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Chemoselective Samarium-Mediated Benzoyloxysulfone Eliminations

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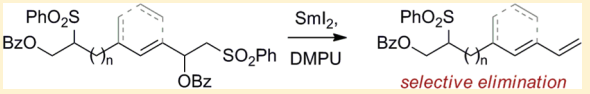
Supporting Information

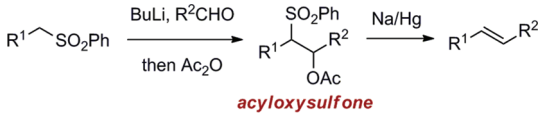
ABSTRACT: An investigation of the substrate dependence on the rate of samarium-mediated reductive elimination of β-acyloxysulfones has provided insights into the mechanism of this transformation and allowed for the development of a chemoselective elimination process.



INTRODUCTION

Nearly 40 years ago, Julia and Paris described a novel alkene synthesis in which β-acyloxysulfones are reductively cleaved to the corresponding predominantly *trans*-olefins.[1] The method was later significantly developed by Lythgoe and Kocienski and has since been used extensively in organic synthesis, particularly as a fragment coupling strategy.[2] Classically, the reaction is carried out in a three-step sequence by addition of an α-metalated sulfone to an aldehyde or ketone, acylation with acetic anhydride (Ac_2O), and reductive elimination of the resulting acyloxysulfone with sodium−mercury amalgam (Na/Hg) (Scheme 1).

Scheme 1. Classical Julia Olefination

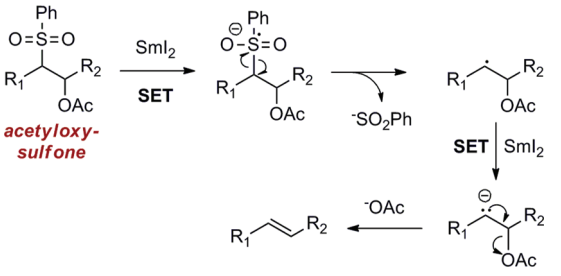


More recently, samarium diiodide (SmI_2) has been shown to be capable of affecting reductive eliminations of this type.[3] Keck and co-workers reported that β-acetyloxysulfones will undergo reductive elimination when treated with SmI_2 in THF and methanol at 25 °C for 1 h (Scheme 2).[4] This reaction was proposed to proceed in an analogous fashion to that originally proposed for the Na/Hg-mediated process involving single-electron transfer (SET) to the sulfone followed by radical decomposition and elimination.

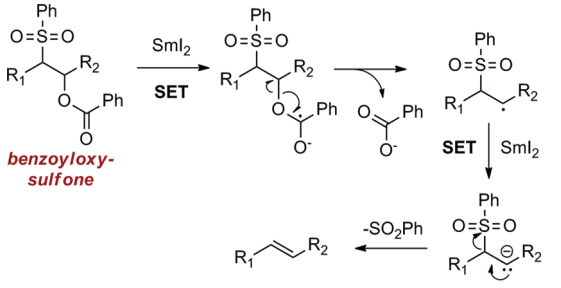
Similarly, Markó and co-workers described an elimination of β-benzoyloxysulfones using SmI_2 in THF in the presence of an additive such as HMPA or DMPU (Scheme 3).[5] Unlike the acetyloxysulfone elimination, the proposed mechanism involves first transfer of an electron to the benzoyl group, followed by loss of benzoate and elimination.

Our own examination into the samarium-mediated reductive elimination of benzoyloxysulfones[6] revealed that the rate of elimination is highly dependent on the substrate structure. For example, while phenylbenzoyloxysulfone **1** rapidly eliminated at −78 °C using SmI_2 and DMPU, alkylbenzoyloxysulfone **2** was

Scheme 2. Proposed Samarium Acetyloxysulfone Elimination



Scheme 3. Proposed Samarium Benzoyloxysulfone Elimination



inert to these conditions (Scheme 4). Even after prolonged reaction times at higher temperatures, only the starting benzoyloxysulfone was recovered. Instead, the corresponding alkene product was obtained using sodium−mercury amalgam which is now known to occur via a different mechanism proceeding through the intermediate vinylsulfone **3**.[4]

This paper describes a closer examination of the substrate dependence on the rate of samarium-mediated elimination

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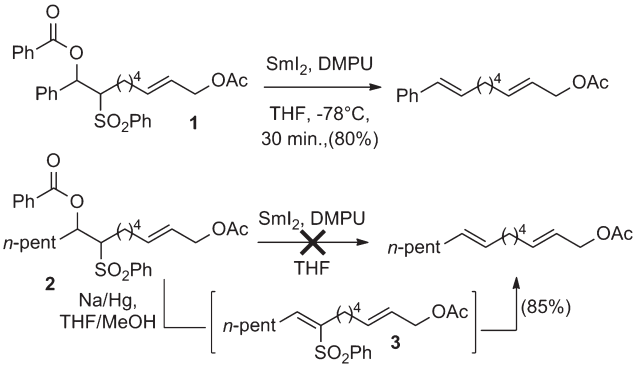
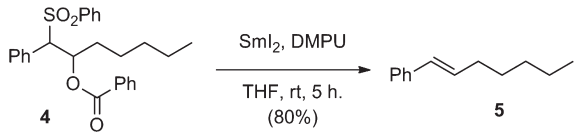
Scheme 4. Differential Acyloxysulfone Reactivity



Scheme 5. Benzylsulfone Samarium Elimination



reactions of β-acyloxysulfones. The results provide evidence that both of the proposed mechanisms do operate, although at substantially different rates. These insights have then allowed for a chemoselective elimination process to be achieved.

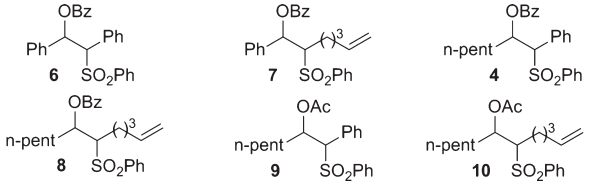
RESULTS AND DISCUSSION

The results in Scheme 4 indicate that substrates with an aryl group adjacent to the benzoylester and an alkyl group adjacent to the sulfone rapidly eliminate when treated with samarium diiodide. Substitution of the aryl with an alkyl group as in compound **2** causes the reaction to fail. To examine the remaining aryl/alkyl combination, benzoyloxysulfone **4** was prepared and treated with SmI_2 in THF and DMPU (Scheme 5). The eliminated product **5** was indeed obtained; however, the reaction required 5 h at rt compared to 30 min at −78 °C for compound **1**.

A series of competition experiments were performed to further test this differential reactivity as described in Table 1. As can be seen from the results, those substrates with an aryl group adjacent to the benzoyl ester (**6** and **7**) were completely consumed when treated with SmI_2 in THF/DMPU at 0 °C for 1 h (entries 1−5). Mixed alkyl/aryl compounds with the aryl group adjacent to the sulfone (**4**) did eliminate under these conditions, but only to the extent of ca. 10% (entries 2, 4, and 6). Dialkyl substrate **8** remained completely intact in all experiments as determined by ^{1}H NMR (entries 3, 5, and 6). Acetyloxysulfone substrates **9** and **10** displayed a similar substrate rate dependence; however, only compound **9** with the phenyl group adjacent to the sulfone gave any elimination product even after prolonged reaction times at elevated temperatures (entry 7).

This elimination profile is not limited to only to aryl-containing substrates. For instance, alkenyl benzoyloxysulfones of type **11** rapidly eliminate when treated with SmI_2 in THF/DMPU at −78 °C generating the corresponding *all-trans* triene as the major product (Scheme 6).[7]

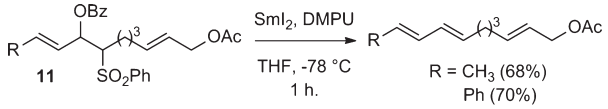
Table 1. Elimination Competition Experiments



entry	compds	conditions[a]	% conversion[b]
1	**6** + **7**	a	**6** = 100%
			7 = 100%
2	**6** + **4**	a	**6** = 100%
			4 = 10%
3	**6** + **8**	a	**6** = 100%
			8 = 0%
4	**7** + **4**	a	**7** = 100%
			4 = 14%
5	**7** + **8**	a	**7** = 100%
			8 = 0%
6	**4** + **8**	a	**4** = 12%
			8 = 0%
7	**9** + **10**	b	**9** = 70%
			10 = 0%

[a] Key: (a) SmI_2 (6 equiv), THF/DMPU (4:1), 0 °C, 60 min; (b) SmI_2 (6 equiv), THF/DMPU (4:1), 22°C, 5 h. [b] Ratios determined by NMR.

Scheme 6. Allylic Benzoyloxysulfone Elimination



Taken together, these results provide support for both of the proposed samarium-mediated acyloxysulfone elimination mechanisms (see Schemes 2 and 3). A comparison of the elimination of compounds **1** and **2** provides further support for the mechanism proposed by Markó[8] and suggests that the rate-determining-step (RDS) involves carbon-radical formation post SET into the benzoylcarbonyl which would be resonance stabilized for compound **1**. This is further supported by the results from each competition experiment involving compound **7** along with the successful elimination of allylic benzoate **11**. Similarly, placement of an aryl substituent adjacent to the phenylsulfone does have an impact on the rate of elimination (entries 6 and 7, Table 1) for both the benzoyloxy and acetoxy series. This data provides strong evidence for Keck's mechanism and suggests that the RDS for this pathway involves carbon-radical formation upon desulfonylation.

Importantly, the competition experiment between compounds **7** and **4** allows for a direct comparison of the rate of the two processes themselves (entry 4, Table 1). The result demonstrates that while both pathways do operate, the mechanism involving SET to the benzoylester is faster (Scheme 7).[9] If the resulting carbon radical is too high in energy, however, the slower SET/sulfone pathway then competes.[10]

As a further demonstration of the substrate dependence on the elimination mechanism, we set out to prepare a

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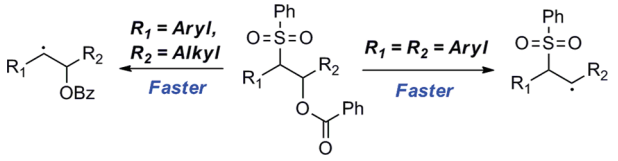
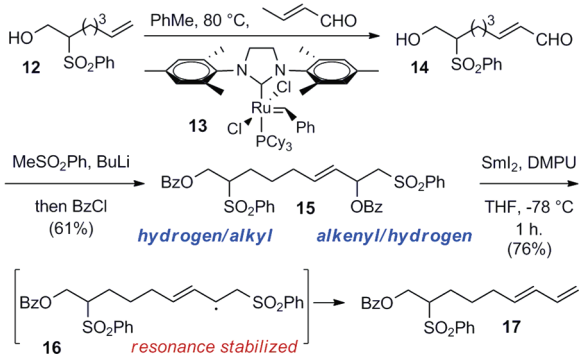
Scheme 7. Relative Elimination Rates



Scheme 8. Chemoselective Samarium-Mediated Elimination



compound that contained two different types of benzoyloxysulfones. To that end, cross-metathesis of alkenyl benzoyloxysulfone **12** with crotonaldehyde using Grubbs' second-generation catalyst (**13**)[11] afforded aldehyde **14** that was immediately treated with the lithium anion of methyl phenyl sulfone (Scheme 8). Methyl phenyl sulfone was chosen to limit the number of stereoisomers that would be produced from the reaction. Acylation with benzoyl chloride (BzCl) gave bis-benzoyloxysulfone **15**, setting the stage for a chemoselective samarium-mediated acyloxysulfone elimination reaction. Specifically, reductive elimination of compound **15** would be expected to proceed by first selective debenzoylation to form the resonance-stabilized radical intermediate **16**. This would then decompose to give diene **17** containing an intact benzoyloxysulfone. In the event, treatment of **15** with samarium diiodide in a mixture of THF and DMPU at −78 °C for 1 h cleanly afforded **17**, thus confirming the substrate dependence of the rate of samarium-mediated acyloxysulfone reductive elimination.

CONCLUSION

The rate of samarium-mediated elimination of β-acyloxysulfones shows a clear substrate dependence as evidenced by a series of competition experiments. These results indicate that both of the proposed mechanisms are indeed operable, and it is the substrate structure that determines by which mechanism elimination occurs. Specifically, electron transfer to the sulfonyl and/or benzoyl group is likely reversible and can occur into both acceptor groups. The next step is fragmentation into a carbon radical, and this is rate-determining. A difference in carbon radical stabilities allowed for the chemoselective reductive-elimination of a bis-benzoyloxysulfone substrate. Efforts are ongoing to design and implement additional permutations of this general concept for the preparation of more complex intermediates.

EXPERIMENTAL SECTION

Competition Experiments (Table 1). To a 1:1 mixture of acyloxysulfones (0.05 mmol/each) in THF (0.4 mL) and DMPU (0.1 mL) at 0 °C was added SmI_2[12] (0.1 M, 2.5 mL), and the mixture was stirred for 1 h. The reaction was quenched with aq NH_4Cl (15 mL) and extracted with EtOAc (15 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. Ratios of starting material(s) and product(s) were determined by ^1H NMR.

Benzoyloxysulfone 6. To a solution of benzyl phenyl sulfone (300 mg, 1.29 mmol) in THF (6.5 mL) at −78 °C was added a solution of *n*-BuLi (1.6 M, 0.97 mL), and the resulting mixture was stirred for 60 min. To the lithiated sulfone thus obtained was added benzaldehyde (0.20 mL, 1.94 mmol), and the resulting mixture was stirred for 1 h. Benzoyl chloride (0.30 mL, 2.58 mmol) was then added, and the mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched with aq NH_4Cl (15 mL) and extracted with EtOAc (2 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica (10:1, 4:1, 1:1 hexanes/ethyl acetate) afforded **6** (512 mg, 90%) as 1.6:1 inseperable mixture of diastereomers: IR (ATR) 3012, 1721, 1447, 1307, 1261, 1140, 1097, 1081, 1070, 1026, 757, 710, 687 cm^{-1}. Signals for the mixture of diastereomers: ^1H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 7.3 Hz, 1H), 8.04 (d, J = 7.3, 2H), 7.95 (d, J = 7.0, 2H), 7.68 (d, J = 6.9 Hz, 2H), 7.43−7.64 (m, 8H), 7.22−7.41 (m, 12H), 7.05−7.19 (m, 14 H), 6.89 (d, J = 10.3 Hz, 1H), 4.91 (d, J = 10.3 Hz, 1H), 4.45 (d, J = 3.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 164.9, 139.5, 138.1, 137.3, 137.0, 133.7, 133.6, 133.3, 133.2, 133.1, 131.5, 130.5, 130.2, 130.1, 129.9, 129.8, 129.7, 129.6, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 127.7, 126.6, 75.6, 75.1, 75.0, 72.5; HRMS (ESI+) calcd for $C_{27}H_{22}O_4SNa$ $(M + Na)^+$ 465.1131, found 465.1134.

Benzoylxysulfone 4. To a solution of benzyl sulfone (100 mg, 0.43 mmol) in THF (2.2 mL) at −78 °C was added a solution of *n*-BuLi (1.6 M, 0.32 mL), and the resulting mixture was stirred for 20 min. To the lithiated sulfone thus obtained was added hexanal (0.10 mL, 0.86 mmol), and the resulting mixture was stirred for 1 h. Benzoic anhydride (292 mg, 1.29 mmol) and DMAP (158 mg, 1.29 mmol) were then added, and the mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched with H_2O (15 mL) and extracted with MTBE (2 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica (10:1, 4:1 hexanes/ethyl acetate) afforded **4** (160 mg, 85%) as 1.7:1 inseperable mixture of diastereomers: IR (ATR) 3063, 2956, 2929, 2860, 1720, 1692, 1602, 1584, 1449, 1317, 1269, 1177, 1147, 1107, 710 cm^{-1}. Signals for the mixture of diastereomers: ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.1, 1.2 Hz, 2H), 7.89 (td, J = 6.9, 1.8 Hz, 2H), 7.60−7.12 (m, 26H), 6.06 (m, 2H), 4.55 (d, J = 8.7 Hz, 1H), 4.24 (d, J = 3.9 Hz, 1H). 1.79−0.90 (m, 16H), 0.80−0.63 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 138.0, 134.0, 133.9, 133.8, 133.7, 133.3, 133.2, 131.5, 131.0, 130.9, 130.7, 130.4, 130.1, 129.3, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 74.8, 73.5, 72.5, 70.0, 69.3, 63.1, 35.0, 34.6, 32.5, 31.6, 31.5, 25.5, 24.3, 24.0, 22.7, 22.6, 22.5, 14.1, 14.0; HRMS (ESI+) calcd for $C_{26}H_{28}O_4SNa$ $(M + Na)^+$ 459.1601, found 459.1600.

Acetyloxysulfone 9. To a solution of benzyl phenyl sulfone (198 mg, 0.85 mmol) in THF (4.3 mL) at −78 °C was added a solution of *n*-BuLi (1.6 M, 0.80 mL), and the resulting mixture was stirred for 20 min. To the lithiated sulfone thus obtained was added hexanal (0.20 mL, 1.71 mmol), and the resulting mixture was stirred for 1 h. Acetic anhydride (261 mg, 2.56 mmol) and DMAP (312 mg, 2.56 mmol) were then added, and the mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched with aq NH_4Cl (15 mL) and extracted with MTBE (2 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column

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chromatography on silica (4:1 hexanes:ethyl acetate) afforded **9** (340 mg, 59%) as 2.6:1 inseperable mixture of diastereomers: IR (ATR) 2958, 2930, 2859, 1737, 1447, 1371, 1308, 1221, 1143, 1085, 1024, 755, 699 cm^{-1}. Signals for the major diastereomer: ^1H NMR (300 MHz, $CDCl_3$) δ 7.46−7.57 (m, 4H), 7.27−7.40 (m, 5H), 7.19−7.24 (m, 4H), 7.14 (dd, J = 7.3, 1.5 Hz, 2H), 5.88−5.94 (m, 2H), 4.42 (d, J = 9.2 Hz, 1H), 1.01−1.19, (m, 4H), 0.77−0.83 (m, 2H). Signals for the mixture of diastereomers: ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 169.8, 151.5, 138.7, 138.2, 133.5, 133.3, 131.3, 130.9, 130.4, 129.9, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 73.5, 73.2, 71.2, 69.8, 33.3, 32.4, 31.3, 24.8, 23.9, 22.4, 22.3, 21.2, 21.1, 13.9, 13.8; HRMS (ESI+) calcd for $C_{21}H_{26}O_4SNa^+$ $(M + Na)^+$ 397.1444, found 397.1463.

Acetyloxysulfone 10. To a solution of 5-hexenyl phenyl sulfone[13] (200 mg, 0.89 mmol) in THF (4.5 mL) at −78 °C was added a solution of *n*-BuLi (1.6 M, 0.67 mL), and the resulting mixture was stirred for 30 min. To the lithiated sulfone thus obtained was added hexanal (0.16 mL, 1.34 mmol), and the resulting mixture was stirred for 1 h. Acetyl chloride (0.126 mL, 1.78 mmol) was then added, and the mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched with aq sodium bicarbonate (15 mL) and extracted with EtOAc (2 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica (4:1 hexanes/ethyl acetate) afforded **10** (204 mg, 63%) as 1.2:1 inseperable mixture of diastereomers: IR (ATR) 2929, 2860, 1739, 1447, 1288, 1232, 1144, 1084, 1024, 998, 911, 753, 728, 699 cm^{-1}. Signals for the mixture of diastereomers: ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (m, 4H), 7.68 (q, J = 8.4 Hz, 2H), 7.60 (q, J = 7.7 Hz, 2H), 7.59 (q, J = 7.4 Hz, 2H), 5.71 (m, 2H), 4.97 (m, 4H), 4.12 (m, 1H), 4.05 (m, 1H), 3.09 (m, 2H), 1.14−2.20 (m, 34H), 0.89 (t, J = 7.0 Hz, 3H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.2, 170.0, 139.2, 139.1, 138.9, 138.5, 138.0, 137.7, 137.6, 137.5, 134.0, 133.8, 133.6, 129.4, 129.2, 129.1, 129.0, 128.6, 128.0, 115.4, 70.4, 70.1, 69.3, 68.8, 68.3, 66.6, 65.9, 56.1, 34.2, 34.0, 33.5, 33.4, 33.3, 33.0, 32.3, 31.6, 31.4, 31.3, 31.2, 31.1, 29.7, 29.6, 28.3, 27.9, 27.4, 26.8, 26.6, 25.6, 25.5, 25.4, 25.3, 25.2, 23.5, 22.6, 22.5, 22.4, 22.1, 22.0, 20.8, 14.0, 13.9; HRMS (ESI+) calcd for $C_{20}H_{30}O_4SNa^+$ $(M + Na)^+$ 389.1757, found 389.1789.

Hydroxysulfone 12. To a solution of 5-hexenyl phenyl sulfone (133 mg, 0.59 mmol) in THF (3.0 mL) at −78 °C was added a solution of *n*-BuLi (1.6 M, 0.71 mL), and the resulting mixture was stirred for 30 min. To the lithiated sulfone thus obtained was added paraformaldehyde (89 mg, 2.96 mmol), and the mixture was allowed to slowly warm to room temperature for 15 h. The reaction was quenched with aq NH_4Cl (20 mL) and extracted with MTBE (2 × 20 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica (4:1 hexanes/ethyl acetate) afforded **12** (151 mg, 76%) as an oil: IR (ATR) 3327, 2928, 2856, 1628, 1447, 1211, 1157, 1085, 1024, 728 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.70 (m, 1H), 7.61 (m, 2H), 5.69 (ddt, J = 13.5, 10.5, 6.6 Hz, 1H), 4.95 (m, 1H), 4.93 (m, 1H), 3.92 (d, J = 2.7 Hz, 2H), 3.10 (m, 1H), 2.02 (m, 2H), 1.76 (m, 1H), 1.68−1.50 (m, 2H), 1.38 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 137.2, 134.1, 129.3, 128.8, 115.4, 65.9, 59.2, 33.2, 25.7, 24.0; HRMS (ESI+) calcd for $C_{13}H_{19}O_3S$ $(M + H)^+$ 255.1077, found 255.1097.

Bisbenzoyloxysulfone 15. To a solution of **12** (115 mg, 0.45 mmol) and crotonaldehyde (316 mg, 4.5 mmol) in toluene (2.3 mL) was added catalyst **13** (19 mg, 0.02 mmol), and the mixture was warmed to 60 °C for 10 h. The reaction was cooled to room temperature and flushed through a plug of silica with EtOAc, and volatiles were removed in vacuo. The crude aldehyde **14** was used immediately in the next reaction.

To a solution of $MeSO_2Ph$ (176 mg, 1.13 mmol) in THF (4.4 mL) at −78 °C was added a solution of *n*-BuLi (1.6 M, 0.71 mL), and the resulting mixture was stirred for 20 min. To the lithiated sulfone thus obtained was added **14** obtained above, and the resulting mixture was stirred for 3 h. Benzoyl chloride (0.15 mL, 1.35 mmol) was then added, and the mixture was allowed to slowly warm to room temperature overnight. The reaction was quenched with aq NH_4Cl (15 mL) and extracted with EtOAc (2 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica (10:1, 4:1, 1:1 hexanes/ethyl acetate) afforded **15** (176 mg, 61%) as an inseperable mixture of diastereomers. Signals for the mixture of diastereomers: ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, J = 8.1, 1.1 Hz, 1H), 7.88 (ddd, J = 14.3, 7.0, 1.1 Hz, 8H), 7.70 (dd, J = 18.3, 8.1 Hz, 8H), 7.60−7.30 (m, 23H), 5.89−5.75 (m, 4H), 5.49, (dd, J = 15.4, 7.0 Hz, 2H), 4.57 (dd, J = 4.8, 2.6 Hz, 4H), 3.72 (dd, J = 8.8, 3.3 Hz, 1H), 3.69 (dd, J = 8.8, 2.9 Hz, 1H), 3.30−3.50, (m, 4H), 1.74, (m, 4H), 1.63 (m, 4H), 1.55 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 164.8, 139.6, 138.4, 135.0, 134.9, 133.8, 133.7, 133.6, 133.4, 133.2, 130.2, 129.6, 129.3, 129.2, 129.0, 128.5, 128.3, 128.2, 128.0, 126.3, 69.4, 63.8, 61.2, 59.8, 31.7, 29.7, 25.7, 24.8; HRMS (ESI+) calcd for $C_{35}H_{34}O_8S_2$ $(M + H)^+$ 647.1773, found 647.1793.

Diene 17. To a solution of **15** (28 mg, 0.04 mmol) in 4:1 THF/DMPU (0.34:0.08 mL) at −78 °C was added SmI_2 (0.1 M, 1.30 mL), and the resulting mixture was stirred for 30 min. The reaction was quenched with aq NH_4Cl (15 mL) and extracted with EtOAc (2 × 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash column chromatography on silica (4:1, 1:1, hexanes/ethyl acetate) afforded **17** (31 mg, 76%): IR (ATR) 2918, 2850, 1721, 1649, 1602, 1448, 1412, 1306, 1270, 1171, 1037, 1008, 831, 711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.69 (dd, J = 7.9, 0.8 Hz, 2H), 7.44−7.63 (m, 4H), 7.35 (t, J = 7.9 Hz, 2H), 6.25 (dt, J = 20.2, 10.1 Hz, 1H), 6.03 (dd, J = 15.8, 13.5 Hz, 1H), 5.60 (dt, J = 14.1, 6.6 Hz, 1H), 5.07 (d, J = 16.7 Hz, 2H), 4.97 (d, J = 10.1 Hz, 2H), 4.60 (d, J = 4.9 Hz, 2H), 3.41 (sextet, J = 4.4 Hz, 1H), 2.13 (m, 2H), 1.65 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 138.5, 136.9, 135.8, 133.7, 133.4, 133.3, 132.0, 130.2, 129.7, 129.3, 129.0, 128.8, 128.5, 128.3, 115.5, 63.9, 61.1, 32.1, 29.7, 29.6, 26.2, 24.8; HRMS (ESI+) calcd for $C_{22}H_{24}O_4SNa$ $(M + Na)^+$ 407.1288, found 407.1302.

■ ASSOCIATED CONTENT

Supporting Information. Copies of ^1H and ^{13}C NMR spectra for new compounds **4**, **6**, **9**, **10**, **12**, **15**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org

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