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Tetrahydrofuran Synthesis via Free Radical Mediated Addition of Functionalized Alkenes to Aryl Vinyl Oxiranes

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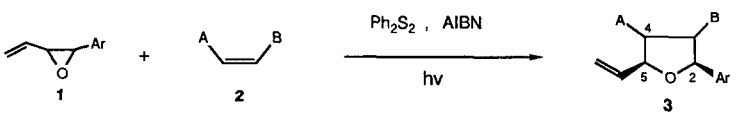
Abstract: Tri- and tetrasubstituted tetrahydrofuran rings can be prepared by phenylthio radical mediated addition of functionalized alkenes across the carbon-carbon bond of aryl substituted vinyl oxiranes. Studies designed both to delineate the scope and limitations and elucidate the mechanistic course of this process are described.

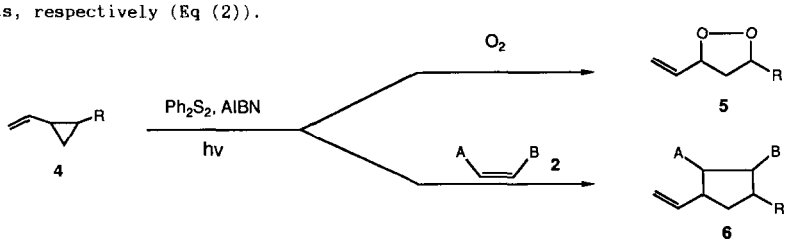
Introduction

The isolation and characterization of numerous tetrahydrofuran-containing natural products has stimulated intense effort toward the development of methodology for the stereoselective synthesis of this heterocycle. Classical strategies, such as furan reduction or cyclization of pentenol derivatives, have been advanced to high levels of stereochemical control.[1] More recently, [3 atom + 2 atom] bond construction approaches have come into prominence.[2] These methods can generally be divided into two categories: 1) dipolar or diyl addition of a three carbon unit to a suitably functionalized aldehyde,[2a-e] or 2) carbonyl ylid/alkene cycloaddition.[2g-p] The utility of the former strategy for the stereoselective preparation of 2,5 disubstituted tetrahydrofurans, crucial for application to many natural product systems, has not been demonstrated. Herein, we describe a novel free radical mediated [3 atom + 2 atom] addition between aryl vinyl oxiranes and alkenes which provides poly-substituted tetrahydrofuran rings featuring complete *cis*-2,5 relative asymmetric induction (Eq (1)).



(1)

This tetrahydrofuran synthesis stems from our exploration of the scope of a free radical mediated [3 atom + 2 atom] addition process developed earlier in our laboratory.[3] These preliminary studies documented the facile addition of either molecular oxygen or functionalized olefins across the carbon-carbon bond of substituted vinyl cyclopropanes to afford 1,2-dioxolane 5 or cyclopentane 6 products, respectively (Eq (2)).



(2)

As with the tetrahydrofuran synthesis described here, we believe that these transformations proceed through a series of free radical intermediates (*vide infra*). Suppression of undesirable (or nonproductive) reaction pathways available to each of these intermediates is crucial for the success of this multistep pathway. The strain energy inherent in the cyclopropane or oxirane ring serves to channel the complex reaction sequence toward the desired product, thus minimizing the intervention of competitive reaction processes.

Results and Discussion

Treatment of a refluxing benzene solution of a vinyl oxirane **1** and excess alkene **2** with a phenylthio radical source leads to formation of the 2,5-*cis* tetrahydrofuran products **3** as a mixture of epimers at C(4). Preliminary experiments indicated that the mixture of oxirane diastereomers **7a**, or the *cis* or *trans* species, used independently, gave identical yields and isomer distributions of tetrahydrofuran products. Therefore, all subsequent experiments utilized a mixture of diastereomeric oxirane isomers for reaction with alkenes. Several specific examples of this process are shown in the Table 1. Use of an aromatic substituent on the oxirane ensures that products from carbon-carbon bond cleavage predominate. Thus, phenyl and 2- or 3-furanyl substituents are effective in this regard (entries a-c, Table). However, vinyl oxiranes **1** bearing ester, alkyl, or vinyl substituents do not produce tetrahydrofuran products upon reaction with methyl acrylate. Fortunately, the consequences of this apparent limitation are minimized by the furan moiety's capacity to serve as a masked carbonyl equivalent.[4] The other component of these cyclizations, a mono- or disubstituted alkene, requires substituents which substantially lower the alkene's LUMO (e.g. phenyl or ester) for successful addition.

Table 1

	7 Ar	A	**8** B	C	**9**	**10**	**11**	yield[a]
a)	Ph	H	CO_2Me	H	*1.8*	*1.0*	----	56 %
b)	2-furanyl	H	CO_2Me	H	*2.2*	*1.0*	----	38 %
c)	3-furanyl	H	CO_2Me	H	*1.9*	*1.0*	----	30 %
d)	Ph	H	CN	H	*2.1*	*1.0*	----	53 %
e)	Ph	H	CO_2t-Bu	H	*3.0* [b]	*1.0*	----	47 %
f)	Ph	H	CO_2(1-ad)	H	*3.4* [b]	*1.0*	----	55 %
g)	Ph	H	Ph	H	*4.0* [b]	*1.0*	----	57 %
h)	Ph	CH_3	CO_2Me	H	*6.8* [b]	*4.6*	*1.0*	56 %
i)	Ph	H	CO_2Me	CH_3	*1.0*	*1.0*	----	55 %

a) Isolated yield based on chromatographically pure products. b) The ratio of these diastereomeric tetrahydrofuran products varied with time over the course of the reaction (GLC analysis). Control experiments indicated that this variation could be attributed to a slow decomposition of the minor stereoisomer under the reaction conditions. The yields reported are for the isolated, chromatographically pure tetrahydrofuran products upon completion of reaction. The diastereomer ratios are reported after short (~20% consumption of starting oxirane) reaction times.

The phenyl, 2-furanyl and 3-furanyl vinyl oxiranes **7a-c** all combine with methyl acrylate to produce the 2,5 *cis* tetrahydrofuran derivatives as epimeric mixtures at C(4). A slight (~2:1) kinetic preference is seen for the *trans* ester products **9a-c**. Independent treatment of either **9a** or **10a** with $NaOCH_3$ in methanol leads to the same equilibrium mixture of stereoisomers (**9a**/**10a** = 5.5:1). The stereoselectivity of product formation appears sensitive to the steric bulk of the alkene addend, as seen by comparison of entries a, e, f, and g (Table 1). Thus, increasing steric bulk results in a corresponding increase in selectivity for the *trans* isomer **9**.

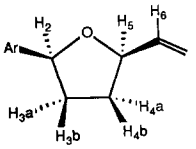
The disubstituted alkenes E-methyl crotonate and methyl methacrylate both undergo addition to phenyl vinyl oxirane (**7a**) to afford the 2,5-*cis*-tetra-substituted tetrahydrofuran adducts **9-11h** and **9-10i**, respectively. The methyl methacrylate adducts **9i** and **10i** are formed with little selectivity,

perhaps reflecting the similarity in size of the two substituents (A values: methyl 1.7 kcal/mol, CO_2CH_3 1.3 kcal/mol).[5] Combination of oxirane **7a** with E-methyl crotonate introduces an additional stereochemical relationship in the product tetrahydrofuran (C(2)–C(3)). This relationship is established with no apparent selectivity (**9h**/**10h**+**11h** = 1.2:1), and furthermore, a typical mixture of ester epimers is produced at C(4).

The stereochemical assignments of the product tetrahydrofurans were based upon homodecoupling and DNOE ^1H NMR studies. The diagnostic DNOE values are compiled in Table 2. In most cases, greater than 10% NOE was detected between H(2) and H(5), in accord with earlier stereochemical studies on five membered heterocycles.[6] In all cases, observable NOE's allowed unambiguous assignment of stereochemistry for substituents at C(3) and C(4).

Table 2

% NOE (reported as a percent of NOE maximum)



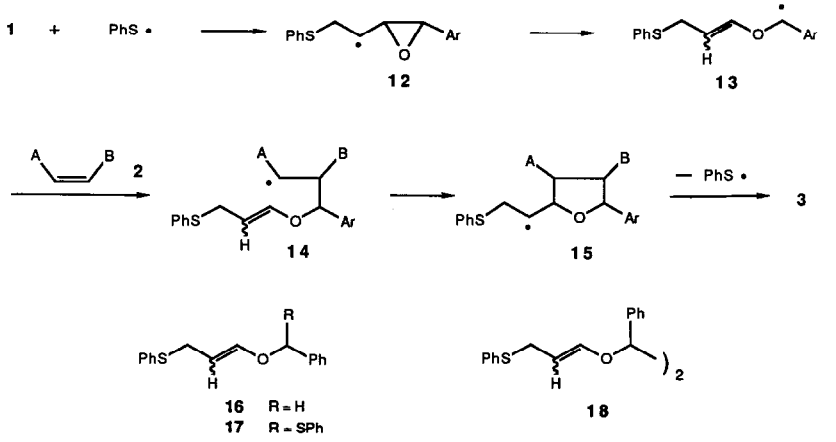
	H 2/H 5	H 2/H 3a	H 5/H 4a	H 6/H 4b	H 3b/H 4b	H 3a/H 4a
9a	13	15	--	12	15	--
10a	7	6	11	--	--	4
9b	12	14	--	9	14	--
10b	5	13	16	--	--	11
9c	10	13	--	8	12	--
10c	9	--	14	--	--	--
9d	12	18	--	13	19	--
10d	17	13	12	--	--	8
9e	18	17	--	--	12	--
10e	6	7	18	--	--	14
9f	14	11	--	12	16	--
10f	7	7	17	--	--	8
9g	16	16	--	11	13	--
10g	5	9	12	--	--	6
9h	7	14	--	10	8(CH_3)	--
10h	5	11(CH_3)	23	--	--	11(CH_3)
11h	7	8(CH_3)	--	10	20	--
9i	22	16	--	26	16(CH_3)	--
10i	10	11	30(CH_3)	--	--	18(CH_3)

The mechanistic course of this transformation is presumed to be similar to one proposed by us for oxygen[3a] or alkene[3b] addition to vinyl cyclopropanes. Key features of the mechanism include 1) initiation by addition of phenylthio radical to the vinyl moiety of oxirane **1** to afford, after carbon-carbon bond cleavage, the homoallylic radical **13**, 2) addition of the alkene **2** to radical **13** to furnish the substituted 5-hexenyl radical **14**, 3) cyclization to the tetrahydrofuranyl carbinyl radical **15**, and 4) termination by ejection of the phenylthio radical (Eq (3)). In general, rearrangement of the oxiranyl carbinyl radical **12** generated by phenylthio radical addition to vinyl oxirane **1** can proceed via either carbon-carbon or carbon-oxygen bond scission.[7] Particularly noteworthy in our tetrahydrofuran synthesis is the complete control of regiochemistry of bond cleavage, leading *only* to alkene addition across the carbon-carbon bond of the oxirane.

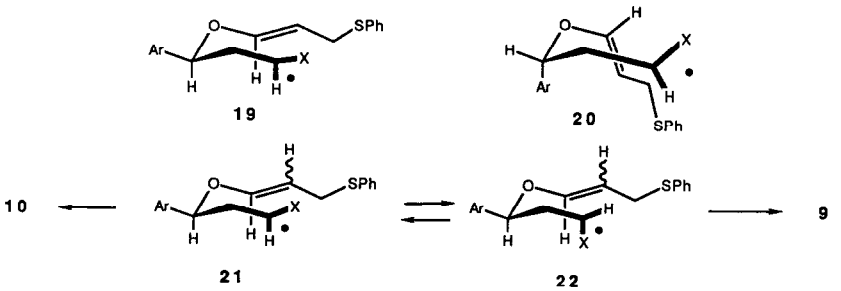
In support of this mechanistic proposal, control experiments indicate that no reaction transpires if any of the reagents necessary to generate the phenylthio radical are omitted. Furthermore, radical intermediates can be trapped as stable adducts by good atom donor reagents. Thus, under standard reaction conditions, omission of the alkene addend leads to isolation of the 1,5-phenyl disulfide adduct **17** (34%, E/Z = 1:1.6) and the radical dimerization product **18** (18%) from phenyl vinyl oxirane **7a**. Finally, substitution of thiophenol for phenyl disulfide in the reaction of oxirane **7a** with methyl acrylate leads to recovery of the 1,5 thiophenol adduct **16** (38%, E/Z = 1:1.1) along with the expected tetrahydrofuran products **9a** and **10a** (39%).

The stereochemical issues raised in this reaction can be addressed through an evaluation of the energetics of the conformations available to the substituted 5-hexenyl radical **14** upon cyclization. Much experimental and theoretical support can be found for a model in which cyclization

occurs through either chair-like or boat-like transition states, as indicated by conformers **19** and **20**.[8] The orientation of the substituents in these conformations and their associated steric interactions determine cyclization selectivity. Our results can be conveniently rationalized by postulating cyclization from either of the chair-like transition states **21** or **22**. Conformer **21** includes a pseudo-equatorial substituent X which experiences some level of eclipsing steric interaction with the olefinic carbon in the transition state for ring closure. This interaction can be alleviated by rotation about the C(3)-C(4) bond to furnish conformer **22**, which now possesses 1,3 diaxial-like steric interactions between the pseudo-axial substituent X and the axial C(2) and C(5)



hydrogens. Our data suggest that the eclipsing interaction in equatorial conformer **21** is both more severe than the 1,3 diaxial interaction in conformer **22** and more sensitive to the steric bulk of the substituent X. This latter conclusion is consistent with the observation that small torsional angle distortions, as might accompany bond formation in **21**, are more energetically costly than small bending distortions, as would result from the axial disposition of X in conformer **22**.[9]



Conclusion

In summary, we have developed methodology for the synthesis of *cis* 2-aryl, 5-vinyl tetrahydrofuran derivatives based on addition of functionalized alkenes to aryl vinyl oxiranes. In favorable cases, further stereoselectivity can be realized for a substituent at C(4). The regioselectivity and stereoselectivity of this transformation can be rationalized by invoking a multi-step reaction pathway featuring stereochemical control through substituent effects upon 5-hexenyl radical cyclization. Further studies designed to delineate the scope and limitations of this process, and applications to the stereorational synthesis of tetrahydrofuran natural products, will be reported in due course.

Acknowledgment: We thank the National Institutes of Health (GM37681) for financial support and Mr. G. D. Harris for his experimental contributions.

Experimental

Infrared spectra were recorded on a Perkin-Elmer model 281B spectrophotometer. Proton and carbon nuclear manetic resonance spectra (^{1}H NMR, ^{13}C NMR) were obtained on Bruker WP-200, WM-360

and AM-300 instruments. ^{1}H NMR signals reported for mixtures include major (M) and minor (m) peak designations. Low resolution mass spectra (MS) were obtained at 50-70 eV by electron impact on a Kratos MS9/50 double-focusing mass spectrometer. High resolution mass spectra (HRMS) were obtained on the Kratos MS 9/50 as well. Combustion analysis were performed by Micro-Tech Laboratories, Skokie, IL. Flash chromatography was performed on ICN 32-63 μm silica gel according to the method of Still.[10] Gas liquid chromatography (GLC) analysis utilized an HP 5890 instrument equipped with a 20 meter methyl silicone capillary column (0.20 mm ID). High pressure liquid chromatography (HPLC) was performed using a Waters 6000A isochratic instrument equipped with a model 440 UV detector, a model R400 differential refractometer, and Dupont Zorbax^R 21.2 mm x 25 cm silica gel column. 2-Phenyl-3-vinyloxirane (**7a**) was prepared by the method of Endo and Kanda.[11] 1-Adamantyl acrylate was synthesized by the method of Orsini.[12]

2-(2-furanyl)-3-vinyloxirane (7b). A solution of 3.2 g (79 mmol) sodium hydroxide in 8 mL water was added dropwise to a vigorously stirring solution of 4.8 g (50 mmol) 2-furaldehyde and allyl dimethyl sulfonium bromide (from 9.6 g (79 mmol) allyl bromide and 5.5 gm (89 mmol) dimethyl sulfide) in 15 mL isopropanol. After 6 h, dimethyl sulfide was removed in vacuo, and the residue was extracted with 4x50 mL ether. The combined ether extracts were washed with brine, dried with sodium sulfate, filtered, concentrated by rotary evaporation, and distilled under vacuum to afford 5.51 g of a pale yellow oil, 69-70°C/13 mm. Redistillation through a 20 cm Vigreaux column resulted in recovery of 3.71 g of a colorless oil, 41.5-42.5°C/1.3 mm (55%, 5:4 trans:cis by ^{1}H NMR). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4 (m, 1H, -OC(H)=), 6.4 (m, 2H, -C(H)=C(H)-), 6.0-5.3 (m, 1H, -C(H)=CH_2), 4.1 (d, J=4.0 Hz, 1H (m), -OC(H)-furanyl), 3.9 (dd, J=6.9, 2.2 Hz, 1H (M), -OC(H)-C(H)=CH_2), 3.8 (d, J=2.2 Hz, 1H (M), -OC(H)-furanyl), 3.7 (dd, J=8.2, 4.0 Hz, 1H (m), -OC(H)-C(H)=CH_2); MS m/z (relative intensity) 136 (13% M^+), 107 (96%, M^+-CHO).

2-(3-furanyl)-3-vinyloxirane (7c). A solution of 2.48 g (62 mmol) sodium hydroxide in 8 mL water was added dropwise to a vigorously stirring solution of 4.65 gm 3-furaldehyde (48 mmol) and allyl dimethyl sulfonium bromide (from 7.5 g (62 mmol) allyl bromide and 4.3 gm (70 mmol) dimethyl sulfide) in 12 mL isopropanol. After 5 h, dimethyl sulfide was removed in vacuo, and the residue was extracted wtih 4x50 mL ether. The combined ether extracts were washed with brine, dried with sodium sulfate, filtered, concentrated by rotary evaporation, and purified by flash chromatography using 2.5% ether/hexane as eluent to afford 2.25 gm of a pale yellow oil (34%, 3:2 trans:cis by ^{1}H NMR). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.5-7.4 (m, 2H, =C(H)OC(H)=), 6.4 (dd, J=1.8, 0.9 Hz, 1H (m), -OC(H)=C(H)-), 6.3 (dd, J=1.8, 0.8 Hz, 1H (M), -OC(H)=C(H)-), 5.8-5.3 (m, 1H, -C(H)=CH_2), 4.1 (d, J=4.0 Hz, 1H (m), -OC(H)-furanyl), 3.7 (d, J=2.1 Hz, 1H (M), -OC(H)-furanyl), 3.6 (m, 1H (m), -OC(H)-C(H)=CH_2), 3.5 (dd, J=7.2, 2.1 Hz, 1H (M), -OC(H)-C(H)=CH_2); MS m/z (relative intensity) 136 (12%, M^+), 107 (65%, M^+-CHO); HRMS. Calcd for $C_8H_8O_2$: 136.0524. Found: 136.0525.

General procedure for the addition of olefins to oxiranes. In a typical experiment, a deoxygenated solution of phenyl disulfide (0.1 M) and AIBN (0.02 M) in benzene is added dropwise (ca. 0.5 mL/h) via syringe pump to a deoxygenated, refluxing benzene solution containing oxirane (0.1 M) and olefin (1.5 M). The reaction solution is subjected to continuous sunlamp irradiation and a inert atmosphere (N_2 or Ar) is maintained throughout. Upon complete consumption of oxirane (TLC or GLC), the reaction solution is concentrated by rotary evaporation and the products isolated by flash chromatography and/or HPLC as pure diastereomers. Individual yields and diastereomer ratios are given in Table 1.

(±)-(2S,4R*,5R*)-Tetrahydro-4-carbomethoxy-2-phenyl-5-vinylfuran (9a).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4-7.2 (m, 5H, Ar-H), 6.0 (ddd, J=17.2, 10.4, 6.3 Hz; 1H; -C(H)=CH_2), 5.4 (dt, J=17.2, 1.3 Hz, 1H, =C(H)H), 5.2 (dt, J=10.3, 1.3 Hz, 1H, = C(H)H), 5.1 (t, J=7.5 Hz, 1H, Ph-C(H)O-), 4.6 (dd, J=7.3, 6.4 Hz, 1H, -OC(H)-C(H)=CH_2), 3.7 (s, 3H, -OCH_3), 2.9 (ddd, J=13.3, 7.3, 6.0 Hz, 1H, -C(H)CO_2Me), 2.7 (ddd, J=12.8, 6.9, 5.9 Hz, 1H, -C(H)H-), 2.1 (ddd, J=12.5, 9.5, 7.9 Hz, 1H, -C(H)H-); ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.5, 141.6, 136.8, 128.3, 127.5, 125.8, 117.0, 83.0, 80.5, 52.1, 49.6, 38.2; IR (CCl_4) 1741 cm^{-1} (C=O); MS m/z (relative intensity) 232 (17%, M^+), 200 (35%, M^+-CH_3OH); HRMS. Calcd for $C_{14}H_{16}O_3$: 232.1099. Found: 232.1100.

(±)-(2S,4S*,5R*)-Tetrahydro-4-carbomethoxy-2-phenyl-5-vinylfuran (10a).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.5-7.2 (m, 5H, Ar-H), 5.9 (ddd, J=17.2, 10.3, 7.1 Hz, 1H, -C(H)=CH_2), 5.4 (ddd, J=17.2, 1.7, 1.2 Hz, 1H, =C(H)H), 5.2 (ddd, J=10.4, 1.6, 1.0 Hz, 1H, =C(H)H), 4.9 (dd, J=10.1, 6.1 Hz, 1H,

Ph-C(H)O-), 4.7 (m, 1H, -OC(H)-C(H)=CH_2), 3.7 (s, 3H, $-OCH_3$), 3.4 (m, 1H, -C(H)-CO_2Me), 2.4 (m, 2H, $-CH_2-$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.2, 140.8, 134.7, 128.3, 127.7, 126.2, 117.9, 81.1, 81.0, 51.7, 49.0, 37.0; IR (CCl_4) 1747 cm^{-1} (C=O); MS m/z (relative intensity) 232 (16%, M$^+$), 200 (57%, M$^+$-CH_3OH); HRMS. Calcd for $C_{14}H_{16}O_3$: 232.1099. Found: 232.1104.

(±)-(2S,4R*,5R*)-Tetrahydro-4-carbomethoxy-2-(2-furanyl)-5-vinylfuran (9b).* ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.4 (dd, J=1.6, 0.9 Hz, 1H, -OC(H)=), 6.3 (m, 2H, -C(H)=C(H)-), 6.0 (ddd, J=17.1, 10.3, 6.7 Hz, 1H, -C(H)=CH_2), 5.4 (dt, J=17.1, 1.3 Hz, 1H, =C(H)H), 5.2 (dt, J=10.3, 1.3 Hz, 1H, =C(H)H), 5.1 (t, J=7.1 Hz, 1H, furanyl-C(H)-O-), 4.5 (t, J=7.0 Hz, 1H, -OC(H)-C(H)=CH_2), 3.7 (s, 3H, $-OCH_3$), 3.0 (dt, J=9.0, 7.3 Hz, 1H, -C(H)-CO_2Me), 2.6 (dt; J=12.7, 7.2 Hz, 1H, -C(H)H-), 2.4 (ddd, J=12.7, 9.0, 6.9 Hz, 1H -C(H)H-); IR (CCl_4) 1742 cm^{-1} (C=O); MS m/z (relative intensity) 222 (7%, M$^+$); HRMS. Calcd for $C_{12}H_{14}O_4$: 222.0892. Found: 222.0891.

(±)-(2S,4S*,5R*)-Tetrahydro-4-carbomethoxy-2(2-furanyl)-5-vinylfuran (10b).* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4 (dd, J=1.8, 0.9 Hz, 1H, -OC(H)=), 6.4 (m, 2H, -C(H)=C(H)-), 5.8 (ddd, J=17.1, 10.3, 7.1 Hz, 1H, -C(H)=CH_2), 5.3 (ddd, J=17.1, 2.1 Hz, 1H, =C(H)H), 5.2 (ddd, J=10.3, 1.6, 1.0 Hz, 1H, =C(H)H), 4.9 (dd, J=10.6, 5.9 Hz, 1H, furanyl -C(H)O-), 4.7 (dd, J=8.4, 7.4 Hz, 1H, -OC(H)-C(H)=CH_2), 3.7 (s, 3H, $-OCH_3$), 3.4 (dt, J=10.4, 8.5 Hz, 1H, -C(H)-CO_2Me), 2.7 (dt, J=12.7, 10.5 Hz, 1H, -C(H)H-), 2.3 (ddd, J=12.7, 7.7, 5.8 Hz, 1H, -C(H)H-); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 152.9, 142.7, 134.8, 118.1, 110.2, 108.0, 80.8, 74.1, 51.8, 48.8, 32.4; IR (CCl_4) 1745cm^{-1} (C=O); MS m/z (relative intensity) 222 (32%, M$^+$); HRMS. Calcd for $C_{12}H_{14}O_4$: 222.0892. Found: 222.0894.

(±)-(2S,4R*,5R*)-Tetrahydro-4-carbomethoxy-2(3-furanyl)-5-vinylfuran (9c).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4 (m, 2H, =C(H)-O-C(H)=), 6.4 (dd, J=1.7, 0.9 Hz, 1H, -OC(H)=C(H)-), 5.9 (ddd, J=17.2, 10.3, 6.3 Hz, 1H, -C(H)=CH_2), 5.4 (dt, J=17.1, 1.3 Hz, 1H, =C(H)H), 5.2 (dt, J=10.3, 1.2 Hz, 1H, =C(H)H), 5.0 (t, J=7.3 Hz, 1H, furanyl-C(H)O-), 4.5 (td, J=6.8, 0.9 Hz, 1H, -OC(H)-C(H)=CH_2), 3.7 (s, 3H, $-OCH_3$), 2.9 (ddd, J=9.3, 7.2, 6.1 Hz, 1H, -C(H)-CO_2Me), 2.6 (ddd, J=12.6, 6.8, 6.0 Hz, 1H, -C(H)H-), 2.2 (ddd, J=12.6, 9.4, 7.7 Hz, 1H, -C(H)H-); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 143.4, 139.5, 136.9, 126.1, 117.0, 108.6, 82.8, 73.6, 52.1, 49.6, 36.7; IR (CCl_4) 1745 cm^{-1} (C=O); MS m/z (relative intensity) 222 (30%, M$^+$); HRMS. Calcd for $C_{12}H_{14}O_4$: 222.0892. Found: 222.0893.

(±)-(2S,4S*,5R*)-Tetrahydro-4-carbomethoxy-2(3-furanyl)-5-vinylfuran (10c).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4 (m, 2H, =C(H)-O-C(H)=), 6.5 (d, J=1.7 Hz, 1H, -OC(H)=C(H)-), 5.8 (ddd, J=17.2, 10.3, 6.9 Hz, 1H, -C(H)=CH_2), 5.3 (ddd, J=17.1, 1.2 Hz, 1H, =C(H)H), 5.2 (ddd, J=10.3, 1.6, 1.0 Hz, 1H, =C(H)H), 4.9 (d, J=8.0 Hz, 1H, furanyl-C(H)O-), 4.6 (tt, J=8, 1 Hz, 1H, -OC(H)-C(H)=CH_2), 3.7 (s, 3H, $-OCH_3$), 3.4 (q, J=8.6 Hz, 1H, -C(H)-CO_2Me), 2.3 (m, 2H, $-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 143.4, 140.0, 134.8, 125.4, 117.9, 109.1, 80.8, 73.6, 51.8, 49.0, 35.3; IR (CCl_4) 1740 cm^{-1} (C=O); MS m/z (relative intensity) 222 (16%, M$^+$); HRMS. Calcd. for $C_{12}H_{14}O_4$: 222.0892. Found: 222.0899.

(±)-(2S,4R*,5R*)-Tetrahydro-4-cyano-2-phenyl-5-vinylfuran (9d).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4-7.2 (m, 5H, Ar-H), 6.0 (ddd, J=17.1, 10.3, 6.3 Hz, 1H, -C(H)=CH_2), 5.6 (dt, J=17.1, 1.2 Hz, 1H, =C(H)H), 5.4 (dt, J=10.3, 1.1 Hz, 1H, =C(H)H), 5.1 (t, J=7.4 Hz, 1H, Ph-C(H)O-), 4.6 (tt, J=6.6, 1.1 Hz, 1H, -OC(H)-C(H)=CH_2), 2.9 (ddd, J=9.6, 7.6, 6.5 Hz, 1H, -C(H)-CN), 2.7 (ddd, J=12.8, 7.2, 6.6 Hz, 1H, -C(H)H-), 2.3 (ddd, J=12.8, 9.6, 7.7 Hz, 1H, -C(H)H-); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 134.5, 128.5, 128.0, 125.6, 119.5, 119.0, 83.2, 80.3, 38.4, 34.2; IR (CCl_4) 2210 cm^{-1} (C$\equiv$N); MS m/z (relative intensity) 199 (10%, M$^+$), 143 (100%); HRMS. Calcd. for $C_{13}H_{13}NO$: 199.0997. Found: 199.0994.

(±)-(2S,4S*,5R*)-Tetrahydro-4-cyano-2-phenyl-5-vinylfuran (10d).* ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4-7.2 (m, 5H, Ar-H), 6.1 (ddd, J=17.1, 10.4, 6.8 Hz, 1H, -C(H)=CH_2), 5.6 (dt, J=17.1, 1.2 Hz, 1H, =C(H)H), 5.5 (dt, J=10.4, 1.1 Hz, 1H, =C(H)H), 4.9 (dd, J=8.6, 6.9 Hz, 1H, Ph-C(H)O-), 4.6 (tt, J=6.9, 1.0 Hz, 1H, -OC(H)-C(H)=CH_2), 3.4 (dt, J=8.6, 6.8 Hz, 1H, -C(H)-CN), 2.8 (ddd, J=13.0, 8.6, 6.9 Hz, 1H, -C(H)H-), 2.3 (ddd, J=13.0, 8.7, 6.7 Hz, 1H, -C(H)H-); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 133.6, 128.6, 128.2, 126.1, 120.0, 119.1, 80.6, 80.2, 38.9, 34.6; IR ($CDCl_3$) 2200 cm^{-1} (C$\equiv$N); MS m/z (relative intensity) 199 (36%, M$^+$), 143 (100%); HRMS. Calcd for $C_{13}H_{13}NO$: 199.0997. Found: 199.1005.

(±)-(2S,4R*,5R*)-Tetrahydro-4-(carbo-t-butoxy)-2-phenyl-5-vinylfuran (9e).* ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.4-7.2 (m, 5H, Ar-H), 6.0 (ddd, J=17.1, 10.4, 6.4 Hz, 1H, -C(H)=CH_2), 5.4 (dt, J=17.1, 1.4 Hz, 1H, =C(H)H), 5.2 (dt, J=10.3, 1.1 Hz, 1H, =C(H)H), 5.0 (t, J=7.4 Hz, 1H, Ph-C(H)O-), 4.5 (dd, J=7.4, 6.4 Hz, 1H, -OC(H)-C(H)=CH_2), 2.8 (ddd, J=9.5, 7.5, 6.1 Hz, 1H, -C(H)-CO_2t-Bu), 2.6

(ddd, J=12.4, 7.0, 6.2 Hz, 1H, -C(H)H-), 2.0 (ddd, J=12.5, 9.4, 7.7 Hz, 1H, -C(H)H-), 1.5 (s, 9H, $-OC(CH_3)_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.1, 141.8, 137.1, 128.2, 127.3, 125.6, 116.5, 83.2, 80.8, 80.3, 50.4, 38.0, 27.9; IR (CCl_4) 1730cm^{-1} (C=O); MS m/z (relative intensity) 217 (100%, M^+-t-Bu); Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.23; H, 8.19.

(±)-(2S,4S*,5R*)-Tetrahydro-4-(carbo-t-butoxy)-2-phenyl-5-vinylfuran (10e).* ^1H NMR (200 MHz, $CDCl_3$) δ 7.5-7.2 (m, 5H, Ar-H), 5.9 (ddd, J=17.1, 10.2, 7.3 Hz, 1H, $-C(H)=CH_2$), 5.4 (ddd, J=17.1, 1.7, 1.1 Hz, 1H, =C(H)H), 5.2 (ddd, J=10.2, 1.6, 0.9 Hz, 1H, =C(H)H), 4.9 (dd, J=10.3, 5.9 Hz, 1H, Ph-C(H)O-), 4.7 (t, J=8.3 Hz, 1H, $-OC(H)-C(H)=CH_2$), 3.3 (dt, J=9.0, 8.4 Hz, 1H, $-C(H)-CO_2$t-Bu), 2.4-2.1 (m, 2H, $-CH_2-$), 1.4 (s, 9H, $-OC(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 141.1, 135.0, 128.3, 127.6, 126.3, 117.8, 81.2, 81.0, 80.9, 49.6, 37.1, 28.1; IR (CCl_4) 1732 cm^{-1} (C=O); MS m/z (relative intensity) 274 (4%, M^+); Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.24; H, 8.12.

(±)-(2S,4R*,5R*)-Tetrahydro-4-(carbo-1-adamantoxy)-2-phenyl-5-vinylfuran (9f).* ^1H NMR (300 MHz, $CDCl_3$) δ 7.4-7.2 (m, 5H, Ar-H), 6.1 (ddd, J=17.2, 10.4, 6.3 Hz, 1H, $-C(H)=CH_2$), 5.4 (dt, J=17.2, 1.4 Hz, 1H, =C(H)H), 5.2 (ddd, J=10.4, 1.5, 1.0 Hz, 1H, =C(H)H), 5.1 (t, J=7.4 Hz, 1H, Ph-C(H)O-), 4.5 (tt, J-7, 1.1 Hz, 1H, $-OC(H)-C(H)=CH_2$), 2.8 (ddd, J=9.5, 7.5, 6.1 Hz, 1H, $-C(H)-CO_2-$(1-Ad)), 2.6 (ddd, J=12.6, 7.1, 6.0 Hz, 1H, -C(H)H-), 2.2-2.1 (m, 9H, $-C'H_2-$, -C(H)-), 2.1 (m, 1H, -C(H)H-), 1.7 (t, J=2.9 Hz, 6H, $-C''H_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 141.9, 137.2, 128.3, 127.3, 125.7, 116.6, 88.3, 81.1, 80.5, 50.7, 41.3, 38.2, 36.1, 30.1; IR (CCl_4) 1735 cm^{-1} (C=O); MS m/z (relative intensity) 352 (4%, M^+); Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.38; H, 8.01. Found: C, 78.27; H, 8.09.

(±)-(2S,4S*,5R*)-Tetrahydro-4-(carbo-1-adamantoxy)-2-phenyl-5-vinylfuran (10f).* ^1H NMR (300 MHz, $CDCl_3$) δ 7.5-7.2 (m, 5H, Ar-H), 6.0 (ddd, J=17.1, 10.4, 7.2 Hz, 1H, $-C(H)=CH_2$), 5.4 (ddd, J=17.1, 1.6, 1.2 Hz, 1H, =C(H)H), 5.2 (ddd, J=10.3, 1.6, 1.1 Hz, 1H, =C(H)H), 4.9 (dd, J=10.4, 5.9 Hz, 1H, Ph-C(H)O-), 4.7 (ddd, J=8.6, 7.4, 1.0 Hz, 1H, $-OC(H)-C(H)=CH_2$, 3.3 (ddd, J=9.3, 8.8, 8.0 Hz, 1H, $-C(H)-CO_2-$(1-Ad)), 2.4 (ddd, J=12.7, 7.9, 5.9 Hz, 1H, -C(H)H-), 2.3 (ddd, J=12.7, 10.3, 9.7 Hz, 1H, -C(H)H-), 2.2-2.1 (m, 9H, $-C'H_2-$, -C(H)-), 1.7 (m, 6H, $-C''H_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 141.1, 135.0, 128.2, 127.6, 126.3, 117.7, 81.2, 81.0, 49.7, 41.4, 37.1, 36.1, 30.7; IR (CCl_4) 1735 cm^{-1} (C=O); MS m/z (relative intensity) 352 (4%, M^+); HRMS. Calcd for $C_{23}H_{28}O_3$: 352.2038. Found: 352.2043.

(±)-(2S,4R*,5R*)-Tetrahydro-2,4-diphenyl-5-vinylfuran (9g).* ^1H NMR (300 MHz, $CDCl_3$) δ 7.5-7.1 (m, 10H, Ar-H), 6.0 (ddd, J=17.2, 10.4, 6.6 Hz, 1H, $-C(H)=CH_2$), 5.3-5.2 (m, 2H, =C(H)H, Ph-C(H)O-), 5.2 (ddd, J=10.4, 1.5, 1.0 Hz, 1H, =C(H)H), 4.5 (ddd, J=8.6, 6.7, 0.9 Hz, 1H, $-OC(H)-C(H)=CH_2$), 3.2 (q, J=8.7 Hz, 1H, Ph-C(H)-), 2.6 (ddd, J=12.6, 8.7, 8.3 Hz, 1H, -C(H)H-), 2.4 (ddd, J=12.7, 8.7, 5.5 Hz, 1H, -C(H)H-); MS m/z (relative intensity) 250 (0.4%, M^+); HRMS. Calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1336.

(±)-(2S,4S*,5R*)-Tetrahydro-2,4-diphenyl-5-vinylfuran (10g).* ^1H NMR (300 MHz, $CDCl_3$) δ 7.5-7.2 (m, 10H, Ar-H), 5.5 (ddd, J=17.1, 10.3, 6.6 Hz, 1H, $-C(H)=CH_2$), 5.3 (dt, J=17.1, 1.5 Hz, 1H, =C(H)H), 5.1 (dd, J=10.3, 5.7 Hz, 1H, Ph-C(H)O-), 5.0 (dt, J=10.3, 1.5 Hz, 1H, =C(H)H), 4.8 (dd, J=8.0, 6.8 Hz, 1H, $-OC(H)-C(H)=CH_2$), 3.8 (dt, J=10.3, 7.7 Hz, 1H, $=C(H)-C(H)=CH_2$), 2.7 (ddd, J=12.5, 7.2, 5.8 Hz, 1H, -C(H)H-), 2.2 (dt, J=12.4, 10.3 Hz, 1H, -C(H)H-); MS m/z (relative intensity) 194 (100%, $M^+-CH_2=C(H)-C(H)O$); HRMS. Calcd for $C_{18}H_{18}O$: 250.1358. Found: 250.1358.

(±)-(2S,3R*,4R*,5R*)-Tetrahydro-4-carbomethoxy-3-methyl-2-phenyl-5-vinylfuran (9h).* ^1H NMR (360 MHz, $CDCl_3$) δ 7.4-7.2 (m, 5H, Ar-H), 6.1 (ddd, J=17.2, 10.4, 6.5 Hz, 1H, $-C(H)=CH_2$), 5.4 (dt, J=17.1, 1.1 Hz, 1H, =C(H)H), 5.3 (dt, J=10.4, 1.0 Hz, 1H, =C(H)H), 5.2 (d, J=7.5 Hz, 1H, Ph-C(H)O-), 4.6 (td, J=7.4, 1.0 Hz, $-OC(H)-C(H)=CH_2$), 3.7 (s, 3H, $-OCH_3$), 2.9 (m, 1H, $-C(H)-CH_3$), 2.6 (dd, J=8.3, 7.5 Hz, 1H, $-C(H)-CO_2Me$), 0.6 (d, J=7.1 Hz, 3H, $-CH_3$); IR (CCl_4) 1739 cm^{-1} (C=O); MS m/z (relative intensity) 246 (3%, M^+); HRMS. Calcd for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1258.

(±)-(2S,3S*,4S*,5R*)-Tetrahydro-4-carbomethoxy-3-methyl-2-phenyl-5-vinylfuran (10h).* ^1H NMR (360 MHz, $CDCl_3$) δ 7.5-7.2 (m, 5H, Ar-H), 5.9 (ddd, J=17.1, 10.2, 7.4 Hz, 1H, $-C(H)=CH_2$), 5.4 (dt, J=17.1, 1.1 Hz, 1H, =C(H)H), 5.2 (dt, J=11.1, 1.1 Hz, 1H, =C(H)H), 4.7 (t, J=8 Hz, 1H, $-OC(H)-C(H)=CH_2$), 4.4 (d, J=9.7 Hz, 1H, Ph-C(H)O-), 3.7 (s, 3H, $-OCH_3$), 3.1 (t, J=9.6 Hz, 1H, $-C(H)-CO_2Me$), 2.5 (m, 1H, $-C(H)-CH_3$), 1.0 (d, J=6.7 Hz, 3H, $-CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ

171.7, 139.7, 135.4, 128.4, 128.1, 126.8, 118.0, 88.1, 80.0, 56.7, 51.8, 44.5, 14.6; IR (CCl_4) 1744 cm^{-1} (C=O); MS m/z (relative intensity) 246 (5%, M^+); HRMS. Calcd for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1250.

(±)-(2S,3S*,4R*,5R*)-Tetrahydro-4-carbomethoxy-3-methyl-2-phenyl-5-vinylfuran (11h).* ^1H NMR (200 MHz, $CDCl_3$) δ 7.4-7.2 (m, 5H, Ar-H), 6.0 (ddd, J=17.1, 10.4, 6.4 Hz, 1H, $-C(H)=CH_2$), 5.4 (dt, J=17.1, 1.4 Hz, 1H, $=C(H)H$), 5.2 (dt, J=10.4, 1.3 Hz, 1H, $=C(H)H$), 4.8 (tt, J=6.5, 1.1 Hz, 1H, $-OC(H)-C(H)=CH_2$), 4.6 (d, J=8.3 Hz, 1H, $Ph-C(H)O-$), 3.7 (s, 3H, $-OCH_3$), 3.0 (dd, J=9.5, 6.5 Hz, 1H, $-C(H)-CO_2Me$), 2.4 (ddd, J=9.5, 8.3, 7.1 Hz, 1H, $-C(H)-CH_3$), 1.0 (d, J=7.0 Hz, $-CH_3$); IR (CCl_4) 1750 cm^{-1} (C=O); MS m/z (relative intensity) 246 (4%, M^+); HRMS. Calcd for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1258.

(±)-(2S,4R*,5R*)-Tetrahydro-4-carbomethoxy-4-methyl-2-phenyl-5-vinylfuran (9i).* ^1H NMR (360 MHz, $CDCl_3$) δ 7.4-7.3 (m, 5H, Ar-H), 5.9 (ddd, J=17.2, 10.5, 6.3 Hz, 1H, $-C(H)=CH_2$), 5.4 (dt, J=17.2, 1.4 Hz, 1H, $=C(H)H$), 5.3 (dt, J=10.4, 1.2 Hz, 1H, $=C(H)H$), 5.0 (t, J=8.2 Hz, 1H, $Ph-C(H)O-$), 4.7 (d, J=6.2 Hz, 1H, $-C(H)-C(H)=CH_2$), 3.8 (s, 3H, $-OCH_3$), 3.0 (dd, J=12.8, 7.4 Hz, 1H, $-C(H)H-$), 1.8 (dd, J=12.8, 8.7 Hz, 1H, $-C(H)H-$), 1.2 (s, 3H, $-CH_3$); IR (CCl_4) 1748 cm^{-1} (C=O); MS m/z (relative intensity) 246 (8%, M^+); HRMS. Calcd for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1258.

(±)-(2S,4S*,5R*)-Tetrahydro-4-carbomethoxy-4-methyl-2-phenyl-5-vinylfuran (10i).* ^1H NMR (360 MHz, $CDCl_3$) δ 7.5-7.3 (m, 5H, Ar-H), 5.8 (ddd, J=17.1, 10.4, 7.0 Hz, 1H, $-C(H)=CH_2$), 5.4 (dd, J=17.1, 1.2 Hz, 1H, $=C(H)H$), 5.2 (dd, J=10.4, 1.4 Hz, 1H, $=C(H)H$), 5.0 (dd, J=10.0, 6.5 Hz, 1H, $Ph-C(H)O-$), 4.2 (d, J=7.3 Hz, 1H, $-C(H)-C(H)=CH_2$), 3.7 (s, 3H, $-OCH_3$), 2.6 (dd, J=12.8, 10.0 Hz, 1H, $-C(H)H-$), 2.2 (dd, J=12.8, 6.5 Hz, 1H, $-C(H)H-$), 1.5 (s, 3H, $-CH_3$); IR (CCl_4) 1753 cm^{-1} (C=O); MS m/z (relative intensity) 246 (11%, M^+); HRMS. Calcd for $C_{15}H_{18}O_3$: 246.1256. Found: 246.1239.

Phenyl disulfide addition to oxirane 7a. A deoxygenated solution of AIBN in benzene (24 mM) was added dropwise (0.3 mL/h) to a deoxygenated, refluxing solution of 103 mg (0.71 mmol) 2-phenyl-3-vinyl oxirane (**7a**) and 164 mg (0.75 mmol) phenyl disulfide in 5 mL benzene under nitrogen, with concommitant sunlamp irradiation. After 8h, GLC indicated that all of the oxirane was consumed. Concentration of the reaction solution by rotary evaporation and purification of the resulting oil by flash chromatography with 2% ether/hexane, and then 25% benzene/hexane as eluent, led to recovery of 88 mg of ether **17** as a pale yellow viscous oil (34%, 1.6:1 Z/E by ^1H NMR) and 32 mg of the homoallylic radical dimerization product **18** as a viscous oil (18%). **17Z.** ^1H NMR (360 MHz, $CDCl_3$) δ 7.4-7.1 (m, 15H, Ar-H), 6.3 (dt, J=6.1, 1.2 Hz, 1H, $-OC(H)=$), 6.0 (s, 1H, $-C(H)(Ph)(SPh)$), 4.7 (td, J=7.7, 6.2 Hz, 1H, $-OC(H)=C(H)-$), 3.7 (m, 2H, $=C(H)-CH_2-SPh$); MS m/z (relative intensity) 364 (0.05%, M^+), 256 (4%, MH^+-SPh); HRMS. Calcd for $C_{22}H_{20}OS_2$: 364.0956. Found: 364.0956.
17E. ^1H NMR (360 MHz, $CDCl_3$) δ 7.3-7.0 (m, 15H, Ar-H), 6.2 (d, J=12.5 Hz, 1H, $-OC(H)=$), 5.9 (s, 1H, $-C(H)(Ph)(SPh)$), 5.0 (dt, J=12.3, 7.7 Hz, 1H, $-OC(H)=C(H)-$), 3.3 (dd, J=7.9, 0.9 Hz, 2H, $=C(H)-CH_2-SPh$); MS m/z (relative intensity) 364 (0.19%, M^+), 199 (100%, $M^+-PhSCH_2-C(H)=C(H)O-$); HRMS. Calcd for $C_{22}H_{20}OS_2$: 364.0956. Found: 364.0955.
18. ^1H NMR (360 MHz, $CDCl_3$) δ 7.5-6.8 (m, 20H, Ar-H), 6.1-5.7 (m, 2H, $-OC(H)=$), 5.0, 4.6-4.4 (m, 2H, $-OC(H)=C(H)-$), 4.9-4.6 (m, 2H, $-OC(H)(Ph)-$), 3.8-3.0 (m, 4H, $PhS-CH_2-$); MS m/z (relative intensity) 401 (3%, M^+-PhS), 345 (43%, $M^+-PhSCH_2C(H)=C(H)OC(H)(Ph)-C(H)(Ph)-$); HRMS. Calcd for $C_{32}H_{30}O_2S_2$: 510.1687. Found: 510.1709.

Thiophenol mediated methyl acrylate addition to oxirane 7a. A deoxygenated solution of AIBN in benzene (26 mM) was added dropwise (0.5 mL/h) to a deoxygenated, refluxing solution of 96 mg (0.66 mmol) 2-phenyl-3-vinyl oxirane (**7a**), 851 mg methyl acrylate (9.9 mmol), and 79 mg thiophenol (0.72 mmol) in 5 mL benzene under nitrogen, with concomitant sunlamp irradiation. After 3.5 h, TLC indicated that all of the oxirane was consumed. Concentration of the reaction solution by rotary evaporation and purification of the resulting oil by flash chromatography with 6% ether/hexane as eluent furnished 59 mg of tetrahydrofurans **9a** and **10a** (39%) and 65 mg of the ether **16** as an oil (38%, 1.1:1 Z/E by ^1H NMR). **16.** ^1H NMR (300 MHz, $CDCl_3$) δ 7.4-7.0 (m, 10H, Ar-H), 6.3-6.1 (m, 1H, $-OC(H)=$), 4.9 & 4.5 (m, 1H, $-OC(H)=C(H)-$), 4.7 & 4.6 (s, 2H, $-OCH_2Ph$), 3.6-3.4 (m, 2H, $PhS-CH_2'$); MS m/z (relative intensity) 256 (2%, M^+), 147 (17%, M^+-PhS); HRMS. Calcd for $C_{15}H_{16}OS$: 256.0922. Found: 256.0918.

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