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S,O-Acetals as Novel "Chiral Aldehyde" Equivalents

Barry M. Trost,* Matthew L. Crawley, and Chul Bom Lee[a]

Abstract: Palladium-catalyzed asymmetric allylic alkylations (AAA) to form "chiral aldehyde" equivalents were investigated. α-Acetoxysulfones were formed in high enantiomeric excess as single regioisomers in AAA reactions of allylic geminal dicarboxylates with sodium benzenesulfinate. The directing ability of this novel functional group was highlighted by a series of dihydroxylations, affording *syn* diols exclusively *anti* to the acetoxy sulfone as single diastereomers in excellent yields. This is the first example of an asymmetric dihydroxylation protocol that gives the equivalent of reaction with a simple enal. The synthetic value of this process was exemplified by subsequent transformations of the diols including the development of a one-pot dihydroxylation–deprotective acyl migration protocol to give differentially protected 1,2-diols.

Keywords: allylation · allylic compounds · asymmetric synthesis · chiral aldehyde equivalents · palladium

Introduction

Stereospecific reactions of double bonds are an important challenge in organic synthesis. In principle there are many approaches to this problem. A particularly efficient solution is to utilize enantioselective catalysis to set an allylic sp^3 stereogenic center that can then direct functionalization of the olefin in a highly diastereoselective fashion. The use of asymmetric allylic alkylation (AAA) reactions has become a vibrant area of research that has specifically addressed this challenge in numerous total syntheses.[1] While there has been considerable progress forming stereogenic carbon–carbon and carbon–heteroatom bonds at a sp^3 center in AAA reactions,[2] successful installation of effective directing groups for acyclic substrates has been limited. An allylic *gem*-diacetate substrate, having two prochiral leaving groups, can undergo selective ionization in the presence of a chiral ligand giving enantioselective addition of a nucleophile.[3] The use of allylic geminal diacetates in the AAA reaction has provided a solution to the selective directing problem with carbon nucleophiles.[4] Addition of malonate nucleophiles proceeds enantioselectively and in the case of azlactones both enantio- and diastereoselectively. Both yield substrates that allow for stereospecific functionalization of the adjacent olefin.[5] This process is useful, though the question remained if a versatile directing group, one that is readily removed, transferred, or transformed could be installed through an asymmetric allylic alkylation.

The flexibility of the functionality contained in an α,β-unsaturated aldehyde led to the search for "chiral aldehyde" equivalents. Simple α,β-unsaturated aldehydes have not been observed to react in asymmetric dihydroxylations such as the Sharpless AD presumably because the aldehyde group is such a strong deactivator.[6] Rather, the corresponding allylic alcohol or enoate must be employed followed by subsequent oxidation or reduction. In some cases, this can be incompatible with other functionality in the substrate. Allylic acetals derived from chiral diols and enals have been used to direct stereocontrolled reactions, including cuprate additions, cyclopropanations, and additions of electrophiles to the adjacent olefin in a number of cases.[7] To evaluate the potential of these "chiral aldehyde" equivalents, two questions needed to be addressed: 1) could such compounds be easily accessed with high enantiopurity from AAA reactions and 2) will such derivatives exercise differential reactivity of the diastereotopic faces of the adjacent double bond? Asymmetric allylic alkylation with sodium benzenesulfinate as nucleophile using *gem*-dicarboxylates as substrates answered the first question through creation of chiral allylic α-acetoxysulfones with high yields and enantiomeric excess.[8] The requisite substrates for the AAA reaction were readily available and their syntheses are reviewed. The

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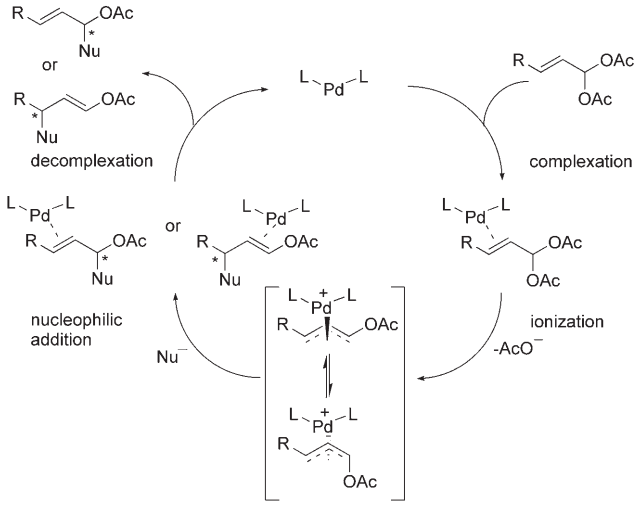
enantiopure substrates' ability to efficiently direct dihydroxylation of the α-olefin with complete stereocontrol is revealed. Discussion of the conversion to functionalized derivatives follows with one-pot dihydroxylation and unmasking reactions highlighted.

Concepts and Previous Work

The catalytic cycle of the AAA reaction with allylic *gem*-diacetates provides an opportunity for enantiotopic ionization of one of the two prochiral acetates (Scheme 1). While the *syn*,*syn* intermediate allyl complex should be formed kinetically, either the *syn*,*syn* or *syn*,*anti* complex may be the more reactive intermediate (Figure 1). Either complex can give rise to two possible regioisomers as adducts.



Scheme 1. Catalytic cycle of Pd-catalyzed alkylation of *gem*-diacetates.

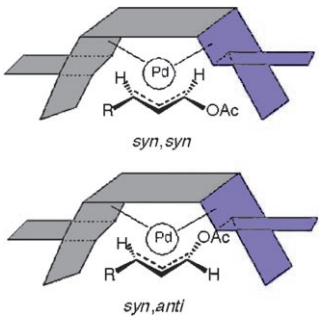
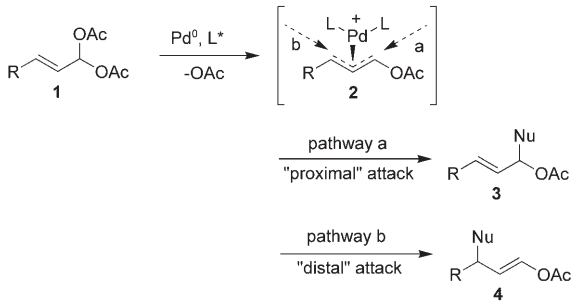


Figure 1. Palladium *syn*,*syn* and *syn*,*anti* ligand cartoons.

The alkylation adduct, a chiral allylic acetal equivalent, can be a versatile building block for synthesis, particularly if the newly formed stereogenic center can effectively direct other reactions with high diastereoselectivity. Formation of only one regioisomeric product resulting from a nucleophilic attack on the carboxy-substituted terminus is required to achieve this goal. Due to the unsymmetrical nature of the π-allyl generated from ionization of **1** either regioisomer in principle could be formed. However, only the "proximal" pathway adduct is observed with carbon or heteroatom nucleophiles when the steric bulk of R is larger than methyl. (Scheme 2). Even when R = methyl the "proximal" adduct **3** is major with a variety of nucleophiles.[9] These concepts were validated by the work of Trost and Lee who examined a variety of carbon nucleophiles with *gem*-diacetates and established the mechanism as outlined above and culminated in a total synthesis of sphingofungins E and F.[10,11]

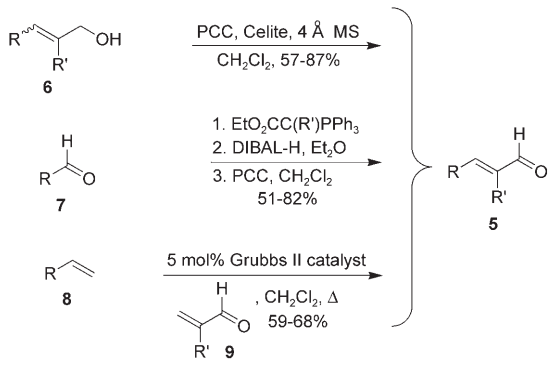


Scheme 2. Regiochemistry of the nucleophilic addition to the π-allyl complex.

Enantioselective synthesis of α-acetoxysulfones

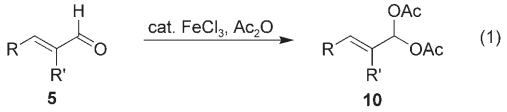
Synthesis of *gem*-diacetates: The synthesis of geminal dicarboxylates from aldehydes is a developed process that has been reported using protic acid catalysts[12] and more efficiently with Lewis acid catalysts.[13,14] An efficient route to the allylic diacetates starts with α,β-unsaturated aldehydes **5**. These aldehydes are readily available via a number of paths, that is, by purchase from commercial sources, through Wittig reactions of commercial alkyl aldehydes **7** followed by reduction–oxidation, through oxidation of *E* or *Z* allylic alcohols **6** with pyridinium chlorochromate, and through cross-metathesis reactions of terminal olefins **8** with enals **9** (Scheme 3).

The *gem*-diacetates were generally prepared by reaction of the enals with acetic anhydride catalyzed by ferric chloride in methylene chloride solution [Eq. (1)]. As summarized in Table 1, most of the aldehydes reacted cleanly with

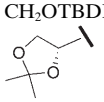


Scheme 3. Synthesis of α,β-unsaturated aldehydes.

Table 1. Preparation of allylic *gem*-1,1-diacetates using ferric chloride catalyst.



5 10 (1)

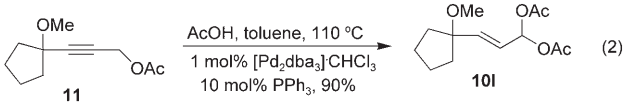
Entry	R	R′	Conditions	Product	Yield [%]
1	Ph	H	4 equiv Ac_2O, 1% $FeCl_3$, 0°C, 2 h	**10a**	87
2	Ph	Me	5 equiv Ac_2O, 1% $FeCl_3$, 0°C, 2 h	**10b**	83
3	(*o*-NO_2)-Ph	H	4 equiv Ac_2O, 1% $FeCl_3$, 0°C, 2 h	**10c**	91
4	(2-furyl)	H	4 equiv Ac_2O, 0.1% $FeCl_3$, 0°C, 0.5 h	**10d**	61
5	Pr	H	3 equiv Ac_2O, 0.5% $FeCl_3$, 0°C, 0.5 h	**10e**	73
6	hexyl	H	3 equiv Ac_2O, 0.2% $FeCl_3$, 0°C, 1 h	**10f**	94
7	*i*Pr	H	4 equiv Ac_2O, 0.5% $FeCl_3$, 0°C, 0.5 h	**10g**	64
8	-$(CH_2)_4$-		5 equiv Ac_2O, 1% $FeCl_3$, RT, 10 h	**10h**	50
9	$CH_2OTBDPS$	H	5 equiv Ac_2O, 0.5% $FeCl_3$, 0°C, 0.5 h	**10i**[a]	85
10		H	2 equiv Ac_2O, 1% $FeCl_3$, 0°C, 3 h	**10j**	79
11	CO_2Et	Me	3 equiv Ac_2O, 1% $FeCl_3$, 0°C, 0.5 h	**10k**	99

[a] Prepared according to ref. [4].

acetic anhydride under these conditions to give the *gem*-diacetates in good to excellent yields. A variety of enals were suitable, including aryl, alkyl, and ester substituted, both with di- and trisubstituted substrates.

The only instance where this method afforded a relatively modest yield (50%) of *gem*-diacetate was in the conversion of enal **5** to acetate **10h** (Table 1, entry 8). In this case not all of the starting material was converted at the specified catalyst loading. Unfortunately, raising the catalyst loading—while it did increase conversion—also resulted in the formation of undesired side products and did not have a positive effect on the overall yield.

While the most convenient route to access the *gem*-diacetates **10** was through the readily available (often commercial) enals **5**, some substrates were more easily accessible through propargylic ester acetates using a palladium-catalyzed redox isomerization–addition process.[15] One example is the case of substrate **11**, derived in four steps from cyclopentanone. This material was converted to *gem*-diacetate **10l** in 90% yield using three equivalents of acetic acid with 1% palladium dibenzylidene acetone catalyst loading [Eq. (2)]. This method was more useful than the conversion of the enal with ferric chloride as the ether of substrate **11** is readily cleaved by a strong Lewis acid.

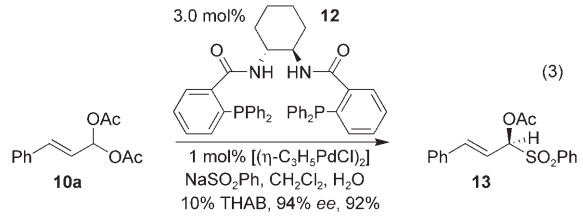


11 10l (2)

These diacetates were mainly crystalline and air stable, and could be stored indefinitely at room temperature under an inert atmosphere. The compounds were stable to both acidic (aqueous 1 N hydrochloric acid) and mild basic (aqueous sodium bicarbonate) conditions. The derivatives were readily distinguished in the ^1H NMR spectrum by the allylic acetal proton that displayed near δ 7.0 as a singlet or as a doublet with 5–8 Hertz coupling constant. These compounds displayed characteristic strong carbonyl bands in IR between 1760 and 1770 cm^{-1}.

Palladium-catalyzed AAA reactions with sodium benzenesulfinate: The versatility of allylic sulfones has been demonstrated by efficient control of diastereoselectivity in addition reactions to double bonds in cyclic systems.[16] These allylic sulfones are readily available in enantiomerically enriched or pure form by asymmetric allylic alkylations with sodium benzenesulfinate. While simple cyclic allylic sulfones exhibit high stereocontrol in the functionalization of the olefin, the selectivity in similarly substituted acyclic systems has been only modest.

A strategy to create a better directing group for acyclic systems was examined based on the observations that sulfinate nucleophiles function well in the asymmetric allylic alkylation (AAA) reaction and that allylic geminal diesters can be readily desymmetrized with carbon nucleophiles.[17] If chiral α-acetoxysulfones were formed with high enantiomeric excess they might subsequently direct a variety of desired transformations of the olefin with good stereocontrol. The observation that this asymmetric transformation could proceed using sodium benzenesulfinate on the prochiral diacetates with good *ee* was first made on a cinnamaldehyde derivative **13a** [Eq. (3); THAB = tetrahexylammonium bromide]; the reaction demonstrated that good enantioselectivity could be achieved.



10a 13 (3)

Expanding upon this promising lead observation, a wide variety of substrates with different substitution patterns was synthesized. Little improvement on the original conditions was necessary. Under optimized conditions the ligand to palladium catalyst ratio was fixed at 3.0:1.0 (1.5:1.0 with respect to palladium) to ensure excess phosphine was present to avoid formation of palladium black. A catalyst load of 1 to 2.5% was necessary to get complete conversion of starting diacetate to the product. Reaction of the *gem*-diacetates

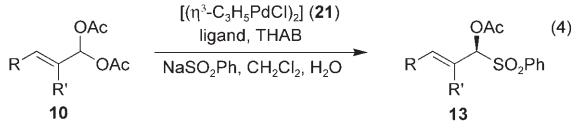
with this heteroatom nucleophile were performed under biphasic conditions (methylene chloride/water) using tetraalkylammonium salts as phase-transfer catalysts. It was also critical that the mixture be thoroughly deoxygenated to avoid formation of an inert ligand–palladium complex in which the amides are deprotonated and bound to palladium. The original conversion issues, where 5% catalyst loading was used, were resolved by this process. The reaction conditions for each substrate varied only with respect to reaction time, concentration, and temperature.

As was observed with carbon nucleophiles excellent control of regioselectivity was achieved (Table 2). Additionally, further reaction of the α-acetoxysulfone did not occur under the reaction conditions. The enantioselectivity of the reactions was determined by examination of the products using chiral high pressure liquid chromatography columns. Comparison of one enantiomer of adduct derived from chiral ligand to the adduct derived from the opposite ligand clearly established the selectivities. The C_2-symmetric ligand **10** derived from *trans*-1,2-diaminocyclohexane and 2-diphenylphosphinobenzoic acid gave *ee* values higher than the other ligands of this class. In some cases the other ligands gave no reaction. For the examples shown both enantiomers of the adduct were synthesized and in all cases similar *ee* values and yields were obtained. The absolute configuration of the products **13** was initially assigned by analogy to the previous results with carbon and other heteroatom nucleophiles. Later, derivatization studies and X-ray crystallography established both the relative and absolute stereochemistry.

The exceptional enantioselectivity and high yields across an array of substrates was notable for this AAA reaction. Both di- and trisubstituted olefins with aryl, alkyl, and ester substituents reacted without formation of byproducts. In all cases where reaction occurred only the desired regioisomer of product was observed. This was verified by ^{1}H NMR spectroscopy where the multiplicity and coupling patterns of the olefinic protons were consistent with the desired addition product.

Adducts **13d**, **13g**, **13h**, and **13k** (Table 2) were formed virtually enantiopure, with the minor enantiomer not detectable in all but one instance. The more sterically encumbered alkenes in some cases did not react completely in 24 h at

Table 2. Alkylations of *gem*-diacetates with sodium benzenesulfinate.



Entry	R	R′	Conditions	Product	Yield [%]	*ee* [%]
1	Ph	H	2 mol% **21**, 6 mol% **10a**, 0°C, 4 h	**13a**	89	98
2	Ph	H	2 mol% **21**, 6 mol% *ent*-**10a**, 0°C, 4 h	*ent*-**13a**	85	96
3	Ph	Me	2.5 mol% **21**, 7.5 mol% **10b**, RT, 24 h	**13b**	85[a]	95
4	Ph	Me	2.5 mol% **21**, 7.5 mol% *ent*-**10b**, RT, 24 h	*ent*-**13b**	86[a]	95
5	(*o*-NO_2)-Ph	H	2 mol% **21**, 6 mol% **10c**, 0°C, 2 h	**13c**	93	85
6	(*o*-NO_2)-Ph	H	2 mol% **21**, 6 mol% *ent*-**10c**, 0°C, 2 h	*ent*-**13c**	93	77
7	(2-furyl)	H	2.5 mol% **21**, 7.5 mol% **10d**, RT, 24 h	**13d**	64	>99
8	(2-furyl)	H	2.5 mol% **21**, 7.5 mol% *ent*-**10d**, RT, 24 h	*ent*-**13d**	64	99
9	Pr	H	2 mol% **21**, 6 mol% **10e**, 0°C, 4 h	**13e**	94	98
10	Pr	H	2 mol% **21**, 6 mol% *ent*-**10e**, 0°C, 4 h	*ent*-**13e**	93	95
11	hexyl	H	2 mol% **21**, 6 mol% **10f**, RT, 6 h	**13f**	73	95
12	hexyl	H	2 mol% **21**, 6 mol% *ent*-**10f**, RT, 6 h	*ent*-**13f**	73	90
13	*i*Pr	H	2 mol% **21**, 6 mol% **10g**, 0°C, 10 h	**13g**	86	>99
14	*i*Pr	H	2 mol% **21**, 6 mol% *ent*-**10g**, 0°C, 10 h	*ent*-**13g**	85	97
15	-$(CH_2)_4$-		2 mol% **21**, 6 mol% **10h**, RT, 48 h	**13h**	85[a]	>99
16	-$(CH_2)_4$-		2 mol% **21**, 6 mol%, *ent*-**10h**, RT, 48 h	*ent*-**13h**	80[a]	>99
17	CH_2OTBDPS	H	2 mol% **21**, 6 mol% **10i**, 0°C, 4 h	**13i**	92	94
18	CH_2OTBDPS	H	2 mol% **21**, 6 mol% *ent*-**10i**, 0°C, 4 h	*ent*-**13i**	91	94
19		H	2 mol% **21**, 6 mol% **10l**, RT, 24 h	**13l**	76[a]	80
20		H	2 mol% **21**, 6 mol% *ent*-**10l**, RT, 24 h	*ent*-**13l**	80	80
21		H	2 mol% **21**, 6 mol% **10j**, 0°C, 4 h	**13j**	86	24:1 *dr*[b]
22		H	2 mol% **21**, 6 mol% *ent*-**10j**, 0°C, 4 h	*ent*-**13j**	89	2:1 *dr*[b]
23	CO_2Et	Me	2 mol% **21**, 6 mol% **10k**, 0°C, 12 h	**13k**	85[a]	99
24	CO_2Et	Me	2 mol% **21**, 6 mol% *ent*-**10k**, 0°C, 12 h	*ent*-**13k**	83	98

[a] brsm = based on recovered starting material. [b] Diastereomeric ratio determined by ^{1}H NMR integration.

ambient temperature. Notably, only two substrates (**13c** and **13l**) gave *ee* values of $<90\%$. This was presumably due to a perturbation in the chiral pocket from adjacent steric encumberance, as simple electron withdrawing substituents did not cause a noticeable change in the enantioselectivity.

The effect of a pre-existing stereogenic center was examined. When the "matched" ligand was utilized, the resulting α-acetoxysulfone *dr* was >20:1 (Table 2, entry 21). However, while the "mismatched" ligand case was able to reduce the directing effect of the dimethylacetal (often 3:1 to 5:1), the result was still *anti* (with respect to the dimethylacetal) substitution, though in a modest 2:1 ratio (Table 2, entry 22). This was the only instance examined of a substrate with a proximal chiral center.

The α-acetoxysulfones in all cases were isolated by silica gel chromatography after separation of the aqueous and organic phases of the reaction. The compounds could be cleaved under basic conditions (using potassium carbonate in methanol, see section on liberation of the aldehyde) but were stable to various Lewis acids, even aqueous 1 N hydrochloric acid. The compounds exhibited longer shelf life when stored at 0 °C under inert atmosphere while storage in solvent at ambient temperature resulted in slow decay to the corresponding enal. The compounds were readily identified by ^{1}H NMR spectroscopy. With respect to the α-acetoxysulfone proton, all of the adducts with trisubstituted olefins had a characteristic singlet between δ 6.00 and 7.00; the disubstituted adducts exhibited a 5 to 8 Hz doublet between δ 6.00 and δ 7.00 ppm. This shift was always upfield (0.3–0.7 ppm) from the corresponding *gem*-diacetate proton.

Diastereoselective dihydroxylations: The products from the asymmetric allylic alkylations of *gem*-diacetates with sodium benzenesulfinate have a unique S,O-mixed acetal structure. We predicted that the electron-withdrawing effect and steric bulk of the phenylsulfonyl group in combination with the electronic effect of the acetoxy moiety together could effectively direct functionalization of the adjacent olefin in a highly diastereoselective fashion. The ground state conformation of the allylic α-acetoxysulfones as predicted by Macromodel using a conformation search with the MM2 force field in solution phase with chloroform as solvent has the phenylsulfonyl moiety nearly perpendicular to the plane of the double bond and the acetoxy group in a *syn* orientation (analogous to the "inside alkoxy" effect).[18] This suggested that high facial selectivity involving attack of an electrophile *anti* to the sulfone would be expected (Figure 2). The phenyl ring of the sulfone was oriented parallel to the olefin, which could allow a favorable π-orbital stacking interaction. Other low energy conformations also favored π-orbital stacking. The nearest low energy conformation that did not have significant overlap of the phenyl ring and the olefin was 0.4 kcal mol^{-1} higher in energy.

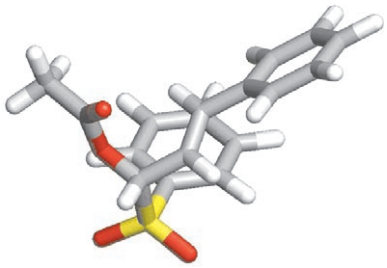
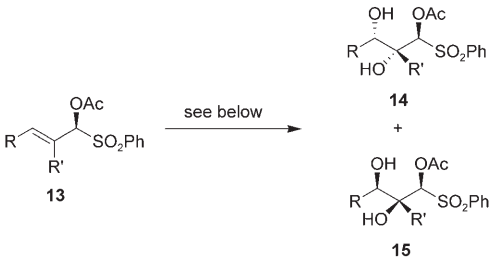


Figure 2. Energy-minimized conformation of α-acetoxysulfone **20a**.

The α-acetoxysulfone **13i** was tested for its reactivity in osmium tetroxide catalyzed dihydroxylation reactions. Using *N*-methylmorpholine-*N*-oxide (NMO) as the stoichiometric reoxidant, osmium tetroxide catalyzed dihydroxylations of the α-acetoxysulfones in methylene chloride initially afforded a modest *dr* of 6.5:1 in Table 3, as shown with the alkoxyalkyl derivative **13i** in its transformation to diols **14** and **15** [Table 3, Equation (5)]. Running the reaction at 0 °C compared with ambient temperature improved the diastereoselectivity to 12.5:1. Decreasing the osmium tetroxide loading from 10 to 5% further increased the dr to 18:1. Employing catalyst loadings under 5 mol% led to incomplete conversion after 24 h and did not further improve the selectivity.

Table 3. Initial results for the dihydroxylation of the allyl sulfone **13i**.



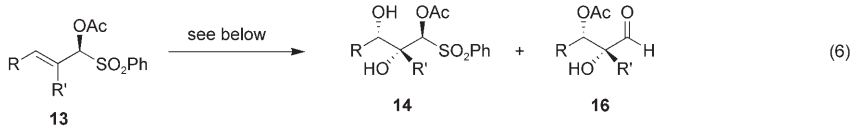
Entry	R	Conditions	Yield [%]	**14**:**15**[a]
1	TBDPSOCH$_2$ (**13i**)	10 mol% OsO_4, 3 equiv NMO, CH_2Cl_2, H_2O, RT, 12 h	87	6.5:1
2	TBDPSOCH$_2$ (**13i**)	10 mol% OsO_4, 3 equiv NMO, CH_2Cl_2, H_2O, 0 °C, 12 h	78	12.5:1
3	TBDPSOCH$_2$ (**13i**)	5 mol% OsO_4, 3 equiv NMO, CH_2Cl_2, H_2O, 0 °C, 24 h	80	18:1

[a] Diastereomeric ratio determined by ^{1}H NMR integration.

Based upon the conformation depicted in Figure 1, the major adduct **14** was tentatively assigned as the *syn* diol configured *anti* to the α-acetoxysulfones; this speculation was later confirmed. Under the optimized conditions (Table 3, entry 3) the other α-acetoxysulfones were dihydroxylated [Table 4, Equation (6)].

The dihydroxylations mainly afforded the expected *anti* diols, though certain substrates either decomposed or rearranged under the reaction conditions. The selectivity on a

Table 4. Dihydroxylations of α-acetoxysulfones using optimized conditions.



Entry	R	R′	Conditions[a]	Adduct	Yield [%]	*dr*[b]
1	Ph	H (**13a**)	standard	**14a**	77	>98:2
2	Ph	H (*ent*-**13a**)	standard	*ent*-**14a**	68	>98:2
3	Ph	H (**13a**)	standard + DABCO, *t*BuOH	*ent*-**14a**	78	>98:2
4	Ph	Me (**13b**)	standard	**14b**	57[c]	>98:2
5	(*o*-NO_2)-Ph	H (**13c**)	standard	**14c**	83	>98:2
6	Pr	H (**13e**)	standard	**14e**	61	95:5[d]
7	hexyl	H (**13f**)	standard	**14f**	84	>98:2
8	*i*Pr	H (*ent*-**13g**)	standard	*ent*-**14g**	81	>98:2
9	CH_2OTBDPS	H (*ent*-**13i**)	standard[d]	*ent*-**14i**	82	12:1
10	CH_2OTBDPS	H (**13i**)	standard	**14i**	81	18:1
11	CH_2OTBDPS	H (*ent*-**13i**)	standard + DABCO, *t*BuOH	*ent*-**14i**	71	11:1
12		H (**13j**)	standard	**14j**	85	6:1
13		H (**13l**)	standard	**14l**	71	96:4
14	CO_2Et	Me (**13k**)	standard	**16k**	94	>98:2[e]

[a] Unless otherwise noted all reactions were run with 5 mol% osmium tetroxide, 3 equiv *N*-methylmorpholine-*N*-oxide, in 0.1 M methylene chloride solution at 0°C. [b] Diastereomeric ratio determined by ^{1}H NMR integration. [c] 5% of the unmasked product formed and was inseparable from the major adduct. [d] 10 mol% osmium tetroxide was used in this case. [e] Diasteromeric and enantiomeric ratio.

wide range of substrates was outstanding and often complete. The conversions and yields were generally high, and the products were isolated by silica gel chromatography. While all adducts resulting from disubstituted olefin starting material were stable for months when stored under argon at 0°C, the adducts that were oils decomposed in a few days upon standing at room temperature.

There were several notable trends in the dihydroxylation reactions. The effect of DABCO and *tert*-butanol was negligible or negative on both yield and selectivity (Table 4, entries 1 vs 3 and 10 vs 11). As expected, smaller side chain groups (Table 4, entries 6, 9, 10) gave good *anti* selectivity though the selectivity was lower than that in the cases of more bulky substrates. Lowering the osmium tetroxide catalyst loading from 10 to 5% had a beneficial effect on diasteroeselectivity for substrate **13i** (Table 4, entries 9 and 10). The lower catalyst loading was then used for all other cases. Trisubstituted olefin **13b** (Table 4, entry 4) gave partial rearrangement to product **16b** under the reaction conditions. However, with the exception of substrate **13k** (Table 4, entry 14) which afforded **16k**, none of the substrates fully converted to a single rearranged product. This led to investigation of additives to force the rearrangement of the initial dihydroxylation adducts (see below).

Another question of interest was how the α-acetoxysulfones would compete against other directing groups. Entry 13 in Table 4 highlights an internal competition for directing the dihydroxylation. The dimethylacetal tends to be modestly *anti* directing (3:1 to 11:1)[19] and was mismatched with the strongly *anti* directing α-acetoxysulfone. The α-acetoxysulfone was the dominant directing group in this case displaying an energy preference of at least 2 kcal mol^{-1}, giving adduct **14j** in 6:1 *dr* (*syn* to the dimethylacetal).

Using a Macromodel driven conformational search with the MM2 force field in solution phase, the minimum energy conformation of diol **14a** was predicted to be consistent with the conformation needed for 1,3-acyl migration. Thus, a key observation from this model shows that the hydroxyl group β to the α-acetoxysulfone had a dihedral angle of 52° with the acetate group, while the α-hydroxyl group was on the opposite face (160°). Ultimately, the conformation that was predicted is nearly identical to that of the X-ray diffraction crystal structure obtained for **14a** (Figure 3). This helps to explain the preference for 1,3 versus 1,2-acyl migration, as discussed later.

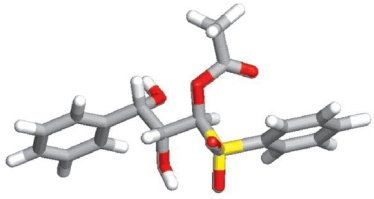


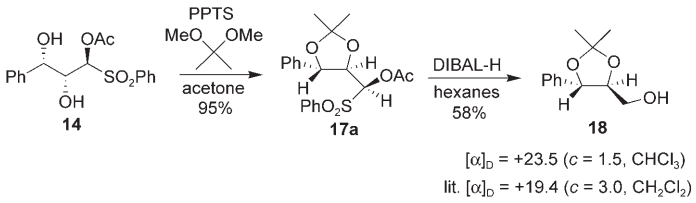
Figure 3. Minimum energy conformation and X-ray structure of diol **14a**.

The utility of this strategy to make diols stereoselectively was exemplified by diol *ent*-**14g** (Table 4, entry 8) obtained enantiomerically pure compared with 70% *ee* in the asymmetric dihydroxylation of methyl (*E*)-4-methyl-2-pente-

noate.[20] The dihydroxylated adduct was used as a key building block in the synthesis of a highly active analogue of *clasto*-lactacystin β-lactone.

The value of this strategy becomes clearer considering enals can not be directly dihydroxylated using the Sharpless methodology.[6] The result from entry 14, Table 4, shows a one pot protocol that afforded the dihydoxylated adduct of an enal with the diol differentially protected.

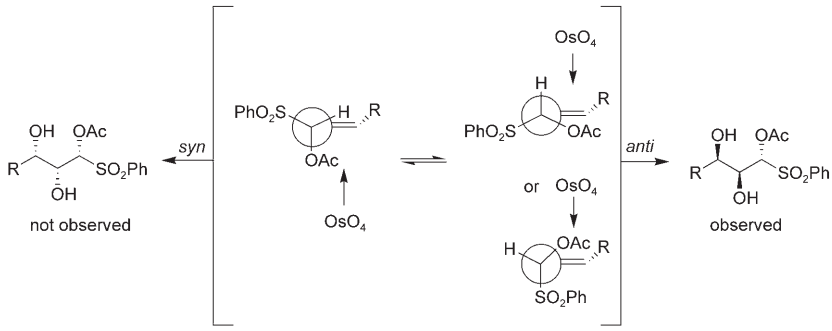
Determination of absolute stereochemistry: X-ray crystallography confirmed that the relative configuration of the diol to the α-acetoxysulfone was indeed *anti* (see Supporting Information for a three dimensional representation and crystal report; see also Figure 3). The absolute stereochemistry of the diol from the dihydroxylated adducts was established by derivatization to a known compound. Diol **14a** was protected as the dimethyl ketal to **17a** and reduced with diisobutylaluminum hydride to afford known triol **18** (Scheme 4). Full characterization data of enantiopure derivative **18** was previously established by Zhou and co-workers and matched the observed optical rotation and spectral data of the isolated product **18**.[21]



Scheme 4. Derivatization of diol **14a** to known triol **18**.

The establishment of the absolute stereochemistry of the two stereogenic centers combined with the relative stereochemistry of the three stereocenters as determined by X-ray crystallography proved the absolute and relative conformation of adduct **14a**. This result also verified that, as predicted, the AAA reactions using sodium benzensulfinate as a nucleophile did indeed proceed to give the same sense of chirality as with stabilized carbon and heteroatom nucleophiles.

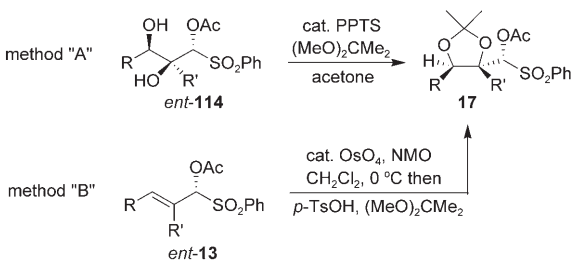
To rationalize the outcome of the dihydroxylation, it was helpful to use both the Stork–Houk–Jaeger "inside alkoxy" model[18] and the Vedejs model[22] for dihydroxylations of chiral allylic ethers. Adaptation of these models to the α-acetoxysulfone system predicts the osmium tetroxide approaching either directly *anti* to the sulfone with the acetate on the same face of the olefin as the approaching electrophile (Houk) or along the same plane as the hydrogen, with the acetate group inside but on the opposite face of the olefin (Vedejs) (Scheme 5). The Kishi model,[23] that would align the hydrogen eclipsing the olefin with the sulfone group on the same face as the approaching electrophile, predicts a conformation that was not compatible with the steric demands of this system.



Scheme 5. Rationale for observed selectivity in the dihydroxylation reaction.

Utility of the α-acetoxysulfones: One advantage presented by the acetoxysulfones for diastereoselective dihydroxylations is the possibility to selectively unmask and transform the substrate. Liberation of the aldehyde before or after protection of the diol, direct nucleophilic substitution on the mixed acetal, and aldehyde formation in situ during the dihydroxylation with simultaneous acyl transfer were all probed as methods to further functionalize the chiral adducts.

Derivatization to acetonides: Several of the *ent*-**14** diols were protected as the dimethyl ketal by treatment with 2,2-dimethoxypropane and pyridinium *p*-toluenesulfonate in acetone at ambient temperature (Scheme 6, method A). More conveniently, the same protection was achieved by direct treatment of the crude adduct of dihydroxylation with 2,2-dimethoxypropane using *p*-toluenesulfonic acid monohydrate as catalyst (Scheme 6, method B). Four acetonides **17** containing both di- and trisubstituted alkenes with both aryl and alkyl substituents were formed in high yields (Table 5). The acetonides were stable, amorphous solids that showed no sign of decomposition after a significant time stored at ambient temperature.



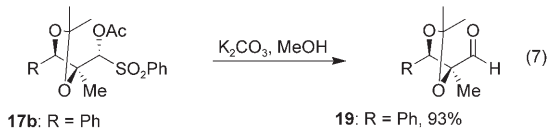
Scheme 6. Protection of the diols as acetonides.

Table 5. Synthesis of acetonide derivatives.

Entry	R	R′	Method	Compound	Yield [%]
1	Ph	H	A	**17a**	92
2	Ph	Me	B	**17b**	81[a]
3	Pr	H	A	*ent*-**17c**	95
4	*i*Pr	H	A	**17d**	83

[a] Two-step one-pot yield from the α-acetoxysulfone.

Liberation of the aldehyde: An obvious way to transform the α-acetoxysulfone to a reactive functional group is direct liberation to the aldehyde under basic conditions. With adducts derived from disubstituted olefins, the conditions for direct liberation led to epimerization of the α-stereogenic center and or elimination/decomposition. However, with trisubstituted alkene **17b** mild conditions (potassium carbonate and methanol) gave α,β-acetonide aldehyde **19** in excellent yield. Tetrasubstitution at the α-stereogenic center prevented epimerization or elimination [Eq. (7)].

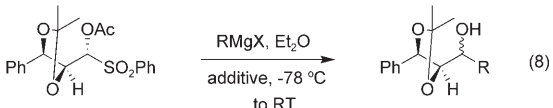


17b: R = Ph

19: R = Ph, 93% (7)

Direct addition of nucleophiles to the α-acetoxysulfone: The dihydroxylation, protection, liberation sequence was highly selective and proceeded in good yield. However, two steps to the aldehyde are required to allow for nucleophilic addition. An alternative envisions a one-pot dihydroxylation protection protocol followed by direct reaction with a nucleophile, one that unmasks and then reacts with the aldehyde in situ.

Initial addition to the cinnamaldehyde derived acetonide **17a** was attempted with alkyl Grignard reagents [Eq. (8)].



17a

21: R = Me
22: R = Et (8)

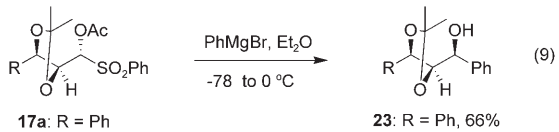
While excess nucleophile liberated the aldehyde in situ and then subsequently added, the diastereoselectivity was poor (Table 6). Variation of the temperature or addition of additives did not improve the result. Despite the low stereoselectivity, this process allows useful access to various substituted alkylketones with a chiral α,β-acetonide after oxidation.

A surprising result, given the poor selectivity the alkyl Grignard reagents, was observed with phenylmagnesium bromide as the nucleophile. Addition to acetoxysulfones **17a** and **17c** afforded only one diastereomeric alcohol, **23** and **24** respectively, in good yield [Eq. (9)]. The relative ster-

Table 6. Addition of alkyl Grignard reactions to acetonide.

Entry	RMgX	Additive	Yield [%]	*dr*[a]
1	MeMgBr	–[b]	87	1.5:1
2	MeMgBr	–[c]	87	1.5:1
3	EtMgBr	–[b]	74	2.2:1
4	MeMgBr	CuBr[c]	88	1.5:1
5	MeMgBr	$MgCl_2$[c]	84	1.5:1

[a] Determined by ^{1}H NMR integration. [b] Reaction run at 0 °C. [c] Reaction run at −78 °C.

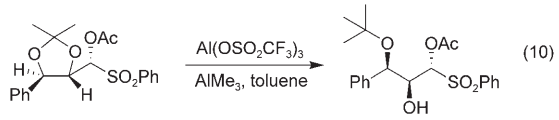


17a: R = Ph
17c: R = *i*Pr

23: R = Ph, 66%
24: R = *i*Pr, 82% (9)

eochemistry of addition was tentatively assigned as shown based on an α-alkoxy chelate controlled model via a five membered-cyclic transition state for addition of the phenyl magnesium bromide. The coupling constants of 5 to 7 Hz for the protons α to the hydroxyl group was also consistent with other *syn* adducts, though this correlation is not always accurate.[18]

Separately, an attempted liberation of the aldehyde from α-acetoxysulfone **17a** in situ followed by addition of a methyl group with trimethylaluminum did not proceed as expected. The Lewis acidity of the aluminum derivatives was strong enough to promote chemoselective cleavage of the acetonide **17a** to afford adduct **25** [Eq. (10)]. This reaction is useful as the acetoxysulfone moiety was not labile under these conditions and afforded a differentially protected triol as the adduct.



17a

25 (10)

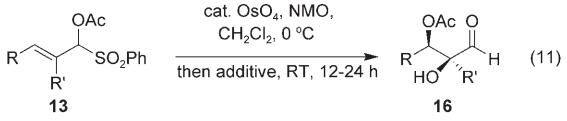
Nucleophilic addition of hydrides, such as utilized in the protocol to establish the absolute stereochemistry, can also directly unmask and subsequently reduce the α-acetoxysulfone to the corresponding alcohol **18**. While only a handful of nucleophiles were examined for direct addition, the results demonstrate the viability of a one-pot unmasking–addition sequence and suggest it may proceed with high diastereoselectivity.

One-pot dihydroxylation–deprotective acyl migration protocol: An arguable disadvantage of the α-acetoxysulfone as a "chiral aldehyde" equivalent is the extra step it takes to prepare the sulfone compared with a direct enantioselective reaction of the olefin.[24] However, it has been noted that such a protocol fails with α,β-unsaturated aldehyde which is

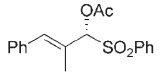
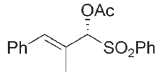
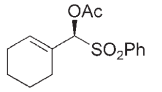
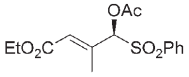
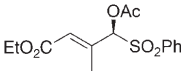
the equivalent of the process reported herein. Furthermore, if, in a one-pot protocol the dihydroxylation, aldehyde unmasking, and differential protection of the diol were possible, an additional advantage to this protocol accrues.

The observation that the diols derived from trisubstituted olefins are relatively unstable led to speculation that slow but spontaneous acyl transfer was occurring. The minimum energy conformation of the dihydroxylated α-acetoxysulfone from Macromodel and X-ray crystal structure indicated the acyl group was nicely aligned for a 1,3-migration. Using intramolecular transesterification catalysts, several direct transformations of acetoxysulfones **13** to differentiated diol **16** were achieved [Table 7, Equation (11)]. While in some instances longer reaction time or dibutyltin oxide were sufficient to promote the acyl migration, the most effective method involved the use of 4-dimethylaminopyridine.

Table 7. Selective one-pot dihydroxylation–differential protection unmasking.



13 16 (11)

Entry	Substrate	Additive	Product	Yield [%][a]	*dr*
1		nBu$_2$SnO	*ent*-**16b**	31	>98:2
2		4-DMAP	*ent*-**16b**	92	>98:2
3		4-DMAP	1,2- and 1,3-acyl transfer, and decomposition products	–	–
4		–	**16k**	94	>98:2
5		4-DMAP	**16k**	98	>98:2

[a] With the exception of entry 7, these reactions were run at 0 °C for 12 h, the additive added, and then at RT for 12 h. The reaction in entry 7 only required 1 h at RT after the dihydroxylation was complete.

Most of these transformations proceeded to give a single adduct with no byproducts. The adducts in entries 1 and 2 (Table 7) were identical to those obtained by a stepwise dihydroxylation and the deprotective acyl-migration protocol. One exception was the case of the cyclic sulfone *ent*-**13i** (Table 7, entry 3), where both 1,2- and 1,3-acyl transfer occurred along with decomposition. It is notable that the overall yields for these processes were significantly higher than for dihydroxylation alone, presumably due to acyl migration during isolation of the free diol. While 4-dimethylaminopyridine was not necessary to facilitate the 1,3-acyl-migration in the case of substrate **16k** (Table 7, entries 4 and 5), it did increase the rate of reaction (completed in 4 h versus 16 h).

Summary

A versatile "chiral aldehyde" equivalent with exceptional directing ability has been discovered and is readily accessible through an asymmetric allylic alkylation of *gem*-diacetates using sodium benzenesulfinate as the nucleophile. The *gem*-diacetate precursors to the sulfones were available in high yields from the corresponding enals or propargylic acetates; those substrates were commercially available or derived in one to two steps. The enantioselectivity created in the α-acetoxysulfone adducts was remarkable, almost always in excess of 95%. The directing ability of this "chiral aldehyde" equivalent was exemplified in diastereoselective dihydroxylations that in all cases proceeded with high diastereoselectivity and often with complete control. The diol derivatives were readily and sometimes spontaneously unmasked, and the unmasking could take place as a one-pot operation with the dihydroxylation. The protocol for chemoselective 1,3-acyl transfer giving a one pot dihydroxylation, differential protection, and aldehyde unmasking was particularly useful as it gave products that the Sharpless asymmetric dihydroxylation could not form from the corresponding enals. The high conformational bias of the acetoxy sulfones provides an opportunity for other diastereoselective elaborations of the adjacent double bond as well as ease of unmasking of the aldehyde. Combined with its robustness to numerous electrophilic reagents, this new type of "chiral aldehyde" complements the use of chiral acetals which typically involve nucleophilic additions rather than electrophilic additions as in the case here.

Experimental Section

General methods: PE = petroleum ether b.p. 40–60 °C.

General procedure for ferric chloride catalyzed preparation of *gem*-diacetates: An aldehyde, neat or dissolved in a minimal amount of methylene chloride at 0 °C, was added to freshly distilled acetic anhydride. After 5 min, a catalytic amount of anhydrous ferric chloride was added to the solution, and stirring was continued at 0 °C or RT. The progress of the reaction was monitored by TLC. After the complete conversion of the starting aldehyde, the reaction mixture was poured into water and extracted with Et_2O. The combined organic extracts were washed with water and dried over anhydrous sodium sulfate. The solution was concen-

trated in vacuo and the residue was purified by silica gel flash chromatography or recrystallization.

(*E*)-1,1-Diacetoxy-2-methyl-3-phenyl-2-propene (10b): Following the general procedure, acetic anhydride (15.3 g, 150 mmol) and α-methyl-*trans*-cinnamaldehyde (**5b**; 4.39 g, 30.0 mmol) in methylene chloride (50 mL) were stirred in the presence of ferric chloride (64.8 mg, 0.400 mmol) at 0 °C for 2 h. Flash chromatography (PE/ethyl acetate 8:1) afforded product **10b** as a colorless oil (6.29 g, 83 %). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.32–7.25 (m, 5H), 7.20 (s, 1H), 6.75 (s, 1H), 2.12 (s, 6H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 136.0, 131.2, 130.9, 129.2, 128.3, 127.4, 92.9, 20.8, 12.3; IR (film): $\tilde{\nu}$ = 2990, 1765, 1493, 1444, 1372, 1241, 1203, 1072, 1007 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{16}O_4$: C 67.73, H 6.50; found: C 67.52, H 6.40.

(*E*)-1,1-Diacetoxy-3-(2-nitrophenyl)-2-propene (10c): Following the general procedure, *trans*-2-nitrocinnamaldehyde (**5c**; 1.77 g, 10.0 mmol) and acetic anhydride (4.08 g, 40.0 mmol) in methylene chloride (10.0 mL) were stirred in the presence of ferric chloride (16.2 mg, 0.100 mmol) for 1 h at 0 °C. Flash chromatography (PE/Et_2O 3:1) afforded diacetate **10c** as a white solid (2.54 g, 91 %). M.p. 73.5–74 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 8.2 Hz, 1H), 7.62–7.60 (m, 2H), 7.52–7.35 (m, 3H), 6.18 (dd, J = 15.7, 5.5 Hz, 1H), 2.15 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.6, 148.0, 133.3, 131.2, 130.6, 129.2, 128.9, 126.9, 124.7, 88.4, 20.6; IR (film): $\tilde{\nu}$ = 2986, 1765, 1608, 1526, 1347, 1240, 1202, 1150, 1009 cm^{-1}; HRMS: m/z: calcd for $C_9H_{10}NO_4$: 220.0611; found: 220.0605 [$M^+ - C_2H_3O_2$].

(*E*)-1,1-Diacetoxy-3-(2-furyl)-2-propene (10d): Following the general procedure, *trans*-3-(2-furyl)-acrolein (**5d**; 1.22 g, 10.0 mmol) and acetic anhydride (4.08 g, 40.0 mmol) in methylene chloride (10.0 mL) was stirred with a few drops of H_2SO_4 for 1 h. Flash chromatography (PE/Et_2O 3:1) afforded the diacetate product **10d** as a clear oil (1.31 g, 61 %). Note: the product decomposes at RT in a matter of days to a brown tar. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (br s, 1H), 7.27 (d, J = 6.4 Hz, 1H), 6.66 (d, J = 16.0 Hz, 1H), 6.40–6.39 (m, 2H), 6.10 (dd, J = 16.0, 6.4 Hz, 1H), 2.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 151.0, 143.2, 123.3, 119.8, 111.6, 111.0, 89.4, 20.8; IR (film): $\tilde{\nu}$ = 2990, 1762, 1664, 1489, 1374, 1239, 1205, 1139, 1051 cm^{-1}.

(*E*)-1,1-Diacetoxy-2-hexene (10e): Following the general procedure, 2-hexenal (**5e**; 1.96 g, 20.0 mmol) and acetic anhydride (6.12 g, 60.0 mmol) were stirred in the presence of ferric chloride (16.2 mg, 0.10 mmol) at 0 °C for 30 min. Flash chromatography (PE/Et_2O 8:1) afforded product **10e** as a clear oil (2.94 g, 73 %). The characterization data matched known values. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (d, J = 6.5 Hz, 1H), 6.00 (dt, J = 15.5, 2.3 Hz, 1H), 5.55 (dd, J = 15.5, 6.5 Hz, 1H), 2.23–2.00 (m, 8H), 1.48–1.34 (m, 2H), 0.84 (t, J = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7, 138.8, 123.3, 89.7, 33.8, 26.4, 20.7, 13.4; IR (film): $\tilde{\nu}$ = 2962, 1763, 1676, 1372, 1242, 1205, 1051 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{16}O_4$: C 59.98, H 8.05; found: C 60.00, H 7.96.

(*E*)-1,1-Diacetoxy-2-nonene (10f): Following the general procedure, *trans*-2-nonenal (**5f**; 2.80 g, 20.00 mmol) and acetic anhydride (6.13 g, 60.0 mmol) were stirred in the presence of ferric chloride (32.4 mg, 0.200 mmol) at 0 °C for 1 h. Flash chromatography (PE/Et_2O 6:1) afforded diacetate **10f** as a clear yellow oil (4.57 g, 94 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (d, J = 6.3 Hz, 1H), 6.00 (dt, J = 15.5, 7.5 Hz, 1H), 5.51 (dd, J = 15.5, 7.5 Hz, 1H), 2.08 (s, 6H), 2.08–2.06 (m, 2H), 1.31–1.18 (m, 8H), 0.85 (t, J = 9.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 138.3, 123.0, 89.8, 31.8, 31.5, 28.6, 28.2, 22.4, 20.8, 13.9; IR (film): $\tilde{\nu}$ = 2929, 1765, 1676, 1459, 1435, 1372, 1241, 1206, 1120 cm^{-1}; HRMS: m/z: calcd for $C_{11}H_{19}O_2$: 183.1378; found: 183.1303 [$M^+ - C_2H_3O_2$].

1,1-Diacetoxy-4-methyl-2-(*E*)-pentene (10g): Following the general procedure, 4-methyl-2-pentenal (**5g**; 1.20 g, 12.2 mmol) and acetic anhydride (5.10 g, 50.0 mmol) were stirred in the presence of ferric chloride (32.4 mg, 0.200 mmol) at 0 °C for 0.5 h. Flash chromatography (PE/Et_2O 6:1) afforded product **10g** as a colorless oil (1.58 g, 64 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (d, J = 6.3 Hz, 1H), 5.99 (dd, J = 15.8, 6.3 Hz, 1H), 5.47 (ddd, J = 15.7, 6.3, 1.4 Hz, 1H), 2.40–2.28 (m, 1H), 2.08 (s, 6H), 1.03 (d, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 144.6, 120.4, 89.8, 30.5, 21.5, 20.9; IR (film): $\tilde{\nu}$ = 1766, 1675, 1372, 1240, 1202, 1008 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{16}O_4$: C 59.98, H 8.05; found: C 59.76, H 8.15.

1-(1′,1′-Diacetoxy)-1-cyclohexene (10h): Following the general procedure, 1-cyclohexene-1-carboxaldehyde (**5h**; 990 mg, 9.00 mmol) and acetic anhydride (4.59 g, 45.0 mmol) were stirred in the presence of ferric chloride (14.5 mg, 0.09 mmol) at 0 °C for 10 h. Flash chromatography (PE/Et_2O 4:1) afforded diacetate **10h** as a clear oil (0.947 g, 50 %). The characterization data matched known values. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.02 (s, 1H), 6.00 (s, 1H), 2.09–2.00 (m, 8H), 1.67–1.60 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.7, 132.0, 128.6, 91.6, 24.6, 22.3, 21.8, 20.8; IR ($CHCl_3$): $\tilde{\nu}$ = 2934, 1764, 1438, 1372, 1240, 1206, 1008 cm^{-1}; HRMS: m/z: calcd for $C_9H_{14}O_3$: 170.0943; found: 170.0940 [$M^+ - C_2H_2O$].

(*S*)-2,2-Dimethyl-4-(3′,3′-diacetoxy-1′-(*E*)-propenyl)-1,3-dioxolane (10j): Following the general procedure, aldehyde **5j**[25] (469 mg, 3.00 mmol) and acetic anhydride (612 mg, 6.00 mmol) were stirred in the presence of ferric chloride (4.8 mg, 0.030 mmol) at 0 °C for 120 min. Flash chromatography (PE/Et_2O 2:1) afforded diacetate **10j** as a clear oil (614 mg, 79 %). $[\alpha]_D$ = +42.5 ± 0.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (d, J = 5.5 Hz, 1H), 5.99 (dd, J = 15.8, 5.6 Hz, 1H), 5.82 (dd, J = 15.8, 5.7 Hz, 1H), 4.55 (q, J = 7.0 Hz, 1H), 4.15 (dd, J = 7.5, 6.4 Hz, 1H), 3.62 (dd, J = 7.5, 6.5 Hz, 1H), 2.09 (s, 6H), 1.44 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 133.9, 125.8, 109.7, 88.3, 75.3, 69.0, 26.4, 25.6, 20.7; IR (film): $\tilde{\nu}$ = 2898, 1765, 1372, 1238, 1203, 1127, 1060 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{18}O_6$: C 55.81, H 7.02; found: C 55.91, H 6.88.

(*E*)-Ethyl 3-methyl-4-diacetoxycrotonate (10k): Following the general procedure, ethyl 3-methyl-4-oxocrotonate (**5k**; 1.42 g, 10.0 mmol) and acetic anhydride (3.06 g, 30.0 mmol) were stirred in the presence of ferric chloride (16.2 mg, 0.100 mmol) at 0 °C for 30 min. Flash chromatography (PE/Et_2O 4:1) afforded product **10k** as a clear oil (2.66 g, 99 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.08 (s, 1H), 6.07 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.18 (s, 3H), 2.13 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 165.8, 148.4, 120.1, 90.5, 60.2, 20.6, 14.1, 13.2; IR (film): $\tilde{\nu}$ = 2984, 1770, 1722, 1667, 1435, 1372, 1225, 1163, 1046, 1008 cm^{-1}; HRMS: m/z: calcd for $C_9H_{16}O_4$: 185.0809; found: 185.0808 [$M^+ - C_2H_3O_2$].

(*E*)-1,1-Diacetoxy-3-(1′-methoxycyclopentyl)-2-propene (10l): $[Pd_2dba_3]\cdot CHCl_3$ (47.0 mg, 0.040 mmol) and PPh_3 (105 mg, 0.400 mmol) were added to a flame dried flask which was then vacuum degassed and filled with argon. Toluene (10 mL) was added and the solution was degassed under vacuum. Acetic acid (720 mg, 12.0 mmol) was added and the solution was stirred for 5 min under argon. A degassed solution of alkyne **11** (786 mg, 4.00 mmol) in toluene (10 mL) was added under argon and the mixture was heated to 110 °C for 4 h. Flash chromatography (PE/Et_2O 5:1) afforded diacetate **10l** as a clear oil (922 mg, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (d, J = 5.8 Hz, 1H), 6.03 (d, J = 15.8 Hz, 1H), 5.67 (dd, J = 15.8, 6.1 Hz, 1H), 3.12 (s, 3H), 2.10 (s, 6H), 1.88–1.57 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8, 139.7, 122.9, 89.3, 86.1, 50.9, 35.7, 23.0, 20.8; IR (film): $\tilde{\nu}$ = 2965, 1765, 1436, 1373, 1241, 1203, 1068 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{20}O$: C 60.92, H 7.87; found: C 60.82, H 7.71.

General procedure for asymmetric alkylation of allylic geminal dicarboxylates with sodium benzenesulfinate: A solution of allylic diacetate **10**, π-allylpalladium chloride dimer, and ligand in methylene chloride was added at 0 °C or RT to a degassed solution of sodium benzenesulfinate and tetraalkylammonium bromide in water. After stirring at 0 °C or RT under argon until TLC indicated the reaction was complete, the mixture was poured into water. The solution was extracted with diethyl ether and the combined organic phases were washed with brine the organic phase dried over magnesium sulfate, and concentrated in vacuo. The residue was purified by silica gel flash chromatography.

(*E*,*S*)-1-Acetoxy-1-phenylsulfonyl-3-phenyl-2-propene (13a): Following the general procedure, a solution of diacetate **10a** (108 mg, 0.462 mmol), π-allylpalladium chloride dimer (3.38 mg, 0.0092 mmol), and ligand **12** (19.0 mg, 0.028 mmol) in methylene chloride (1.00 mL) was added at 0 °C to sodium benzenesulfinate (114.9 mg, 0.700 mmol) and tetrahexylammonium bromide (39.14 mg, 0.0920 mmol) in water (1.00 mL). The reaction

mixture was stirred at 0 °C for 2 h. Flash chromatography (PE/ethyl acetate 6:1) afforded **13a** a white solid (140 mg, 89 %). M.p. 116–117 °C; $[\alpha]_D = -19.9 \pm 0.1$ ($c = 1.32$, $CHCl_3$); $t_r(S) = 12.85$ min, $t_r(R) = 15.24$ min, 98 % *ee*, (Chiralcel OD, $\lambda = 254$ nm, heptane/*i*PrOH 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.89 (m, 2H), 7.68 (t, $J = 7.4$ Hz, 1H), 7.54 (t, $J = 8.1$ Hz, 2H), 7.36–7.31 (m, 5H), 6.75 (dd, 15.9, 0.9 Hz, 1H), 6.40 (dd, $J = 7.3$, 1.0 Hz, 1H), 6.17 (dd, $J = 16.1$, 7.2 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 139.4, 135.8, 134.9, 134.5, 129.8, 129.2, 128.8, 127.2, 115.9, 86.8, 20.4; IR (film): $\tilde{\nu}$ = 1765, 1448, 1372, 1324, 1204, 1151, 1082, 1032 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{16}O_4S$: C 64.54, H 5.10; found: C 64.60, H 5.28.

(*E*,*R*)-1-Acetoxy-1-phenylsulfonyl-3-phenyl-2-propene (*ent*-13a): Following the general procedure, a solution of diacetate **10a** (108 mg, 0.462 mmol), π-allylpalladium chloride dimer (3.38 mg, 0.0092 mmol), and ligand **12** (19.0 mg, 0.028 mmol) in methylene chloride (1.00 mL) was added at 0 °C to sodium benzenesulfinate (114.9 mg, 0.700 mmol) and tetrahexylammonium bromide (39.14 mg, 0.0920 mmol) in water (1.00 mL). The reaction mixture was stirred at 0 °C for 2 h. Flash chromatography (PE/ethyl acetate 6:1) afforded *ent*-**13a** as a white solid (134 mg, 85 %). M.p. 116.5–117 °C; $[\alpha]_D = +20.6 \pm 0.3$ ($c = 1.10$, $CHCl_3$); $t_r(S) =$ 12.92 min, $t_r(R) = 15.00$ min, 96 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 9:1).

(*E*,*S*)-1-Acetoxy-2-methyl-1-phenylsulfonyl-3-phenyl-2-propene (13b): Following the general procedure, a solution of diacetate **13b** (248 mg, 1.00 mmol), π-allylpalladium chloride dimer (9.10 mg, 0.025 mmol), and ligand **12** (51.0 mg, 0.075 mmol) in methylene chloride (2.50 mL) was added at RT to sodium benzenesulfinate (492 mg, 3.00 mmol) and tetramethylammonium bromide (30.8 mg, 0.200 mmol) in water (2.50 mL). The reaction mixture was stirred at RT for 24 h. Flash chromatography (PE/Et_2O 3:1) to afford starting material (161 mg) and product as a white solid (97 mg, 30 %, 85 % based on recovered material (brsm)). Both the IR and ^{1}H NMR characterization data matched known values. The sign of rotation was opposite to that of **13b**; the magnitude of the rotation was similar. M.p. 95–96 °C; $[\alpha]_D = +45.7 \pm 0.1$ ($c = 1.06$, $CHCl_3$); $t_r(S) = 15.05$ min, $t_r(R) = 19.69$ min, 95 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.89 (m, 2H), 7.70 (t, $J = 7.4$ Hz, 1H), 7.59–7.54 (m, 2H), 7.36–7.19 (m, 5H), 6.48 (s, 1H), 6.24 (s, 1H), 2.12 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 135.9, 135.8, 134.5, 134.4, 129.8, 129.1, 128.3, 127.7, 127.0, 124.8, 124.7, 90.3, 20.4, 15.3; IR (film): $\tilde{\nu}$ = 2965, 1760, 1586, 1493, 1447, 1323, 1204, 1150, 1058 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{18}O_4S$: C 65.47, H 5.49; found: C 65.59, H 5.57.

(*E*,*R*)-1-Acetoxy-2-methyl-1-phenylsulfonyl-3-phenyl-2-propene (*ent*-13b): Following the general procedure, a solution of diacetate **10b** (248 mg, 1.00 mmol), π-allylpalladium chloride dimer (9.10 mg, 0.025 mmol), and ligand *ent*-**12** (51.0 mg, 0.075 mmol) in methylene chloride (2.50 mL) was added at RT to sodium benzenesulfinate (492 mg, 3.00 mmol) and tetramethylammonium bromide (30.8 mg, 0.200 mmol) in water (2.50 mL). The reaction mixture was stirred at RT for 24 h. Flash chromatography (PE/Et_2O 3:1) to afford starting material (93 mg) and product *ent*-**13b** as a white solid (130 mg, 54 %, 86 % brsm). M.p. 95–96 °C; $[\alpha]_D = -48.8 \pm 0.1$ ($c = 2.10$, $CHCl_3$); $t_r(S) = 14.36$ min, $t_r(R) =$ 17.88 min, >95 % *ee*, (Chiralcel OD, $\lambda = 254$ nm, heptane/*i*PrOH 95:5).

(*E*,*S*)-1-Acetoxy-1-phenylsulfonyl-3-(2-nitrophenyl)-2-propene (13c): Following the general procedure, a solution of allylic diacetate **10c** (140 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.0100 mmol), and ligand *ent*-**12** (20.7 mg, 0.0300 mmol) in methylene chloride (1.00 mL) was added at 0 °C to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.4 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred at 0 °C for 2 h. Flash chromatography (PE/Et_2O 1:1) afforded **13c** as a white solid (168 mg, 93 %). M.p. 162–163 °C; $[\alpha]_D = +8.6 \pm 0.6$ ($c = 1.30$, $CHCl_3$); $t_r(S) = 21.80$ min, $t_r(R) =$ 23.05 min, 85 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02–7.90 (m, 3H), 7.72–7.49 (m, 6H), 7.25 (d, $J = 4.5$ Hz, 1H), 6.48 (d, 6.9 Hz, 1H), 6.28 (dd, $J = 9.5$, 6.2 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.8, 147.8, 135.5, 134.7, 133.7, 133.5, 131.0, 129.7, 129.6, 129.1, 129.0, 124.8, 121.5, 85.8, 20.2; IR (film): $\tilde{\nu}$ = 3069, 2926, 1770, 1608, 1524, 1448, 1327, 1202, 1153 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{15}NO_6S$: C 64.54, H 5.10; found C 64.36, H 5.20.

(*E*,*R*)-1-Acetoxy-1-phenylsulfonyl-3-(2-nitrophenyl)-2-propene (*ent*-13c): Following the general procedure, a solution of allylic diacetate **10c** (140 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.0100 mmol), and ligand *ent*-**12** (20.7 mg, 0.0300 mmol) in methylene chloride (1.00 mL) was added at 0 °C to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.4 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred at 0 °C for 2 h. Flash chromatography (PE/Et_2O 1:1) afforded *ent*-**13c** as a white solid (168 mg, 93 %). M.p. 163–166 °C; $[\alpha]_D = -7.8 \pm 0.2$ ($c = 1.30$, $CHCl_3$); $t_r(S) = 21.93$ min, $t_r(R) = 23.11$ min, 77 % *ee*, (Chiralcel OD, $\lambda =$ 230 nm, heptane/*i*PrOH 9:1).

(*E*,*S*)-1-Acetoxy-1-phenylsulfonyl-3-(2-furyl)-2-propene (13d): Following the general procedure, a solution of furan **10d** (112 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.010 mmol), and ligand **12** (20.7 mg, 0.030 mmol) in methylene chloride (1.00 mL) was added at RT to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.5 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred at RT for 24 h. Flash chromatography (PE/Et_2O 2:1) afforded **13d** as a white solid (99 mg, 64 %). M.p. 89–89.5 °C; $[\alpha]_D = -70.9 \pm 0.1$ ($c = 1.05$, $CHCl_3$); $t_r(S) = 11.46$ min, 100 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.89 (m, 2H), 7.68 (dd, $J = 6.0$, 1.2 Hz, 1H), 7.59–7.54 (m, 2H), 7.39 (br s, 1H), 6.57 (d, $J = 15.0$ Hz, 1H), 6.40–6.34 (m, 3H), 6.08 (dd, $J = 15.0$, 7.0 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.9, 150.8, 143.5, 135.6, 134.4, 129.7, 129.0, 126.5, 113.7, 111.7, 111.6, 86.6, 20.5; IR (film): $\tilde{\nu}$ = 2927, 1766, 1653, 1325, 1202, 1152, 1012 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{13}H_{15}O_2$: 247.0249; found: 247.0427 [$M^+ - C_2H_3O_2$].

(*E*,*R*)-1-Acetoxy-1-phenylsulfonyl-3-(2-furyl)-2-propene (*ent*-13d): Following the general procedure, a solution of furan **10d** (112 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.010 mmol), and ligand **10** (20.7 mg, 0.030 mmol) in methylene chloride (1.00 mL) was added at RT to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.5 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred at RT for 24 h. Flash chromatography (PE/Et_2O 2:1) afforded *ent*-**13d** as a white solid (99 mg, 64 %). M.p. 88–89 °C; $[\alpha]_D = +69.6 \pm 0.1$ ($c = 0.81$, $CHCl_3$); $t_r(S) = 11.46$ min, $t_r(R) = 14.30$ min, 97 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 9:1).

(*E*,*S*)-1-Acetoxy-1-phenylsulfonyl-2-hexene (13e): Following the general procedure, a solution of substrate **10e** (100 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.0100 mmol), and ligand **12** (20.7 mg, 0.0300 mmol) in methylene chloride (1.00 mL) was added at RT to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.4 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred at RT for 4 h. Flash chromatography (PE/Et_2O 4:1) afforded **13e** as a clear oil (133 mg, 94 %). $[\alpha]_D = +20.9 \pm 0.1$ ($c = 1.5$, $CHCl_3$); $t_r(R) = 8.50$ min, $t_r(S) = 9.81$ min, 98 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, $J = 8.4$ Hz, 2H), 7.72–7.52 (m, 3H), 6.19 (d, $J = 7.3$ Hz, 1H), 6.00 (dt, $J = 15.5$ Hz, 8.4 Hz, 1H), 5.50 (dd, $J = 15.5$, 7.4 Hz, 1H), 2.13–2.02 (m, 5H), 1.44–1.33 (m, 2H), 0.87 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.5, 142.8, 135.9, 129.8, 117.4, 86.6, 34.4, 21.4, 20.4, 13.4; IR (film): $\tilde{\nu}$ = 2960, 1764, 1659, 1448, 1325, 1205, 1153, 1083 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{18}O_4S$: C 59.55, H 6.43; found: C 59.65, H 6.62.

(*E*,*R*)-1-Acetoxy-1-phenylsulfonyl-2-hexene (*ent*-13e): Following the general procedure, a solution of substrate **10e** (100 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.0100 mmol), and ligand *ent*-**12** (20.7 mg, 0.0300 mmol) in methylene chloride (1.00 mL) was added at RT to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.4 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred at RT for 4 h. Flash chromatography (PE/Et_2O 4:1) afforded *ent*-**13e** as a clear oil (131 mg, 93 %). $[\alpha]_D = -22.9 \pm 0.2$ ($c =$ 1.0, $CHCl_3$); $t_r(R) = 8.10$ min, $t_r(S) = 9.71$ min, 95 % *ee*, (Chiralcel OD, $\lambda =$ 230 nm, heptane/*i*PrOH 95:5).

(*E*,*S*)-1-Acetoxy-1-phenylsulfonyl-2-nonene (13f): Following the general procedure, a solution of alkyl diacetate **10f** (484 mg, 2.00 mmol), π-allylpalladium chloride dimer (14.6 mg, 0.040 mmol), and ligand **12** (82.8 mg,

0.120 mmol) in methylene chloride (5.00 mL) was added at RT to sodium benzenesulfinate (492 mg, 2.00 mmol) and tetrahexylammonium bromide (173.8 mg, 0.400 mmol) in water (5.00 mL). The reaction mixture was stirred at RT for 6 h. Flash chromatography (PE/Et_2O 5:1) afforded **13 f** as a white solid (476 mg, 73 %). M.p. 42–43.5 °C; $[\alpha]_D = +22.3 \pm 0.1$ ($c = 1.20$, $CHCl_3$); $t_r(S) = 7.69$ min, $t_r(R) = 8.87$ min, 95 % *ee*, (Chiralcel OD, $\lambda =$ 230 nm, heptane/*i*PrOH 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.86 (m, 2H), 7.69–7.52 (m, 3H), 6.18 (d, $J = 7.3$ Hz, 1H), 5.97 (dt, $J =$ 8.8, 7.3 Hz, 1H), 5.50 (dd, $J = 8.5$, 7.3 Hz, 1H), 2.16–20.7 (m, 2H), 2.04 (s, 3H), 1.34–1.26 (m, 8H), 0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 143.0, 135.7, 134.3, 129.7, 129.0, 117.1, 86.6, 32.4, 31.5, 28.6, 28.1, 22.4, 20.3, 13.9; IR (film): $\tilde{\nu}$ = 2929, 2857, 1767, 1664, 1448, 1327, 1206, 1154, 1084, 1026 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{24}O_4S$: C 62.93, H 7.46; found: C 62.93, H 7.45.

(*E*,*R*)-1-Acetoxy-1-phenylsulfonyl-2-nonene (*ent*-13 f): Following the general procedure, a solution of alkyl diacetate **10 f** (484 mg, 2.00 mmol), π-allylpalladium chloride dimer (14.6 mg, 0.040 mmol), and ligand *ent*-**12** (82.8 mg, 0.120 mmol) in methylene chloride (5.00 mL) was added at RT to sodium benzenesulfinate (492 mg, 2.00 mmol) and tetrahexylammonium bromide (173.8 mg, 0.400 mmol) in water (5.00 mL). The reaction mixture was stirred at RT for 6 h. Flash chromatography (PE/Et_2O 5:1) afforded *ent*-**13 f** as a white solid (476 mg, 73 %). M.p. 41.5–42.5 °C; $[\alpha]_D = -16.9 \pm 0.1$ ($c = 1.20$, $CHCl_3$); $t_r(S) = 7.70$ min, $t_r(R) = 8.85$ min, 90 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 95:5).

(*E*,*S*)-1-Acetoxy-4-methyl-1-phenylsulfonyl-2-pentene (13 g): Following the general procedure, a solution of acetate **10 g** (100 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.010 mmol), and ligand **12** (20.7 mg, 0.030 mmol) in methylene chloride (1.00 mL) was added at 0 °C to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.4 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred for 10 h at RT. Flash chromatography (PE/Et_2O 3:1) afforded **13 g** as a clear oil (122 mg, 86 %). $[\alpha]_D = -34.0 \pm 0.1$ ($c = 5.00$, $CHCl_3$); $t_r(S) = 7.81$ min, $t_r(R) = 8.65$ min, >99 % *ee*, (Chiralcel OD, $\lambda =$ 230 nm, heptane/*i*PrOH 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, $J = 7.3$ Hz, 2H), 7.68–7.66 (m, 1H), 7.55 (d, $J = 7.3$ Hz, 2H), 6.19 (d, $J =$ 7.1 Hz, 1H), 5.90 (dd, $J = 15.6$, 5.6 Hz, 1H), 5.45 (dd, $J = 15.6$, 6.9 Hz, 1H), 2.37–2.30 (m, 1H), 2.07 (s, 3H), 0.96 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 148.8, 135.6, 134.3, 129.7, 128.9, 114.7, 86.5, 31.0, 21.5, 21.3, 20.5; IR (film): $\tilde{\nu}$ = 2962, 1766, 1662, 1448, 1372, 1326, 1207, 1154, 1084 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{12}H_{15}O_2S$: 223.0788; found: 223.0792 [$M^+ + C_2H_3O_2$].

(*E*,*R*)-1-Acetoxy-4-methyl-1-phenylsulfonyl-2-pentene (*ent*-13 g): Following the general procedure, a solution of acetate **10 g** (100 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.010 mmol), and ligand *ent*-**12** (20.7 mg, 0.030 mmol) in methylene chloride (1.00 mL) was added at 0 °C to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.4 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred for 10 h at RT. Flash chromatography (PE/Et_2O 3:1) afforded *ent*-**13 g** as a clear oil (119 mg, 85 %). $[\alpha]_D = +42.6 \pm 0.1$ ($c = 4.00$, $CHCl_3$); $t_r(S) = 7.80$ min, $t_r(R) = 8.65$ min, 97 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, hepütane/*i*PrOH 95:5).

1-((*E*,*S*)-1′-Acetoxy-1′-phenylsulfonyl)-1-cyclohexene (13 h): Following the general procedure, a solution of diacetate **10 h** (420 mg, 2.00 mmol), π-allylpalladium chloride dimer (18.2 mg, 0.050 mmol), and ligand **12** (103 mg, 0.150 mmol) in methylene chloride (5.00 mL) was added at RT to sodium benzenesulfinate (985 mg, 6.00 mmol) and tetrahexylammonium bromide (261 mg, 0.600 mmol) in water (5.00 mL). The reaction mixture was stirred at RT for 24 h. Flash chromatography (PE/Et_2O 4:1) afforded diacetate **10 h** (168 mg, 40 %) and product **13 i** as a white solid (291 mg, 51 %, 85 % brsm). M.p. 82.5–83.5 °C; $[\alpha]_D = +48.5 \pm 0.4$ ($c =$ 0.750, $CHCl_3$); $t_r(S) = 6.66$ min, 100 % *ee*, (Chiralcel OD, $\lambda = 254$ nm, heptane/*i*PrOH 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, $J = 7.0$ Hz, 2H), 7.69–7.52 (m, 3H), 6.03 (s, 1H), 5.84 (s, 1H), 2.14–2.03 (m, 2H), 2.03–2.00 (m, 5H), 1.65–1.58 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 136.1, 134.2, 133.6, 129.6, 128.9, 127.6, 89.0, 25.3, 22.1, 21.5, 20.4; IR (film): $\tilde{\nu}$ = 2965, 1762, 1445, 1323, 1213, 1153, 1083 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{15}H_{18}O_4$: 295.0976; found: 295.1000 [M^++H].

1-((*E*,*R*)-1′-Acetoxy-1′-phenylsulfonyl)-1-cyclohexene (*ent*-13 h): Following the general procedure, a solution of diacetate **10 h** (210 mg, 1.00 mmol), π-allylpalladium chloride dimer (9.1 mg, 0.025 mmol), and ligand *ent*-**12** (51.0 mg, 0.075 mmol) in methylene chloride (5.00 mL) was added at RT to sodium benzenesulfinate (492 mg, 3.00 mmol) and tetrahexylammonium bromide (130 mg, 0.300 mmol) in water (5.00 mL). The reaction mixture was stirred at RT for 24 h. Flash chromatography (PE/Et_2O 4:1) afforded diacetate **10 h** (131 mg, 62 %) and product *ent*-**13 h** as a white solid (94 mg, 30 %, 80 % brsm). M.p. 82–83.5 °C; $[\alpha]_D = -41.6 \pm$ 0.2 ($c = 2.60$, $CHCl_3$); $t_r(S) = 6.66$ min, $t_r(R) = 6.66$ min, 100 % *ee*, (Chiralcel OD, $\lambda = 254$ nm, heptane/*i*PrOH 9:1).

(*E*,*S*)-1-Acetoxy-1-phenylsulfonyl-4-(*tert*-butyldiphenylsilyloxy)-2-butene (13 i): Following the general procedure, a solution of substrate **10 i** (100 mg, 0.230 mmol), π-allylpalladium chloride dimer (1.60 mg, 0.0047 mmol), and ligand **12** (9.7 mg, 0.014 mmol) in methylene chloride (1.00 mL) was added at 0 °C to sodium benzenesulfinate (67.3 mg, 0.410 mmol) and tetrahexylammonium bromide (20.3 mg, 0.047 mmol) in water (1.00 mL). The reaction mixture was stirred at 0 °C for 2 h. Flash chromatography (PE/ethyl acetate 10:1) afforded **13 i** as a clear oil (110 mg, 92 %). $[\alpha]_D = +2.7 \pm 0.1$ ($c = 6.00$, $CHCl_3$); $[\alpha]_D = +3.0$ ($c =$ 6.00, $CHCl_3$); $t_r(S) = 7.05$ min, $t_r(R) = 7.98$ min, 94 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.87 (m, 2H), 7.67–7.61 (m, 5H), 7.54–7.49 (m, 2H), 7.45–7.38 (m, 6H), 6.32 (d, $J = 6.3$ Hz, 1H), 6.00 (dt, $J = 15.5$, 3.3 Hz, 1H), 5.95–5.91 (m, 1H), 4.21 (br s, 2H), 2.09 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 139.9, 135.7, 135.5, 134.3, 133.1, 133.0, 129.9, 129.8, 129.0, 127.8, 116.6, 86.2, 62.8, 26.6, 20.4, 19.1; IR ($CHCl_3$): $\tilde{\nu}$ = 1767, 1672, 1588, 1327, 1206, 1153, 1113 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{24}H_{23}O_5SSi$: 451.1035; found: 451.1048 [$M^+ + C_4H_9$].

(*E*,*R*)-1-Acetoxy-1-phenylsulfonyl-4-(*tert*-butyldiphenylsilyloxy)-2-butene (*ent*-13 i): Following the general procedure, a solution of diacetate **10 i** (100 mg, 0.230 mmol), π-allylpalladium chloride dimer (1.6o mg, 0.0047 mmol), and ligand *ent*-**12** (9.7 mg, 0.014 mmol) in methylene chloride (1.00 mL) was added at 0 °C to sodium benzenesulfinate (67.3 mg, 0.410 mmol) and tetrahexylammonium bromide (20.34 mg, 0.047 mmol) in water (1.00 mL). The reaction mixture was stirred at RT for 2 h. Flash chromatography (PE/ethyl acetate 10:1) afforded *ent*-**13 i** as a clear oil (108 mg, 91 %). $[\alpha]_D = -2.5 \pm 0.7$ ($c = 1.05$, $CHCl_3$); $[\alpha]_D = -3.0$ ($c =$ 5.93, $CHCl_3$); $t_r(S) = 7.17$ min, $t_r(R) = 8.05$ min, 94 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 9:1).

(*E*,*S*)-1-Acetoxy-1-phenylsulfonyl-3-(1′-methoxycyclopentyl)-2-propene (13 l): Following the general procedure, a solution of allylic diacetate **10 l** (256 mg, 1.00 mmol), π-allylpalladium chloride dimer (7.32 mg, 0.020 mmol), and ligand **12** (41.4 mg, 0.060 mmol) in methylene chloride (2.00 mL) was added at RT to sodium benzenesulfinate (246 mg, 1.50 mmol) and tetrahexylammonium bromide (86.8 mg, 0.200 mmol) in water (2.00 mL). The reaction mixture was stirred at RT for 4 h. Flash chromatography (PE/Et_2O 2:1) afforded starting material (138 mg) and **13 l** as a clear oil (118 mg, 35 %, 76 % brsm). $[\alpha]_D = +24.2 \pm 0.1$ ($c =$ 1.20, $CHCl_3$); $t_r(S) = 11.23$ min, $t_r(R) = 12.93$ min, 80 % *ee*, (Chiralcel OD, $\lambda = 230$ nm, heptane/*i*PrOH 95:5); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, $J = 7.4$ Hz, 2H), 7.69–7.66 (m, 1H), 7.59–7.54 (m, 2H), 6.28 (d, $J =$ 7.4 Hz, 1H), 5.93 (d, $J = 16.1$ Hz, 1H), 5.67 (dd, $J = 15.9$, 6.7 Hz, 1H), 3.05 (s, 3H), 2.09 (s, 3H), 1.85–1.47 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 143.8, 135.7, 134.5, 129.8, 129.1, 117.2, 86.3, 86.2, 51.0, 35.8, 35.6, 23.0, 22.9, 20.4; IR (film): $\tilde{\nu}$ = 2962, 1768, 1447, 1372, 1326, 1203, 1153, 1081 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{15}H_{19}O_3S$: 279.1058; found: 279.1053 [$M^+ + C_2H_3O_2$].

(*E*,*R*)-1-Acetoxy-1-phenylsulfonyl-3-(1′-methoxycyclopentyl)-2-propene (*ent*-13 l): Following the general procedure, a solution of allylic diacetate **10 l** (128 mg, 0.50 mmol), π-allylpalladium chloride dimer (3.60 mg, 0.010 mmol), and ligand *ent*-**12** (41.4 mg, 0.060 mmol) in methylene chloride (2.00 mL) was added at RT to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred at RT for 4 h. Flash chromatography (PE/Et_2O 2:1) afforded starting material (68 mg, 53 %) and a clear oil *ent*-**13 l** (57 mg, 34 %, 80 % brsm). The sign of rotation was opposite to that of **13 l** and the magnitude of rotation was similar. $[\alpha]_D =$

-24.6 ± 0.2 ($c=1.20$, $CHCl_3$); $t_r(S)=11.47$ min, $t_r(R)=13.02$ min, 80% *ee*, (Chiralcel OD, $\lambda=230$ nm, heptane/*i*PrOH 95:5).

(*S*,*S*)-2,2-Dimethyl-4-(3′-acetoxy-3′-phenylsulfonyl-1′(*E*)-propenyl)-1,3-dioxolane (13j): Following the general procedure, a solution of diacetate **10j** (103 mg, 0.400 mmol), π-allylpalladium chloride dimer (2.92 mg, 0.0040 mmol), and ligand **12** (16.6 mg, 0.024 mmol) in methylene chloride (2.00 mL) was added at 0°C to sodium benzenesulfinate (98.4 mg, 0.400 mmol) and tetrahexylammonium bromide (34.8 mg, 0.080 mmol) in water (2.00 mL). The reaction mixture was stirred at 0°C for 4 h. Flash chromatography (PE/Et_2O 1:1) afforded **13j** as a white solid (107 mg, 79%). ^{1}H NMR indicated a diastereomeric ratio >20:1 in favor of "*anti*" based on separated peaks for the acetate methyl protons (major peak 2.09 ppm, minor peak 2.06 ppm). M.p. 110–111°C; $[\alpha]_D = +69.9\pm0.2$ ($c=3.10$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.89$ (d, $J=7.8$ Hz, 2H), 7.71–7.53 (m, 3H), 6.30 (d, $J=3.2$ Hz, 1H), 5.91–5.87 (m, 2H), 4.55–4.50 (m, 1H), 4.07 (dd, $J=9.2$, 8.2 Hz, 1H), 3.50 (dd, $J=9.1$, 8.5 Hz, 1H), 2.09 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.8$, 137.6, 135.4, 134.5, 129.8, 129.1, 120.0, 110.0, 85.3, 75.2, 68.9, 26.4, 25.6, 20.3; IR (film): $\tilde{\nu} = 2986$, 1768, 1448, 1372, 1326, 1205, 1153, 1060 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{12}H_{12}O_4$: 325.0752; found: 325.0733 $[M^+-CH_3]$.

(*S*,*S*+*R*)-2,2-Dimethyl-4-(3′-acetoxy-3′-phenylsulfonyl-1′(*E*)-propenyl)-1,3-dioxolane (*ent*-13j): Following the general procedure, a solution of diacetate **10j** (51.6 mg, 0.200 mmol), π-allylpalladium chloride dimer (1.46 mg, 0.0040 mmol), and ligand *ent*-**12** (8.3 mg, 0.012 mmol) in methylene chloride (1.00 mL) was added at 0°C to sodium benzenesulfinate (49.2 mg, 0.200 mmol) and tetrahexylammonium bromide (17.4 mg, 0.040 mmol) in water (1.00 mL). The reaction mixture was stirred at 0°C for 4 h. Flash chromatography (PE/Et_2O 1:1) afforded *ent*-**13j** as a clear oil (59 mg, 86%). ^{1}H NMR indicated a diastereomeric ratio of 2:1 in favor of "*anti*" on separated peaks for the acetate protons. Minor adduct: $[\alpha]_D = +53.9\pm0.1$ ($c=4.80$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.89 (d, $J=7.8$ Hz, 2H), 7.71–7.53 (m, 3H), 6.30 (d, $J=3.2$ Hz, 1H), 5.91–5.87 (m, 2H), 4.55–4.50 (m, 1H), 4.07 (dd, $J=9.2$, 8.2 Hz, 1H), 3.50 (dd, $J=9.1$, 8.5 Hz, 1H), 2.06 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H); IR (film): $\tilde{\nu} = 2987$, 1768, 1448, 1372, 1326, 1205, 1154, 1060 cm^{-1}.

(*E*,*S*)-Ethyl 4-acetoxy-3-methyl-4-phenylsulfonylcrotonate (13k): Following the general procedure, a solution of allylic diacetate **10k** (134 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.0100 mmol), and ligand **12** (20.7 mg, 0.0300 mmol) in methylene chloride (1.00 mL) was added at RT to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.4 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred for 12 h at 0°C. Flash chromatography (PE/Et_2O 2:1) afforded starting diacetate **10k** (163 mg, 40%) and product **13k** as a clear oil (252 mg, 51%, 85% brsm). $[\alpha]_D = +68.1\pm0.1$ ($c=1.20$, $CHCl_3$); $t_r(S)=8.08$ min, $t_r(R)=11.17$ min, 98% *ee*, (Chiralcel OD, $\lambda=254$ nm, heptane/*i*PrOH 90:10); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.89 (d, $J=7.5$ Hz, 2H), 7.71–7.55 (m, 3H), 6.13 (s, 1H), 5.87 (s, 1H), 4.16 (q, $J=7.1$ Hz, 2H), 2.31 (s, 3H), 2.07 (s, 3H), 1.27 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.6$, 165.0, 144.7, 134.6, 129.6, 129.4, 129.1, 123.5, 88.7, 60.3, 20.3, 16.6, 14.1; IR (film): $\tilde{\nu} = 2984$, 1771, 1719, 1652, 1448, 1372, 1329, 1202, 1158, 1065 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{13}H_{15}O_4$: 267.0691; found: 267.0686 $[M^+-C_2H_3O_2]$.

(*E*,*R*)-Ethyl-4-acetoxy-3-methyl-4-phenylsulfonylcrotonate (*ent*-13k): Following the general procedure, a solution of allylic diacetate **10k** (134 mg, 0.500 mmol), π-allylpalladium chloride dimer (3.66 mg, 0.0100 mmol), and ligand *ent*-**12** (20.7 mg, 0.0300 mmol) in methylene chloride (1.00 mL) was added at RT to sodium benzenesulfinate (123 mg, 0.750 mmol) and tetrahexylammonium bromide (43.4 mg, 0.100 mmol) in water (1.00 mL). The reaction mixture was stirred for 12 h at 0°C. Flash chromatography (PE/Et_2O 2:1) afforded starting diacetate **10k** (160 mg, 38%) and product *ent*-**13k** as a clear oil (251 mg, 50%, 83% brsm). $[\alpha]_D = +69.1\pm0.1$ ($c=1.20$, $CHCl_3$); $t_r(S)=8.07$ min, $t_r(R)=11.13$ min, 98% *ee*, (Chiralcel OD, $\lambda=254$ nm, heptane/*i*PrOH 90:10).

General procedure for osmium catalyzed diastereoselective dihydroxylations: α-Acetoxysulfone, 4% aqueous osmium tetroxide solution, and *N*-methylmorpholine-*N*-oxide (NMO) were stirred at 0–5°C for 24 h. In some cases DABCO and *tert*-butanol were added. The crude mixture was poured into ethyl acetate and the organic phase was washed with 1N aqueous sodium bisulfite solution. The organic phase was dried over magnesium sulfate and concentrated in vacuo. The residue was purified by flash chromatography.

(1*S*,2*R*,3*S*)-1-Acetoxy-1-phenylsulfonyl-3-phenyl-2,3-propandiol (14a): Following the general procedure, α-acetoxysulfone *ent*-**13a** (40 mg, 0.126 mmol), 4% aqueous osmium tetroxide solution (40 μL, 1.60 mg, 0.0063 mmol), and NMO (44.4 mg, 0.379 mmol) in methylene chloride (1.50 mL) were stirred at 0–5°C for 12 h. Flash chromatography (PE/ethyl acetate 3:1) afforded product *ent*-**14a** as a white solid (29.0 mg, 66%). ^{1}H NMR indicated the product was a single diastereomer. M.p. 134–136 (decomp); $[\alpha]_D = +57.3\pm0.2$ ($c=1.14$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 7.93–7.90 (m, 2H), 7.68–7.66 (m, 1H), 7.59–7.54 (m, 2H), 7.36–7.29 (m, 5H), 5.97 (d, $J=8.5$ Hz, 1H), 4.77 (brs, 1H), 4.36–4.35 (m, 1H), 3.15 (d, $J=5.3$ Hz, 1H), 2.77 (d, $J=6.4$ Hz, 1H), 1.96 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 167.8$, 139.8, 137.0, 134.6, 129.4, 129.3, 128.7, 128.6, 128.2, 126.3, 84.8, 72.5, 20.1; IR (film): $\tilde{\nu} =$ 3490, 3064, 3030, 2935, 1777, 1448, 1372, 1309, 1210, 1151, 1049 cm^{-1}; elemental analysis calcd (%) for: C 58.27, H 5.18; found: C 58.36, H 5.30.

(1*R*,2*S*,3*R*)-1-Acetoxy-1-phenylsulfonyl-3-phenyl-2,3-propandiol (*ent*-14a): ***Method A***: Following the general procedure, acetoxysulfone **13a** (40.0 mg, 0.1264 mmol), 4% aqueous osmium tetroxide solution (40 μL, 1.60 mg, 0.0063 mmol), NMO (44.4 mg, 0.379 mmol), DABCO (0.86 mg, 0.0076 mmol), and *tert*-butanol (one drop) were stirred in methylene chloride (1.50 mL) at 0–5°C for 24 h. Flash chromatography (PE/ethyl acetate 3:1) afforded product *ent*-**14a** as a white solid (34.0 mg, 77%). ^{1}H NMR indicated the product was a single diastereomer. M.p. 134–136°C; $[\alpha]_D = -58.3\pm0.1$ ($c=1.12$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.93–7.90 (m, 2H), 7.68–7.66 (m, 1H), 7.59–7.54 (m, 2H), 7.36–7.29 (m, 5H), 5.97 (d, $J=8.5$ Hz, 1H), 4.77 (brs, 1H), 4.36–4.35 (m, 1H), 3.15 (d, $J=5.3$ Hz, 1H), 2.77 (d, $J=6.4$ Hz, 1H), 1.96 (s, 3H); IR (film): $\tilde{\nu} = 3490$, 3064, 3030, 2935, 1777, 1448, 1372, 1309, 1210, 1151, 1049 cm^{-1}.

Method 2: Following the general procedure, acetoxysulfone **13** (40.0 mg, 0.1264 mmol), 4% aqueous osmium tetroxide solution (40 μL, 1.60 mg, 0.0063 mmol), and NMO (44.4 mg, 0.379 mmol) were stirred in methylene chloride (1.50 mL) at 0–5°C for 24 h. Flash chromatography (PE/ethyl acetate 3:1) afforded product *ent*-**14a** as a white solid (35.0 mg, 78%). ^{1}H NMR indicated the product was a single diastereomer.

(1*S*,2*R*,3*S*)-1-Acetoxy-2-methyl-1-phenylsulfonyl-3-phenyl-2,3-propandiol (14b): Following the general procedure, acetoxysulfone **13b** (33.0 mg, 0.100 mmol), 4% aqueous osmium tetroxide solution (30 μL, 1.20 mg, 0.0050 mmol), and NMO (35.1 mg, 0.300 mmol) in methylene chloride (1.00 mL) were stirred at 0–5°C for 12 h. Flash chromatography (PE/ethyl acetate 3:1) afforded product **14b** as a colorless stick oil (20.6 mg, 57%). ^{1}H NMR indicated the product was a single diastereomer. $[\alpha]_D = +80.1\pm0.2$ ($c=0.610$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.98$ (d, $J=7.2$ Hz, 2H), 7.66–7.58 (m, 3H), 7.39–7.33 (m, 5H), 6.16 (s, 1H), 4.57 (d, $J=5.5$ Hz, 1H), 3.59 (s, 1H), 2.81 (d, $J=5.5$ Hz, 1H), 2.01 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 196.9$, 168.2, 134.4, 129.2, 129.1, 128.4, 128.2, 128.1, 86.4, 76.3, 68.7, 28.8, 20.1, 19.3. IR (film): $\tilde{\nu} =$ 3498, 2938, 1766, 1448, 1371, 1309, 1202, 1149, 1050 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{18}H_{20}O_6S$: 347.0981; found: 347.0955 $[M^+-OH]$.

(1*S*,2*R*,3*S*)-1-Acetoxy-1-phenylsulfonyl-3-(2-nitrophenyl)-2,3-propandiol (14c): Following the general procedure, acetoxysulfone **13c** (72.3 mg, 0.200 mmol), 4% aqueous osmium tetroxide solution (63 μL, 2.54 mg, 0.010 mmol), and NMO (70.3 mg, 0.600 mmol) in methylene chloride (2.00 mL) were stirred at 0–5°C (cold room) for 12 h. Flash chromatography (PE/Et_2O 1:3) afforded product **14c** as a white solid (64.0 mg, 81%). ^{1}H NMR indicated the product was a single diastereomer. M.p. 94–95.5°C; $[\alpha]_D = +31.0\pm0.2$ ($c=1.00$, CH_3OH); ^{1}H NMR (200 MHz, CD_3OD): $\delta =$ 7.88–7.81 (m, 4H), 7.62–7.40 (m, 5H), 5.96 (d, $J=9.4$ Hz, 1H), 5.16 (s, 1H), 4.21 (d, $J=9.5$ Hz, 1H), 2.01 (s, 3H); ^{13}C NMR (50 MHz, CD_3OD): $\delta =$ 169.7, 149.0, 139.0, 138.5, 135.4, 134.0, 132.1, 130.6, 130.3, 129.4, 125.2, 86.9, 72.2, 68.6, 20.2; IR (film): $\tilde{\nu} = 3489$, 2925, 1776, 1610, 1525, 1344, 1200, 1151, 1052 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{11}H_{12}NO_6$: 254.0664; found: 254.0651 $[M^+-C_6H_5SO_2]$.

(1*S*,2*R*,3*S*)-1-Acetoxy-1-phenylsulfonyl-2,3-hexandiol (14e): Following the general procedure, acetoxysulfone **13e** (282 mg, 1.00 mmol), 4% aqueous osmium tetroxide solution (318 μL, 12.7 mg, 0.050 mmol), and NMO (352 mg, 3.00 mmol) in methylene chloride (5.00 mL) were stirred at 0–5 °C (cold room) for 5 h. Flash chromatography (PE/Et_2O 1:3) afforded product **14e** as a white solid (194 mg, 61%). The diastereomeric ratio was >95:5 as determined by ^{1}H NMR integration by comparison of the acetate protons (major δ 2.03, minor 2.09 ppm). M.p. 88–89 °C; $[\alpha]_D = +20.5 \pm 0.2$ (c=2.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, J=8.1 Hz, 2H), 7.72–7.56 (m, 3H), 5.93 (d, J=8.8 Hz, 1H), 4.09–4.02 (m, 1H), 3.59–3.56 (m, 1H), 3.36–3.28 (m, 1H), 2.15–2.07 (m, 1H), 2.03 (s, 3H), 1.76–1.31 (m, 4H), 0.92 (t, J=7.4 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.9, 136.6, 134.5, 129.3, 129.2, 84.8, 70.4, 69.7, 35.5, 20.2, 18.9, 13.9; IR (film): $\tilde{\nu}$ = 3503, 2960, 1738, 1448, 1372, 1310, 1202, 1153, 1048 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{20}O_6S$: C 53.15, H 6.37; found: C 53.27, H, 6.50.

(1*S*,2*R*,3*S*)-1-Acetoxy-1-phenylsulfonyl-2,3-nonandiol (14f): Following the general procedure, acetoxysulfone **13f** (32.4 mg, 0.100 mmol), 4% aqueous osmium tetroxide solution (32 μL, 1.27 mg, 0.005 mmol), and NMO (35.1 mg, 0.300 mmol) in methylene chloride (1.00 mL) were stirred at 0–5 °C (cold room) for 12 h. Flash chromatography (PE/ethyl acetate 1:1) afforded product **14f** as a white glass (30.2 mg, 84%). ^{1}H NMR indicated the product was a single diastereomer. M.p. 72–73 °C; $[\alpha]_D = +30.7 \pm 0.2$ (c=1.80, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.97–7.92 (m, 2H), 7.74–7.54 (m, 3H), 5.93 (d, J=8.8 Hz, 1H), 4.12–4.03 (m, 1H), 3.60–3.57 (m, 1H), 3.20 (d, J=5.7 Hz, 1H), 2.03 (s, 3H), 1.94 (d, J=8.8 Hz, 1H), 1.64–1.55 (m, 2H), 1.47–1.22 (m, 8H), 0.85 (t, J=6.8 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.9, 136.7, 134.6, 129.4, 129.3, 84.8, 70.4, 70.0, 33.5, 31.6, 29.1, 25.6, 22.5, 20.1, 14.0; IR (film): $\tilde{\nu}$ = 3497, 2929, 2858, 1779, 1448, 1373, 1310, 1203, 1153, 1051 cm^{-1}; elemental analysis calcd (%) for $C_{17}H_{26}O_6S$: C 57.00, H 7.31; found: C 57.22, H 7.50.

(1*R*,2*S*,3*R*)-1-Acetoxy-4-methyl-1-phenylsulfonyl-2,3-pentandiol (*ent*-14g): Following the general procedure, acetoxysulfone *ent*-**13g** (84.7 mg, 0.300 mmol), 4% aqueous osmium tetroxide solution (95 μL, 3.81 mg, 0.015 mmol), and NMO (105 mg, 0.900 mmol) in methylene chloride (3.00 mL) were stirred at 0–5 °C for 4 h. Flash chromatography (PE/Et_2O 1:2) afforded product *ent*-**14g** as a white solid (76 mg, 81%). ^{1}H NMR indicated the product was a single diastereomer. M.p. 121–122 °C; $[\alpha]_D = -143.7 \pm 0.1$ (c=2.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, J=8.3 Hz, 2H), 7.72–7.67 (m, 1H), 7.60–7.55 (m, 2H), 5.94 (d, J=8.8 Hz, 1H), 4.31–4.27 (m, 1H), 3.31 (d, J=6.3 Hz, 1H), 3.16–3.10 (m, 1H), 2.22 (d, J=8.6 Hz, 1H), 2.01 (s, 3H), 1.92–1.85 (m, 1H), 1.00 (d, J=6.6 Hz, 3H), 0.91 (d, J=6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.9, 136.7, 134.5, 129.3, 129.2, 85.0, 75.3, 68.4, 30.6, 20.2, 19.2, 18.8; IR (film): $\tilde{\nu}$ = 3613, 3354, 2966, 1781, 1473, 1450, 1370, 1302, 1194, 1150, 1045 cm^{-1}; HRMS: m/z: calcd for $C_{11}H_{13}O_6S$: 273.0433; found: 273.0435 [$M^+ - C_3H_7$].

(1*R*,2*S*,3*R*)-1-Acetoxy-1-phenylsulfonyl-4-(*tert*-butyldiphenylsilyloxy)-2,3-butandiol (*ent*-14i): Following the general procedure, acetoxysulfone *ent*-**13i** (36.0 mg, 0.0707 mmol), 4% aqueous osmium tetroxide solution (44 μL, 0.0071 mmol), and NMO (26.0 mg, 0.2200 mmol) in methylene chloride (1.00 mL) were stirred at 0–5 °C for 12 h. Flash chromatography (PE/ethyl acetate 3:1) afforded product *ent*-**14i** as a colorless sticky oil (31.5 mg, 82%). The diastereomeric ratio was 12.5:1 as determined as determined by ^{1}H NMR integration by comparison of the acetate protons (major δ 2.04, minor 2.10 ppm). $[\alpha]_D = -20.6 \pm 0.4$ (c=1.20, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.94 (d, J=8.1 Hz, 2H), 7.90–7.54 (m, 7H), 7.47–7.39 (m, 6H), 5.94 (d, J=8.8 Hz, 1H), 4.26 (dd, J=8.8, 5.9 Hz, 1H), 3.78–3.69 (m, 3H), 3.06 (d, J=5.9 Hz, 1H), 2.45 (d, J=6.3 Hz, 1H), 2.04 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 167.9, 136.9, 135.6, 135.5, 134.5, 132.7, 130.0, 129.5, 127.9, 84.5, 69.5, 68.4, 64.6, 26.7, 20.2, 19.0; IR (film): $\tilde{\nu}$ = 3510, 1776, 1428, 1310, 1202, 1152, 1113, 1053 cm^{-1}; HRMS: m/z: calcd for $C_{22}H_{22}O_5SSi$: 425.0642; found: 425.0879 [$M^+ - C_4H_9 - C_2H_3O_2$].

Method B: Following the general procedure, acetoxysulfone *ent*-**13i** (36.0 mg, 0.0707 mmol), 4% aqueous osmium tetroxide solution (44 μL, 0.0071 mmol), DABCO (0.53 mg, 0.0047 mmol) *tert*-butanol (1 drop), and NMO (26.0 mg, 0.2200 mmol) in methylene chloride (1.00 mL) were stirred at 0–5 °C for 12 h. Flash chromatography (PE/ethyl acetate 3:1) afforded product *ent*-**14i** as a colorless oil (27.4 mg, 71%). The diastereomeric ratio was 11:1 as determined by ^{1}H NMR integration by comparison of the acetate protons (major δ 2.04, minor 2.10 ppm).

(1*S*,2*R*,3*S*)-1-Acetoxy-1-phenylsulfonyl-4-(*tert*-butyldiphenylsilyloxy)-2,3-butandiol (14i): Following the general procedure, acetoxysulfone **13i** (36.0 mg, 0.0707 mmol), 4% aqueous osmium tetroxide solution (22 μL, 0.915 mg, 0.0036 mmol), and NMO (26.0 mg, 0.220 mmol) in methylene chloride (1.00 mL) were stirred at 0–5 °C for 24 h. Flash chromatography (PE/ethyl acetate 3:1) afforded product **14i** as a colorless oil (31.0 mg, 81%). The diastereomeric ratio was 18:1 as determined as determined by ^{1}H NMR integration by comparison of the acetate protons (major δ 2.04, minor 2.10 ppm). $[\alpha]_D = +20.9 \pm 0.4$ (c=1.60, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.94 (d, J=8.1 Hz, 2H), 7.90–7.54 (m, 7H), 7.47–7.39 (m, 6H), 5.94 (d, J=8.8 Hz, 1H), 4.26 (dd, J=8.8, 5.9 Hz, 1H), 3.78–3.69 (m, 3H), 3.06 (d, J=5.9 Hz, 1H), 2.45 (d, J=6.3 Hz, 1H), 2.04 (s, 3H), 1.04 (s, 9H); IR (film): $\tilde{\nu}$ = 3510, 1776, 1428, 1310, 1202, 1152, 1113, 1053 cm^{-1}; HRMS: m/z: calcd for $C_{22}H_{22}O_5SSi$: 425.0642; found: 425.0879 [$M^+ - C_4H_9 - C_2H_3O_2$].

(1′*R*,2′*R*,3′*S*,4*S*)-2,2-Dimethyl-4-(3′-acetoxy-1′,2′-dihydroxy-3′-phenylsulfonyl-1′-propan)-1,3-dioxolane (14j): Following the general procedure, acetoxysulfone **13j** (170 mg, 0.500 mmol), 4% aqueous osmium tetroxide solution (159 μL, 6.36 mg, 0.025 mmol) and NMO (176 mg, 1.50 mmol) in methylene chloride (5.00 mL) were stirred at 0–5 °C for 12 h. Flash chromatography (PE/Et_2O 1:3) afforded product **14j** as a white solid (158 mg, 85%). The diastereomeric ratio was >6:1), as determined by ^{1}H NMR integration by comparison of the acetate protons, (major acetate peak δ 2.02, minor acetate peak 2.11 ppm) favoring the typical "*anti*" product (1st cmpd.). M.p. 146–148 °C; $[\alpha]_D = +30.5 \pm 0.1$ (c=1.00, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.92 (d, J=7.0 Hz, 2H), 7.71–7.55 (m, 3H), 5.88 (d, J=8.7 Hz, 1H), 4.27–4.04 (m, 3H), 3.81 (dd, J=8.7, 7.0 Hz, 1H), 3.55–3.48 (m, 1H), 3.17 (d, J=5.2 Hz, 1H), 2.59 (d, J=7.7 Hz, 1H), [2.11 (s, 0.43H), 2.02 (s, 2.58H)], 1.38 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.2, 137.8, 134.8, 129.8, 129.5, 110.4, 84.8, 77.6, 70.8, 69.4, 66.3, 26.5, 25.3, 20.3; IR (film): $\tilde{\nu}$ = 3490, 2397, 1778, 1448, 1373, 1310, 1203, 1153, 1063 cm^{-1}; HRMS: m/z: calcd for $C_{15}H_{19}O_8S$: 359.0801; found: 359.0792 [$M^+ - CH_3$].

(2*R*,3*R*)-Ethyl 2-acetoxy-3-hydroxy-3-methyl-4-oxodihydrocrotonate (14k): Following the general procedure, acetoxysulfone **13k** (32.6 mg, 0.100 mmol), 4% aqueous osmium tetroxide solution (32 μL, 1.27 mg, 0.005 mmol) and NMO (35.1 mg, 0.300 mmol) in methylene chloride (1.00 mL) were stirred at 0–5 °C (cold room) for 12 h. Flash chromatography (PE/Et_2O 1:3) afforded product **14k** as a clear oil (20.4 mg, 94%). ^{1}H NMR indicated the product was a single diastereomer. $[\alpha]_D = +11.6 \pm 0.2$ (c=1.80, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.60 (s, 1H), 5.16 (s, 1H), 4.26 (q, J=6.0 Hz, 2H), 3.59 (s, 1H), 2.15 (s, 3H), 1.44 (s, 3H), 1.29 (t, J=6.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 199.4, 169.6, 167.1, 74.9, 62.1, 52.0, 20.3, 19.3, 13.9; IR (film): $\tilde{\nu}$ = 3462, 2918, 1734, 1447, 1373, 1200, 1063 cm^{-1}; HRMS: m/z: calcd for $C_9H_{15}O_6$: 219.0798; found: 219.0868 [M^++H].

(4*S*,5*R*)-4-((1′*R*)-1′-Acetoxy-1′-phenylsulfonylmethyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (17a): Diol *ent*-**14a** (170 mg, 0.485 mmol), 2,2-dimethoxypropane (2,2-DMP) (5.00 mL), acetone (5.00 mL), and PPTS (one crystal) were mixed at RT and stirred for 24 h. The mixture was poured into diethyl ether (20 mL), washed with 10% aqueous sodium bicarbonate solution (20 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded product **17a** as a white solid (174 mg, 92%). ^{1}H NMR indicated adduct was a single diastereomer. M.p. 61–62 °C; $[\alpha]_D = -13.6 \pm 0.1$ (c=2.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J=7.4 Hz, 2H), 7.67–7.64 (m, 1H), 7.56–7.51 (m, 2H), 7.35–7.26 (m, 5H), 5.97 (d, J=8.0 Hz, 1H), 4.87 (d, J=7.6 Hz, 1H), 4.41–4.35 (m, 1H), 1.81 (s, 3H), 1.51 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.0, 136.9, 136.8, 134.3, 129.6, 128.9, 128.8, 128.5, 127.2, 111.1, 84.9, 81.5, 78.7, 27.1, 26.3, 20.3; IR ($CHCl_3$): $\tilde{\nu}$ = 2988, 1772, 1448, 1373, 1328, 1198, 1155, 1057 cm^{-1}; HRMS: m/z: calcd for $C_{19}H_{19}O_6S$: 375.0896; found: 375.0920 [$M^+ - CH_3$].

(4*R*,5*S*)-4-((1′*S*)-1′-Acetoxy-1′-phenylsulfonylmethyl)-2,2-dimethyl-5-phenyl-1,3-dioxolane (*ent*-17a): Diol *ent*-**14a** (170 mg, 0.485 mmol), 2,2-DMP (5.00 mL), acetone (5.00 mL), and PPTS (one crystal) were mixed at RT and stirred for 24 h. The mixture was poured into diethyl ether (20 mL), washed with 10% aqueous sodium bicarbonate solution (20 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded product **17a** as a white solid (176 mg, 93%). ^{1}H NMR indicated adduct was a single diastereomer. M.p. 60–62 °C; $[\alpha]_D = +14.5 \pm 0.1$ ($c = 2.00$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 7.4$ Hz, 2H), 7.67–7.64 (m, 1H), 7.56–7.51 (m, 2H), 7.35–7.26 (m, 5H), 5.97 (d, $J = 8.0$ Hz, 1H), 4.87 (d, $J = 7.6$ Hz, 1H), 4.41–4.35 (m, 1H), 1.81 (s, 3H), 1.51 (s, 3H), 1.33 (s, 3H); IR ($CHCl_3$): $\tilde{\nu} = 2988, 1772, 1448, 1373, 1328, 1198, 1155, 1057\ cm^{-1}$.

(4*S*,5*R*)-4-((1′*R*)-1′-Acetoxy-1′-phenylsulfonylmethyl)-5-phenyl-2,2,4-trimethyl-1,3-dioxolane (17b): A 4% aqueous solution of osmium tetroxide (0.12 mL, 0.0462 mmol) was added to a solution of substrate *ent*-**13b** (305 mg, 0.923 mmol) and *N*-methylmorpholine-*N*-oxide (324 mg, 2.77 mmol) in methylene chloride (5.00 mL). The solution was stirred for 16 h at 0 °C. The organic layer was separated, the organic phase dried over sodium sulfate, and treated with 2,2-dimethoxypropane (1.00 mL) and 2 crystals of toluenesulfonic acid monohydrate. The solution was stirred for 8 h at RT. Flash chromatography (PE/Et_2O 2:1) afforded acetonide **17b** as a colorless oil (303 mg, 81%). $[\alpha]_D = +0.8 \pm 0.1$ ($c = 2.60$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.01$ (dd, $J = 6.4$, 2.0 Hz, 2H), 7.68–7.66 (m, 1H), 7.59–7.56 (m, 2H), 7.36–7.32 (m, 5H), 5.76 (s, 1H), 5.31 (s, 1H), 2.04 (s, 3H), 1.55 (s, 3H), 1.16 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 168.6, 138.8, 135.2, 134.0, 129.5, 128.9, 128.5, 128.2, 126.8, 109.0, 87.6, 84.0, 83.1, 28.3, 25.7, 20.4, 18.6$; IR (film): $\tilde{\nu} = 2990, 2937, 1764, 1602, 1448, 1375, 1326, 1203, 1153, 1055\ cm^{-1}$; HRMS: m/z: calcd for $C_{18}H_{16}O_6S$: 389.1059; found: 389.1065 [$M^+ - CH_3$].

4*R*,5*S*)-4-((1′*S*)-1′-Acetoxy-1′-phenylsulfonylmethyl)-2,2-dimethyl-5-propyl-1,3-dioxolane (17c): Diol **14c** (63.3 mg, 0.200 mmol), 2,2-dimethoxypropane (2.00 mL), acetone (2.00 mL), and pyridinium *p*-toluenesulfonate (one crystal) were mixed at RT and stirred for 24 h. The mixture was poured into diethyl ether (20 mL), washed with 10% aqueous sodium bicarbonate solution (10 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded acetonide **17c** as a white solid (67.5 mg, 95%). ^{1}H NMR indicated the product was a single diastereomer. M.p. 67–68.5 °C; $[\alpha]_D = -13.3 \pm 0.1$ ($c = 2.00$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.93$ (d, $J = 7.4$ Hz, 2H), 7.70–7.65 (m, 1H), 7.59–7.54 (m, 2H), 5.90 (d, $J = 6.6$ Hz, 1H), 4.25 (dd, $J = 6.6$, 6.4 Hz, 1H), 4.10–4.04 (m, 1H), 2.07 (s, 3H), 1.71–1.40 (m, 6H), 1.37 (s, 3H), 1.16 (s, 3H), 0.94 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.0, 137.0, 134.4, 129.5, 110.1, 84.9, 78.2, 76.6, 36.1, 27.4, 26.5, 20.2, 19.0, 13.9$; IR ($CHCl_3$): $\tilde{\nu} = 2968, 1756, 1450, 1380, 1316, 1215, 1168, 1062\ cm^{-1}$; HRMS: m/z: calcd for $C_{17}H_{24}O_6S$: 341.1065; found: 341.1051 [$M^+ - CH_3$].

(4*S*,5*R*)-4-((1′*R*)-1′-Acetoxy-1′-phenylsulfonylmethyl)-2,2-dimethyl-5-isopropyl-1,3-dioxolane (17d): Diol **14d** (31.6 mg, 0.100 mmol), 2,2-dimethoxypropane (1.00 mL), acetone (1.00 mL), and pyridinium *p*-toluenesulfonate (one crystal) were mixed at RT and stirred for 24 h. The mixture was poured into diethyl ether (20 mL), washed with 5% aqueous sodium bicarbonate solution (20 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded acetonide **17d** as a clear oil (29 mg, 83%). ^{1}H NMR indicated the product was a single diastereomer. $[\alpha]_D = +19.4 \pm 0.3$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 7.1$ Hz, 2H), 7.67–7.64 (m, 1H), 7.56–7.53 (m, 2H), 7.35–7.26 (m, 5H), 5.85 (d, $J = 8.1$ Hz, 1H), 4.42–4.38 (m, 1H), 3.75 (dd, $J = 5.6$, 2.1 Hz, 1H), 2.08 (s, 3H), 1.86–1.82 (m, 1H), 1.35 (s, 3H), 1.06 (s, 3H), 0.96–0.93 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.1, 137.5, 134.3, 129.6, 129.0, 110.7, 85.4, 75.4, 31.1, 27.5, 26.8, 20.3, 19.4, 17.1$; IR ($CHCl_3$): $\tilde{\nu} = 2964, 1774, 1471, 1448, 1372, 1328, 1199, 1156, 1055\ cm^{-1}$; elemental analysis calcd (%) for $C_{17}H_{26}O_6S$: C 57.29, H 6.79; found: C 57.22, H 6.91.

(3*R*,4*R*)-2,2-Dimethyl-4-(hydroxymethyl)-3-phenyl-1,3-dioxolane (18): DIBAL-H (1.0 M in hexanes, 0.300 mL, 42 mg, 0.300 mmol) was added to a solution of acetal **17a** (39.0 mg, 0.100 mmol) in hexanes (1 mL) at −78 °C. The solution was allowed to warm to RT overnight with stirring. The mixture was washed with 5% aqueous ammonium chloride solution (10 mL), diluted with methylene chloride (20 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 1:1) afforded product as a clear oil (12 mg, 58%). ^{1}H NMR and optical rotation matched literature values.[26] $[\alpha]_D = -22.1 \pm 0.3$ ($c = 0.300$, $CHCl_3$); lit.:[26] $[\alpha]_D = -19.5 \pm 0.3$ ($c = 3.10$, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.41–7.32$ (m, 5H), 4.92 (d, $J = 8.5$ Hz, 1H), 3.91–3.84 (m, 2H), 3.68–3.64 (m, 1H), 1.95–1.89 (m, 1H), 1.59 (s, 3H), 1.53 (s, 3H); IR ($CHCl_3$): $\tilde{\nu} = 3451, 1605, 1372, 1240, 1056\ cm^{-1}$.

(3*S*,4*S*)-2,2-Dimethyl-4-(hydroxymethyl)-3-phenyl-1,3-dioxolane (18): DIBAL-H (1.0 M in hexanes, 0.50 mL, 0.500 mmol) was added to a solution of acetal **17a** (39.0 mg, 0.100 mmol) in THF (1 mL) at −78 °C. The solution was allowed to warm to RT overnight with stirring. The mixture was washed with 5% aqueous ammonium chloride solution (10 mL), diluted with methylene chloride (10 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 1:1) afforded product **18** as a clear oil (17 mg, 84%). ^{1}H NMR and optical rotation matched literature values.[26] $[\alpha]_D = +23.5 \pm 0.2$ ($c = 1.50$, $CHCl_3$); lit.:[26] $[\alpha]_D = +19.4 \pm 0.2$ ($c = 3.00$, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.42–7.30$ (m, 5H), 4.92 (d, $J = 8.5$ Hz, 1H), 3.91–3.84 (m, 2H), 3.68–3.62 (m, 1H), 1.87 (brs, 1H), 1.60 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 137.6, 128.6, 128.3, 126.5, 109.3, 83.5, 78.6, 60.3, 27.2, 27.1$; IR ($CHCl_3$): $\tilde{\nu} = 3460, 2986, 2933, 1495, 1455, 1372, 1240, 1166, 1082, 1056\ cm^{-1}$.

(4*S*,5*R*)-4-Formyl-5-phenyl-2,2,4-trimethyl-1,3-dioxolane (19): Acetoxysulfone **17b** (81 mg, 0.200 mmol) and potassium carbonate (55.3 mg, 0.400 mmol) were stirred in methanol (1.00 mL) for 4 h at RT. The mixture was filtered, concentrated in vacuo, diluted with methylene chloride (5.0 mL) and water (5.0 mL), the organic layer separated, the organic phase dried over magnesium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 3:1) afforded aldehyde **19** as a colorless oil (41 mg, 93%). $[\alpha]_D = -82.7 \pm 0.3$ ($c = 1.3$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 9.82$ (s, 1H), 7.37–7.31 (m, 5H), 5.30 (s, 1H), 1.67 (s, 3H), 1.52 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 202.2, 135.4, 128.3, 128.1, 126.3, 109.6, 86.7, 78.9, 27.8, 26.0, 18.1$; IR (film): $\tilde{\nu} = 2989, 2936, 1735, 1496, 1456, 1376, 1249, 1220, 1181, 1053, 995\ cm^{-1}$; HRMS: m/z: calcd for $C_{12}H_{15}O_2$: 191.1073; found: 191.1067 [$M^+ - CHO$].

(4*R*,5*S*)-2,2-Dimethyl-4-((1′*R*)-1′-hydroxyethyl)-5-phenyl-1,3-dioxolane (22)—General procedure: Acetal **17a** (39.0 mg, 0.100 mmol) in diethyl ether (1.00 mL) was added at the stated temperature under argon to an diethyl ether solution of methyl magnesium bromide (0.200 mL, 71.7 mg, 0.600 mmol) and additive (see Table 8). After stirring at the state temperature for 1 h, the mixture was allowed to warm to RT and diluted with diethyl ether (10 mL). The mixture was then quenched with 10% aqueous ammonium chloride solution (10 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded alcohol **35** as a clear gel. $[\alpha]_D = -36.0 \pm 0.3$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.45–7.30$ (m, 5H), 4.91 (dd, $J = 12.4$, 11.2 Hz, 1H), 4.06–3.69 (m, 2H), 2.16–2.10 (m, 1H), 1.58 (s, 3H), 1.51 (s, 3H), [1.14 (d, $J = 6.4$ Hz, 1.3H), 1.08 (d, $J = 6.4$ Hz, 1.8H) together 3H)]; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.7, 128.6, 128.4, 127.6, 127.0, 97.8, 86.7, 86.0, 79.5, 78.8, 66.7, 65.6, 27.2, 27.0, 18.2$; IR ($CHCl_3$): $\tilde{\nu} = 3468, 2985, 1604, 1456, 1372, 1239, 1169, 1060\ cm^{-1}$; HRMS: m/z: calcd for $C_{13}H_{18}O_3$: 222.1256; found: 222.1251 [M^+].

Table 8. Additions of methyl magnesium bromide to acetal **17a**.

Entry	T [°C]	Additive (wt./mg)	Amount [mg]/% Yield	*dr* (*syn*:*anti*)[a]
1	0	none	19.3/87	1.5:1.0
2	−78	CuBr (71.7)	19.6/88	1.5:1.0
3	−78	$MgCl_2$ (9.5)	18.7/84	1.5:1.0

[a] The *dr* was determined by proton NMR integration of the methyl proton doublets (δ 1.14, $J = 6.4$ Hz, minor peak, δ 1.08, $J = 6.4$ Hz, major peak).

(4*S*,5*R*)-2,2-Dimethyl-4-((1′*R*)-1′-hydroxypropyl)-5-phenyl-1,3-dioxolane (22): Acetal **17a** (39.0 mg, 0.100 mmol) in diethyl ether (1.00 mL) was added at −78 °C under argon to an 1.0 M diethyl ether solution of ethylmagnesium bromide (0.600 mL, 80 mg, 0.600 mmol). After stirring for 1 h, the mixture was allowed to warm to RT and diluted with diethyl ether (20 mL). The mixture was then quenched with 10% aqueous ammonium chloride solution (20 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded alcohol **22** as a clear gel (17.5 mg, 74%). The product was a 2:1 mixture of diastereomers as determined by ^1H NMR integration of the methyl protons (triplet) of the ethyl group (δ = 0.91, J = 7 Hz, minor peak, δ = 0.85, J = 6.8 Hz, major peak). $[\alpha]_D = -14.2 \pm 0.1$ (c = 1.00, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 7.44–7.36 (m, 10H), 5.00–4.96 (m, 1H), 3.99–3.93 (m, 1H), 3.82–3.76 (m, 1H), 2.07 (d, J = 2.4 Hz, 1H), 1.58 (s, 3H), 1.56 (s, 3H), 1.45–1.33 (m, 2H), [0.91 (t, J = 7.1 Hz, 1H) (minor), 0.85 (t, J = 6.8 Hz, 1H) (major)]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5, 128.7, 128.6, 128.4, 127.8, 126.9, 108.9, 85.3, 85.3, 85.1, 79.4, 78.7, 72.3, 70.2, 28.2, 27.3, 27, 25.5, 10.1; IR ($CHCl_3$): $\tilde{\nu}$ = 3461, 2984, 2934, 1457, 1371, 1236, 1168, 1062 cm^{-1}; HRMS: m/z: calcd for $C_{13}H_{17}O_3$: 221.1181; found: 221.1183 [$M^+ - CH_3$].

(4*S*,5*R*)-2,2-Dimethyl-4-((1′*R*)-1′-hydroxy-1′-phenyl)-5-phenyl-1,3-dioxolane (23): Acetal **17a** (58.5 mg, 0.150 mmol) in diethyl ether (2.00 mL) was added at −78 °C under argon to an diethyl ether solution of phenylmagnesium bromide (0.90 mL, 163 mg, 0.900 mmol). After stirring for 1 h, the mixture was allowed to warm to RT and diluted with diethyl ether (20 mL). The mixture was then quenched with 10% aqueous ammonium chloride solution (20 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded alcohol **23** as a clear gel (28 mg, 66%). ^1H NMR indicated that the product was a single diastereomer. $[\alpha]_D = -0.83 \pm 0.1$ (c = 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.16 (m, 10H), 4.96 (d, J = 8.3 Hz, 1H), 4.68 (dd, J = 7.0, 3.8 Hz, 1H), 4.12 (dd, J = 8.3, 3.9 Hz, 1H), 2.77 (d, J = 7.1 Hz, 1H), 1.57 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5, 137.8, 128.5, 128.2, 128.1, 126.9, 126.8, 121.1, 109.9, 86.5, 79.8, 72.6, 27.3, 27.1; IR ($CHCl_3$): $\tilde{\nu}$ = 3451, 2986, 2917, 1604, 1495, 1454, 1380, 1238, 1164, 1052 cm^{-1}; HRMS: m/z: calcd for $C_{17}H_{17}O_3$: 269.1178; found: 269.1168 [$M^+ - CH_3$].

(4*S*,5*R*)-2,2-Dimethyl-4-((1′*R*)-1′-hydroxy-1′-phenyl)-5-isopropyl-1,3-dioxolane (24): Acetal **17c** (17.8 mg, 0.050 mmol) in diethyl ether (1.00 mL) was added at −78 °C under argon to an diethyl ether solution of PhMgBr (0.300 mL, 54.5 mg, 0.300 mmol). After stirring for 1 h, the mixture was allowed to warm to RT and diluted with diethyl ether (10 mL). The mixture was then quenched with 10% aqueous ammonium chloride solution (10 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded alcohol **24** as a clear gel (10.2 mg, 82%). ^1H NMR confirmed the product was a single diastereomer. $[\alpha]_D = +49.9 \pm 0.4$ (c = 0.25, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 7.37–7.32 (m, 5H), 4.59 (dd, J = 5.5, 5.2 Hz, 1H), 3.97 (dd, J = 6.2, 6.1 Hz, 1H), 3.73 (dd, J = 6.1, 5.6 Hz, 1H), 2.90 (d, J = 4.6 Hz, 1H), 1.49 (s, 3H), 1.42 (s, 3H), 0.85 (d, J = 6.4 Hz, 3H), 0.69 (d, J = 6.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.5, 128.5, 128.2, 126.9, 109.4, 83.2, 83.0, 75.2, 30.6, 27.7, 19.2, 17.2; IR ($CHCl_3$): $\tilde{\nu}$ = 3457, 2962, 1605, 1451, 1370, 1243, 1166, 1039 cm^{-1}; HRMS: m/z: calcd for $C_{14}H_{19}O_3$: 235.1330; found: 235.1328 [$M^+ - CH_3$].

(1*R*,2*S*,3*R*)-1-Acetoxy-3-*tert*-butylhydroxy-1-phenylsulfonyl-3-phenyl-2-propanol (25): Trimethylaluminum (2.0 M in toluene, 0.300 mL, 43.2 mg, 0.600 mmol) was added at 0 °C to a degassed solution of trifluoromethanesulfonic acid (135.0 mg, 0.900 mmol). After the reaction mixture was stirred for 20 min, a solution of acetal **17a** (39.0 mg, 0.100 mmol) in toluene (0.50 mL) was added at 0 °C and the solution was stirred for 1 h. The mixture was washed with water (25 mL), diluted with methylene chloride (20 mL), the organic phase dried over sodium sulfate, and concentrated in vacuo. Flash chromatography (PE/Et_2O 2:1) afforded the unexpected product **25** as a clear oil (22 mg, 48%). $[\alpha]_D = -54.5 \pm 0.7$ (c = 0.70, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 7.92 (d, J = 5.8 Hz, 2H), 7.65–7.60 (m, 3H), 7.34–7.26 (m, 5H), 5.81 (d, J = 7.3 Hz, 1H), 4.66 (d, J = 3.5 Hz, 1H), 4.00 (m, 1H), 2.86 (d, J = 7.1 Hz, 1H), 2.05 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.2, 141.4, 139.7, 134.0, 129.6, 128.9, 128.3, 127.9, 127.1, 85.6, 76.1, 73.9, 73.0, 28.7, 20.3; IR ($CHCl_3$): $\tilde{\nu}$ = 3511, 2974, 1774, 1448, 1370, 1310, 1201, 1152, 1054 cm^{-1}; HRMS: m/z: calcd for $C_{17}H_{17}O_5S$ ($M^+ - C_4H_9O$): 333.0791; found: 333.0796.

127.1, 85.6, 76.1, 73.9, 73.0, 28.7, 20.3; HRMS: m/z: calcd for $C_{17}H_{17}O_5S$: 333.0791; found: 333.0796 [$M^+ - C_4H_9O$].

(2*S*,3*R*)-2-Hydroxy-2-methyl-3-acetoxy-3-phenylpropanal (*ent*-16b): A 4% aqueous osmium tetroxide solution (31 μL, 0.005 mmol) was added at 0 °C to a solution of substrate *ent*-**14b** (33.0 mg, 0.100 mmol) and NMO (35.1 mg, 0.300 mmol) in methylene chloride (1.00 mL). After 12 h at 0 °C 4-dimethylaminopyridine (12.2 mg, 0.100 mmol) was added and the solution was stirred for 6 h at RT. Flash chromatography (PE/Et_2O 1:1) afforded aldehyde *ent*-**16b** as a colorless oil (20.5 mg, 92%). $[\alpha]_D = -4.6 \pm 0.1$ (c = 1.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 9.68 (s, 1H), 7.41–7.36 (m, 5H), 5.90 (s, 1H), 3.36 (s, 1H), 2.08 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.3, 169.6, 134.4, 128.8, 128.2, 79.6, 76.9, 20.9, 19.6; IR (film): $\tilde{\nu}$ = 3488, 2935, 1736, 1496, 1456, 1373, 1234, 1107, 1026, 926 cm^{-1}; HRMS: m/z: calcd for $C_{12}H_{14}O_4$: 223.0970; found: 223.0968 [$M^+ + H$].

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