Radical β-Elimination of a Sulfinyl Group to Afford Allenes

Virginie Mouriès,[a] Bénédicte Delouvrié,[a] Emmanuel Lacôte,[a] Louis Fensterbank,*[a] and Max Malacria*[a]

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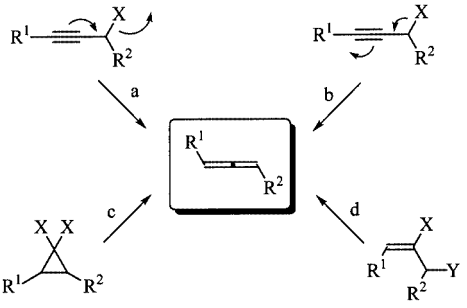
An unprecedented radical β-elimination of vinyl sulfoxides has opened a new route to functionalized allenes. The radical precursors were obtained in two steps from a carbonyl derivative and a vinyl sulfoxide. The radical translocation stratagem could also be used to trigger the β-elimination of the sulfinyl radical. Variation of the nature of the sulfur group on a common precursor gave no allene with the thio, sulfonyl, and iminosulfinyl moieties, in contrast to the analogous vinyl sulfoxide and vinylsulfimide precursors.

Introduction

Allenes are versatile partners for a variety of synthetic applications including, for instance, oxidations, cycloadditions, metal-catalyzed cycloisomerizations, formation of π-allyl complexes, and electrocyclizations.[1] This partly explains the constant interest in the invention of new allene syntheses.

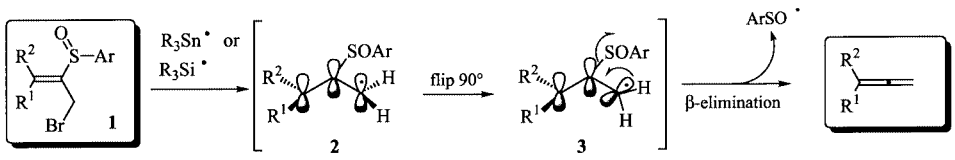
Several preparative routes are now well established, and are outlined in Scheme 1. Among them, the S_N2' displacement of a propargylic leaving group (pathway a) has attracted a lot of attention,[2] and has allowed the preparation of enantiopure allenes.[3,4] Propargylic precursors can also be used to generate propargylic metallic entities that can be trapped in the allenic form (pathway b).[5−7] Two alternative approaches have relied on monounsaturated precursors. Dihalogenated cyclopropyl derivatives can be conveniently transformed into allenes by the Skattebøl rearrangement (pathway c).[8,9] On the other hand, a large family of reactions has involved elimination of X and Y from a vinyl precursor (pathway d). For instance, where X is a leaving group and with displacement of the C−Y bond, elimination can proceed to afford allenes under various conditions.[10−12] Wittig-[13−16] or Peterson-type[17] approaches have also been devised, including transition metal mediated variants.[18−21] In these elimination reactions, vinyl sulfoxides have played an important role. Nucleophilic attack of an organometallic reagent on the sulfinyl group (X) of β-mesyloxy- or β-acetoxyvinyl sulfoxides with subsequent elimination of the mesylate or acetate group (Y) has been reported.[22] The second route has consisted of the formation of an allylic carbanion stabilized by a chelate involving the sulfinyl group and subsequent β-elimination.[23,24] This has recently been developed into a one-pot sequence involving carbocupration of an alkynyl sulfoxide, followed by zinc carbenoid homologation and final β-elimination of the sulfinyl group.[25]



Scheme 1

Probably because allenes are excellent radical acceptors[26,27] that have served in total synthesis of natural products,[28−31] their synthesis by radical approaches has remained largely unexplored. Two isolated reports have mentioned that allenes, in admixture with other compounds, can be obtained through the addition of halogens[32] or selenosulfonates[33] to cyclopropylacetylene and that the reaction proceeds by the rearrangement of an α-cyclopropylvinyl radical. Tin hydride reduction of this type of radicals has also been studied by Crandall, who showed that the allene functionality could be obtained only under slow addition conditions.[34] Recently, a notable breakthrough has been accomplished by Myers, who developed a single-step transformation of propargyl alcohols into allenes, through a radical fragmentation of diazene intermediates, corresponding to pathway b in Scheme 1.[35,36]

[a] Université P. et M. Curie, Laboratoire de Chimie Organique de Synthèse associé au CNRS, Tour 44−54, Case 229
4, place Jussieu, 75252 Paris Cedex 05, France
Fax: (internat.) + 33-1/44277360
E-mail: fensterb@ccr.jussieu.fr
malacria@ccr.jussieu.fr



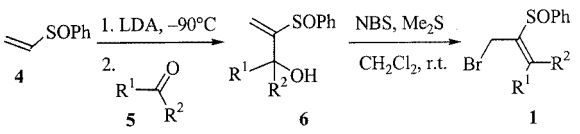
Scheme 2

We have recently reported a new radical synthesis of allenes from allyl bromide precursors **1** (Scheme 2), based on the β-elimination of a sulfinyl radical[37,38] and corresponding to pathway d in Scheme 1.[39] While β-elimination of sulfinyl radicals has been estimated to be a very fast process (ca. 10^9 s^{-1}),[40,41] no data, to the best of our knowledge, have been reported in the case of an aryl sulfoxide borne by a sp^2-C center. A noteworthy feature of this system is that we are now dealing with a conjugated radical **2** that needs to flip by 90° to provide **3**, which can then undergo β-elimination. Initially, we feared that the required energy barrier to break the conjugation of the allylic radical might be quite high, especially since the closely related reverse pathways selenosulfonation,[42] iodosulfonation,[43] and hydrosulfurization[44] of allenes involving the initial addition of a sulfonyl or thio radical were documented.[45,46] In these reactions, the addition of the S-centered radical can take place at the terminal or at the central position of the allene, but the former is reversible in the absence of efficient trapping, whilst addition at the central position results in a highly stabilized allyl radical, thus generating a driving force. Nevertheless, we decided to examine this chemistry in order to prepare variously substituted allenes. We also varied the nature of the sulfur group (thio, sulfonyl, iminosulfinyl, iminothio) to delineate the scope and limitations of the β-elimination process. Finally, we have identified an intriguing competition between a 6-*exo*-*trig* cyclization and a 1,5-H transfer/β-elimination tandem, which can be controlled by the nature of the incoming radical.

Results and Discussion

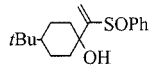
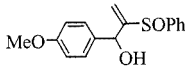
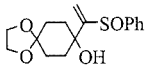
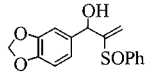
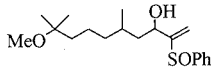
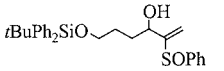
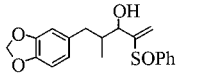
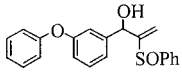
Synthesis of Precursors

To test this strategy, we initially focused on terminally unsubstituted allenes, and prepared the allyl bromides **1** in a two-step procedure (Scheme 3) based on chemistry developed by Maignan.[47] The first step involved the alkylation of the vinylic carbanion of phenyl vinyl sulfoxide **4** with readily available carbonyl derivatives **5** to give alcohols **6** in moderate (though consistent with the literature; Table 1[48]) yields and diastereoselectivities. The diastereomeric mixtures of alcohols **6** were then treated with NBS in the presence of dimethyl sulfide to give the allyl bromides **1**, generally in good yields and with high to complete (*E*) selectivity (Table 2).



Scheme 3

Table 1. Preparation of the sulfinyl alcohols **6**

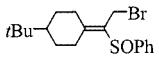
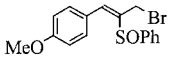
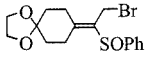
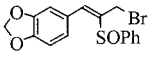
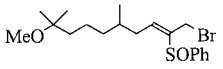
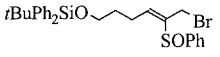
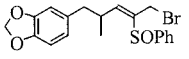
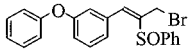
Entry	Alcohol **6**	Yield, (%)	*de* (%)
1		**6a**, 50	22
2		**6b**, 54	20
3		**6c**, 40	–
4		**6d**, 45	18
5		**6e**, 51	–[a]
6		**6f**, 50	–[a]
7		**6g**, 53	–[a]
8		**6h**, 48	4

[a] Not determined.

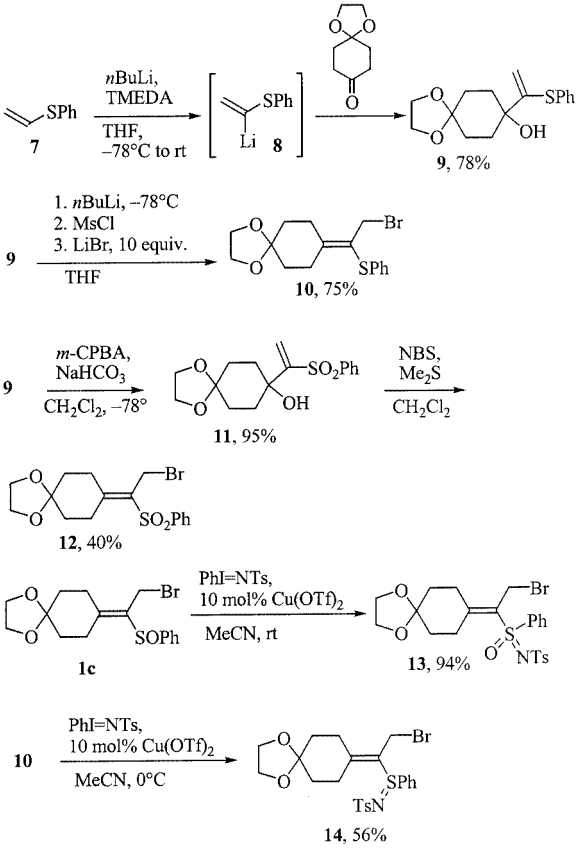
We also prepared the thio, sulfonyl, iminosulfinyl, and iminothio analogues of **1c**, the syntheses of which have no precedent and are presented in Scheme 4. Deprotonation of the vinyl sulfide **7** with *n*BuLi in the presence of TMEDA[49,50] generated the α-thiovinyl anion **8**, which was quenched with 1,4-cyclohexanedione monoethylene ketal to provide the tertiary alcohol **9** in fair yield. The best bromination conditions were devised by first forming the mesylate, and then treating it with an excess of lithium bromide, to furnish a 75% yield of allyl bromide **10**. Thioether **9** could also be efficiently oxidized at the sulfone stage with *m*-CPBA (95% of **11**),[49] and further transformed into bromide **12** under NBS/dimethyl sulfide conditions. Finally, the allyl bromides **1c** and **10** could be iminated by use of [(*p*-tolylsulfinyl)imino]phenyliodinane and copper(II) catalysis, to provide the corresponding sulfoximine **13** (94%)[51] and sulfimide **14** (56%),[52] respectively.

With a view to obtaining allenes by initial hydrogen transfer, we also synthesized precursors **18** and **23**

Table 2. Preparation of the allyl bromides **1**

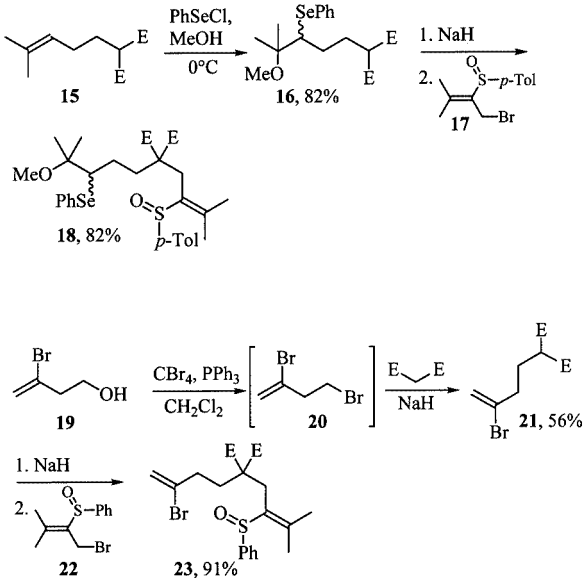
Entry	Bromide **1**	Yield, (%)	*E* : *Z*
1		**1a**, 64	–[a]
2		**1b**, 86	100 : 0
3		**1c**, 49	–
4		**1d**, 80	100 : 0
5		**1e**, 68	–[b]
6		**1f**, 83	91 : 9
7		**1g**, 73	95 : 5
8		**1h**, 75	100 : 0

[a] *de* = 24%. [b] No *de* determination.



Scheme 4

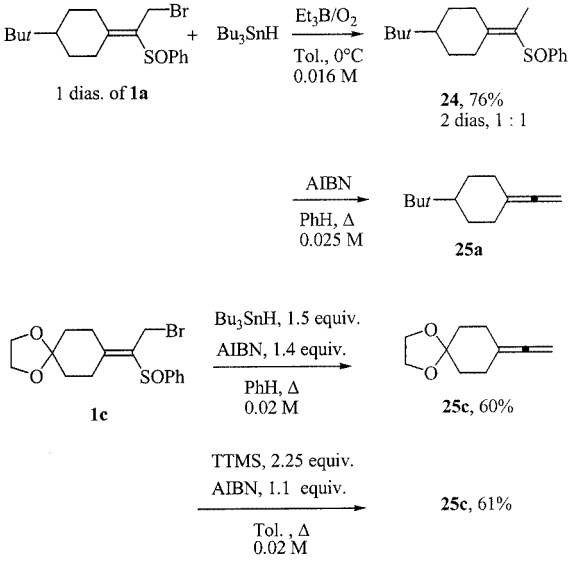
(Scheme 5). Methoxyselenation[53] of malonate **15** smoothly provided **16**. The sodium salt of **16** could be subjected to malonyl coupling with allyl bromide **17** to give a good yield of the diastereomeric mixture of **18**. Precursor **23** was prepared uneventfully by alkylation of dimethyl malonate, first with homoallyl bromide **20** (56%) and then with allyl bromide **22** (91%).



Scheme 5

β-Elimination Reactions

To test the feasibility of the reaction, we initially looked at the behavior of precursor **1a**, and tried several radical reaction conditions (Scheme 6). We first found that, at low temperature (0 °C) with the triethylborane/oxygen initiating system, the β-elimination did not take place, and that only reduced adducts **24** were isolated. In refluxing benzene, however, allene **25a** was formed. Although it was contamin-

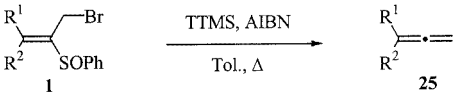


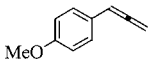
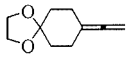
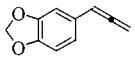
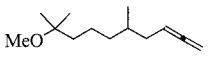
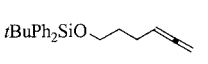
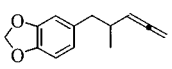
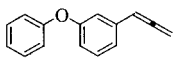
Scheme 6

ated with tin residues, its structure was fully confirmed by comparison with the literature spectroscopic data.[54] While the same type of behavior was observed with aromatic precursor **1h**, our initial assumption that a certain amount of energy had to be provided to the reacting system to trigger the β-elimination was corroborated. We also looked at the behavior of an analogue precursor (**1c**), bearing some polar functionality to assist separation from tin by-products and checked that a fair yield of allene **25c** could be obtained with tin hydride in refluxing benzene. Alternatively, the use of Chatgilialoglu's tris(trimethylsilyl)silane (TTMS) and AIBN as an initiator in refluxing toluene proved as rewarding.

We therefore applied the latter conditions to other precursors, with the idea that the TTMS, a slower hydrogen donor than tin hydride,[55] should also minimize the formation of reduced products and facilitate purification of the reaction products. This method proved successful, as shown in Table 3. Aliphatic substrates (Entries 4−6), including ketone-derived ones (Entry 2), gave satisfactory yields of allenes. More interestingly, highly stabilized radicals (Entries 1, 3, and 7) could also undergo the β-elimination. The sulfinyl radical generated during the course of the reaction presumably dimerized, and disproportionation then occurred to furnish an arylthio and an arylsulfonyl radical.[41] This was evidenced by isolation of the $ArSSi(SiMe_3)_3$ adduct in several of our reactions, suggesting that the radical chain was not properly maintained. Thus, excesses of TTMS (1.5−2.5 equiv.) and of AIBN (0.75−1.50 equiv.) had to be used to guarantee complete conversion in these reactions.

Table 3. Formation of the allenes **25**

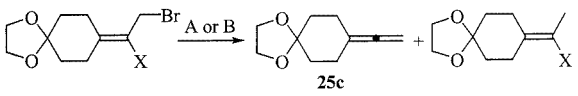


Entry	Bromide **1**	Allene **30**	Yield, (%)
1	**1b**		**25b**, 56
2	**1c**		**25c**, 61
3	**1d**		**25d**, 57
4	**1e**		**25e**, 53
5	**1f**		**25f**, 55
6	**1g**		**25g**, 80[a]
7	**1h**		**25h**, 70

[a] Reaction was run in benzene.

Variation of the sulfur group gave new insights into the reactivity of this system. For this study, we used tin hydride as a mediator, as it proved more versatile, notably for slow addition conditions. Surprisingly, no β-elimination was observed with thioether **10**, even under slow addition conditions (Table 4, Entries 1−2). In both cases, only the reduction product **26** was obtained. The same pattern of reactivity was observed for the sulfonyl and iminosulfinyl precursors **12** and **13** (Table 1, Entries 3−6). The sulfimide, however, displayed some interesting behavior. Under direct addition conditions (Entry 7), allene **25c** was obtained in admixture with reduced adduct **29**. The slow addition technique permitted the formation of allene **25c** in high yield, at the expense of the reduction product **29**. More interestingly, only a catalytic amount of AIBN (0.2 equiv.) was required in these reactions, suggesting that the iminothio radical propagates the radical chain. In contrast, the same conditions (B) applied to sulfoxide precursor **1c** gave only traces of allene **25c**, with almost no conversion of the starting material (< 10%). This difference in behavior could be explained in terms of the known stability of the (tosylimino)thiyl radical.[56]

Table 4. Variation of the sulfur moiety



A: 0.025 M, Bu_3SnH (1.3 equiv.), AIBN (0.2 equiv.), PhH, Δ

B: 0.02 M, Bu_3SnH (1.3 equiv., 2.10^{-4} mol.h^{-1}), AIBN (0.2 equiv.), PhH, Δ

Entry	Precursor	X	Method	Yield of **25c** (%)	Reduction product[a], yield (%)
1	**10**	SPh	A	0	**26**, 62
2	**10**	SPh	B	0	**26**, 97
3	**12**	SO_2Ph	A	0	**27**, 92
4	**12**	SO_2Ph	B	0	**27**, –[b]
5	**13**	SOPhNTs	A	0	**28**, 94
6	**13**	SOPhNTs	B	0	**28**, 94
7	**14**	SPhNTs	A	40	**29**, 55
8	**14**	SPhNTs	B	90	**29**, 8

[a] The reduction products were contaminated (< 5%) with the product resulting from reduction at the tertiary position. [b] The ^{1}H NMR spectrum of the crude product showed that only **27** was formed.

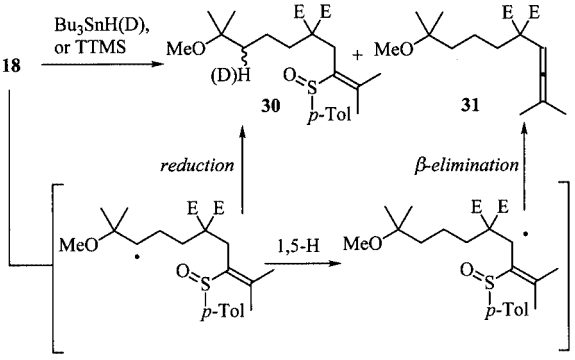
Whereas β-eliminations of arylthio, arylsulfonyl, and arylsulfinyl radicals are well established, and their rates have been compared [$k(PhSO_2^•) \approx 1.1{\cdot}10^7\ s^{-1} < k(PhS^•) \approx 1.9{\cdot}10^8\ s^{-1} < k(ArSO^•) \approx 1.1{\cdot}10^9\ s^{-1}$],[40] only one example of β-elimination of arylsulfimides has to the best of our knowledge been reported,[57] and no data are available for

sulfoximines. As previously stated by Chatgilialoglu in the saturated series,[41] the "kinetic stability" of the expelled radical could also be the crucial factor in these reactions. The sulfonyl **12** and its close analogue, the iminosulfinyl **13** precursor, would behave similarly, being unable to undergo any β-elimination. The same would still apply to thioether **10**, although in the saturated series, the thio radical β-eliminates ten times more rapidly than the sulfonyl one. A possible alternative explanation would be that β-elimination of the thio and sulfonyl radicals might indeed proceed, but that these radicals would keep re-adding to the allene. Reduction of the resulting allyl radical would not then distinguish between the "no β-elimination" pathway and the "β-elimination/re-addition" pathway. However, a few elements point against this proposal. As mentioned above, the work of Heiba on thio radicals[44] and Truce on sulfonyl radicals[43] strongly suggest that the attack of the S-centered radical takes place at both positions (terminal and central), but that under equilibrating conditions (no efficient trapping), only the product resulting from the central attack is observed, because of the formation of a stabilized allyl radical intermediate. In our case, as in the thiol addition study, we have a reducing agent (Bu_3SnH) that should, to some extent, trap the vinyl radical originating from the terminal attack. This would be especially true under direct tin hydride addition conditions (conditions A). No such adducts have been detected, however. Another fate for the β-eliminated radicals could be reduction by tin hydride, preventing any readdition, and thus conserving the allene. However, as previously mentioned, no allene **25c** was observed. Although we have to be cautious on this, it would appear likely that β-elimination simply does not operate.

Thus, only the generation of the sulfinyl and its aza analogue radicals could be triggered under these reactions. The two compounds **1c** and **14** exhibited some reactivity in common, though with certain distinctions: no reduction adduct was obtained from precursor **1c**, in contrast with **14**, and the iminothio radical propagated the radical chain while the sulfinyl one did not. Clearly, more physical data on these radicals are required to clarify all these findings.

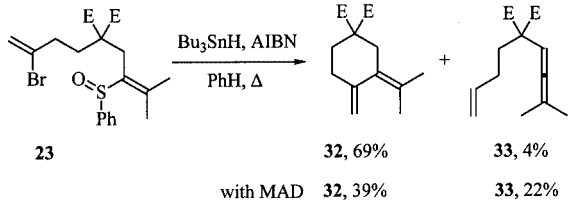
We next examined the behavior of precursor **18** under radical reactions conditions. No 6-*exo*-*trig* cyclization took place at 10 °C, with only reduction being observed (88% of **30**). However, doubt persisted concerning the nature of this reduction: intermolecular vs. intramolecular through a 1,5-H transfer from the activated allylic position. To obtain a better understanding of this, we performed the same reaction with tin deuteride under reflux conditions, and obtained two products (Scheme 7): the reduced adduct **30D**, in which deuterium incorporation was shown by ^1H NMR and ^2H NMR to be $> 95\%$ at the initial radical position, and the minor trisubstituted allene **31**, which indicated that some 1,5-H transfer, followed by β-elimination of the sulfinyl radical, had taken place.[58] Use of TTMS under the same conditions confirmed these findings and resulted in an increase in the yield of the allene (61% of **31**).

In contrast, the vinyl precursor **23** mainly underwent a 6-*exo*-*trig* cyclization to produce diene **32**, accompanied by



conditions	30(D), %	31, %
Bu_3SnH, AIBN Tol., hv, 10°C	88	
Bu_3SnD, AIBN PhH, Δ	32	50
TTMS, AIBN Tol., Δ	18	61

Scheme 7



Scheme 8

traces of allene **33** (Scheme 8). Presumably, the smaller vinyl radical can find a way to cyclize. The competitive 1,5-H transfer pathway is minor. Interestingly, in the presence of MAD [methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide)], which presumably coordinates the sulfoxide oxygen atom[37,59] and results in higher steric hindrance at the cyclization site, the amount of 1,5-H transfer giving rise to the allene increases. These two related examples also demonstrate the power of the radical translocation stratagem, pioneered by Curran.[60] In that case, it spared us the preparation of allyl bromide precursors and allowed the construction of trisubstituted allenes.

Conclusion

In summary, we have devised the first efficient and general radical synthesis of variously substituted allenes, based on the β-elimination of a sulfinyl radical. This reaction does not proceed at low temperature, nor with sulfur groups other than sulfoxide and sulfimide. A further incentive is also the fact that the chiral sulfinyl group might induce some stereoselectivity in the β-elimination step to provide diastereo- or enantioenriched allenes. However, presumably because of the high energy of activation, our preliminary results on disubstituted allenes have been disappointing.

Further work to solve this issue is now being addressed and will be reported in due time.

Experimental Section

General Remarks: Reactions were carried out under an inert gas, with magnetic stirring and degassed solvents when necessary. Ether and THF were distilled from sodium/benzophenone under nitrogen before use. CH_2Cl_2, benzene, and toluene were dried and distilled from CaH_2. Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel. Merck Geduran SI 60 A silica gel (35−70 μm) was used for column chromatography. PE, EE, and EA are petroleum ether, diethyl ether, and ethyl acetate. The melting points reported were measured with a Reichert hot stage apparatus and are uncorrected. IR spectra were recorded with a Perkin−Elmer 1420 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with 200 MHz AC 200 and 400 MHz ARX 400 Bruker spectrometers. Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents (δ = 7.26 for $CDCl_3$). Coupling constants (*J*) are given in Hertz (Hz). The terms m, s, d, t, q, quint mean multiplet, singlet, doublet, triplet, quadruplet, quintuplet, respectively. The term br means that the signal is broad. Elemental analyses were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie (Paris VI).

Allyl Alcohols 6a−h. General Procedure: *n*-Butyllithium (2.5 M in hexanes, 4.40 mL, 11 mmol, 1.1 equiv.) was added at 0 °C to a solution of diisopropylamine (1.68 mL, 12 mmol, 1.2 equiv.) in THF (30 mL). The reaction mixture was cooled to −90 °C, and phenyl vinyl sulfoxide (**4**) (1.52 g, 10 mmol, 1 equiv.) in THF (15 mL) was added by cannula. After 20 min, the ketone or the aldehyde **5** (20 mmol, 2 equiv.) in THF (15 mL) was added. The reaction mixture was allowed to warm to 0 °C and then diluted with CH_2Cl_2 and quenched with a saturated solution of ammonium chloride. The aqueous layer was extracted three times with CH_2Cl_2, and the combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated.

Compound 6a: Chromatography (PE/EA, 50:50) afforded 1.55 g (50%) of **6a** as a mixture of two separated diastereomers (*de* = 22%). *Minor diastereomer:* yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.72 (s, 9 H, *t*Bu), 0.50−1.50 (m, 8 H, CH_2 + C*H*-*t*Bu), 1.90 (m, 1 H, CH*H*), 5.67 (s, 1 H, =CH*H*), 5.99 (s, 1 H, =C*H*H), 7.32−7.70 (m, 5 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.0 and 22.2 (CH_2), 27.5 (3 CH_3), 32.4 [*C*(CH_3)$_3$], 38.9, 39.5 and 47.2 (2 CH_2 + *C*H-*t*Bu), 73.9 (C-OH), 114.5 (=CH_2), 126.3, 129.0, 131.1, 144.6 (3 CH arom. + 1 C arom.), 162.6 (C=). *Major diastereomer:* yellow oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.61 (s, 9 H, *t*Bu), 0.50−1.50 (m, 7 H, CH_2 + C*H*-*t*Bu), 1.88 (m, 1 H, CH*H*), 2.18 (m, 1 H, C*H*H), 5.77 (s, 1 H, =CH*H*), 6.04 (s, 1 H, =C*H*H), 7.20−7.60 (m, 5 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.9 and 24.1 (CH_2), 27.5 (3 CH_3), 32.1 [*C*(CH_3)$_3$], 38.0 and 46.9 (2 CH_2 + *C*H-*t*Bu), 74.0 (C-OH), 118.0 (=CH_2), 125.9, 128.9, 131.1, 144.1 (3 CH arom. + 1 C arom.), 158.3 (C=). $C_{18}H_{26}O_2S$ (306.46): calcd. C 70.55, H 8.55; found C 70.45, H 8.59.

Compound 6b: Chromatography (PE/EA, 40:60 to 30:70) afforded 1.56 g (54%) of **6b** as a pale yellow oil and as an inseparable mixture of two diastereomers (*de* = 20%). IR (neat): $\tilde{\nu}$ = 3350, 3060, 2830, 1610, 1510, 1250, 1030 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.72 (s, 3 H, OCH_3 two dias.), 5.04 (s, 1 H, C*H*OH one dias.), 5.14 (s, 1 H, C*H*OH one dias.), 5.41 (s, 1 H, =CH*H* one dias.), 5.69 (s, 1 H, =CH*H* one dias.), 6.05 (s, 1 H, =C*H*H one dias.), 6.10 (s, 1 H, =C*H*H one dias.), 6.74 (d, *J* = 8.7 Hz, 2 H, arom. two dias.), 7.00 (d, *J* = 8.7 Hz, 2 H, arom. one dias.), 7.06 (d, *J* = 8.7 Hz, 2 H arom. one dias.), 7.35−7.65 (m, 5 H, arom. two dias.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 70.9 and 71.6 (C-OH), 113.8 and 113.9 (CH arom.), 117.8 and 119.2 (=CH_2), 125.3 and 125.8, 128.1 and 128.3, 129.2 and 129.3 (CH arom.), 131.4 (2 CH arom.), 131.7 and 132.9, 141.7 and 142.7, 156.0 and 157.5 (C arom.), 159.3 and 159.4 (C=).

Compound 6c: Chromatography (PE/EA, 40:60 to 30:70) afforded 1.23 g (40%) of **6c** as a white solid. M.p. 137−139 °C. IR (neat): $\tilde{\nu}$ = 3350, 2920, 1440, 1360, 1100, 1030 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41−1.51 (m, 4 H, CH_2), 1.90−1.77 (m, 4 H, CH_2), 3.85−3.91 (m, 4 H, CH_2O), 5.80 (s, 1 H, =C*H*H), 6.03 (s, 1 H, =CH*H*), 7.43−7.49 (m, 3 H, arom.), 7.65−7.68 (m, 2 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.0 (2 CH_2), 36.4 (2 CH_2), 64.1 (2 CH_2O), 73.7 (C-OH), 107.9 (O−C−O), 115.7 (=CH_2), 126.0, 129.2, and 131.2 (CH arom.), 144.1 (C arom.), 160.9 (C=). $C_{16}H_{20}O_4S$ (308.40): calcd. C 62.31, H 6.54; found C 62.33, H 6.61.

Compound 6d: Chromatography (PE/EA, 80:20 to 40:60) afforded 1.36 g (45%) of **6d** as an orange foam and as a mixture of two diastereomers (*de* = 18%). IR (neat): $\tilde{\nu}$ = 3320, 3050, 2880, 1495, 1440, 1240, 1030 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.98 (s, 1 H, C*H*OH one dias.) and 5.37 (s, 1 H, C*H*OH one dias.), 5.78 (s, 1 H, =CH*H* one dias.), 5.84 (s, 1 H, =CH*H* one dias.), 5.84 (m, 2 H, OCH_2O two dias.), 5.97 (s, 1 H, =C*H*H one dias.), 6.05 (s, 1 H, =C*H*H one dias.), 6.48 (m, 1 H, arom. two dias.), 6.58 (d, *J* = 3.0 Hz, 1 H, arom. one dias.), 6.60 (d, *J* = 3.0 Hz, 1 H, arom. one dias.), 7.07 (m, 1 H, arom. two dias.), 7.36−7.45 (m, 5 H, arom. two dias.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 70.9 and 71.6 (C-OH), 101.1 (2 OCH_2O), 107.3 and 107.4 (CH arom.), 107.9 and 108.0 (CH arom.), 117.6 and 118.6 (=CH_2), 120.4 and 120.8 (CH arom.), 125.4 and 125.9 (CH arom.), 129.3 (2 CH arom.), 131.5 (2 CH arom.), 133.8 and 134.9, 141.7 and 142.5, 147.3 and 147.4 (C arom.), 147.7 (2 C arom.), 155.9 and 157.3 (C=).

Compound 6e: Chromatography (PE/EA, from 70:30 to 40:60) afforded 1.73 g (51%) of **6e** as a yellow oil and as a mixture of two diastereomers (*de* impossible to determine by ^{1}H NMR). IR (neat): $\tilde{\nu}$ = 3360, 2930, 1440, 1375, 1080 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.62−1.70 (m, 18 H, alkyl), 3.14 (s, 3 H, OCH_3), 4.30 (m, 1 H, C*H*OH), 5.87 (m, 1 H, =CH*H*), 6.07 (m, 1 H, =C*H*H), 7.48−7.52 (m, 3 H, arom.), 7.61−7.70 (m, 2 H, arom.).

Compound 6f: Chromatography (PE/EA, from 80:20 to 40:60) afforded 2.39 g (50%) of **6f** as a yellow oil and as a mixture of two diastereomers (*de* impossible to determine by ^{1}H NMR). IR (neat): $\tilde{\nu}$ = 3340, 3060, 2930, 1420, 1100 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.03 (s, 9 H, *t*Bu two dias.), 1.47−1.76 (m, 4 H, CH_2 two dias.), 3.56 (m, 2 H, CH_2O two dias.), 4.09 (dd, *J* = 14.2, 7.1 Hz, 1 H, C*H*OH two dias.), 5.83 (s, 1 H, =CH*H* one dias.), 5.91 (s, 1 H, =CH*H* one dias.), 6.09 (s, 2 H, =C*H*H two dias.), 7.33−7.42 (m, 9 H, arom. two dias.), 7.56−7.67 (m, 6 H, arom. two dias.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.2 [*C*(CH_3)$_3$], 26.9 (3 CH_3), 28.1 and 28.3 (CH_2), 32.8 and 33.6 (CH_2), 63.6 and 63.9 (CH_2O), 68.1 and 68.7 (C-OH), 116.7 and 117.0 (=CH_2), 125.4 and 125.6 (CH arom.), 127.7 (2 CH arom.), 129.2 and 129.3 (CH arom.), 129.7 (2 CH arom.), 131.2 and 131.5 (2 CH arom.), 133.4 and 133.6 (C arom.), 135.5 (2 CH arom.) 142.3 and 142.8 (C arom.), 156.6 and 157.2 (C=).

Compound 6g: Chromatography (PE/EA, from 80:20 to 0:100) afforded 1.83 g (53%) of **6g** as a yellow foam and as a mixture of four diastereomers (two are distinct on ^{1}H NMR, and four on ^{13}C NMR). IR (neat): $\tilde{\nu}$ = 3360, 3050, 2870, 1480, 1240, 1035 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.56 (d, *J* = 6.6 Hz, 3 H, CH_3 one dias.) and 0.79 (d, *J* = 6.7 Hz, 3 H, CH_3 one dias.), 1.60−2.90 (m, 4 H, C*H*$_2$Ar + C*H*CH_3 + C*H*OH two dias.), 3.61−4.07 (m, 2 H, OCH_2O two dias.), 5.82−5.91 (m, 3 H, 2 =CH*H* + 1 =C*H*H two dias.), 6.10 (m, 1 H, =C*H*H one dias.), 6.38−6.50 (m, 1 H, arom. two dias.), 6.55−6.65 (m, 1 H, arom. two dias.), 7.27−7.62 (m, 6 H, arom. two dias.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.6, 12.8, 15.7, and 15.8 (CH_3), 36.4, 36.7, 39.6, and 39.7 (CH_2), 39.4 and 39.8 (C*H*CH_3), 68.9, 70.3, 72.4, and 73.4 (C-OH), 100.7 (OCH_2O), 108.0 and 108.1 (CH arom.), 109.5 and 109.7 (CH arom.), 115.7, 117.7, 118.4, and 119.3 (=CH_2), 122.0 and 122.1 (CH arom.), 125.3, 125.5, 125.6, and 125.7 (CH arom.), 129.1, 129.3, and 129.4 (CH arom.) 131.1, 131.4, 131.6, and 131.7 (C arom.), 134.3 and 134.4 (CH arom.), 142.01, 142.07, 142.1, and 142.7 (C arom.), 145.6 and 145.7 (C arom.), 147.4 (C arom.), 155.7, 155.9, and 156.2 (C=).

Compound 6h: Chromatography (PE/EA, from 80:20 to 50:50) afforded 1.68 g (48%) of **6h** as a white foam and as a mixture of two diastereomers (*de* = 4%). IR (neat): ṽ = 3320, 3050, 1580, 1040 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.08 (s, 1 H, =CH*H* one dias.), 5.22 (s, 1 H, =CH*H* one dias.), 5.46 (s, 1 H, =C*H*H one dias.), 5.69 (s, 1 H, =C*H*H one dias.), 6.08 (s, 1 H, C*H*OH one dias.), 6.10 (s, 1 H, C*H*OH one dias.), 6.75−7.70 (m, 14 H, arom. two dias). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.6 and 71.4 (C-OH), 117.1 and 117.2 (CH arom.), 118.2 (2 CH arom.), 118.8 (2 CH arom.), 118.4 and 120.1 (=CH_2), 121.5 (2 CH arom.), 123.3 (2 CH arom.), 125.0 (2 CH arom.), 125.7 (2 CH arom.), 129.20 and 129.26 (CH arom.), 129.7 (2 CH arom.), 131.3 and 131.4 (CH arom.), 141.4 and 141.6 (C arom.), 142.4 and 142.7 (C arom.), 155.6 (2 C arom.), 156.8 and 157.2 (2 C arom. + C=).

Allyl Bromides 1a−h. General Procedure:[47] Dimethyl sulfide (1.10 mL, 15 mmol, 3.0 equiv.) was added at 0 °C in the absence of light to a solution of *N*-bromosuccinimide (2.23 g, 12.5 mmol, 2.5 equiv.) in CH_2Cl_2 (30 mL). A yellow precipitate appeared. After 15 min, the sulfinyl alcohol **6** (5 mmol, 1.0 equiv.) in CH_2Cl_2 (15 mL) was added dropwise. The reaction mixture was allowed to warm to room temp. and monitored by TLC until completion (about 24 h), and was then diluted in Et_2O, washed with water and brine, dried with $MgSO_4$, filtered, and concentrated.

Compound 1a: Chromatography (PE/EA, 80:20) afforded 1.18 g of **1a** (64%) as a mixture of two separable diastereomers (*de* = 24%). *Major diastereomer:* white foam. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.79 (s, 9 H, *t*Bu), 1.08−1.37 (m, 3 H, CH_2 + C*H*-*t*Bu), 1.80−2.15 (m, 4 H, CH_2), 2.75 (m, 1 H, C*H*H), 3.54 (m, 1 H, C*H*H), 3.90 (A of AB, *J* = 11.6 Hz, 1 H, C*H*HBr), 4.16 (B of AB, *J* = 11.6 Hz, 1 H, CH*H*Br), 7.27−7.52 (m, 5 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.4 (CH_2Br), 27.5 (3 CH_3), 27.9, 28.6, 31.8, and 32.5 (CH_2), 32.8 [*C*(CH_3)$_3$], 47.6 (*C*H-*t*Bu), 124.3, 129.0, and 130.5 (CH arom.), 132.8 (C=), 142.7 (C arom.), 156.9 (=C−S=O). *Minor diastereomer:* white foam. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.81 (s, 9 H, *t*Bu), 1.00−1.37 (m, 3 H, CH_2 + C*H*-*t*Bu), 1.80−2.20 (m, 4 H, CH_2), 2.75 (m, 1 H, C*H*H), 3.49 (m, 1 H, C*H*H), 3.87 (A of AB, *J* = 11.6 Hz, 1 H, C*H*HBr), 4.17 (B of AB, *J* = 11.6 Hz, 1 H, CH*H*Br), 7.34−7.55 (m, 5 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.7 (CH_2Br), 27.6 (3 CH_3), 28.1, 29.1, and 31.5 (CH_2), 32.5 [*C*(CH_3)$_3$], 32.8 (CH_2), 47.5 (*C*H-*t*Bu), 124.5, 129.1, and 130.6 (CH arom.), 132.5 (C=), 141.9 (C arom.), 157.9 (=C−S=O).

Compound 1b: Chromatography (PE/EA, 50:50) afforded 1.51 g (86%) of **1b** as a white solid. M.p. 93−95 °C. IR (neat): ṽ = 3030, 2960, 1600, 1500, 1255, 1175, 1040 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, OCH_3), 4.10 (A of AB, *J* = 11.7 Hz, 1 H, C*H*HBr), 4.17 (B of AB, *J* = 11.7 Hz, 1 H, CH*H*Br), 6.93 (d, *J* = 8.7 Hz, 2 H, arom.), 7.52 (m, 4 H, arom. + H−C=), 7.60 (d, *J* = 8.7 Hz, 2 H, arom.), 7.67 (m, 2 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.9 (CH_2Br), 55.6 (OCH_3), 114.8 and 125.6 (CH arom.), 126.1 (C arom.), 129.5, 131.7, 132.2, and 136.7 (CH arom. + H−C=), 138.8 and 142.5 (C arom.), 161.1 (=C−S=O). $C_{16}H_{15}BrO_2S$ (351.26): calcd. C 54.71, H 4.30; found C 54.83, H 4.37.

Compound 1c: Chromatography (PE/EA, 50:50) afforded 910 mg (49%) of **1c** as an orange oil. IR (neat): ṽ = 3050, 2950, 1440, 1100, 1030 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.81−1.92 (m, 4 H, CH_2), 2.53−2.57 (m, 2 H, CH_2), 2.88−3.10 (m, 2 H, CH_2), 3.98−3.92 (s + A of AB, 5 H, CH_2O + C*H*HBr), 4.22 (B of AB, *J* = 11.6 Hz, 1 H, CH*H*Br), 7.43−7.54 (m, 5 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 16.1 (CH_2Br), 28.4, 29.5, 34.4, 35.2 (CH_2), 64.5 (2 CH_2O), 107.4 (O−C−O), 124.2 and 129.0 (CH arom.), 129.1 (C=), 130.6 (CH arom.), 134.4 (C arom.), 154.1 (=C−S=O).

Compound 1d: Chromatography (PE/EA, from 90:10 to 50:50) afforded 1.46 g (80%) of **1d** as an orange foam. IR (neat): ṽ = 3050, 2950, 1440, 1100, 1030 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.06 (A of AB, *J* = 8.1 Hz, 1 H, C*H*HBr), 4.12 (B of AB, *J* = 8.1 Hz, 1 H, CH*H*Br), 5.92 (s, 2 H, OCH_2O), 6.79 (d, *J* = 8.1 Hz, 1 H, arom.), 7.04 (d, *J* = 8.1 Hz, 1 H, arom.), 7.06 (s, 1 H, arom.), 7.38 (s, 1 H, H−C=), 7.40−7.45 (m, 3 H, arom.), 7.62−7.66 (m, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9 (CH_2Br), 102.1 (CH_2O), 109.2, 109.8, 125.6, and 125.9 (CH arom.), 127.6 (C arom.), 129.6 and 131.8 (CH arom.), 136.4 (H−C=), 139.4, 142.7, 148.7 and 149.3 (C arom. + =C−S=O).

Compound 1e: Chromatography (PE/EA, 80:20) afforded 1.19 g (68%) of **1e** as an orange oil and as a mixture of two diastereomers (*de* impossible to determine with ^{1}H NMR). IR (neat): ṽ = 3050, 2940, 1440, 1080, 1040 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (d, *J* = 6.6 Hz, 3 H, CHC*H*$_3$ two dias.), 1.02 (s, 6 H, 2 CH_3, one dias.), 1.03 (s, 6 H, 2 CH_3, one dias.), 1.09−1.72 (m, 7 H, 3 CH_2 + C*H*CH_3 two dias.), 2.03−2.11 (m, 1 H, C*H*HCH= two dias.), 2.18−2.23 (m, 1 H, CH*H*CH= two dias.), 3.15 (s, 3 H, OCH_3 one dias.), 3.16 (s, 3 H, OCH_3 one dias.), 3.85 (A of AB, *J* = 11.7 Hz, 1 H, C*H*HBr two dias.), 3.92 (B of AB, *J* = 11.7 Hz, 1 H, CH*H*Br two dias.), 6.70 (t, *J* = 7.6 Hz, 1 H, H−C= one dias.), 6.70 (t, *J* = 7.1 Hz, 1 H, H−C= one dias.), 7.48−7.49 (m, 3 H, arom. two dias.), 7.63−7.65 (m, 2 H, arom. two dias.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.3 (CH_2Br), 19.8 (CH_3), 21.3 (CH_2), 25.0 (2 CH_3), 33.0 (*C*H−CH_3), 36.0, 37.3, and 40.1 (CH_2), 49.2 (OCH_3), 74.5 (*C*−OCH_3), 125.2, 129.3, and 131.4 (CH arom.), 140.3 (H−C=), 141.7 and 142.2 (C arom. + =C−S=O).

Compound 1f: Chromatography (PE/EA, from 100:0 to 90:10) afforded 2.25 g (83%) of **1f** as an orange oil and a mixture of two diastereomers [(*E*)/(*Z*) = 91:9]. *(E) isomer:* IR (neat): ṽ = 3060, 2920, 1420, 1090, 1040 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 9 H, *t*Bu), 1.80 (m, 2 H, CH_2), 2.47 (m, 2 H, C*H*$_2$CH=), 3.75 (m, 2 H, CH_2O), 3.90 (A of AB, *J* = 11.6 Hz, 1 H, C*H*HBr), 3.96 (B of AB, *J* = 11.6 Hz, 1 H, CH*H*Br), 6.72 (t, *J* = 7.7 Hz, 1 H, H−C=), 7.28−7.47 (m, 9 H, arom.), 7.65−7.71 (m, 6 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.1 (CH_2Br), 19.3 (*C*-(CH_3)$_3$], 25.5 (CH_2), 27.0 (3 CH_3), 31.0 (*C*H_2CH=), 62.9 (CH_2O), 125.2, 127.9, 129.3, 129.8, 131.4 and 135.6 (CH arom.), 133.7 (C arom.), 140.9 (H−C=), 141.8 and 142.8 (C arom. + =C−S=O). $C_{28}H_{33}BrO_2SSi$ (541.64): calcd. C 62.09, H 6.14; found C 62.05, H 6.18.

Compound 1g: Chromatography (PE/EA, from 85:15 to 60:40) afforded 1.49 g (73%) of **1g** as a mixture of two separable diastereo-

mers [(*E*)/(*Z*) = 95:5]. *(Z) isomer:* orange oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 6.6 Hz, 3 H, CH_3), 2.65 (A of ABX, *J* = 13.7, 7.6 Hz, 1 H, C*H*HAr), 2.74 (B of ABX, *J* = 13.7, 6.6 Hz, 1 H, CH*H*Ar), 3.49 (m, 1 H, C*H*−CH_3), 3.91 (A of AB, *J* = 12.2 Hz, 1 H, C*H*HBr), 4.09 (B of AB, *J* = 12.2 Hz, 1 H, CH*H*Br), 5.94 (s, 2 H, OCH_2O), 6.33 (d, *J* = 10.7 Hz, 1 H, H−C=), 6.64−6.78 (m, 3 H, arom.), 7.47−7.58 (m, 5 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (CH_3), 24.6 (CH_2Br), 35.8 [*C*H-(CH_3)], 43.1 (CH_2Ar), 101.2 (OCH_2O), 108.6, 109.9, 122.5, 124.6 129.6 and 131.2 (CH arom.), 133.2, 139.9, 142.2, 146.5, 148.1 (4 C arom. + =C−S=O), 148.6 (H−C=). *(E) isomer:* Two diastereomers were observed. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 8.1 Hz, 3 H, CH_3 one dias.), 1.20 (d, *J* = 7.1 Hz, 3 H, CH_3 one dias.), 2.55−2.64 (m, 1 H, C*H*HAr two dias.), 2.78−2.59 (m, 1 H, CH*H*Ar two dias.), 2.88−2.96 (m, 1 H, C*H*−CH_3 two dias.), 3.51 (A of AB, *J* = 11.5 Hz, 1 H, C*H*HBr one dias.), 3.76 (A of AB, *J* = 11.5 Hz, 1 H, CH*H*Br one dias.), 3.78 (s, 2 H, CH_2Br one dias.), 5.89 (s, 2 H, OCH_2O one dias), 5.91 (m, 2 H, OCH_2O one dias.), 6.56 (m, 1 H, =C−H, two dias.), 6.64−6.81 (m, 3 H, arom. two dias.), 7.52−7.60 (m, 5 H, arom. two dias.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.0 and 20.7 (CH_2Br), 19.7 and 20.0 (CH_3), 36.5 and 36.6 (*C*H−CH_3), 42.4 and 42.7 (CH_2), 101.1 and 101.2 (OCH_2O), 108.5 (2 CH arom.), 109.6 and 109.7 (CH arom.), 122.3 (2 CH arom), 125.3 and 126.0 (CH arom.), 129.4 and 129.6 (CH arom.), 131.4 and 131.9 (CH arom.), 133.3 and 133.4 (C arom.), 140.5 and 140.7, 142.2 and 142.5, 146.3 and 146.4 (2 C arom. + =C−S=O), 142.9 and 146.9 (=C−H), 147.9 and 148.0 (C arom.).

Compound 1h: Chromatography (PE/EA, 85:15) afforded 1.55 g (75%) of **1h** as an orange oil. IR (neat): $\tilde{\nu}$ = 3050, 2980, 1570, 1045 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.02 (A of AB, *J* = 11.5 Hz, 1 H, C*H*HBr), 4.12 (B of AB, *J* = 11.5 Hz, 1 H, CH*H*Br), 7.05−7.80 (m, 15 H, arom. + =C−H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1 (CH_2Br), 118.9 (CH arom.), 119.3 (2 CH arom.), 123.8, 124.0, 125.3, 129.2, 129.8, 130.2, 131.6, and 134.4 (7 CH arom. + =C−H), 134.8, 141.9, 142.2, 156.1, and 158.0 (4 C arom. + =C−S=O).

Thio-Substituted Alcohol 9: Phenyl vinyl sulfide (**7**) (500 mg, 3.67 mmol) in THF (3 mL) was added under nitrogen at −78 °C to a THF (11 mL) solution of *n*-butyllithium (2.15 M in hexanes, 2.05 mL, 4.4 mmol, 1.2 equiv.) and TMEDA (555 μL, 3.67 mmol, 1 equiv.). The reaction mixture was allowed to warm to room temp. for 1 h and 1,4-cyclohexanedione monoethylene ketal (687 mg, 4.4 mmol, 1.2 equiv.) in THF (3 mL) was added at −78 °C. The reaction mixture was allowed to warm to room temp. and then quenched with saturated aqueous ammonium chloride and extracted with ether. The organic layer was washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (PE/EA, 70:30) to give 786 mg (73%) of **9** as an oil. IR (neat): $\tilde{\nu}$ = 3550, 3440, 3200, 2940, 2910, 1700, 1590, 1470, 1430, 1100 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.50−2.10 (m, 8 H, CH_2), 3.94 (s, 4 H, CH_2O), 4.80 (s, 1 H, =*CH*H), 5.50 (s, 1 H, =CH*H*), 7.28−7.32 (m, 5 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 30.5 (2 CH_2), 36.6 (2 CH_2), 64.3 and 64.4 (OCH_2), 73.8 (C-OH), 108.5 (O−C−O), 112.1 (=CH_2), 128.0 (CH arom.), 129.4 (2 CH arom.), 133.4 (2 CH arom.), 133.8 (C arom.), 154.2 (=C). MS (CI): *m*/*z* (%) = 310 (35) [M + NH_4^+], 293 (59) [MH^+]. $C_{16}H_{20}O_3S$ (292.39): calcd. C 65.72, H 6.89; found C 65.56, H 7.06.

Thioallyl Bromide 10: *n*-Butyllithium (2.20 M in hexanes, 1.63 mL, 3.59 mmol, 1.05 equiv.) was added at −78 °C to a stirred solution of **9** (1.00 g, 3.42 mmol) in THF (6 mL), and MsCl (431 mg, 3.76 mmol, 1.1 equiv.) was added dropwise under nitrogen. After 30 min, LiBr (3.00 g, 34.2 mmol, 10 equiv.) was added. The mixture was allowed to warm to room temp. for 1 h, then quenched with saturated aqueous ammonium chloride and extracted with ether. The organic layer was washed with brine, dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography (PE/EA, 70:30) to give 909 mg (75%) of an oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.70 (m, 2 H, CH_2), 1.81 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.58 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.79 (m, 2 H, CH_2), 3.97 (s, 4 H, CH_2O), 4.15 (s, 2 H, CH_2Br), 7.16−7.27 (m, 5 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.4, 30.1, 33.1, 35.0, and 35.2 (4 CH_2 + CH_2Br), 64.4 (CH_2O), 108.0 (O−C−O), 126.1 (2 CH arom.), 128.7 (2 CH arom.) and 129.0 (CH arom.), 131.3, 133.1 and 152.3 (2 =C and C arom.). MS (CI): *m*/*z* (%) = 372−374 (100) [M + NH_4^+], 355−357 (35) [MH^+].

Sulfonyl-Substituted Alcohol 11: A solution of *m*-CPBA (70%, 1.80 g, 7.28 mmol, 2.1 equiv.) in CH_2Cl_2 (55 mL) was added dropwise at −78 °C under argon to a solution of **9** (1.04 g, 3.47 mmol) and $NaHCO_3$ (728 mg, 8.67 mmol, 2.5 equiv.) in CH_2Cl_2 (56 mL). The mixture was stirred for 4 h and then allowed to warm to room temp. Basic workup (CH_2Cl_2, K_2CO_3) and flash chromatography (PE/EA, 50:50) gave 1.06 g (95%) of pure product **11** as a white solid. M.p. 77−79 °C. IR (neat): $\tilde{\nu}$ = 3530, 3000, 2960, 2920, 1750, 1460, 1390 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.48−1.54 (m, 2 H, CH_2), 1.82−1.95 (m, 6 H, CH_2), 3.87−3.90 (m, 4 H, CH_2O), 6.03 (s, 1 H, =C*H*H), 6.38 (s, 1 H, =C*H*H), 7.46−7.54 (m, 3 H, arom.), 7.85−7.90 (m, 2 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.9 (2 CH_2), 35.5 (2 CH_2), 64.0 and 64.2 (CH_2O), 72.2 (C-OH), 107.7 (O−C−O), 125.4 (=CH_2), 127.5 (2 CH arom.), 129.0 (2 CH arom.), 133.2 (CH arom.), 141.1 and 156.5 (=C and C arom.). MS (CI): *m*/*z* (%) = 342 (100) [M + NH_4^+].

Sulfonylallyl Bromide 12: This compound was prepared by the general procedure for allyl bromides **1**, with NBS (685 mg), DMS (340 μL), and **11** (500 mg). Chromatography (PE/EA, 90:10) afforded 229 mg (40%) of **12** as an oil. IR (neat): $\tilde{\nu}$ = 2980, 2960, 2900, 1615, 1450, 1100 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32 (m, 2 H, CH_2), 1.78 (m, 2 H, CH_2), 2.54 (m, 2 H, CH_2), 2.73 (m, 2 H, CH_2), 3.90 (s, 4 H, CH_2O), 4.55 (s, 2 H, CH_2Br), 7.47−7.63 (m, 3 H, arom.), 8.00−8.03 (m, 2 H, arom.). ^{13}C NMR (62.2 MHz, $CDCl_3$): δ = 25.6, 29.0, 30.7, 34.2 and 34.9 (4 CH_2 and CH_2Br), 64.5 (2 CH_2O), 107.0 (O−C−O), 127.2 (2 CH arom.), 129.1 (2 CH arom.), 133.2 (CH arom.), 133.5, 142.3 and 160.3 (C arom. and 2 =C). MS (CI): *m*/*z* (%) = 404−406 (27) [M + NH_4^+], 387−389 (63) [MH^+]. $C_{16}H_{19}BrSO_4$ (387.29): calcd. C 49.62, H 4.94; found C 49.74, H 5.03.

(Iminosulfinyl)allyl Bromide 13: Compound **1c** (274 mg, 0.74 mmol) was added at room temp. to a solution of $Cu(OTf)_2$ (27 mg, 0.074 mmol, 0.1 equiv.) in acetonitrile (8 mL). The phenyl iodinane TsN=IPh (358 mg, 0.96 mmol, 1.3 equiv.) was then added in one batch. The reaction was monitored by the rapid disappearance of the yellowish powder from the reaction mixture, which then turned homogeneous and green. Acetonitrile was removed in vacuo, and the crude product was purified by chromatography (CH_2Cl_2/EA, 90:10) to give 374 mg (94%) of **13** as a white solid, m.p. 88−90 °C. IR (neat): $\tilde{\nu}$ = 3080, 2980, 1620, 1485, 1455, 1320, 1270, 1235 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.92 (m, 1 H, CH_2), 1.40 (m, 1 H, CH_2), 1.63−1.88 (m, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 2.50−2.62 (m, 4 H, CH_2), 3.83−3.90 (m, 4 H, CH_2O), 4.54 (A of AB, *J* = 12.3 Hz, 1 H, C*H*HBr), 4.82 (B of AB, *J* = 12.3 Hz, 1 H, C*H*HBr), 7.24 (d, *J* = 8.0 Hz, 2 H, arom.), 7.46−7.64 (m, 3 H, arom.), 7.82 (d, *J* = 8.0 Hz, 2 H, arom.), 8.10−8.13 (m, 2 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4 (CH_3), 25.8, 29.0, 31.1, 33.36, and 34.6

(4 CH_2 and CH_2Br), 64.4 (2 CH_2O), 106.7 (O−C−O), 126.5 (2 CH arom.), 127.5 (2 CH arom.), 129.2 (2 CH arom.), 129.2 (2 CH arom.), 133.9 (CH arom.), 129.5, 139.5, 140.4, 142.8, 160.7 (3 C arom. and 2 =C). MS (CI): *m*/*z* (%) = 540−542 (10) [MH^+].

(Iminothio)allyl Bromide 14: First TsN=IPh (868 mg, 2.32 mmol, 1.3 equiv.) and then $Cu(OTf)_2$ (65 mg, 0.179 mmol, 0.1 equiv.) were added to a solution of **10** (637 mg, 1.79 mmol) in acetonitrile (20 mL), and the resulting mixture was stirred under nitrogen at 0 °C for 1.5 h. The mixture was concentrated and purified by chromatography (PE/EA, 50:50) to give 512 mg (56%) of **14** as a white solid. M.p. 130−132 °C. IR (neat): $\tilde{\nu}$ = 3105, 2980, 2400, 2380, 1640, 1470, 1320, 1310 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.71 (m, 4 H, CH_2), 2.33 (s, 3 H, CH_3), 2.45 (m, 2 H, CH_2), 2.85 (m, 2 H, CH_2), 3.83 (A of AB, *J* = 12.5 Hz, 1 H, C*H*HBr), 3.93 (s, 4 H, CH_2O), 4.25 (B of AB, *J* = 12.5 Hz, 1 H, C*H*HBr), 7.17 (d, *J* = 1 0.0 Hz, 2 H, arom.), 7.44 (m, 3 H, arom.), 7.64 (m, 2 H, arom.), 7.70 (d, *J* = 1 0.0 Hz, 2 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.3 (CH_2Br), 20.9 (CH_3), 29.4 (2 CH_2), 29.7 (2 CH_2), 64.6 (2 CH_2O), 106.9 (O−C−O), 126.2, 126.3, 126.5, 129.1, and 129.6 (5 CH arom.), 131.9, 132.0, 141.3, 141.8, and 159.4 (3 C arom. and 2 =C) − MS (CI): *m*/*z* (%) = 524−526 (6) [MH^+], 444 (2) [M^+ − HBr], 167 (100) [$M^+ - C_{13}H_{12}S_2O_2Br$].

Malonate 16:[53] Monoalkylmalonate **15** (924 mg, 4.3 mmol, 1 equiv.) in MeOH (35 mL) was cooled to 0 °C. A solution of phenylselenenyl chloride (840 mg, 4.3 mmol, 1 equiv.) in CH_2Cl_2 (1 mL) was added dropwise. The solution turned orange, and then yellow. After 0.5 h, the reaction mixture was allowed to warm to room temp., concentrated in vacuo, diluted with Et_2O, washed with brine, dried with $MgSO_4$, filtered, and concentrated. Chromatography (PE/EA, 85:15) afforded 1.41 g (82%) of **16** as a yellow oil, which was carried forward directly. IR (neat): $\tilde{\nu}$ = 2970, 2940, 1750, 1730 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, MeCC*H*$_3$), 1.29 (s, 3 H, C*H*$_3$CMe), 1.41−1.60 (m, 1 H, CH_2CH*H*), 1.89−2.08 (m, 2 H, CH*H*CH_2+CH_2C*H*H), 2.31−2.49 (m, 1 H, C*H*HCH_2), 3.02−3.10 (m, 1 H, CHSe), 3.11 (s, 3 H, COMe), 3.30 (t, *J* = 7.4 Hz, 1 H, ECHE), 3.69 (s, 3 H, CO_2Me), 3.70 (s, 3 H, CO_2Me), 7.21−7.24 (m, 3 H, arom.), 7.54−7.61 (m, 2 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.0 (*CH*$_3$CCH$_3$), 23.8 (CH$_3$C*CH*$_3$), 28.1 (CH_2), 28.9 (CH_2), 49.3 (OMe), 51.4 (CO*OMe*+CHSe), 52.4 (CO*OMe*), 57.1 (E*CH*E), 78.2 (Me$_2$-*C*OMe), 127.2 (CH arom.), 129.0 (CH arom.), 131.4 (C arom.), 134.0 (CH arom.), 169.6 (C=O), 169.7 (C=O).

Selenyl Precursor 18: This compound was prepared according to the previously described procedure,[37] with **16** (620 mg, 1.47 mmol) and **17** (430 mg, 1 equiv.). Chromatography (PE/EA, 60:40) afforded 728 mg (82%) of **18** as a white foam (two inseparable diastereomers). IR (neat): $\tilde{\nu}$ = 3060, 2980, 2950, 1730, 1045 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.04−1.25 (m, 2 H, SeHCC*H*$_2$ two dias.), 1.22 (s, 6 H, MeCC*H*$_3$ two dias.), 1.26 (s, 3 H, C*H*$_3$CMe one dias.), 1.27 (s, 3 H, C*H*$_3$CMe one dias.), 1.41−1.53 (m, 2 H, SeHCC*H*$_2$ two dias.), 1.82 (s, 3 H, =CMe one dias.), 1.83 (s, 3 H, =CMe one dias.), 1.75−1.90 (m, 2 H, CHSe two dias.), 2.13 (s, 3 H, =CMe one dias.), 2.14 (s, 3 H, =CMe one dias.), 2.18−2.30 (m, 2 H, E_2CCH*H* two dias.), 2.33 (s, 6 H, Tol two dias.), 2.34 (B of AB, *J* = 15.8 Hz, 1 H, =CCH*H* one dias.), 2.50−2.56 (m, 1 H, E_2CC*H*H one dias.), 2.78 (A of AB, *J* = 15.8 Hz, 1 H, =CC*H*H one dias.), 2.80 (B of AB, *J* = 1 5.0 Hz, 1 H, =CCH*H* one dias.), 2.97−3.00 (m, 1 H, E_2CC*H*H one dias.), 3.08 (s, 3 H, COMe one dias.), 3.10 (s, 3 H, COMe one dias.), 3.14 (A of AB, *J* = 1 5.0 Hz, 1 H, =CC*H*H one dias.), 3.65 (s, 6 H, CO_2Me two dias.), 3.69 (s, 3 H, CO_2Me one dias.), 3.74 (s, 3 H, CO_2Me one dias.), 7.18−7.25 (m, 10 H, arom. two dias.), 7.29−7.38 (m, 4 H, arom. two dias.), 7.51−7.61 (m, 4 H, arom., two dias.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2 (CH_3), 22.3 (CH_3), 23.2 (CH_3), 23.3 (CH_3), 23.5 (CH_3), 23.9 (CH_3), 26.7 (*CH*$_2$CH$_2$, two dias.), 30.1 (CH$_2$*CH*$_2$, one dias.), 30.2 (CH$_2$*CH*$_2$ one dias.), 33.9 (=C*CH*$_2$ one dias.), 34.1 (=C*CH*$_2$ one dias.), 49.2 (Me$_2$C*OMe* two dias.), 52.3 (CO*OMe* two dias.), 57.8 (CHSe one dias.), 57.9 (CHSe one dias.), 58.1 (E*C*E one dias.), 58.3 (E*C*E one dias.), 78.2 (Me$_2$*C*OMe one dias.), 78.3 (Me$_2$*C*OMe one dias.), 124.3 (CH arom. one dias.), 124.4 (CH arom. one dias.), 126.8 (CH arom. one dias.), 127.0 (CH arom. one dias.), 128.9 (CH arom. one dias.), 129.0 (CH arom. one dias.), 129.6 (CH arom. two dias.), 131.9 (CSe one dias.), 132.1 (CSe one dias.), 133.3 (CH arom. one dias.), 134.0 (CH arom. one dias.), 136.9 (C arom. two dias.), 140.3 (C arom. two dias.), 141.4 (C arom. two dias.), 145.3 (CH_2*C*SO one dias.), 145.6 (CH_2*C*SO one dias.), 171.8 (C=O two dias.), 172.0 (C=O one dias.), 172.3 (C=O one dias.).

Malonate 21: 2-Bromobut-1-en-3-ol (1.00 g, 6.6 mmol, 1 equiv.) and tetrabromomethane (3.10 g, 9.3 mmol, 1.4 equiv.) were dissolved in CH_2Cl_2 (27 mL). Triphenylphosphane (4.89 g, 18.5 mmol, 2.8 equiv.) in CH_2Cl_2 (8 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temp. and left for 2 h. Most of the phosphorus-containing by-products were precipitated in pentane (250 mL) at 0 °C and removed by filtration through Celite®. Residual by-products were eliminated by filtration through a short pad of silica (eluent pentane). Solvents were distilled and crude 2,4-dibromobut-1-ene was carried forward directly. Dimethyl malonate (870 mg, 6.6 mmol, 1 equiv.) in THF (10 mL) was added dropwise to a suspension of sodium hydride (60 wt.%, 265 mg, 6.6 mmol, 1 equiv.) in THF (16 mL). The mixture was left at room temp. for 1 h, and HMPA (1.2 mL, 6.6 mmol, 1 equiv.) was then added, followed by bromide **20** in THF (7 mL). The reaction mixture was heated under reflux overnight, allowed to cool to room temp., diluted with Et_2O, washed with sat. aq. NH_4Cl and brine, dried with $MgSO_4$, filtered, and concentrated. Chromatography (PE/EA, 85:15) afforded 975 mg (56%) of **21** as a slightly yellow oil, which was carried forward directly. IR (neat): nu (tilde) = 3070, 2990, 2940, 1730, 1675, 1640 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.09 (dt, *J* = 7.4, 7.1 Hz, 2 H, CHC*H*$_2$), 2.42 (t, *J* = 7.1 Hz, 2 H, =CCH$_2$), 3.34 (t, *J* = 7.4 Hz, 1 H, ECHE), 3.68 (s, 6 H, CO_2Me), 5.38 (br. s, 1 H, =CH), 5.53 (br. s, 1 H, =CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.9 (CH*CH*$_2$), 36.7 (=C*CH*$_2$), 50.0 (CH), 52.6 (OMe), 118.1 (=CH_2), 132.3 (=C), 169.4 (C=O).

Vinyl Bromide Precursor 23: This compound was prepared according to the previously described procedure,[37] with **21** (975 mg, 3.67 mmol) and **22** (1.02 g. 1 equiv.). Chromatography (PE/EA, 70:30) afforded 1.49 g (91%) of **23** as a colorless oil. IR (neat): $\tilde{\nu}$ = 2950, 2820, 1730, 1630, 1080 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.84 (s, 3 H, =CMe), 1.85−1.94 (m, 1 H, =CCH*H*), 2.19 (s, 3 H, =CMe), 2.09−2.27 (m, 2 H, =CCH$_2$CH*H*+=CC*H*H), 2.49−2.61 (m, 1 H, =CCH$_2$C*H*H), 2.72 (B of AB, *J* = 15.6 Hz, 1 H, =CCH*H*), 3.08 (A of AB, *J* = 15.6 Hz, 1 H, =CC*H*H), 3.64 (s, 3 H, CO_2Me), 3.70 (s, 3 H, CO_2Me), 5.32 (br. s, 1 H, =CH), 5.55 (br. s, 1 H, =CH), 7.33−7.43 (m, 5 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.7 [*CH*$_3$C(=)CH$_3$], 23.3 [CH$_3$C(=)*CH*$_3$], 29.8 (=CCH$_2$*CH*$_2$), 32.6 (=C*CH*$_2$), 37.2 (=C*CH*$_2$), 52.5 (OMe), 57.4 (E*C*E), 116.9 (=CH_2), 124.4 (CH arom.), 129.0 (CH arom.), 130.2 (CH arom.), 133.5 (C), 136.3 (C), 144.3 (C), 146.6 (C), 171.5 (C=O), 171.9 (C=O). $C_{20}H_{25}BrO_5S$ (457.38): calcd. C 52.52, H 5.51; found C 52.31, H 5.56.

Vinyl Sulfoxide 24: Bu_3SnH (100 μL, 0.36 mmol, 1.5 equiv.) and Et_3B (1 M solution in hexanes, 1 mL, 1 mmol, 4 equiv.) were added to a cooled (0 °C) solution of the major diastereoisomer of bromide

1a (89 mg, 0.24 mmol, 1 equiv.) in toluene (15 mmol). Air was injected by syringe. After 15 min, the reaction mixture was subjected to a KF/MeOH workup (see below). Two diastereomers of reduced product **24** were separated by chromatography (PE/EA, 70:30). **Compound 24a:** 28 mg (40%) of **24a** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (s, 9 H, *t*Bu), 1.10−1.40 (m, 3 H, cyc.), 1.64 (s, 3 H, =CMe), 1.80−2.10 (m, 4 H, cyc.), 2.65−2.69 (m, 1 H, cyc.), 3.63−3.66 (m, 1 H, cyc.), 7.35−7.55 (m, 5 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.5 (=C*Me*), 27.6 (*t*Bu), 28.1 (=CCH_2CH_2), 28.7 (=CCH_2CH_2), 31.5 (=CCH_2), 32.0 (=CCH_2), 32.6 (Me_3C), 48.1 (CH), 124.2 (CH arom.), 128.9 (CH arom.), 129.9 (CH arom.), 131.8 (*C*=CSO), 143.8 (C arom.), 149.1 (C=*C*SO). **Compound 24b:** 25 mg (36%) of **24b** was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (s, 9 H, *t*Bu), 1.05−1.40 (m, 3 H, cyc.), 1.60 (s, 3 H, =CMe), 1.85−2.20 (m, 4 H, cyc.), 2.58−2.70 (m, 1 H, cyc.), 3.53−3.65 (m, 1 H, CH_2), 7.35−7.55 (m, 5 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.8 (=CMe), 27.9 (*t*Bu), 28.4 (=CCH_2CH_2), 29.0 (=CCH_2CH_2), 31.8 (=CCH_2), 32.3 (=CCH_2), 32.9 (Me_3C), 48.4 (CH), 124.5 (CH arom.), 129.2 (CH arom.), 130.2 (CH arom.), 132.1 (C=CSO), 144.1 (C arom.), 149.4 (C=CSO).

Allenes 25b−h. General Procedure: AIBN (62 mg, 0.38 mmol, 0.75 equiv.) and TTMS (230 μL, 0.75 mmol, 1.5 equiv.) were added to a benzene or toluene solution of bromide **1** (0.02 M, 0.5 mmol, 1 equiv.). The mixture was heated under reflux under nitrogen for 2 h. Monitoring by TLC indicated whether AIBN (by portions of 30 mg, 0.37 equiv.) and TTMS (by portions of 80 μL, 0.25 mmol, 0.5 equiv.) had to be re-added. After the necessary time, the solvent was evaporated. The crude product was purified by flash chromatography.

Compound 25b: Chromatography (pentane/EE, from 100:0 to 95:5) afforded 41 mg (56%) of **25b** as an oil. IR (neat): $\tilde{\nu}$ = 3005, 2950, 1940, 1600, 1505, 1240 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OCH_3), 5.15 (d, *J* = 6.8 Hz, 2 H, =CH_2), 6.15 (t, *J* = 6.8 Hz, 1 H, =C−H), 6.88 (d, *J* = 8.7 Hz, 2 H, arom.), 7.25 (d, *J* = 8.7 Hz, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7 (OCH_3), 79.2 (=CH_2), 93.7 (CH), 114.5 (CH arom.), 128.1 (CH arom.), 126.5 (C arom.), 159.1 (C arom.), 209.7 (=C=).

Compound 25c: Chromatography (PE/EE, from 97:3 to 95:5) afforded 51 mg (61%) of **25c** as an oil. IR (neat): $\tilde{\nu}$ = 3005, 2920, 1960, 1440, 1250, 1110, 1065 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.65 (m, 4 H, CH_2), 2.21 (m, 4 H, CH_2), 3.88 (s, 4 H, CH_2O), 4.50 (m, 2 H, =CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.1 and 35.1 (CH_2), 64.3 (CH_2O), 73.1 (=CH_2), 98.7 (CH_2-*C*=), 108.0 (O−C−O), 203.0 (=C=).

Compound 25d: Chromatography (PE/EA, from 100:0 to 95:5) afforded 46 mg (57%) of **25d** as an oil. ^{1}H NMR (200 MHz, CDCl3): δ = 5.17 (d, *J* = 6.8 Hz, 2 H, =CH_2), 5.96 (m, 2 H, OCH_2O), 6.14 (t, *J* = 6.8 Hz, 1 H, =C−H), 6.74−6.88 (m, 3 H, arom.). ^{13}C NMR (100 MHz, CDCl3): δ = 79.1 (=CH_2), 93.9 (CH), 101.1 (OCH_2O), 106.7, 108.4, and 120.5 (CH arom.), 128.0, 146.8 and 148.2 (C arom.), 209.4 (=C=).

Compound 25e: Chromatography (pentane/EE, from 100:0 to 98:2) afforded 52 mg (53%) of **25e** as an oil. IR (neat): $\tilde{\nu}$ = 2960, 2920, 1950, 1455, 1370, 1080 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 7.1 Hz, 3 H, CH_3), 1.14 (s, 6 H, 2 CH_3), 1.23−1.42 (m, 6 H, CH_2), 1.52 (m, 1 H, $CHCH_3$), 1.85 (m, 1 H, C*H*HCH=), 2.00 (m, 1 H, CH*H*CH=), 3.17 (s, 3 H, OCH_3), 4.62 (dt, *J* = 7.1, 3.0 Hz, 2 H, =CH_2), 5.04 (quint, *J* = 7.1 Hz, 1 H, H−C=). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4 (CH_3), 21.2 (CH_2), 25.0 (2 CH_3), 33.2 (*C*HCH_3), 35.9, 36.7, and 40.0 (CH_2), 49.0 (OCH_3), 73.8 (CH_2), 74.8 (C−OCH_3), 88.3 (=C−H), 209.1 (=C=).

Compound 25f: Chromatography (PE/EA, from 100:0 to 90:10) afforded 93 mg (55%) of **25f** as an oil. IR (neat): $\tilde{\nu}$ = 3060, 2920, 2825, 1950, 1420, 1105 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.06 (s, 9 H, *t*Bu), 1.70 (m, 2 H, CH_2), 2.06−2.20 (m, 2 H, CH_2CH=), 3.70 (t, *J* = 6.3 Hz, 2 H, CH_2O), 4.64 (dt, *J* = 6.7, 3.3 Hz, 2 H, =CH_2), 5.10 (quint, *J* = 6.7 Hz, 1 H, =CH), 7.33−7.47 (m, 6 H, arom.), 7.63−7.72 (m, 4 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4 [*C*(CH_3)], 24.7 (CH_2), 27.0 (3 CH_3), 32.0 (CH_2CH=), 63.3 (CH_2O), 75.1 (=CH_2), 89.9 (=CH), 129.7 (CH arom.), 134.2 (C arom.), 127.8 and 135.7 (CH arom.), 208.7 (=C=).

Compound 25g: Chromatography (PE/EA, from 100:0 to 96:4) afforded 81 mg (80%) of **25g** as an oil. IR (neat): $\tilde{\nu}$ = 2950, 1950, 1480, 1240 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.00 (d, *J* = 6.5 Hz, 3 H, CH_3), 2.22−2.67 [m, 3 H, CH_2Ar + C*H*(CH_3)], 4.67 (dd, *J* = 6.6, 2.8 Hz, 2 H, =CH_2), 5.11 (q, *J* = 6.5 Hz, 1 H, = CH), 5.91 (s, 2 H, OCH_2O), 6.57−6.74 (m, 3 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.5 (CH_3), 34.5 [*C*H(CH_3)], 43.1 (CH_2Ar), 75.9 (=CH_2), 95.4 (=C−H), 100.7 (OCH_2O), 107.9 and 109.5 (2 CH arom.), 122.0 (CH arom.), 129.2 (C arom.), 145.6 and 147.3 (C arom.), 207.4 (=C=).

Compound 25h: Chromatography (pentane) afforded 73 mg (70%) of **25h** as a colorless oil. IR (neat): $\tilde{\nu}$ = 3050, 2940, 1955, 1575, 1480 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.20 (d, *J* = 6.7 Hz, 2 H, =CH_2), 6.20 (t, *J* = 6.7 Hz, 1 H, =CH), 6.92 (m, 1 H, arom.), 7.07−7.19 (m, 5 H, arom.),7.31−7.42 (m, 3 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.0 (=CH_2), 93.6 (=C−H), 117.1, 117.4, 118.7, 121.7, 123.1, 129.7, and 129.8 (CH arom.), 135.9, 157.2, and 157.4 (C arom.), 209.8 (=C=).

Reactions of 10, 12, 13, and 14

Conditions A: AIBN (16 mg, 0.1 mmol, 0.2 equiv.) and Bu_3SnH (175 μL, 0.65 mmol, 1.3 equiv.) were added to a benzene solution of bromide (0.025 M, 0.5 mmol, 1equiv.). After 1 h at reflux, the mixture was allowed to cool to room temp. and the benzene was removed in vacuo. The crude product was subjected to treatment with KF (5 equiv.) in methanol (10 mL) for 2 h. After removal of the solvent, the mixture was dissolved in CH_2Cl_2, filtered through Celite®, and concentrated. The crude product was purified by flash chromatography.

Conditions B: A benzene solution (6 mL) of Bu_3SnH (175 μL, 0.65 mmol, 1.3 equiv.) containing AIBN (4 mg, 0.025 mmol, 0.05 equiv.) was added by syringe pump ($2\cdot10^{-4}$ mol·h^{-1}) to a solution of bromide (0.5 mmol, 1 equiv.) and AIBN (12 mg, 0.075 mmol, 0.15 equiv.) in refluxing benzene (19 mL) under argon. The benzene was removed in vacuo and the crude product was treated as above.

Vinyl Sulfide 26: Chromatography (PE/EA, 90:10) afforded 134 mg (97%) of **26** as an oil. IR (neat): $\tilde{\nu}$ = 2950, 2920, 2880, 1600, 1580, 1475, 1435 cm^{-1-1}H NMR (200 MHz, $CDCl_3$): 1.72 (m, 4 H, CH_2), 1.97 (s, 3 H, CH_3), 2.50 (m, 2 H, CH_2), 2.75 (m, 2 H, CH_2), 3.97 (s, 4 H, CH_2O), 7.12−7.30 (m, 5 H, arom.). ^{13}C NMR (50 MHz): δ = 20.3 (CH_3), 27.9, 29.5, 35.4 and 35.7 (CH_2), 64.3 (2 CH_2O), 108.4 (O−C−O), 119.4 (=C), 125.3 (CH arom.), 128.3

(2 CH arom.), 128.8 (2 CH arom.), 129.1 (C arom.), 144.4 (=C). MS (CI): *m*/*z* (%) = 277 (100) [MH^+], 167 (50) [M^+ − SPh].

Vinyl Sulfone 27: Chromatography (PE/EA, 40:60) afforded 141 mg (92%) as an oil. IR (neat): $\tilde{\nu}$ = 3000, 2950, 2880, 1740, 1700, 1625, 1445, 1300 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.50−1.72 (m, 4 H, CH_2), 2.05 (s, 3 H, CH_3), 2.40 (m, 2 H, CH_2), 2.92 (m, 2 H, CH_2), 3.90 (s, 4 H, CH_2O), 7.43−7.54 (m, 3 H, arom.), 7.80−7.82 (m, 2 H, arom.). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.4 (CH_3), 27.5, 30.1, 35.9 and 35.0 (CH_2), 64.4 (2 CH_2O), 107.5 (O−C−O), 126.7 (2 CH arom.), 130.0 (2 CH arom.),130.2 (=C), 132.8 (CH arom.), 142.3, 151.4 (C arom. and =C).

Vinyl Sulfoximine 28: Chromatography (PE/EA, 90:10) afforded 201 mg (94%) as an oil. IR (neat): $\tilde{\nu}$ = 2940, 2900, 2350, 1725, 1630, 1600, 1320 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.66 (m, 4 H, CH_2), 2.06 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 2.36 (m, 2 H, CH_2), 2.72 (m, 2 H, CH_2), 3.84 (m, 4 H, CH_2O), 7.15−7.19 (m, 2 H, arom.), 7.41−7.53 (m, 3 H, arom.), 7.75−7.86 (m, 4 H, arom.). ^{13}C NMR (62.2 MHz, $CDCl_3$): δ = 16.0 and 21.4 (CH_3), 27.7, 30.8, 34.3 and 34.9 (CH_2), 64.4 (CH_2O), 107.3 (O−C−O), 126.6 (2 CH arom.), 127.0 (2 CH arom.), 129.1 (2 CH arom.), 129.2 (2 CH arom.), 133.5 (CH arom.), 129.5, 140.2, 141.1, 142.5, 153.7 (3 C arom. and 2 =C).

Vinyl Sulfimine 29: Chromatography (PE/EA, 50:50) afforded 113 mg (55%) of **29** as an oil. IR (neat): $\tilde{\nu}$ = 2980, 2940, 2380, 2350, 1730, 1640, 1600, 1480, 1450, 1300 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.51−1.75 (m, 7 H, 2 CH_2 and CH_3), 2.20−2.34 (m, 5 H, CH_2, CH_3), 2.66−2.92 (m, 2 H, CH_2), 3.95 (s, 4 H, CH_2O), 7.18 (d, *J* = 8.0 Hz, 2 H, arom.), 7.43−7.60 (m, 5 H, arom.), 7.75 (d, *J* = 8.0 Hz, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.1 (CH_3), 21.4 (CH_3), 28.8, 29.0, 34.8, and 35.1 (4 CH_2), 64.5 and 64.5 (OCH_2), 107.4 (O−C−O), 125.9 (2 CH arom.), 126.3 (2 CH arom.), 129.1 (2 C arom.), 129.6 (2 CH arom.), 131.2 (CH arom.), 121.75, 133.6, 141.6, 142.0, 152.0 (3 C arom. and 2 =C). MS (CI): *m*/*z* (%) = 446 (35) [MH^+], 277 (100) [M^+ − $C_{13}H_{12}S_2O_2N$].

Reaction of 18: Precursor **18** (182 mg, 0.30 mmol, 1 equiv.), AIBN (35 mg, 0.21 mmol, 0.7 equiv.), and Bu_3SnH (120 μL, 0.45 mmol, 1.5 equiv.) were dissolved in dry toluene (12 mL). The reaction mixture was irradiated (OSRAM 300 W sunlamp) for 2 h, concentrated in vacuo, and purified by chromatography (PE/EA, 60:40) to yield 119 mg (88%) of **30** as a colorless oil.

Reduced Product 30: IR (neat): $\tilde{\nu}$ = 3060, 2980, 2950, 2840, 1730, 1580, 1045 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 6 H, Me_2C), 1.33−1.47 (m, 4 H, CH_2CH_2), 1.60−1.70 (m, 1 H, MeO_2CCH*H*), 1.84 (s, 3 H, =CMe), 1.95−2.05 (m, 1 H, MeO_2CCH*H*), 2.18 (s, 3 H, =CMe), 2.35 (s, 3 H, Tol.), 2.74 (B of AB, *J* = 15.6 Hz, 1 H, =CC*H*H), 3.07 (A of AB, *J* = 15.6 Hz, 1 H, =CC*H*H), 3.12 (s, 3 H, COMe), 3.66 (s, 3 H, CO_2Me), 3.71 (s, 3 H, CO_2Me), 7.22 (d, *J* = 8.1 Hz, 2 H, arom.), 7.33 (d, *J* = 8.1 Hz, 2 H, arom.). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.4 ($CH_2CH_2CH_2$), 21.3 (Tol.), 22.5 (=CCH_3), 23.3 (=CCH_3), 25.1 (CH_3CCH_3), 25.2 (CH_3CCH_3), 29.6 (CH_2CSO), 34.5 (E_2CCH_2), 39.7 (Me_2CCH_2), 49.1 (Me_2COMe), 52.3 (CO*OMe*), 58.3 (E*C*E), 74.4 (Me_2COMe), 124.5 (CH arom.), 129.7 (CH arom.), 137.0, 140.4, 141.4 and 145.8 (2 C arom. + C=C), 172.1 (C=O) 172.2 (C=O). $C_{24}H_{36}O_6S$ (452.60): calcd. C 63.69, H 8.02; found C 63.58, H 8.16. Compound **30D** was obtained from the reduction of **18** with Bu_3SnD. Spectroscopic data corresponded to those of the nondeuterated product. ^2H NMR (46 MHz, $CHCl_3$): δ = 1.43 ($CHDCH_2CH_2$). MS (CI): *m*/*z* = 454 (100) [$MH]^+$, 422 (51), 406 (15), 314 (17). Alternatively, precursor **18** (149 mg, 0.25 mmol, 1 equiv.) and AIBN (5 mg) were dissolved in toluene (10 mL). The solution was heated under reflux and a solution of tris(trimethylsilyl)silane (120 μL, 0.38 mmol, 1.5 equiv.) and AIBN (53 mg, 0.32 mmol, 1.3 equiv.) in toluene (4 mL) was added by syringe pump (rate [TTMS] = 0.064 $mmol \cdot h^{-1}$). At the end of the addition, the reaction mixture was heated for an additional hour, and then concentrated in vacuo. Chromatography (PE/EA, 90:10) afforded 20 mg (18%) of reduced **30** and 48 mg (61%) of allene **31** as a colorless oil.

Allene 31: IR (neat): $\tilde{\nu}$ = 2960, 2930, 1965, 1730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 (s, 6 H, Me_2C), 1.18−1.29 (m, 2 H, CH_2), 1.39−1.49 (m, 2 H, CH_2), 1.67 (s, 3 H, =CMe), 1.68 (s, 3 H, =CMe), 1.91−1.98 (m, 2 H, CH_2), 3.12 (s, 3 H, COMe), 3.70 (s, 6 H, CO_2Me), 5.48−5.52 (m, 1 H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8 ($CH_2CH_2CH_2$), 20.1 [$CH_3C(=)CH_3$], 23.6 [$CH_3C(=)CH_3$], 25.0 (Me_2COMe), 34.8 ($CH_2CH_2CH_2$), 40.2 ($CH_2CH_2CH_2$), 49.1 (Me_2COMe), 52.7 (CO*OMe*), 58.3 (E*C*E), 74.5 (Me_2COMe), 88.6 (=CH), 99.8 (Me_2C=), 171.2 (*C*OOMe), 201.5 (=C=). $C_{17}H_{28}O_5$ (312.41): calcd. C 66.36, H 9.03; found C 66.92, H 8.92.

Reaction of 23: Precursor **23** (184 mg, 0.41 mmol, 1 equiv.), AIBN (80 mg, 0.41 mmol, 1 equiv.), and Bu_3SnH (140 μL, 0.53 mmol, 1.3 equiv.) were heated under reflux in benzene (20 mL) for 2 h, then allowed to cool to room temp. Additional AIBN (50 mg, 0.25 mmol, 0.6 equiv.) and Bu_3SnH (140 μL, 0.53 mmol, 1.3 equiv.) were added, and the reaction mixture was again heated under reflux for 2 h and allowed to cool to room temp. Aq. sodium carbonate (10 wt.%, 20 mL) was added and the mixture was vigorously stirred for 1 h. The organic phase was dried with $MgSO_4$, filtered, and concentrated. Chromatography (PE/EA, 95:5) yielded **32** and **33**, which could not be separated. For reactions run in the presence of MAD, a solution of precursor **23** in benzene (6 mL) was added dropwise to a MAD solution (4 equiv.), previously prepared in situ from $AlMe_3$ (2 M solution in toluene, 760 μL, 1.52 mmol, 4 equiv.) and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (670 mg, 3.04 mmol, 8 equiv.) in benzene (20 mL). The reaction mixture was left standing at room temp. for 20 min before addition of tin hydride and AIBN as described above.

Mixture of Diene 32 and Allene 33: Chromatography (PE/EA, 95:5) yielded 75 mg (73%) of a slightly yellow oil, corresponding to the mixture of **32** and **33** (95:5) that could not be separated. **Compound 32:** IR (neat): $\tilde{\nu}$ = 3070, 2950, 2860, 1730, 1640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.74 (s, 3 H, =CMe), 1.74 (s, 3 H, =CMe), 2.14−2.17 (m, 2 H, CH_2), 2.27−2.30 (m, 2 H, CH_2), 2.81 (s, 2 H, $=CCH_2CE_2$), 3.71 (s, 6 H, CO_2Me), 4.60 (br. s, 1 H, =CH), 4.95 (br. s, 1 H, =CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (=C*Me*), 22.2 (=C*Me*), 32.9 (CH_2), 33.2 (CH_2), 36.0 (CH_2), 52.6 (OMe), 52.8 (OMe), 56.4 (E*C*E), 111.3 (=CH_2), 127.9 (=C), 128.8 (=C), 146.8 (=C), 171.8 (*C*OOMe). **Compound 33:** IR (neat): $\tilde{\nu}$ = 3070, 2950, 2860, 1730, 1640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3 H, =CMe), 1.71 (s, 3 H, =CMe), 1.97−2.13 (m, 4 H, CH_2CH_2), 3.74 (s, 6 H, CO_2Me), 4.95−5.10 (m, 2 H, CH_2=CH), 5.51−5.58 (m, 1 H, C=C=CH), 5.52−5.72 (m, 1 H, CH_2=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2 (=C*Me*), 22.2 (=C*Me*), 29.9 (CH_2), 30.5 (CH_2), 52.7 (OMe), 52.8 (OMe), 58.2 (E*C*E), 88.5 (C=C=*CH*), 99.9 (*C*=C=CH), 115.1 (=CH_2), 137.9 (=CH), 171.2 (*C*OOMe), 201.3 (C=*C*=CH). $C_{14}H_{20}O_4$ (252.31): calcd. C 66.65, H 7.99; found C 66.61, H 8.08.

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