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Exclusively *endo*-Selective Lewis Acid-Catalyzed Hetero Diels-Alder Reactions of (*E*)-1-Phenylsulfonyl-3-alken-2-ones with Vinyl Ethers

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Abstract: (*E*)-1-Phenylsulfonyl-3-alken-2-ones as new hetero 1,3-dienes undergo smooth hetero Diels-Alder reactions with vinyl ethers in the presence of a catalytic amount of Lewis acid such as ZnI_2, $Eu(fod)_3$, and $TiCl_2(i\text{-}PrO)_2$. The reactions are absolutely *endo*-selective producing 2,4-*cis*-3,4-dihydro-2*H*-pyrans in excellent yields, the configuration at 3-position depending upon the stereochemistry of the starting vinyl ethers. Reductive ring opening reactions of the 3,4-dihydro-2*H*-pyran cycloadducts with $Et_3SiH/TiCl_4$ lead to 6-alkoxy-1-phenylsulfonyl-2-hexanones, and the sulfonyl-stabilized carbanions derived from the 3,4-dihydro-2*H*-pyran cycloadducts are alkylated followed by reductive desulfonylation to give 2,4,6-trisubstituted 3,4-dihydro-2*H*-pyran derivatives.

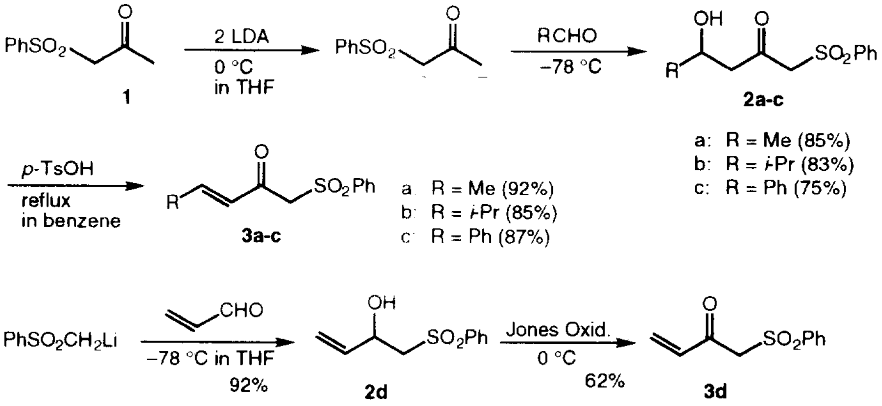
We have recently reported that 2-oxo-3-alkenylphosphonates, phosphoryl-substituted α,β-unsaturated ketones, serve as useful hetero 1,3-dienes in the Lewis acid-catalyzed hetero Diels-Alder reactions using vinyl ether dienophiles.[1a] They can be activated so effectively by chelate formation with a Lewis acid such as $ZnCl_2$ or $ZnBr_2$ that 2-alkoxy-3,4-dihydro-2*H*-pyrans are produced stereoselectively without serious polymerization of vinyl ethers. The resulting heterocycles are useful synthetic equivalents of 5-oxoalkanals through a simple hydrolytic procedure.[2] Such Lewis acid catalysis must be especially noteworthy since the undesired polymerization of vinyl ethers has been a serious problem in the Lewis acid-catalyzed hetero Diels-Alder reactions of simple α,β-unsaturated aldehydes and ketones.[3] Uncatalyzed reactions often require higher reaction temperatures, e.g. above 100 °C in a sealed tube, leading to poor stereoselectivity.[4]

A stoichiometric amount of Lewis acid was needed in the above catalyzed reactions, indicating a lack of efficiency of the catalytic cycle. If effective catalytic efficiency is established, a new entry to catalyzed asymmetric hetero Diels-Alder reaction methodology leading to enantiomers of 2-alkoxy-3,4-dihydro-2*H*-pyran derivatives would be open.[5] For this purpose, it has been strongly desired to develop new α,β-unsaturated carbonyl compounds which can be highly activated by chelate formation with a Lewis acid and then release the catalyst after the completion of the cycloaddition.[6]

In the present paper, we report the synthesis of (*E*)-1-phenylsulfonyl-3-alken-2-ones as new effective hetero 1,3-dienes and their use in Lewis acid-catalyzed hetero Diels-Alder reactions with vinyl ethers.[6] The sulfonyl group accelerates the reactions in the presence of a Lewis acid catalyst, the reactions are exclusively *endo*-selective, and the sulfonyl group can be finally utilized for the further transformation via carbon-carbon bond formation.

Results and Discussion

Synthesis of (E)-1-Phenylsulfonyl-3-alken-2-ones. (*E*)-1-Phenylsulfonyl-3-alken-2-ones **3a-c**, as hetero 1,3-dienes employed in the present work, could be easily prepared by the application of our synthetic method of 2-oxo-3-alkenylphosphonates via dianion intermediates.[1b] According to the Belletire's method, 1-phenylsulfonylpropanone (**1**) was treated with two equimolar amounts of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at 0 °C for 4 h to give a solution of the dianion.[7] This solution was allowed to react with aldehydes such as acetaldehyde, 2-methylpropionaldehyde, and benzaldehyde at –78 °C to give the corresponding aldol adducts **2a-c** in satisfactory yields based on the starting ketone **1**. They were then subjected to dehydration by treatment with a catalytic amount of *p*-toluenesulfonic acid under reflux in benzene to produce the desired (*E*)-1-phenylsulfonyl-3-alken-2-ones **3a-c** in excellent yields. Since the stereoselectivities at the dehydration steps were almost exclusive in all cases, single purification procedure through a silica gel column chromatography afforded the pure samples of *E*-isomers of **3a-c**.



Scheme 1.

On the other hand, 1-phenylsulfonyl-3-buten-2-one (**3d**) as β-unsubstituted enone was prepared through two steps starting from propenal. The 1,2-addition of phenylsulfoylmethyllithium, which was generated from methyl phenyl sulfone and *n*-BuLi in THF at –78 °C, to propenal gave 1-phenylsulfonyl-3-buten-2-ol (**2d**) in 92% yield. Subsequent Jones oxidation of the resulting alcohol **2d** at 0 °C produced **3d** in 62% yield.

Hetero Diels-Alder Reactions of (E)-1-Phenylsulfonyl-3-alken-2-ones with Vinyl Ethers. In order to evaluate the reactivity of 1-sulfonyl-3-alken-2-ones **3a-d** and the stereoselectivity in their hetero Diels-Alder reactions, they were allowed to react with vinyl ethers **4a-e** in dichloromethane in the absence or presence of Lewis acid. Lewis acids such as ZnI_2, $Eu(fod)_3$, and $TiCl_2(i\text{-}PrO)_2$ were employed (Scheme 2 and Table 1), and stereoselectivity was determined in each case on the basis of ^1H and/or ^{13}C NMR spectra of the crude reaction mixtures.

The reaction of enone **3a** as a typical hetero 1,3-diene in the absence of Lewis acid required the use of a large excess of vinyl ether **4b** (20 equiv), and a high reaction temperature and some prolonged reaction time were needed for the completion of the reaction (48 h at 130-135 °C in a sealed tube). A 34:66 mixture of *cis*- and *trans*-isomers **6b, 5b** of the cycloadduct, which correspond to the *endo*- and *exo*-cycloadducts respectively, was produced in 85% of combined yield (entry 3). The low reactivity and poor selectivity observed resemble those of the related reactions of simple α,β-unsaturated aldehydes and ketones.[4]

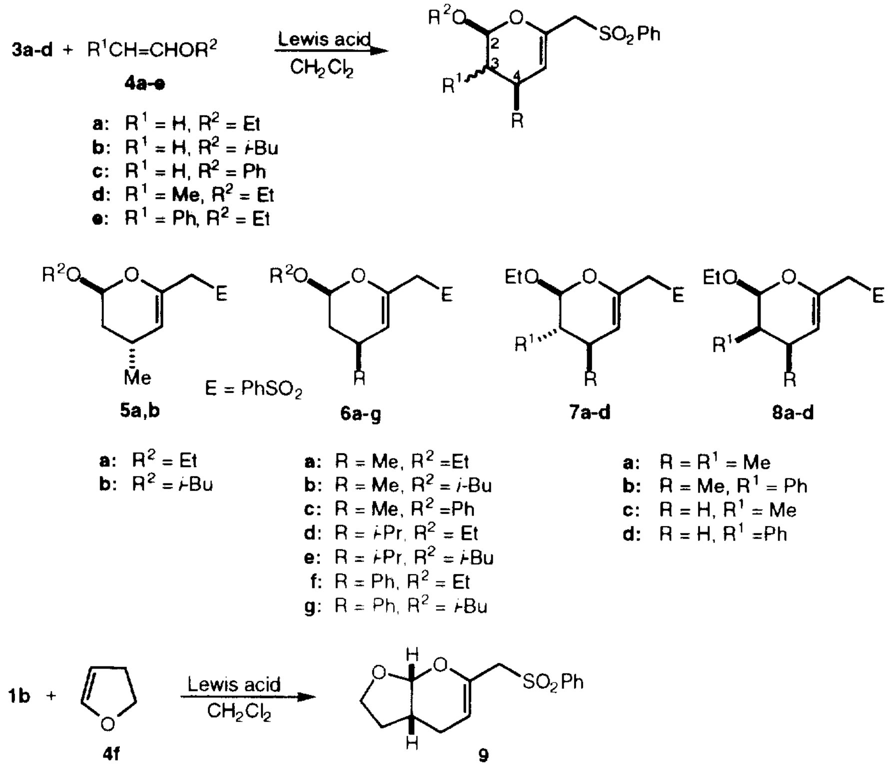
To our delight, however, the same reaction using vinyl ether **4b** (5 equiv) was highly accelerated (15 h at -30 °C) in the presence of a catalytic amount of $TiCl_2(i\text{-}PrO)_2$ (10 mol%) and became exclusively stereoselective to give the 2,4-*cis*-isomer of **6b** as a single isomer in 91% yield (entry 4).[8] No serious polymerization of vinyl ether **4b** was observed, indicating that the Lewis acid effectively accelerated the hetero Diels-Alder reaction rather than the polymerization. The reaction of enone **3a** with vinyl ether **4c** also proceeded stereoselectively in the presence of $TiCl_2(i\text{-}PrO)_2$ to give the *cis*-isomer **6c** as a single isomer in 97% yield (entry 5).

Table 1. Lewis Acid-Catalyzed Hetero Diels-Alder Reactions of Enones **3a-d** with Vinyl Ethers **4a-f**[a]

Entry	Enone	Vinyl ether (*E*/*Z*, equiv)	Lewis acid (mol%)	Reaction conditions Temp/°C	Time/h	Product (yield/%)[b]	Isomer ratio[c]
1	**3a**	**4a** (5)	ZnI_2 (3)	rt	86	**6a+5a** (92)	92/8
2	**3a**	**4a** (5)	$TiCl_2(i\text{-}PrO)_2$ (10)	-50	15	**6a+5a** (90)	98/2
3[d]	**3a**	**4b** (20)	-	130-135	48	**6b+5b** (85)	34/66
4	**3a**	**4b** (5)	$TiCl_2(i\text{-}PrO)_2$ (10)	-30	15	**6b** (91)	
5	**3a**	**4c** (5)	$TiCl_2(i\text{-}PrO)_2$ (10)	-50	90	**6c** (97)	
6	**3a**	**4a** (5)	$Eu(fod)_3$ (1)	-5	40	**6a** (95)	
7	**3a**	**4a** (5)	$Eu(fod)_3$ (0.5)	-10	72	**6a** (91)	
8	**3b**	**4a** (5)	$Eu(fod)_3$ (3)	rt	90	**6d** (80)	
9	**3b**	**4b** (5)	$Eu(fod)_3$ (3)	rt	99	**6e** (71)	
10	**3c**	**4a** (5)	$Eu(fod)_3$ (3)	rt	43	**6f** (85)	
11	**3c**	**4b** (5)	$Eu(fod)_3$ (3)	rt	92	**6g** (89)	
12	**3a**	**4d** (1/1, 5)	$Eu(fod)_3$ (1)	rt	80	**7a+8a** (65)	1/1
13	**3a**	**4d** (1/19, 5)	$Eu(fod)_3$ (5)	-5	96	**7a+8a** (95)	1/19
14	**3a**	*E*-**4e** (3)	$Eu(fod)_3$ (3)	rt	65	**7b** (53)	
15	**3a**	*E*-**4e** (3)	$Eu(fod)_3$ (3)	-10	240	**7b** (80)	
16	**3a**	*E*-**4e** (3)	$TiCl_2(i\text{-}PrO)_2$ (10)	-30	38	**7b** (97)	
17	**3a**	*Z*-**4e** (3)	$TiCl_2(i\text{-}PrO)_2$ (10)	-30	97	**8b** (97)	
18	**3d**	**4d** (1/1, 5)	$Eu(fod)_3$ (1)	-20	40	**7c+8c** (95)	1/1
19	**3d**	**4e** (5.5/1, 3)	$Eu(fod)_3$ (10)	rt	38	**7d+8d** (41)	9/1
20	**3d**	*Z*-**4e** (3)	$TiCl_2(i\text{-}PrO)_2$ (10)	-78	41	**7d+8d** (57)	4/96
21	**3d**	**4f** (5)	$Eu(fod)_3$ (1)	-10/rt	73/16	**9** (24)	
22	**3d**	**4f** (5)	ZnI_2 (3)	rt	25	**9** (90)	

[a] All reactions were carried out in CH_2Cl_2. [b] Yields of isolated cycloadducts. [c] Determined by ^1H NMR and/or ^{13}C NMR. [d] In a sealed tube in benzene.

Other Lewis acid catalysts such as ZnI_2 and $Eu(fod)_3$ can be effectively used in a catalytic amount (0.5-3 mol%). The titanium catalyst $TiCl_2(i\text{-}PrO)_2$ was a little better than the zinc catalyst ZnI_2 in selectivity (entry 1 *vs* entry 2). The europium catalyst $Eu(fod)_3$ showed effective catalysis as a catalytic amount exclusively produced *cis*-isomers of the dihydropyran derivatives **6a,d-g** in excellent yields for all combinations of enones **3a-c** and vinyl ethers **4a,b** (entries 6-11). This high efficiency of catalytic cycle makes a striking contrast with the reactions of 2-oxo-3-alkenylphosphonates.[1a] Although we employed excess (5 equiv) of vinyl ethers **4a-c** in fear of their partial loss by a possible Lewis acid-catalyzed polymerization, less amounts are probably enough, especially in the reactions performed at low temperatures (entries 2 and 4-7).

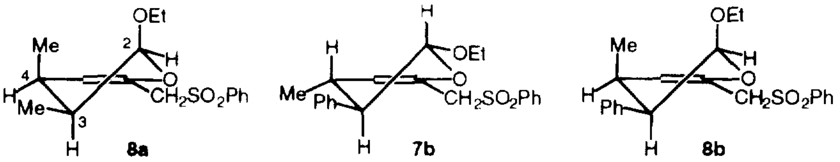


Scheme 2.

Such remarkable rate acceleration, high stereoselectivity, and high catalytic efficiency, all observed in the Lewis acid-catalyzed hetero Diels-Alder reactions of 2-oxo-1-sulfonyl-3-alkenes **3a-c**, are no doubt based on their capability of effective chelate formation with a Lewis acid by the aid of the sulfonyl moiety. The coordination makes **3a-c** themselves activated as hetero 1,3-dienes. We further investigated the stereospecificity of the Lewis acid-catalyzed hetero Diels-Alder reactions by using β-substituted vinyl ethers **4d,e**.

The reaction using vinyl ether **4d** (*E/Z*-mixture, 5 equiv) was activated in the presence of a catalytic amount (1 mol%) of Eu(fod)$_3$ at or below room temperature in dichloromethane. A 1:1 stereoisomeric mixture of *r*-2-ethoxy-*t*-3,*c*-4-dimethyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2*H*-pyran (**7a**) and *r*-2-ethoxy-*c*-3,*c*-4-dimethyl-6-(phenylsulfonymethyl)-3,4-dihydro-2*H*-pyran (**8a**) was produced from the reaction using a 1:1 mixture of *E/Z* stereoisomers of vinyl ether **4d** (65%, entry 12), and a 1:19 mixture of **7a and 8a** from a 1:19 mixture of *E/Z* stereoisomers (95%, entry 13). These results indicate that (1) the reactions are exclusively 2,4-*cis*-selective or *endo*-selective, (2) the Eu(fod)$_3$-catalyzed hetero Diels-Alder reactions of **3a** with **4d** are exclusively stereospecific, and (3) the *E*- and *Z*-isomers of vinyl ether **4d** have comparable reactivities toward enone **3a**.

(*E*)-1-Ethoxy-2-phenylethene (*E*-**4e**) showed comparable reactivity toward enone **3a** in the reactions catalyzed by Eu(fod)$_3$ to give the *endo*-cycloadduct, *r*-2-ethoxy-*c*-4-methyl-*t*-3-phenyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2*H*-pyran (**7b**), as a single stereoisomer (entries 14, 15). Use of TiCl$_2$(*i*-PrO)$_2$ was even more effective and satisfactory rate enhancement was observed. For example, the reaction of **3a** with *E*-**4e** was completed at –30 °C to produce **7b** in the presence of 10 molar percent of TiCl$_2$(*i*-PrO)$_2$ without polymerization of vinyl ether **4e** (entry 16). On the other hand, the reaction with (*Z*)-1-ethoxy-2-phenylethene (*Z*-**4e**) provided also the *endo*-cycloadduct, *r*-2-ethoxy-*c*-4-methyl-*c*-3-phenyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2*H*-pyran (**8b**), as single stereoisomer (entry 17). The β-unsubstituted enone **3d** showed the same reactivity to vinyl ethers **4d,e** as that of **3a**, while stereospecificity was a little lower than **3a** (entries 18-20). With cyclic vinyl ether **4f**, the cycloadditions took place (entries 21, 22).



8a **7b** **8b**

NOE H-2 $\rightleftarrows$ H-3
H-3 $\rightleftarrows$ H-4
$J_{2\text{-}3}$ = 1.8; $J_{3\text{-}4}$ =7.0 Hz

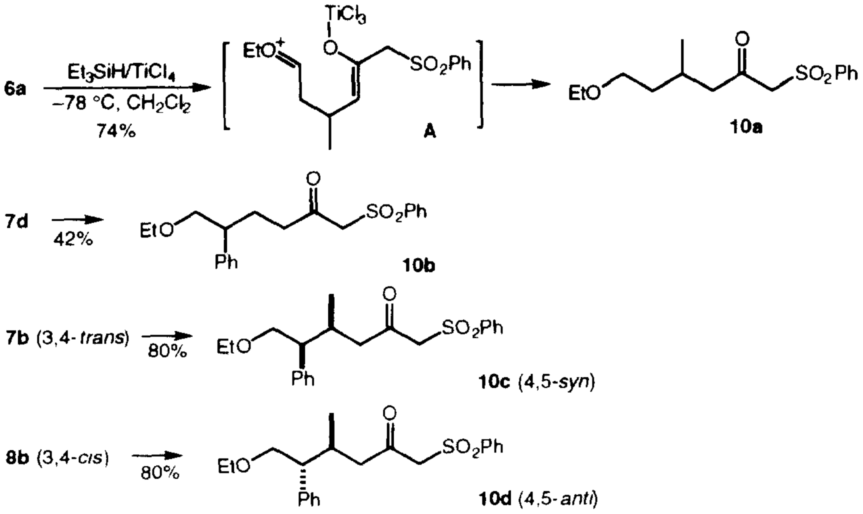
$J_{2\text{-}3}$=8.1, $J_{3\text{-}4}$=9.9 Hz

NOE H-2 $\rightleftarrows$ H-3
H-3 $\rightleftarrows$ H-4
$J_{2\text{-}3}$ = 2.2; $J_{3\text{-}4}$ =6.8 Hz

Figure 1. Stereochemical assignment of 2,3-*trans*-3,4-*trans*-cycloadduct **7b** and 2,3-*cis*-3,4-*cis*-cycloadducts **8a,b** on the basis of NOE spectra and coupling constants.

Stereochemistry of the above 3,4-dihydro-2*H*-pyran derivatives was determined on the basis of spectral data, especially ^{1}H NMR spectra, typical examples of which are shown in Figure 1. The *endo*-cycloadducts **8a** and **8b** from the *Z*-isomers of vinyl ether dienophiles **4d** and **4e** could be easily assigned by their NOE spectra. Notable signal enhancement was observed between H-2/H-3 and H-3/H-4, and the small coupling constant between H-2 and H-3 (**8a**: $J_{2\text{-}3}$ = 1.8 Hz, **8b**: $J_{2\text{-}3}$ = 2.2 Hz) showed the *cis*-relationship of these hydrogens. On the other hand, the *endo*-cycloadduct **7b** from the *E*-isomer of **4e** bears all the substituents at equatorial positions in its stable conformer. Thus, the relatively large diaxial coupling constants $J_{2\text{-}3}$ (8.1 Hz) and $J_{3\text{-}4}$ (9.9 Hz) observed between H-2/H-3 and H-3/H-4, respectively, are consistent with the proposed stereochemistry.

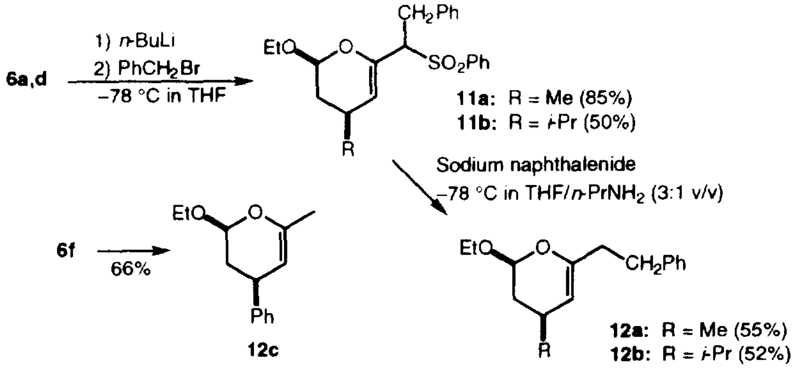
Transformation of 2-Alkoxy-3,4-dihydro-2H-dihydropyran Cycloadducts. The aforementioned stereospecific and *endo*-selective hetero Diels-Alder reactions of sulfonyl-substituted enones **3** with *E*- and *Z*-isomers of vinyl ethers **4d,e** offer a convenient route to sterically defined 2-alkoxy-3,4-dihydro-2*H*-pyrans. We already reported that hydrolytic cleavage of the acetal moiety led to 5-oxo-6-sulfonylalkanal intermediates which then underwent ready dehydrative cyclizations to give 2-cyclohexen-1-one derivatives.[6b] In the present work, we examined other transformations of the 2-alkoxy-3,4-dihydro-2*H*-pyran cycloadducts.



Scheme 3.

When dihydropyran **6a** was treated with triethylsilane and titanium tetrachloride in dichloromethane at -78 °C,[9] the reduction occurred at the acetal moiety to give 6-ethoxy-4-methyl-1-phenylsulfonyl-2-hexanone (**10a**). This indicates that the Lewis acid $TiCl_4$ coordinated at the ring oxygen atom, rather than the ethoxyl oxygen atom, to induce the formation of the ring-opened oxonium intermediate **A** (Scheme 3). Its reduction by the silane reagent led to the ether derivative **10a**. Similarly, dihydropyran **7d** was converted into **10b**.

This facile reductive ring opening reaction could be successfully applied to the 3,4-*trans*-isomer **7b** and the 3,4-*cis*-isomer **8b** which had been obtained in the stereospecific hetero Diels-Alder reactions of **3d** with *E*-**4e** and *Z*-**4e**, respectively. Thus, 4,5-*syn*-isomer **10c** and 4,5-*anti*-isomer **10d** were selectively prepared.



Scheme 4.

The sulfonyl moiety of cycloadducts **5-8** has a synthetic advantage since it should mediate the generation of an anionic center at the α-position which would be then utilized for the introduction of a substituent by alkylation. Thus, the sulfonyl-stabilized carbanion of dihydropyran **6a** was generated by treatment with butyllithium at –78 °C and allowed to react with benzyl bromide at the same temperature to provide benzylated product **11a** as a single isomer in 85% yield (Scheme 4). Similar benzylation of **6d** gave **11b** (90% de) in 50% yield. The phenylsulfonyl group in the alkylated **11a,b** and unalkylated **6f** were successfully removed by reduction. Treatment with sodium naphthalenide (4 equiv.), generated from naphthalene and metal sodium under ultrasonic conditions in THF,[10] at –78 °C in THF/*n*-$PrNH_2$ (3:1 v/v) gave the desulfonylated products **12a-c** in 55, 52, and 66% yields, respectively.

In conclusion, the exclusively stereoselective formation of 2,4-*cis*-3,4-dihydro-2*H*-pyrans **6-9** and **12** has been achieved by a sequence based on the hetero Diels-Alder reactions of 1-phenylsulfonyl-3-alken-2-ones **3** with vinyl ethers **4** in the presence of a catalytic amount of $Eu(fod)_3$ or $TiCl_2(i\text{-}PrO)_2$. The sulfonyl moiety of enones **3** is an excellent reactivity-enhancing auxiliary. A new method of stereocontrolled construction of acyclic framework has been also demonstrated by regiocontrolled reductive ring cleavage reaction of stereochemically defined dihydropyran cycloadducts **7b** and **8b**.

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Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO A-720 spectrometer. ^1H NMR spectra were recorded on a JEOL JNM-EX90 (90 MHz) or a JEOL GSX-270 instrument (270 MHz) and ^{13}C NMR spectra on a JEOL GSX-270 spectrometer (67.94 MHz). Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL-01SG-2 or a JEOL JMS-AM 20 spectrometer. Elemental analyses were performed on a Hitachi 026 CHN or a Yanaco CHN Corder MT-5 analyzer. For preparative column chromatography, silica gel 60 (Merk, size: 0.04–0.063 mm) was employed. Flash chromatography was carried out on a Yamazen YFLC 540 apparatus using a column (15 x 350 mm) or (20 x 350 mm) packed with silica gel 60 (Merk). Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at room temperature unless otherwise stated.

Materials. The following reagents were prepared by literature methods: methyl phenyl sulfone,[11] 1-phenylsulfonylpropanone (**1**),[12] dichlorodiisopropoxytitanium,[13] (*E*)-1-ethoxy-2-phenylethene (*E*-**4e**),[14] and (*Z*)-1-ethoxy-2-phenylethene (*Z*-**4e**).[15] Complete separation of the (*E*)- and (*Z*)-isomers **4e** was accomplished by flash chromatography (silica gel, hexane). Dichloromethane was purified by distillation on calcium hydride. THF was distilled on lithium aluminum hydride under nitrogen just before its use.

General Procedure for the Preparation of 4-Hydroxy-1-phenylsulfonyl-2-alkanones 2a-c. As a typical example the preparation of **2a** is described as follows: To a solution of LDA, prepared from diisopropylamine (3.36 g, 36 mmol) and butyllithium (in hexane, 23.2 ml, 36 mmol) at -78 °C in THF (20 ml), was added 1-phenylsulfonylpropanone (**1**) (2.97 g, 15 mmol) in THF (20 ml) under nitrogen. The reaction mixture was warmed to 0 °C and stirred for 4 h. To the resulting THF suspension of the dianion of **1** was added acetaldehyde (792 mg, 1.08 ml, 18 mmol) dropwise at 0 °C. After stirred at 0 °C for 1 h, the mixture was acidified with 1 mol/l hydrochloric acid. The THF was removed in vacuo and the aqueous residue was extracted with dichloromethane (40 ml x 3). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product (4 g) was chromatographed on silica gel with hexane–EtOAc (1:1 v/v) to give **2a** (3.06 g, 85%). Other β-keto alcohols **2b,c** were also prepared in 83 and 75 % yields, respectively, under similar reaction conditions.

4-Hydroxy-1-phenylsulfonyl-2-pentanone (2a): Colorless prisms (Et_2O-hexane); mp 75-77 °C; IR (KBr) 3520, 2950, 2900, 1710, 1450, 1390, 1360, 1305, 1280, 1200, 1150, 1050, 950, 860, 730, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.22 (3H, d, $J_{Me\text{-}4}$ = 6.2 Hz, Me), 2.51 (1H, br. s, OH), 2.80 (1H, dd, J_{gem} = 17.6 and $J_{3\text{-}4}$ = 7.7 Hz, one of H-3), 2.87 (1H, dd, J_{gem} = 17.6 and $J_{3\text{-}4}$ = 4.4 Hz, the other of H-3), 4.16-4.32 (1H, m, H-4), 4.24 (2H, s, H-1), 7.5-7.7 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 22.65 (C-5), 52.57 (C-3), 63.80 (C-4), 67.36 (C-1), 128.26, 129.43, 134.41, 138.71 (each Ph), and 198.70 (C=O); MS (20 eV, rel. intensity, %) *m/z* 227 (M^+-Me, 13), 224 (M^+-H_2O, 5), 199 (22), 198 (base peak), 156 (46), 141 (47), 134 (62), 126 (24), 125 (58), 101 (78), 77 (25), 69 (34), and 43 (63). Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82%. Found: C, 54.70; H, 5.99%.

4-Hydroxy-5-methyl-1-phenylsulfonyl-2-hexanone (2b): Separated and purified by silica gel column chromatography using hexane–EtOAc (1:1 v/v). Colorless viscous oil; IR (neat) 3500, 3050, 2970, 1710, 1580, 1445, 1375, 1310, 1240, 1150, 1075, 1040, 1000, 800, 730, and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.92, 0.93 (each 3H, each d, *J* = 6.9 Hz, Me), 1.69 (1H, oct, $J_{5\text{-}4}$ = $J_{5\text{-}Me2}$ = 6.9 Hz, H-5), 2.14 (1H, br. s, OH), 2.79 (1H, dd, J_{gem} = 17.2 and $J_{3\text{-}4}$ = 7.7 Hz, one of H-3), 2.86 (1H, dd, J_{gem} = 17.2 and $J_{3\text{-}4}$ = 4.8 Hz, the other of H-3), 3.83 (1H, ddd, $J_{4\text{-}3}$ = 7.7, 4.8, and $J_{4\text{-}5}$ = 6.9 Hz, H-4), 4.20, 4.26 (each 1H, each d, J_{gem} = 13.5 Hz, H-1), 7.5-7.7 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 17.55, 18.30 (each 5-Me or C-6), 33.26 (C-5), 48.28 (C-3), 67.40 (C-1), 72.24 (C-4), 128.28, 129.40, 134.48, 138.66 (each Ph), and 199.22 (C=O); MS (20 eV, rel. intensity, %) *m/z* 252 (M^+-H_2O, 3), 227 (base peak), 199 (31), and 111 (26). Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.76; H, 6.71%. Found: C, 58.08; H, 6.95%.

4-Hydroxy-4-phenyl-1-phenylsulfonyl-2-butanone (2c): Separated and purified by silica gel column chromatography using hexane–EtOAc (1:1 v/v). Colorless solids (Et_2O); mp 69-70 °C; IR (KBr) 3350, 3050, 2900, 1710, 1580, 1450, 1300, 1150, 1070, 1050, 900, 750, 730, 700 and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.23 (1H, br. s, OH), 3.06 (1H, dd, J_{gem} = 17.6 and $J_{3\text{-}4}$ = 3.7 Hz, one of H-3), 3.19 (1H, dd, J_{gem} = 17.6 and $J_{3\text{-}4}$ = 8.8 Hz, the other of H-3), 4.19, 4.23 (each 1H, each d, J_{gem} = 13.2 Hz, H-1), 5.15 (1H, dd, $J_{4\text{-}3}$ = 8.8 and 3.7 Hz, H-4), 7.2-7.4 (5H, m, Ph), 7.5-7.7 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 52.76 (C-3), 67.40 (C-1), 69.80 (C-3), 125.70, 127.97, 128.28, 128.65, 129.38, 134.38, 138.48, 142.28 (each Ph), and 197.40 (C=O); MS (70 eV, rel. intensity, %) *m/z* 288 (M^+-16, 14), 287 (26), 164 (21), 163 (76), 162 (24), 107 (52), 104 (62), 103 (33), 97 (22), 92 (29), 90 (24), 80 (25), 79 (34), 78 (46), 76 (96), 75 (26), 74 (24), 65 (50), 52 (32), and 50 (base peak). Anal. Calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30%. Found: C, 63.10; H, 5.38%.

Preparation of 1-Phenylsulfonyl-3-buten-2-ol (2d). To a solution of methyl phenyl sulfone (5 g, 32 mmol) in THF (100 ml) was added butyllithium (in hexane, 22.7 ml, 35.2 mmol) by the aid of a syringe at -78 °C under nitrogen. The mixture was stirred at -78 °C for 1 h and the addition of acrolein (1.96 g, 2.3 ml, 35 mmol) was followed. The reaction mixture was stirred at room temperature for 30 min, poured to saturated aqueous NH_4Cl. The THF was removed in vacuo and the aqueous residue was extracted with CH_2Cl_2 (50 ml x 3). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product (6.7 g) was chromatographed on silica gel with hexane-EtOAc (1:1 v/v) to give alcohol **2d** (6.22 g, 92%): Colorless oil; IR (neat) 3470, 3050, 2970, 2900, 1630, 1580, 1440, 1300, 1140, 1080, 990, 930, 840, 790, 750, and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 3.25 (1H, dd, J_{gem} = 14.3 and $J_{1\text{-}2}$ =3.3 Hz, one of H-1), 3.33 (1H, dd, J_{gem} = 14.3 and $J_{1\text{-}2}$ = 8.4 Hz, the other of H-1), 3.38 (1H, br. s, OH), 4.65-4.74 (1H, m, H-2), 5.18 (1H, ddd, $J_{4\text{-}3\,(cis)}$ = 10.6, J_{gem} = 1.5, and $J_{4\text{-}2}$ = 1.1 Hz, one of H-4), 5.34 (1H, ddd, $J_{4\text{-}3\,(trans)}$ = 17.6, J_{gem} = 1.5, and $J_{4\text{-}2}$ = 1.1 Hz, the other of H-4), 5.78 (1H, ddd, $J_{3\text{-}4\,(trans)}$ = 17.6, $J_{3\text{-}4\,(cis)}$ = 10.6, and $J_{3\text{-}2}$ = 5.5 Hz, H-3), 7.5-7.7 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 61.83 (C-1), 66.98 (C-2), 116.68 (C-4), 128.00, 129.46, 134.12 (each Ph), 136.78 (C-3), and 139.25 (Ph); MS (70 eV, rel intensity, %) *m/z* 212 (M^+, 20), 129 (33), 109 (base peak), 108 (80), 107 (35), 81 (29), 57 (33), and 55 (34). Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.59; H, 5.70%. Found: C, 56.37; H, 5.72%.

General Procedure for the Dehydration of 2a-c Leading to (E)-1-Phenylsulfonyl-3-alken-2-ones 3a-c. As a typical example the conversion of **2a** into **3a** is described as follows: To a solution of β-keto alcohol **2a** (1.69 g, 6.98 mmol) in dry benzene (60 ml) was added *p*-toluenesulfonic acid monohydrate (190 mg, 1 mmol). The reaction mixture was heated under reflux for 2 h with continual azeotropic removal of water by aid of a Dean-Stark trap. The mixture was evaporated in vacuo and the residue was chromatographed on silica gel with hexane–EtOAc (2:3 v/v) to give enone **3a** (1.43 g, 92%). Other enones **3b,c** were also prepared in 85 and 87 % yields, respectively, under similar reaction conditions.

(E)-1-Phenylsulfonyl-3-penten-2-one (3a). This compound was previously prepared[16] and full data are as follows. Colorless needles (Et_2O-hexane); mp 73-75 °C; IR (KBr) 3000, 2910, 1670, 1620, 1450, 1380, 1300, 1150, 1075, 975, 770, 710, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.96 (3H, dd, $J_{5\text{-}4}$ = 7.0 and $J_{5\text{-}3}$ = 1.5 Hz, Me), 4.28 (2H, s, H-1), 6.31 (1H, dq, $J_{3\text{-}4}$ = 15.8 and $J_{3\text{-}Me}$ = 1.5 Hz, H-3), 6.99 (1H, dq, $J_{4\text{-}3}$ = 15.8 and $J_{4\text{-}Me}$ = 7.0 Hz, H-4), 7.5-7.7 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 18.65 (C-5), 65.25 (C-1), 128.42, 129.27 (each Ph), 131.00 (C-3), 134.24, 138.69 (each Ph),

147.91 (C-4), and 186.86 (C=O); MS (75 eV, rel intensity, %) *m/z* 224 (M^+, 8), 160 (28), 77 (39), 69 (base peak), and 41 (21). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.91; H, 5.39%. Found: C, 59.27; H, 5.41%.

(E)-5-Methyl-1-phenylsulfonyl-3-hexen-2-one **(3b)**. Separated and purified by silica gel column chromatography using hexane–EtOAc (2:1 v/v). Colorless prisms (Et_2O-hexane); mp 30-31 °C, IR (neat) 3050, 2950, 1670, 1625, 1590, 1450, 1400, 1325, 1300, 1150, 1070, 980, 900, 755, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.07 (6H, d, $J_{Me\text{-}5}$ =7.0 Hz, 2xMe), 2.28 (1H, doct, $J_{5\text{-}4} = J_{5\text{-}Me2}$ = 7.0 and $J_{5\text{-}3}$ = 1.5 Hz, H-5), 4.31 (2H, s, H-1), 6.19 (1H, dd, $J_{3\text{-}4}$ = 15.8 and $J_{3\text{-}5}$ = 1.5 Hz, H-3), 6.91 (1H, dd, $J_{4\text{-}3}$ = 15.8 and $J_{4\text{-}5}$ = 7.0 Hz, H-4), 7.5-7.7 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 21.02 (2xMe), 31.43 (C-5), 65.27 (C-1), 126.69 (C-3), 128.45, 129.25, 134.41,138.86 (each of Ph), 158.41 (C-4), and 187.45 (C=O); MS (20 eV, rel. intensity, %) *m/z* 252 (M^+, 10), 188 (33), 111 (base peak), and 110 (21). Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39%. Found: C, 61.68; H, 6.35%.

(E)-4-Phenyl-1-phenylsulfonyl-3-buten-2-one (3c). Separated and purified by silica gel column chromatography using hexane–EtOAc (2:1 v/v). Colorless needles (Et_2O); mp 96-98 °C; IR (KBr) 2970, 2900, 1650, 1575, 1440, 1400, 1280, 1145, 1060, 980, 875, 790, 760, 710, and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 4.40 (2H, s, H-1), 6.94 (1H, d, $J_{3\text{-}4}$ = 15.8 Hz, H-3), 7.4-7.7 (9H, m, H-4 and Ph), and 7.8- 7.9 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 66.22 (C-1), 124.64 (C-3), 128.39, 128.88, 129.04, 129.27, 131.43, 133.70, 134.26, 138.55 (each Ph), 146.46 (C-4), and 186.86 (C=O); MS (75 eV, rel. intensity, %) *m/z* 286 (M^+, 7), 145 (77), 144 (46), 131 (base peak), 103 (42), 77 (44), and 50 (20). Anal. Calcd for $C_{16}H_{14}O_3S$: C, 67.11; H, 4.93%. Found: C, 67.24; H, 4.91%.

Preparation of 1-Phenylsulfonyl-3-buten-2-one (3d) by Jones Oxidation of Alcohol 2d. The chromic acid oxidizing reagent is prepared by dissolving chromium trioxide (1.5 g, 15 mmol) in water (3 ml) and adding concentrated sulfuric acid (1.3 ml). To a solution of alcohol **2** (2.12 g, 10 mmol) in acetone (35 ml) was added dropwise the chromic acid reagent at -10-0 °C. The resulting mixture was stirred at 0 °C for 30 min and the remaining oxidizing agent was consumed by addition of isopropyl alcohol (2 ml). The resulting green precipitates were filtered off through Celite 545, the filtrate was concentrated, and extracted with CH_2Cl_2 (50 ml x 3). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product was chromatographed on silica gel with CH_2Cl_2-Et_2O (50:1 v/v) to give enone **3d** (1.3 g, 62%). Colorless needles (Et_2O-hexane); mp 36-37 °C; IR (KBr) 3070, 2970, 2920, 1675, 1610, 1450, 1400, 1310, 1150, 1090, 1060, 980, 900, 785, 755, 725, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 4.35 (2H, s, H-1), 6.01 (1H, dd, $J_{4\text{-}3\,(cis)}$ = 10.3 and J_{gem} = 0.7 Hz, one of H-4), 6.33 (1H, dd, $J_{4\text{-}3\,(trans)}$ = 17.6 and J_{gem} = 0.7 Hz, the other of H-4), 6.52 (1H, dd, $J_{3\text{-}4\,(trans)}$ = 17.6 and $J_{3\text{-}4\,(cis)}$ = 10.3 Hz, H-3), 7.5-7.7 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 64.75 (C-1), 128.38, 129.33 (each Ph), 132.32 (C-3), 134.35 (Ph), 135.33 (C-4), 138.61 (Ph), and 187.74 (C=O); MS (20 eV, rel intensity, %) *m/z* 210 (M^+, 4), 146 (base peak), and 55 (47). Anal. Calcd for $C_{10}H_{10}O_3S$: C, 57.13; H, 4.79%. Found: C, 56.98; H, 4.89%.

Thermal Hetero Diels-Alder Reaction of Enone 3a with Vinyl Ether 4b Leading to 2-Isobutoxy-4-methyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (6b+5b). A mixture of **3a** (89 mg, 0.4 mmol) and isobutyl vinyl ether **4b** (800 mg, 8 mmol) in benzene (1 ml) was heated in a sealed tube at 130-135 °C for 48 h. The mixture was condensed in a vacuo and the residue was chromatographed on silica gel with hexane-EtOAc (6:1 v/v) to give **6b, 5b** (110 mg, 85%) as inseparable mixture of *cis*- and *trans*-isomers. According to the ^1H NMR analysis of crude reaction mixture, the ratio of **6b** and **5b** was 1:2; *trans*-isomer **5b**: ^1H NMR (C_6D_6) δ = 0.69 (3H, d, $J_{Me\text{-}4}$ = 7.3 Hz, 4-Me), 0.87, 0.89 (each 3H, each d, J = 6.6 Hz, Me of 2-*i*-BuO), 1.08 (1H, ddd, J_{gem} = 12.8, $J_{3\text{-}4}$ = 10.3, and $J_{3\text{-}2}$ = 2.9 Hz, one of H-3), 1.5-1.9 (2H, m, CH of 2-*i*-BuO and the other of H-3), 2.2-2.4 (1H, m, H-4), 3.04 (1H, dd, J_{gem} = 9.2 and J = 6.6 Hz, one of CH_2 of 2-*i*-BuO), 3.55, 3.61 (each 1H, each d, J_{gem} = 12.6 Hz, 6-CH_2SO_2Ph), 3.64 (1H, dd, J_{gem} = 9.2 and J = 6.6 Hz, the other of CH_2 of 2-*i*-BuO), 4.73 (1H, t, $J_{2\text{-}3}$ = 2.9 Hz, H-2), 6.9-7.0 (3H, m, Ph), 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 19.44 (Me of 2-*i*-BuO), 20.85 (4-Me), 22.74 (C-3), 28.80 (CH of 2-*i*-BuO), 34.56 (C-4), 61.55 (6-CH_2SO_2Ph), 75.17 (CH_2 of 2-*i*-BuO), 97.64 (C-2), 111.52 (C-5), 128.71, 128.98, 133.14 (each Ph), 139.88, and 140.00 (Ph and C-6). The data of *cis*-isomer **6b** are presented below.

General Procedure for the Lewis Acid-Catalyzed Hetero Diels-Alder Reactions of Enones 3a-c with Vinyl Ethers 4 Leading to Dihydropyran Cycloadducts 5-9. As a typical example the reaction of **3a** with ethyl vinyl ether **4a** in the presence of $Eu(fod)_3$ is described as follows: To a solution of enone **3a** (224 mg, 1 mmol) and $Eu(fod)_3$ (31 mg, 0.03 mmol) in CH_2Cl_2 (3 ml) was added ethyl vinyl ether **4a** (360 mg, 5 mmol) at -78 °C under argon. The mixture was warmed to -5 °C and allowed to stand for 40 h. The resulting mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (30 ml x 3). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product (350 mg) was chromatographed on silica gel with hexane–EtOAc (7:1 v/v) to give **6a** (276 mg, 95%) as a single isomer. Other hetero Diels-Alder reactions were performed under the reaction conditions shown in Table 1. The yields as well as the diastereoselectivities are also summarized in Table 1. *trans*-Isomer **5a** (entries 1 and 2 in Table 1) was characterized on the basis of ^1H and ^{13}C NMR spectra data as a mixture with *cis*-isomer **6a**.

cis-2-Ethoxy-4-methyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**6a**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless prisms (cyclohexane); mp 88-89 °C; IR (KBr) 2950, 1665, 1580, 1450, 1375, 1290, 1255, 1180, 1155, 1125, 1050, 1025, 980, 900, 855, 810, 750, and 690 cm^{-1}; ^1H NMR (C_6D_6) δ = 0.73 (3H, d, J_{Me-4} = 7.3 Hz, 4-Me), 1.03 (3H, t, J = 7.0 Hz, 2-EtO), 1.29 (1H, ddd, J_{gem} = 13.2, J_{3-4} = 9.5, and J_{3-2} = 8.1 Hz, one of H-3), 1.64 (1H, dddd, J_{gem} = 13.2, J_{3-4} = 6.0, J_{3-2} = 2.2, and J_{3-5} = 1.1 Hz, the other of H-3), 1.92-2.18 (1H, m, H-4), 3.12 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 3.48 (1H, dd, J_{gem} = 13.2 and J_{CH2-5} = 1.1 Hz, one of 6-CH_2SO_2Ph), 3.55 (1H, dd, J_{gem} = 13.2 and J_{CH2-5} = 0.7 Hz, the other of 6-CH_2SO_2Ph), 3.60 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, the other of 2-EtO), 4.35 (1H, br. d, J_{5-4} = 2.6 Hz, H-5), 4.49 (1H, dd, J_{2-3} = 8.1 and 2.2 Hz, H-2), 6.9-7.0 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.29 (2-EtO), 20.88 (4-Me), 26.62 (C-4), 35.85 (C-3), 61.40 (6-CH_2SO_2Ph), 64.26 (2-EtO), 100.15 (C-2), 110.65 (C-5), 128,74, 128.95, 133.01 (each Ph), 140.15, and 140.96 (Ph and C-6); MS (70 eV, rel intensity, %) *m/z* 296 (M^+, 25), 155 (40), 111 (23), 109 (59), 85 (24), 81 (48), 77 (90), 72 (100), 69 (31), 57 (27), 55 (27), 51 (29), 45 (64), 44 (84), and 40 (30). Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80%. Found: C, 60.72; H, 6.97%.

trans-2-Ethoxy-4-methyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**5a**). ^1H NMR (C_6D_6) δ = 0.66 (3H, d, J_{Me-4} = 7.3 Hz, 4-Me), 1.09 (3H, t, J = 7.3 Hz, EtO), 2.20-2.40 (1H, m, H-4), 3.28, 3.89 (each 1H, dq, J_{gem} = 9.5 and J = 7.3 Hz, one of 2-EtO), 4.25-4.28 (1H, m, H-5), and 4.73 (1H, t, J_{2-3} = 2.8 Hz, H-2); ^{13}C NMR (C_6D_6) δ = 20.83 (4-Me), 22.71 (C-4), 34.61 (C-3), 61.55 (6-CH_2SO_2Ph), 64.00 (2-EtO), 97.32 (C-2), 111.53 (C-5), 128.68 (Ph), and 140.18 (Ph and C-6). Other signals are overlapped with those of the *cis*-isomer **6a**.

cis-2-Isobutoxy-4-methyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**6b**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless needles (Et_2O-hexane); mp 57-58 °C; IR (KBr) 2900, 1660, 1445, 1360, 1300, 1260, 1130, 1125, 1060, 975, 825, 745, and 690 cm^{-1}; ^1H NMR (C_6D_6) δ = 0.75 (3H, d, J_{Me-4} = 7.0 Hz, 4-Me), 0.84, 0.85 (each 3H, each d, J_{Me-CH} = 6.6 Hz, Me of 2-*i*-BuO), 1.28 (1H, ddd, J_{gem} = 13.2 , J_{3-2} = 8.1, and J_{3-4} = 9.2 Hz, one of H-3), 1.64 (1H, dddd, J_{gem} = 13.2, J_{3-2} = 2.2, J_{3-4} = 6.6, and J_{3-5} = 1.1 Hz, the other of H-3), 1.75 (1H, ninefold, J = 6.6 Hz, CH of 2-*i*-BuO), 1.92-2.18 (1H, m, H-4), 2.82, 3.35 (each 1H, each dd, J_{gem} = 9.3 and J_{CH2-CH} = 6.6 Hz, CH_2 of 2-*i*-BuO), 3.49, 3.56 (each 1H, each br. d, J_{gem} = 14.3 Hz, 6-CH_2SO_2Ph), 4.35 (1H, br. d, J_{5-4} = 2.6 Hz, H-5), 4.47 (1H, dd, J_{2-3} = 8.1 and 2.2 Hz, H-2), 6.9-7.0 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 19.40, 19.44 (each Me of 2-*i*-BuO), 20.89 (4-Me), 26.58 (C-4), 28.74 (CH of 2-*i*-BuO), 35.71 (C-3), 61.40 (6-CH_2SO_2Ph), 75.56 (CH_2 of 2-*i*-BuO), 100.50 (C-2), 110.65 (C-5), 128.76, 128.95, 133.07 (each Ph), 140.25, and 140.93 (Ph and C-6); MS (70 eV, rel intensity, %) *m/z* 324 (M^+, 21), 235 (30), 226 (23), 225 (base peak), 184 (76), 182 (36), 140 (30), 128 (22), 126 (46), 112 (34), 108 (30), 101 (32), and 91 (23). Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.94; H, 7.46%. Found: C, 63.16; H, 7.43%.

cis-4-Methyl-2-phenoxy-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**6c**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless needles (Et_2O); mp 133-135 °C; IR (KBr) 3050, 2900, 1660, 1580, 1475, 1440, 1375, 1290, 1225, 1140, 1065, 980, 890, 805, 740, and 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.08 (3H, d, J_{Me-4} = 7.3 Hz, 4-Me), 1.65 (1H, ddd, J_{gem} =13.4, J_{3-2} = 7.9, and J_{3-4} = 9.0 Hz, one of H-3), 2.11 (1H, dddd, J_{gem} = 13.4, J_{3-2} = 2.6, J_{3-4} = 6.4, and J_{3-5} = 0.7 Hz, the other of H-3), 2.38-2.55 (1H, m, H-4), 3.81 (2H, br. s, 6-CH_2SO_2Ph), 4.76 (1H, br. d, J_{5-4} = 2.2 Hz, 5-H), 5.43 (1H, dd, J_{2-3} = 7.9 and 2.2 Hz, H-2), 6.8-6.9 (2H, m, Ph), 7.0-7.1 (1H, m, Ph), 7.2-7.3 (2H, m, Ph), 7.4-7.5 (2H, m, Ph), 7.5-7.6 (1H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 20.81 (4-Me), 25.93 (C-4), 34.97 (C-3), 61.05 (6-CH_2SO_2Ph), 97.55 (C-2), 111.50 (C-5), 116.47, 122.31, 128.53, 128.87, 129.41, 133.66 (each Ph), 138.71, 138.74 (Ph and C-6), and 156.74 (Ph); MS (20 eV, rel intensity, %) *m/z* 344 (M^+, 13), 251 (23), 249 (30), 235 (base peak), 109 (52), and 108 (62). Anal. Calcd for $C_{19}H_{20}O_4S$: C, 66.26; H, 5.85%. Found: C, 66.13; H, 5.93%.

cis-2-Ethoxy-4-isopropyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**6d**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless solids (Et_2O-hexane); mp 91-93 °C; IR (KBr) 2850, 1650, 1440, 1350, 1255, 1120, 1025, 900, 850, 825, 800, 770, 745, and 675 cm^{-1}; ^1H NMR (C_6D_6) δ = 0.67, 0.68 (each 3H, each d, J = 6.6 Hz, Me of 4-*i*-Pr), 1.04 (3H, t, J = 7.0 Hz, 2-EtO), 1.31 (1H, oct, J = 6.6 Hz, CH of 4-*i*-Pr), 1.43 (1H, ddd, J_{gem} = 13.0, J_{3-2} = 9.0, and J_{3-4} = 10.8 Hz, one of H-3), 1.63 (1H, dddd, J_{gem} = 13.0, J_{3-2} = 2.2, and J_{3-4} = 6.0 and J_{3-5} = 1.0 Hz, the other of H-3), 1.76-1.88 (1H, m, H-4), 3.12 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 3.51 (1H, d, J_{gem} = 13.9 Hz, one of 6-CH_2SO_2Ph), 3.57 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, the other of 2-EtO), 3.58 (1H, d, J_{gem} = 13.9 Hz, the other of 6-CH_2SO_2Ph), 4.50 (1H, dd, J_{2-3} = 9.0 and 2.2 Hz, H-2), 6.8-7.0 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.35 (2-EtO), 17.22, 19.64 (each Me of 4-*i*-Pr), 31.00 (CH of 4-*i*-Pr), 31.68 (C-4), 38.43 (C-3), 61.45 (6-CH_2SO_2Ph), 64.25 (2-EtO), 100.82 (C-2), 107.92 (C-5), 128.81, 128.92, 133.06 (each Ph), 140.28, and 142.00 (Ph and C-6); MS (75 eV, rel intensity, %) *m/z* 324 (M^+, 74), 281 (36), 235 (base peak), and 72 (48). Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.94; H, 7.46%. Found: C, 63.00; H, 7.20%.

cis-2-Isobutoxy-4-isopropyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**6e**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless needles (Et_2O-hexane); mp 83-84 °C; IR (KBr) 2900, 2850, 1650, 1440, 1350, 1290, 1260, 1125, 1055, 1010, 915, 890, 855, 800, 770, 740, and 675 cm^{-1}; ^{1}H NMR (C_6D_6) $\delta = 0.69$, 0.70 (each 3H, each d, $J = 7.0$ Hz, Me of 4-*i*-Pr), 0.85, 0.87 (each 3H, each d, $J = 6.6$ Hz, Me of 2-*i*-BuO), 1.35 (1H, oct, $J = 7.0$ Hz, CH of 4-*i*-Pr), 1.42 (1H, ddd, $J_{gem} = 13.0$, $J_{3\text{-}2} = 8.8$, and $J_{3\text{-}4} = 10.8$ Hz, one of H-3), 1.62 (1H, dddd, $J_{gem} = 13.0$, $J_{3\text{-}2} = 2.2$, $J_{3\text{-}4} = 6.0$, and $J_{3\text{-}5} = 1.0$ Hz, the other of H-3), 1.76 (1H, ninefold, $J = 6.6$ Hz, CH of 2-*i*-BuO), 1.78-1.91 (1H, m, H-4), 2.83, 3.33 (each 1H, each dd, $J_{gem} = 9.2$ and $J = 6.6$ Hz, CH_2 of 2-*i*-BuO), 3.51, 3.60 (each 1H, each d, $J_{gem} = 13.9$ Hz, 6-CH_2SO_2Ph), 4.48 (1H, dd, $J_{2\text{-}3} = 8.8$ and 2.2 Hz, H-2), 4.52 (1H, br. s, H-5), 6.8-7.0 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) $\delta = 19.19$, 19.42, 19.47, 19.67 (each Me of 2-*i*-BuO and 4-*i*-Pr), 28.78 (CH of 2-*i*-BuO), 30.83 (CH of 4-*i*-Pr), 31.71 (C-4), 38.42 (C-3), 61.45 (6-CH_2SO_2Ph), 75.55 (CH_2 of 2-*i*-BuO), 101.15 (C-2), 107.93 (C-5), 128.81, 128.91, 133.07 (each Ph), 140.43, and 142.00 (Ph and C-6); MS (75 eV, rel intensity, %) *m/z* 352 (M^+, 8), 309 (44), 235 (base peak), 57 (36), 56 (21), and 41 (24). Anal. Calcd for $C_{19}H_{28}O_4S$: C, 64.74; H, 8.01%. Found: C, 64.71; H, 7.95%.

cis-2-Ethoxy-4-phenyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**6f**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless solids (Et_2O-hexane); mp 88-90 °C; IR (KBr) 2980, 2900, 2870, 1675, 1600, 1580, 1445, 1380, 1320, 1305, 1225, 1175, 1160, 1130, 1080, 1040, 1025, 950, 930, 890, 800, 750, and 690 cm^{-1}; ^{1}H NMR (C_6D_6) $\delta = 1.01$ (1H, t, $J = 7.0$ Hz, 2-EtO), 1.73 (1H, ddd, $J_{gem} = 13.2$, $J_{3\text{-}2} = 9.2$, and $J_{3\text{-}4} = 11.0$ Hz, one of H-3), 1.94 (1H, dddd, $J_{gem} = 13.2$, $J_{3\text{-}2} = 2.2$, $J_{3\text{-}4} = 6.6$, and $J_{3\text{-}5} = 1.1$ Hz, the other of H-3), 3.16 (1H, dq, $J_{gem} = 9.5$ and $J = 7.0$ Hz, one of 2-EtO), 3.09- 3.35 (1H, m, H-4), 3.49 (1H, dd, $J_{gem} = 13.9$ and $J = 1.1$ Hz, one of 6-CH_2SO_2Ph), 3.59 (1H, br. d, $J_{gem} = 13.9$ Hz, the other of 6-CH_2SO_2Ph), 3.60 (1H, dq, $J_{gem} = 9.5$ and $J = 7.0$ Hz, the other of 2-EtO), 4.56 (1H, br. s, H-5), 4.58 (1H, dd, $J_{2\text{-}3} = 9.2$ and 2.2 Hz, H-2), 6.8-7.2 (8H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) $\delta = 15.28$ (2-EtO), 37.16 (C-4), 38.40 (C-3), 61.35 (6-CH_2SO_2Ph), 64.27 (2-EtO), 100.41 (C-2), 108.43 (C-5),126.85, 127.50, 127.67, 128.02, 128.38, 133.19 (each Ph), 140.20, 142.79 (Ph and C-6), and 144.19 (Ph); MS (70 eV, rel intensity, %) *m/z* 359 (M^++1, 4), 313 (M^+-EtO, 66), 218 (72), 216 (base peak), 173 (49), 170 (49), 147 (39), 141 (23), 117 (25), 115 (54), 103 (61), 91 (38), 77 (86), and 74 (42). Anal. Calcd for $C_{20}H_{22}O_4S$: C, 67.02; H, 6.19%. Found: C, 66.82; H, 6.34%.

cis-2-Isobutoxy-4-phenyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**6g**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless viscous oil; IR (neat) 3050, 2950, 2850, 1660, 1600, 1445, 1310, 1150, 1075, 1060,1025, 950, 890, 800, 750, and 680 cm^{-1}; ^{1}H NMR (C_6D_6) $\delta = 0.82$, 0.83 (each 3H, each d, $J = 7.0$ Hz, Me of 2-*i*-BuO), 1.60-1.85 (2H, m, one of H-3 and CH of 2-*i*-BuO), 1.92 (1H, dddd, $J_{gem} = 12.8$, $J_{3\text{-}2} = 2.2$, $J_{3\text{-}4} = 6.6$, and $J_{3\text{-}5} = 1.1$ Hz, the other of H-3), 2.86 (1H, dd, $J_{gem} = 9.2$ and $J = 7.0$ Hz, one of CH_2 of 2-*i*-BuO), 3.19-3.29 (1H, m, H-4), 3.36 (1H, dd, $J_{gem} = 9.2$ and $J = 7.0$ Hz, the other of CH_2 of 2-*i*-BuO), 3.51 (1H, dd, $J_{gem} = 13.4$ and $J = 1.1$ Hz, one of 6-CH_2SO_2Ph), 3.61 (1H, br. d, $J_{gem} = 13.4$ Hz, the other of 6-CH_2SO_2Ph), 4.56 (1H, dd, $J_{2\text{-}3} = 9.2$ and 2.2 Hz, H-2), 4.61 (1H, dd, $J_{5\text{-}4} = 2.2$ and $J_{5\text{-}3} = 1.1$ Hz, H-5), 6.8-7.2 (8H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) $\delta = 19.35$, 19.41 (each Me of 2-*i*-BuO), 28.71 (CH of 2-*i*-BuO), 37.05 (C-4), 38.34 (C-3), 61.38 (6-CH_2SO_2Ph), 75.53 (CH_2 of 2-*i*-BuO), 100.05 (C-2), 108.38 (C-5), 126.84, 127.48, 128.75, 133.13 (each Ph), 140.43, 142.79 (Ph and C-6), and 144.21 (Ph); MS (75 eV, rel intensity, %) *m/z* 386 (M^+, 5), 245 (25), 244 (62), 171 (71), 170 (30), 145 (base peak), 144 (53), 143 (34), 141 (43), 131 (55), 129 (29), 128 (31), 100 (27), 77 (46), 57 (86), 56 (55), and 41 (29). Anal. Calcd for $C_{22}H_{26}O_4S$: C, 68.37; H, 6.78%. Found: C, 68.12; H, 6.62%.

r-2-Ethoxy-t-3,c-4-dimethyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**7a**). Purified as an inseparable 1:1 mixture (entry 12 in Table 1) of stereoisomers **7a** and **8a** by silica gel column chromatography using hexane–EtOAc (5:1 v/v). The compound **7a** was characterized on the basis of ^{1}H and ^{13}C NMR spectral data. ^{1}H NMR (C_6D_6) $\delta = 0.77$, 0.84 (each 3H, each d, $J = 7.3$ Hz, each 3-Me or 4-Me), 1.02 (3H, t, $J = 7.0$ Hz, 2-EtO), 1.33 (1H, dquint, $J_{3\text{-}2} = J_{3\text{-}Me} = 7.3$ and $J_{3\text{-}4} = 8.1$ Hz, H-3), 1.54-1.68 (1H, m, H-4), 3.14 (1H, dq, $J_{gem} = 9.5$ and $J = 7.0$ Hz, one of 2-EtO), 3.51 (2H, s, 6-CH_2SO_2Ph), 3.63 (1H, dq, $J_{gem} = 9.5$ and $J = 7.0$ Hz, the other of 2-EtO), 4.22 (1H, $J_{2\text{-}3} = 7.3$ Hz, H-2), 4.33 (1H, d, $J_{5\text{-}4} = 2.6$ Hz, H-5), 6.8-7.0 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) $\delta = 14.95$, 15.21 (each 2-EtO or 3-Me), 19.57 (4-Me), 30.04 (C-4), 38.83 (C-3), 61.27 (6-CH_2SO_2Ph), 64.45 (2-EtO), 104.06 (C-2), 110.68 (C-5), 128.91, 128.95, 133.06 (each Ph), and 140.40 (Ph and C-6). Other signals are overlapped with those of the compound **8a**.

r-2-Ethoxy-c-3,c-4-dimethyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**8a**). Purified as an inseparable 1:19 mixture (entry 13 in Table 1) of *trans* **7a** and *cis* **8a** by silica gel column chromatography using hexane–EtOAc (5:1 v/v). Recrystallization of a mixture of stereoisomers **7a** and **8a** from Et_2O-hexane gave **8a** as a single isomer. Colorless prisms (Et_2O-hexane); mp 82-84 °C; IR (KBr) 2850, 1660, 1440, 1300, 1260, 1130, 1020, 940, 840, 810, 740, 675 and 645 cm^{-1}; ^{1}H NMR (C_6D_6) $\delta = 0.77$, 0.86 (each 3H, each d, $J = 7.3$ Hz, each 3-Me or 4-Me), 1.02 (3H, t, $J = 7.0$ Hz, 2-EtO), 1.68 (1H, dquint, $J_{3\text{-}2} = 1.8$ and $J_{3\text{-}Me} = J_{3\text{-}4} = 7.0$ Hz, H-3), 1.99-2.15 (1H, m, H-4), 3.12 (1H, dq, $J_{gem} = 9.5$ and $J = 7.0$ Hz, one of 2-EtO), 3.51 (2H, s, 6-CH_2SO_2Ph), 3.65 (1H, dq, $J_{gem} = 9.5$ and $J = 7.0$ Hz, the other of 2-EtO), 4.23 (1H, $J_{5\text{-}4} = 3.3$ Hz, H-5), 4.50 (1H, d, J_{2-3} = 1.8 Hz, H-2), 6.8-7.0 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 8.57 (3-Me), 15.31 (2-EtO), 16.21 (4-Me), 30.70 (C-4), 34.80 (C-3), 61.16 (6-CH_2SO_2Ph), 64.56 (2-EtO), 102.63 (C-2), 109.83 (C-5), 128.75, 128.97, 133.03 (each Ph), and 140.25 (Ph and C-6); MS (20 eV, rel intensity, %) *m/z* 310 (M^+, 18) and 86 (base peak). Anal. Calcd for $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14%. Found: C, 61.95; H, 7.14%.

r-2-Ethoxy-c-4-methyl-t-3-phenyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**7b**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless needles (Et_2O-hexane); mp 111-112 °C; IR (KBr) 2900, 1650, 1440, 1300, 1255, 1130, 1075, 995, 820, 745, 680, and 625 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.69 (3H, d, J_{Me-4} = 6.6 Hz, 4-Me), 0.78 (3H, t, J = 7.0 Hz, 2-EtO), 2.22-2.35 (1H, m, H-4), 2.41 (1H, dd, J_{3-2} = 8.1 and J_{3-4} = 9.9 Hz, H-3), 3.03, 3.48 (each 1H, each dq, J_{gem} = 9.5 and J = 7.0 Hz, 2-EtO), 3.53, 3.64 (each 1H, each d, J_{gem} = 13.9 Hz, 6-CH_2SO_2Ph), 4.54 (1H, d, J_{5-4} = 2.2 Hz, H-5), 4.67 (1H, d, J_{2-3} = 8.1 Hz, H-2), 6.8-7.2 (8H, m, Ph), 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ =14.96 (2-EtO), 19.24 (4-Me), 34.59 (C-4), 51.95 (C-3), 61.21 (6'-CH_2SO_2Ph), 64.66 (2-EtO), 103.04 (C-2), 111.26 (C-5), 126.94, 128.55, 128.62, 128.89, 133.16 (each Ph), 140.44, and 140.82 (Ph and C-6); MS (20 eV, rel intensity, %) *m/z* 372 (M^+, 6), 149 (11), and 148 (base peak). Anal. Calcd for $C_{21}H_{24}O_4S$: C, 67.72; H, 6.49%. Found: C, 68.08; H, 6.53%.

r-2-Ethoxy-c-4-methyl-c-3-phenyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**8b**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless prisms (Et_2O-hexane); mp 91-92 °C; IR (KBr) 2900, 1650, 1440, 1300, 1150, 1125, 1105, 1085, 1050, 1015, 980, 880, 845, 740, and 680 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.81 (3H, d, J = 7.3 Hz, 4-Me), 1.03 (3H, t, J = 7.0 Hz, 2-EtO), 2.18-2.34 (1H, m, 4-H), 2.93 (1H, dd, J_{3-2} = 2.2 and J_{3-4} = 6.8 Hz, 3-H), 3.21 (1H, dq, J_{gem} = 9.5 and J = 7.3 Hz, one of 2-EtO), 3.52, 3.62 (each 1H, each d, J_{gem} = 14.3 Hz, 6-CH_2SO_2Ph), 3.86 (1H, dq, J_{gem} = 9.5 and J = 7.3 Hz, the other of 2-EtO), 4.39 (1H, br. d, J_{5-4} = 4.0 Hz, H-5), 4.92 (1H, d, J_{2-3} = 2.2 Hz, H-2), 6.9-7.4 (8H, m, Ph), and 7.8-8.0 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.18 (2-EtO), 16.60 (4-Me), 31.39 (C-4), 46.48 (C-3), 61.24 (6'-CH_2SO_2Ph), 64.76 (2-EtO) 100.80 (C-2), 111.72 (C-5), 126.88, 127.66, 128.02, 128.38, 130.00, 133.26 (each Ph), 138.53, 139.78, and 139.86 (Ph and C-6); Mass (75 eV, rel. intensity, %) *m/z* 372 (M^+, 2), 148 (base peak), 120 (29), and 91 (28). Anal. Calcd for $C_{21}H_{24}O_4S$: C, 67.72; H, 6.49%. Found: C, 67.31; H, 6.36%.

trans- and cis-2-Ethoxy-3-Methyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**7c**) and (**8c**). Purified as an inseparable 1:1 mixture (entry 18 in Table 1) of **7c** and **8c** by silica gel column chromatography using hexane–EtOAc (5:1 v/v). Colorless oil; IR (neat) 2950, 2900, 1675, 1580, 1445, 1370, 1310, 1250, 1210, 1150, 1125, 1080, 1060, 1025, 980, 960, 920, 850, 790, 745, and 680 cm^{-1}; ^{1}H NMR (C_6D_6) **7c**: δ = 0.78 (3H, d, J = 6.9 Hz, 3-Me), 1.06 (3H, t, J = 7.0 Hz, 2-EtO), 1.33 (1H, dt, J_{gem} = 12.5 and J_{4-3} = J_{4-5} = 4.8 Hz, one of 4-H), 2.01-2.15 (1H, m, the other of 4-H), 3.24 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 3.51 (2H, br. s, 6-CH_2SO_2Ph), 3.78 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 4.83 (1H, d, J_{2-3} = 4.8 Hz, H-2), and 4.41 (1H, t, J_{5-4} = 4.8 Hz, 5-H); **8c**: δ = 0.82 (3H, d, J = 6.6 Hz, 3-Me), 1.06 (3H, t, J = 7.0 Hz, 2-EtO), 3.28 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 3.47, 3.58 (each 1H, each br. d, J_{gem} = 13.9 Hz, 6-CH_2SO_2Ph), 3.90 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, the other of 2-EtO), 4.40 (1H, dd, J_{5-4} = 4.7 and 2.5 Hz, 5-H), and 4.56 (1H, d, J_{2-3} = 2.5 Hz, H-2). Other signals (H-3 and Ph) of **7c** are overlapped with those (H-3, 4 and Ph) of the compound **8c**: 1.5-1.9 (4H, m, H-3 of **7c** and H-3, 4 of **8c**) and 6.7-7.0 (3H, m, Ph), and 7.7-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) **7c**: δ = 15.26 (3-Me), 16.18 (2-EtO), 25.77 (C-4), 30.05 (C-3), 61.34 (6-CH_2SO_2Ph), 64.09 (2-EtO), 102.40 (C-2), 103.77 (C-5), 128.75, 128.81, 133.06 (each Ph), 140.28 (Ph or C-6), and 140.33 (Ph or C-6); **8c**: δ = 15.12 (3-Me), 15.62 (2-EtO), 25.15 (C-4), 30.58 (C-3), 61.34 (6-CH_2SO_2Ph), 64.16 (2-EtO), 100.40 (C-2), 104.95 (C-5), 128.71, 128.92, 133.06 (each Ph), 140.28, and 140.33 (Ph and C-6). Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.79; H, 6.80%. Found: C, 60.05; H, 6.62%.

trans-2-Ethoxy-3-phenyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**7d**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless prisms (*i*-PrOH-hexane); mp 102-103 °C; IR (KBr) 2900, 1660, 1430, 1280, 1240, 1120, 1075, 980, 870, 790, 740, and 675 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.93 (3H, t, J = 7.0 Hz, 2-EtO), 1.94 (1H, ddd, J_{gem} = 18.0, J_{4-3} = 6.6, and J_{4-5} = 4.0 Hz, one of H-4), 2.27 (1H, ddd, J_{gem} = 18.0, J_{4-3} = 6.6, J_{4-5} = 4.0 Hz, the other of H-4), 2.82 (1H, dt, J_{3-2} = 5.1 and J_{3-4} = 6.6 Hz, H-3), 3.16 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz one of 2-EtO), 3.50 (2H, s, CH_2SO_2Ph), 3.70 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, the other of 2-EtO), 4.53 (1H, t, J_{5-4} = 4.0 Hz, H-5), 4.72 (1H, d, J_{2-3} = 5.1 Hz, H-2), 6.8-7.0 (3H, m, Ph), 7.0-7.3 (5H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ =15.09 (2-EtO), 26.38 (C-4), 41.97 (C-3), 61.28 (6-CH_2SO_2Ph), 64.32 (2-EtO), 101.52 (C-2), 104.61 (C-5), 126.95, 128.15, 128.68, 128.71, 128.81, 132.97 (each Ph), 140.51, 141.28, and 141.59 (Ph and C-6); Mass (70 eV, rel. intensity, %) *m/z* 358 (M^+, 9), 171 (52), 149 (87), 147 (34), 119 (23), 92 (22), 91 (70), 78 (23), 77 (base peak), 65 (34), 55 (27), and 51 (33). Anal. Calcd for $C_{20}H_{22}O_4S$: C, 67.02; H, 6.19%. Found: C, 67.19; H, 6.31%.

cis-2-Ethoxy-3-phenyl-6-(phenylsulfonylmethyl)-3,4-dihydro-2H-pyran (**8d**). Separated and purified by silica gel column chromatography using hexane–EtOAc (7:1 v/v). Colorless prisms (*i*-PrOH-hexane); mp 93-95 °C; IR (KBr) 2900, 1670, 1440, 1305, 1160, 1130, 1100, 1080, 1040, 980, 930, 870, 850, 800, 740, and 690 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.97 (3H, t, J = 7.0 Hz, 2-EtO), 1.77 (1H, dt, J_{gem} = 16.9 and J_{4-3} = J_{4-5} = 5.5 Hz, one of H-4), 2.52 (1H, br. dd, J_{gem} = 16.9 and J_{4-3} = 12.8 Hz the other of H-4), 2.78 (1H, ddd, $J_{3\text{-}4}$ = 12.8, $J_{3\text{-}4}$ = 5.5, and $J_{3\text{-}2}$ = 1.8 Hz, H-3), 3.16 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 3.54, 3.66 (each 1H, each d, J_{gem} = 14.3 Hz, 6-CH_2SO_2Ph), 3.86 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, the other of 2-EtO), 4.50 (1H, dd, $J_{5\text{-}4}$ = 5.5 and 2.2 Hz, H-5), 4.88 (1H, d, $J_{2\text{-}3}$ = 1.8 Hz, H-2), 6.8-7.3 (8H, Ph), and 7.7-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 14.97 (2-EtO), 23.70 (C-4), 42.63 (C-3), 61.32 (C-6'), 64.43 (2-EtO), 99.77 (C-2), 105.60 (C-5), 127.17, 128.69, 128.84, 128.94, 129.34, 133.07 (each Ph), 140.13, 140.23, and140.67 (Ph and C-6); Mass (70 eV, rel. intensity, %) *m/z* 358 (M^+, 49), 312 (21), 171 (54), 149 (70), 147 (base peak), 143 (35), 142 (22), 141 (69), 129 (24), 128 (68), 127 (21), 121 (32), 119 (45), 115 (69), 105 (37), 104 (31), 103 (20), 92 (26), and 51 (50). Anal. Calcd for $C_{20}H_{22}O_4S$: C, 67.02; H, 6.19%. Found: C, 67.25; H, 6.35%.

cis-6-(Phenylsulfonylmethyl)-2,3,3a,7a-tetrahydro-4H-furo[2,3-b]pyran (**9**). Separated and purified by silica gel column chromatography using hexane–EtOAc (4:1 v/v). Colorless prisms (Et_2O-hexane); mp 79-81 °C; IR (KBr) 2900, 1670, 1440, 1270, 1040, 990, 920, 800, 750, 690, and 610 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 1.20-1.90 (4H, m, H-3, H-3a, and H-4), 3.5-3.6 (1H, m, one of H-2), 3.53 (2H, s, 6-CH_2SO_2Ph), 3.82 (1H, ddd, J_{gem} = 9.2, $J_{2\text{-}3}$ = 8.4, and 2.9 Hz, the other of H-2), 4.45 (1H, dd, $J_{5\text{-}4}$ = 5.1 and 2.6 Hz, H-5), 4.85 (1H, d, $J_{7a\text{-}3a}$ = 3.7 Hz, H-7a), 6.9-7.0 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 21.66 (C-4), 27.75 (C-3), 36.59 (C-3a), 61.58 (6-CH_2SO_2Ph), 67.90 (C-2), 99.82 (C-7a), 100.51 (C-5), 128.69, 128.84, 133.17 (each Ph), 140.60, and 141.21 (Ph and C-6); MS (75 eV, rel intensity, %) *m/z* 280 (M^+, 11), 139 (28), and 70 (base peak). Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75%. Found: C, 60.18; H, 5.80%.

General Procedure for the Transformation of 2-Ethoxy-3,4-dihydro-2H-pyran Cycloadducts 6a, 7b,d, and 8b to 6-Ethoxy-1-phenylsulfonyl-2-hexanone Derivatives 10a-d. As a typical example the transformation of **6a** to **10a** is described as follows: To a solution of **6a** (148 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) was added $TiCl_4$ (2 M in CH_2Cl_2, 0.06 ml, 0.55 mmol) under nitrogen. The mixture was stirred at -78 °C for 10 min and the addition of triethyl silane (64 mg, 0.088 ml, 0.55 mmol) was followed. The reaction mixture was stirred at -78 °C for 1 h. The resulting mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (30 ml x 3). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product (139 mg) was chromatographed on silica gel with hexane-EtOAc (4:1 v/v) to give keto ether **10a** (111 mg, 74%). Other keto ethers **10b-d** were also prepared in 42, 80, and 80 % yields, respectively, by the similar reaction method.

6-Ethoxy-4-methyl-1-phenylsulfonyl-2-hexanone (**10a**). Colorless oil; IR (neat) 2900, 1720, 1445, 1375, 1320, 1150, 1080, 1040, 980, 740, and 680 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.81 (3H, d, $J_{\text{Me-4}}$ = 6.6 Hz, 4-Me), 1.09 (3H, t, J = 7.0 Hz, 2-EtO), 1.21-1.51 (2H, m, H-5), 2.05-2.22 (1H, m, H-4), 2.26 (1H, dd, J_{gem} = 17.2 and $J_{3\text{-}4}$ = 7.3 Hz, one of H-3), 2.46 (1H, dd, J_{gem} = 17.2 and $J_{3\text{-}4}$ = 5.5 Hz, the other of H-3), 3.15-3.30 (4H, m, H-6 and 6-EtO), 3.64 (2H, s, 1-CH_2SO_2Ph), 6.8-7.0 (3H, m, Ph), and 7.8-7.9 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.48 (6-EtO), 19.97 (4-Me), 26.41 (C-4), 36.50 (C-5), 51.33 (C-3), 66.22 (C-1), 66.99 (6-EtO), 68.54 (C-6), 128.55, 129.08, 133.60, 139.97 (each Ph), and 197.27 (C=O); MS (70 eV, rel intensity, %) *m/z* 254 (M^+-EtOH, 5), 158 (28), 145 (30), 142 (57), 141 (21), 126 (46), 117 (28), 116 (91), 115 (34), 113 (33), 112 (58), 111 (74), 110 (48), 100 (37), 96 (33), 94 (31), 81 (48), 78 (87), 77 (47), 72 (24), 70 (63), 60 (86), 56 (base peak), 55 (22), and 52 (53). Anal. Calcd for $C_{15}H_{22}O_4S$: C, 60.38; H, 7.43%. Found: C, 60.48; H, 7.30%.

6-Ethoxy-5-phenyl-1-phenylsulfonyl-2-hexanone (**10b**). Separated and purified by silica gel column chromatography using hexane–EtOAc (4:1 v/v). Colorless oil; IR (neat) 2850, 1700, 1575, 1440, 1370, 1275, 1220, 1140, 1080, 1020, 875, 825, 725, and 680 cm^{-1}; ^{1}H NMR (C_6D_6) δ =1.04 (3H, t, J = 7.0 Hz, 2-EtO), 1.74-1.78 (1H, m, one of H-4), 2.10-2.43 (3H, m, H-3 and the other of H-4), 2.66-2.80 (1H, m, H-5), 3.21 (2H, q, J = 7.0 Hz, 2-EtO), 3.30 (1H, dd, J_{gem} = 9.5 and $J_{6\text{-}5}$ = 7.0 Hz, one of H-6), 3.36 (1H, dd, J_{gem} = 9.5 and $J_{6\text{-}5}$ = 5.9 Hz, the other of H-6), 3.43 (2H, s, H-1), 6.8-7.2 (8H, m, Ph), and 7.7-7.8 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.32 (6-EtO), 26.64 (C-4), 42.29 (C-5), 45.60 (C-3), 66.46 (C-1), 66.61 (6-EtO), 75.46 (C-6), 126.92, 128.30, 128.53, 129.08, 129.04, 133.56, 139.23, 142.79 (each Ph), and 197.27 (C=O); MS (70 eV, rel intensity, %) *m/z* 315 (M^+-EtO, 25), 314 (M^+-EtOH, 25), 174 (39), 173 (84), 172 (52), 160 (38), 159 (base peak), 158 (59), 141 (50), 140 (25), 117 (38), 116 (23), 104 (58), 103 (41), 91 (45), 77 (51), 59 (63), and 58 (23). Anal. Calcd for $C_{20}H_{24}O_4S$: C, 66.64; H, 6.71%. Found: C, 66.25; H, 6.71%.

4,5-syn-6-Ethoxy-4-methyl-5-phenyl-1-phenylsulfonyl-2-hexanone (**10c**). Separated and purified by silica gel column chromatography using hexane–EtOAc (4:1 v/v). Colorless oil; IR (neat) 2950, 2850, 1710, 1575, 1440, 1370, 1320, 1150, 1100, 1025, 900, 730, 700, and 675 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.73 (3H, d, J = 6.2 Hz, 4-Me), 1.02 (3H, t, J = 7.0 Hz, 2-EtO), 2.36 (1H, dd, J_{gem} = 17.6 and $J_{3\text{-}4}$ = 7.0 Hz, one of H-3), 2.49-2.70 (2H, m, H-4 and H-5), 2.76 (1H, dd, J_{gem} = 17.6 and $J_{3\text{-}4}$ = 4.8 the other of H-3), 3.18 (2H, q, J = 7.0 Hz, 2-EtO), 3.41 (1H, dd, J_{gem} = 9.5 and $J_{6\text{-}5}$ = 4.8 Hz, one of H-6), 3.49 (1H, dd, J_{gem} = 9.5 and $J_{6\text{-}5}$ = 6.6 Hz, the other of H-6), 3.68, 3.74 (each 1H, each d, J_{gem} = 13.6 Hz, H-1), 6.8-7.2 (8H, m, Ph), and 7.7-7.8 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.32 (6-EtO), 17.98 (4-Me), 31.35 (C-4), 49.83 (C-5), 50.81 (C-3), 66.42 (C-1), 67.00 (6-EtO), 73.07 (C-6), 126.79, 128.55, 128.58, 128.88, 129.08, 133.59, 140.04, 142.27 (each Ph), and 197.29 (C=O); MS (70 eV, rel intensity, %) *m/z* 329 (M^+-EtO, 74), 328 (M^+-EtOH, 77), 188 (83), 184 (22), 174 (43), 173 (base peak), 172 (46), 171

(35), 170 (58), 169 (99), 168 (39), 153 (39), 140 (45), 131 (29), 119 (20), 116 (47), 115 (31), 104 (33), 103 (32), 90 (32), 76 (23), and 58 (44). Anal. Calcd for $C_{21}H_{26}O_4S$: C, 67.35 H, 7.00%. Found: C, 67.43; H, 6.98%.

4,5-anti-6-Ethoxy-4-methyl-5-phenyl-1-phenylsulfonyl-2-hexanone (**10d**). Separated and purified by silica gel column chromatography using hexane–EtOAc (4:1 v/v). Colorless oil; IR (neat) 2950, 2850, 1710, 1575, 1440, 1370, 1320, 1140, 1100, 1025, 880, 730, 700, and 675 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.98 (3H, d, J = 5.5 Hz, 4-Me),1.02 (3H, t, J = 7.0 Hz, 2-EtO), 2.27 (1H, dd, J_{gem} = 18.3 and $J_{3\text{-}4}$ = 9.2 Hz, one of H-3), 2.49-2.65 (3H, m, the other of H-3, H-4, and H-5), 3.15, 3.20 (each 1H, each dq, J_{gem} = 9.2 and J = 7.0 Hz, 6-EtO), 3.42, 3.48 (each 1H, each d, J_{gem} = 13.2 Hz, 1-CH_2SO_2Ph), 3.48 (2H, d, $J_{6\text{-}5}$ = 4.8 Hz, H-6), 6.8-7.2 (8H, m, Ph), and 7.7-7.8 (2H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.31 (6-EtO), 17.98 (4-Me), 31.52 (C-4), 49.48 (C-5), 50.87 (C-3), 66.52 (C-1), 66.90 (6-EtO), 72.19 (C-6), 126.79, 128.31, 128.59, 128.97, 129.05, 133.57, 139.88, 143.06 (each Ph), and 197.46 (C=O); MS (70 eV, rel intensity, %) *m/z* 329 (M$^+$-EtO, 33), 328 (M$^+$-EtOH, 53), 188 (25), 187 (84), 186 (base peak), 185 (24), 173 (50), 171 (20), 170 (36), 169 (79), 156 (87), 155 (76), 154 (58), 145 (59), 143 (20), 142 (23), 141 (97), 140 (23), 132 (20), 131 (29), 130 (25), 118 (41), 117 (46), 77 (24), and 59 (41). Anal. Calcd for $C_{21}H_{26}O_4S$: C, 67.35 H, 7.00%. Found: C, 67.72; H, 7.09%.

General Procedure for the Transformation of 2-Ethoxy-3,4-dihydro-2H-pyran Cycloadducts 6a,d,f to Desulfonylated 6-Ethoxy-1-phenylsulfonyl-2-hexanone Derivatives 12a-c.

Benzylation of Dihydropyran 6a,d. As a example benzylation of **6a** to **11a** is described as follows: To a solution of dihydropyran **6a** (593 mg, 2.0 mmol) in THF (6 ml) was added butyllithium (in hexane, 1.4 ml, 2.2 mmol) by the aid of a syringe under nitrogen at -78 °C. After stirred at room temperature for 20 min, the mixture was again cooled to -78 °C and the addition of benzyl bromide (376 mg, 0.26 ml, 2.2 mmol) was followed. The reaction mixture was stirred at -78 °C for 30 min and quenched with saturated aqueous NH_4Cl. The THF was removed in vacuo and the aqueous residue was extracted with CH_2Cl_2 (30 ml x 3). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product (715 mg) was chromatographed on silica gel with hexane-EtOAc (7:1 to 5:1 v/v) to give **11a** (662 mg, 85%) as a single stereoisomer.

Another benzylated dihydropyran **11b** (90% de) was also prepared in 50% yield by the similar reaction method.

cis-2-Ethoxy-4-methyl-6-(2-phenyl-1-phenylsulfonylethyl)-3,4-dihydro-2H-pyran (**11a**). Colorless prisms (Et_2O-hexane); mp 79-81 °C; IR (KBr) 2950, 2850, 1660, 1440, 1280, 1220, 1175, 1125, 1050, 1010, 980, 850, 800, 745, 690, and 630 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.55 (3H, d, $J_{Me\text{-}4}$ = 7.0 Hz, 4-Me), 1.07 (3H, t, J = 7.0 Hz, 2-EtO), 1.19 (1H, ddd, J_{gem} = 13.2, $J_{3\text{-}4}$ = 10.3 and $J_{3\text{-}2}$ = 8.8 Hz, one of H-3), 1.63 (1H, br. dd, J_{gem} = 13.2 and $J_{3\text{-}4}$ = 6.6 Hz, the other of H-3), 1.80-1.96 (1H, m, H-4), 3.25 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 3.40 (1H, dd, J_{gem} = 13.2 and $J_{CH2\text{-}1'}$ = 12.1 Hz, one of 1'-CH_2Ph), 3.58 (1H, dd, J_{gem} = 13.2 and $J_{CH2\text{-}1'}$ = 3.3 Hz, the other of 1'-CH_2Ph), 3.71 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 3.73 (1H, dd, $J_{1'\text{-}CH2}$ = 12.1 and 3.3 Hz, H-1'), 4.16 (1H, dd, $J_{5\text{-}4}$ = 2.2 and $J_{5\text{-}3}$ = 1.1 Hz, H-5), 4.52 (1H, dd, $J_{2\text{-}3}$ = 8.8 and 2.2 Hz, H-2), 6.9-7.2 (8H, m, Ph), and 7.8-7.9 (3H, Ph); ^{13}C NMR (C_6D_6) δ = 15.44 (2-EtO), 20.72 (4-Me), 26.80 (C-4), 31.91 (1'-CH_2Ph), 36.31 (C-3), 64.61 (2-EtO), 72.68 (C-1'), 100.64 (C-2), 111.53 (C-5), 126.84, 128.49, 128.69, 129.54, 129.61, 133.08, 137.63 (each Ph), 139.41, and 142.60 (Ph and C-6); MS (20 eV, rel intensity, %) *m/z* 386 (M$^+$, 43), 245 (base peak), and 199 (61). Anal. Calcd for $C_{22}H_{26}O_4S$: C, 68.37; H, 6.78%. Found: C, 68.43; H, 6.67%.

cis-2-Ethoxy-4-isopropyl-6-(2-phenyl-1-phenylsulfonylethyl)-3,4-dihydro-2H-pyran (**11b**). major isomer: Colorless prisms (Et_2O-hexane); mp 87-89 °C; IR (KBr) 2900, 2850, 1660, 1440, 1370, 1280, 1210, 1180, 1120, 1045, 1010, 970, 900, 850, 740, 680, and 630 cm^{-1}; ^{1}H NMR (C_6D_6) δ = 0.43, 0.49 (each 3H, each d, J = 7.0 Hz, Me of 4-*i*-Pr), 1.11 (3H, t, J = 7.0 Hz, 2-EtO), 1.13 (1H, oct, J = 7.0 Hz, CH of 4-*i*-Pr), 1.35 (1H, ddd, J_{gem} = 12.8, $J_{3\text{-}4}$ = 11.2 and $J_{3\text{-}2}$ = 9.2 Hz, one of H-3), 1.58 (1H, dddd, J_{gem} = 12.8, $J_{3\text{-}4}$ = 6.6, $J_{3\text{-}2}$ = 2.2, and $J_{3\text{-}5}$ = 1.1 Hz, the other of H-3), 1.73-1.85 (1H, m, H-4), 3.29 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 3.43 (1H, dd, J_{gem} = 12.8 and $J_{CH2\text{-}1'}$ = 11.7 Hz, one of 1'-CH_2Ph), 3.54 (1H, dd, J_{gem} = 12.8 and $J_{CH2\text{-}1'}$ = 3.3 Hz, the other of 1'-CH_2Ph), 3.72 (1H, dd, $J_{1'\text{-}CH2}$ = 11.7 and 3.3 Hz, H-1'), 3.76 (1H, dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 4.20 (1H, dd, $J_{5\text{-}4}$ = 2.2 and $J_{5\text{-}3}$ = 1.1 Hz, H-5), 4.57 (1H, dd, $J_{2\text{-}3}$ = 9.2 and 2.2 Hz, H-2), 6.9-7.2 (8H, m, Ph), and 7.8-8.0 (3H, Ph); ^{13}C NMR (C_6D_6) δ = 15.52 (2-EtO), 18.46, 19.18 (each Me of 4-*i*-Pr), 30.63 (C-4), 31.30 (1'-CH_2Ph), 31.72 (CH of 4-*i*-Pr), 38.31 (C-3), 64.69 (2-EtO), 73.01 (C-1'), 101.32 (C-2), 109.32 (C-5), 126.81, 128.53, 128.75, 129.47, 129.63, 133.08, 137.55 (each Ph), 139.96, and 143.39 (Ph and C-6); MS (75 eV, rel intensity, %) *m/z* 414 (M$^+$, 43), 325 (42), 227 (68), 97 (26), 91 (base peak), 77 (66), and 41 (35). Anal. Calcd for $C_{24}H_{30}O_4S$: C, 69.54; H, 7.29%. Found: C, 69.61 H, 7.31%. minor isomer: This product could not be separated from the mixture with major isomer because of the low yield. Its patial ^{13}C NMR spectrum was abstracted (C_6D_6) δ = 15.39 (2-EtO), 19.05, 19.73 (each Me of 4-*i*-Pr), 30.88 (C-4), 31.62 (1'-CH_2Ph), 31.88 (CH of 4-*i*-Pr), 38.08 (C-3), 64.29 (2-EtO), 72.15 (C-1'), 100.67 (C-2), 108.77 (C-5), 128.65, 129.23, and 129.33 (each Ph).

Reductive Desulfonylation of 11a,b and 6f Leading to 12a-c. As a typical example reductive desulfonylation of **11a** to **12a** is described as follows: A mixture of metal sodium and naphthalene (1:1 mol equiv.) in THF at 5 °C under nitrogen was ultrasonified for 40 min to afford lithium naphthalenide reducing reagent as a dark green solution. To a solution of **11a** (270 mg, 0.7 mmol) in isopropylamine (2ml) was added the freshly prepared sodium naphthalenide (0.5 M in THF, 5.6 ml, 2.8 mmol) at -78 °C under nitrogen. The reaction mixture was stirred at -78 °C for 10 min, quenched with water and extracted with CH_2Cl_2 (30 ml x 3). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The crude product (400 mg) was chromatographed on silica gel with hexane-Et_2O (49:1 v/v) to give **12a** (95 mg, 55%). Other desulfonylated dihydropyran **12b,c** were also prepared in 52 and 66 % yields, respectively, by the similar reaction method.

cis-2-Ethoxy-4-methyl-6-phenethyl-3,4-dihydro-2H-pyran (**12a**). Separated and purified by silica gel column chromatography using hexane–Et_2O (99:1 v/v). Colorless oil; IR (neat) 3050, 2950, 2900, 2850, 1675, 1610, 1500, 1455, 1380, 1330, 1290, 1260, 1220, 1190, 1130, 1060, 980, 910, 875, 780, 750, and 700 cm^{-1}; ^1H NMR (C_6D_6) δ = 0.90 (3H, d, $J_{Me\text{-}4}$ = 7.0 Hz, 4-Me), 1.15 (3H, t, J = 7.0 Hz, 2-EtO), 1.52 (1H, ddd, J_{gem} = 12.8, $J_{3\text{-}4}$ = 9.2 and $J_{3\text{-}2}$ = 8.1 Hz, one of H-3), 1.86 (1H, dddd, J_{gem} = 12.8, $J_{3\text{-}4}$ = 6.6, $J_{3\text{-}2}$ = 2.2, and $J_{3\text{-}5}$ = 1.1 Hz, the other of H-3), 1.99-2.25 (1H, m, H-4), 2.35 (2H, t, J = 7.3 Hz, 6-CH_2CH_2Ph), 2.83 (2H, t, J = 7.3 Hz, 6-CH_2CH_2Ph), 3.40, 3.93 (each 1H, each dq, J_{gem} = 9.5 and J = 7.0 Hz, 2-EtO), 4.28 (1H, br. s, H-5), 4.82 (1H, dd, $J_{2\text{-}3}$ = 8.8 and 2.2 Hz, H-2), and 7.0-7.2 (5H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.54 (2-EtO), 21.80 (4-Me), 26.48 (C-4), 33.92 (6-CH_2CH_2Ph), 36.33, 36.82 (C-3 and 6-CH_2CH_2Ph), 64.10 (2-EtO), 100.05 (C-2), 102.91 (C-5), 126.10, 128.52, 128.84, 142.08 (each Ph), and 150.45 (C-6); MS (75 eV, rel intensity, %) *m/z* 246 (M^+, 82), 231 (31), 200 (24), 174 (78), 159 (95), 105 (31), 104 (20), 91 (95), 72 (54), 69 (base peak), 44 (35), and 41 (28). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00%. Found: C, 78.07; H, 8.86%.

cis-2-Ethoxy-4-isopropyl-6-phenethyl-3,4-dihydro-2H-pyran (**12b**). Separated and purified by silica gel column chromatography using hexane–Et_2O (99:1 v/v). Colorless oil; IR (neat) 2950, 2850, 1675, 1600, 1490, 1450, 1375, 1300, 1260, 1125, 1055, 975, 910, 890, 860, 775, 740, and 700 cm^{-1}; ^1H NMR (C_6D_6) δ = 0.75, 0.77 (each 3H, each d, J = 7.0 Hz, Me of 4-*i*-Pr), 1.18 (3H, t, J = 7.0 Hz, 2-EtO), 1.42 (1H, oct, J = 7.0 Hz, CH of 4-*i*-Pr), 1.64 (1H, ddd, J_{gem} = 12.8, $J_{3\text{-}4}$ = 11.0 and $J_{3\text{-}2}$ = 8.8 Hz, one of H-3), 1.76-1.86 (1H, m, the other of H-3), 1.91-2.02 (1H, m, H-4), 2.37 (2H, t, J = 7.3 Hz, 6-CH_2CH_2Ph), 2.84 (2H, t, J = 7.3 Hz, 6-CH_2CH_2Ph), 3.43, 3.98 (each1H, each dq, J_{gem} = 9.5 and J = 7.0 Hz, one of 2-EtO), 4.34 (1H, br. d, H-5), 4.82 (1H, dd, $J_{2\text{-}3}$ = 8.8 and 2.2 Hz, H-2), and 7.0-7.2 (5H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.59 (2-EtO), 19.34, 19.77 (each Me of 4-*i*-Pr), 31.94, 32.14 (each C-4 or CH of 4-*i*-Pr), 33.89 (6-CH_2CH_2Ph), 36.34 (6-CH_2CH_2Ph), 38.40 (C-3), 64.19 (2-EtO), 99.88 (C-2), 100.81 (C-5), 126.10, 128.53, 128.87, 142.03 (each Ph), and 151.54 (C-6); MS (70 eV, rel intensity, %) *m/z* 274 (M^+, 33), 230 (42), 229 (37), 159 (base peak), 134 (56), 133 (35),120 (20), 119 (22), and 77 (27). Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55%. Found: C, 78.59; H, 9.35%.

cis-2-Ethoxy-6-methyl-4-phenyl-3,4-dihydro-2H-pyran (**12c**). Separated and purified by silica gel column chromatography using hexane–Et_2O (99:1 v/v). Colorless oil; IR (neat) 2950, 2900, 2850, 1675, 1600, 1490, 1440, 1375, 1300, 1270, 1175, 1125, 1065, 1030, 940, 885, 865, 760, and 700 cm^{-1}; ^1H NMR (C_6D_6) δ = 1.15 (3H, t, J = 7.0 Hz, 2-EtO), 1.77 (1H, dd, $J_{Me\text{-}5}$ = 2.2 and $J_{Me\text{-}4}$ = 1.1 Hz, 6-Me), 1.94 (1H, ddd, J_{gem} = 12.8, $J_{3\text{-}4}$ = 10.6 and $J_{3\text{-}2}$ = 8.8 Hz, one of H-3), 2.11 (1H, dddd, J_{gem} = 12.8, $J_{3\text{-}4}$ = 6.6, $J_{3\text{-}2}$ = 2.2, and $J_{3\text{-}5}$ = 1.5 Hz, the other of H-3), 3.34-3.47 (1H, m, H-4), 3.40, 3.93 (each 1H, each dq, J_{gem} = 9.5 and J = 7.0 Hz, 2-EtO), 4.50 (1H,m, H-5), 4.82 (1H, dd, $J_{2\text{-}3}$ = 8.8 and 2.2 Hz, H-2), and 7.0-7.2 (5H, m, Ph); ^{13}C NMR (C_6D_6) δ = 15.45 (2-EtO), 19.97 (6-Me), 37.67 (C-4), 38.62 (C-3), 64.07 (2-EtO), 100.14, 100.36 (C-2 and C-5), 126.59, 127.60, 128.69, 145.70 (each Ph), and 149.82 (C-6); MS (70 eV, rel intensity, %) *m/z* 218 (M^+, 17), 173 (41), 172 (base peak), 171 (31), 161 (39),146 (22), 145 (42), 103 (40), 102 (23), and 85 (24). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%. Found: C, 77.08; H, 8.28%.

References and Note

1. (a) Wada, E.; Kanemasa, S.; Tsuge, O. *Chem. Lett.* **1989**, 675-678. (b) Wada, E.; Kanemasa, S.; Tsuge, O. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 860-868.
2. (a) Boquel, P.; Chapleur, Y. *Tetrahedron Lett.* **1990**, *31*, 1869-1872. (b) Tursch, B.; Chome, C.; Braekman, J. C. *Bull. Soc. Chim. Belg.* **1973**, *82*, 699-702. (c) Longley, R. I. Jr.; Emerson, W. S. *J. Am. Chem. Soc.* **1950**, *72*, 3079-3081.
3. (a) Hall, S. S.; Weber, G. F.; Duggan, A. J. *J. Org. Chem.* **1978**, *43*, 667-672. A lanthanoid catalyst is an effective catalyst in the Diels-Alder reactions of 2-alkenals: (b) Chapleur, Y.; Euvrard, M. -N. *J. Chem. Soc. Chem. Commun.* **1987**, 884-885. (c) Danishefsky, S.; Bednarski; Bednarski, M. *Tetrahedron Lett.* **1984**, *25*, 721-724.
4. (a) Boger, D. L.; Weinreb, S.M. "Hetero Diels-Alder Methodology in Organic Synthesis," as Vol. 47 of "Organic Chemistry, A Series of Monographs," ed by Wasserman, H. H. , Academic Press, San Diego (1987), Chap. 7, pp. 167-213. (b) Schmidt, R. R. *Acc. Chem. Res.*, **1986**, *19*, 250-259. (c) Tietze, L. F. "Selectivity–a Goal for Synthetic

Efficiency," ed by Bartmann, W.; Trost, B. M., Verlag Chemie GmbH, Weinheim (1984), pp 299-316. (d) G. Desimoni and G. Tacconi, *Chem. Rev.* **75**, 651-692 (1975).

5. Catalyzed intramolecular asymmetric hetero Diels-Alder reactions: Tietze, L. F.; Saling, P. *Synlett.* **1992**, 281-282.
6. As preliminary works: (a) Wada, E.; Yasuoka, H.; Kanemasa, S. *Chem. Lett.* **1994**, 145-148. (b) Wada, E.; Yasuoka, H.; Kanemasa, S. *Chem. Lett.* **1994**, 1637-1640.
7. Belletire, J. L.; Spletzer, E. G. *Synth. Commun.* **1987**, *17*, 1701-1707.
8. John, R. A.; Schmid, V.; Wyler, H. *Helv. Chim. Acta.* **1987**, *70*, 600-606.
9. (a) Sammakia, T.; Smith, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 3949-3950. (b) Mori, A.; Ishihara, K.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 987-990.
10. Steven, V. L.; Lygo, B.; Sternfeld, F.; Wonnacott, A. *Tetrahedron.* **1986**, *42*, 4333-4342.
11. Oxley, P.; Partridge, M. W.; Robson, T. D.; Short, W. F. *J. Chem. Soc.* **1946**, 763-771.
12. Tavares, D. F.; O'sullivan, W. I.; Hauser, C. R. *J. Org. Chem.* **1962**, *27*, 1251-1254.
13. (a) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949-3954. (b) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340-5345 and references cited therein.
14. Subramanyam, V.; Silver, E. H.; Soloway, A. H. *J. Org. Chem.* **1976**, *41*, 1272-1273.
15. (a) Baldwin, J. E.; Walker, L. E. *J. Org. Chem.* **1966**, *31*, 3985-3989. (b) Miller, S. I. *J. Am. Chem. Soc.* **1956**, *78*, 6091-6095.
16. Lansbury, P. T.; Bebernitz, G. E.; Maynard, S. C.; and Spsgnolo, C. J. *Tetrahedron Lett.* **1985**, *26*, 169-172.

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