# Progressive Studies on the Novel Samarium-Catalyzed Diastereoselective Tandem Semipinacol Rearrangement/Tishchenko Reduction of Secondary $\alpha$-Hydroxy Epoxides

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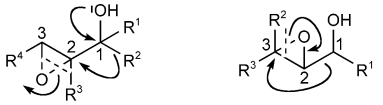
**Abstract:** A novel and highly diastereoselective samarium-catalyzed tandem rearrangement/reduction of secondary $\alpha$-hydroxy epoxides, which involves a C1 to C3 carbon migration rearrangement and a very interesting hetero-Tishchenko reduction of the intermediate aldehyde and the reductant aldehyde, has been reported. This reaction could be developed to provide a facile and stereoselective construction of 2-quarternary 1,3-diol units with an hydroxymethyl moiety attached to the diastereogenic quaternary carbon center. Detailed investigations have been carried out concerning the screening of the aldehydes as a reductant, the optimization of reaction conditions, and the substrate scope of this tandem reaction. A catalytic cycle for this reaction, the electronic and steric effects of the reductant aldehydes, and the mechanism for the acyl migration of 1,3-diol monoesters are proposed.

**Keywords:** alcohols · diastereoselectivity · rearrangement · samarium · Tishchenko reaction

## Introduction

The tandem semipinacol rearrangement/reduction of $\alpha$-hydroxy epoxides is of considerable synthetic importance, as in one step and with high diastereoselectivity it efficiently generates 2-quarternary 1,3-diol units,[1] which are used extensively as key building blocks in organic synthesis[2] or as important chiral ligands for asymmetric reactions.[3] As part of our efforts to design and develop this kind of tandem reaction, we described a samarium-catalyzed tandem reaction of tertiary $\alpha$-hydroxy epoxides,[1b] which involves the rearrangement of the migrating group $R^2$ from C1 to C2 (rate-controlling step), as shown in structure **I** of Figure 1, and subsequently an immediate Tishchenko reduction of the potential $\beta$-hydroxy ketone with perfect diastereocontrol.

Recently our investigation has resulted in another novel samarium-catalyzed diastereoselective tandem rearrangement/reduction of secondary $\alpha$-hydroxy epoxides **1**. To the best of our knowledge, this new kind of catalytic tandem reaction has not been reported. It involves another semi




I II

Figure 1. Comparison of two types of semipinacol rearrangement of $\alpha$-hydroxy epoxides.

pinacol-type rearrangement with C1 to C3 carbon migration and concomitant formation of an intermediate aldehyde at the original C2 position, as seen in structure **II** of Figure 1, and a subsequent slower hetero-Tishchenko reduction of the intermediate aldehyde and the reductant aldehyde (rate-determining step) to afford another kind of 2-quarternary 1,3-diol unit. The synthetic value of this sequence lies in the stereoselective derivation of two adjacent stereocenters, one being a quaternary center bearing a hydroxymethyl moiety, which are widely present in many chiral reagents[3a–e,g,i] and biologically active molecules.[2, 4] Additionally, of particular importance is the stereoselective construction of the quaternary carbon, which has long been an important class of structural unit.[5]

The one-step rearrangement in our samarium-mediated Lewis acid catalyzed tandem reaction of $\alpha$-hydroxy-unprotected substrates was not readily accessible for some cases using the conventional Lewis acid, even though it is equivalent to that reported by Yamamoto et al.[6] However, their reported one-step transformation required up to two equivalents of the highly sterically hindered, aluminum-based

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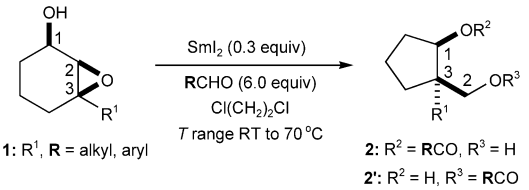
Lewis acid MABR [methylaluminum bis(4-bromo-2,6-*tert*-butylphenoxide)] and was only applicable to hydroxy-protected substrates. Consequently, it is of significant interest that substoichiometric amounts of the easily accessible $SmI_2$ promoted the semipinacol rearrangement/Tishchenko reaction of $\alpha$-hydroxy-unprotected substrates.

Since the introduction of the first useful method for the generation of samarium(II) diiodide ($SmI_2$) by Kagan and coworkers in 1980,[7] $SmI_2$ has received considerable attention and has been widely used in modern organic synthesis, especially as a single-electron reducing reagent in stoichiometric amounts or in excess.[7, 8] However, only a few reactions with substoichiometric amounts of $SmI_2$ have been investigated.[1b, 9] Moreover, to the best of our knowledge, very few were effective in employing $SmI_2$ to react with epoxides, whether in a stoichiometric or catalytic fashion. For example, $SmI_2$ has been applied to promote the deoxygenation,[7, 10] ring opening,[11] and the reductive coupling of epoxides,[8x] and to catalyze the rearrangement[9b] and the rearrangement/reduction of epoxides.[1b] Additionally, $SmI_2$ has also been used in Tishchenko reactions,[1b, 9c,e,k–o] generally in which the hydride is smoothly transferred from the aldehyde to the inter- or intramolecular ketone group. But, to the best of our knowledge, there were few examples of homo- or hetero-Tishchenko reactions of two aldehydes catalyzed by $SmI_2$,[9l, 12] in which the hydride is transferred from one aldehyde to the other. As a result, it is particularly important that we present our studies towards the tandem rearrangement/Tishchenko reaction of $\alpha$-hydroxy epoxides promoted by substoichiometric amounts of $SmI_2$, in which the interesting hetero-Tishchenko reaction of the reductant aldehyde and the intermediate aldehyde derived from the semipinacol rearrangement takes place.

Herein, we disclose our detailed research results on this novel samarium-catalyzed tandem reaction.

## Results and Discussion

The secondary $\alpha$-hydroxy epoxides **1** examined were prepared in racemic form from the corresponding allylic alcohols through epoxidation with *m*-chloroperbenzoic acid (*m*CPBA).[13] As described in Scheme 1, a solution of **1**




Scheme 1. Samarium-catalyzed tandem reaction of secondary $\alpha$-hydroxy epoxides.

(1.0 equiv), $SmI_2$ (0.3 equiv), and the reductant aldehyde **R**CHO (6.0 equiv) in $Cl(CH_2)_2Cl$ was stirred at between room temperature and approximately 70 °C (as applicable) under an argon atmosphere, and a tandem semipinacol rearrangement/Tishchenko reduction proceeded smoothly with high diastereoselectivity to generate the 2-quaternary 1,3-diol monoesters **2** and/or the corresponding acyl migration product **2′**.[1b, 9l, 16b,d,f,k,p] Products **2** and **2′** were identified to have the same 2-quaternary 1,3-diol core structure by NMR spectroscopy analysis of the products of their methanolysis with NaOH/MeOH.[14a] To further investigate the relative stereochemistry at C1 and C3 of the products **2** and **2′**, we prepared the acetonide[14b] of the 2-quaternary 1,3-diol obtained by methanolysis of **2** and/or **2′**. The two-dimensional NOESY spectrum revealed an obvious spatial correlation between the group $R^1$ and H, as shown in *cis*-**A** in Figure 2. If the group $CH_2OR^3$ were *trans* to $OR^2$ in **2** and/or **2′**, no spatial correlation would occur in the acetonide *trans*-**B** (Figure 2); therefore, the group $CH_2OR^3$ is *cis* to $OR^2$ on the five-membered ring in **2** and/or **2′**.

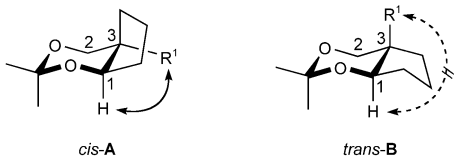



Figure 2. The determination of C1 and C3 relative stereochemistry in the product **2** and/or **2′**.

In connection with our previous work,[1b] we first screened the active aldehydes as an effective reductant for this catalytic tandem reaction. Initially, we selected the secondary $\alpha$-hydroxy epoxide **1a** ($R^1 = Ph$) as a model substrate, and benzaldehyde (**R** = Ph) as a reductive agent. Following the above-mentioned general procedure, the 2-quaternary 1,3-diol monoesters **2aa/2′aa** were obtained, but only in a moderate yield of 47%. It occurred to us that this fact could be caused by the weak hydride-transfer ability of the reductant PhCHO in this reaction.[1b, 16g] Based on this consideration, a series of aldehydes with different electronic and/or steric effects were employed to investigate the tandem reaction of **1a** under parallel experimental conditions, and the results are tabulated in Table 1.

From Table 1 we can see that the yields were dependent, to some extent, upon the electronic and/or steric effects of the reductant aldehydes. For example, among the substituted benzaldehydes used, the aldehydes bearing the *meta*- or *para*-electron-withdrawing groups (entries 3, 4, 6, and 7) gave better results; the *p*Cl-$C_6H_4$CHO was the best. In contrast, unfavorable electronic effects of the electron-donating groups in the *meta*- or *para*-substituted benzaldehydes (entries 9, 10, and 12) led to much lower yields than PhCHO. These facts indicated that reductants based on electron-rich substituted benzaldehydes could severely retard this reaction. Use of *ortho*-substituted benzaldehydes, no matter whether it has an electron-withdrawing group (entry 2) or electron-donating group (entry 8), resulted in much lower yields. This fact may be ascribed to the steric effect of the *ortho* substituents. To support this assertion, *o*F-$C_6H_4$CHO, which contains the less bulky *ortho*-fluoro substituent,[15] was subjected to this model reaction and indeed produce the 1,3-diol monoesters **2ad/2′ad** in higher yield (40%) compared with entries 2 and 8. Accordingly, the steric effect of bulky *ortho* substituents on substituted benzaldehydes may be the principal factor that

Table 1. Samarium-catalyzed rearrangement/reduction of the secondary $\alpha$-hydroxy epoxide **1a** with various reductant aldehydes **R**CHO.[a]

| Entry | **R** | $T$ [°C] | $t$ [h] | Product | **2**:**2′**[b] | Yield [%][c] |
|---|---|---|---|---|---|---|
| 1 | Ph | 65 | 3 | **2aa/2′aa** | 72:28 | 47 |
| 2 | *o*-$C_6H_4Cl$ | 65 | 4 | **2ab/2′ab** | 80:20 | 11 |
| 3 | *m*-$C_6H_4Cl$ | 65 | 2 | **2ac/2′ac** | 60:40 | 60 |
| 4 | *p*-$C_6H_4Cl$ | 65 | 1.5 | **2a/2′a** | 90:10 | 63 |
| 5 | *o*-$C_6H_4F$ | 60 | 7 | **2ad/2′ad** | 63:27 | 40 |
| 6 | *p*-$C_6H_4CF_3$ | 60 | 1.5 | **2ae/2′ae** | > 98:2 | 62 |
| 7 | *p*-$C_6H_4NO_2$ | 60 | 0.25 | **2af/2′af** | 82:18 | 55 |
| 8 | *o*-$C_6H_4Me$ | 60 | 2[d] | **2ag/2′ag** | > 99:< 1 | 2 |
| 9 | *m*-$C_6H_4Me$ | 60 | 4 | **2ah/2′ah** | > 99:< 1 | 17 |
| 10 | *p*-$C_6H_4Me$ | 60 | 5[e] | **2ai/2′ai** | > 99:< 1 | 7 |
| 11 | *m*-$C_6H_4OMe$ | 60 | 3.5 | **2aj/2′aj** | 80:20 | 52 |
| 12 | *p*-$C_6H_4OMe$ | 60 | 2[d] | – | – | trace |
| 13 | 2-Furyl | 60 | 4.5 | – | – | [f] |
| 14 | Cyclohexyl | 60 | 3 | **2ak/2′ak** | 85:15 | 50 |
| 15 | *i*Pr | 60 | 3.5 | **2al/2′al** | > 98:2 | 41 |
| 16 | *n*Pr | 60 | 3.5 | **2am/2′am** | 24:76 | 56 |

[a] All reactions proceeded with $SmI_2$ (0.3 equiv), the substrate **1a** ($R^1$ = Ph, 1.0 equiv) and the reductant aldehyde **R**CHO (6.0 equiv) in $Cl(CH_2)_2Cl$ following the general procedure (see Experimental Section). [b] The ratios were determined by $^1$H NMR spectroscopy. [c] Total yields of isolated product **2** and/or **2′**. [d] Prolongation of the reaction time led to more unidentified by-products, as monitored by TLC. [e] After continuing to run for 19 h at 60 °C, the result obtained was similar to that for 5 h. [f] No desired product **2** and/or **2′** was observed; the semipinacol rearrangement product ($\beta$-hydroxy aldehyde) was obtained in 43% yield.

gives rise to the lower yield for this tandem reaction. To our surprise, *m*MeO-$C_6H_4CHO$ (entry 11) gave a good yield of 52% for reasons that remain unclear. In addition, another type of aromatic aldehyde, 2-furaldehyde, was found to be ineffective in this reaction. Furthermore, three aliphatic aldehydes (entries 14–16) gave results approximately equal to those obtained using PhCHO; the less bulky *n*PrCHO even provided a slightly higher yield. To the best of our knowledge, these facts mentioned above have not been reported in detail in the previous Tishchenko reactions.[1b, 9c,e,k–o, 16]

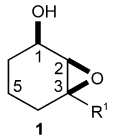
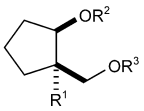
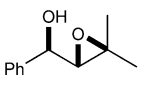
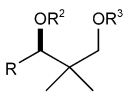
On the basis of the above evaluation, the cheap *p*Cl-$C_6H_4CHO$ was finally chosen as the reductant for this catalytic tandem reaction. Additionally, for this model experiment, we found that further decreasing the amounts of aldehydes employed made this reaction slow, and so we generally used six equivalents of aldehyde as a reductant for this reaction.

Notably, the intermediate aldehyde, which arose from the semipinacol rearrangement of **1a** during the above reactions, was observed on TLC, and was further characterized by NMR spectroscopy. Importantly, this fact shows that the hetero-Tishchenko reaction of the intermediate aldehyde and the reductant aldehyde, which has seldom been mentioned in the previously reported Tishchenko reaction promoted by $SmI_2$,[1b, 9c,e,k–o] is a rate-determining step in this tandem sequence.

Our further investigations were aimed at the optimization of other reaction conditions, the scope of the substrates, and the ratios of the two monoester products **2** and **2′**; the corresponding experimental results are listed in Table 2.

Generally we employed 0.3 equivalents of $SmI_2$ in the typical procedure, as using less $SmI_2$ (e.g., 0.2 equiv; Table 2, entry 5) prolonged the reaction time and lowered the reaction yield. Of all the solvents examined, toluene and 1,2-dichloroethane ($Cl(CH_2)_2Cl$) proved to be compatible with this reaction (e.g., entries 4 and 6), but use of coordinative media, such as THF (entry 7) and $CH_3CN$ (entry 8), had a significant influence on the reaction and gave lower yields and longer reaction times. This may arise from weakening the samarium-mediated Lewis acidic property by coordination with the lone pair of electrons of the solvents. Moreover, temperatures of approximately 70 °C were generally necessary for this tandem reaction to proceed readily. As compared with the Evans

Table 2. Samarium-catalyzed tandem reaction of secondary $\alpha$-hydroxy epoxides with *p*Cl-$C_6H_4CHO$.

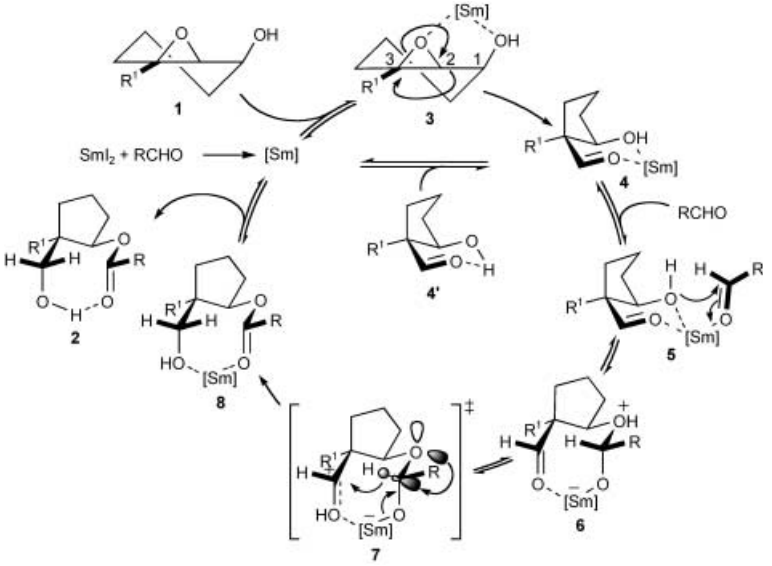
| Entry | Substrate[a] | $SmI_2$ [equiv] | Solvent | $T$ [°C] | $t$ [h] | Product[b] | **2**:**2′**[c] | Yield [%][d] |
|---|---|---|---|---|---|---|---|---|
| |  | | | | |  | | |
| | **1** | | | | | | | |
| 1 | **1a** ($R^1$ = Ph) | 0.3 | $Cl(CH_2)_2Cl$ | 65 | 1.5 | **2a/2′a** | 90:10 | 63 |
| 2 | **1a** | 0.3 | $Cl(CH_2)_2Cl$ | 65 | 3 | **2a/2′a** | 45:55 | 63 |
| 3 | **1a** | 0.3 | $Cl(CH_2)_2Cl$ | 85 | 1 | **2a/2′a** | 72:28 | 62 |
| 4 | **1b** ($R^1$ = Et) | 0.3 | $PhCH_3$ | 80 | 1 | **2b/2′b** | 80:20 | 75 |
| 5 | **1b** | 0.2 | $PhCH_3$ | 80 | 2.5 | **2b/2′b** | 67:33 | 55 |
| 6 | **1b** | 0.3 | $Cl(CH_2)_2Cl$ | 70 | 1.5 | **2b/2′b** | > 99:< 1 | 73 |
| 7 | **1b** | 0.3 | THF | reflux | 8 | **2b/2′b** | 19:81 | 58 |
| 8 | **1b** | 0.3 | $CH_3CN$ | 70 | 4 | **2b/2′b** | 50:50 | 65 |
| 9 | **1c** ($R^1$ = Bn) | 0.3 | $Cl(CH_2)_2Cl$ | 70 | 2.5 | **2c/2′c** | 60:40 | 82 |
| 10 | **1d** ($R^1$ = *n*Bu) | 0.3 | $Cl(CH_2)_2Cl$ | 70 | 2 | **2d/2′d** | > 98:2 | 76 |
| 11 | **1e** ($R^1$ = allyl) | 0.3 | $Cl(CH_2)_2Cl$ | 70 | 1 | **2e/2′e** | < 1:> 99 | 82 |
| |  | | | | |  | | |
| 12 | **1f**[e] | 0.3 | $Cl(CH_2)_2Cl$ | RT | 2 | **2f/2′f**[f] | < 1:> 99 | 89 |

[a] All substrates were racemic. [b] 1,3-Diol monoesters **2**: $R^2$ = *p*Cl-$C_6H_4CO$, $R^3$ = H; **2′**: $R^2$ = H, $R^3$ = *p*Cl-$C_6H_4CO$. [c] The ratios were determined by $^1$H NMR spectroscopy. [d] Total yields of isolated product **2** and/or **2′**. [e] After purification by column chromatography, one single diastereoisomer (*threo*:*erythro* 100:0) was obtained as identified by $^1$H NMR spectroscopy; also see ref. [13a]. [f] R = *p*Cl-$C_6H_4$.

condition for the Tishchenko reactions of $\beta$-hydroxy ketones,[9e] the relatively higher temperatures may be responsible for the semipinacol rearrangement of $\alpha$-hydroxy epoxides and the hetero-Tishchenko reduction of the intermediate $\alpha$-quaternary $\beta$-hydroxy aldehydes.

As can be seen in Table 2, this catalytic tandem reaction was effective for six-membered cyclic substrates **1a**–**1e**, and the substituent $R^1$ could be Et, *n*Bu, allyl, Bn, or Ph. The comparison of these substituents showed that an $sp^3$-hybridized alkyl group gave a higher yield than an $sp^2$-hybridized aryl one. This may be due to the fact that the $sp^2$-hybridized substituent $R^1$ could stabilize the transition state generated from C3–O bond cleavage of the type shown in structure **II** of Figure 1 (also, see below and **3** in Scheme 2), and the resultant




Scheme 2. Proposed catalytic cycle for rearrangement/reduction of secondary $\alpha$-hydroxy epoxides.

delocalization, to some extent, may inhibit the C1 to C3 concerted migration catalyzed by the samarium-mediated Lewis acid.

To extend the substrate scope, one tandem reaction of the acyclic substrate **1f** was conducted. Surprisingly, at room temperature, a new tandem semipinacol rearrangement/Tishchenko reaction involving an additional aldol-transfer process[17] took place to furnish the unusual product **2′f** in good yield; this product is in fact a very useful chiral resolving agent intermediate.[3a,g,h] To the best of our knowledge, this is the first report of such a tandem transformation in the presence of substoichiometric amounts of $SmI_2$.[9l, 16k,p, 17] In comparison with the tandem reaction of cyclic substrates **1a**–**1e**, this acyclic case shows that once the enolate precursor (i.e., the intermediate $\beta$-hydroxy aldehyde) was formed through semipinacol rearrangement, in the presence of the reductant *p*Cl-$C_6H_4CHO$, a stepwise retro-aldol aldolisation process took place faster than the direct Tishchenko reduction.

Furthermore, the success of the tandem reaction was dependent on substrate structure. For example, when $R^1$ was an sp-hybridized substituent, such as 1-heptynyl ($CH_3(CH_2)_4C{\equiv}C-$) or 1-phenylacetylenyl ($C_6H_5C{\equiv}C-$), complex unidentified products formed. Additionally, for the substrate **1** ($R^1$ = Ph) with a C2 substituent (such as methyl, other than the hydrogen), only uncharacterized mixtures were observed in our experiments, possibly as a result of competition between C2–O bond cleavage and the expected C3–O bond cleavage. Moreover, the substrate **1** ($R^1$ = Me) with two sterically hindered C5-methyl groups, which was prepared from isophorol, was also examined, but the desired 1,3-diol monoesters **2**/**2′** were afforded in a much lower yield of 17%. With the seven-membered cyclic substrate *cis*-2,3-epoxy-3-*n*-butyl-cycloheptanol, we only obtained the expected product **2**/**2′** in 21% yield.

In addition, the ratios of the 2-quaternary 1,3-diol monoesters **2** and **2′** relied primarily on the temperature, the reaction time, and the structure of product **2**. Usually, increasing the temperature (entry 3 of Table 2) and prolonging the reaction time (entry 2) should favor the formation of the product **2′** through acyl migration. Moreover, the structure of **2** could also affect the ratios of **2** and **2′**. For example (entry 12), at room temperature for 2 h, the product **2f** was nearly completely converted into the more stable **2′f**. These facts imply that **2′** could be a thermodynamic product and that **2** could be a kinetic product.[1b, 9l, 16b,d,f,k,p]

In the general procedure, when substoichiometric amounts of $SmI_2$ in THF were added to the solution of the secondary $\alpha$-hydroxy epoxide **1** and the reductant **R**CHO in aprotic solvent ($PhCH_3$, $Cl(CH_2)_2Cl$, THF, or $CH_3CN$), the deep blue color of freshly prepared $SmI_2$ in THF disappeared immediately. This observation suggests that $SmI_2$ is not the actual catalyst, but only a catalyst precursor.[1b, 9e,g,j] Based on previous reports,[7, 8d] we know that in the presence of the $\alpha$-hydroxy epoxide **1** containing a secondary hydroxy group ($R^4R^5COH$), a direct reduction of the reductant **R**CHO by $SmI_2$ could also take place in the first stage of our reported tandem reaction and produce $Sm^{III}$-mediated alkoxides ($I_2Sm{-}OCH_2\mathbf{R}$ and $I_2Sm{-}OCR^4R^5$) as the catalytically active species. In fact, both aromatic and aliphatic aldehydes are effective in the present reaction (see Table 1). Thus, when aromatic aldehydes were used as reductants in the reaction, we could not exclude the possibility that the $Sm^{III}$-mediated pinacol adduct ($I_2Sm{-}O{-}CH\mathbf{R}{-}CH\mathbf{R}{-}O{-}SmI_2$), which was generated from the pinacol coupling of the aromatic aldehyde,[9e,i, 18] serves as an active catalyst. According to these considerations, whether the $Sm^{III}$-mediated alkoxide, the $Sm^{III}$-mediated pinacol adduct, or a combination of the two are the catalytically active species remains to be determined.

At present, we think the active samarium catalyst may well be some samarium(III) entity (a $Sm^{III}$-mediated Lewis acid, represented by [Sm] in Scheme 2).

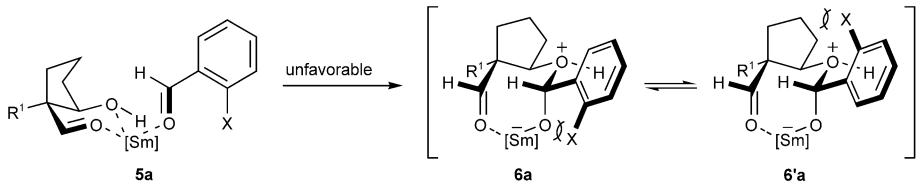
On the basis of the experimental results above and the literature reports,[1b, 9c,e,g,j–l,o, 7, 8d, 16, 18] a possible catalytic cycle for this tandem reaction is proposed as depicted in Scheme 2. The catalyst [Sm] is firstly formed in situ from $SmI_2$ and the reductant **R**CHO, and then coordinates with the epoxy oxygen atom and the hydroxy oxygen atom in **1** to afford the complex **3**. Subsequently, cleavage of the activated C3–O bond of the epoxide occurs concomitantly with a C1 to C3 concerted migration with inversion of the configuration at C3 position, and then the complex **4** is formed. Because the intermediate aldehyde **4′** was observed during the reaction, it shows that the irreversible semipinacol rearrangement (**3** → **4**) is faster than the subsequent Tishchenko reduction (**7** → **8**) in this tandem reaction. Consequently, the catalyst [Sm] can be rapidly released from **4**, and again it coordinates with two oxygen atoms of **1** to continuously transform **1** into **4** as described above. Simultaneously, the catalyst [Sm] in the complex **4** further coordinates with the reductant **R**CHO to readily afford the complex **5**, and subsequently a [Sm]-catalyzed nucleophilic attack of the secondary hydroxy to the carbonyl of **R**CHO furnishes the hemiacetal **6**, then a fast proton transfer results in the formation of **7**. So, an irreversible intramolecular 1,5-hydride transfer (rate-controlling step) occurs in the transition state **7**, and gives the [Sm]-coordinated 1,3-diol monoesters **8**, which further generates the final 1,3-diol monoesters **2** by releasing the catalyst [Sm] for the next cycle. As shown in **7**, the hemiacetal hydride transfer may be promoted by not only the transfer of the negative charge from the catalyst [Sm] to the hemiacetal carbon, but also the effective overlap of the antibonding orbital of the hemiacetal C–H bond with one lone pair on the hemiacetal oxygen.[19]

From the above-proposed mechanism, we could know that the formation of the samarium-bound hemiacetal **6** is the premise for the hydride transfer in transition state **7**. As a consequence, any factor influencing the formation of **6** in the reversible **5** → **6** equilibrium could affect the rate-controlling irreversible transformation of **7** into **8**. Accordingly, some characteristic properties of this catalytic tandem reaction can be explained. For example, when the substituted benzaldehydes with a bulky *ortho*-substituent group X (X = Me, Cl) as a reductant were subjected to this reaction, the formations of the hemiacetal intermediates **6a** and **6′a** (corresponding to **6** in Scheme 2), as indicated in Scheme 3, were unfavorable because of steric hindrance between X and [Sm]–O–C in **6a** or the cyclopentane moiety in **6′a**. Thus, entries 2 (X = Cl, electron-withdrawing group (EWG)) and 8 (X = Me, electron-donating group (EDG)) in Table 1 afforded much lower yields. This fact also indicates that the electronic effects of the *ortho* substituents have minor influence on this reaction. As expected, when the group X was a less bulky *ortho* substituent, such as fluorine (entry 5 of Table 1),[15] a higher yield of 40% was obtained compared with 11% for entry 2 and 2% for entry 8. In contrast, as shown in Scheme 4, it is reasonable that no steric effect was observed in this tandem reaction with the *meta*- or *para*-substituted benzaldehydes. For the *meta*- or *para*-substituted benzaldehydes bearing an electron-withdrawing group X (X = *m*Cl, *p*Cl, *p*$CF_3$, *p*$NO_2$; see **5b** in Scheme 4), the electrophilic reactivity of the carbonyl group of the reductant aldehydes, to some extent, can be increased by the electron-deficient substituted phenyls, which is favorable for the formation of the hemiacetal **6b** (corresponding to **6** of Scheme 2), and then the expected higher yields (55–63%) were achieved (entries 3, 4, 6, and 7 in Table 1). However, if the *meta* or *para* substituent X is *m*Me, *p*Me, or *p*OMe (see **5′b** of Scheme 4), the opposite electronic effect can be found in the present reaction, and a decrease of the electrophilic reactivity of the carbonyl group of the reductant aldehydes results in lower yields (entry 9, 10, and 12 in Table 1).

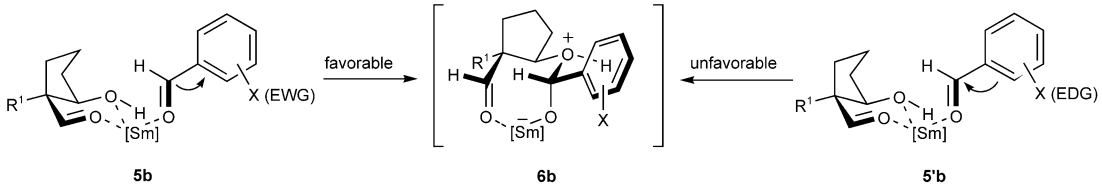
In addition, the formation of the thermodynamic product **2′** through acyl migration[1b, 9l, 16b,d,f,k,p] of the kinetic product **2** can be understood from Scheme 5. Here the driving force for converting **2** into **2′** may result from the fact that the acyl group (RCO) tends to attach to the primary hydroxyl group rather than the crowded secondary hydroxyl group.

## Conclusion

In conclusion, we have discovered a novel, highly stereoselective, samarium-catalyzed tandem semipinacol rearrangement/Tishchenko reduction of secondary $\alpha$-hydroxy epoxides. The two different processes in this tandem reaction, namely, a semipinacol rearrangement of the secondary $\alpha$-hydroxy

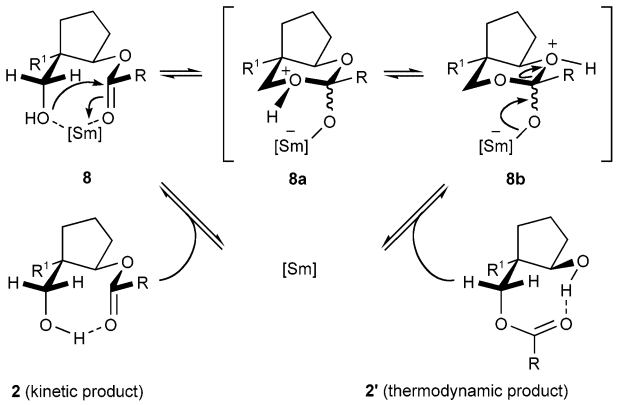



Scheme 3. Steric effect of *ortho* substituents on substituted benzaldehydes in the tandem reaction.




Scheme 4. Electronic effect of *meta* and *para* substituents on substituted benzaldehydes in the tandem reaction.




Scheme 5. Proposed mechanism for the formation of regioisomeric product **2′**.

epoxides and a hetero-Tishchenko reduction of the intermediate $\beta$-hydroxy aldehydes, could be realized by substoichiometric amounts of the easily accessible $SmI_2$ as a catalyst precursor. Moreover, the latter process could be significantly affected by the reductant aldehydes with different steric and electronic effects. We found *p*Cl-$C_6H_4CHO$ was the most effective reductant in this reaction, and by further optimizing the reaction conditions this sequence has been applied to the one-step construction of another class of 2-quaternary 1,3-diol unit comprising an hydroxymethyl moiety bearing the diastereogenic quaternary carbon center. On the basis of our detailed studies, a mechanism for this catalytic tandem reaction was proposed. According to the catalytic cycle, we explained the steric effect of *ortho* substituents and the electronic effect of *meta* or *para* substituents on the substituted benzaldehydes, and additionally a rationalization was also proposed for the formation of the thermodynamic acyl migration product **2′**.

## Experimental Section

**General**: All anhydrous solvents ($Cl(CH_2)_2Cl$, $PhCH_3$, $CH_3CN$, and THF) were dried by standard techniques and freshly distilled before use. All aldehyde reductants were purchased from Fluka, and also freshly distilled, except for the *p*$NO_2$-$C_6H_4CHO$, under an argon atmosphere under ordinary or reduced pressure prior to use. Samarium(II) diiodide ($SmI_2$) was prepared from samarium (Fluka) and iodine in dried THF under Ar as described in the literature.[20] All reactions were monitored by thin-layer chromatography (TLC) on gel $F_{254}$ plates. The silica gel (200–300 mesh) for column chromatography was from the Qingdao Marine Chemical Factory in China, and the distillation range of light petroleum is 60–90 °C. $^1$H NMR and $^{13}$C NMR spectra were recorded in $CDCl_3$ solution (unless otherwise noted) on an Avance DRX-200 or Bruker AM-400 MHz instrument. Spectral data are reported in ppm relative to tetramethylsilane (TMS) as internal standard. The GC-MS and MS data were obtained with EI (70 eV), and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the ESI technique.

**General procedure for the synthesis of the secondary $\alpha$-hydroxy epoxides (1)**: *m*CPBA (1.1 equiv) was added to a stirred solution of the allylic alcohol (1.0 equiv) in $CH_2Cl_2$ at 0 °C.[13] After complete consumption of the substrate (as monitored by TLC), the reaction mixture was diluted with $CH_2Cl_2$, washed with 10% aqueous $K_2CO_3$ solution, and brine, and dried ($MgSO_4$) overnight. Evaporation of the solvent under reduced pressure gave the crude product **1**, which was purified by column chromatography on silica gel eluting with a mixture solvent of light petroleum and ethyl acetate to yield the secondary $\alpha$-hydroxy epoxide **1**.

***cis*-2,3-Epoxy-3-phenylcyclohexanol (1a)**: $^1$H NMR (200 MHz, $(CD_3)_2CO$): $\delta$ = 7.40–7.25 (m, 5H), 4.12–4.00 (m, 1H), 3.10 (d, $J$ = 2.2 Hz, 1H), 3.05 (br s, 1H; OH), 2.35–2.21 (m, 1H), 1.96–1.82 (m, 1H), 1.73–1.61 (m, 2H), 1.57–1.40 ppm (m, 2H); $^{13}$C NMR (50 MHz, $(CD_3)_2CO$): $\delta$ = 142.2, 128.2, 128.2, 127.1, 125.2, 125.2, 66.5, 65.0, 62.6, 28.0, 27.8, 19.4 ppm.

***cis*-2,3-Epoxy-3-ethylcyclohexanol (1b)**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 4.05–3.90 (m, 1H), 3.16 (d, $J$ = 3.0 Hz, 1H), 2.51 (d, $J$ = 9.2 Hz, 1H; OH), 1.81–1.15 (m, 8H), 0.95 ppm (t, $J$ = 7.6 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 67.2, 64.9, 61.2, 30.1, 28.5, 26.1, 18.7, 8.6 ppm.

***cis*-2,3-Epoxy-3-benzylcyclohexanol (1c)**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.34–7.19 (m, 5H), 4.07–3.95 (m, 1H), 3.20 (d, $J$ = 3.0 Hz, 1H), 2.90, 2.84 (ABq, $J$ = 14.4 Hz, 2H), 2.39 (d, $J$ = 8.4 Hz, 1H; OH), 1.74–1.10 ppm (m, 6H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 136.5, 129.4, 129.4, 128.3, 128.3, 126.6, 66.6, 64.1, 60.8, 43.5, 29.1, 26.6, 17.8 ppm.

***cis*-2,3-Epoxy-3-*n*-butylcyclohexanol (1d)**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 4.06–3.89 (m, 1H), 3.14 (d, $J$ = 2.8 Hz, 1H), 2.75 (d, $J$ = 9.0 Hz, 1H; OH), 1.80–1.19 (m, 12H), 0.90 ppm (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 67.0, 64.3, 61.5, 37.1, 28.7, 26.8, 26.5, 22.6, 18.5, 13.9 ppm.

***cis*-2,3-Epoxy-3-allylcyclohexanol (1e)**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 5.89–5.68 (m, 1H), 5.18–5.15 (m, 1H), 5.10–5.08 (m, 1H), 4.08–3.93 (m, 1H), 3.20 (d, $J$ = 2.8 Hz, 1H), 2.82 (br s, 1H; OH), 2.38–2.32 (m, 2H), 1.80–1.20 ppm (m, 6H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 132.7, 118.1, 67.0, 63.4, 60.9, 41.7, 28.5, 26.4, 18.5 ppm.

***threo*-1-Phenyl-2,3-epoxy-3-methylbutanol (1f)**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.42–7.33 (m, 5H), 4.59 (d, $J$ = 8.2 Hz, 1H), 3.06 (br s, 1H; OH), 3.01 (d, $J$ = 8.2 Hz, 1H), 1.46 (s, 3H), 1.32 ppm (s, 3H).

**General procedure for $Sm^{III}$-catalyzed tandem semipinacol rearrangement/Tishchenko reduction of the secondary $\alpha$-hydroxy epoxides**: Unless otherwise noted, a solution of $SmI_2$ (0.1 M in THF, 1.2 mL, 0.3 equiv) was added dropwise to a stirred solution of the substrate **1** (0.4 mmol, 1.0 equiv) and the reductant aldehyde (2.4 mmol, 6.0 equiv) in dried $Cl(CH_2)_2Cl$ (4.0 mL) at room temperature under an argon atmosphere. The resulting reaction mixture was stirred at between room temperature and approximately 80 °C (as necessary). When TLC analysis indicated that the substrate **1** had disappeared completely, the reaction mixture was treated with a saturated aqueous $NaHCO_3$ solution (3 mL) followed by $CH_2Cl_2$ (10 mL). The organic layer was separated, and the aqueous phase was carefully extracted with $CH_2Cl_2$ (3 × 10 mL), and the combined extracts were dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel (eluting with 5→10% EtOAc in light petroleum) to afford **2** and/or **2′**.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 4′-chlorobenzoate (2a) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl 4′-chlorobenzoate (2′a)**: By following the typical procedure described above for entry 1 in Table 2 and entry 4 in Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *p*Cl-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1 M, 1.2 mL, 0.3 equiv) for 1.5 h at 65 °C to give the products **2a**/**2′a** (90:10, 83.3 mg) in a total yield of 63%. For entries 2 and 3 in Table 2, the experimental operation was analogous to that described above, and the reactions were stirred for 3 h at 65 °C and for 1 h at 85 °C, respectively, to afford the products **2a**/**2′a** in 63% and 62% yield and with the ratios of 45:55 and 72:28. **2a**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.04–8.01, 7.47–7.45 (AA′BB′, 4H), 7.46–7.27 (m, 5H), 5.78 (dd, $J$ = 3.7, 6.4 Hz, 1H), 3.97, 3.80 (ABq, $J$ = 11.3 Hz, 2H), 2.32–2.10 (m, 3H), 2.02–1.90 (m, 1H), 1.90–1.80 (m, 1H), 1.80–1.65 ppm (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 165.4, 142.6, 139.6, 130.9, 130.9, 128.8, 128.8, 128.8, 128.6, 128.6, 126.9, 126.9, 126.9, 82.2, 67.4, 56.1, 32.0, 31.1, 20.6 ppm; MS (70 eV): *m*/*z* (%): 191 (0.4) [$M$ − $ClC_6H_4CO$]$^+$, 174 (9) [$M$ − $ClC_6H_4CO_2H$]$^+$, 144 (68), 141 (33) [$^{37}ClC_6H_4CO$]$^+$, 139 (100) [$^{35}ClC_6H_4CO$]$^+$, 131 (16), 118 (51), 113 (8) [$^{37}ClC_6H_4$]$^+$, 111 (25) [$^{35}ClC_6H_4$]$^+$, 91 (18), 77 (10); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}O_3ClNa$: 353.0915; found: 353.0911 [$M$+Na]$^+$.

**2′a**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.83–7.81, 7.48–7.46 (AA′BB′, 4H), 7.40–7.25 (m, 5H), 4.79, 4.47 (ABq, $J$ = 11.4 Hz, 2H), 4.55 (dd, $J$ = 5.1, 6.3 Hz, 1H), 2.21–2.17 (m, 2H), 2.07–1.95 (m, 1H), 1.95–1.85 (m, 1H), 1.84–1.74 (m, 1H), 1.71–1.60 ppm (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 166.2, 143.6, 139.5, 130.9, 130.9, 128.7, 128.7, 128.5, 128.3, 128.3, 126.8, 126.8, 126.6, 78.5, 69.0, 54.3, 32.9, 32.0, 19.6 ppm; MS (70 eV): *m*/*z* (%): 191 (0.08) [$M$ − $ClC_6H_4CO$]$^+$, 174 (21) [$M$ − $ClC_6H_4CO_2H$]$^+$, 144 (6), 141 (12)

$[^{37}ClC_6H_4CO]^+$, 139 (33) $[^{35}ClC_6H_4CO]^+$, 131 (28), 118 (100), 113 (6) $[^{37}ClC_6H_4]^+$, 111 (20) $[^{35}ClC_6H_4]^+$, 91 (20), 77 (13); HRMS (ESI): *m/z* calcd for $C_{19}H_{20}O_3Cl$: 331.1095; found: 331.1095 $[M+H]^+$.

***cis*-1-Ethyl-1-hydroxymethylcyclopent-2-yl 4′-chlorobenzoate (2b) and *cis*-(1-ethyl-2-hydroxycyclopent-1-yl)methyl 4-chlorobenzoate (2′b)**: By following the typical procedure described above for entry 4 of Table 2, a solution of the epoxide **1b** (56.8 mg, 0.4 mmol, 1.0 equiv) and *p*Cl-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $PhCH_3$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 1 h at 80 °C to give the 2-quaternary 1,3-diol monoesters products **2b/2′b** (80:20, 84.7 mg) in a total yield of 75%. For entry 5 of Table 2, 0.2 equiv $SmI_2$ was used in the catalytic tandem reaction; the mixture was stirred for 2.5 h at 80 °C, and the products **2b/2′b** (67:33, 62.1 mg, 55%) were obtained. For entries 6–8 in Table 2, $Cl(CH_2)_2Cl$, THF, and $CH_3CN$ were used as solvents in this reaction, respectively, and the experimental process was analogous to the typical procedure; for detailed data see entries 6–8 in Table 2. **2b**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.95-7.92$, 7.42–7.39 (AA′BB′, 4H), 5.14 (dd, $J =$ 3.2, 5.9 Hz, 1H), 3.57, 3.53 (ABq, $J = 11.6$ Hz, 2H), 2.25–2.15 (m, 2H), 1.92–1.76 (m, 2H), 1.76–1.60 (m, 2H), 1.60–1.50 (m, 1H), 1.35–1.25 (m, 1H), 0.92 ppm (t, $J = 7.4$ Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 165.9$, 139.6, 130.9, 130.9, 128.8, 128.8, 128.8, 82.6, 63.4, 51.0, 31.5, 30.5, 26.1, 21.0, 8.2 ppm; GC-MS (70 eV): *m/z* (%): 143 (1) $[M-ClC_6H_4CO]^+$, 141 (35) $[^{37}ClC_6H_4CO]^+$, 139 (100) $[^{35}ClC_6H_4CO]^+$, 126 (5) $[M-ClC_6H_4CO_2H]^+$, 113 (8) $[^{37}ClC_6H_4]^+$, 111 (26) $[^{35}ClC_6H_4]^+$, 98 (19), 82 (36), 67 (26), 55 (14), 41 (14); HRMS (ESI): *m/z* calcd for $C_{15}H_{20}O_3Cl$: 283.1095; found: 283.1096 $[M+H]^+$.

**2′b**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.98-7.95$, 7.42–7.39 (AA′BB′, 4H), 4.58, 4.23 (ABq, $J = 11.6$ Hz, 2H), 3.85–3.82 (m, 1H), 2.69 (d, $J = 3.8$ Hz, 1H; OH), 2.21–1.26 (m, 8H), 0.95 ppm (t, $J = 7.4$ Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 166.3$, 139.6, 130.9, 130.9, 128.6, 128.6, 128.5, 78.4, 65.9, 50.3, 33.2, 30.0, 26.5, 20.4, 8.4 ppm; GC-MS (70 eV): *m/z* (%): 143 (0.5) $[M-ClC_6H_4CO]^+$, 141 (25) $[^{37}ClC_6H_4CO]^+$, 139 (79) $[^{35}ClC_6H_4CO]^+$, 126 (3) $[M-ClC_6H_4CO_2H]^+$, 113 (14) $[^{37}ClC_6H_4]^+$, 111 (41) $[^{35}ClC_6H_4]^+$, 108 (62), 98 (49), 82 (100), 67 (60), 55 (40), 41 (40); HRMS (ESI): *m/z* calcd for $C_{15}H_{20}O_3Cl$: 283.1095; found: 283.1096 $[M+H]^+$.

***cis*-1-Benzyl-1-hydroxymethylcyclopent-2-yl 4′-chlorobenzoate (2c) and *cis*-(1-benzyl-2-hydroxycyclopent-1-yl)methyl 4′-chlorobenzoate (2′c)**: By following the typical procedure described above for entry 9 in Table 2, a solution of the substrate **1c** (81.6 mg, 0.4 mmol, 1.0 equiv) and *p*Cl-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 2.5 h at 70 °C to give **2c/2′c** (113.0 mg, 82%) in the ratio of 60:40. **2c**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.94-7.90$, 7.44–7.40 (AA′BB′, 4H), 7.34–7.20 (m, 5H), 5.27 (dd, $J = 2.6$, 6.1 Hz, 1H), 3.50, 3.45 (ABq, $J = 11.8$ Hz, 2H), 3.05, 2.53 (ABq, $J = 13.2$ Hz, 2H), 2.42–2.30 (m, 1H), 1.97–1.80 (m, 3H), 1.60–1.53 (m, 1H), 1.47–1.39 ppm (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 166.0$, 139.7, 137.6, 131.0, 131.0, 130.6, 130.6, 128.8, 128.8, 128.6, 128.1, 128.1, 126.3, 82.3, 63.0, 52.4, 38.6, 31.1, 29.9, 20.6 ppm; MS (70 eV): *m/z* (%): 326 (0.01) $[M-H_2O]^+$, 253 (0.1) $[M-Bn]^+$, 205 (0.1) $[M-ClC_6H_4CO]^+$, 188 (18) $[M-ClC_6H_4CO_2H]^+$, 157 (60), 141 (37) $[^{37}ClC_6H_4CO]^+$, 139 (100) $[^{35}ClC_6H_4CO]^+$, 113 (12) $[^{37}ClC_6H_4]^+$, 111 (35) $[^{35}ClC_6H_4]^+$, 91 (72), 57 (20), 41 (19); HRMS (ESI): *m/z* calcd for $C_{20}H_{22}O_3Cl$: 345.1252; found: 345.1261 $[M+H]^+$.

**2′c**: $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 8.03-8.00$, 7.48–7.46 (AA′BB′, 4H), 7.34–7.22 (m, 5H), 4.53, 4.12 (ABq, $J = 11.6$ Hz, 2H), 4.01 (dd, $J = 3.4$, 6.1 Hz, 1H), 2.78, 2.60 (ABq, $J = 13.5$ Hz, 2H), 2.25–2.15 (m, 1H), 1.97–1.85 (m, 1H), 1.85–1.71 (m, 2H), 1.62–1.50 ppm (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 166.3$, 139.7, 137.7, 131.0, 131.0, 130.2, 130.2, 128.9, 128.9, 128.5, 128.4, 128.4, 126.5, 78.0, 65.8, 51.3, 39.5, 32.6, 29.9, 20.1 ppm; MS (70 eV): *m/z* (%): 326 (0.1) $[M-H_2O]^+$, 253 (0.06) $[M-Bn]^+$, 188 (10) $[M-ClC_6H_4CO_2H]^+$, 170 (23), 141 (22) $[^{37}ClC_6H_4CO]^+$, 139 (65) $[^{35}ClC_6H_4CO]^+$, 113 (12) $[^{37}ClC_6H_4]^+$, 111 (33) $[^{35}ClC_6H_4]^+$, 91 (100), 57 (16), 41 (26); HRMS (ESI): *m/z* calcd for $C_{20}H_{22}O_3Cl$: 345.1252; found: 345.1256 $[M+H]^+$.

***cis*-1-*n*-Butyl-1-hydroxymethylcyclopent-2-yl 4′-chlorobenzoate (2d)**: By following the typical procedure described above for entry 10 of Table 2, a solution of the substrate **1d** (68.0 mg, 0.4 mmol, 1.0 equiv) and *p*Cl-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 2 h at 70 °C to give **2d/2′d** (94.4 mg, 76%) in >98:2 ratio. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.96-7.93$, 7.44–7.41 (AA′BB′, 4H), 5.14 (dd, $J = 3.1$, 5.9 Hz, 1H), 3.56, 3.53 (ABq, $J = 12.0$ Hz, 2H), 2.25–2.15 (m, 1H), 1.94–1.78 (m, 2H), 1.78–1.68 (m, 1H), 1.68–1.48 (m, 3H), 1.45–1.19 (m, 5H), 0.92 ppm (t, $J = 7.2$ Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta = 166.0$, 139.6, 130.9, 130.9, 128.8, 128.8, 128.6, 82.9, 63.9, 50.9, 33.6, 31.5, 30.9, 26.0, 23.5, 21.0, 14.1 ppm; MS (70 eV): *m/z* (%): 171 (0.5) $[M-ClC_6H_4CO]^+$, 154 (4) $[M-ClC_6H_4CO_2H]^+$, 141 (30) $[^{37}ClC_6H_4CO]^+$, 139 (100) $[^{35}ClC_6H_4CO]^+$, 113 (10) $[^{37}ClC_6H_4]^+$, 111 (34) $[^{35}ClC_6H_4]^+$, 98 (47), 67 (25), 55 (21), 41 (30); HRMS (ESI): *m/z* calcd for $C_{17}H_{24}O_3Cl$: 311.1408; found: 311.1414 $[M+H]^+$.

***cis*-(1-Allyl-2-hydroxycyclopent-1-yl)methyl 4′-chlorobenzoate (2′e)**: By following the typical procedure described above for entry 11 in Table 2, a solution of the substrate **1e** (61.6 mg, 0.4 mmol, 1.0 equiv) and *p*Cl-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv), and stirred for 1 h at 70 °C to give the products **2e/2′e** (<1:>99, 96.6 mg, 82%). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 8.00-7.95$, 7.45–7.40 (AA′BB′, 4H), 6.00–5.79 (m, 1H), 5.12 (d, $J =$ 10.8 Hz, 1H), 5.11 (d, $J = 16.4$ Hz, 1H), 4.56, 4.22 (ABq, $J = 11.6$ Hz, 2H), 3.90 (dd, $J = 2.4$, 5.6 Hz, 1H), 2.71 (brs, 1H; OH), 2.25–1.95 (m, 3H), 1.95–1.50 ppm (m, 5H); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta = 166.2$, 139.6, 134.0, 131.0, 131.0, 128.8, 128.8, 128.5, 118.3, 78.0, 66.4, 50.2, 38.7, 33.0, 30.3, 20.2 ppm; MS (70 eV): *m/z* (%): 276 (0.04) $[M-H_2O]^+$, 253 (0.04) $[M-CH_2CH{=}CH_2]^+$, 141 (23) $[^{37}ClC_6H_4CO]^+$, 139 (75) $[^{35}ClC_6H_4CO]^+$, 138 (2) $[M-ClC_6H_4CO_2H]^+$, 113 (12) $[^{37}ClC_6H_4]^+$, 111 (36) $[^{35}ClC_6H_4]^+$, 94 (48), 79 (100), 55 (27), 41 (47); HRMS (ESI): *m/z* calcd for $C_{16}H_{20}O_3Cl$: 295.1095; found: 295.1094 $[M+H]^+$.

**1-(4′-Chlorophenyl)-1-hydroxy-2,2-dimethylprop-3-yl 4′-chlorobenzoate (2′f)**: By following the typical procedure described above for entry 12 of Table 2, a solution of the substrate **1f** (71.2 mg, 0.4 mmol, 1.0 equiv) and *p*Cl-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 2 h at room temperature to give the products **2f/2′f** (<1:>99, 113.3 mg, 89%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta = 7.95-7.92$, 7.45–7.42 (AA′BB′, 4H), 7.33–7.25 (AA′BB′, 4H), 4.62 (d, $J = 2.2$ Hz, 1H), 4.43, 4.01 (ABq, $J = 10.9$ Hz, 2H), 2.56 (d, $J = 2.2$ Hz, 1H; OH), 1.00 (s, 3H), 0.95 ppm (s, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta = 165.8$, 139.6, 139.4, 133.3, 130.9, 130.9, 128.9, 128.9, 128.8, 128.8, 128.4, 127.9, 127.9, 77.2, 71.0, 39.5, 21.5, 19.4 ppm; GC-MS (70 eV): *m/z* (%): 213 (0.2) $[M(^{37}Cl)-ClC_6H_4CHOH]^+$, 211 (0.6) $[M(^{35}Cl)-ClC_6H_4CHOH]^+$, 198 (0.3) $[M(^{37}Cl)-ClC_6H_4CO_2H]^+$, 196 (0.9) $[M(^{35}Cl)-ClC_6H_4CO_2H]^+$, 157 (32), 143 (26) $[^{37}ClC_6H_4CHOH]^+$, 141 (100) $[^{35}ClC_6H_4CHOH+{}^{37}ClC_6H_4CO]^+$, 139 (50) $[^{35}ClC_6H_4CO]^+$, 113 (12) $[^{37}ClC_6H_4]^+$, 111 (19) $[^{35}ClC_6H_4]^+$, 77 (36), 56 (68) $[CH_2{=}C(CH_3)_2]$; HRMS (ESI): *m/z* calcd for $C_{18}H_{22}Cl_2O_3N$: 370.0971; found: 370.0977 $[M+NH_4]^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl benzoate (2aa) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl benzoate (2′aa)**: By following the typical procedure described above for entry 1 in Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and PhCHO (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 3 h at 65 °C to give the products **2aa/2′aa** (72:28, 55.6 mg, 47%). **2aa**: $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 8.03-8.00$, (m, 2H), 7.57–7.17 (m, 8H), 5.72 (dd, $J = 3.6$, 6.4 Hz, 1H), 3.91, 3.76 (ABq, $J = 11.2$ Hz, 2H), 2.70 (brs, 1H; OH), 2.21–1.60 ppm (m, 6H); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta = 166.2$, 142.8, 133.1, 130.3, 129.6, 129.6, 128.6, 128.6, 128.5, 128.5, 126.9, 126.9, 126.8, 82.0, 67.5, 56.1, 32.0, 31.1, 20.6 ppm; GC-MS (70 eV): *m/z* (%): 191 (0.6) $[M-PhCO]^+$, 174 (27) $[M-PhCO_2H]^+$, 144 (12), 131 (31), 118 (100), 105 (88) $[PhCO]^+$, 91 (21), 77 (50), 51 (12); HRMS (ESI): *m/z* calcd for $C_{19}H_{20}O_3Na$: 319.1305; found: 319.1296 $[M+Na]^+$.

**2′aa**: $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.85-7.81$ (m, 2H), 7.57–7.17 (m, 8H), 4.69, 4.39 (ABq, $J = 11.4$ Hz, 2H), 4.46 (t, $J = 6.0$ Hz, 1H), 2.70 (brs, 1H; OH), 2.21–1.60 ppm (m, 6H); $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta = 167.0$, 143.7, 133.0, 130.0, 129.6, 129.6, 128.3, 128.3, 128.2, 128.2, 126.9, 126.9, 126.5, 78.5, 68.8, 54.2, 32.8, 32.0, 19.8 ppm; GC-MS (70 eV): *m/z* (%): 174 (16) $[M-PhCO_2H]^+$, 144 (23), 131 (22), 118 (71), 105 (100) $[PhCO]^+$, 91 (17), 77 (53), 51 (15); HRMS (ESI): *m/z* calcd for $C_{19}H_{20}O_3Na$: 319.1305; found: 319.1296 $[M+Na]^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 2′-chlorobenzoate (2ab) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl 2′-chlorobenzoate (2′ab)**: By following the typical procedure described above for entry 2 of Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *o*Cl-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 4 h at 65 °C to give the products **2ab/2′ab** (80:20, 14.5 mg, 11%). **2ab**: $^1H$ NMR (200 MHz, $CDCl_3$): $\delta = 7.92-7.89$ (m,

1H), 7.53–7.29 (m, 8H), 5.85 (dd, $J=3.2$, 6.2 Hz, 1H), 4.00, 3.84 (ABq, $J=11.2$ Hz, 2H), 2.30–1.60 ppm (m, 6H).

**2′ab**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta=7.60-7.28$ (m, 9H), 4.80, 4.56 (ABq, $J=11.2$ Hz, 2H), 4.58 (t, $J=6.2$ Hz, 1H), 2.40–1.60 ppm (m, 6H).

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 3′-chlorobenzoate (2ac) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl 3′-chlorobenzoate (2′ac)**: By following the typical procedure described above for entry 3 in Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *m*Cl-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 2 h at 65 °C to give the products **2ac**/**2′ac** (60:40, 79.3 mg, 60%). **2ac**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta=8.03-7.93$ (m, 2H), 7.57–7.15 (m, 7H), 5.78 (dd, $J=3.2$, 6.2 Hz, 1H), 3.95, 3.80 (ABq, $J=11.2$ Hz, 2H), 2.65 (brs, 1H; OH), 2.31–1.50 ppm (m, 6H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=165.0$, 142.6, 134.6, 133.1, 132.0, 129.8, 129.6, 129.6, 128.7, 128.7, 127.7, 126.9, 126.9, 82.4, 67.4, 56.2, 32.0, 31.1, 20.6 ppm; GC-MS (70 eV): *m*/*z* (%): 191 (0.4) $[M-ClC_6H_4CO]^+$, 174 (17) $[M-ClC_6H_4CO_2H]^+$, 144 (84), 141 (35) $[^{37}ClC_6H_4CO]^+$, 139 (100) $[^{35}ClC_6H_4CO]^+$, 131 (28), 118 (78), 113 (12) $[^{37}ClC_6H_4]^+$, 111 (35) $[^{35}ClC_6H_4]^+$, 91 (30), 77 (10); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}O_3ClNa$: 353.0915; found: 353.0911 $[M+Na]^+$.

**2′ac**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta=7.83-7.72$ (m, 2H), 7.57–7.15 (m, 7H), 4.74, 4.46 (ABq, $J=11.2$ Hz, 2H), 4.52 (t, $J=6.8$ Hz, 1H), 2.65 (brs, 1H; OH), 2.31–1.50 ppm (m, 6H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=165.7$, 143.5, 134.4, 133.0, 131.8, 129.6, 128.3, 128.3, 127.6, 126.9, 126.8, 126.8, 126.6, 78.6, 69.2, 54.1, 32.9, 31.9, 19.8 ppm; GC-MS (70 eV): *m*/*z* (%): 174 (26) $[M-ClC_6H_4CO_2H]^+$, 144 (7), 141 (11) $[^{37}ClC_6H_4CO]^+$, 139 (30) $[^{35}ClC_6H_4CO]^+$, 131 (32), 118 (100), 113 (6) $[^{37}ClC_6H_4]^+$, 111 (20) $[^{35}ClC_6H_4]^+$, 91 (20), 77 (8); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}O_3ClNa$: 353.0915; found: 353.0911 $[M+Na]^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 2′-fluorobenzoate (2ad) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl 2′-fluorobenzoate (2′ad)**: By following the typical procedure described above for entry 5 of Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *o*F-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 7 h at 60 °C to give the products **2ad**/**2′ad** (63:37, 50.2 mg, 40%). **2ad**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta=8.05-8.01$ (m, 1H), 7.59–7.51 (m, 1H), 7.50–7.10(m, 7H), 5.81 (dd, $J=4.3$, 6.6 Hz, 1H), 3.99, 3.85 (ABq, $J=11.4$ Hz, 2H), 2.28–2.12 (m, 2H), 2.08–1.80 (m, 2H), 1.80–1.60 ppm (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=164.3$, 161.9 (d, $^1J(C,F)=256.4$ Hz), 143.2, 134.7 (d, $^3J(C,F)=8.7$ Hz), 132.4, 128.6, 128.6, 126.9, 126.9, 126.9, 124.2 (d, $^3J(C,F)=3.6$ Hz), 118.6 (d, $^2J(C,F)=10.2$ Hz), 117.1 (d, $^2J(C,F)=22.8$ Hz), 82.9, 67.8, 55.6, 32.3, 31.4, 20.7 ppm; GC-MS (70 eV): *m*/*z* (%): 191 (0.1) $[M-FC_6H_4CO]^+$, 174 (10) $[M-FC_6H_4CO_2H]^+$, 144 (54), 131 (13), 123 (100) $[FC_6H_4CO]^+$, 118 (41), 95 (17), 91 (13), 77 (5); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}FO_3Na$: 337.1210; found: 337.1205 $[M+Na]^+$.

**2′ad**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta=7.83-7.78$ (m, 1H), 7.50–7.10 (m, 8H), 4.73, 4.54 (ABq, $J=11.4$ Hz, 2H), 4.60 (t, $J=5.9$ Hz, 1H), 2.28–2.12 (m, 2H), 2.08–1.80 (m, 2H), 1.80–1.60 ppm (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=164.5$, 161.9 (d, $^1J(C,F)=256.4$ Hz), 143.8, 134.5 (d, $^3J(C,F)=8.9$ Hz), 132.2, 128.3, 128.3, 126.9, 126.9, 126.5, 124.0 (d, $^3J(C,F)=3.6$ Hz), 118.5 (d, $^2J(C,F)=10.2$ Hz), 117.0 (d, $^2J(C,F)=22.6$ Hz), 79.1, 69.6, 53.7, 33.2, 32.4, 20.0 ppm; GC-MS (70 eV): *m*/*z* (%): 174 (22) $[M-FC_6H_4CO_2H]^+$, 144 (11), 131 (29), 123 (67) $[FC_6H_4CO]^+$, 118 (100), 95 (21) $[FC_6H_4]^+$, 91 (21), 77 (9); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}FO_3Na$: 337.1210; found: 337.1205 $[M+Na]^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 4′-trifluoromethylbenzoate (2ae)**: By following the typical procedure described above for entry 6 in Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *p*$CF_3$-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 1.5 h at 60 °C to give the products **2ae**/**2′ae** (>98:2, 90.2 mg, 62%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta=8.22-8.20$, 7.77–7.75 (AA′BB′, 4H), 7.48–7.27 (m, 5H), 5.83 (dd, $J=3.4$, 6.3 Hz, 1H), 4.00, 3.83 (ABq, $J=11.4$ Hz, 2H), 2.35–2.15 (m, 3H), 2.05–1.95 (m, 1H), 1.95–1.83 (m, 1H), 1.83–1.70 ppm (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=165.1$, 142.5, 134.7 (q, $^2J(C,F)=32.2$ Hz), 133.6, 130.0, 130.0, 128.8, 128.8, 127.1, 126.9, 126.9, 125.6, 125.6, 123.6 (q, $^1J(C,F)=271.4$ Hz), 82.6, 67.5, 56.2, 32.2, 31.2, 20.6 ppm; GC-MS (70 eV): *m*/*z* (%): 191 (0.1) $[M-CF_3C_6H_4CO]^+$, 174 (24) $[M-CF_3C_6H_4CO_2H]^+$, 173 (40) $[CF_3C_6H_4CO]^+$, 145 (36) $[CF_3C_6H_4]^+$, 144 (15), 131 (30), 118 (100), 91 (21), 77 (8); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{19}O_3F_3Na$: 387.1179; found: 387.1182 $[M+Na]^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 4′-nitrobenzoate (2af) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl 4′-nitrobenzoate (2′af)**: By following the typical procedure described above for entry 7 of Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *p*$NO_2$-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 0.25 h at 60 °C to give the products **2af**/**2′af** (82:18, 75.0 mg, 55%). **2af**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta=8.34-8.32$, 8.27–8.25 (AA′BB′, 4H), 7.49–7.45 (m, 2H), 7.41–7.39 (m, 2H), 7.31–7.27 (m, 1H), 5.85 (dd, $J=3.4$, 6.2 Hz, 1H), 3.99, 3.81 (ABq, $J=11.2$ Hz, 2H), 2.31–2.15 (m, 3H), 2.05–1.85 (m, 2H), 1.83–1.65 ppm (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=164.4$, 150.6, 142.3, 135.7, 130.7, 130.7, 128.8, 128.8, 127.1, 126.8, 126.8, 123.7, 123.7, 82.9, 67.5, 56.3, 32.2, 31.1, 20.6 ppm; GC-MS (70 eV): *m*/*z* (%): 191 (1.4) $[M-NO_2C_6H_4CO]^+$, 174 (10) $[M-NO_2C_6H_4CO_2H]^+$, 150 (72) $[NO_2C_6H_4CO]^+$, 144 (100), 131 (23), 118 (57), 104 (42), 91 (39), 77 (14); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}NO_5Na$: 364.1155; found: 364.1151 [M+Na]$^+$.

**2′af**: $^1$H NMR (400 MHz, $CDCl_3$): $\delta=8.25-8.23$, 8.04–8.02 (AA′BB′, 4H), 7.49–7.25 (m, 5H), 4.83, 4.54 (ABq, $J=11.2$ Hz, 2H), 4.56 (t, $J=5.8$ Hz, 1H), 2.31–1.65 ppm (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta=165.0$, 150.5, 143.4, 140.4, 130.6, 130.6, 128.4, 128.4, 126.9, 126.7, 126.7, 123.5, 123.5, 78.7, 69.6, 57.1, 33.1, 32.0, 19.8 ppm; GC-MS (70 eV): *m*/*z* (%): 174 (16) $[M-NO_2C_6H_4CO_2H]^+$, 150 (14) $[NO_2C_6H_4CO]^+$, 144 (5), 131 (31), 118 (100), 104 (20), 91 (21), 77 (8); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}NO_5Na$: 364.1155; found: 364.1151 $[M+Na]^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 2′-methylbenzoate (2ag)**: By following the typical procedure described above for entry 8 in Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *o*Me-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 2 h at 60 °C to give the products **2ag**/**2′ag** (>99:<1, 2.5 mg, 2%). $^1$H NMR (200 MHz, $CDCl_3$): $\delta=7.96-7.93$ (m, 1H), 7.53–7.26 (m, 8H), 5.81 (dd, $J=3.2$, 6.2 Hz, 1H), 3.96, 3.79 (ABq, $J=11.0$ Hz, 2H), 2.66 (s, 3H), 2.30–1.50 ppm (m, 6H).

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 3′-methylbenzoate (2ah)**: By following the typical procedure described above for entry 9 of Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *m*Me-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 4 h at 60 °C to give the products **2ah**/**2′ah** (>99:<1, 21.1 mg, 17%). $^1$H NMR (200 MHz, $CDCl_3$): $\delta=7.89$ (brs, 2H), 7.49–7.22 (m, 7H), 5.79 (dd, $J=3.4$, 6.2 Hz, 1H), 3.98, 3.83 (ABq, $J=11.4$ Hz, 2H), 2.44 (s, 3H), 2.36–1.69 ppm (m, 6H); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{22}O_3Na$: 333.1461; found: 333.1456 $[M+Na]^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 4′-methylbenzoate (2ai)**: By following the typical procedure described above for entry 10 in Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *p*Me-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 5 h at 60 °C to give the products **2ai**/**2′ai** (>99:<1, 8.6 mg, 7%). $^1$H NMR (200 MHz, $CDCl_3$): $\delta=7.99-7.95$ (m, 2H), 7.49–7.27 (m, 7H), 5.78 (dd, $J=3.4$, 6.2 Hz, 1H), 3.97, 3.82 (ABq, $J=11.4$ Hz, 2H), 2.44 (s, 3H), 2.36–1.60 ppm (m, 6H).

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl 3′-methoxylbenzoate (2aj) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl 3′-methoxylbenzoate (2′aj)**: By following the typical procedure described above for entry 11 of Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *m*MeO-$C_6H_4CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 3.5 h at 60 °C to give the products **2aj**/**2′aj** (80:20, 67.8 mg, 52%). **2aj**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta=7.69-7.10$ (m, 9H), 5.78 (dd, $J=3.4$, 6.2 Hz, 1H), 3.98, 3.89 (ABq, $J=11.4$ Hz, 2H), 3.88 (s, 3H), 2.28–1.68 ppm (m, 6H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=166.1$, 159.6, 142.8, 131.6, 129.5, 128.6, 128.6, 126.9, 126.9, 126.9, 121.9, 119.4, 114.3, 82.1, 67.5, 56.1, 55.4, 32.0, 31.1, 20.6 ppm; GC-MS (70 eV): *m*/*z* (%): 191 (0.6) $[M-MeOC_6H_4CO]^+$, 174 (33) $[M-MeOC_6H_4CO_2H]^+$, 152 (45) $[MeOC_6H_4CO_2H]^+$, 144 (27), 135 (100) $[MeOC_6H_4CO]^+$, 118 (88), 107 (28) $[MeOC_6H_4]^+$, 91 (20), 77 (30); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{22}O_4Na$: 349.1410; found: 349.1417 $[M+Na]^+$.

**2′aj**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta=7.69-7.10$ (m, 9H), 4.77, 4.45 (ABq, $J=11.2$ Hz, 2H), 4.54 (t, $J=6.8$ Hz, 1H), 3.80 (s, 3H), 2.28–1.68 ppm (m, 6H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta=166.1$, 159.5, 142.8, 132.0–126.0 (3C), 129.3, 128.2, 128.2, 126.5, 121.9, 119.7, 113.8, 78.4, 68.8, 55.4, 54.2, 32.8,

32.0, 19.8 ppm; GC-MS (70 eV): *m*/*z* (%): 174 (48) [*M* – $MeOC_6H_4CO_2H$]$^+$, 152 (56) [$MeOC_6H_4CO_2H$]$^+$, 144 (26), 135 (100) [$MeOC_6H_4CO$]$^+$, 118 (92), 107 (26) [$MeOC_6H_4$]$^+$, 91 (19), 77 (24); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{22}O_4Na$: 349.1410; found: 349.1417 [*M*+Na]$^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl cyclohexanecarboxylate (2ak) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl cyclohexanecarboxylate (2′ak)**: By following the typical procedure described above for entry 14 in Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and $C_6H_{11}CHO$ (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 3 h at 60 °C to give the products **2ak**/**2′ak** (85:15, 60.4 mg, 50%). **2ak**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 7.44-7.20$ (m, 5H), 5.55 (dd, $J = 3.4$, 6.0 Hz, 1H), 3.84, 3.70 (ABq, $J = 11.2$ Hz, 2H), 2.45–1.20 ppm (m, 17H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta = 175.7$, 142.8, 128.5, 128.5, 126.8, 126.8, 126.7, 81.0, 67.6, 55.7, 43.4, 32.0, 31.0, 29.1, 28.9, 25.7, 25.4, 25.3, 20.5 ppm; GC-MS (70 eV): *m*/*z* (%): 191 (0.4) [$M - C_6H_{11}CO$]$^+$, 174 (26) [$M - C_6H_{11}CO_2H$]$^+$, 144 (36), 131 (36), 118 (100), 111 (9) [$C_6H_{11}CO$]$^+$, 91 (25), 83 (89) [$C_6H_{11}$]$^+$, 77 (7), 55 (36), 41 (14); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{26}O_3Na$: 325.1774; found: 325.1774 [*M*+Na]$^+$.

**2′ak**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 7.44-7.24$ (m, 5H), 4.52, 4.22 (ABq, $J = 11.2$ Hz, 2H), 4.47 (dd, $J = 5.2$, 6.0 Hz, 1H), 2.45–1.20 ppm (m, 17H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta = 176.5$, 143.6, 128.1, 128.1, 126.4, 126.4, 126.8, 78.4, 68.0, 54.0, 43.1, 32.8, 32.2, 29.5, 28.8, 25.8, 25.7–25.3 (2C), 19.8 ppm; GC-MS (70 eV): *m*/*z* (%): 174 (19) [$M - C_6H_{11}CO_2H$]$^+$, 144 (12), 131 (34), 118 (100), 111 (4) [$C_6H_{11}CO$]$^+$, 91 (21), 83 (40) [$C_6H_{11}$]$^+$, 77 (7), 55 (27), 41 (12); HRMS (ESI): *m*/*z* calcd for $C_{19}H_{26}O_3Na$: 325.1774; found: 325.1774 [*M*+Na]$^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl isobutanoate (2al)**: By following the typical procedure described above for entry 15 of Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *i*PrCHO (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 3.5 h at 60 °C to give the products **2al**/**2′al** (>98:2, 42.9 mg, 41%). $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 7.42-7.21$ (m, 5H), 5.53 (dd, $J = 3.4$, 6.2 Hz, 1H), 3.84, 3.70 (ABq, $J = 11.4$ Hz, 2H), 2.62 (m, 1H), 2.21–1.50 (m, 6H), 1.23 (d, $J = 7.0$ Hz, 3H), 1.21 ppm (d, $J = 7.0$ Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta = 176.7$, 142.8, 128.5, 128.5, 126.8, 126.8, 126.7, 81.2, 67.5, 55.8, 34.3, 31.9, 31.0, 20.5, 19.0, 18.9 ppm; GC-MS (70 eV): *m*/*z* (%): 191 (0.4) [$M - i$PrCO]$^+$, 174 (16) [$M - i$PrCO$_2$H]$^+$, 144 (28), 131 (31), 118 (100), 91 (29), 77 (10), 71 (25) [*i*PrCO]$^+$, 43 (68) [*i*Pr]; HRMS (ESI): *m*/*z* calcd for $C_{16}H_{22}O_3Na$: 285.1461; found: 285.1467 [*M*+Na]$^+$.

***cis*-1-Hydroxymethyl-1-phenylcyclopent-2-yl butanoate (2am) and *cis*-(1-phenyl-2-hydroxycyclopent-1-yl)methyl butanoate (2′am)**: By following the typical procedure described above for entry 16 in Table 1, a solution of the substrate **1a** (76.0 mg, 0.4 mmol, 1.0 equiv) and *n*PrCHO (2.4 mmol, 6.0 equiv) in $Cl(CH_2)_2Cl$ (4.0 mL) was treated with $SmI_2$ (0.1M, 1.2 mL, 0.3 equiv) for 3.5 h at 60 °C to give the products **2am**/**2′am** (24:76, 58.6 mg, 56%). **2am**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 7.43-7.20$ (m, 5H), 5.57 (dd, $J = 3.6$, 6.0 Hz, 1H), 3.86, 3.72 (ABq, $J = 11.4$ Hz, 2H), 3.30 (br s, 1H; OH), 2.38 (t, $J = 7.6$ Hz, 2H), 2.25–1.49 (m, 8H), 0.99 ppm (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta = 173.4$, 142.8, 128.5, 128.5, 126.7, 126.7, 126.7, 81.2, 67.6, 55.6, 36.5, 32.0, 31.0, 20.5, 18.5, 13.6 ppm; GC-MS (70 eV): *m*/*z* (%): 191 (0.3) [$M - n$PrCO]$^+$, 174 (14) [$M - n$PrCO$_2$H]$^+$, 144 (24), 131 (30), 118 (100), 91 (26), 77 (10), 71 (30) [*n*PrCO]$^+$, 43 (29) [*n*Pr]$^+$; HRMS (ESI): *m*/*z* calcd for $C_{16}H_{22}O_3Na$: 285.1461; found: 285.1469 [*M*+Na]$^+$.

**2′am**: $^1$H NMR (200 MHz, $CDCl_3$): $\delta = 7.43-7.20$ (m, 5H), 4.53, 4.24 (ABq, $J = 11.2$ Hz, 2H), 4.49 (t, $J = 5.8$ Hz, 1H), 3.30 (br s, 1H; OH), 2.21 (t, $J = 7.4$ Hz, 2H), 2.14–1.49 (m, 8H), 0.85 ppm (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta = 174.1$, 143.6, 128.2, 128.2, 126.8, 126.8, 126.4, 78.5, 68.1, 53.9, 36.2, 32.8, 32.1, 19.8, 18.3, 13.5 ppm; GC-MS (70 eV): *m*/*z* (%): 174 (15) [$M - n$PrCO$_2$H]$^+$, 144 (10), 131 (30), 118 (100), 91 (22), 77 (8), 71 (17) [*n*PrCO]$^+$, 43 (19) [*n*Pr]$^+$; HRMS (ESI): *m*/*z* calcd for $C_{16}H_{22}O_3Na$: 285.1461; found: 285.1469 [*M*+Na]$^+$.

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