

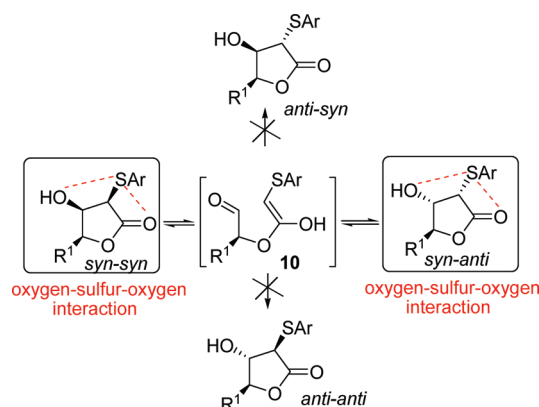
Stereoisomerization of β -Hydroxy- α -sulfenyl- γ -butyrolactones Controlled by Two Concomitant 1,4-Type Nonbonded Sulfur–Oxygen Interactions As Analyzed by X-ray Crystallography

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We have synthesized nine β -hydroxy- α -sulfenyl- γ -butyrolactones having different substituents. The *syn-anti* or *syn-syn* lactones (or any mixture of both) invariably isomerized into *syn-anti*/*syn-syn* lactones in a ratio of $\sim 6/4$. The other two possible isomeric lactones (*anti-syn* or *anti-anti*) were never observed. The crystal structures of *syn-syn* lactones have been determined. We found sulfur–oxygen distances to be less than the sum of the van der Waals radii (3.3 Å), with the angle formed among the hydroxylic oxygen, sulfur, and quaternary aromatic carbon being close to 180°. In addition, carbonylic oxygen–sulfur is directed $< 40^\circ$ from the perpendicular to the C–S–C. Theoretical calculations were performed which emphasize the directionality of the sulfur–oxygen interaction. The X-ray and theoretical studies demonstrate that two concomitant, attractive 1,4 intramolecular interactions of divalent sulfur with both carbonyl and hydroxyl oxygens are the driving force for the aforementioned stereochemical preference. Then nonbonded sulfur–oxygen interactions would control the stereoselectivity of the reaction. The same features are observed in the X-ray structure of a β -hydroxy- α -sulfinyl- γ -butyrolactone.

Introduction

The steric energy of a molecule, which accounts for its geometry at the energy minimum, is expressed in terms of a

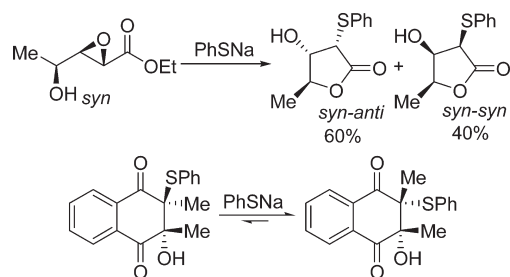
number of contributions such as nonbonded interactions.¹ Attractive nonbonded interactions can play an important role in determining the stereoselectivity of chemical processes.² Specifically, intramolecular reactions often benefit from greater control of stereoselectivity relative to their intermolecular counterparts.²

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SCHEME 1. Isomerization of β -Hydroxy- α -sulfenyl Carbonyl Compounds



During the course of a preceding study related to the synthesis of β -hydroxy- α -sulfenyl- γ -butyrolactones from γ -hydroxy- α,β -epoxy esters,³ we made a curious observation: an approximately 6/4 ratio of a mixture of *syn-anti*/*syn-syn* lactones was always obtained, regardless of the stereoisomeric ratio of the starting epoxides (Scheme 1). This tendency of α -sulfenyl carbonyl compounds to isomerize into an isomer displaying a *syn* relative stereochemistry has been reported previously by Silverman for dihydronaphthoquinones (Scheme 1).⁴

Weak nonbonding interactions between sulfur and oxygen atoms have been invoked to explain the control of conformations in a large number of organosulfur compounds,⁵ including molecules which play important roles in biological systems.⁶ Usually, these interactions are based on the distances between sulfur and oxygen atoms being less than the sum of S and O van der Waals radii (3.3 Å) as measured in X-ray structures.

The sulfur–oxygen interactions in organic compounds are usually formed between the nonbonding atoms separated by three or four covalent bonds (1,4- or 1,5-type sulfur–oxygen interactions, respectively), while those in proteins are much more widely separated throughout the polypeptide backbone.^{6h}

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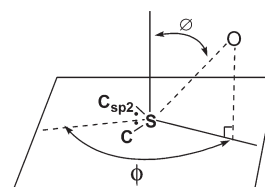
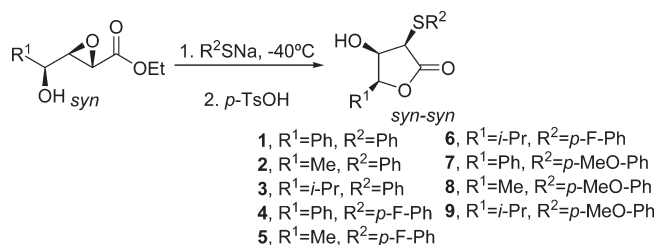


FIGURE 1. Polar coordinates (polar θ and azimuthal ϕ angles) to specify the direction of S...O.

SCHEME 2. Syntheses of β -Hydroxy α -Sulfenyl γ -Butyrolactones



According to the seminal work by Parthasarathy and co-workers,⁷ two types of sulfur–oxygen interactions can be identified: nucleophilic oxygens, which tend to approach along the extension of one of the covalent bonds to sulfur ($60^\circ < \theta < 90^\circ$) ($110^\circ < \phi < 150^\circ$), and electrophilic oxygens, which tend to approach sulfur from the direction perpendicular to the plane through the C–S–C atoms ($\theta < 40^\circ$) (Figure 1).

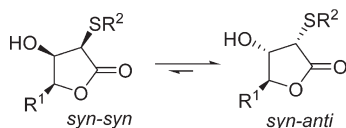
Herein, we report a general study of the isomerization process as applied to β -hydroxy- α -sulfenyl- γ -butyrolactones. We have determined the crystal structures of *syn-syn* β -hydroxy- α -sulfenyl- γ -butyrolactones **1–9**. Both of the aforementioned types of sulfur–oxygen contacts are observed in lactones **1–9**, with the sulfur atom in contact with both the nucleophilic hydroxyl oxygen and with the electrophilic carbonyl oxygen. We hypothesized these two concomitant, attractive 1,4 intramolecular interactions of divalent sulfur with both carbonyl and hydroxyl oxygens to be the driving force for the aforementioned stereochemical preference. Curiously, the same features are observed in the X-ray structure of β -hydroxy- α -sulfenyl- γ -butyrolactone **11** readily obtained by oxidation in a stereoselective fashion.

Results and Discussion

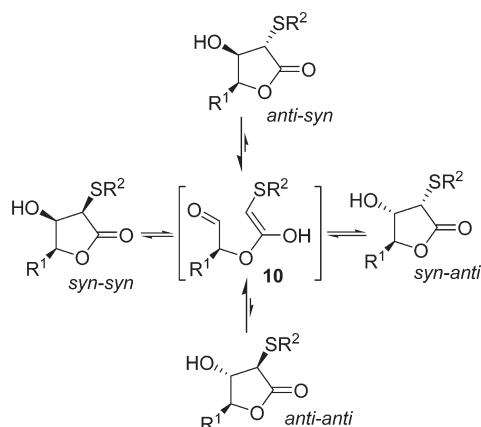
A series of β -hydroxy- α -sulfenyl- γ -butyrolactones having different R¹ and R² substituents were prepared in order to study the influence of these substituents on the isomerization process. We also wanted to study how the sulfur–oxygen interactions are influenced by different R² substituents having an electron-withdrawing group (fluorine) or an electron-donating group (methoxy) in the aromatic ring.² We have synthesized *syn-syn* β -hydroxy- α -sulfenyl- γ -butyrolactones **1–9** from γ -hydroxy- α,β -epoxy esters as previously reported (Scheme 2).³

These *syn-syn* lactones **1–9** (or *syn-anti* isomers, or any mixture of both) invariably isomerized into *syn-anti*/*syn-syn* lactones in a ratio of $\sim 6/4$ (Scheme 3 and Table 1). The isomerization occurred easily under basic conditions (stirring at room temperature with triethylamine), neat upon heating, or in a polar solvent like DMSO at room temperature (see the Experimental Section).

The isomerization process can be rationalized through a retroaldol–aldol sequence⁸ as previously reported by

SCHEME 3. Isomerization of β -Hydroxy α -Sulfenyl γ -Butyrolactones

TABLE 1. Ratio of *Syn-Syn*/*Syn-Anti* Lactones 1–9 Resulting from Isomerization

lactone	basic conditions <i>syn-syn</i> / <i>syn-anti</i>	neat upon heating <i>syn-syn</i> / <i>syn-anti</i>	DMSO at rt <i>syn-syn</i> / <i>syn-anti</i>
1	40/60	34/66	31/69
2	32/68	40/60	33/67
3	33/67	39/61	35/65
4	46/54	44/56	36/64
5	36/64	40/60	32/68
6	42/58	33/67	30/70
7	35/65	40/60	34/66
8	29/71	30/70	35/65
9	33/67	33/67	41/59

SCHEME 4. Retroaldol–Aldol Sequence


Silverman^{4a} (Scheme 4). The other two possible isomeric lactones (*anti-syn* or *anti-anti*) were never observed.

We hypothesized that the distinctive nonbonding sulfur–oxygen contacts are at the origin of this phenomenon.⁹

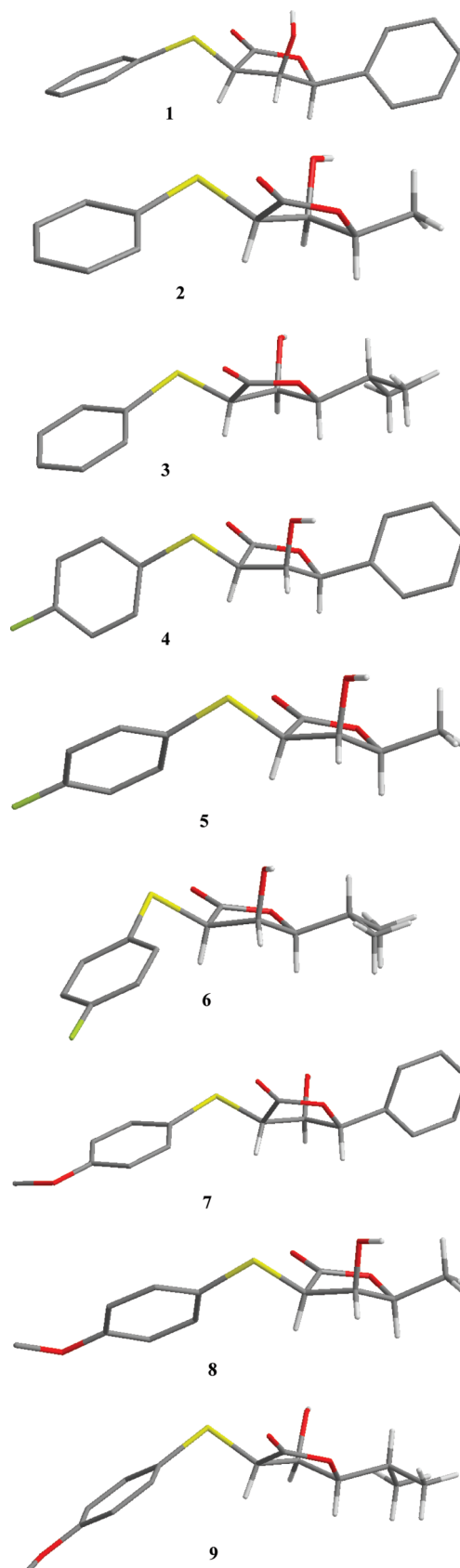
In order to confirm it, the crystal structures of *syn-syn* lactones (1–9) have been determined (Figure 2).¹⁰ Geometric features were essentially similar for 1–9, with the

(8) Aldehyde **10** was trapped as an alkene when treated with a base in the presence of a phosphonium salt. See also ref 3c

(9) We ruled out the intermediacy of hydrogen bonding between OH and the sulfur atom as the driving force of the phenomenon under the reaction conditions for several reasons: 1) The isomerization takes place in THF as solvent which it is known to be a high hydrogen bonding acceptor. 2) Hydroxylic peak of the lactones in ¹H NMR shifted considerably when changing the solvent from CDCl₃ to CD₃CN ($\Delta\delta$ = 2.85 ppm in CDCl₃ and 3.72 ppm in CD₃CN for compound **2**; $\Delta\delta$ = 2.74 ppm in CDCl₃ and 3.73 ppm in CD₃CN for compound **5**).

(10) The crystal structures have been deposited at the CCDC and allocated the deposition numbers: CCDC 603611, 293151, 293009, 714594, 714595, 714596, 714597, 714598 and 714599 for 1–9, respectively.

(11) It is well-known that different crystal ordering (and accordingly intermolecular contacts) may affect intramolecular bond distances and therefore comparisons between compounds with different crystal packing must be undertaken with caution. This particularly holds for compound **6**, for which a different crystal packing is observed as compared with the rest of the series. Consequently, intramolecular S⋯O contacts in compound **6** fall outside of the general trend determined for 1–5 and 7–9 as well as for the vast majority of closely related compounds.


FIGURE 2. X-ray structures of compounds 1–9.

only exception being compound **6**.¹¹ The distances between the hydroxyl oxygen and sulfur and between the carbonyl

TABLE 2. Sulfur–Oxygen Distances (from Hydroxyl Groups) and Polar and Azimuthal Angles in X-ray Structures of Lactones

lactone	S···O _{hydroxyl}	ϕ_{hydroxyl} (deg)	θ_{hydroxyl} (deg)
1	2.937	107.1	97.3
2	2.871	106.7	95.6
3	2.896	107.1	92.5
4	2.853	106.1	84.3
5	2.886	105.8	83.7
6	3.104	68.6	41.8
7	2.876	107.0	94.6
8	2.865	103.8	94.9
9	2.952	109.5	103.6

TABLE 3. Sulfur–Oxygen Distances (from Carbonyl Groups) and Polar and Azimuthal Angles X-ray Structures of Lactones

lactone	S···O _{carbonyl}	ϕ_{carbonyl} (deg)	θ_{carbonyl} (deg)
1	3.197	33.6	42.7
2	3.178	39.9	41.0
3	3.214	38.0	42.6
4	3.202	35.5	40.7
5	3.165	40.7	40.7
6	3.054	98.3	63.8
7	3.211	41.8	41.1
8	3.213	30.7	42.1
9	3.200	60.2	40.7

oxygen and sulfur are less than the sum of S and O van der Waals radii (3.3 Å) in all compounds (Tables 2 and 3).

The short atomic distances observed in *syn-syn* lactones are interpreted as nonbonded interactions between oxygen and sulfur atoms. For all structures, the distances between the hydroxyl oxygen and sulfur atoms are less than the distances between the carbonyl oxygen and sulfur atoms, with the exception of compound **6**.¹¹

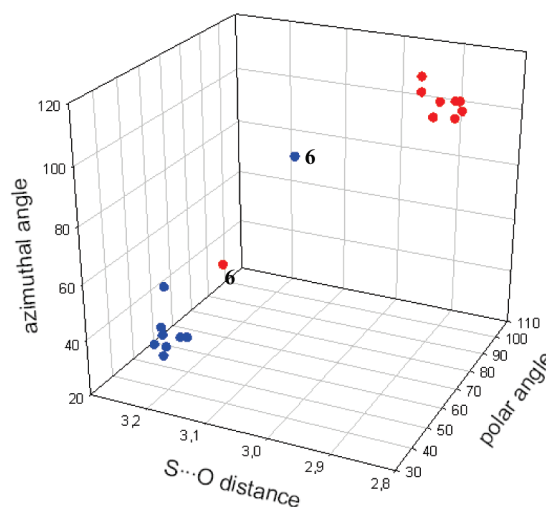
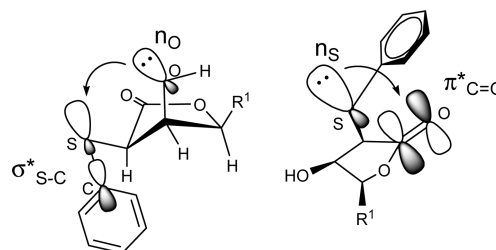
The distances between oxygen atoms (either carbonyl or hydroxyl) and the sulfur atom depend on the substituent on the aromatic ring.

Azimuthal angles for sulfur–hydroxyl oxygen contacts are very similar, around 107° (Table 2), and polar angles for sulfur–carbonyl oxygen contacts are also similar, being around 41° (Table 3). Curiously, lactone **6** shows angles that have a reversed relationship of magnitude ($\phi_{\text{carbonyl}} = 98.3^\circ$ and $\theta_{\text{hydroxyl}} = 41.8^\circ$).

Figure 3 shows a 3D representation of S···O contacts, the azimuthal and polar angles involving O atoms from the carbonyl and hydroxyl groups (see also Tables 2 and 3). It reflects graphically that the sulfur–oxygen contacts from the hydroxyl oxygens have azimuthal and polar angles that are very similar for all compounds and so is the case for the sulfur–oxygen contacts from carbonyl oxygens.

Both types of sulfur–oxygen contacts are observed concomitantly in lactones **1–9**, with the sulfur atom in contact with both the nucleophilic hydroxyl oxygen and with the electrophilic carbonyl oxygen. This configuration is reversed in the case of compound **6**, as illustrated by the outlying blue and red dots midway between the other data points in Figure 3. This is the first report of such a spatial disposition, with both types of sulfur–oxygen interactions present at the same time.

The linear alignment of the C–S covalent bond and the coordinating hydroxyl oxygen should allow an effective orbital interaction between the oxygen lone pair and σ^* orbital of the S–C bond (see Figure 4), which may elongate the S–C bond (1.76–1.78 Å for **1–9**, 1.75 Å for the diphenyl

**FIGURE 3.** 3D representation of S···O distances and polar and azimuthal angles for compounds **1–9**. Red dots represent sulfur–oxygen contacts from hydroxyl oxygens, and blue dots represent sulfur–oxygen contacts from carbonyl oxygens.**FIGURE 4.** Electron delocalization from the oxygen lone pair (n_O) to the antibonding orbital of a S–C bond (σ^*) and from the sulfur lone pair to the π^* of the C=O bond.

disulfide). The phenyl ring attached to the sulfur atom is oriented in the direction opposite to the hydroxyl, permitting the interaction to take place (see Figure 2). On the other hand, the carbonyl oxygen is positioned $\sim 40^\circ$ from the perpendicular to the C–S–C plane and should allow orbital interactions between π^* of the C=O bond and the sulfur lone pair electrons (see Figure 4). In the case of compound **6**, the phenyl ring attached to the sulfur atom is oriented in the direction opposite to that of the carbonyl oxygen, permitting an orbital interaction between the carbonyl oxygen lone pair and σ^* orbital of the S–C bond.

We performed theoretical calculations for the *syn-syn* and *syn-anti* lactones **1**. Their geometries were fully optimized in vacuo using the B3LYP¹² exchange-correlation functionals together with the standard 6-31+G(d,p) basis set.¹³ The electronic structures of the geometries associated with the *syn-syn* and *syn-anti* lactones were analyzed using the Wiberg bond order (BO)¹⁴ (Table 4). The BO values between the sulfur atom and the hydroxyl oxygen are very similar in both lactones, as are their interatomic distances. However, differences are evident when the BO between the sulfur and

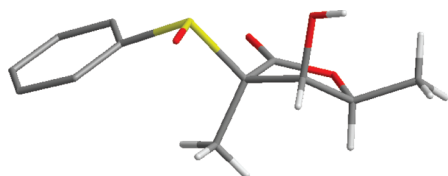
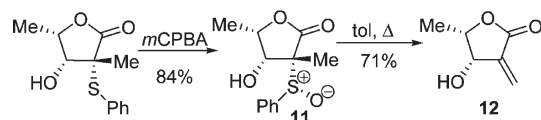
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TABLE 4. Theoretical Sulfur–Oxygen Distances and Bond Order (BO) (B3LYP/6-311+G**)

entry ^a	lactone	S···O _{hydroxyl}	S···O _{carbonyl}	BO (S···OH)	BO (S···OC)
1	<i>syn-syn</i> - 1	3.093	3.429	0.014	0.023
2	<i>syn-anti</i> - 1	3.010	3.248	0.014	0.009

^aSulfur–oxygen distances (Å) and BO of the *syn-syn*- and *syn-anti*-**1** B3LYP/6-311+G(d,p) geometries.**FIGURE 5.** X-ray structure of compound **11**.**SCHEME 5.** Synthesis of Sulfoxide **11**

carbonyl oxygen are compared. Although the S···O carbonyl bond of *syn-anti* **1** is ~0.18 Å shorter than that of the corresponding *syn-syn* **1**, the carbonyl BO of the *syn-syn* **1** is 2.5 times greater than *syn-anti* **1**. This difference emphasizes the directionality of the sulfur–oxygen interaction.

Interestingly, a very similar spatial disposition is also observed in the structure of sulfoxide **11**. Compound **11** is an intermediate in the synthesis of the natural product **12** (Scheme 5).¹⁵ It is obtained through oxidation of the preceding sulfide as a single isomer (Scheme 5). It is well-known that the oxidation of the thioether group is strongly influenced by neighboring atoms.¹⁶

The X-ray crystal structure of sulfoxide **11** shows the configuration of the sulfur atom to be *R* (Figure 5).¹⁷ The distance between the hydroxyl oxygen and sulfur is 2.734 Å and between the carbonyl oxygen and sulfur is 3.177 Å. Azimuthal and polar angles are $\phi = 109.6^\circ$ and $\theta = 96^\circ$ for the sulfur–hydroxyl oxygen contact and $\phi = 23.7^\circ$ and $\theta = 38.3^\circ$ for the sulfur–carbonyl oxygen contact, respectively. These geometric features are similar to the ones depicted for *syn-syn* lactones **1–9**. The double sulfur–oxygen interaction would stabilize the *R* configuration of the sulfur atom during oxidation.

In summary, two attractive 1,4 intramolecular interactions of divalent sulfur with both carbonyl and hydroxyl oxygens are observed in the X-ray structures of β -hydroxy- α -sulfinyl- γ -butyrolactones and a β -hydroxy- α -sulfinyl- γ -butyrolactone. Sulfur–oxygen interactions can be invoked to account for the tendency of β -hydroxy α -sulfinyl γ -butyrolactones to assume the *syn* configuration. Our synthetic α -sulfinyl carbonyl systems should contribute to the understanding of the role played by these subtle noncovalent interactions in determining the preferred conformation in biochemical and molecular recognition processes.

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(17) The crystal structure has been deposited at the CCDC and allocated the deposition number CCDC 752570.

Experimental Section

General Experimental Methods. All solvents used in reactions were freshly distilled from appropriate drying agents before use. ¹H NMR spectra and ¹³C NMR spectra were measured in CDCl₃ (¹H, 7.24 ppm; ¹³C 77.0 ppm) solution at 30 °C on a 300 MHz or a 500 MHz NMR spectrometer. Mass spectra were measured in a hybrid quadrupole-t-TOF mass spectrometer operating at a resolution ca. 15000 fwhm (W-mode) with an orthogonal Z-spray-electrospray interface. The drying gas as well as nebulizing gas was nitrogen at a flow of 400 and 60 L/h, respectively. The temperature of the source block was set to 120 °C and the desolvation temperature to 150 °C. A capillary voltage of 3 kV was used in the positive scan mode, and the cone voltage was set to 15 V. Sample solutions were infused via syringe pump directly connected to the ESI source at a flow rate of 10 μ L/min. ESI mass spectra were dominated by the presence of sodium adducts of the target compound. For the accurate mass measurements, a 2 mg/L standard solution of leucine enkephalin was introduced via the lock spray needle at a cone voltage set to 45 V and a flow rate of 30 μ L/min. IR spectra were recorded as oily films on NaCl plates on a FT-IR spectrometer. EM Science silica gel 60 was used for column chromatography, while TLC was performed with precoated plates (Kieselgel 60, *F*₂₅₄, 0.25 mm). Unless otherwise specified, all reactions were carried out under nitrogen atmosphere with magnetic stirring.

General Procedure for the Syntheses of *syn-syn*-Lactones **1–9.** A –40 °C cold suspension of NaH (60% in mineral oil) (1.12 mmol) in THF (1 mL) was treated with thiophenol (2.25 mmol). The mixture was stirred at –40 °C for 15 min, a solution of *syn*-epoxy ester (0.75 mmol) in THF (1 mL) was added dropwise, and the resulting mixture was stirred at –40 °C for 1.5 h. Brine was added, the mixture was extracted with Et₂O (3 \times 20 mL), and the organic layers were washed (brine), dried (Na₂SO₄), and concentrated. The crude oil which contained the corresponding diols was directly submitted for cyclization without further purification.

A solution of diol in CHCl₃ (2 mL) was treated with *p*-toluenesulfonic acid (catalytic amount). The resulting mixture was stirred at room temperature for 1 h. NaHCO₃ (saturated aqueous solution) was added, and the mixture was extracted with Et₂O (3 \times 20 mL), and the organic layers were washed (brine), dried (Na₂SO₄), and concentrated. The crude was purified through chromatography (silica gel, hexanes/EtOAc (7:3) and (6:4)).

Compound *syn,syn*-1**:** ¹H NMR (CDCl₃, 500 MHz) δ 7.50–7.53 (m, 2H), 7.35–7.45 (8H, m), 5.47 (1H, d, *J* = 3.0 Hz), 4.56 (1H, ddd, *J* = 4.0, 3.0, 2.0 Hz), 4.35 (1H, d, *J* = 4.0 Hz), 2.37 (1H, d, *J* = 2.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 172.6, 133.0, 132.6, 129.6, 129.1, 128.7, 128.6, 126.5, 83.0, 71.4, 56.6; IR (NaCl) ν 3460, 3060, 2916, 1951, 1886, 1752, 1581, 1498, 1456, 1438, 1326, 1290, 1214, 1179, 1110, 1024, 994, 954, 942, 815, 790, 701, 634 cm^{–1}; HRMS *m/z* calcd for C₁₆H₁₄O₃Na [M + Na⁺] 309.0562, found 309.0580 (recrystallized from hexanes/EtOAc, mp 151.5–154.5 °C).

Compound *syn,syn*-2**:** ¹H NMR (CDCl₃, 500 MHz) δ 7.33–7.57 (m, 5H), 4.51 (1H, dq, *J* = 6.5, 3 Hz), 4.24 (2H, m), 2.75 (1H, s), 1.50 (3H, d, *J* = 6.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 172.9, 132.4, 129.7, 128.7, 79.0, 69.9, 57.3, 14.1; IR (NaCl) ν 3381, 2921, 2860, 1752, 1630, 1436, 1174, 1113 cm^{–1}; HRMS *m/z* calcd for C₁₁H₁₂O₃Na [M + Na⁺] 247.0405, found 247.0376.

Compound *syn,syn*-3: ^1H NMR (CDCl_3 , 500 MHz) δ 7.52–7.54 (2H, m), 7.33–7.36 (3H, m), 4.31 (1H, m), 4.24 (1H, d, $J = 4.0$ Hz), 3.86 (1H, dd, $J = 10.0, 2.5$ Hz), 2.75 (1H, s), 2.27 (1H, m), 1.11 (3H, d, $J = 7.0$ Hz), 0.99 (3H, d, $J = 6.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.2, 132.4, 132.0, 129.7, 128.7, 88.3, 68.6, 57.6, 27.6, 19.8, 17.5; IR (NaCl) ν 3423, 2965, 1760, 1471, 1440, 1392, 1339, 1171, 1072, 1026, 873, 778, 745, 690 cm^{-1} ; HRMS m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{SNa}$ [$\text{M} + \text{Na}^+$] 275.0718, found 275.0706 (recrystallized from hexanes/EtOAc, mp 147.8–148.5 $^\circ\text{C}$).

Compound *syn,syn*-4: ^1H NMR (CDCl_3 , 500 MHz) δ 7.62–7.65 (2H, m), 7.37–7.45 (5H, m), 7.04–7.07 (2H, m), 5.45 (1H, d, $J = 2.0$ Hz), 4.55 (1H, ddd, $J = 4.5, 3.0, 2.0$ Hz), 4.22 (1H, d, $J = 4.5$ Hz), 2.26 (1H, br s); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.7, 163.2 ($J = 252.5$ Hz), 135.6 ($J = 8.4$ Hz), 132.9, 129.2, 128.8, 127.7, 126.5, 116.7 ($J = 22.0$ Hz), 82.9, 71.6, 57.0; IR (NaCl) ν 3483, 2925, 1951, 1758, 1590, 1498, 1456, 1492, 1456, 1363, 1398, 1320, 1234, 1172, 1093, 998, 932, 942, 843, 827, 817, 747, 697, 634, 508 cm^{-1} ; HRMS m/z calcd for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{SFNa}$ [$\text{M} + \text{Na}^+$] 327.0462, found 327.0471 (recrystallized from hexanes/EtOAc, mp 176–178 $^\circ\text{C}$).

Compound *syn,syn*-5: ^1H NMR (CDCl_3 , 500 MHz) δ 7.56–7.59 (2H, m), 7.04–7.07 (2H, m), 4.51 (1H, dq, $J = 7.0, 3.5$ Hz), 4.23 (1H, dd, $J = 4.5, 3.0$ Hz), 4.14 (1H, d, $J = 4.5$ Hz), 2.73 (1H, d, $J = 2.5$ Hz), 1.50 (3H, d, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.2, 163.2 ($J = 248.6$ Hz), 135.4 ($J = 8.3$ Hz), 127.2 ($J = 3.5$ Hz), 116.9 ($J = 22.0$ Hz), 79.0, 70.0, 57.7, 14.1; IR (NaCl) ν 3487, 2908, 1755, 1589, 1491, 1340, 1232, 1186, 818 cm^{-1} ; HRMS m/z calcd for $\text{C}_{11}\text{H}_{11}\text{O}_3\text{SFNa}$ [$\text{M} + \text{Na}^+$] 265.0305, found 265.0312 (recrystallized from hexanes/EtOAc, mp 143–144 $^\circ\text{C}$).

Compound *syn,syn*-6: ^1H NMR (CDCl_3 , 500 MHz) δ 7.55–7.58 (2H, m), 7.05–7.08 (2H, m), 4.29 (1H, s), 4.14 (1H, d, $J = 4.0$ Hz), 3.84 (1H, dd, $J = 10.5, 3.0$ Hz), 2.69 (1H, s), 2.24–2.29 (1H, m), 1.12 (3H, d, $J = 7.0$ Hz), 1.00 (3H, d, $J = 6.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.1, 163.2 ($J = 248.5$ Hz), 135.3 ($J = 8.5$ Hz), 127.0 ($J = 3.6$ Hz), 116.9 ($J = 22.0$ Hz), 88.3, 68.7, 58.2, 27.6, 19.8, 17.5; IR (NaCl) ν 3441, 2967, 1747, 1589, 1493, 1389, 1341, 1315, 1224, 1183, 1159, 1127, 1083, 988, 947, 826, 777, 734, 638, 616 cm^{-1} ; HRMS m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3\text{SFNa}$ [$\text{M} + \text{Na}^+$] 293.0618, found 293.0622. (Recrystallized from hexanes/EtOAc, mp 173–174 $^\circ\text{C}$).

Compound *syn,syn*-7: ^1H NMR (CDCl_3 , 300 MHz) δ 7.54–7.57 (2H, m), 7.37–7.43 (5H, m), 6.87–6.90 (2H, m), 5.42 (1H, d, $J = 3.0$ Hz), 4.49 (1H, ddd, $J = 4.5, 3.0, 1.8$ Hz), 4.22 (1H, d, $J = 4.5$ Hz), 3.81 (3H, s), 2.49 (1H, d, $J = 2.1$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz) δ 172.5, 160.6, 135.7, 133.2, 129.0, 128.7, 126.5, 122.4, 115.2, 82.9, 71.2, 57.8, 55.5; IR (NaCl) ν 3369, 3064, 2914, 1864, 1770, 1595, 1494, 1451, 1408, 1321, 1282, 1239, 1181, 1158, 1148, 1123, 1084, 1008, 931, 847, 814, 742, 697, 642, 627, 544, 516 cm^{-1} ; HRMS m/z calcd for $\text{C}_{17}\text{H}_{16}\text{O}_4\text{SNa}$ [$\text{M} + \text{Na}^+$] 339.0662, found 339.0653 (recrystallized from hexanes/EtOAc, mp 165–166 $^\circ\text{C}$).

Compound *syn,syn*-8: ^1H NMR (CDCl_3 , 500 MHz) δ 7.51 (2H, d, $J = 8.0$ Hz), 6.87 (2H, d, $J = 8.5$ Hz), 4.47 (1H, dq, $J = 6.5$ and 3.5 Hz), 4.16 (1H, s), 4.12 (1H, d, $J = 4.5$ Hz), 3.81 (3H, s), 2.90 (1H, br s), 1.50 (3H, d, $J = 6.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.2, 160.6, 135.5, 122.0, 115.3, 78.9, 70.0, 58.4, 55.5, 14.1; IR (NaCl) ν 3482, 3028, 2978, 2935, 2896, 2836, 1750, 1595, 1497, 1439, 1341, 1290, 1250, 1180, 1134, 1122, 1030, 1010, 944, 816 cm^{-1} ; HRMS m/z calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{SNa}$ [$\text{M} + \text{Na}^+$] 277.0505, found 277.0501 (recrystallized from hexanes/EtOAc, mp 133–135 $^\circ\text{C}$).

Compound *syn,syn*-9: ^1H NMR (CDCl_3 , 500 MHz) δ 7.50–7.52 (2H, m), 6.88–6.90 (2H, m), 4.23 (1H, dq, $J = 3.0$ and 2.0 Hz), 4.12 (1H, d, $J = 4.0$ Hz), 3.81 (3H, s), 2.86 (1H, s), 2.25–2.29 (1H, m), 1.10 (3H, d, $J = 7.0$ Hz), 0.99 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.2, 160.6, 135.5, 121.9,

115.3, 88.3, 68.4, 58.8, 55.5, 27.7, 19.9, 17.5; IR (NaCl) ν 3480, 3068, 2965, 2923, 1753, 1591, 1494, 1459, 1337, 1284, 1247, 1201, 1172, 1078, 1035, 1004, 940, 818, 775, 734, 640, 516 cm^{-1} ; HRMS m/z calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{SNa}$ [$\text{M} + \text{Na}^+$] 305.0818, found 305.0820 (recrystallized from hexanes/EtOAc, mp 148–150 $^\circ\text{C}$).

General Procedure for the Isomerization of Lactones 1–9. **Method 1.** A solution of *syn,syn*-lactone (0.25 mmol) in THF (2 mL) was treated with Et_3N (0.25 mmol). The reaction mixture was stirred at room temperature for 12 h and then quenched with 1 M HCl and extracted with Et_2O (3×20 mL). The organic layers were washed with saturated aqueous NaHCO_3 solution and brine and then dried (Na_2SO_4) and concentrated. **Method 2.** A solution of *syn,syn*-lactone (0.25 mmol) in DMSO- d_6 (2 mL) was heated at 50 $^\circ\text{C}$ for 1 h. **Method 3.** Pure solid *syn,syn*-lactone was heated to its melting point for 5 min and then cooled to room temperature.

Compound *syn,anti*-1: ^1H NMR (CDCl_3 , 500 MHz) δ 7.48–7.50 (m, 2H), 7.24–7.35 (8H, m), 5.49 (1H, d, $J = 4.0$ Hz), 4.38 (1H, dd, $J = 4.0, 1.0$ Hz), 3.89 (1H, d, $J = 1.0$ Hz), 2.20 (1H, s); ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.1, 132.9, 132.5, 131.2, 129.5, 129.1, 129.0, 128.9, 126.3, 83.3, 75.5, 52.2; IR (NaCl) ν 3389, 3053, 2987, 1776, 1440, 1265, 1156, 1070, 1023, 909, 650 cm^{-1} ; HRMS m/z calcd for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{SNa}$ [$\text{M} + \text{Na}^+$] 309.0562, found 309.0562 (recrystallized from hexanes/EtOAc, mp 142.5–144.3 $^\circ\text{C}$).

Compound *syn,anti*-2: ^1H NMR (CDCl_3 , 500 MHz) δ 7.33–7.57 (m, 5H), 4.65 (1H, dq, $J = 6.6, 4.4$ Hz), 4.31 (1H, dd, $J = 4.4, 2.8$ Hz), 3.81 (1H, d, $J = 2.8$ Hz), 1.40 (3H, d, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.9, 133.2, 132.3, 129.5, 129.5, 128.9, 78.7, 74.7, 53.0, 13.7; IR (NaCl) ν 3399, 2922, 2853, 1759, 1721, 1623, 1439, 1313, 1259, 1113, 1052 cm^{-1} ; HRMS m/z calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_3\text{SNa}$ [$\text{M} + \text{Na}^+$] 247.0405, found 247.0412.

Compound *syn,anti*-3: ^1H NMR (CDCl_3 , 500 MHz) δ 7.52–7.54 (2H, m), 7.33–7.36 (3H, m), 4.35 (1H, m), 4.06 (1H, dd, $J = 10.0, 3.0$ Hz), 3.80 (1H, s), 2.42 (1H, d, $J = 5.0$ Hz), 2.15 (1H, m), 1.10 (3H, d, $J = 6.5$ Hz), 0.95 (3H, d, $J = 7.0$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.5, 132.8, 131.6, 129.5, 128.8, 88.4, 74.0, 53.5, 27.0, 19.9, 17.6; IR (NaCl) ν 3449, 3060, 2965, 2876, 1759, 1583, 1471, 1440, 1391, 1370, 1340, 1199, 1173, 1121, 1070, 1024, 955, 916, 821, 778, 747, 690 cm^{-1} ; HRMS m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{SNa}$ [$\text{M} + \text{Na}^+$] 275.0718, found 275.0721.

Compound *syn,anti*-4 + compound *syn,syn*-4: ^1H NMR (CDCl_3 , 500 MHz) δ 7.58–7.63 (4H, m) (*syn,syn* and *syn-anti*), 7.34–7.45 (10H, m) (*syn,syn* and *syn-anti*), 7.03–7.09 (4H, m) (*syn,syn* and *syn-anti*), 5.59 (1H, d, $J = 3.5$ Hz) (*syn-anti*), 5.45 (1H, d, $J = 2.5$ Hz) (*syn,syn*), 4.55 (1H, t, $J = 7.5$) (*syn,syn*), 4.46 (1H, t, $J = 4.0$) (*syn-anti*), 4.22 (1H, d, $J = 4.5$ Hz) (*syn,syn*), 3.87 (1H, s) (*syn-anti*), 2.28 (1H, s) (*syn,syn*), 1.69 (1H, s) (*syn-anti*); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.7 (*syn,syn*), 172.7 (*syn-anti*), 164.5 (*syn,syn*), 164.2 (*syn-anti*), 162.5 (*syn,syn*), 162.2 (*syn-anti*), 136.3 (*syn,syn*), 136.2 (*syn,syn*), 135.6 (*syn-anti*), 135.5 (*syn-anti*), 132.9 (*syn,syn*), 132.4 (*syn-anti*), 129.3 (*syn,syn*), 129.2 (*syn-anti*), 129.1 (*syn,syn*), 128.8 (*syn-anti*), 126.5 (*syn-anti*), 126.3 (*syn,syn*), 116.9 (*syn,syn*), 116.8 (*syn-anti*), 116.7 (*syn,syn*), 116.6 (*syn-anti*), 83.2 (*syn,syn*), 82.9 (*syn-anti*), 75.4 (*syn,syn*), 71.5 (*syn-anti*), 56.9 (*syn-anti*). 56.8 (*syn,syn*).

Compound *syn,anti*-5 + compound *syn,syn*-5: ^1H NMR (CDCl_3 , 500 MHz) δ 7.53–7.58 (2H, m) (*syn,syn* and *syn-anti*), 7.02–7.06 (2H, m) (*syn,syn* and *syn-anti*), 4.62 (1H, dq, $J = 6.5, 5.0$ Hz) (*syn-anti*), 4.52 (1H, dq, $J = 7.0, 3.5$ Hz) (*syn,syn*), 4.28 (1H, dd, $J = 4.5, 3.0$ Hz) (*syn-anti*), 4.25 (1H, dd, $J = 4.5, 3.0$ Hz) (*syn,syn*), 4.14 (1H, d, $J = 4.5$ Hz) (*syn,syn*), 3.72 (1H, d, $J = 3.0$ Hz) (*syn-anti*), 2.89 (1H, br s) (*syn-anti*), 2.78 (1H, br s) (*syn,syn*), 1.49 (3H, d, $J = 7.0$ Hz) (*syn,syn*), 1.39 (3H, d, $J = 6.5$ Hz) (*syn-anti*); ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.3 (*syn-anti*), 172.8 (*syn,syn*), 164.4 (*syn anti*), 164.1 (*syn,syn*), 162.4 (*syn anti*), 162.1 (*syn,syn*), 136.3 (*syn-anti*), 136.2 (*syn-anti*), 135.3 (*syn,syn*), 135.2 (*syn,syn*), 116.9 (*syn,syn*), 116.8 (*syn-anti*), 116.7 (*syn,syn*), 116.6

(*syn-anti*), 79.2 (*syn-syn*), 79.0 (*syn-anti*), 74.4 (*syn-anti*), 70.1 (*syn-syn*), 57.6 (*syn-syn*), 53.4 (*syn-anti*), 14.0 (*syn-syn*), 13.6 (*syn-anti*).

Compound *syn,anti-6* + compound *syn,syn-6*: ^1H NMR (CDCl_3 , 500 MHz) δ 7.53–7.58 (2H, m) (*syn-syn* and *syn-anti*), 7.04–7.08 (2H, m) (*syn-syn* and *syn-anti*), 4.35 (1H, d, $J = 3.0$ Hz) (*syn-anti*), 4.29 (1H, s) (*syn-syn*), 4.14 (1H, d, $J = 4.5$) (*syn-syn*), 4.06 (1H, dd, $J = 10.5, 3.5$ Hz) (*syn-anti*), 3.85 (1H, dd, $J = 10.5, 3.0$) (*syn-syn*), 3.71 (1H, s) (*syn-anti*), 2.72 (1H, s) (*syn-syn*), 2.24–2.29 (1H, m) (*syn-syn*), 2.10–2.18 (1H, m) (*syn-anti*), 1.11 (3H, d, $J = 7.0$ Hz) (*syn-syn* and *syn-anti*), 0.99 (3H, d, $J = 6.5$ Hz) (*syn-syn*), 0.97 (3H, d, $J = 7.0$ Hz) (*syn-anti*); ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.5 (*syn-anti*), 172.5 (*syn-syn*), 164.4 (*syn-anti*), 164.2 (*syn-syn*), 162.4 (*syn-anti*), 162.2 (*syn-syn*), 136.0 (*syn-anti*), 136.0 (*syn-anti*), 135.3 (*syn-syn*), 135.2 (*syn-syn*), 122.1 (*syn-syn*), 127.1 (*syn-anti*), 127.0 (*syn-syn*), 116.9 (*syn-syn*), 116.8 (*syn-syn* and *syn-anti*), 116.6 (*syn-anti*), 88.5 (*syn-anti*), 88.4 (*syn-syn*), 73.7 (*syn-anti*), 68.7 (*syn-syn*), 58.1 (*syn-syn*), 53.9 (*syn-anti*), 27.6 (*syn-syn*), 27.0 (*syn-anti*), 19.9 (*syn-anti*), 19.8 (*syn-syn*), 17.6 (*syn-anti*), 17.5 (*syn-syn*).

Compound *syn,anti-7* + compound *syn,syn-7*: ^1H NMR (CDCl_3 , 300 MHz) δ 7.54–7.57 (4H, m) (*syn-syn* and *syn-anti*), 7.31–7.43 (10H, m) (*syn-syn* and *syn-anti*), 6.89–6.92 (4H, m) (*syn-syn* and *syn-anti*), 5.49 (1H, d, $J = 3.6$ Hz) (*syn-anti*), 5.41 (1H, d, $J = 3.3$ Hz) (*syn-syn*), 4.47 (1H, ddd, $J = 1.2, 2.1, 3.9$ Hz) (*syn-syn* and *syn-anti*), 4.22 (1H, s) (*syn-anti*), 4.21 (1H, s) (*syn-syn*), 3.81 (3H, s) (*syn-anti*), 3.81 (3H, s) (*syn-syn*), 2.51 (1H, s) (*syn-anti*), 2.27 (1H, s) (*syn-syn*); ^{13}C NMR (CDCl_3 , 75 MHz) δ 173.2 (*syn-anti*), 172.7 (*syn-syn*), 160.9 (*syn-anti*), 160.5 (*syn-syn*), 136.6 (*syn-anti*), 135.7 (*syn-syn*), 133.2 (*syn-syn*), 132.7 (*syn-anti*), 129.0 (*syn-anti*), 128.6 (*syn-syn*), 126.5 (*syn-syn*), 126.3 (*syn-anti*), 122.4 (*syn-syn*), 120.9 (*syn-anti*), 115.2 (*syn-syn* and *syn-anti*), 83.2 (*syn-anti*), 82.9 (*syn-syn*), 75.5 (*syn-anti*), 71.2 (*syn-syn*), 57.7 (*syn-syn*), 55.4 (*syn-syn* and *syn-anti*), 53.1 (*syn-anti*).

Compound *syn,anti-8* + compound *syn,syn-8*: ^1H NMR (CDCl_3 , 500 MHz) δ 7.48–7.51 (2H, m) (*syn-syn* and *syn-anti*), 6.85–6.88 (2H, m) (*syn-syn* and *syn-anti*), 4.54 (1H, dq, $J = 6.5, 5.0$ Hz) (*syn-anti*), 4.47 (1H, dq, $J = 7.0, 3.5$ Hz) (*syn-syn*), 4.28

(1H, t, $J = 6.5$ Hz) (*syn-anti*), 4.18 (1H, t, $J = 8.0$ Hz) (*syn-syn*), 4.11 (1H, d, $J = 4.5$ Hz) (*syn-syn*), 3.80 (3H, s) (*syn-syn* and *syn-anti*), 3.65 (1H, d, $J = 2.5$ Hz) (*syn-anti*), 1.48 (3H, d, $J = 6.5$ Hz) (*syn-syn*), 1.36 (3H, d, $J = 6.5$ Hz, (*syn-anti*); ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.9 (*syn-anti*), 173.0 (*syn-syn*), 160.7 (*syn-anti*), 160.4 (*syn-syn*), 136.5 (*syn-anti*), 135.3 (*syn-syn*), 122.1 (*syn-syn*), 121.0 (*syn-anti*), 115.2 (*syn-syn*), 115.0 (*syn-anti*), 79.2 (*syn-syn* and *syn-anti*), 74.5 (*syn-anti*), 69.9 (*syn-syn*), 58.1 (*syn-syn*), 55.4 (*syn-syn*), 55.4 (*syn-anti*), 53.8 (*syn-anti*), 14.0 (*syn-syn*), 13.6 (*syn-anti*).

Compound *syn,anti-9* + compound *syn,syn-9*: ^1H NMR (CDCl_3 , 500 MHz) δ 7.46–7.50 (2H, m) (*syn-syn* and *syn-anti*), 6.85–6.89 (2H, m) (*syn-syn* and *syn-anti*), 4.32 (1H, s) (*syn-anti*), 4.23 (1H, d, $J = 3.5$ Hz) (*syn-syn*), 4.11 (1H, d, $J = 4.5$) (*syn-syn*), 3.99 (1H, dd, $J = 9.5, 3.5$ Hz) (*syn-anti*), 3.80 (3H, s) (*syn-syn*), 3.79 (3H, s) (*syn-anti*), 2.94 (1H, s) (*syn-syn*), 2.68 (1H, s) (*syn-anti*), 2.23–2.27 (1H, m) (*syn-syn*), 2.12–2.16 (1H, m) (*syn-anti*), 1.09 (3H, d, $J = 6.5$ Hz) (*syn-syn*), 1.07 (3H, d, $J = 6.5$ Hz) (*syn-anti*), 0.97 (3H, d, $J = 7.0$ Hz) (*syn-syn*), 0.93 (3H, d, $J = 7.0$ Hz) (*syn-anti*); ^{13}C NMR (CDCl_3 , 125 MHz) δ 174.1 (*syn-anti*), 172.8 (*syn-syn*), 160.6 (*syn-anti*), 160.4 (*syn-syn*), 136.2 (*syn-syn*), 135.3 (*syn-anti*), 122.0 (*syn-syn*), 121.3 (*syn-anti*), 115.2 (*syn-syn*), 115.0 (*syn-anti*), 88.6 (*syn-syn*), 88.4 (*syn-anti*), 73.6 (*syn-anti*), 68.5 (*syn-syn*), 58.5 (*syn-syn*), 55.4 (*syn-syn*), 55.3 (*syn-anti*), 54.4 (*syn-anti*), 27.5 (*syn-syn*), 26.9 (*syn-anti*), 19.8 (*syn-anti*), 19.7 (*syn-syn*), 17.6 (*syn-anti*), 17.4 (*syn-syn*).

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Supporting Information Available: Crystallographic data (CIF), theoretical calculations, graphical NMR spectra of all compounds, and ORTEP representations. This material is available free of charge via the Internet at <http://pubs.acs.org>.