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# Preparation of Olefins and Acetylenes *via* Reductive Elimination with $SmI_2$–HMPA

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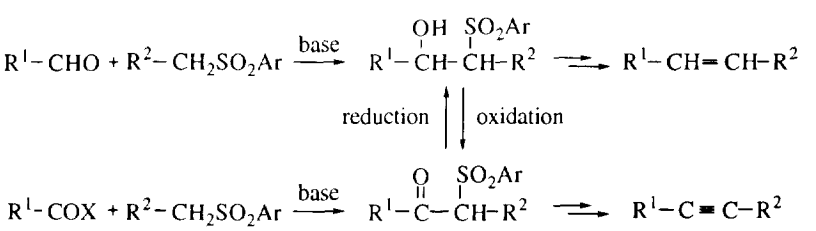
***Abstract***: Reaction of β-hydroxy or acetoxy sulfones with $SmI_2$ in the presence of HMPA caused effectively reductive elimination to provide olefins. Treatment of enol phosphates, readily synthesized from β-hydroxy sulfones *via* keto sulfones, under the same conditions efficiently produced mono- and disubstituted acetylenes.

## Introduction

Transformation of carbonyl compounds to olefins is a useful carbon-carbon bond forming method in organic synthesis. Among numerous reports for synthesis of olefins,[1] Julia olefination[2] is frequently utilized as a regio- and stereoselective preparation,[3] and the synthetic significance is reflected by its widespread use in total syntheses of natural products. The Julia's procedure was also used for preparation of acetylenes.[4,5] The central to their utility is the easy preparation of β-hydroxy sulfones and β-keto sulfones by coupling reaction of sulfones with carbonyl compounds (Scheme 1).[6] We now report improved methods for syntheses of various olefins and acetylenes employing the reductive elimination with $SmI_2$–HMPA.[7]

**Scheme 1**



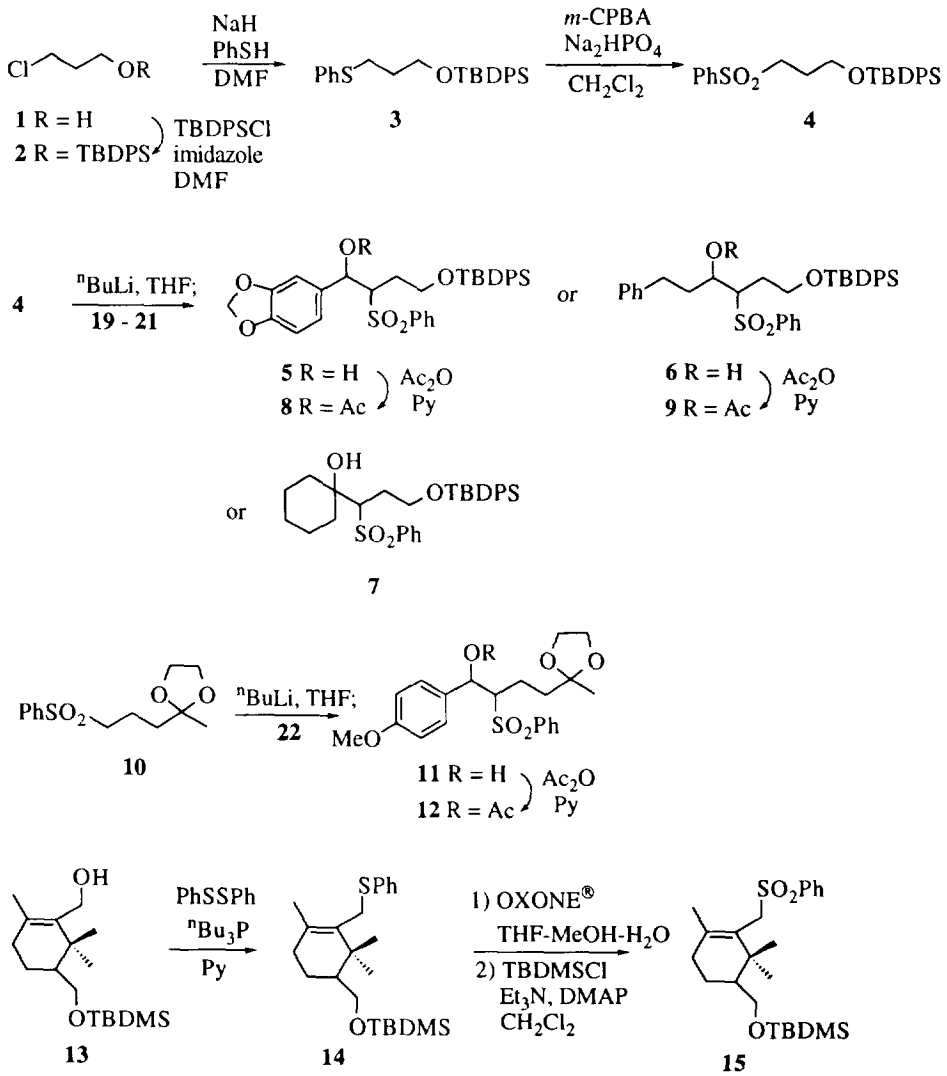

## Results and Discussion

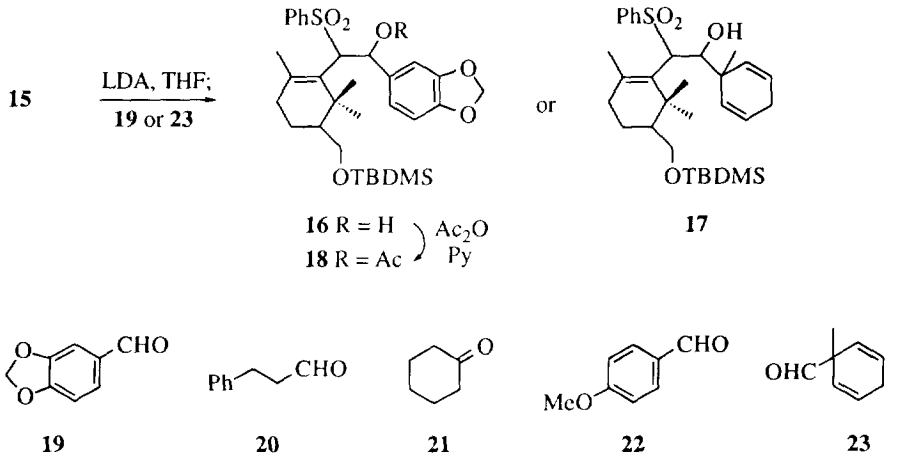
**Preparation of olefins**. β-Hydroxy or acetoxy sulfones for the key reductive elimination were readily prepared through coupling of corresponding carbonyl compounds (**19–23**) with sulfones **4**, **10**[8] and **15** as summarized in Scheme 2. Sulfone **4** was prepared from 3-chloro-1-propanol **1** as follows. After protection of hydroxy group of **1** with *tert*-butyldiphenylsilyl (TBDPS) group (81% yield), treatment of **2** with thiophenol (PhSH) in the presence of sodium hydride (NaH) in DMF gave **3** in quantitative yield. Oxidation of **3** with *m*-CPBA afforded sulfone **4** in 96% yield. On the other hand, sulfone **15** was synthesized starting with the known alcohol **13**.[9] After conversion of **13** into sulfide **14** by means of the Hata's method[10] in 95% yield,

oxidation of **14** with OXONE®,[11] followed by reprotection with *tert*-butyldimethylsilyl (TBDMS) group provided sulfone **15** in 96% overall yield.

Reaction of **4** with carbonyl compounds **19–21** in the presence of $^{n}$BuLi afforded hydroxy sulfones **5–7** in 90, 99 and 94% yields, respectively. Hydroxy sulfone **11** was also prepared in 98% yield by treatment of *p*-anisaldehyde **22** with sulfone **10**[8] as above. Coupling of **15** with aldehydes **19** and **23**[12] was carried out using LDA to give **16** and **17** in 92 and 80% yields, respectively. Furthermore, resulting hydroxy sulfones **5**, **6**, **11** and **16** were converted into acetates **8**, **9**, **12** and **18** by the established method in high yields. However, acetylation of **7** and **17** was failed because of their steric hindrance.

**Scheme 2**






Reductive elimination of β-substituted sulfones was carried out with $SmI_2$[13] in the presence of HMPA[14] in THF at ambient temperature (Table 1). In order to compare with the ordinary method, several results using Na(Hg) in the presence of $Na_2HPO_4$[15] in a 1 : 1 (v/v) mixture of THF–MeOH are also listed.

There were some reports about reduction of sulfones using $SmI_2$ as an electron transfer reagent. Inanaga reported deoxygenation of sulfones with $SmI_2$–HMPA,[16] while desulfonylation using the same reagents was observed by Künzer.[17] Furthermore, Kende recorded a poor result in the reductive elimination of the β-hydroxy phenyl sulfone with $SmI_2$ without HMPA.[18]

At the beginning of this study, the influence due to reaction temperature was examined. On treatment of acetate **12** for 0.25 h with $SmI_2$–HMPA at ambient temperature, a 3 : 1 mixture of (*E*)- and (*Z*)-olefins **25** was obtained in 92% yield (entry 6). On the other hand, the reaction of **12** for 3 h at between –30 and –10 °C gave a 3.6 : 1 mixture of olefins **25** in 78% yield. It was revealed from the above outcome that ratio of (*E*)- and (*Z*)-olefins was not fundamentally changed by the reaction temperature.

In all cases, the $SmI_2$–HMPA method gave better results than the method using Na(Hg) as a reductant. Although the reductive elimination of β-hydroxy sulfones with Na(Hg) had provided a less satisfactory result except special cases,[3] the present method effectively caused reductive elimination to afford olefins in reasonable yields (entries 1, 5, 9, 10 and 14) except the entry 7. Desulfonated products **30**–**33** were also produced (**31**: 35% yield, **33**: 31% yield, but **30** and **32** could not be isolated as pure forms). Particularly, it is noteworthy that treatment of **17**, acetylation of which was failed, with $SmI_2$–HMPA furnished olefin **29** in 82% yield (entry 14). On the other hand, retro aldol type reaction took place to some extent in reactions of **16** and **17** with Na(Hg) as shown in the experimental section (entries 11 and 15).

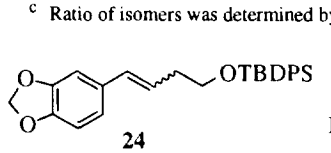
**Table 1. Reductive Elimination of β-Substituted Sulfones [a]**

| entry | substrates | reagents[b] | reaction time (h) | olefins | yield (%) (ratio of *E*:*Z*)[c] |
|---|---|---|---|---|---|
| 1 | **5** | A | 2 | **24** | 73 (3 :1) |
| 2 | **5** | B | 2 | **24** | 68 (2.1 : 1) |
| 3 | **8** | A | 1 | **24** | 95 (3.1 : 1) |
| 4 | **8** | B | 2 | **24** | 88 (3.7 : 1) |
| 5 | **11** | A | 2 | **25** | 59 (7 : 1) |
| 6 | **12** | A | 0.25 | **25** | 92 (3 : 1) |
| 7 | **6** | A | 1 | **26** | 30 (2.9 : 1) |
| 8 | **9** | A | 0.5 | **26** | 81 (1.1 : 1) |
| 9 | **7** | A | 0.5 | **27** | 53 |
| 10 | **16** | A | 2 | **28** | 75 (100 : 0) |
| 11 | **16** | B | 3 | **28** | 39 (100 : 0) |
| 12 | **18** | A | 1 | **28** | 83 (100 : 0) |
| 13 | **18** | B | 2 | **28** | 77 (100 : 0) |
| 14 | **17** | A | 2 | **29** | 82 (100 : 0) |
| 15 | **17** | B | 2 | **29** | 58 (100 : 0) |

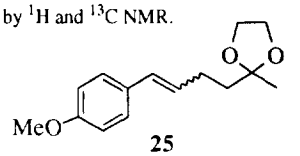
[a] All reactions were carried out at ambient temperature.

[b] A: $SmI_2$, HMPA in THF; B: Na(Hg), $Na_2HPO_4$ in THF-MeOH (1 : 1 v/v).

[c] Ratio of isomers was determined by $^1H$ and $^{13}C$ NMR.




**24**

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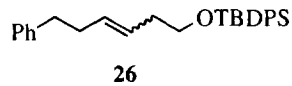


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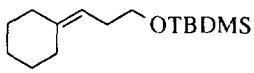


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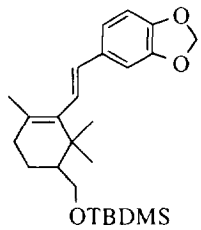


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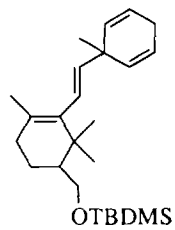
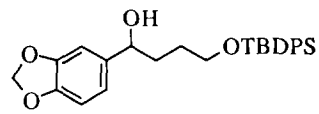
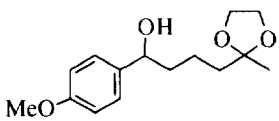


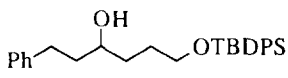

**29**



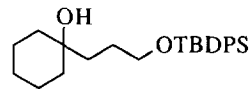

**30**




**31**



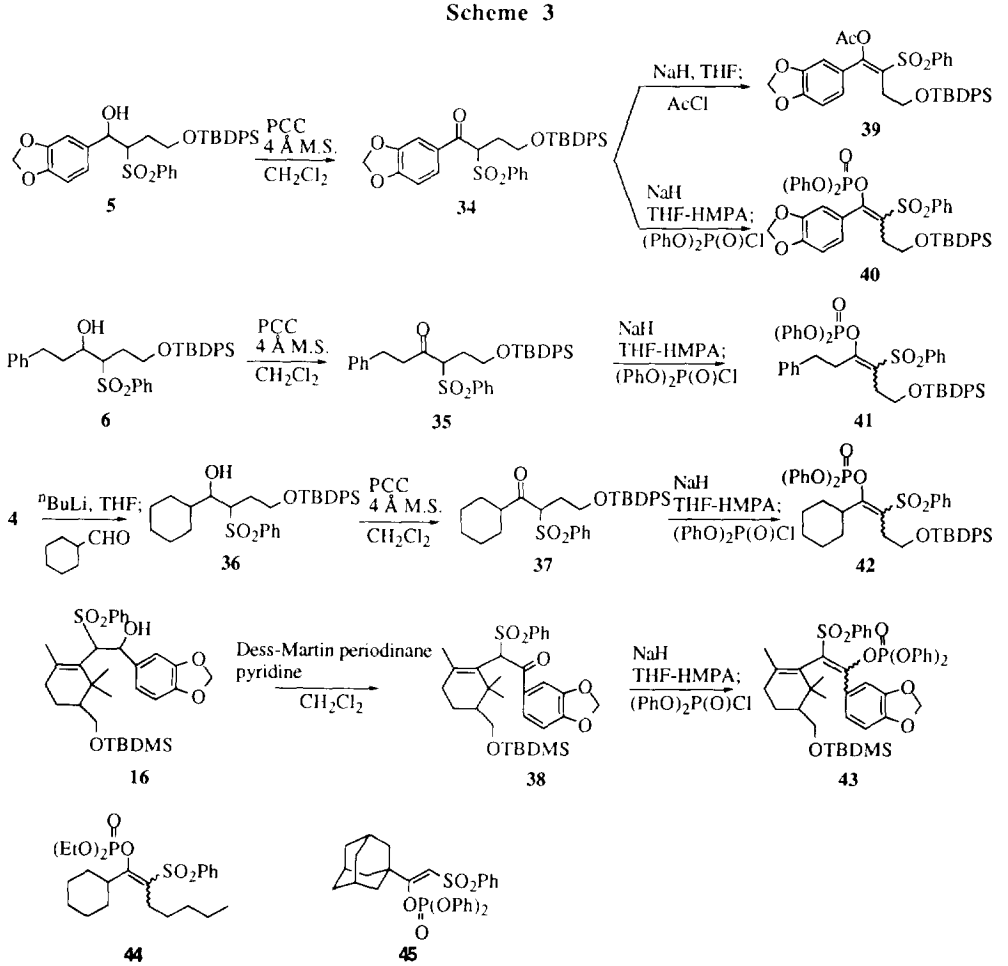

**32**




**33**

**Preparation of acetylenes**. Enol acetate **39** and enol phosphates **40–43** for reductive elimination were prepared as described in Scheme 3. β-Hydroxy sulfone **36** was synthesized by coupling of sulfone **4** with cyclohexanecarboxaldeyde in 96% yield. Oxidation of hydroxy sulfones **5**, **6** and **36** with PCC in the presence of 4 Å molecular sieves gave β-keto sulfones **34**, **35** and **37** in 93, 94 and 98% yields, respectively. Furthermore, **16** was oxidized with Dess–Martin periodinane[19] to afford **38** in 98% yield. Reaction of β-keto sulfone **34** with NaH followed by addition of acetyl chloride gave the (*Z*)-enol acetate **39**. The selective formation of the (*Z*)-isomer is presumably due to an internally chelated enolate.[20] On the other hand, β-keto sulfones **34**, **35**, **37** and **38** were converted into mixtures of (*Z*)- and (*E*)-enol phosphates **40** (5.3 : 1, 95%), **41** (2.3 : 1, 91%), **42** (1.4 : 1, 92%), and **43** (2.5 : 1, 60%) by treatments with diphenyl phosphorochloridate in the presence of NaH and HMPA.[4c]

**Scheme 3**




Results of acetylene synthesis using $SmI_2$–HMPA are summarized in Table 2. Treatment of enol acetate **39** with $SmI_2$–HMPA provided a 5 : 1 inseparable mixture of **46** and (*Z*)-olefin **24** in 81% yield (entry 1).

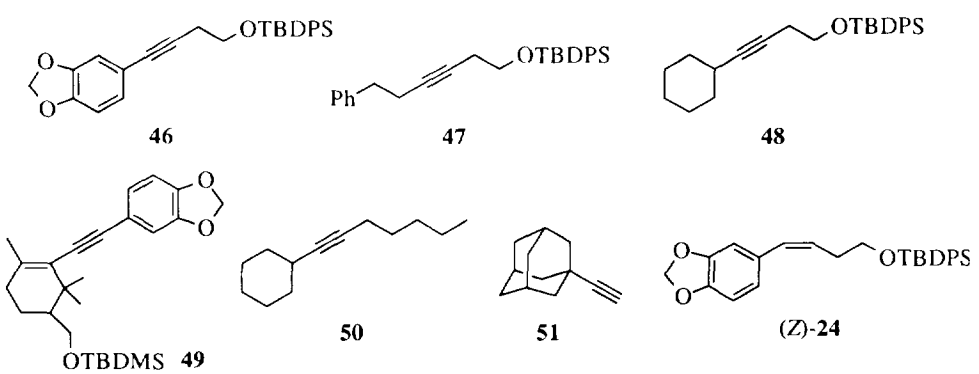
Although Bartlett and co-workers recorded a considerable formation of β-keto sulfones by reduction of phenylsulfonyl enol acetates or enol carbonates with Na in liquid $NH_3$ or Na(Hg),[4c] no reverting back to β-keto sulfone was observed by using $SmI_2$-HMPA. The desired compound **46** was obtained in 94% yield by treatment of enol phosphate **40** under the same reduction conditions (entry 2). Three disubstituted acetylenes **47–49** were produced in high yields by reactions of corresponding enol phosphates **41–43** (entries 3–5).

In order to compare with classical methods, known enol phosphates **44**[4b] and **45**[4c] were treated with the present procedure. On reaction of **44**, acetylene **50** was obtained in 75% yield (entry 6), although Lythgoe and Waterhouse reported the formation of **50** in 64.5% yield together with a considerable amount of the β-keto sulfone using Na(Hg) as a reductant in THF–DMSO.[4b] The β-keto sulfone was not detected in entry 6. Bartlett and co-workers synthesized the monosubstituted acetylene **51** in 51% yield (60% yield of 85% pure material) by reaction of **45** with Na in liquid $NH_3$.[4c] On the other hand, acetylene **51** was obtained in 57% yield (65% of 87% pure material) by the reductive elimination of **45** using $SmI_2$–HMPA (entry 7).

**Table 2. Synthesis of Acetylenes** [a]

| entry | substrates | acetylenes | yield (%) |
|---|---|---|---|
| 1 | **39** | **46** | 68[b,d] |
| 2 | **40** | **46** | 94[b] |
| 3 | **41** | **47** | 87[b] |
| 4 | **42** | **48** | 82[b] |
| 5 | **43** | **49** | 92[b] |
| 6 | **44** | **50** | 75[c] |
| 7 | **45** | **51** | 57[c,e] |

[a] Reactions were carried out for 30 min at ambient temperature.
[b] Products were purified by column chromatography on silica gel.
[c] Products were purified by distillation.
[d] (Z)-**24** was also obtained in 14% yield.
[e] 65% yield of 87% pure materials.



It has been made clear that the present procedure using $SmI_2$–HMPA provides effective methods for the preparation of various types of olefins and acetylenes. The present method possesses several advantages comparing with the classical methods due to the requirement of mild reaction conditions; for example i) no retro aldol type reaction during olefin synthesis and ii) no formation of β-keto sulfones during acetylene synthesis.

## Experimental Section

### General.

All reactions were carried out under $N_2$ or Ar atmosphere. Solvents were distilled prior to use: THF was distilled from Na–benzophenone; $CH_2Cl_2$, DMF and HMPA were distilled from $CaH_2$ and stored over 4 Å molecular sieves; MeOH was distilled from Mg–$I_2$ and stored over 3 Å molecular sieves; pyridine and $Et_3N$ were distilled from KOH and stored over KOH. Unless otherwise noted, all extracts were dried over $MgSO_4$, and the solvents were removed by rotary evaporation under reduced pressure. NMR spectra were taken in $CDCl_3$. Colunm chromatography was performed on Merck Kieselgel 60 Art. 7734.

### 3-*tert*-Butyldiphenylsiloxy-1-chloropropane (2).

To a stirred solution of **1** (3.0 g, 31.7 mmol) and imidazole (2.8 g, 41.1 mmol) in DMF (45 mL) at rt was added TBDPSCl (8.3 mL, 31.9 mmol), and the mixture was stirred for 19 h at rt. The resulting mixture was partitioned between $H_2O$ and $Et_2O$. The organic layer was washed with brine, dried, and evaporated to give a residue, which was purified by column chromatography. Elution with $Et_2O$–hexane (1 : 100 v/v) afforded **2** (8.6 g, 81%) as a colorless oil: IR (neat, $cm^{-1}$) 1470, 1430; $^1H$ NMR (300 MHz) δ 1.05 (s, 9H), 1.95–2.03 (m, 2H), 3.72 (t, $J$ = 6.2 Hz, 2H), 3.79 (t, $J$ = 5.8 Hz, 2H), 7.35–7.46 (m, 6H), 7.64–7.68 (m, 4H); MS *m/z* 297 ($M^+$ –Cl), 275 ($M^+$ –$^t$Bu). Anal. Calcd for $C_{19}H_{25}ClOSi$: C, 68.65; H, 7.59; Cl, 10.53. Found: C, 68.56; H, 7.62; Cl, 10.31.

### (3-*tert*-Butyldiphenylsiloxy)propyl Phenyl Sulfide (3).

To a stirred suspension of NaH (60 w/w% in mineral oil, 387 mg, 9.68 mmol) in DMF (30 mL) at 0 °C was slowly added PhSH (1.13 mL, 11.0 mmol), and the mixture was stirred for 20 min at 0 °C. To the resulting mixture was added a solution of **2** (2.14 g, 6.44 mmol) in DMF (10 mL) at the same temperature. After 6 h of stirring at rt, the mixture was diluted with $Et_2O$ and then washed with $H_2O$, 10% aqueous NaOH, and brine, dried, and evaporated. Column chromatography of the residue with $Et_2O$–hexane (1 : 50 v/v) as eluent gave **3** (2.64 g, 100%) as a colorless oil: IR (neat, $cm^{-1}$) 1590, 1480, 1470, 1430; $^1H$ NMR (300 MHz) δ 1.05 (s, 9H), 1.82–1.91 (m, 2H), 3.06 (t, $J$ = 7.3 Hz, 2H), 3.76 (t, $J$ = 5.9 Hz, 2H), 7.15–7.43 (m, 11H), 7.63–7.67 (m, 4H); MS *m/z* 349 ($M^+$ –$^t$Bu). Anal. Calcd for $C_{25}H_{30}OSSi$: C, 73.84; H, 7.44. Found: C, 74.06; H, 7.40.

### (3-*tert*-Butyldiphenylsiloxy)propyl Phenyl Sulfone (4).

To a stirred mixture of **3** (8.3 g, 20.4 mmol) and $Na_2HPO_4$ (14.5 g, 102 mmol) in $CH_2Cl_2$ (160 mL) at 0 °C was slowly added *m*-CPBA (8.8 g, 51.0 mmol). After being stirred for 50 min at rt, followed by dilution

with $Et_2O$ and addition of 0.1 N aqueous $Na_2S_2O_3$, the mixture was stirred for 10 min at rt. The organic layer was washed with 10% aqueous NaOH and brine, dried, and evaporated to give a residue, which was subjected to column chromatography. Elution with AcOEt–hexane (1 : 7 v/v) gave **4** (8.64 g, 96%) as a colorless oil: IR (neat, $cm^{-1}$) 1590, 1475, 1450, 1430, 1320, 1150; $^1H$ NMR (300 MHz) δ 1.00 (s, 9H), 1.85–1.95 (m, 2H), 3.22–3.27 (m, 2H), 3.66 (t, $J$ = 5.7 Hz, 2H), 7.32–7.44 (m, 6H), 7.54–7.59 (m, 6H), 7.63–7.66 (m, 1H), 7.87–7.91 (m, 2H); MS *m/z* 381 ($M^+$ –$^t$Bu). Anal. Calcd for $C_{25}H_{30}O_3SSi$: C, 68.47; H, 6.90; S, 7.30: Found: C, 68.35; H, 6.90; S, 7.57.

**5-*tert*-Butyldimethylsiloxymethyl-1-phenylthiomethyl-2,6,6-trimethyl-1-cyclohexene (14).**

A mixture of **13**[9] (18.0 g, 0.06 mol), diphenyl disulfide (39.5 g, 0.18 mol), and $^n$Bu$_3$P (45 mL, 0.18 mol) in pyridine (49 mL) was stirred for 9 h at rt. After dilution with $Et_2O$, the mixture was washed with 10% aqueous NaOH and brine, dried, and evaporated to give a residue, which was purified by column chromatography. Elution with AcOEt–hexane (1 : 50 v/v) gave **14** (22.4 g, 95%) as a colorless oil: IR (neat, $cm^{-1}$) 1580, 1465, 1250; $^1H$ NMR (300 MHz) δ 0.05 (s, 6H), 0.90 (s, 9H), 0.94 (s, 3H), 1.19 (s, 3H), 1.36–1.52 (m, 2H), 1.77 (s, 3H), 1.78–1.87 (m, 1H), 1.97–2.05 (m, 2H), 3.38 (dd, $J$ = 8.4, 9.5 Hz, 1H), 3.55–3.64 (m, 2H), 3.78 (dd, $J$ = 3.7, 9.5 Hz, 1H), 7.11–7.18 (m, 1H), 7.23–7.34 (m, 4H); MS m/z 390 ($M^+$). Anal. Calcd for $C_{23}H_{38}OSSi$: C, 70.71; H, 9.81; S, 8.19. Found: C, 70.77; H, 9.84; S, 7.97.

**5-*tert*-Butyldimethylsiloxymethyl-1-phenylsulfonylmethyl-2,6,6-trimethyl-1-cyclohexene (15).**

To a stirred solution of **14** (900 mg, 2.31 mmol) in THF–MeOH–$H_2O$ (3 : 1 : 1, 22.5 mL) at 0 °C was slowly added OXONE®[11] (4.0 g, 6.5 mmol), and the mixture was stirred for 4 h at rt. After being poured into $H_2O$, the mixture was extracted with AcOEt. The extract was washed with brine, dried, and evaporated to give the sulfone alcohol, which was used in the following reaction without purification.

To a stirred solution of the above product, TBDMSCl (491 mg, 3.26 mmol), DMAP (27 mg, 0.22 mmol) in $CH_2Cl_2$ (20 mL) at 0 °C was added $Et_3N$ (0.91 mL, 6.53 mmol). After being stirred for 12 h at rt, the mixture was partitioned between $H_2O$ and $Et_2O$. The organic layer was washed with brine, dried, and evaporated to give a residue, which was subjected to column chromatography. Elution with AcOEt-hexane (1 : 20 v/v) afforded **15** (880 mg, 96% for 2 steps) as a colorless solid, mp 77–78 °C: IR ($CHCl_3$, $cm^{-1}$) 1305, 1155; $^1H$ NMR (300 MHz) δ 0.05 (s, 6H), 0.89 (s, 9H), 0.93 (s, 3H), 1.12 (s, 3H), 1.68 (s, 3H), 1.79–1.88 (m, 1H), 2.04–2.12 (m, 2H), 3.38 (dd, $J$ = 8.8, 9.5 Hz, 1H), 3.76 (dd, $J$ = 3.7, 9.5 Hz, 1H), 3.91–4.02 (m, 2H), 7.50–7.65 (m, 3H), 7.88–7.95 (m, 2H); $^{13}C$ NMR (75 MHz) δ 141.8, 139.5, 133.2, 129.1, 127.8, 126.0, 63.5, 57.8, 47.0, 36.7, 31.7, 28.3, 26.0, 23.3, 22.0, 20.9, 18.3, –5.3; MS *m/z* 281 ($M^+$ –$SO_2Ph$). Anal. Calcd for $C_{23}H_{38}O_3SSi$: C, 65.37; H, 9.07; S, 7.57. Found: C, 65.17; H, 8.81; S, 7.28.

**4-*tert*-Butyldiphenylsiloxy-1-(3,4-methylenedioxyphenyl)-2-phenylsulfonyl-1-butanol (5).**

To a stirred solution of **4** (1.51 g, 3.45 mmol) in THF (35 mL) at –78 °C was added 1.56 M $^n$BuLi in hexane (2.2 mL, 3.43 mmol), and the mixture was stirred for 20 min at the same temperature. To the resulting mixture was slowly added a solution of piperonal (**19**) (525 mg, 3.50 mmol) in THF (5 mL) at –78 °C, and the mixture was stirred for 20 min at the same temperature. After dilution with $Et_2O$, the mixture was quenched with saturated $NH_4Cl$. The organic layer was washed with brine, dried, and evaporated. Silica gel column

chromatography of the residue with AcOEt–hexane (1 : 3 v/v) as eluent gave a 1 : 1 diastereoisomeric mixture of **5** (1.82 g, 90%) as a colorless oil: IR (neat, $cm^{-1}$) 3510, 1305; $^1H$ NMR (300 MHz) δ 0.88 and 0.91 [each s, 9H (1 : 1)], 1.52–1.63 (m, 0.5H), 1.90–2.02 (m, 0.5H), 2.07–2.23 (m, 1H), 2.81–2.88 (m, 0.5H), 3.20–3.28 (m, 1H), 3.37–3.45 (m, 0.5H), 3.50 (d, $J$ = 2.2 Hz, 0.5H), 3.66–3.70 (m, 0.5H), 3.75–3.81 (m, 0.5H), 4.53 (d, $J$ = 2.6 Hz, 0.5H), 5.01 (dd, $J$ = 2.6, 8.4 Hz, 0.5H), 5.41 (br s, 0.5H), 5.85–5.90 (m, 2H), 6.65–6.84 (m, 3H), 7.30–7.71 (m, 13H), 7.86–7.95 (m, 2H); MS *m/z* 588 ($M^+$), 531 ($M^+ - {}^t$Bu); HRMS calcd for $C_{29}H_{27}O_6SSi$ ($M^+ - {}^t$Bu) 531.1298, found 531.1276.

**6-*tert*-Butyldiphenylsiloxy-1-phenyl-4-phenysulfonyl-3-hexanol (6).**

Coupling of **4** (338 mg, 0.771 mmol) with hydrocinnamaldehyde (**20**) (105 mg, 0.783 mmol) as above gave a 1 : 1 mixture of **6** (441 mg, 99%) as a colorless oil: IR (neat, $cm^{-1}$) 3550, 1305; $^1H$ NMR (300 MHz) δ 0.98 and 1.00 [each s, 9H (1 : 1)], 1.58–1.68 (m, 0.5H), 1.90–2.17 (m, 3.5H), 2.53–2.79 (m, 1.5H), 2.86–2.95 (m, 0.5H), 3.18 (d, $J$ = 3.3 Hz, 0.5H), 3.33 (br t, $J$ = 5.1 Hz, 0.5H), 3.44 (dt, $J$ = 4.4, 4.4 Hz, 0.5), 3.53–3.77 (m, 2.5H), 3.94–4.01 (m, 0.5H), 4.11–4.17 (m, 0.5H), 7.00–7.80 (m, 20H); MS *m/z* 572 ($M^+$), 515 ($M^+ - {}^t$Bu); HRMS calcd for $C_{30}H_{31}O_4SSi$ ($M^+ - {}^t$Bu) 515.1713, found 515.1694.

**3-*tert*-Butyldiphenylsiloxy-1-(1-hydroxycyclohexyl)-1-phenylsulfonylpropane (7).**

Coupling of **4** (294 mg, 0.67 mmol) with cyclohexanone (**21**) (55 mg, 0.56 mmol) gave **7** (338 mg, 94%) as a colorless oil: IR (neat, $cm^{-1}$) 3520, 1295; $^1H$ NMR (300 MHz) δ 0.94 (s, 9H), 3.21–3.27 (m, 1H), 3.34–3.40 (m, 2H), 3.81 (br s, 1H), 7.32–7.58 (m, 13H), 7.79–7.83 (m, 1H); $^{13}C$ NMR (75 MHz) δ 140.7, 135.4, 133.5, 133.0, 129.8, 129.2, 128.0, 127.7, 74.8, 69.8, 61.9, 36.3, 33.9, 29.2, 26.8, 25.4, 21.4, 19.1; MS *m/z* 479 ($M^+ - {}^t$Bu); HRMS calcd for $C_{27}H_{31}O_4SSi$ ($M^+ - {}^t$Bu) 479.1713, found 479.1684.

**5,5-Ethylenedioxy-1-(4-methoxyphenyl)-2-phenylsulfonyl-1-hexanol (11).**

Coupling of **10**[8] (3.0 g, 11.1 mmol) with *p*-anisaldehyde (**22**) (1.15 g, 8.45 mmol) was carried out at between –40 – 0 °C to afford a 1 : 1 mixture of **11** (3.37 g, 98%) as a colorless oil: IR (neat, $cm^{-1}$) 3520; $^1H$ NMR (300 MHz) δ 0.95 and 1.02 [each s, 3H (1 : 1)], 1.15–1.24 (m, 1H), 1.30–1.48 (m, 1.5H), 1.91–2.09 (m, 1H), 4.36 (d, $J$ = 2.2 Hz, 0.5H), 4.93–5.00 (m, 0.5H), 5.33 (br s, 0.5H), 6.77–6.88 (m, 2H), 7.14 (d, $J$ = 8.8 Hz, 1H), 7.24 (d, $J$ = 8.8 Hz, 1H), 7.52–7.75 (m, 3H), 7.86–8.02 (m, 2H); MS *m/z* 406 ($M^+$); HRMS calcd for $C_{21}H_{26}O_6S$ ($M^+$) 406.1450, found 406.1465.

**5-*tert*-Butyldimethylsiloxymethyl-1-[2-hydroxy-2-(3,4-methylenedioxy-phenyl)-1-phenylsulfonylethyl]-2,6,6-trimethyl-1-cyclohexene (16).**

To a stirred solution of LDA, prepared form $^i Pr_2NH$ (0.43 mL, 3.07 mmol) and 1.56 M $^n$BuLi in haxane (1.82 mL, 2.84 mmol) in THF (10 mL) at 0 °C, was added a solution of **15** (1.00 g, 2.37 mmol) in THF (5 mL), and the mixture was stirred for 30 min at the same temperature. After the reaction mixture was cooled to –78 °C, a solution of piperonal (**19**) (391 mg, 2.60 mmol) was slowly added to the above mixture. The reaction mixture was stirred for 1 h at the same temperature, and poured into a stirred mixture of saturated $NH_4Cl$ and $Et_2O$. The aqueous layer was extracted with $Et_2O$, and the extract was washed with brine, dried, and evaporated. Column chromatography of the residue with AcOEt–haxane (1 : 3 v/v) as eluent gave a 1.5 : 1 mixture of **16** (1.25 g, 92%) as a pale yellowish solid, which was recrystallized from AcOEt-hexane to provide

a colorless solid as a 4.5 : 1 diastereomeric mixture: IR ($CHCl_3$, $cm^{-1}$) 3350: $^1H$ NMR (500 MHz) δ –0.21 (s, 0.55H), –0.03–0.02 (m, 8.45H), 0.68 and 0.82 [each s, 3H (4.5 : 1)], 0.84 and 0.87 [each s, 9H (1 : 4.5)], 2.14 and 2.15 [each s, 3H (4.5 : 1)], 3.07 (dd, *J* = 9.8, 9.8 Hz, 0.18H), 3.37 (dd, *J* = 9.8, 9.8 Hz, 0.82H), 3.43 (dd, *J* = 4.8, 9.8 Hz, 0.18H), 3.61 (dd, *J* = 4.9, 9.8 Hz, 0.82H), 3.87 (d, *J* = 3.7 Hz, 0.82H), 4.01 (d, *J* = 9.8 Hz, 0.18H), 4.06 (d, *J* = 9.8 Hz, 0.82H), 4.09 (d, *J* = 3.1 Hz, 0.18H), 5.62–5.67 (m, 1H), 5.89–5.91 (m, 2H), 6.67 and 6.68 [each br s, 2H (1 : 4.5)], 6.76 and 6.77 [each br s, 1H (4.5 : 1)], 7.54–7.64 (m, 3H), 8.04–8.10 (m, 2H); Anal. Calcd for $C_{31}H_{44}O_6SSi$: C, 65.01; H, 7.75; S, 5.59. Found: C, 65.08; H, 7.85; S, 5.69.

**5-*tert*-Butyldimethylsiloxymethyl-1-[2-(1-methyl-2,5-cyclohexadien-1-yl)-2-hydroxy-1-phenylsulfonylethyl]-2,6,6-trimethyl-1-cyclohexene (17).**

Coupling of **15** (5.00 g, 11.8 mmol) with **23**[12] (1.88 g, 15.4 mmol) using LDA as above gave a 2.2 : 1 mixture of **17** (5.13 g, 80%) as a pale yellowish solid: IR ($CHCl_3$, $cm^{-1}$) 3400; $^1H$ NMR (500 MHz) δ 0.03 (s, 1.88H), 0.05 (s, 2.06H), 0.06 (s, 2.06H), 0.88 and 0.90 [each s, 9H (1 : 2.2)], 0.98 (s, 0.94H), 1.02 (s, 2.06H), 1.11 (s, 2.06H), 1.14 (s, 0.94H), 1.16 (s, 2.06H), 1.18 (s, 0.94H), 1.43 and 1.62 [each s, 3H (1 : 2.2)], 2.60–2.67 (m, 2H), 3.24 (dd, *J* = 9.2, 9.7 Hz, 0.31H), 3.44 (dd, *J* = 9.8, 9.8 Hz, 0.69H), 3.67 (dd, *J* = 3.7, 9.7 Hz, 0.31H), 3.72 (dd, *J* = 4.3, 9.8 Hz, 0.69H), 3.96 and 4.05 [each d, each *J* = 4.9 Hz, 1H (1 : 2.2)], 4.38–4.43 (m, 1H), 5.39–5.79 (m, 4H), 7.47–7.51 (m, 2H), 7.57–7.61 (m, 1H), 7.90–7.92 (m, 2H); MS *m/z* 487 ($M^+ - {}^t$Bu). Anal. Calcd for $C_{31}H_{48}O_4SSi$: C, 68.34; H, 8.89; S, 5.87. Found: C, 68.41; H, 8.94; S, 5.77.

**4-*tert*-Butyldiphenylsiloxy-1-cyclohexyl-2-phenylsulfonyl-1-butanol (36).**

Coupling of **4** (1.01 g, 2.31 mmol) with cyclohexanecarboxaldehyde (200 mg, 1.78 mmol) as described in the preparation of **5** gave a 1 : 1 mixture of **36** (941 mg, 96%) as a colorless oil: IR (neat, $cm^{-1}$) 3530, 1310; $^1H$ NMR (300 MHz) δ 0.98 and 1.03 [each s, 9H (1 : 1)], 3.00 (d, *J* = 2.6 Hz, 0.5H), 3.30 (d, *J* = 7.7 Hz, 0.5H), 3.61–3.81 (m, 4H), 7.32–7.64 (m, 13H), 7.81–7.88 (m, 2H); MS *m/z* 493 ($M^+ - {}^t$Bu). Anal. Calcd for $C_{32}H_{42}O_4SSi$: C, 69.78; H, 7.69. Found: C, 69.48; H, 7.70.

**4-*tert*-Butyldiphenylsiloxy-1-(3,4-methylenedioxyphenyl)-2-phenylsulfonyl-but-1-yl Acetate (8).**

A mixture of **5** (110 mg, 0.187 mmol) and $Ac_2O$ (0.35 mL, 3.7 mmol) in pyridine (2 mL) was stirred for 13 h at rt. After dilution with benzene, the mixture was washed with 10% aqueous $KHSO_4$ and brine, dried, and evaporated to give a residue, which was subjected to column chromatography. Elution with AcOEt–hexane (1 : 3 v/v) afforded a 1 : 1 mixture of **8** (115 mg, 98%) as a colorless oil: IR (neat, $cm^{-1}$) 1750, 1310; $^1H$ NMR (300 MHz) δ 0.89 and 1.00 [each s, 9H (1 : 1)], 1.68 and 1.96 [each s, 3H (1 : 1)], 2.11–2.30 (m, 2H), 3.31 (dt, *J* = 5.5, 11.6 Hz, 0.5H), 3.51 (dt, *J* = 5.1, 10.3 Hz, 0.5H), 3.64 (dt, *J* = 6.2, 11.6 Hz, 0.5H), 3.71–3.79 (m, 1H), 4.06 (dt, *J* = 6.0, 8.8 Hz, 0.5H), 5.86–5.92 (m, 2H), 6.03 (d, *J* = 8.8 Hz, 0.5H), 6.40 (br s, 0.5H), 6.56–6.78 (m, 3H), 7.30–7.68 (m, 13H), 7.85–7.91 (m, 2H); MS *m/z* 630 ($M^+$), 573 ($M^+ - {}^t$Bu); HRMS calcd for $C_{31}H_{29}O_7SSi$ ($M^+ - {}^t$Bu) 573.1415, found 573.1403.

**6-*tert*-Butyldiphenylsiloxy-1-phenyl-4-phenysulfonylhex-3-yl Acetate (9).**

By means of the above procedure, **6** (70 mg, 0.12 mmol) was converted into a 1 : 1 mixture of **9** (70 mg, 93%) as a colorless oil: IR (neat, $cm^{-1}$) 1745, 1310; $^1H$ NMR (300 MHz) δ 0.98 and 1.01 [each s, 9H (1 : 1)], 1.83 and 1.84 [each s, 3H (1 : 1)], 5.05–5.11 (m, 0.5H), 5.41–5.46 (m, 0.5H), 6.99–7.83 (m, 20H); MS *m/z* 614 ($M^+$). Anal. Calcd for $C_{36}H_{42}O_5SSi$: C, 70.32; H, 6.88. Found: C, 70.28; H, 6.93.

**5,5-Ethylenedioxy-1-(4-methoxyphenyl)-2-phenylsulfonylhex-1-yl Acetate (12).**

By means of the above procedure, **11** (1.6 g, 4.0 mmol) was converted into a 1 : 1 mixture of **12** (1.75 g, 99%) as a colorless oil: IR (neat, $cm^{-1}$) 1745–1735; $^1H$ NMR (300 MHz) δ 1.07 and 1.15 [each s, 3H (1 : 1)], 1.65 and 1.94 [each s, 3H (1 : 1)], 6.05 (d, $J$ = 8.8 Hz, 0.5H), 6.36 (d, $J$ = 2.2 Hz, 0.5H), 6.80 and 6.85 [each d, each $J$ = 8.8 Hz, 2H (1 : 1)], 7.04 and 7.25 [each d, each $J$ = 8.8 Hz, 2H (1 : 1)], 7.49–7.72 (m, 3H), 7.82–8.00 (m, 2H); MS *m/z* 448 ($M^+$); HRMS calcd for $C_{23}H_{28}O_7S$ ($M^+$) 448.1556, found 448.1528.

**1-[2-Acetoxy-2-(3,4-methylenedioxyphenyl)-1-phenylsufonylethyl]-5-*tert*-butyldimethylsiloxymethyl-2,6,6-trimethyl-1-cyclohexene (18).**

By means of the above procedure, **16** (200 mg, 0.35 mmol) was converted into a 4.5 : 1 mixture of **18** (215 mg, 100%) as a colorless solid: IR ($CHCl_3$, $cm^{-1}$) 1745, 1300; $^1H$ NMR (300 MHz) δ –0.02–0.14 (m, 9H), 0.85 and 0.87 [each s, 9H (1 : 4.5)], 0.99 and 1.09 [each s, 3H (4.5 : 1)], 1.93 and 2.02 [each s, 3H (4.5 : 1)], 2.22 (br s, 3H), 3.03 (dd, $J$ = 9.2, 9.2 Hz, 0.18H), 3.41 (dd, $J$ = 9.5, 9.5 Hz, 0.82H), 3.45 (dd, $J$ = 4.7, 9.2 Hz, 0.18H), 3.65 (dd, $J$ = 4.8, 9.5 Hz, 0.82H), 4.25 (d, $J$ = 10.6 Hz, 0.18H), 4.31 (d, $J$ = 11.0 Hz, 0.82H), 5.89–5.91 (m, 2H), 6.54–6.68 (m, 4H), 7.54–7.68 (m, 3H), 7.95–8.00 (m, 2H); MS *m/z* 497 ($M^+$ –$^t$Bu). Anal. Calcd for $C_{33}H_{46}O_7SSi$: C, 64.46; H, 7.54. Found: C, 64.18; H, 7.66.

**(*E*)- and (*Z*)-4-*tert*-Butyldiphenylsiloxy-1-(3,4-methylenedioxyphenyl)-1-butene (24) and 4-*tert*-Butyldiphenylsiloxy-1-(3,4-methylenedioxyphenyl)-1-butanol (30).**

**Reduction of 5.**

(A) To a stirred solution of 0.1 M $SmI_2$[13] in THF (4.3 mL, 0.43 mmol) at rt was added HMPA (0.22 mL), and the color of the $SmI_2$ solution changed to purple. To the resulting mixture was quickly added a solution of **5** (49 mg, 0.083 mmol) in THF (0.5 mL), and the mixture was stirred for 2 h at the same temperature. After dilution with $Et_2O$, the mixture was washed with 10% aqueous HCl, $H_2O$, saturated $NaHCO_3$ and brine, dried, and evaporated to give a residue, which was subjected to column chromatography. Elution with $Et_2O$–hexane (1 : 30 v/v) afforded the 3 : 1 mixture of (*E*)- and (*Z*)-**24** (26 mg, 73%) as a colorless oil: IR (neat, $cm^{-1}$) 1610, 1605, 1590; $^1H$ NMR (300 MHz) δ 1.04 and 1.05 [each s, 9H (1 : 3)], 2.40–2.47 and 2.53–2.60 [each m, 2H (3 : 1)], 3.70–3.83 (m, 2H), 5.62 (dt, $J$ = 7.0, 11.7 Hz, 0.25H), 5.93 and 5.95 [each s, 2H (3 : 1)], 6.02 (dt, $J$ = 7.0, 15.7 Hz, 0.75H), 6.32 (br d, $J$ = 15.7 Hz, 0.75H), 6.39 (br d, $J$ = 11.7 Hz, 0.25H), 6.73 and 6.75 [each br s, 2H (3 : 1)], 6.82 and 6.86 [each br s, 1H (1 : 3)], 7.26–7.57 (m, 6H), 7.65–7.69 (m, 4H); MS *m/z* 430 ($M^+$). Anal. Calcd for $C_{27}H_{30}O_3Si$: C, 75.31; H, 7.02. Found: C, 75.31; H, 7.03.

(B) A mixture of **5** (48 mg, 0.082 mmol), 5% Na(Hg) (188 mg, 0.409 mmol), and $Na_2HPO_4$ (81 mg, 0.57 mmol) in THF–MeOH (1 : 1, 2 mL) was stirred for 2 h at rt. After decantation into $Et_2O$, the organic solution was washed with $H_2O$ and brine, dried, and evaporated. Purification as described above gave a 2.1 : 1 mixture of (*E*)- and (*Z*)-**24** (24 mg, 68%). Further elution with AcOEt-hexane (1 : 5 v/v) afforded **30** (7 mg,

20%) as a colorless oil: IR (neat, $cm^{-1}$) 3410; $^1H$ NMR (300 MHz) δ 1.05 (s, 9H), 2.45 (br s, 1H), 3.68 (t, $J$ = 5.9 Hz, 2H), 4.61 (br t, $J$ = 6.6 Hz, 1H), 5.94 (s, 2H), 6.77 (br s, 2H), 6.86 (br s, 1H), 7.32–7.45 (m, 6H), 7.63–7.68 (m, 4H); MS *m/z* 448 ($M^+$); HRMS calcd for $C_{27}H_{32}O_4Si$ ($M^+$) 448.2070, found 448.2093.

**Reduction of 8.**

(A) Reduction of **8** (60 mg, 0.095 mmol) with 0.1 M $SmI_2$ in THF (5.0 mL, 0.50 mmol) and HMPA (0.25 mL) as above afforded a 3.1 : 1 mixture of (*E*)- and (*Z*)-**24** (39 mg, 95%).

(B) Reduction of **8** (55 mg, 0.087 mmol) with 5% Na(Hg) (200 mg, 0.44 mmol) in the presence of $Na_2HPO_4$ (87 mg, 0.61 mmol) as above afforded a 3.7 : 1 mixture of (*E*)- and (*Z*)-**24** (33 mg, 88%).

**(*E*)- and (*Z*)-5,5-Ethylenedioxy-1-(4-methoxyphenyl)-1-hexene (25) and 5,5-Ethylenedioxy-1-(4-methoxyphenyl)-1-hexanol (31).**

**Reduction of 11.**

**11** (125 mg, 0.31 mmol) was treated with 0.1 M $SmI_2$ in THF (15.4 mL, 0.15 mmol) and HMPA (7.7 mL) as above. Silica gel column chromatography with $Et_2O$–hexane (1 : 10 v/v) as eluent gave a 7 : 1 mixture of (*E*)- and (*Z*)-**25** (45 mg, 59%) as a colorless oil: IR (neat, $cm^{-1}$) 1607, 1510; $^1H$ NMR (300 MHz) δ 1.33 and 1.35 [each s, 3H (1 : 3)], 1.74–1.85 (m, 2H), 2.22–2.75 (m, 1.5H), 2.38–2.48 (m, 0.5H), 3.79 and 3.80 [each s, 3H (3 : 1)], 3.82–4.00 (m, 4H), 5.56 (dt, $J$ = 7.3, 11.7 Hz, 0.5H), 6.08 (dt, $J$ = 7.0, 15.7 Hz, 0.5H), 6.28–6.39 (m, 1H), 6.78–6.89 (m, 2H), 7.18–7.30 (m, 2H); MS *m/z* 248 ($M^+$); HRMS calcd for $C_{15}H_{20}O_3$ ($M^+$) 248.1412, found 248.1422.

Further elution with AcOEt–hexane (1 : 1 v/v) afforded **31** (29 mg, 35%) as a colorless oil: IR (neat, $cm^{-1}$) 3442, 1610, 1512; $^1H$ NMR (300 MHz) δ 1.29 (s, 3H), 3.80 (s, 3H), 3.82–3.98 (m, 4H), 4.55–4.67 (m, 1H), 6.87 (d, $J$ = 8.8 Hz, 2H), 7.26 (d, $J$ = 8.8 Hz, 2H); MS *m/z* 266 ($M^+$); HRMS calcd for $C_{15}H_{22}O_4$ ($M^+$) 266.1518, found 266.1566.

**Reduction of 12.**

Reduction of **12** (100 mg, 0.223 mmol) with 0.1 M $SmI_2$ in THF (11 mL, 1.1 mmol) and HMPA (5.5 mL) afforded a 3 : 1 mixture of (*E*)- and (*Z*)-**25** (51 mg, 92%).

**1-*tert*-Butyldiphenylsiloxy-6-phenyl-3-hexene (26).**

**Reduction of 6.**

Reduction of **6** (93 mg, 0.163 mmol) with 0.1 M $SmI_2$ in THF (8.1 mL, 0.81 mmol) and HMPA (0.41 mL) as above afforded a 2.9 : 1 mixture of (*E*)- and (*Z*)-**26** (20 mg, 30%) as a colorless oil: IR (neat, $cm^{-1}$) 1590, 1430; $^1H$ NMR (300 MHz) δ 1.04 and 1.05 [each s, 9H (1 : 2.9)], 2.21–2.34 (m, 4H), 2.58–2.67 (m, 2H), 3.59 and 3.66 [each t, each $J$ = 7.0 Hz, 2H (1 : 2.9)], 5.36–5.55 (m, 2H), 7.13–7.68 (m, 15H); $^{13}C$ NMR (75 MHz) δ 142.2 (*E*), 142.0 (*Z*), 135.6, 134.1 (*E*), 134.0 (*Z*), 131.7 (*E*), 130.7 (*Z*), 129.6, 128.5, 128.3, 127.6, 127.3, 126.5 (*Z*), 125.7 (*E*), 64.1 (*E*), 63.7 (*Z*), 36.1 (*E*), 36.0, 34.7 (*E*), 31.0 (*Z*), 29.3 (*Z*), 27.0, 19.4; MS *m/z* 357 ($M^+$ –$^t$Bu). Anal. Calcd for $C_{28}H_{34}OSi$: C, 81.10; H, 8.26. Found: C, 80.77; H, 8.42.

**Reduction of 9.**

Reduction of **9** (46 mg, 0.075 mmol) with 0.1 M $SmI_2$ in THF (3.8 mL, 0.38 mmol) and HMPA (0.19 mL) as above afforded a 1.1 : 1 mixture of (*E*)- and (*Z*)-**26** (25 mg, 81%).

**3-*tert*-Butyldiphenysiloxy-1-cyclohexylidenepropane (27) and 1-(3-*tert*-Butyldiphenylsiloxyprop-1-yl)-1-cyclohexanol (33).**

**7** (93 mg, 0.17 mmol) was reduced with 0.1 M $SmI_2$ in THF (8.7 mL, 0.87 mmol) and HMPA (0.44 mL) as above. Silica gel column chromatography with $Et_2O$–hexane (1 : 50 v/v) as eluent afforded **27** (35 mg, 53%) as a colorless oil: IR (neat, $cm^{-1}$) 1590, 1475, 1430; $^1H$ NMR (300 MHz) δ 1.05 (s, 9H), 1.40–1.55 (m, 6H), 2.00–2.05 (m, 4H), 2.25 (dt, *J* = 7.3, 7.3 Hz, 2H), 3.61 (t, *J* = 7.3 Hz, 2H), 5.03 (br t, *J* = 7.3 Hz, 1H), 7.25–7.44 (m, 6H), 7.66–7.69 (m, 4H); MS *m/z* 321 ($M^+$ –$^t$Bu); HRMS calcd for $C_{21}H_{25}OSi$ ($M^+$ –$^t$Bu) 321.1674, found 321.1700.

Further elution with $Et_2O$–hexane (1 : 3 v/v) afforded **33** (21 mg, 31%) as a colorless oil: IR (neat, $cm^{-1}$) 3430; $^1H$ NMR (300 MHz) δ 1.00 (s, 9H), 3.68 (t, *J* = 7.2 Hz, 2H), 7.25–7.42 (m, 6H), 7.65–7.69 (m, 4H); MS *m/z* 339 ($M^+$ –$^t$Bu); HRMS calcd for $C_{21}H_{27}O_2Si$ ($M^+$ –$^t$Bu) 339.1780, found 339.1779.

**(*E*)-5-*tert*-Butyldimethylsiloxymethyl-1-[2-(3,4-methylenedioxyphenyl)ethen-1-yl]-2,6,6-trimethyl-1-cyclohexene (28).**

**Reduction of 16.**

(A) **16** (50 mg, 0.087 mmol) was reduced with 0.1 M $SmI_2$ in THF (4.37 mL, 0.437 mmol) and HMPA (0.22 mL) as above. Silica gel column chromatography with $Et_2O$-hexane (1 : 50 v/v) as eluent afforded **28** (27 mg, 75%) as a solid, which was recrystallized from $Et_2O$–MeOH to provide colorless prisms, mp 70–71 °C: IR ($CHCl_3$, $cm^{-1}$) 1605, 1490; $^1H$ NMR (300 MHz) δ 0.06 (s, 6H), 0.89 (s, 3H), 0.90 (s, 9H), 1.12 (s, 3H), 1.39–1.54 (m, 2H), 1.73 (s, 3H), 1.81–1.91 (m, 1H), 2.01–2.07 (m, 2H), 3.39 (dd, *J* = 8.8, 9.5 Hz, 1H), 3.80 (dd, *J* = 3.7, 9.5 Hz, 1H), 5.95 (s, 2H), 6.20 (d, *J* = 16.1 Hz, 1H), 6.47 (br d, *J* = 16.1 Hz, 1H), 6.76 (d, *J* = 8.1 Hz, 1H), 6.81 (dd, *J* = 1.5, 8.1 Hz, 1H), 6.97 (d, *J* = 1.5 Hz, 1H); MS *m/z* 414 ($M^+$); HRMS calcd for $C_{25}H_{38}O_3Si$ ($M^+$) 414.2590, found 414.2582.

(B) Reduction of **16** (50 mg, 0.087 mmol) with 5% Na(Hg) (200 mg, 0.437 mmol) in the presence of $Na_2HPO_4$ (87 mg, 0.61 mmol) as described in the preparation of **24** gave a residue, which was subjected to silica gel column chromatography with $Et_2O$-hexane (1 : 100 v/v) as eluent to afford 4-*tert*-butyldimethylsiloxymethyl-1,2,3,3-tetramethyl-1-cyclohexene (5 mg, 20%) as a colorless oil: IR (neat, $cm^{-1}$) 1535, 1435; $^1H$ NMR (300 MHz) δ 0.05 (s, 6H), 0.83 (s, 3H), 0.90 (s, 9H), 1.05 (s, 3H), 1.55 (br s, 3H), 1.58 (br s, 3H), 1.75–1.85 (m, 1H), 1.89–1.98 (m, 2H), 3.36 (dd, *J* = 9.8, 9.9 Hz, 1H), 3.78 (dd, *J* = 4.0, 9.9 Hz, 1H); MS *m/z* 282 ($M^+$); HRMS calcd for $C_{17}H_{34}OSi$ ($M^+$) 282.2379, found 282.2401.

Further elution with $Et_2O$–hexane (1 : 100 v/v) provided **28** (14 mg, 39%) and elution with AcOEt–hexane (1 : 10 v/v) gave **15** (14 mg, 38%).

**Reduction of 18.**

(A) Reduction of **18** (50 mg, 0.081 mmol) with 0.1 M $SmI_2$ in THF (4.1 mL, 0.41 mmol) and HMPA (0.21 mL) afforded **28** (28 mg, 83%).

(B) Reduction of **16** (50 mg, 0.081 mmol) with 5% Na(Hg) (187 mg, 0.407 mmol) in the presence of $Na_2HPO_4$ (81 mg, 0.57 mmol) afforded **28** (26 mg, 77%).

**(*E*)-5-*tert*-Butyldimethylsiloxymethyl-1-[2-(1-methyl-2,5-cyclohexadien-1-yl)-ethen-1-yl]-2,6,6-trimethyl-1-cyclohexene (29).**

(A) **17** (100 mg, 0.184 mmol) was reduced with 0.1 M $SmI_2$ in THF (6.43 mL, 0.643 mmol) and HMPA (0.23 mL) as above. Silica gel column chromatography with $Et_2O$–hexane (1 : 500 v/v) as eluent afforded **29** (58 mg, 82%) as a colorless oil: IR (neat, $cm^{-1}$) 1470, 1460, 1360; $^1H$ NMR (300 MHz) δ 0.04 (s, 6H), 0.80 (s, 3H), 0.89 (s, 9H), 1.02 (s, 3H), 1.17 (s, 3H), 1.35–1.50 (m, 2H), 1.63 (s, 3H), 1.78–1.85 (m, 1H), 1.94–1.99 (m, 2H), 2.59–2.64 (m, 2H), 3.36 (dd, *J* = 9.2, 9.9 Hz, 1H), 3.76 (dd, *J* = 4.0, 9.9 Hz, 1H), 5.30 (d, *J* = 16.1 Hz, 1H), 5.53 - 5.57 (m, 2H), 5.65–5.75 (m, 3H); $^{13}C$ NMR (75 MHz) δ 142.4, 137.7, 133.2, 127.7, 125.0, 121.9, 64.0, 46.9, 38.9, 36.4, 31.4, 28.5, 27.9, 26.1, 22.6, 21.6, 18.4, –5.1; MS *m/z* 386 ($M^+$). Anal. Calcd for $C_{25}H_{42}OSi$: C, 77.65; H, 10.95. Found: C, 77.52; H, 10.99.

(B) Reduction of **17** (100 mg, 0.184 mmol) with 5% Na(Hg) (422 mg, 0.918 mmol) in the presence of $Na_2HPO_4$ (183 mg, 1.29 mmol) as above afforded **29** (41 mg, 58%) and a considerable amount of crude **15**.

**4-*tert*-Butyldiphenylsiloxy-1-(3,4-methylenedioxyphenyl)-2-phenylsulfonyl-1-butanone (34).**

A mixture of **5** (1.68 g, 2.86 mmol), PCC (1.23 g, 5.71 mmol), and 4 Å molecular sieves (1.5 g) in $CH_2Cl_2$ (35 mL) was stirred for 2 h at rt. After dilution with $Et_2O$, the reaction mixture was filtered through Florisil. Evaporation of the filtrate afforded a residue, which was recrystallized from AcOEt-hexane to provide **34** (1.56 g, 93%) as colorless prisms, mp 125–126 °C: IR ($CHCl_3$, $cm^{-1}$) 1675, 1320; $^1H$ NMR (300 MHz) δ 0.92 (s, 9H), 2.15–2.40 (m, 2H), 3.34–3.47 (m, 1H), 3.62–3.71 (m, 1H), 5.45 (dd, *J* = 3.3, 10.6 Hz, 1H) 6.06–6.07 (m, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 7.23–7.79 (m, 17H); $^{13}C$ NMR (75 MHz) δ 189.9, 152.7, 148.4, 136.6, 135.4, 135.3, 134.1, 132.8, 132.1, 129.8, 129.7, 128.9, 127.7, 127.6, 126.4, 108.6, 108.0, 102.2, 66.8, 60.4, 31.4, 26.7, 19.1; MS *m/z* 529 ($M^+$ –$^t$Bu). Anal. Calcd for $C_{33}H_{34}O_6SSi$: C, 67.55; H. 5.84; S, 5.46. Found: C, 67.53; H, 5.97; S, 5.43.

**6-*tert*-Butyldiphenylsiloxy-1-phenyl-4-phenylsulfonyl-3-hexanone (35).**

Oxidation of **6** (97 mg, 0.17 mmol) with PCC (73 mg, 0.34 mmol) as above gave the residue, which was subjected to silica gel column chromatography. Elution with AcOEt–hexane (1 : 8 v/v) afforded **35** (91 mg, 94%) as a colorless oil: IR (neat, $cm^{-1}$) 1720, 1310; $^1H$ NMR (300 MHz) δ 0.99 (s, 9H), 2.00–2.14 (m, 2H), 2.81–2.92 (m, 3H), 3.24–3.35 (m, 1H), 3.36 - 3.48 (m, 1H), 3.57–3.67 (m, 1H), 4.46 (dd, *J* = 4.4, 9.9 Hz, 1H), 7.14–7.68 (m, 20H); MS *m/z* 513 ($M^+$ –$^t$Bu); HRMS calcd for $C_{30}H_{29}O_4SSi$ ($M^+$ –$^t$Bu) 513.1556, found 513.1527.

**4-*tert*-Butyldiphenylsiloxy-1-cyclohexyl-2-phenylsulfonyl-1-butanone (37).**

Oxidation of **36** (941 mg, 1.71 mmol) with PCC (740 mg, 3.43 mmol) as above afforded **37** (920 mg, 98%) as a colorless oil: IR (neat, $cm^{-1}$) 1710, 1320; $^1H$ NMR (300 MHz) δ 1.02 (s, 9H), 2.76–2.86 (m, 1H), 3.26–3.37 (m, 1H), 3.59–3.65 (m, 1H), 4.80 (dd, *J* = 3.7, 10.2 Hz, 1H), 7.34–7.78 (m, 15H); $^{13}C$ NMR (75 MHz) δ 205.3, 136.6, 135.5, 135.4, 134.1, 133.0, 132.9, 129.88, 129.85, 129.5, 129.0, 127.79, 127.76, 69.5, 60.0, 52.8, 30.7, 28.4, 27.3, 26.9, 25.9, 25.8, 25.1, 19.1; MS *m/z* 491 ($M^+$ –$^t$Bu); HRMS calcd for $C_{28}H_{31}O_4SSi$ ($M^+$ –$^t$Bu) 491.1713, found 491.1715.

**(*Z*)-1-Acetoxy-4-*tert*-butyldiphenylsiloxy-1-(3,4-methylenedioxyphenyl)-2-phenylsulfonyl-1-butene (39).**

To a stirred suspension of NaH (60 w/w% in mineral oil, 9 mg, 0.23 mmol) in THF (2 mL) at rt was slowly added a solution of **34** (96 mg, 0.16 mmol) in THF (1 mL), and the mixture was stirred for 1 h at rt. To the resulting mixture at 0 °C was added acetyl chloride (20 μL, 0.28 mmol). After being stirred for 20 min at rt, the mixture was diluted with $Et_2O$ and then washed with saturated $NaHCO_3$ and brine, dried, and evaporated. Silica gel column chromatography of the residue with AcOEt–hexane (1 : 3 v/v) as eluent gave **39** (94 mg, 91%) as a colorless oil: IR (neat, $cm^{-1}$) 1780, 1635, 1310; $^1H$ NMR (300 MHz) δ 1.01 (s, 9H), 2.07 (s, 3H), 2.87 (t, $J$ = 6.5 Hz, 2H), 3.94 (t, $J$ = 6.5 Hz, 2H), 5.96 (s, 2H), 6.67 (d, $J$ = 8.1 Hz, 1H), 6.91 (d, $J$ = 1.8 Hz, 1H), 6.97 (dd, $J$ = 1.8, 8.1 Hz, 1H), 7.31–7.62 (m, 13H), 7.93 (dd, $J$ = 1.5, 7.3 Hz, 2H); MS m/z 571 ($M^+$ –$^t$Bu); HRMS calcd for $C_{31}H_{27}O_7SSi$ ($M^+$ –$^t$Bu) 571.1247, found 571.1258.

**(*E*)- and (*Z*)-4-*tert*-Butyldiphenylsiloxy-1-(diphenoxyphosphinyl)oxy-1-(3,4-methylenedioxyphenyl)-2-phenylsulfonyl-1-butene (40).**

To a stirred suspension of NaH (60 w/w% in oil, 18 mg, 0.45 mmol) in THF–HMPA (3 : 1 v/v, 4.8 mL) at rt was slowly added a solution of **34** (200 mg, 0.341 mmol) in THF (1.2 mL), and the mixture was stirred for 1 h at rt. To the resulting mixture at 0 °C was added $(PhO)_2P(O)Cl$ (105 μL, 0.507 mmol), and the mixture was stirred for 20 min at rt. The mixture was quenched with saturated $NH_4Cl$ under ice cooling, and the aqueous layer was extracted with AcOEt. The organic layer was washed with $H_2O$ and brine, dried, and evaporated to give a residue, which was subjected to silica gel column chromatography. Elution with AcOEt–hexane (1 : 2 v/v) gave a 5.3 : 1 mixture of enol phosphates **40** (266 mg, 95%) as an oil: IR (neat, $cm^{-1}$) 1630, 1310, 970; $^1H$ NMR (300 MHz) δ 0.99 and 1.09 [each s, 9H (5.3 : 1)], 2.79 and 3.00 [each br t, each $J$ = 7.0 Hz, 2H (5.3 : 1)], 3.90 and 3.95 [each t, each $J$ = 7.0 Hz, 2H (5.3 : 1)], 5.89 and 5.91 [each s, 2H (1 : 5.3)], 6.46–8.04 (m, 28H); MS *m/z* 761 ($M^+$ –$^t$Bu); HRMS calcd for $C_{41}H_{34}O_9PSSi$ ($M^+$ –$^t$Bu) 761.1430, found 761.1398.

**(*E*)- and (*Z*)-1-*tert*-Butyldiphenylsiloxy-4-(diphenoxyphosphinyl)oxy-6-phenyl-2-phenylsulfonyl-3-hexene (41).**

By means of the above procedure, **35** (85 mg, 0.15 mmol) was converted into a 2.3 : 1 mixture of **41** (109 mg, 91%) as an oil: IR (neat, $cm^{-1}$) 1640, 1310, 980; $^1H$ NMR (300 MHz) δ 1.01 and 1.03 [each s, 9H (1 : 3)], 2.39 (t, $J$ = 7.5 Hz, 1.39H), 2.68– 2.86 (m, 4H), 3.33 (t, $J$ = 7.5 Hz, 0.61H), 3.65–3.73 (m, 2H), 6.76–7.87 (m, 30H); MS *m/z* 745 ($M^+$ –$^t$Bu); HRMS calcd for $C_{42}H_{38}O_7PSSi$ ($M^+$ –$^t$Bu) 745.1845, found 745.1841.

**(*E*)- and (*Z*)-4-*tert*-Butyldiphenylsioxy-1-cyclohexyl-1-(diphenoxyphos-phinyl)oxy-2-phenylsulfonyl-1-butene (42).**

By means of the above procedure, **37** (560 mg, 1.02 mmol) was converted into a 1.4 : 1 mixture of **42** (733 mg, 92%) as an oil: IR (neat, $cm^{-1}$) 1620, 1310, 965; $^1H$ NMR (300 MHz) δ 1.02 and 1.05 [each s, 9H (1.4 : 1)], 2.50– 2.61 (m, 0.42H), 2.81 (t, $J$ = 7.3 Hz, 0.83H), 3.00 (t, $J$ = 7.0 Hz, 1.17H), 3.83 (t, $J$ = 7.3 Hz, 0.83H), 3.89 (t, $J$ = 7.0 Hz, 1.17H), 7.13–7.99 (m, 25H); MS *m/z* 723 ($M^+$ –$^t$Bu); HRMS calcd for $C_{40}H_{40}O_7PSSi$ ($M^+$ –$^t$Bu) 723.2001, found 723.1989.

**(*E*)- and (*Z*)-5-*tert*-Butyldimethylsiloxymethyl-1-[2-(diphenoxyphosphinyl)-oxy-2-(3,4-methylenedioxyphenyl)-1-phenysulfonyl]ethenyl-2,6,6-trimethyl-1-cyclohexene (43).**

To a stirred solution of Dess–Martin periodinane[19] (300 mg, 0.707 mmol) and pyridine (0.15 mL, 1.9 mmol) in $CH_2Cl_2$ (4 mL) at rt was added a solution of **16** (200 mg, 0.35 mmol) in $CH_2Cl_2$ (2 mL). After being stirred for 30 min at the same temperature, the resulting mixture was diluted with $Et_2O$, and poured into a mixture of saturated $NaHCO_3$ and 5% aqueous $Na_2S_2O_3$, and the mixture was stirred for 1 h. The organic layer was washed with saturated $NaHCO_3$ and brine, dried, and evaporated to give a residue, which was subjected to silica gel column chromatography. Elution with AcOEt–hexane (1 : 3 v/v) afforded **38** (196 mg, 98%) as an oil: IR (neat, $cm^{-1}$) 1690, 1325.

The above keto sulfone (145 mg, 0.254 mmol) was treated with NaH (60 w/w% in oil, 15 mg, 0.38 mmol) and $(PhO)_2P(O)Cl$ (85 μL, 0.41 mmol) as described above. Column chromatography of the product on silica gel with AcOEt–hexane (1 : 4 v/v) as eluent gave a 2.5 : 1 mixture of **43** (123 mg, 60%) as an oil: IR ($CHCl_3$, $cm^{-1}$) 1590, 1310, 950; $^1H$ NMR (300 MHz) δ −0.04 (s, 0.86H), −0.03 (s, 0.86H), 0.00 (s, 4.28H), 0.38 and 0.48 [each s, 3H (1 : 2.5)], 0.84 and 0.86 [each s, 9H (1 : 2.5)], 1.02 and 1.21 [each d, 3H (2.5 : 1)], 2.04 and 2.06 [each s, 3H (2.5 : 1)], 2.96 (dd, $J$ = 9.5, 9.9 Hz, 0.29H), 3.26 (dd, $J$ = 4.4, 9.9 Hz, 0.29H), 3.38 (dd, $J$ = 9.2, 9.9 Hz, 0.71H), 3.66 (dd, $J$ = 9.4, 9.9 Hz, 0.71H), 5.92 and 5.94 [each s, 2H (2.5 : 1)], 6.64–7.61 (m, 16H), 8.21–8.25 (m, 2H); MS *m/z* 802 ($M^+$), 745 ($M^+$ −$^t$Bu); HRMS calcd for $C_{39}H_{42}O_9PSSi$ ($M^+$ −$^t$Bu) 745.2056, found 745.2045.

**4-*tert*-Butyldiphenylsiloxy-1-(3,4-methylenedioxyphenyl)-1-butyne (46).**

To a stirred mixture of 0.1 M $SmI_2$ in THF (8.7 mL, 0.87 mmol) and HMPA (0.44 mL) was added a solution of **40** (142 mg, 0.17 mmol) in THF (1 mL), and the mixture was stirred for 30 min at the same temperature. After dilution with $Et_2O$, the mixture was washed with 10% aqueous HCl, saturated $NaHCO_3$ and brine, dried, and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with $Et_2O$–hexane (1 : 75 v/v) afforded **46** (70 mg, 94%) as a colorless oil: IR (neat, $cm^{-1}$) 1605, 1590; $^1H$ NMR (300 MHz) δ 1.07 (s, 9H), 2.65 (t, $J$ = 7.0 Hz, 2H), 3.84 (t, $J$ = 7.0 Hz, 2H), 5.94 (s, 2H), 6.70 (d, $J$ = 8.1 Hz, 1H), 6.81 (d, $J$ = 1.5 Hz, 1H), 6.88 (dd, $J$ = 1.5, 8.1 Hz, 1H), 7.33–7.45 (m, 6H), 7.70 (dd, $J$ = 1.8, 7.7 Hz, 2H); $^{13}C$ NMR (75 MHz) δ 147.4, 147.3, 135.8, 135.5, 133.7, 129.81, 129.76, 129.68, 127.8, 127.7, 126.0, 117.1, 111.7, 108.4, 101.2, 85.6, 81.4, 62.6, 26.9, 23.7, 19.4; MS *m/z* 428 ($M^+$). Anal. Calcd for $C_{27}H_{28}O_3Si$: C, 75.66; H, 6.58. Found: C, 75.52; H, 6.74.

**1-*tert*-Butyldiphenylsiloxy-6-phenyl-3-hexyne (47).**

The enol phosphate **41** (105 mg, 0.131 mmol) was treated with 0.1 M $SmI_2$ in THF (6.5 mL, 0.65 mmol) and HMPA (0.33 mL) as above to give **47** (47 mg, 87%) as a colorless oil: IR (neat, $cm^{-1}$) 1605, 1590; $^1H$ NMR (300 MHz) δ 1.06 (s, 9H), 2.35–2.45 (m, 4H), 2.77 (br t, $J$ = 7.3 Hz, 2H), 3.73 (t, $J$ = 7.3 Hz, 2H), 7.16–7.27 (m, 5H), 7.34–7.45 (m, 6H), 7.68 (dd, $J$ = 1.8, 8.1 Hz, 4H); $^{13}C$ NMR (75 MHz) δ 141.0, 135.7, 135.5, 133.8, 129.7, 128.4, 127.7, 126.2, 80.8, 77.8, 63.0, 35.6, 26.9, 23.0, 21.1, 19.3; MS *m/z* 355 ($M^+$ −$^t$Bu). Anal. Calcd for $C_{28}H_{32}OSi$: C, 81.50; H, 7.82. Found: C, 81.56; H, 7.92.

**4-*tert*-Butyldiphenylsiloxy-1-cyclohexyl-1-butyne (48).**

The enol phosphate **42** (93 mg, 0.12 mmol) was treated with 0.1 M $SmI_2$ in THF (6.3 mL, 0.63 mmol) and HMPA (0.32 mL) as above to give **48** (38 mg, 82%) as a colorless oil: IR (neat, $cm^{-1}$) 1590, 1470, 1450, 1430; $^1H$ NMR (300 MHz) δ 1.05 (s, 9H), 2.25–2.38 (m, 1H), 2.44 (dt, $J$ = 2.2, 7.0 Hz, 2H), 3.74 (t, $J$ = 7.0 Hz, 2H), 7.34–7.45 (m, 6H), 7.67–7.70 (m, 4H); MS $m/z$ 333 ($M^+ - {}^t$Bu); HRMS calcd for $C_{22}H_{25}OSi$ ($M^+ - {}^t$Bu) 333.1674, found 333.1685.

**5-*tert*-Butyldimethylsiloxymethyl-1-(3,4-methylenedioxyphenylethynyl)-2,6,6-trimethyl-1-cyclohexene (49).**

The enol phosphate **43** (55 mg, 0.069 mmol) was treated with 0.1 M $SmI_2$ in THF (3.5 mL, 0.35 mmol) and HMPA (0.2 mL) as above to give **49** (26 mg, 92%) as a colorless solid, which was recrystallized from $Et_2O$–MeOH to give prisms, mp 87– 88 °C: IR ($CHCl_3$, $cm^{-1}$) 2200, 1505; $^1H$ NMR (300 MHz) δ 0.06 (s, 6H), 0.90 (s, 9H), 1.01 (s, 3H), 1.27 (s, 3H), 1.95 (s, 3H), 2.07–2.11 (m, 2H), 3.39 (dd, $J$ = 9.5, 9.9 Hz, 1H), 3.80 (dd, $J$ = 4.4, 9.8 Hz, 1H), 5.95 (s, 2H), 6.74 (d, $J$ = 8.1 Hz, 1H), 6.88 (d, $J$ = 1.5 Hz, 1H), 6.95 (dd, $J$ = 1.5, 8.1 Hz, 1H); $^{13}C$ NMR (75 MHz) δ 147.4, 147.3, 141.2, 125.6, 124.6, 117.8, 111.3, 108.4, 101.2, 93.0, 87.1, 64.0, 46.2, 36.3, 31.3, 31.2, 28.5, 26.1, 22.9, 21.4, 18.4, –5.1; MS $m/z$ 412 ($M^+$). Anal. Calcd for $C_{25}H_{36}O_3Si$: C, 72.77; H, 8.79. Found: C, 72.64; H, 8.87.

**1-Cyclohexyl-1-heptyne (50).**

The enol phosphate **44** (2.16 g, 4.58 mmol) was treated with 0.1 M $SmI_2$ in THF (229 mL, 22.9 mmol) and HMPA (11 mL) as above, and the residue was finally distilled with a Kugelrohr at 140 °C and 40 mm Hg to give a **50** (610 mg, 75%) as a colorless oil, whose IR, $^1H$ NMR, $^{13}C$ NMR, and MS spectral data were consistent with reported ones.[4b]

**1-Ethynyladamantane (51).**

The enol phosphate **45** (925 mg, 1.68 mmol) was treated with 0.1 M $SmI_2$ in THF (84 mL, 8.4 mmol) and HMPA (4.2 mL) as above to give **51** (175 mg, 65%) of a semisolid after distillation with Kugelrohr (150 °C, 25 mmHg). The $^1H$ NMR spectrum revealed the presence of 13% of 1-vinyladamantane, the acetylene derivative **51** could be purified by recrystalization from MeOH to yield a colorless solid, mp 79–81 °C (lit.[4c] 80–81 °C), and IR, $^1H$ NMR and $^{13}C$ NMR spectral data were consisted with reported ones.[4c]

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