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Organothiosilanes in the synthesis of functionalized benzothiophenes and benzofurans

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This paper is dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday and retirement.

Fluoride-ion-induced reactivity of bromo(phenylthio)methyltrimethylsilane with *o*-hydroxy benzaldehyde and *o*-mercaptobenzyl alcohol afforded direct and simple access to 2,3-dihydro-2-phenylthio-3-hydroxybenzofuran and 2-phenylthio-3-hydroxy-2,3-dihydrobenzothiophene, respectively. 2-Phenoxy-3-hydroxy-2,3-dihydrobenzo-thiophene could be similarly obtained through a slightly modified procedure.

Keywords: 2,3-dihydrobenzothiophene; 2,3-dihydrobenzofuran; organothiosilanes; fluoride ion

1. Introduction

The last decades have witnessed a very rapid growth of a number of different organometallic reagents in organic synthesis. Such compounds have in fact expanded from the classical organoalkali or Grignard reagents to organometallics containing metals, such as Si, Sn, Cu, B, Al, Zn. The utility of such reagents relies mainly on the fact that they are virtually "non-basic organometallics" and can tolerate polar functional groups, this conferring them a very high versatility.

In this context, organosilicon chemistry has recently witnessed very rapid growth (*1*, *2*), and reagents and methods based on organosilicon chemistry today comprise an area of increasing interest in organic synthesis. Application, for instance, of heterocyclic silanes to organic synthesis offers the opportunity for new synthetic strategies, since these compounds can behave as effective precursors of heterocyclic carbanions and as masked functional group equivalents. In this field, the reactivity of 2-(trimethylsilyl)thiazolidines (*3*) as powerful building blocks and their synthetic utility with respect to the corresponding 2-lithio derivatives have been reported. Particular focus

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has been on silylated synthons (*4*, *5*), easily available today through a large number of silylation reactions.

The C−Si bond in fact can be activated by specific catalysts, such as fluoride (*5–9*) or phenoxide ion (*10–12*), to generate a nucleophilic species, capable of interacting with different electrophiles, thus avoiding the use of strong metalating agents. This reactivity turns out to be particularly enhanced when a heteroatom, such as sulfur, is present in the α position.

Silyl thioacetals are probably one of the most representative and versatile classes of acyl anion equivalents, and among them heterocyclic ones offer a variety of methods for the development of umpolung reactivity. For a long time, one of the most commonly used classes of cyclic *S*, *S*-acetals are 1,3-dithianes, which are useful carbonyl-protecting groups and can react as masked acyl carbanions (*13–17*).

1,3-Dithianes can be easily metalated with BuLi and reacted with a wide range of electrophiles, thus evidencing their behavior as useful synthons and umpoled reagents (*13–15*, *18*, *19*). On the other hand, deprotonation of the related 1,3-dithiolanes invariably leads to the generation of unstable anions, and cleavage of the heterocyclic ring is always reported, thus limiting their functionalization under strong basic conditions (*20–22*).

These drawbacks can be efficiently overcome through the use of silyl dithianes (*16*, *23*) and silyl dithiolanes (*5*, *23*, *24–26*). The peculiar characteristics of the reactivity of the carbon–silicon bond, which reacts without the generation of a real carbanionic species, but rather through a pentacoordinated intermediate, have led to the efficient functionalization of such organosilanes.

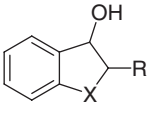
Several different sulfur-containing acyclic derivatives have also been shown to react as masked formyl and acyl anion synthons. Some selected examples are α-silyl sulfides $PhSCH_2TMS$ (*27*, *28*) and MeO(PhS)CHTMS (*29*). Phenylseleno methyl trimethylsilane (*30–33*) has also been used in useful synthetic transformations.

2. Results and discussion

During the course of an investigation on different heterocyclic derivatives of type **1** (Scheme 1), we needed a possibly simple and stereoselective synthetic route to access 2-functionalized-3-hydroxy-2,3-dihydro-benzofurans and -thiophenes. However, to the best of our knowledge, only one example through a radical reaction is reported in the literature for their synthesis (*34*), and consequently we had to devise a novel strategy to access such compounds. In this context, we reasoned that the reactivity of sulfur-containing silanes could provide a possible access to these molecules through an intramolecular cyclization reaction of an activated silyl moiety with a suitable electrophile present in the same framework.

A retrosynthetic analysis of compounds **1** shows that, in principle, they could be accessible through the reaction of the synthons (*35*) in Scheme 2.

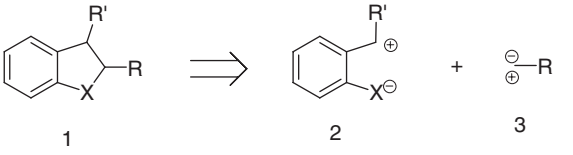
While the synthetic equivalent of synthon **2** could be easily envisaged in *o*-hydroxy- or *o*-mercapto benzaldehyde, synthon **3** could originate from bromo(phenylthio)methyltrimethylsilane **4** (*36*, *37*).



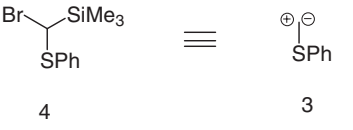
1

a X = O
b X = S

Scheme 1.



Scheme 2.



Scheme 3.

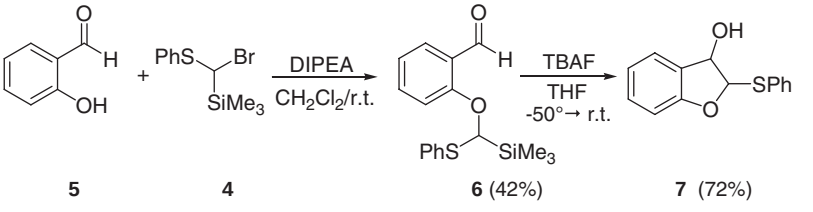
This molecule in fact, due to the presence of a C−Br bond and a C−Si bond activated by a sulfur moiety, could in principle behave as the synthetic equivalent of polysynthon **3** (Scheme 3).

Bromo(phenylthio)methyltrimethylsilane **4** (*36, 37*) is easily accessible from phenylthiomethyltrimethylsilane upon reaction with NBS.

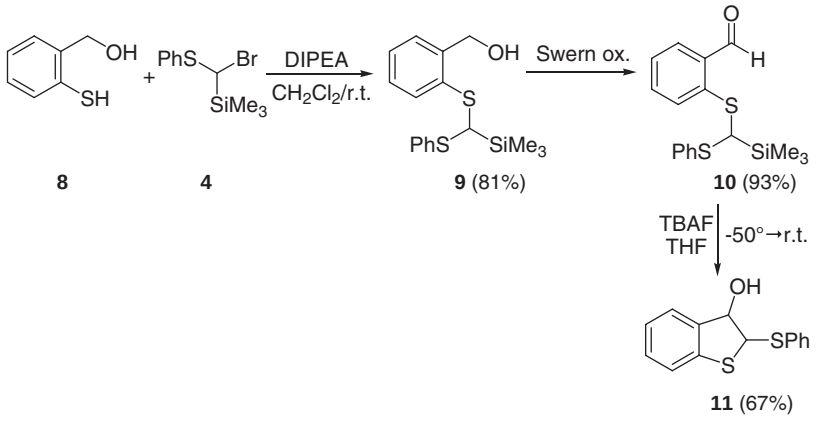
Thus, the reaction of *o*-hydroxy benzaldehyde **5** with bromo(phenylthio)methyltrimethylsilane **4** in the presence of diisopropylethylamine (DIPEA) afforded in 42% yield the corresponding adduct **6** (Scheme 4), which, taking advantage of the already developed methodology of C–Si functionalization under fluoride ion conditions, could be easily reacted to afford an intramolecular cyclization leading in 72% yield to the expected 2,3-dihydro-2-phenylthio-3-hydroxy-benzofuran **7** as an equimolar mixture of diastereomers (Scheme 4). This reaction then showed the real ability of compound **4** to act as the synthetic equivalent of **3**, and leading to a simple and efficient access to the functionalized dihydrobenzofuran **7**.

The extension of the present methodology to the thiophene series could be obtained under similar conditions. In this case, due to the difficult access to *o*-mercaptobenzaldehyde, we had to use *o*-mercaptobenzyl alcohol **8** as the starting material. Thus, bromo(phenylthio)methyltrimethylsilane **4** (Scheme 5) was reacted with *o*-mercaptobenzyl alcohol to afford the functionalized benzyl alcohol **9**. Oxidation of **9** under Swern conditions afforded the corresponding aldehyde **10**, which, again subjected to fluoride-ion-induced intramolecular cyclization, led smoothly and in good yield to 2-phenylthio-3-hydroxy-2,3-dihydrobenzothiophene **11**. Interestingly, such a compound has been obtained in a nice diastereomeric ratio (84% d.e.), affording as the major isomer the *anti* diastereomer. The identity of such compounds has been deducted through a careful analysis of the ^{1}H NMR coupling constants of the protons at positions 2 and 3 of the ring.

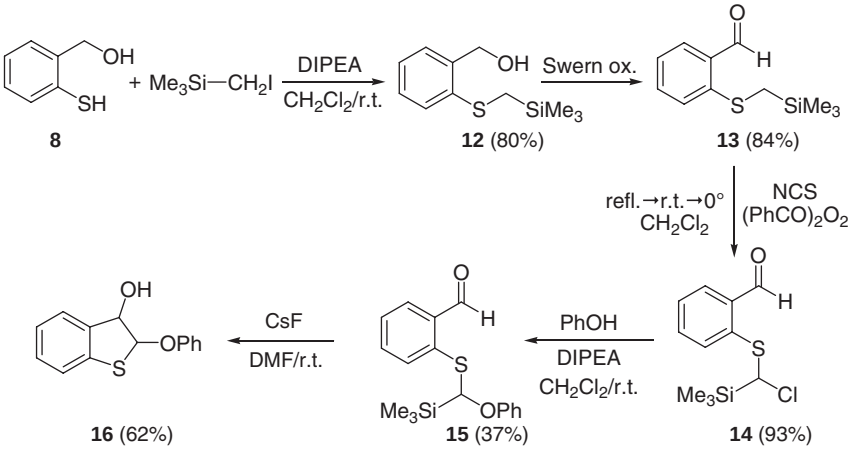
Finally, in order to test the generality of the proposed methodology in accessing differently functionalized 2,3-dihydro benzothiophene systems, we developed a novel synthesis of the phenoxy-substituted system **16** (Scheme 6).



Scheme 4.



Scheme 5.



Scheme 6.

In this case, a slightly different approach was used because of difficulties in obtaining synthetically useful yields of $PhOCHBrSiMe_3$. Thus, *o*-mercaptobenzyl alcohol **8** was reacted with (iodomethyl)trimethylsilane to afford compound **12,** which under Swern conditions was oxidized to yield the corresponding aldehyde **13**. Further treatment of **13** with NCS afforded the chloro derivative **14**, which, upon treatment with phenol and exposure to fluoride ions, afforded in good yields the expected dihydrobenzothiophene **16**.

3. Conclusions

In conclusion, we have shown that bromo(phenylthiomethyl)trimethylsilane could be considered the synthetic equivalent of polysynthon **3**, and that such a molecule can be efficiently used in carbocyclization reactions leading to variously polyfunctionalized dihydrobenzofurans and -thiophenes. Investigation on further applications of compound **3** in organic synthesis is still underway in our laboratory.

4. Experimental

2-(Phenylthio(trimethylsilyl)methoxy)benzaldehyde (6)

A solution of 2-hydroxybenzaldehyde (122 mg, 1 mmol) in 5 ml of CH_2Cl_2 was treated under inert atmosphere with bromo(phenylthio)methyl(trimethylsilane) (275 mg, 1 mmol) and DIPEA (129 mg, 1 mmol). The mixture was stirred in the dark at room temperature overnight. The reaction was quenched with water and the product was extracted with CH_2Cl_2 (5 ml), and the organic layer washed with brine, dried over Na_2SO_4, and evaporated under vacuum. Preparative TLC purification (petroleum ether/ethyl acetate 4:1) afforded 134 mg of **6** (42%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.32 (9H, s), 5.58 (1H, s), 6.80–8.00 (9H, m), 10.66 (1H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: −2.9, 71.9, 116.9, 121.6, 122.3, 125.1, 129.5, 126.8, 130.6, 139.0, 161.9, 190.8. Anal. calcd for $C_{17}H_{20}O_2SSi$: C, 64.51; H, 6.37. Found: C, 64.30; H, 6.52%.

2-(Phenylthio)-2,3-dihydrobenzofuran-3-ol (7)

A solution of **6** (134 mg, 0.42 mmol) in dry tetrahydrofuran (THF) (4 ml) was stirred for 20 min at room temperature and under N_2 over 300 mg of 4 Å molecular sieves, then cooled to −50 °C and treated with 420 µl of a 1 M solution of tetrabutyl ammonium fluoride (TBAF) in THF. Stirring was continued for 10 min at −50 °C, and then the mixture was warmed to RT and stirred overnight. The reaction was quenched with water, extracted with CH_2Cl_2 (5 ml), and washed with brine. The organic layer was dried over Na_2SO_4, and the solvent removed *in vacuo* to afford the crude product **7** as a 1:1 mixture of diastereoisomers. Preparative TLC purification (petroleum ether/ethyl acetate 6:1, two elutions) afforded 74 mg of **6** (72%). Diastereomer A: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.14 (1H, bd, $J = 7.6$ Hz), 5.25 (1H, dd, $J = 7.6$ Hz, $J = 2.4$ Hz), 5.88 (1H, d, $J = 2.4$ Hz), 6.90–7.03 (2H, m), 7.31–7.46 (5H, m), 7.54–7.67 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 73.5, 95.6, 111.3, 121.7, 125.5, 127.3, 127.8, 129.0, 131.1, 132.0, 132.8, 155.6. Diastereomer B: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.26 (1H, bd, $J = 8.0$ Hz), 5.46 (1H, dd, $J = 8.0$ Hz, $J = 5.8$ Hz), 6.01 (1H, d, $J = 5.8$ Hz), 6.90–7.03 (2H, m), 7.31–7.46 (5H, m), 7.54–7.67 (2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 77.8, 95.6, 110.8, 121.8, 125.4, 127.3, 127.6, 129.1, 131.0, 131.5, 133.6, 155.9. Anal. calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.75; H, 5.07%.

[2-(Phenylthio(trimethylsilyl)methylthio)phenyl)methanol] (9)

A solution of (2-mercaptophenyl)methanol (185 mg, 1.32 mmol) in CH_2Cl_2 (5 ml) was treated under inert atmosphere with bromo(phenylthio)methyl(trimethylsilane) (363 mg, 1.32 mmol) and DIPEA (204 mg, 1.58 mmol). The solution was stirred overnight at room temperature in the dark. The reaction mixture was quenched with water and extracted with CH_2Cl_2, the organic layer washed with brine, dried over Na_2SO_4, and evaporated under vacuum to afford 420 mg of **9**, which was purified on silica gel (358 mg, 81%).^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.26 (9H, s), 3.98 (1H, s), 4.63 (1H, d, $J = 12.6$ Hz), 4.85 (1H, d, $J = 12.6$ Hz), 7.00–7.50 (9H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: −2.2, 46.6, 63.4, 126.9, 128.0, 128.5, 131.4, 133.7, 134.2, 135.9, 142.0. Anal. calcd for $C_{17}H_{22}OS_2Si$: C, 61.03; H, 6.63. Found: C, 60.87; H, 6.75%.

2-(Phenylthio(trimethylsilyl)methylthio)benzaldehyde (10)

A solution of oxalyl chloride (200 mg, 1.58 mmol) in dry THF (3 ml) in a Schlenk tube was treated at −78 °C with dry dimethyl sulphoxide (DMSO) (186 mg, 2.38 mmol). The mixture was stirred

for 20 min at −78 °C and then treated with a solution of **9** (265 mg, 0.79 mmol) in dry THF (1 ml). After stirring for 20 min, Et_3N was added (481 mg, 4.76 mmol) and the solution warmed to room temperature and stirred for 2 h. Progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate 4:1). Purification on silica gel (petroleum ether/ethyl acetate 4:1) afforded 244 mg of **10** (93%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.26 (9H, s), 4.04 (1H, s), 7.10–7.80 (9H, m), 10.51 (1H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: −2.1, 46.2, 127.1, 127.7, 128.7, 129.3, 131.2, 133.6, 133.9, 135.6, 136.5, 140.1, 191.8. Anal. calcd for $C_{17}H_{20}OS_2Si$: C, 61.40; H, 6.06. Found: C, 61.12; H, 6.29%.

2-(Phenylthio)-2,3-dihydrobenzo[b]thiophen-3-ol (11)

A solution of **10** (122 mg, 0.36 mmol) in dry THF (4 ml) was stirred at room temperature for 20 min and under N_2 over 300 mg of 4 Å molecular sieves. After cooling to −50 °C, the solution was treated with 360 µl of a 1 M solution of TBAF in THF. The reaction was kept at −50 °C for 10 min and then let to RT and stirred overnight. The reaction was quenched with water, extracted with CH_2Cl_2, and washed with brine. The organic phase was dried over sodium sulphate, and the solvent removed *in vacuo* to afford 76 mg of crude **11** as a mixture of diastereoisomers (d.e. 84%). Preparative TLC purification (hexanes/ethyl acetate 4:1) gave 63 mg of **11** (67%). Major isomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.90 (1H, bs), 5.19 (1H, d, $J = 8$ Hz), 5.38 (1H, d, $J = 8$ Hz), 7.10–7.60 (9H, m,). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 63.1, 82.4, 124.5, 125.2, 127.8, 128.0, 129.5, 130.7, 131.6, 131.9, 132.7, 141.3. Minor isomer: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.90 (1H, bs), 5.03 (1H, d, $J = 2.8$ Hz), 5.18 (1H, d, $J = 2.8$ Hz), 7.10–7.60 (9H, m). Anal. calcd for $C_{14}H_{12}OS_2$: C, 64.58; H, 4.65. Found: C, 64.33; H, 4.81%.

[2-((Trimethylsilyl)methylthio)phenyl]methanol (12)

A solution of 2-mercaptophenyl)methanol **8** (689 mg, 4.92 mmol) in CH_2Cl_2 (7 ml) was treated with iodo(methyl)trimethylsilane (1.52 g, 7.10 mmol) and DIPEA (635 mg, 4.92 mmol). The solution was stirred overnight at room temperature. After quenching with water, the product was extracted with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent under vacuum afforded 1.03 g of **12**, which was purified on silica gel (petroleum ether/ethyl acetate 4:1) to obtain 0.89 g of **12** (80%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.18 (9H, s), 2.15 (2H, s), 4.73 (2H, s), 7.09–7.37 (4H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ: −1.7, 18.2, 63.0, 124.9, 125.8, 127.5, 127.9, 138.2, 138.4. Anal. calcd for $C_{11}H_{18}OSSi$: C, 58.35; H, 8.01. Found: C, 58.12; H, 8.29%.

2-[(Trimethylsilyl)methylthio]benzaldehyde (13)

A solution of oxalyl chloride (391 mg, 3.10 mmol) in dry THF (6 ml) in a Schlenk tube was cooled to −78 °C and treated with dry DMSO (363 mg, 4.65 mmol). The mixture was stirred for 20 min at −78 °C and then treated with a solution of **12** (350 mg, 1.55 mmol) in dry THF (2 ml). After stirring for 20 min, Et_3N was added (939 mg, 9.30 mmol) and the solution warmed to room temperature and stirred for 2 h. The progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate 4:1). Purification on silica gel with petroleum ether/ethyl acetate (4:1) and evaporation of the solvent under vacuum afforded 290 mg of **13** (84%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.21 (9H, s), 2.14 (2H, s), 7.20–7.28 (1H, m), 7.46–7.52 (2H, m), 7.78–7.82 (1H, m), 10.33 (1H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: −1.8, 17.9, 126.4, 127.2, 130.8, 136.1, 142.2, 190.5. Anal. calcd for $C_{11}H_{16}OSSi$: C, 58.88; H, 7.19. Found: C, 58.61; H, 7.35%.

2-(Chloro(trimethylsilyl)methylthio)benzaldehyde (14)

A solution of *N*-chlorosuccinimide (56 mg, 0.42 mmol) in CCl_4 was treated under N_2 with **13** (94 mg, 0.42 mmol) and a crystal of benzoyl peroxide. The solution was refluxed for 3 h, cooled to RT and then to 0 °C. After filtration and evaporation of the solvent, purification on silica gel (hexanes/ethyl acetate 8:1) afforded 100 mg of **14** (93%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.31 (9H, s), 4.85 (1H, s), 7.38–7.46 (1H, m), 7.58–7.66 (1H, m), 7.77–7.81 (1H, m), 7.87–7.92 (1H, m), 10.36 (1H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: −3.0, 56.6, 126.9, 131.8, 134.1, 134.6, 139.7, 191.4. Anal. calcd for $C_{11}H_{15}ClOSSi$: C, 51.04; H, 5.84. Found: C, 50.83; H, 6.07%.

2-(Phenoxy(trimethylsilyl)methylthio)benzaldehyde (15)

A solution of aldehyde **14** (44 mg, 0.17 mmol) in 4 ml of CH_2Cl_2 was treated at RT under N_2 with phenol (16 mg, 0.17 mmol) and DIPEA (22.2 mg, 0.172 mmol). The progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate 4:1). The reaction mixture was quenched with water, extracted with CH_2Cl_2, the organic layer washed with brine, and dried over Na_2SO_4. Evaporation of the solvent under vacuum afforded crude **15**, which was purified by TLC (petroleum ether/ethyl acetate 8:1) to give 20 mg of the pure compound (37%). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.14 (9H, s), 5.40 (1H, s), 6.81–6.94 (2H, m), 7.11–7.47 (5H, m), 7.54–7.58 (1H, m), 7.79–7. 83 (1H, m), 10.45 (1H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ: −0.9, 74.3, 115.2, 125.3, 126.5, 127.9, 129.1, 133.4, 136.5, 137.0, 142.1, 158.3, 190.2. Anal. calcd for $C_{17}H_{20}O_2SSi$: C, 64.51; H, 6.37. Found: C, 64.29; H, 6.44%.

2-Phenoxy-2,3-dihydrobenzo[b]thiophen-3-ol (16)

A solution of **15** (39 mg, 0.12 mmol) in dry dimethyl formammide (DMF) (3.5 ml) was treated under inert atmosphere with CsF (22.5 mg, 0.148 mmol). The progress of the reaction was monitored by TLC (petroleum ether/ethyl acetate 4:1). The reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was washed with water and brine, and dried over Na_2SO_4. The solvent was removed under vacuum to afford 22.2 mg of crude **16** as a mixture of diastereoisomers (d.e. 43%). TLC purification (hexanes/ethyl acetate 8:1) afforded 18 mg of **16** (62%). Diastereomer A: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.24 (1H, bs, OH), 5.45–5.50 (1H, m), 5.99 (1H, d, $J = 1.8$ Hz), 6.90–7.60 (9H, m). Diastereomer B: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.91 (1H9, bd, OH), (5.45–5.50 (1H, m), 5.93 (1H, d, $J = 4.8$ Hz), 6.90–7.60 (9H, m). Anal. calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.70; H, 5.12%.

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