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Efficient preparation of trisubstituted alkenes using the SmI_2 modification of the Julia–Lythgoe olefination of ketones and aldehydes

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Dedicated with deep respect to Professor Henri B. Kagan

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Abstract—High yields of di- and tri-substituted alkenes are obtained by a modification of the Julia–Lythgoe olefination reaction involving the in situ capture of intermediate β-alkoxy-sulfones by benzoyl or trimethylsilyl chloride, followed by SmI_2-mediated reductive elimination. This novel protocol also provides a connective preparation of dienyl ethers, which are important partners in Diels–Alder cycloadditions.

The formation of carbon–carbon double bonds is of paramount importance in organic chemistry.[1] Amongst the plethora of methods known for the connective synthesis of alkenes, the Julia–Lythgoe olefination, the combination of a sulfone **2** with a carbonyl derivative **1** followed by reductive elimination, occupies a cardinal position (Fig. 1).[2]

The versatility of this procedure has been demonstrated by its numerous applications in the synthesis of complex natural products.[3] Despite its prominence, the Julia–Lythgoe method suffers from a number of drawbacks, including the production of mixtures of *E*/*Z* olefinic isomers and the poor yields of trisubstituted alkenes obtained during attempted coupling between ketones and primary sulfone anions. An elegant solution to the first problem has been recently provided by Kocienski et al., who showed that sulfones bearing a modified phenyltetrazolyl substituent afforded disubstituted alkenes with virtually complete control of the double bond geometry in favour of the *E*-isomer.[4]

In this article, we wish to describe in full detail our contribution to the establishment of a novel and efficient procedure for the preparation of trisubstituted olefins by the direct coupling between primary sulfone anions and ketones.[5] In addition, this methodology offers an easy access to dienyl ethers, which are important partners in Diels–Alder cycloadditions.[6]

Examination of the literature revealed that trisubstituted alkenes **8** are usually prepared by the coupling of disubstituted sulfone anions such as **4** with aldehydes **5**, followed by the reductive elimination of the corresponding β-hydroxy sulfones **7** with Na amalgam. The high yields obtained using this protocol stem from the equilibrium between reactants **4** and **5** and alkoxide **6** largely favouring the addition product **6**. In stark contrast, the same equilibrium is strongly shifted to the left in the case of the addition of a primary sulfone anion **9** to a ketone **10** and only poor conversions to the desired β-hydroxy sulfone **12** can be achieved.[7] Moreover, the reductive elimination employing Na(Hg) not only affords the corresponding alkene **8**, but also produces, even under buffered conditions, some alkoxide **11** which undergoes competitive retro-aldol type reaction, regenerating the starting material and decreasing even further the overall yields of this olefination process (Fig. 2).

In order to improve this approach and transform it into a

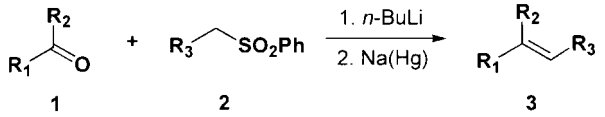

Figure 1.

Keywords: alkenes; olefination; sulfones; Julia reaction; samarium.
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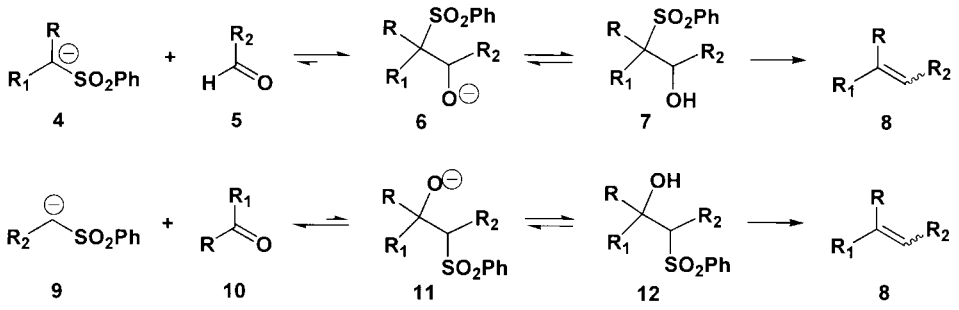


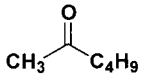
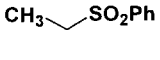
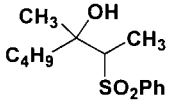
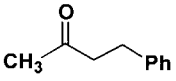
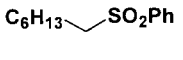
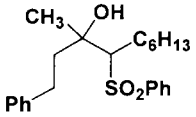
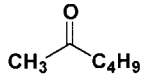
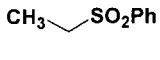
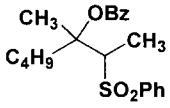
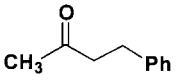
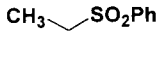
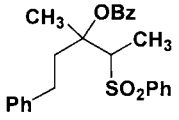
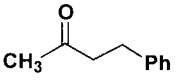
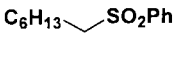
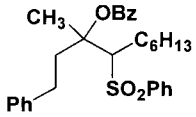
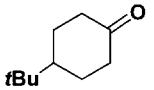
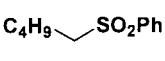
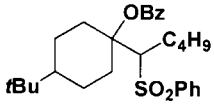
Figure 2.

viable synthetic methodology, two key problems have to be solved: (1) shifting the unfavorable equilibrium towards the product β-hydroxy sulfone **12**, and (2) defining neutral conditions for the reductive elimination of **12** in order to minimise any competing retrograde process.

Inspired by some elegant solutions used in reluctant aldol condensations between enolates and ketones,[8] we decided to enhance the yields of the sulfone anion addition reaction by capturing the intermediate β-alkoxy-sulfone **11** by an oxophilic reactant such as trimethylsilyl chloride or a suitable acyl halide. Gratifyingly, addition of either TMSCl or PhCOCl to the in situ generated tertiary alkoxide **11** resulted in excellent yields of β-hydroxy sulfones **12** and the corresponding β-benzoyloxy sulfones, respectively (Table 1).

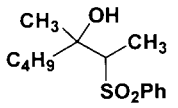
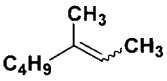
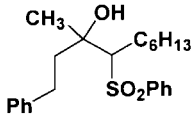
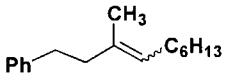
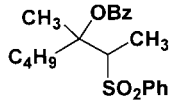
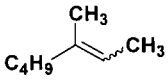
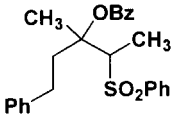
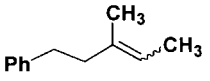
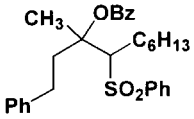
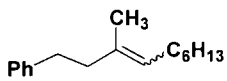
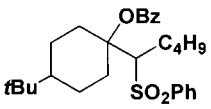
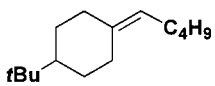
As can be seen from Table 1, both acyclic and cyclic

Table 1. Synthesis of β-alkoxy- and β-benzoyloxy-sulfones by in situ electrophilic trapping

Entry	Substrate	Reagent	Product	Yields[a]
1				86%[b]
2				69%[b]
3				93%[c]
4				82%[c]
5				85%[c]
6				76%[c]

[a] All yields are for pure, isolated products. A 70:30 mixture of diastereoisomers was obtained in entries 1–5.
[b] The reaction mixture was quenched by addition of TMSCl at −78°C.
[c] The reaction mixture was quenched by addition of PhCOCl at −78°C.

Table 2. SmI_2-mediated reductive elimination

Entry	Substrate	Product	Yields[a]
1			69%[b]
2			66%[b]
3			73%[c]
4			84%[d]
5			72%[c]
6			85%[b]

[a] All yields are for pure, isolated products.
[b] The reaction was performed at 0°C.
[c] The reaction mixture was effected at −78°C.
[d] The reaction was performed at −84°C. The *E*/*Z* ratios are typically in the range of 2:1.

ketones reacted efficiently with a variety of primary sulfone anions. Apart from entry 6, the addition products were typically obtained as a 70:30 mixture of diastereoisomers.

With an expedient and high-yielding method to access the desired adducts in hand, attention was focused on the reductive elimination step. The use of Na(Hg), whether buffered or not rapidly proved to be unsuitable for our purposes, resulting either in poor yields of the alkene, large amounts of retro-aldol product or complete decomposition of the starting material. Several other standard reducing agents were shown to be equally ineffective. The powerful, though selective, reducing abilities of the lanthanides and of some of their complexes triggered our interest and we decided to investigate the use of SmI_2 in this transformation.[9]

Disappointingly, SmI_2 in THF proved to be completely unreactive in the reductive elimination of β-hydroxy sulfones, even after prolonged reaction times at room temperature. This lack of reactivity has been observed by Kende[10], who used the *N*-phenyl imidazolyl sulfone, a better single electron acceptor, as a surrogate for the inert phenyl sulfonyl group. Whilst this substitution provides an elegant solution to this problem, we decided to test the influence of various adjuvants, known to modify the reactivity of SmI_2,[11] on the outcome of the reductive elimination of the more commonly employed phenylsulfonyl derivatives.

Much to our delight, the addition of 1–5 mol% of HMPA or DMPU to SmI_2 in THF resulted in the smooth transformation of the β-benzoyloxy sulfones into the desired alkenes, in good to excellent yields, at temperatures as low as −84°C. Table 2 summarises some of our results.

As can be seen from Table 2, a range of trisubstituted alkenes may efficiently be prepared by the SmI_2-mediated reductive elimination (entries 3–6). Unfortunately, no reaction took place with the corresponding β-hydroxy sulfones under the same reaction conditions and the starting material was recovered unchanged. Gratifyingly, increasing the temperature to 0°C resulted in the rapid formation of the desired olefins in good to excellent yields (Table 2, entries 1–2).

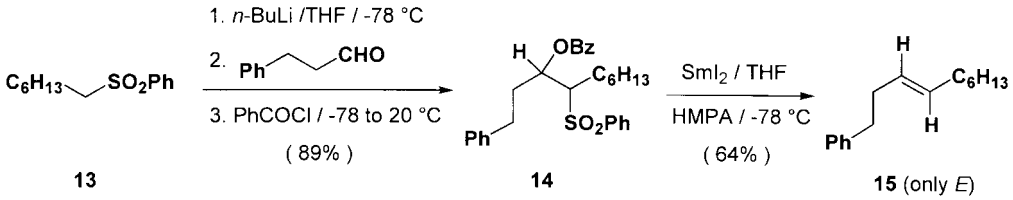


Figure 3.

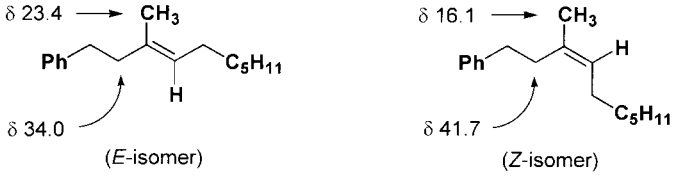


Figure 4.

From these results, it transpires that the use of a suitable in situ oxophilic trapping reagent, combined with a neutral SmI_2-mediated reductive elimination, provides for the first time an efficient access to trisubstituted alkenes by the previously inaccessible condensation of ketones with primary sulfone anions. This methodology can also be applied to the preparation of disubstituted olefins as illustrated in Fig. 3.

Thus, deprotonation of sulfone **13**, followed by sequential addition of dihydrocinnamaldehyde and benzoyl chloride, afforded benzoate ester **14** in 89% yield, as a 60:40 mixture of diastereoisomers. Subsequent reductive elimination of **14** using SmI_2 in THF/HMPA, at −78°C for 1 h, smoothly led to the desired disubstituted alkene **15** (64% yield). In contrast to the trisubstituted alkenes, which are typically obtained as mixtures of isomers, olefin **15** was shown to possess solely the *E*-double bond geometry. The stereochemistry of the trisubstituted olefinic linkage was assigned in each case using the ^{13}C chemical shift method, as illustrated in Fig. 4.[12]

It is interesting to note that the ratio of trisubstituted olefinic isomers is independent of the relative stereochemistry of the starting hydroxide or benzoate derivatives. For example, the same 1.7:1 ratio of alkenes **18** and **19** was obtained by

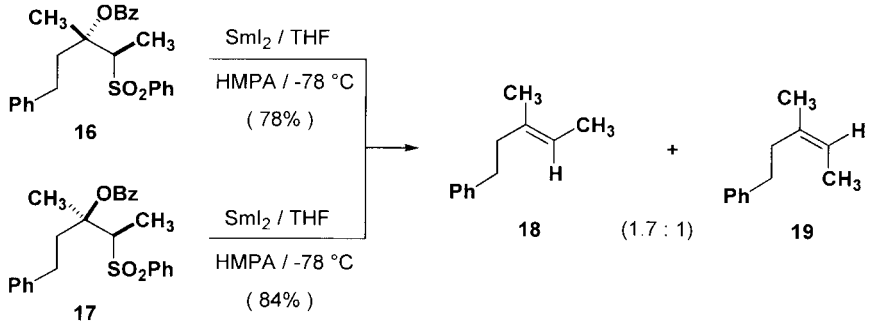


Figure 5.

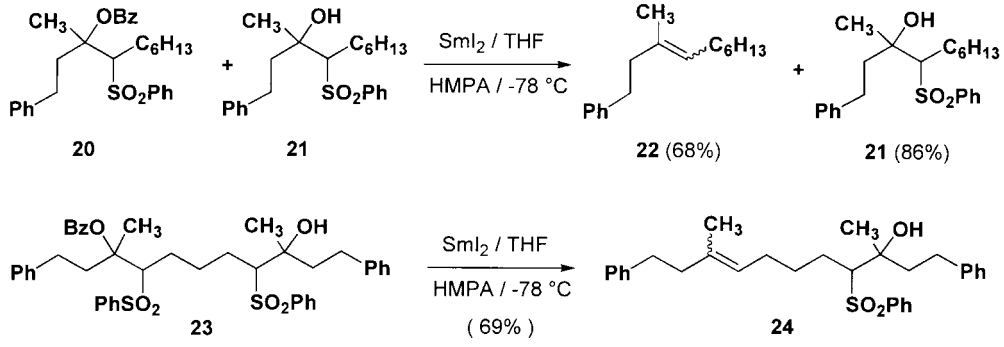


Figure 6.

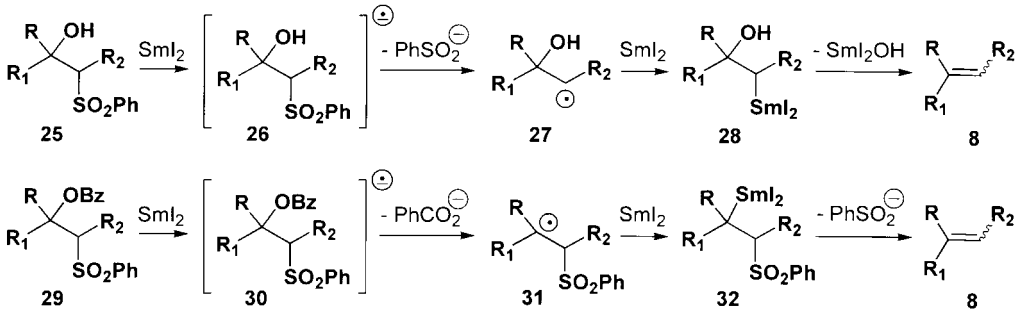


Figure 7.

the SmI_2-mediated reductive elimination of a 4:96 or 90:10 ratio of the diastereoisomeric β-benzoyloxy sulfones **16** and **17** (Fig. 5).

During the course of this work, Fukumoto[13] and Keck,[14] independently reported a similar use of the SmI_2/HMPA system in the preparation of disubstituted olefins. Furthermore, Sinaÿ and co-workers have also successfully employed the Inanaga's conditions for the reductive elimination of a variety of β-acetoxy sulfone derivatives.[15]

The large difference in reactivity between the β-hydroxy sulfones and the corresponding β-benzoyloxy sulfones can be further illustrated using competition experiments (Fig. 6).

For example, treatment of an equimolar mixture of sulfones **20** and **21** with SmI_2, in THF/HMPA, at −78°C for 1 h, resulted in the chemoselective transformation of benzoate **20** into alkene **22**. After work-up, olefin **22** could be isolated in 68% yield and the starting β-hydroxy sulfone **21** was recovered unchanged in 86% yield. Similarly, bis-sulfone **23**, bearing a free hydroxyl function and a benzoate substituent reacted smoothly with SmI_2, at −78°C, affording exclusively and in good yields the unsaturated hydroxysulfone **24**, resulting from the chemo- and regio-selective elimination of the benzoate moiety.

The enormous difference in reactivity between the β-hydroxy sulfones and the β-benzoyloxy sulfones strongly suggests that the reductive elimination of these substrates proceeds via a different mechanism (Fig. 7).

We believe that in the case of the β-hydroxy sulfones, a single electron transfer from SmI_2 to the aromatic sulfone nucleus takes place, generating the radical anion **26**. This step, which appears to be rather unfavourable, is followed by the ejection of phenylsulfinate ion, producing the new radical species **27**. A second electron transfer from SmI_2 to radical **27** then affords the intermediate organosamarium derivative **28**, which undergoes β-elimination, leading to the observed alkene product **8**.

In contrast to this mechanism, the transfer of a single electron to the benzoate moiety appears to be an easier process, taking place rapidly even at −84°C and leading to radical anion **30**. Subsequent collapse of this intermediate liberates the benzoate ion and produces radical **31**.[16] Further transformation of **31** into the organosamarium intermediate **32** and elimination of the phenylsulfinyl group eventually affords the olefin **8**. It is noteworthy that, in accord with the results of Keck, no deuterium incorporation could be detected in the alkene product upon attempted quenching of a putative vinyl anion intermediate using MeOD as an additive in the SmI_2 reductive elimination. This observation, which contrasts with the passage via a vinyl anion in the Na(Hg) mediated reductive elimination, offers further evidence for our proposed reaction mechanism.[14,17] This powerful methodology was then applied to the preparation of dienyl ethers, which are useful substrates for Diels–Alder cycloadditions (Fig. 8).

The requisite β-sulfonyl benzoates were readily prepared by sequential deprotonation of α-benzyloxy sulfone **33** with BuLi, addition of cinnamaldehyde (or its 2-methyl

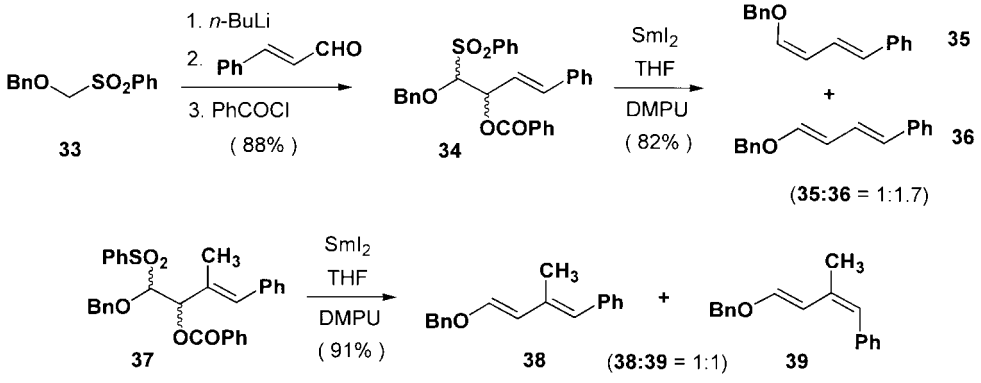


Figure 8.

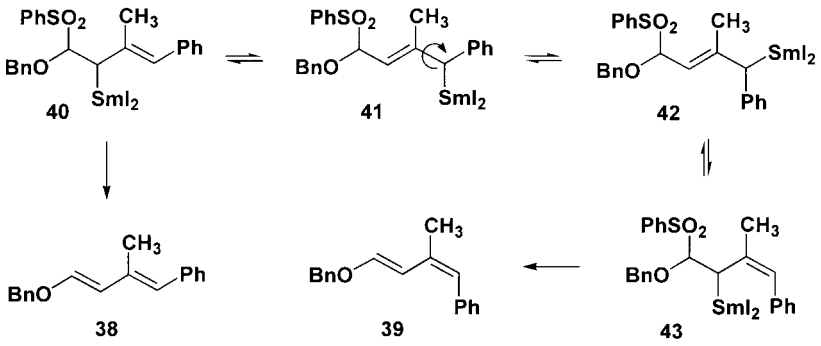


Figure 9.

derivative) and capture of the in situ generated β-alkoxy sulfones with benzoyl chloride. In both cases, the products **34** and **37** consisted of a mixture of *syn*- and *anti*-diastereoisomers. However, the geometric integrity of the C–C double bond of the substrate aldehydes was retained in the products. Reductive elimination of benzoates **34** and **37**, using SmI_2 in THF, in the presence of DMPU, proceeded smoothly, affording the desired dienyl ethers **35/36** and **38/39** in excellent yields. Interestingly, the transformation of sulfones **34** and **37** into the corresponding enol ethers displayed noteworthy differences.

Indeed, dienes **36** and **35** are obtained as a 1.7:1 mixture of *E*/*Z*-isomers at the newly formed enol–ether double bond. No isomerisation of the styrenyl double bond occured under these conditions. In sharp contrast, products **38** and **39** were isolated as a 1:1 mixture of (*E*,*E*)/(*E*,*Z*) geometric isomers, resulting from the loss of the stereochemical integrity of the trisubstituted olefin.

These observations can be rationalised by invoking the intermediacy of either an allylic radicalor the corresponding allylic organosamarium species **40** (Fig. 9).

Based upon our previous explanation (Fig. 7), treatment of benzoate **37** with SmI_2 should result in the formation of the allylsamarium species **40**. The fate of this key intermediate is decisive for the ultimate ratio of (*E*,*E*)/(*E*,*Z*) isomeric dienyl ethers **38** and **39**. Direct β-elimination of phenylsulfinyl anion should lead to the (*E*,*E*)-geometric isomer **38**, via a transition state that should minimise $A^{1,3}$ repulsive interactions between the benzyloxy moiety and the adjacent methyl substituent. However, a competitive [1,3]-shift of SmI_2 might also take place, affording samarium derivative **41**. Rapid rotation around the newly formed C–C bond, followed by another [1,3]-shift then leads to allylic samarium species **43**, in which the trisubstituted double bond has undergone *E*/*Z* isomerisation. Examination of molecular models clearly reveals negligeable differences in steric interactions between intermediates **41** and **42**, further supporting our hypothesis of a rapid equilibrium between these two conformers. Finally, β-elimination of phenylsulfinate ion from **43**, via a transition state with minimum $A^{1,3}$-strain, ultimately forms the (*E*,*Z*)-isomer **39** (Fig. 9).

We believe that the 1:1 ratio of (*E*,*E*)/(*E*,*Z*) isomers obtained in this reaction not only supports our assumption of a rapid equilibrium between the various allylsamarium species **40**, **41**, **42** and **43**,[18] but also lends further credit to our proposed mechanism for the reductive elimination of β-benzoyloxy sulfones.

In summary, we have developed a novel variant of the Julia–Lythgoe olefination reaction, involving the addition of a suitable oxophilic electrophile and the utilisation of SmI_2 to promote, under neutral conditions, the subsequent reductive elimination. This novel methodology allows for the first time, the efficient preparation of trisubstituted alkenes directly from ketones and primary sulfone anions, a transformation that only proceeded previously with extremely poor yields. The synthetic utility of this protocol was further extended to the preparation of disubstituted olefins anddienyl ethers.

1. Experimental

1.1. General methods

All the reactions were carried out under anhydrous conditions and in an atmosphere of argon unless otherwise stated. NMR spectra were recorded on Varian XL-200, Gemini 200 and 300 and Brucker 270 MHz instruments. Chemical shifts are expressed as parts per million (δ) downfield from tetramethylsilane or calibrated from $CDCl_3$. The chemical shifts of the minor diastereoisomers are highlighted whenever discernable from the major isomers and are underlined. Mass spectra were obtained using Varian MAT-44 and Finnigan MAT-TSQ 70 spectrometers with electron impact (70 eV) and chemical ionisation (100 eV, ionisation gas, isobutane). IR spectra were taken with a Perkin–Elmer 681 spectrometer. Thin layer chromatography was performed on Merck 0.2 mm aluminium-backed TLC plates and visualised using UV light followed by development with iodine, alkaline $KMnO_4$ and/or cerium (IV) nitrate solution. Column chromatography was performed using Merck silica gel 60 (230–400 mesh) under pressure. Microanalyses were provided by the analytical department, University College, London. We are grateful to Professors John S. Svendsen and Ari M. P. Koskinen for performing the HRMS analysis.

1.2. General procedure for the addition of a primary sulfone to a ketone. Method A: capture by TMSCl

1.2.1. 3-Methyl-2-phenylsulfonyl heptan-3-ol (Table 1, entry 1). A solution of ethyl phenyl sulfone (0.5 g,

2.9 mmol) in anhydrous THF (9.0 mL) at −78°C was treated with a solution of *n*-BuLi in hexane (1.6 M, 2.2 mL, 3.5 mmol). After stirring for 30 min, a solution of 2-hexanone (0.44 mL, 3.5 mmol) in THF (5.0 mL) was added dropwise and the yellow solution was stirred for another 45 min at −78°C. Trimethylsilyl chloride (0.49 mL, 3.8 mmol) was then added. The cooling bath was removed and, after stirring for 60 min, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with water (30 mL). The aqueous phase was extracted with CH_2Cl_2 (2×20 mL) and the combined organic extracts were washed sequentially with 10% H_2SO_4 (2×20 mL), 5% $NaHCO_3$ (20 mL) and brine (20 mL). After removal of the solvents in vacuo, purification of the residue on silica gel using 8:2 Et_2O/hexane as the eluent, gave 0.685 g (86%) of the title compound as a clear oil. IR (neat) ν_{max}=3518, 3067, 2954, 1584, 1298, 1161, 1139, 720 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ_H=0.89 (3H, t, *J*=7.2 Hz), *0.93* (3H, t, *J*=7.3 Hz), 1.18–1.36 (6H, m), 1.32 (3H, d, *J*=7.2 Hz), 1.53 (3H, s), *3.12* (1H, q, *J*=7.3 Hz), 3.31 (1H, q, *J*=7.2 Hz), 7.54–7.7 (3H, m), 7.87–7.96 (2H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=11.36, 11.41, 13.55, *13.65*, 22.49, *22.68*, 23.80, 24.26, *25.10*, *25.18*, *37.68*, 40.70, 66.86, *68.24*, 74.24, *74.73*, *127.86*, 127.90, *128.80*, 128.84, *133.32*, 133.41, 139.06, *139.16*. HRMS: Calcd mass for $C_{14}H_{22}O_3S$: [M^+], 270.3920. Found: 270.3922.

1.2.2. 3-Methyl-1-phenyl-4-phenylsulfonyl decan-3-ol (Table 1, entry 2). Following Method A, a solution of phenyl heptyl sulfone (1.0 g, 5.90 mmol) in THF (20 mL) was treated with *n*-BuLi in hexane (1.6 M, 4.1 mL, 6.5 mmol) and 4-phenyl-2-butanone (0.99 mL, 6.5 mmol) in THF (9 mL). After addition of trimethylsilyl chloride (2.58 mL, 16 mmol), the cooling bath was removed and the solution stirred for 60 min. Usual work-up gave a crude mixture which was bulb–bulb distilled (150°C, 0.5 mmHg), affording 3.87 g of essentially pure product as a 7:3 mixture of diastereoisomers. This material was recrystallised from hot Et_2O–hexane, providing the title compound as a white solid in analytically pure form (3.58 g, 69%). Mp: 54–56°C. IR (neat) ν_{max}=3507, 3062, 1601, 1288, 1143, 722 cm^{-1}. MS (EI) *m*/*z*=283 (3), 299 (32), 143 (100), 125 (10), 91 (18), 57 (15). ^1H NMR ($CDCl_3$, 300 MHz) δ_H=0.76 (3H, t, *J*=7.1 Hz), 0.89–1.46 (10H, m), *1.41* (3H, s), 1.57 (3H, s), 1.60–2.41 (2H, m), 2.61–2.97 (2H, m), *3.17* (1H, dd, *J*=5.6, 4.9 Hz), 3.24 (1H, dd, *J*=5.7, 3.5 Hz), *4.25* (1H, s), 4.56 (1H, s), 7.11–7.30 (5H, m), 7.49–7.66 (3H, m), 7.85–7.96 (2H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=13.74, 22.29, 24.18, 25.99, *27.01*, 27.15, *28.78*, 28.96, 29.05, 29.45, *29.62*, *29.89*, 31.13, *40.27*, 43.52, 73.30, *74.45*, 75.35, *76.03*, *125.80*, 125.85, 128.18, *128.31*, 128.37, 128.42, 129.20, 133.62, *140.69*, 141.10, 142.07. Anal. Calcd for $C_{23}H_{32}O_3S$: C, 71.10, H, 8.30; S, 8.25. Found: C, 70.85; H, 8.12; S, 8.25.

1.3. General procedure for the addition of a primary sulfone to a ketone. Method B: capture by PhCOCl

1.3.1. 1-Methyl-1-(1-phenylsulfonylethyl) pentyl benzoate (Table 1, entry 3). A solution of ethyl phenyl sulfone (0.5 g, 2.94 mmol) in anhydrous THF (9.0 mL) at −78°C was treated with *n*-BuLi in hexane (1.6 M, 2.20 mL, 3.53 mmol). After stirring for 30 min, a solution of 2-hexanone (0.441 mL, 3.53 mmol) in THF (5.0 mL) was added dropwise and the yellow solution was stirred at −78°C for 2 h. Benzoyl chloride (0.64 mL, 5.50 mmol) was then added. The cooling bath was removed and the reaction mixture was stirred for 50 min before adding 3-dimethylaminopropylamine (0.70 mL, 5.50 mmol). The mixture was diluted with ether (50 mL) and washed with water (30 mL). The aqueous phase was washed with ether (2×20 mL) and the combined organic layers washed sequentially with 10% HCl (20 mL), 5% $NaHCO_3$ (20 mL) and brine (20 mL). Purification of the residue on silica gel using 3:1 hexane–ether as the eluent gave the title compound (1.03 g, 93%, d.r.=7:3) as a clear oil. IR (neat) ν_{max}=3065, 1713, 1601, 1584, 1315, 1147, 1070, 714 cm^{-1}. MS (CI) *m*/*z*=375 (3), 234 (10), 205 (100), 179 (65), 171 (24), 123 (94), 111 (54), 105 (34). ^1H NMR ($CDCl_3$, 300 MHz) δ_H=0.91 (3H, t, *J*=7.2 Hz), *0.92* (3H, t, *J*=7.2 Hz), *1.30* (3H, d, *J*=7.2 Hz), 1.33 (3H, d, *J*=7.1 Hz), 1.17–1.54 (6H, m), *1.74* (3H, s), 1.90 (3H, s), *4.50* (1H, q, *J*=7.2 Hz), 4.55 (1H, q, *J*=7.1 Hz), 7.45–7.58 (6H, m), 7.84–7.96 (4H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=11.20, *11.40*, 13.93, 21.90, *22.02*, 22.77, 24.98, *25.69*, 35.68, *36.71*, 64.18, *64.45*, 85.07, *85.39*, 128.13, *128.22*, 128.40, 128.93, *128.99*, *129.51*, 129.54, *130.63*, 130.76, 132.82, *132.89*, 133.18, *133.30*, 140.10, 165.78. Anal. Calcd for $C_{21}H_{26}O_4S$: C, 67.35; H, 7.00; S, 8.56. Found: C, 67.42; H, 7.18; S, 8.15.

1.3.2. 1-Methyl-3-phenyl-1-(1-phenylsulfonylethyl) propyl benzoate (Table 1, entry 4). According to Method B, a solution of phenylethyl sulfone (1.0 g; 5.90 mmol) in THF (20 mL) was treated with *n*-BuLi in hexane (1.6 M, 4.1 mL, 6.5 mmol) and 4-phenyl-2-butanone (0.99 mL, 6.5 mmol) in THF (9 mL) and benzoyl chloride (1.18 mL, 10 mmol). The title compound was isolated in 93% yield (2.35 g) after purification by the following procedure. A first crop of pure material was obtained by trituration of the crude product with hexane (40%, 1.0 g). The mother liquors were pooled and the solvent was evaporated in vacuo. The residue was bulb-to-bulb distilled (60°C, 0.2 mmHg) to remove traces of 4-phenyl-2-butanone. The remaining solid was recrystallised from hot hexane–ether, affording an additional 1.35 g (53%) of pure compound as a white solid. It is interesting to note that the first crop consisted of a 4:96 mixture of diastereoisomers while the second crop was composed of a 90:10 mixture of isomers. Mp=106–107°C. IR (neat) ν_{max}=3068, 1712, 1601, 1586, 1315, 1149, 1069, 703 cm^{-1}. MS (EI) *m*/*z*=423 (3), 345 (5), 159 (72), 158 (100), 143 (16), 105 (17). ^1H NMR ($CDCl_3$, 300 MHz) δ_H=*1.31* (3H, d, *J*=7.0 Hz), 1.32 (3H, d, *J*=7.2 Hz), *1.84* (3H, s), 2.0 (3H, s), 2.19–2.33 (1H, m), 2.52–3.09 (3H, m), *4.52* (1H, q, *J*=7.0 Hz), 4.59 (1H, q, *J*=7.2 Hz), 7.14–7.28 (5H, m), 7.36–7.58 (6H, m), 7.86–7.95 (4H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=11.28, *11.51*, *22.00*, 22.24, 29.46, *30.09*, *38.86*, 38.94, 64.09, *64.42*, 84.78, *85.14*, *125.97*, 126.04, 128.24, *128.34*, *128.36*, 128.40, 128.46, *128.49*, 129.00, *129.08*, *129.62*, 129.64, *130.56*, 130.65, 132.97, *133.09*, 133.29, *133.43*, *139.93*, 139.99, 140.07, *141.38*, *165.72*, 165.85. Anal. Calcd for $C_{25}H_{26}O_4S$: C, 71.01; H, 6.20; S, 7.59. Found: C, 71.01; H, 6.16; S, 7.62.

1.3.3. 1-Methyl-1-(2-phenylethyl)-2-phenylsulfonyloctyl benzoate (Table 1, entry 5). According to Method B, a

solution of heptyl phenyl sulfone (0.842 g; 3.50 mmol) in THF (10 mL) was treated with *n*-BuLi in hexane (1.6 M, 2.38 mL, 3.8 mmol) and 4-phenyl-2-butanone (0.575 g, 3.8 mmol) in THF (5 mL) and benzoyl chloride (0.77 mL, 6.60 mmol). The title compound was isolated in 85% yield (1.46 g), after purification by silica gel column chromatography using 3:1 hexane–ether as the eluent, as a clear, colourless oil. IR (neat) ν_{max}=3062, 1714, 1602, 1314, 1146, 1070, 700 cm^{-1}. MS (EI) *m/z*=289 (2), 148 (65), 123 (20), 105 (71), 91 (25), 85 (91), 84 (100). ^1H NMR ($CDCl_3$, 200 MHz) δ_H=0.72 (3H, t, *J*=6.7 Hz), *0.74* (3H, t, *J*=6.5 Hz), 0.82–1.40 (10H, m), 1.60–2.42 (2H, m), *1.83* (3H, s), 1.98 (3H, s), 2.60–2.96 (2H, m), *4.43* (1H, dd, *J*=6.0, 3.0), 4.46 (1H, dd, *J*=5.8, 3.0 Hz), 7.10–7.28 (5H, m), 7.36–7.58 (6H, m), 7.86–7.95 (4H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=13.63, 22.02, *22.26*, 22.51, 26.24, *26.39*, *28.73*, 29.26, 29.42, *29.84*, 30.82, 38.71, *69.05*, 69.15, 85.07, *85.47*, *125.75*, 125.86, 128.03, *128.25*, 128.30, 128.78, *129.34*, 129.40, 130.56, *130.63*, 132.77, *133.03*, 133.08, *140.52*, 140.64, 141.12, *141.24*, *165.54*, 165.64. HRMS: Calcd mass for $C_{30}H_{36}O_4S$: [M^+], 492.6780. Found: 492.6784.

1.3.4. 4-*tert*-Butyl-1-benzoyloxy-1-(1-phenylsulfonyl pentyl) cyclohexane (Table 1, entry 6). According to Method B, a solution of pentyl phenyl sulfone (6.36 g; 29 mmol) in THF (90 mL) was treated with *n*-BuLi in hexane (1.6 M, 22 mL, 35.2 mmol) and 4-*tert*-butylcyclohexane (5.1 g, 29 mmol) in THF (30 mL), benzoyl chloride (5.8 mL, 56.3 mmol) and dimethylaminopropyl amine (7 mL). The title compound was isolated in 85% yield (10.4 g) as a white solid, after purification by recrystallisation from heptane. Mp=137°C. IR (neat) ν_{max}=2951, 2869, 1711, 1336, 1142 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ_H=0.67 (3H, t, *J*=6.9 Hz), 0.78 (9H, s), 1.1–1.4 (7H, m), 1.6–1.85 (4H, m), 2.0 (2H, m), 2.56 (1H, dq, *J*=14.1, 3.3 Hz), 2.86 (1H, dq, *J*=14.4, 3.0 Hz), 4.48 (1H, dd, *J*=4.8, 3.6 Hz), 7.35 (5H, m), 7.5 (1H, tt, *J*=7.2, 1.5 Hz), 7.84 (4H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=14.21, 22.68, 23.01, 23.17, 26.58, 28.07, 32.43, 32.62, 32.79, 33.03, 47.36, 68.97, 86.07, 128.90, 129.23, 129.59, 130.23, 131.63, 133.61, 133.75, 141.59, 166.47. Anal. Calcd for $C_{28}H_{38}O_4S$: C, 71.49; H, 8.09; S, 6.81. Found: C, 71.59; H, 8.16; S, 6.92.

1.4. Method A. General procedure for the reductive elimination of β-hydroxy sulfones

1.4.1. 3-Methyl-1-phenyl dec-3-ene[19] (Table 2, entry 2). Freshly distilled HMPA (2.0 mL, 11.4 mmol) was added to a solution of *3-Methyl-1-phenyl-4-phenylsulfonyl decan-3-ol* (0.4 g, 1.03 mmol, d.r.=7:3) dissolved in 0.1 M SmI_2 in THF (52 mL, 5.2 mmol) at 0°C and the solution was stirred for 1 h. Saturated NH_4Cl (15 mL) was then added and, upon warming to room temperature, the solution was diluted with ether (300 mL) and washed with 10% aq. sodium thiosulfate (200 mL). The aqueous layers were extracted with ether (2×65 mL) and the combined organic layers were washed with water (65 mL), dried and the solvents were removed in vacuo. The crude product was purified by column chromatography on silica gel using 100% petroleum ether as the eluent. The title compound was obtained as a colourless liquid (0.156 g, 66%, 1.2:1 mixture of *E*/*Z* isomers).

1.5. Method B. General procedure for the reductive elimination of β-benzoyloxy sulfones

1.5.1. 3-Methyl-1-phenyl dec-3-ene[19] (Table 2, entry 5). Freshly distilled HMPA (1.3 mL, 7.4 mmol) was added to a solution of *1-methyl-1-(2-phenylethyl)-2-phenylsulfonyl-octyl benzoate* (0.642 g, 1.3 mmol, d.r.=7:3) dissolved in 0.1 M SmI_2 in THF (65 mL, 6.5 mmol) at −78°C and the solution was stirred for 1 h. Saturated NH_4Cl (10 mL) was then added and, upon warming to room temperature, the solution was diluted with ether (200 mL) and washed with 10% aq. sodium thiosulfate (150 mL). The aqueous layer was extracted with ether (2×50 mL) and the combined organic layers were washed with water (50 mL), dried and the solvents were removed in vacuo. The crude product was purified by column chromatography on silica gel using 100% petroleum ether as the eluent. The title compound was obtained as a colourless liquid (0.22 g, 72%, 2.5:1 mixture of *E*/*Z* isomers). IR (neat) ν_{max}=3070, 3030, 1675, 1600, 1495, 1454, 742, 697 cm^{-1}. MS (EI) *m/z*= 231 (13), 230 (100), 146 (14), 104 (73), 91 (98), 83 (51). ^1H NMR ($CDCl_3$, 300 MHz) δ_H=*0.877* (3H, t, *J*=7.2 Hz), 0.883 (3H, t, *J*=6.9 Hz), 1.18–1.32 (8H, m), 1.64 (3H, s, (*E*)), *1.72* (3H, s, (*Z*)), 1.84–1.98 (2H, m), 2.24–2.34 (2H, m), 2.64–2.72 (2H, m), 5.10–5.17 (1H, m), 7.14–7.31 (5H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=14.10, 16.08 (*E*), 22.68, *23.43* (*Z*), *27.83*, 27.95, 29.00, *29.11*, 29.79, *29.97*, 31.85, *34.02* (*Z*), *34.52*, 34.80, 41.67 (*E*), 125.41, 125.59, *125.70*, *126.29*, 128.18, *128.22*, 128.36, *134.13*, 134.17, *142.46*, 149.50.

1.5.2. 3-Methyl-1-phenyl pent-3-ene[20] (Table 2, entry 4). Prepared according to Method B. Freshly distilled HMPA (0.8 mL, 4.6 mmol) was added to a solution of *1-methyl-3-phenyl-1-(1-phenylsulfonylethyl) propyl benzoate* (0.33 g, 0.8 mmol, d.r.=7:3) dissolved in 0.1 M SmI_2 in THF (40 mL, 4.0 mmol) at −84°C and the solution was stirred for 1 h. Saturated NH_4Cl (10 mL) was then added and, upon warming to room temperature, the milky white suspension was diluted with ether (200 mL) and washed with 10% aq. sodium thiosulfate (100 mL). The aqueous layer was extracted with ether (2×50 mL) and the combined organic layers were washed with water (50 mL), dried and the solvents were removed in vacuo. The crude product was purified by column chromatography on silica gel using 100% pentane as the eluent. The title compound was obtained as a colourless liquid (0.108 g, 84%, 1.7:1 mixture of *E*/*Z* isomers). IR (neat) ν_{max}=3063, 1670, 1604, 1495, 1454, 742, 698 cm^{-1}. MS (EI) *m/z*=161 (5), 160 (52), 145 (14), 91 (100), 69 (28). ^1H NMR ($CDCl_3$, 200 MHz) δ_H= 1.47 (3H, bd, *J*=6.6 Hz), 1.56 (3H, bd, *J*=6.7 Hz), 1.65 (3H, bs), 1.72 (3H, bs), 2.23–2.36 (2H, m), 2.62–2.74 (2H, m), 5.226 (1H, m), 5.232 (1H, m), 7.09–733 (5H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=*13.00*, 13.27, *15.76*, 23.38, *33.60*, 34.15, *34.79*, 41.63, *118.78*, 119.66, 125.62, *125.70*, 128.21, *128.34*, 135.23, *135.30*, 142.46, *142.58*.

1.5.3. 4-*tert*-Butyl cyclohexylidenyl butane[21] (Table 2, entry 6). Prepared according to Method B. Freshly distilled HMPA (4 mL, 23 mmol) was added to a solution of *1-methyl-3-phenyl-1-(1-phenylsulfonylethyl) propyl benzoate* (0.94 g, 2.0 mmol) dissolved in 0.1 M SmI_2 in THF (250 mL, 24 mmol) at −78°C and the solution was stirred

for 15 h at room temperature. Saturated NH_4Cl (30 mL) was then added and the solution was diluted with ether (400 mL) and washed with 10% aq. sodium thiosulfate (400 mL). The aqueous layer was extracted with ether (2×100 mL) and the combined organic layers were washed with water (2× 100 mL), dried and the solvents were removed in vacuo. The crude product was purified by column chromatography on silica gel using 100% hexane as the eluent. The title compound was obtained as a colourless liquid (0.350 g, 85%). IR (neat) ν_{max}=2957, 2856, 1735 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz) δ_H=0.82 (9H, s), 0.87 (3H, bt, *J*= 6.9 Hz), 0.88 (1H, m), 1.05 (1H, qt, *J*=11.7, 2.7 Hz), 1.24 (5H, m), 1.62 (1H, tm, *J*=13.5 Hz), 1.8 (2H, m), 1.96 (3H, m), 2.19 (1H, dq, *J*=14.1, 3.0 Hz), 2.61 (1H, dq, *J*=13.5, 2.7 Hz), 5.04 (1H, t, *J*=7.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ_C=14.80, 23.12, 27.67, 28.37, 28.40, 28.46, 29.28, 30.11, 32.23, 37.84, 49.38, 121.91, 139.97.

1.5.4. 1-(2-Phenylethyl)-2-phenylsulfonyloctyl benzoate 14. Prepared according to Method B using the following quantities: phenylheptyl sulfone (0.842 g, 3.50 mmol), 3-phenyl-1-propanal (0.537 g, 3.80 mmol). The crude product was purified by column chromatography on silica gel using 2:1 hexane–ether as the eluent, affording the title compound (colourless oil) as a 3:2 mixture of diastereoisomers in 89% yield (1.483 g). IR (neat) ν_{max}=3064, 1721, 1603, 1315, 1149, 1070, 700 cm^{-1}. MS (EI) *m/z*= 223 (23), 134 (37), 122 (51), 105 (59), 84 (77), 56 (100). ^1H NMR ($CDCl_3$, 200 MHz) δ_H=*3.31* (1H, ddd, *J*=7.9, 5.2, 2.7 Hz), 3.48 (1H, ddd, *J*=6.0, 6.0, 2.7 Hz), 5.30 (1H, ddd, *J*=10.2, 2.7, 2.7 Hz), *5.55* (1H, ddd, *J*=7.5, 5.2, 2.2 Hz), 7.10–7.62 (11H, m), 7.72–8.06 (4H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=13.73, *13.83*, 22.23, *22.33*, *23.53*, 24.52, 27.51, *28.06*, 28.73, *28.97*, 31.10, *31.21*, 31.81, *31.90*, 33.57, 65.64, *66.96*, 71.09, *71.20*, 126.00, 126.09, 128.11, 128.22, 128.30, 128.40, 128.50, 128.60, *128.91*, 129.04, 129.49, 129.50, *132.97*, 133.16, *133.28*, 133.49, *138.65*, 138.82, *140.25*, 140.60, 165.14. Anal. Calcd for $C_{29}H_{34}O_4S$: C, 72.77; H, 7.16; S, 6.70. Found: C, 73.02; H, 7.27; S, 6.32.

1.5.5. (*E*)-1-Phenyl dec-3-ene 15. Prepared according to Method B using the following quantities: *1-(2-phenylethyl)-2-phenylsulfonyloctyl benzoate* **14** (0.488 g, 1.02 mmol), SmI_2 (0.1 M, 51 mL, 5.10 mmol) and HMPA (2.03 mL, 11.6 mmol) at −78°C. The crude product was purified by column chromatography on silica gel using 100% hexane as the eluent, affording the title compound as a clear oil (0.164 g, 64%). IR (neat) ν_{max}=3030, 1630, 1496, 1455, 745, 698 cm^{-1}. MS (EI) *m/z*=217 (14), 216 (100), 104 (35), 91 (38), 69 (13). ^1H NMR ($CDCl_3$, 300 MHz) δ_H=0.88 (3H, t, *J*=6.8 Hz), 1.21–1.34 (8H, m), 1.92–2.22 (2H, m), 2.39–2.45 (2H, m), 2.62–3.72 (2H, m), 5.36–5.45 (2H, m), 7.14–7.28 (5H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=14.06, 22.63, 28.80, 29.53, 31.76, 32.56, 34.43, 36.19, 125.68, 128.22, 128.48, 129.31, 131.22, 142.21. Anal. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18. Found: C, 88.65; H, 11.30.

1.5.6. 3,9-Dimethyl-1,11-diphenyl-4-phenylsulfonyl undec-8-en-3-ol 24. Freshly distilled HMPA (0.26 mL, 1.49 mmol), was added to a solution of *bis*-sulfone **23** (0.1 g, 0.13 mmol) dissolved in 0.1 M SmI_2 in THF (6.5 mL, 0.65 mmol) at −78°C. The solution was stirred for 30 min. Saturated NH_4Cl (0.8 mL) was then added, the cooling bath was removed and the mixture stirred vigorously for 30 min. After dilution with ether (30 mL), the mixture was washed with 10% aq. $Na_2S_2O_3$ (15 mL) and the aqueous layers extracted with ether (2×10 mL). The combined organic phases were washed with water (10 mL), dried and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel using 95:5 hexane–ether as the eluent, affording the title compound as a clear colourless oil (45 mg, 69%, mixture of isomers). IR (neat) ν_{max} =3504, 3064, 2934, 1603, 1448, 1312, 1145, 1045, 723 cm^{-1}. MS (EI) *m/z*=472 (23), 342 (95), 331 (100), 239 (19), 227 (80), 185 (20), 131 (55), 91 (53). ^1H NMR ($CDCl_3$, 200 MHz) δ_H=0.58–2.10 (10H, m), 1.33 (3H, s), 1.43 (3H, s), 1.50 (3H, s), 1.59 (3H, s), 2.10–3.16 (5H, m), 4.45 (1H, s, OH), 4.47 (1H, s, OH), 4.67–4.78 (1H, m), 4.96–5.12 (1H, m), 7.08–7.28 (10H, m), 7.38–7.61 (3H, m), 7.79–7.93 (2H, m). ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C=16.09 (*Z*), 23.37 (*E*), 24.17, 25.98, 26.63, 26.67, 27.26, 27.32, 27.47, 27.58, 29.32, 29.43, 29.56, 29.89, 29.99, 30.37, 34.67 (*E*), 40.29, 41.40 (*Z*), 42.02, 43.55, 43.75, *73.30*, 74.37, *75.33*, 76.00, *123.52*, 124.44, *125.70*, 125.82, 128.04, 128.22, 128.30, 128.41, 129.18, 133.48, 133.66, 135.39, 135.48, 135.53, 135.61, 140.56, *140.64*, 140.96, *141.01*, 142.07, 142.18. Anal. Calcd for $C_{31}H_{38}O_3S$: C, 75.88; H, 7.81. Found: C, 75.96; H, 7.95.

1.5.7. (*E*)-1-Benzyloxy-1-phenylsulfonyl-2-benzoyloxy-5-phenyl but-3-ene 34. Prepared according to Method B using the following quantities: sulfone **33** (0.212 g, 0.81 mmol), *n*-BuLi (0.4 mL, 0.97 mmol), THF (5 mL), cinnamaldehyde (0.122 mL, 0.97 mmol) dissolved in 5 mL of THF and PhCOCl (0.112 mL, 0.97 mmol) at −78°C. After warming to room temperature over 45 min, the reaction mixture was diluted with sat. NH_4Cl (50 mL) and ether (50 mL). The organic layer was separated and the aqueous phase extracted with ether (3×30 mL). The combined organic layers were washed with water (50 mL), brine (50 mL), dried over $MgSO_4$ and the solvents removed in vacuo. The crude product was purified by column chromatography on silica gel using 70:30 petroleum ether/AcOEt as the eluent, affording the title compound as a colourless solid (0.358 g, 88%). Mp=108–110°C. IR (neat) ν_{max}=2900, 1720, 1260, 1147, 1115 cm^{-1}. MS (CI) *m/z*=516, 357, 280, 266, 149, 84, 49. ^1H NMR ($CDCl_3$, 270 MHz) δ_H= 4.71 (1H, d, *J*=3.01 Hz), 4.87 (1H, d, *J*=5.1 Hz), 4.91 (1H, d, *J*=11.8 Hz), 5.03 (1H, d, *J*=11.6 Hz), 5.07 (1H, d, *J*=11.8 Hz), 5.23 (1H, d, *J*=11.6 Hz), 5.87 (1H, dd, *J*=7.9, 5.08 Hz), 5.98 (1H, dd, *J*=15.5, 7.6 Hz), 5.99 (1H, dd, *J*=15.7, 7.9 Hz), 6.07 (1H, dd, *J*=7.6, 3.0 Hz), 6.62 (1H, d, *J*=15.7 Hz), 6.64 (1H, d, *J*=15.5 Hz), 7.1–8.0 (20H, m). HRMS: Calcd mass for $C_{30}H_{30}NO_5S$: $[M+NH_4^+]$, 516.1845. Found: 516.1863.

1.5.8. (*E*)-1-Benzyloxy-1-phenylsulfonyl-2-benzoyloxy-3-methyl-5-phenyl but-3-ene 37. Prepared according to Method B using the following quantities: *n*-BuLi (0.318 mL, 0.795 mmol), sulfone **33** (0.189 g, 0.723 mmol), THF (6 mL), α-methyl cinnamaldehyde (0.116 g, 0.795 mmol) dissolved in 6 mL of THF and PhCOCl (0.1 mL, 0.867 mmol). Usual work-up gave a crude product which was purified by column chromatography on silica gel

using 70:30 petroleum ether/AcOEt as the eluent, affording the title compound as a colourless oil (0.092 g, 25%). IR (neat) ν_{max}=2918, 1719, 1445, 1310, 1282, 1143, 1103, 1070, 743 cm^{-1}. MS (CI) *m/z*=530, 408, 372, 371, 251, 249, 233, 159, 108, 105, 91. ^1H NMR ($CDCl_3$, 270 MHz) Diastereoisomer 1, δ_H=1.7 (3H, s), 4.83 (1H, d, *J*=11.3 Hz), 4.89 (1H, d, *J*=8.3 Hz), 5.05 (1H, d, *J*=11.1 Hz), 5.48 (1H, d, *J*=8.3 Hz), 6.6 (1H, s), 7.2–8.1 (10H, m). Diastereoisomer 2, δ_H=1.7 (3H, s), 4.78 (1H, d, *J*=3.3 Hz), 5.03 (1H, d, *J*=11.0 Hz), 5.22 (1H, d, *J*=11.0 Hz), 5.87 (1H, d, *J*=3.3 Hz), 6.45 (1H, s), 7.2–8.1 (10H, m).

1.5.9. 1-Benzyloxy-4-phenyl-1,3-butadiene 35/36. A solution of sulfone **34** (0.113 g, 0.227 mmol) and DMPU (0.433 mL, 3.585 mmol) in 2.4 mL of THF was treated with SmI_2 (12 mL of a 0.1 M solution in THF, 1.195 mmol). The resulting blue–green solution was stirred at room temperature for 2 h. The reaction was quenched by the addition of a saturated solution of NH_4Cl (20 mL) and extracted with ether (3×50 mL). The combined organic layers were washed with 10% $Na_2S_2O_3$ (50 mL), water (50 mL), brine (50 mL), dried over $MgSO_4$ and the solvents were removed in vacuo. The residue was purified by column chromatography on silica gel using 9:1 petroleum ether–AcOEt as the eluent, affording the title compound as a colourless oil (0.044 g, 82%, *E*/*Z*=1.7:1). IR (neat) ν_{max}= 3027, 2926, 1638, 1611, 1593, 1160, 1064, 743 cm^{-1}. MS (CI) *m/z*=237, 219, 145, 117, 108, 91. ^1H NMR ($CDCl_3$, 270 MHz) Compound **36**, δ_H=4.84 (2H, s), 5.87 (1H, dd, *J*=12.3, 10.9 Hz), 6.38 (1H, d, *J*=15.5 Hz), 6.69 (1H, dd, *J*=15.7, 10.9 Hz), 6.79 (1H, dd, *J*=15.7, 10.9 Hz), 7.15 (10H, m). Compound **35**, δ_H=4.88 (2H, s), 5.31 (1H, ddd, *J*=11.1, 6.2, 0.7 Hz), 6.16 (1H, dt, *J*=6.2, 0.9 Hz), 6.45 (1H, d, *J*=14.6 Hz), 7.15 (10H, m+1H, dd, *J*=14.6, 11.1 Hz).

1.5.10. 1-Benzyloxy-3-methyl-4-phenyl-1,3-butadiene 38/39. A solution of sulfone **37** (0.042 g, 0.082 mmol) and DMPU (0.212 mL, 1.76 mmol) in 1.1 mL of THF was treated with SmI_2 (5.8 mL of a 0.1 M solution in THF, 0.58 mmol). The resulting blue–green solution was stirred at room temperature for 2 h. The reaction was quenched by the addition of a saturated solution of NH_4Cl (20 mL) and extracted with ether (3×50 mL). The combined organic layers were washed with 10% $Na_2S_2O_3$ (50 mL), water (50 mL), brine (50 mL), dried over $MgSO_4$ and the solvents were removed in vacuo. The residue was purified by column chromatography on silica gel using 97:3 petroleum ether–AcOEt as the eluent, affording the title compound as a colourless oil (0.019 g, 91%, (*E*,*E*)/(*E*,*Z*)=1/1). IR (neat) ν_{max}=2957, 2831, 1550, 1449, 1131, 1021, 742 cm^{-1}. MS (CI) *m/z*=251, 233, 159, 131, 108, 91. ^1H NMR ($CDCl_3$, 270 MHz) Compound **38**, δ_H=1.7 (3H, s), 4.82 (2H, s), 6.19 (1H, s), 6.25 (1H, d, *J*=12.7 Hz), 6.78 (1H, d, *J*=13.2 Hz), 7.2–7.5 (10H, m). Compound **39**, δ_H=1.7 (3H, s), 4.87 (2H, s), 5.89 (1H, d, *J*=12.7 Hz), 6.36 (1H, s), 6.73 (1H, d, *J*=13.2 Hz), 7.2–7.5 (10H, m).

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