracts were dried over anhydrous sodium sulfate and evaporated to leave a residue, which was chromatographed on silica gel with hexane−AcOEt (5:1) to give **9**.

2-Phenyl-1-azulenyl *p*-tolyl sulfone (9a): 90%; violet powder; mp 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (3H, s), 7.02 (2H, d, J = 8.1 Hz), 7.23 (1H, s), 7.38 (7H, m), 7.52 (1H, t, J = 9.7 Hz), 7.67 (1H, t, J = 10.0 Hz), 7.87 (1H, t, J = 9.8 Hz), 8.44 (1H, d, J = 9.6 Hz), 9.84 (1H, d, J = 10.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 120.3, 120.5, 126.3, 127.2, 127.8, 127.9, 128.5, 128.9, 130.2, 136.1, 137.4, 138.6, 139.4, 139.6, 141.3, 142.2, 142.6, 153.1; IR (KBr) 1448, 1411, 1328, 1280, 1136, 770, 731, 659, 571 cm^{-1}. Anal. Calcd for $C_{23}H_{18}O_2S$: C, 77.07; H, 5.06. Found: C, 77.19; H, 5.29.

1-(*p*-Tolylsulfonyl)-2,2′-biazulene (9b): 62%; violet powder; mp 192−194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (3H, s), 6.96 (2H, d, J = 8.2 Hz), 7.18 (2H, t, J = 9.8 Hz), 7.47 (2H, d, J = 8.3 Hz), 7.53 (1H, s), 7.54 (1H, t, J = 9.4 Hz), 7.58 (1H, t, J = 9.9 Hz), 7.66 (1H, t, J = 10.1 Hz), 7.73 (2H, s), 7.82 (1H, t, J = 9.8 Hz), 8.33 (2H, d, J = 9.4 Hz), 8.46 (1H, d, J = 9.5 Hz), 9.86 (1H, d, J = 10.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 120.5, 121.8, 123.4, 126.2, 127.9, 128.8, 129.0, 137.4, 137.5, 137.6, 138.5, 139.2, 139.9, 140.9, 141.5, 142.3, 142.6, 144.4, 148.9; one carbon signal was too weak to be assigned; IR (KBr) 1439, 1395, 1333, 1285, 1145, 802, 662, 600, 540 cm^{-1}. Anal. Calcd for $C_{27}H_{20}O_2S$: C, 79.38; H, 4.93. Found: C, 79.10; H, 5.11.

General Procedure of Desulfonylation. To a solution of **9** (1 mmol) in 1-methyl-2-pyrrolidone was added at room temperature a solution containing sodium hydrogen carbonate (6 mmol) and sodium dithionite (3 mmol) in distilled water (7 mL). The resulting mixture was stirred at 90 °C for 12 h. The reaction mixture was extracted with ether (3 × 10 mL) and the solvent was evaporated to leave a residue, which was purified by column chromatography on silica gel with hexane−AcOEt (5:1) to give **10**.

2-Phenylazulene (10a): 98%; reddish violet powder; mp 228 °C (lit.[24] mp 234 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (2H, t, J = 9.8 Hz), 7.36 (1H, t, J = 7.4 Hz), 7.48 (2H, t, J = 7.8 Hz),

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7.52 (1H, t, $J = 9.8$ Hz), 7.69 (2H, s), 7.98 (2H, d, $J = 7.2$ Hz), 8.30 (2H, d, $J = 9.6$ Hz).

Azulene-2-boronic Acid. To a solution of azulene-2-boronic acid pinacol ester[9] (1.0 mmol) in ethanol (7 mL) was added phenylboronic acid (1.2 mmol) followed by a diluted aqueous solution of hydrochloric acid (5 mL, pH 3) at room temperature, then the mixture was stirred for 5 h. After concentration of the reaction mixture, an aqueous solution of potassium hydroxide (10%, 10 mL) was added and the resulting mixture was washed with ether (3 × 10 mL). The water layer was acidified with a diluted aqueous solution of hydrochloric acid (10 mL) and extracted with ether (3 × 10 mL). The organic layer was dried with Na_2SO_4 and the solvent was evaporated to give the crude product. Purification by recrystallization from hexane—AcOEt (5:1) afforded the pure product.

Blue solids; yield 58%; mp 256−259 °C dec; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.13 (2H, t, $J = 9.7$ Hz), 7.61 (1H, t, $J = 9.9$ Hz), 7.72 (2H, s), 8.20 (2H, br s), 8.35 (2H, d, $J = 9.5$ Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 122.9, 125.2, 137.8, 138.7, 140.5, 146.1. Anal. Calcd for $C_{10}H_9BO_2$: C, 69.84; H, 5.27. Found: C, 70.11; H, 5.48.

2,2′-Biazulene (10b): 85%; green powder; mp >300 °C (lit.[25] mp >300 °C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.21 (4H, t, $J = 10.0$ Hz), 7.58 (2H, t, $J = 10.0$ Hz), 8.37 (4H, d, $J = 10.0$ Hz), 7.94 (4H, s).

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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