Chelation and stereodirecting group effects on regio- and diastereoselective samarium(II)-water allylic benzoate reductions.

Trevor F. Stockdale
Michael A. Leitch
Gregory W. O'Neil*

Department of Chemistry, Western Washington University,
516 High Street, Bellingham, WA 98225, USA.

* indicates the main/corresponding author.

oneilg@wwu.edu

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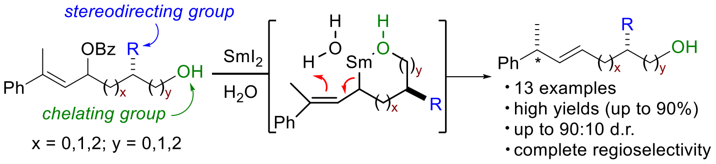

- 13 examples
- high yields (up to 90%)
- up to 90:10 d.r.
- complete regioselectivity

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Abstract $SmI_2(H_2O)_n$ reductions of allylic benzoates adjacent to a trisubstituted alkene occur in high yield with complete regioselectivity and good diastereoselectivity (up to 90:10) for substrates containing properly positioned stereodirecting- and chelating groups. The outcome of these reactions can be rationalized by ring conformation considerations of a proposed chelated organosamarium intermediate, and a mechanism involving intramolecular protonation by a samarium-bound water.

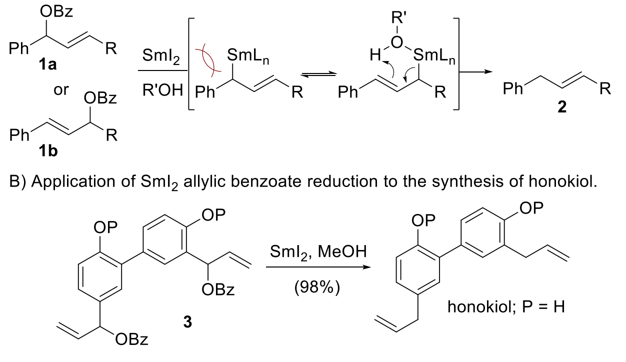
Key words samarium, reduction, diastereoselective, regioselective, chelation

Since its introduction more than 40 years ago,[1] samarium(II) iodide (SmI_2) has proven to be an extremely useful and versatile reductant available to the synthetic chemist.[2] Much of this success relies on the use of certain additives which change the coordination sphere and redox potential of the reagent,[3] allowing for the selective and efficient reduction of a wide range of functional groups. Among the additives commonly employed, proton donors are of special interest.[4] In particular, the addition of water to SmI_2 (often represented as $SmI_2(H_2O)_n$) has been shown to have a significant impact on its reducing capability,[5] enabling for instance the reduction of carboxylic acid derivatives[6] while avoiding the use of toxic and/or less green additives like HMPA, DMPU, or TPPA.[3b,7] A number of investigations have been conducted to understand the special role of water in these transformations that have revealed higher redox potentials[8] and rate enhancements for water relative to other proton sources (e.g. methanol).[9] Recent studies indicate that the mechanism for many of these processes may involve both concerted and asynchronous proton-coupled electron-transfer.[10]

Our group became interested in the use of SmI_2 for the reduction of acyloxysulfones as part of a masked-alkene metathesis protocol.[11] More recently we reported that allylic benzoates (**1a** or **1b**) can be reduced with SmI_2 in the presence of an alcohol additive (R'OH),[12] converging to the corresponding reduced products **2** with high regioselectivity (Scheme 1). The regioselectivity of this reaction can be rationalized by steric considerations of the organosamarium intermediate, and a pericyclic protonation mechanism involving a samarium-bound alcohol molecule. This method then featured in our synthesis of the biologically active natural product honokiol to simultaneously install both allyl substituents found in the target compound from the *bis*-allylic benzoate precursor **3**.[13]

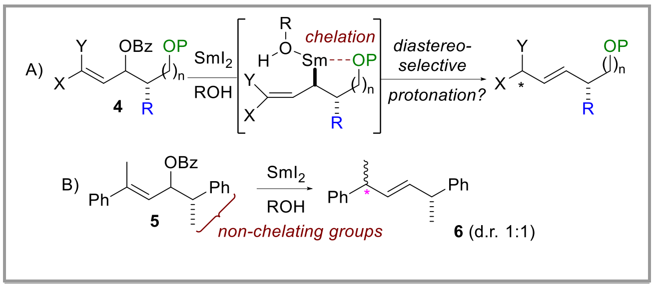
A) SmI_2 reduction of **1a** or **1b** and origin of selectivity for forming **2**.

B) Application of SmI_2 allylic benzoate reduction to the synthesis of honokiol.



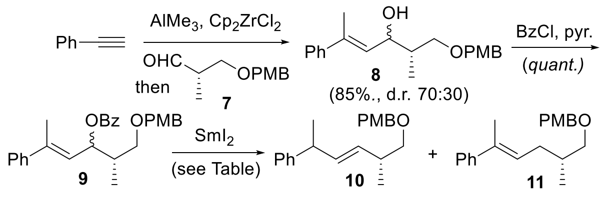
Scheme 1 (A) Regioselective SmI_2 allyl benzoate reductions and (B) its application to a synthesis of honokiol.

Applied to trisubstituted alkene-containing substrates, we recognized that the reaction would generate a new stereocenter (*), and became interested in finding ways to develop this reaction as a new strategy for stereoselective synthesis (Scheme 2).[14] We hypothesized that incorporation of a Lewis-basic chelating element (e.g. OP) and stereodirecting group (R) would render $SmI_2(H_2O)_n$ reductions of compounds of type **4** both regio- and diastereoselective. Together, these groups could impart facial selectivity during the intramolecular protonation event from a chelated intermediate. The importance of chelation to our design was supported by the reduction of compound **5** to product **6** which proved to be non-diastereoselective.



Scheme 2 (A) Proposed regio- and diastereoselective allylic benzoate reductions proceeding through a chelated organosamarium intermediate. (B) The importance of chelation for stereoselectivity is supported by the non-diastereoselective reaction of compound **5** which lacks this ability.

For the chelating element we chose to focus on oxygen given the well-established oxophilicity of samarium.[15] This also introduced an obvious synthetic disconnection (i.e. a carbonyl addition) when designing the synthesis of our desired substrates. With these considerations in mind, initial investigations began with the preparation of compound **8** by zirconium-catalyzed carboalumination[16] of phenyacetylene and addition of the resulting vinylalane into Roche ester-derived aldehyde (*S*)-**7**[17] (Scheme 3). The stereochemistry of the newly formed hydroxyl in **8** for the major isomer is assumed to be (*S*) arising from chelation control,[18] but was not rigorously determined as this stereocenter proved unimportant for the subsequent eliminations (*vide infra*). After benzoylation, unfortunately the reduction of **9** in the presence of various additives proceeded with low diastereoselectivity (50:50 to 60:40) and only modest regioselectivity (up to 5:1).

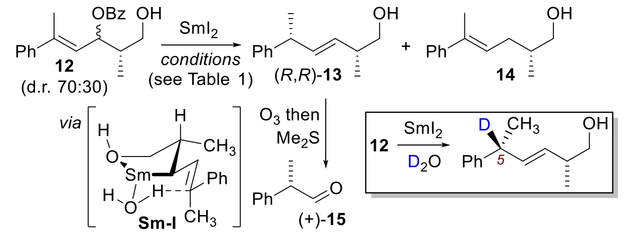


Entry	Additive[a]	10:11[b]	10 d.r.[b]
1.	DMPU	1.3:1	60:40
2.	*t*-BuOH	3:1	69:31
3.	MeOH	3:1	60:40
4.	H_2O	5:1	50:50

Notes: [a]Reactions were performed by adding the additive (16 equiv. DMPU or 1400 equiv. ROH) to SmI_2 (7 equiv.) followed by the substrate at room temperature. [b]Determined by NMR

Scheme 3 Synthesis of substrate **9** and initial screening of its reduction with $SmI_2(H_2O)_n$ in the presence of various additives.

Gratifyingly after PMB-removal, reduction of the corresponding free hydroxyl compound **12** proceeded with both enhanced regio- and diastereoselectivity (d.r.), presumably as a result of greater chelation to samarium,[19] although secondary coordination sphere effects (e.g. hydrogen-bond networks) cannot be ruled out at this time (Scheme 4, Table 1).[8,10a] The impact of different additives on the outcome of the reaction with **12** were investigated as outlined in Table 1. Interestingly, the highest (and nearly identical) diastereoselectivities were obtained using either anhydrous conditions (DMPU, entry 1) followed by quenching (aq. NH_4Cl) or in the presence of water (entry 5),[20] suggestive against an internal protonation by the hydroxyl group per se (performing the reaction in D_2O resulted in >90% deuterium incorporation by ^1H NMR at C5). Both reactions produced compound **13** as a 3:1 mixture of diastereomers and exclusively as the *trans*-isomer, however regioselectivity for the DMPU reaction was much lower (2:1 vs 15:1 for H_2O). Colder conditions (i.e. 0 °C, Entry 6) also led to an erosion of regioselectivity. The reaction proved non-stereospecific to the stereochemistry of the -OBz stereocenter, with identical results obtained when **12** was used as a 50:50 (Entry 7) or 70:30 (Entry 5, *ref.* Scheme 3) mixture of diastereomers.[21] This is attractive from a synthetic standpoint, allowing us to prepare and use substrates epimeric at this position without any impact on the subsequent reductions. The amount of water used also had little effect on the d.r. of the reactions (e.g. 76:24 for 70 equivalents (Entry 8) vs. 75:25 for 1400 equivalents (Entry 5)), consistent with other studies showing that even high concentrations of water do not lead to complete saturation of Sm(II).[3b] Regioselectivity, however, tended to be higher at fewer equivalents of H_2O, perhaps as a result of a competing intermolecular protonation at the higher equivalents (*ref.* Scheme 1). Yields also increased with decreased H_2O (with the exception of 1 equivalent (66% yield)), where side-products that we have tentatively assigned as radical dimers were observed.[22] The absolute configuration of the newly formed stereocenter was determined by ozonolysis of **13** and comparison of the optical activity of the resulting aldehyde **15** to that previously reported.[23] This analysis revealed that the sample was enriched in the (*S*)-(+)-enantiomer, indicating that the major diastereomer of **13** had the (2*R*,5*R*)-configuration. Our working model to explain the stereochemical outcome of this reaction is based on the ring-conformation energetics of a fused 5,6-bicyclic organosamarium transition state structure **Sm-I**,[24] involving hydroxyl chelation of samarium[25] followed by intramolecular protonation by a coordinated water molecule.



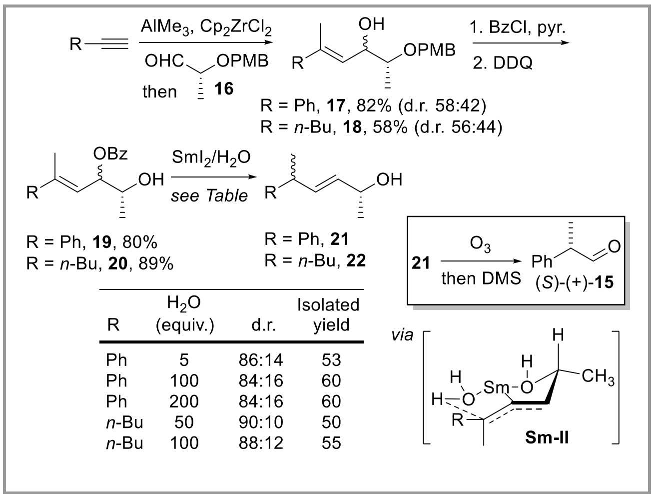
Scheme 4 SmI_2 reduction of compound **12** and determination of absolute stereochemistry by ozonolysis of **13**.

Table 1 Additive effects on SmI_2 reductions of compound 12 (*ref.* Scheme 4).

Entry	Additive[a]	13:14[b]	Compound 13 d.r.[b]
1.	DMPU	2:1	75:25
2.	*t*-BuOH	1:0[c]	67:33
3.	*i*-PrOH	2.3:1	67:33
4.	MeOH	1:0[c]	60:40
5.	H_2O	15:1	76:24
6.	H_2O[d]	5:1	75:25
7.	H_2O[e]	15:1	76:24
8.	H_2O[f]	15:1	76:24

Notes for Table 1: [a] Reactions were performed by adding the additive (16 equiv. DMPU or 1400 equiv. ROH) to SmI_2 (7 equiv.) followed by the substrate and stirring for 30 min. [b] Determined by ^1H NMR. [c] **14** was not detected by NMR. [d] Performed at 0 °C. [e] Compound **12** was used as a 1:1 mixture of diastereomers. [f] Performed using 70 equiv. of H_2O.

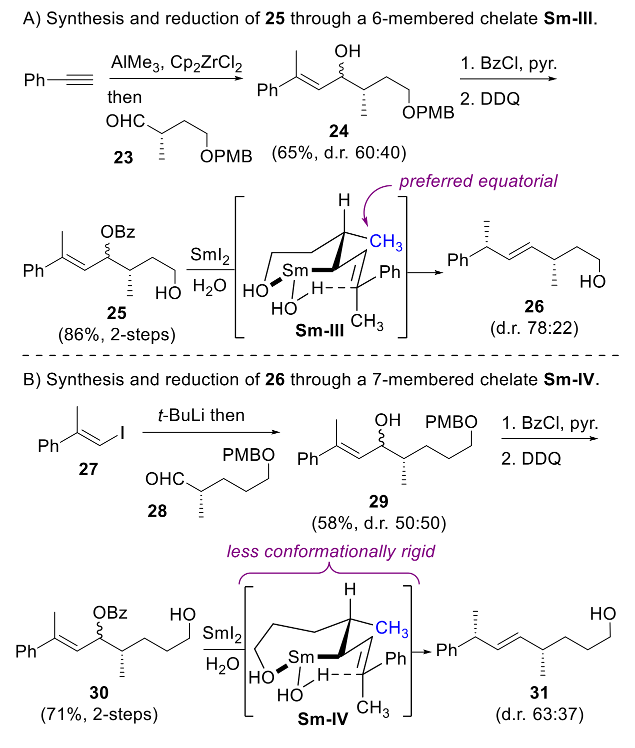
In thinking about other suitable and available aldehyde starting materials from which we could prepare additional substrates to further investigate this transformation, we were drawn to lactate-derived aldehyde **16**[26] (Scheme 5). Using similar chemistry to that employed in the synthesis of **12**, we prepared compounds **19** and **20** and investigated their reduction with $SmI_2(H_2O)_n$. Treatment of **19** or **20** to our optimized conditions from experiments with **12** (e.g. 15 equivalents H_2O relative to SmI_2, room temperature) gave the desired products **21** or **22** with complete regioselectivity and high diastereoselectivity (84:16; higher than for compound **12** (75:25)), however in low yield due to a competing elimination and formation of the corresponding diene (presumably beta-elimination of the hydroxyl group after benzoate cleavage). Increasing the equivalents of water to either 100 or 200 equivalents suppressed this elimination to some extent (presumably by increasing the rate of protonation), allowing for the isolation of **21** in 60% yield. The highest d.r. (90:10) was obtained for the *n*-butyl substrate **20** using 50 equivalents of water, giving compound **22** in 50% isolated yield. The absolute configuration of the newly formed stereocenter was determined by ozonolysis of the product which produced primarily (*S*)-(+)-aldehyde **15** by polarimetry.[23] A possible model to explain this selectivity based on that previously proposed for the one-carbon homologated samarium intermediate is shown in Scheme 5, with the organosamarium transition state structure **Sm-II** existing in this case as an η[3]-complex.[27]



R	H_2O (equiv.)	d.r.	Isolated yield
Ph	5	86:14	53
Ph	100	84:16	60
Ph	200	84:16	60
n-Bu	50	90:10	50
n-Bu	100	88:12	55

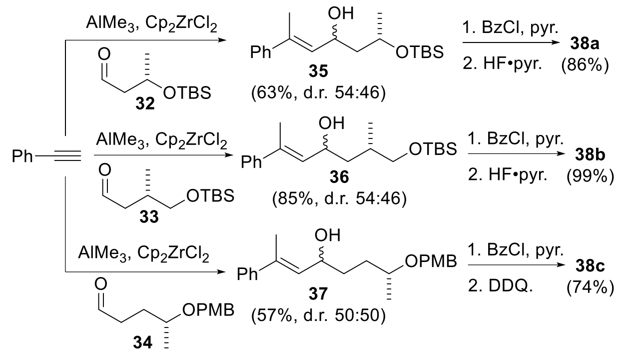
Scheme 5 Synthesis and elimination of lactate-derived compounds **21** and **22**.

Comparing results for lactate substrate **19** and Roche ester-derived compound **12** demonstrates that the location of the hydroxyl group (i.e. linker length) can impact both the yield and selectivity for this reaction. To further investigate this effect, we synthesized and examined the $SmI_2(H_2O)_n$ reductions of compounds **25** and **30** which contain hydroxyl groups three- and four-carbons away (as opposed to one- and two-carbons for compounds **19** and **12** respectively) from the allylic benzoate position (Scheme 6). The reduction of **25** proceeded with comparable diastereoselectivity (78:22) to compound **12**, giving **26** via a mechanism presumably involving the 6-membered chelate **Sm-III**. The methyl group in **Sm-III** assumes a preferred equatorial conformation, controlling the facial selectivity of the protonation event and explaining the stereochemistry observed in the final product. It was anticipated that the reaction of compound **30** would give lower selectivity as the 7-membered organosamarium ring chelate **Sm-IV** would be less stable and/or less conformationally rigid than 5- and 6- membered chelate substrates.[28] Indeed, the reaction of **30** with $SmI_2(H_2O)_n$ gave **31** with not only a lower diastereomeric ratio (63:37), but was accompanied by large amounts of what we have assigned as radical dimers.[22] This result indicates that favorable chelation not only improves d.r., but also controls the product selectivity in these reactions.



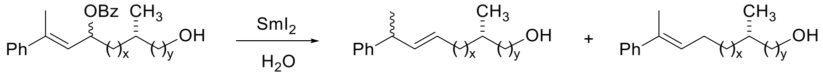
Scheme 6 Comparison of chelation size effects on $SmI_2(H_2O)_n$ allylic benzoate reductions. The reaction of **30** (B) gave lower diastereoselectivity than compound **25** (A), presumably due to formation of a less conformationally rigid 7-membered organosamarium chelate **Sm-IV**.

Within the 5- and 6-membered chelate series we also set out to evaluate the impact of stereodirecting group location. To that end, several additional substrates **38a-c** were prepared (Scheme 7). Combined with compounds **12** and **25**, we obtained data for $SmI_2(H_2O)_n$ reductions for all permutations of compounds proceeding through 5- or 6-membered chelates containing an α, β, or γ methyl stereodirecting group (Table 2). From these results certain trends emerged. For instance, comparing results for compounds **12** and **38a** (Entries 2 and 4) indicates that shifting the stereocenter away from the allylic benzoate position results in a slight loss of diastereoselectivity (75:25 for **12** vs 70:30 for **38a**) with essentially no change in regioselectivity. This could potentially be explained by the difference between the primary alcohol in **12** and a secondary alcohol in **38a**, with a more sterically hindered alcohol resulting in a loss of samarium chelation and therefore a less conformationally restricted transition state. However, a similar shift of the methyl group in the 6-membered chelate system (Entries 3 and 5) resulted in a significant loss of diastereoselectivity (78:22 for **25** vs 57:43 for **38b**). This result cannot be explained by a change in the strength of the chelating group as both **25** and **38b** contain primary alcohols. Rather, it seems that having the stereodirecting group closest to the allylic benzoate position (and thus the resulting carbon-bound samarium) is optimal for maximizing the diastereoselectivity of this reaction. Further evidence is provided from the reduction of compound **38c** (Entry 6), with the stereodirecting methyl group now further remote, and the reaction giving low (and essentially identical to compound **38b**) diastereoselectivity.

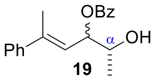
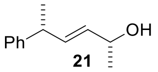
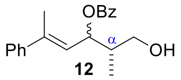
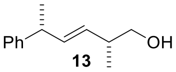
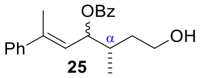
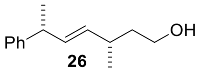
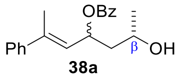
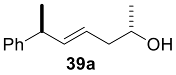
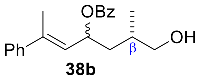
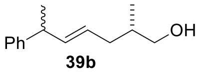
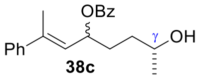
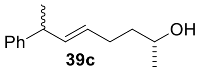


Scheme 7 Synthesis of additional elimination substrates **37a-c** containing differing methyl stereocenter positioning.

Table 2 Comparison of chelation size and methyl stereocenter position on regio- and diastereoselectivity for SmI$_2$(H$_2$O)$_n$ allylic benzoate reductions.

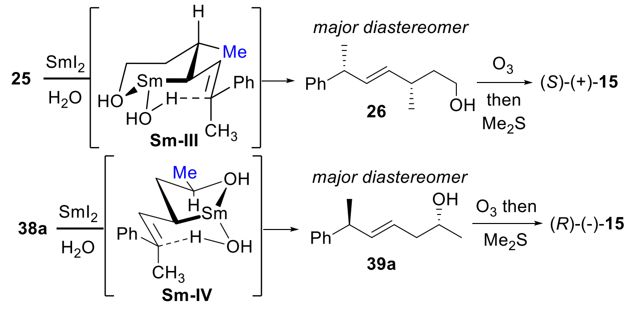


12, 25, 38a-c see Table[a] **15, 26, 39a-c**

Entry	Starting Material	Product	Diastereoselectivity[b]	Regioselectivity[b]
1.	 **19**	 **21**	86:14	98:2
2.	 **12**	 **13**	75:25	98:2
3.	 **25**	 **26**	70:30	100:0
4.	 **38a**	 **39a**	78:22	88:12
5.	 **38b**	 **39b**	57:43[c]	94:6
6.	 **38c**	 **39c**	56:44	83:17

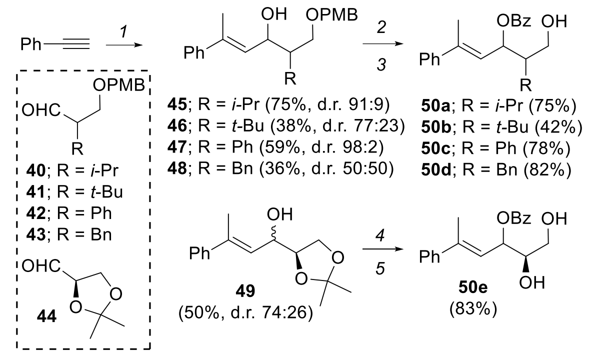
Notes for Table 2: [a]All reactions were preformed using 105 equiv. of H_2O and 7 equiv. of SmI$_2$ in degassed THF at rt under N$_2$. [b]Determined by 1H NMR and GC-FID. [c]Identical results were obtained when the reaction was performed under Ar.

Ozonolysis of the product mixtures obtained from the reductions of compounds **25** and **38a** produced oppositely enantioenriched mixtures of aldehyde **15**. From **25** we obtained primarily *S*-(+)-**15** whereas **38a** gave primarily the *R*-(-)-enantiomer.[23] Both results are consistent with the formation of chelated organosamarium transition state structures **Sm-III** and **Sm-IV**, with the methyl group (Me) assuming a preferred equatorial position (Scheme 8).



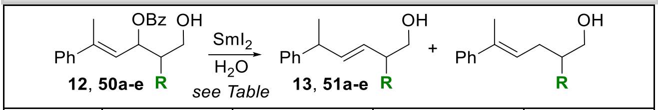
Scheme 8 Determination of absolute stereochemistry for the major diastereomers produced from the reactions of compounds **25** and **38a** and models **Sm-III** and **Sm-IV** to explain the outcome.

We also prepared a series of compounds (**50a-e**) in order to examine the effect of stereodirecting group identity in these reactions (Scheme 9, Table 3). It was hypothesized that larger groups might impart better diastereoselectivities based on for instance larger energy differences between axial and equatorial conformations. With the exception of substrates containing a hydroxyl- (**50e**, Entry 6) or phenyl (**50c**, Entry 4) stereodirecting group where elimination was an issue, all other substrates gave the desired products in good yield and diastereoselectivity. Increasing the size of the stereodirecting group appears to play a modest role in the diastereoselectivity of the reaction. For instance, a change in stereocenter identity from methyl (**12**, Entry 1) to isopropyl (**50a**, Entry 2) resulted in an increase in diastereoselectivity from 75:25 to 83:17, however incorporation of an even larger *tert*-butyl group (**50b**, Entry 3) showed no further increase but rather a small drop in diastereoselectivity (80:20). Reduction of the substrate **50c** containing a phenyl stereocenter (Entry 4) gave the product with a d.r. similar to that of a methyl stereodirecting group (73:27 vs 75:25) but with a lower isolated yield (25%) due to competing elimination to form the fully conjugated diene. The use of a benzyl (Bn) stereocenter (**50d**, Entry 5) resulted in a d.r. similar to that obtained for an *i*-Pr group (81:19). Regioselectivity for all reactions was high (from 93:7 to 100:0) suggestive of a dominant intramolecular protonation pathway.



Scheme 9 Reagents: (1) $AlMe_3$, Cp_2ZrCl_2, then **40**, **41**, **42**, **43**, or **44**; (2) BzCl, pyridine; (3) DDQ; (4) BzCl, pyridine; (5) pTSA, MeOH.

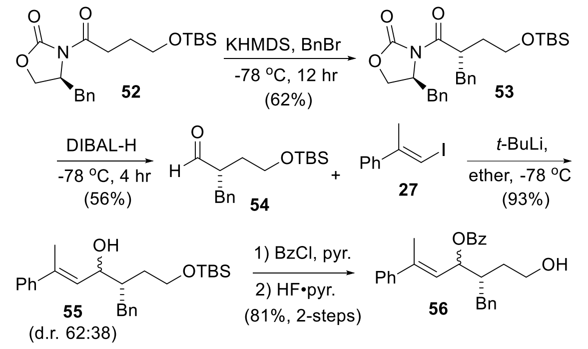
Table 3 Stereodirecting group identify effects on regio- and diastereoselectivity for $SmI_2(H_2O)_n$ allylic benzoate reductions.



Entry	R	d.r.[a]	Regioselectivity[a]	Yield%[b]
1.	Me (12)	75:25	98:2	90
2.	*i*-Pr (50a)	83:17	93:7	80
3.	*t*-Bu (50b)	80:20	95:5	73
4.	Ph (50c)	73:27	100:0	25
5.	Bn (50d)	81:19	96:4	82
6.	OH (50e)	-	-	0

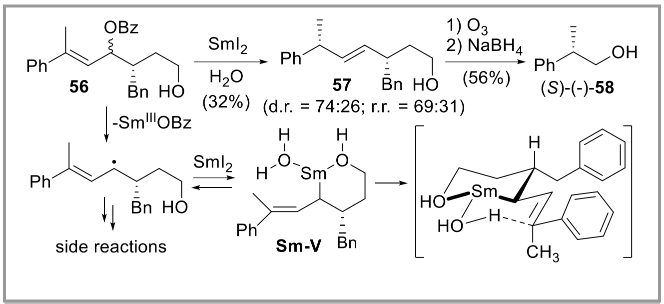
Notes for Table 3: All reductions were performed at room temp. using 7 equiv of SmI2 and 105 equiv of water. [a]Determined by 1H NMR. [b]Isolated yield.

Based the results in Tables 2 and 3, we sought to design an optimized substrate for maximizing diastereoselectivity in our $SmI_2(H_2O)_n$ allylic benzoate reductions. For instance, comparing results for compounds **12** and **25** (Table 2, Entries 1 and 3) indicates a slightly higher d.r. from a 6-membered ring chelated organosamarium intermediate over a 5-membered ring chelate. Additionally, we also observed an enhancement in d.r. by incorporation of *i*-Pr or Bn-stereodirecting groups (Table 3, Entries 2 and 5). Combining these effects we thought might therefore lead to even further enhanced d.r. while still maintaining high yield and regioselectivity. In order to test this hypothesis, we synthesized the 6-membered chelate Bn-stereocenter containing substrate **56** (Scheme 10). The synthesis began by alkylation of oxazolidinone **52**[29] with benzyl bromide giving **53** in 62% yield as a single diastereomer after chromatography on silica. DIBAL-H reduction of **53** gave aldehyde **54** to which was then added the lithium anion generated from vinyl iodide **27**[30] by lithium-halogen exchange. This reaction produced secondary alcohol **55** as a 62:38 mixture of diastereomers in 93% yield. Benzoylation followed by deprotection of the TBS ether using HF·pyr then gave the final allylic benzoate “optimized substrate” **56** in 81% over the two steps.



Scheme 10 Synthesis of an optimized substrate **56** based on results from Tables 2 and 3.

Surprisingly upon reduction of **56** with $SmI_2(H_2O)_n$, the expected product **57** was obtained in only 32% yield with a d.r. of 74:26 and as a 69:31 mixture of regioisomers (r.r., Scheme 111). The low yield was due in part to a significant level of side-product formation (e.g. radical dimers) which were observed in the ^1H NMR spectrum of the crude reaction mixture. Other studies have shown that larger ions such as samarium prefer smaller ring systems.[31] This may explain the higher d.r. and regioselectivity obtained with the lactate derived substrate **20** (90:10) as it had the smallest ring chelate size (nominal 4-membered[32]). Additionally as the stereodirecting group becomes larger, steric strain may be introduced into the rigid chelated organosamarium **Sm-V**. Formation of the 6-membered chelate **Sm-V** from reduction of **56** may therefore not be as favorable, leading to a greater percentage of side-products and lower d.r. and regioselectivity. Nonetheless, sufficient amounts of **57** were obtained to determine its absolute configuration. Ozonolysis of **57** followed by reduction with $NaBH_4$ gave (*S*)-(-)-**58**[33] indicating the absolute stereochemistry of the major diastereomer of **57** is (*3S,6R*). This is consistent with a mechanism involving the 6-6 bicyclic organosamarium transition state structure **Sm-V**, with the benzyl stereodirecting group occupying a preferred equatorial position, followed by intramolecular proton delivery from a samarium bound water.



Scheme 11 Results from the $SmI_2(H_2O)_n$ reduction of an "optimized" substrate **56**. The d.r. and regioselectivity (r.r.) obtained suggest that the trends observed in Tables 2 and 3 may not be additive.

In summary, samarium mediated allylic benzoate reductions can occur diastereoselectively when adjacent to a tri-substituted alkene and flanked by a stereodirecting and chelating group. The reaction can achieve high yields, regioselectivity, and diastereoselectivity (up to 90:10). Stereodirecting- and chelating group location appear to have the most significant impact on yield and selectivity in these reactions. Diastereoselectivity tends to increase with shorter chain lengths between the allylic benzoate and the chelating group (e.g. 63:37 d.r. when separated by four carbons vs 90:10 when separated by two). However, the highest diastereoselectivity obtained (90:10) by having a chelating hydroxyl immediately adjacent (α) to the allylic benzoate, was accompanied by competing beta-elimination leading to lower yields. Increasing the size of the stereodirecting group also increased diastereoselectivity, although to a lesser extent (e.g. 75:25 for methyl vs 80:20 for *tert*-butyl). Combining the results from experiments investigating stereodirecting- and chelating group location along with stereodirecting group identity effects led to the design and synthesis of an "optimized substrate" containing an α-benzyl stereodirecting group and a hydroxyl group that would generate a 6-membered ring chelate organosamarium intermediate. Reduction of this compound with $SmI_2(H_2O)$, however, proceeded with low yield (32%) of the desired product and modest diastereoselectivity (74:26). The low yield was the result of moderate regioselectivity (69:31) and the formation of side-products that we assume may include radical dimerization processes. Formation of larger ring-chelated organosamarium intermediates containing sterically demanding groups might therefore not be favorable. Models have been proposed to account for these results based on ring-conformation considerations of a chelated organosamarium intermediate and a mechanism involving intramolecular protonation by a samarium-bound water.

The experimental section has no title; please leave this line here.

All reactions were carried out under N_2 in flame-dried glassware unless otherwise specified. The solvents used were dried by passing the solvent through a column of activated alumina under nitrogen immediately prior to use. Samarium(II) iodide was prepared according to the method of Procter.[34] All other reagents were purchased and used as received unless otherwise mentioned. TLC analysis used 0.25 mm silica layer fluorescence UV_{254} plates. Flash chromatography: silica gel (230-400 mesh). NMR: Spectra were recorded on a Varian Mercury 300 or Bruker 500 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm, coupling constants (*J*) in Hz. The solvent signals were used as references ($CDCl_3$: $\delta_c \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm). MS (EI): Bruker MaXis Impact mass spectrometer. Spectral data listed is for a mixture of stereoisomers unless specifically labelled to the contrary.

Procedures

General procedure for zirconium-catalyzed carboalumination: To a schlenk tube filled with dichloromethane (DCM) (0.3 M relative to alkyne) and Cp_2ZrCl_2 (0.1 eq) at -20 ^{0}C was added trimethyl aluminum (2.0 eq) dropwise resulting in a yellow solution which was stirred for 10 min. Deionized H_2O (1.0 eq) was then added dropwise turning the solution a darker shade of yellow which was then stirred for another 10 min. The reaction was then warmed to room temperature for ten min and then cooled to 0 ^{0}C. Phenyl acetylene (1.0 eq) was added dropwise and the solution was stirred for 40 min at 0 ^{0}C. The aldehyde (0.8 eq) was then added dropwise and the mixture was stirred for 1 h at 0 ^{0}C. The reaction was quenched slowly with cold H_2O and then aq. HCl, and extracted with DCM (x3). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*.

General Procedure for alcohol benzoylation: Pyridine (2 equiv.) was added to a schlenk tube containing substrate (1 equiv.) in DCM (0.2 M relative to substrate). The mixture was then cooled to 0 ^{o}C followed by the addition of benzoyl chloride (1.2 equiv.). The reaction was allowed to warm to rt for 15 h., before quenching with aq. $NaHCO_3$ and extracting with DCM (3x). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*.

General procedure for DDQ removal of a PMB: Substrate was added to a round bottom containing a 50:50 mixture of DCM:pH 7 buffer (0.1 M relative to substrate). The reaction mixture was cooled to 0 ^{o}C and stirred vigorously at which time DDQ (3 equiv.) was added portion wise over 30 min. The reaction was stirred vigorously for 1 h. and then quenched with aq. NaOH (1.0 M) and extracted with DCM (3x). The combined organic extracts were washed with brine (2x), dried over $MgSO_4$, and concentrated *in vacuo*

General procedure for $SmI_2(H_2O)_n$ reductions: To a dry schlenk tube containing a solution of SmI_2 in THF (0.1 M, 7 equiv.) was added degassed nano-pure H_2O (105 equiv.) turning the solution a deep red color. The solution was stirred for 5 min. before the substrate (1 equiv) was then added. After 30 min. the reaction was quenched with aq. $NaHCO_3$ and extracted with EtOAc (3x). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*.

(E)-2,5-diphenylhex-4-en-3-yl benzoate (**5**). Prepared according to the general benzoylation procedure using (E)-2,5-diphenylhex-4-en-3-ol[35] (0.5 g, 1.98 mmol). Purification by flash chromatography on silica gave **5** (0.64 g, 90%) as a colorless oil (d.r. 80:20).

R_f = 0.52 in 4:1 hexanes:EtOAc)

IR (ATR): 3059, 3028, 2970, 1712, 1601, 1584, 1494, 1450, 1377, 1265, 998, 864, 710, 696 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.08 (ddd, *J* = 8.2, 3.2, 1.9 Hz, 2H), 7.57 (dd, *J* = 6.8, 1.3 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.33 (m, 2H), 7.33 – 7.26 (m, 5H), 7.26 – 7.20 (m, 3H), 6.01 (dd, *J* = 9.4, 7.5 Hz, 1H), 5.64 (dq, *J* = 9.3, 1.4 Hz, 1H), 3.29 (dq, *J* = 7.1 Hz, 1H), 2.01 (d, *J* = 1.4 Hz, 3H), 1.47 (d, *J* = 7.0 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 165.97, 143.02, 142.29, 139.89, 132.94, 130.60, 129.68, 128.42, 128.41, 128.27, 128.19, 127.35, 126.79, 125.99, 124.75, 76.04, 44.62, 17.16, 16.72.

HRMS (ES+): *m/z* $[379.1674]^+$ calcd for $C_{25}H_{24}O_2Na^+$ $[M+Na]^+$; found: 379.1640.

(2S,E)-1-((4-methoxybenzyl)oxy)-2-methyl-5-phenylhex-4-en-3-ol (**8**). Prepared according to the general zirconium-catalyzed carboalumination procedure using aldehyde **7**[17] (1.0 g, 4.7 mmol). Purification by flash chromatography on silica gave **8** (1.31 g, 85%) as a colorless oil (d.r. 70:30).

R_f = 0.65 in 1:1 hexanes:EtOAc.

IR (ATR): 3320, 3028, 2986, 2962, 2851, 1713, 1611, 1595, 1576, 1440, 1246, 1035, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.43 (d, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 8.7 Hz 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 5.78 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.50 (d, *J* = 11.7, 1H), 4.51 (m, 1H), 4.47 (d, *J* = 11.7Hz, 1H), 3.83 (s, 3H), 3.66 (dd, *J* = 9.3, 4.3 Hz, 1H), 3.51 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.12 (d, *J* = 1.4 Hz, 3H), 2.03 (qd, *J* = 7.4, 4.3 Hz, 1H). 0.93 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.27, 143.22, 137.42, 129.87, 129.50, 129.34, 128.15, 127.10, 125.88, 113.84, 74.49, 73.11, 73.10, 55.25, 39.34, 16.52, 13.45.

HRMS (ES+): *m/z* [349.1780]$^+$ calcd for $C_{21}H_{26}O_3Na^+$ [M+Na]$^+$; found: 349.1771.

(2S,E)-1-((4-methoxybenzyl)oxy)-2-methyl-5-phenylhex-4-en-3-yl benzoate (**9**). Prepared according to the general benzoylation procedure using **8** (1.31 g, 4.00 mmol). Purification by flash chromatography on silica gave **9** (1.72 g, *quant*) as a colorless oil.

R_f = 0.48 in 4:1 hexanes:EtOAc

IR (ATR): 3063, 3032, 2999, 2962, 2934, 2917, 2851, 1786, 1713, 1611, 1599, 1584, 1450, 1246, 1035, 699 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.02 (dd, *J* = 7.0, 1.3 Hz, 2H), 7.54 (dd, *J* = 8.2, 7.6 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.25-7.21 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.96 (dd, *J* = 9.5, 6.8 Hz, 1H), 5.77 (dq, *J* = 9.5, 1.4 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 3.77 (s, 3H), 3.49 (t, *J* = 7.0 Hz, 1H), 3.44 (dd, *J* = 6.0, 9.2 Hz, 1H), 2.35 (hept, *J* = 6.9 Hz, 1H), 2.27 (d, *J* = 1.3 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 165.73, 159.06, 143.00, 140.35, 134.54, 132.73, 130.59, 129.59, 129.24, 128.89, 128.29, 128.21, 127.40, 126.00, 124.06, 113.70, 73.37, 72.79, 71.60, 55.23, 38.33, 16.81, 13.09.

HRMS (ES+): *m/z* [453.2042]$^+$ calcd for $C_{28}H_{30}O_4Na^+$ [M+Na]$^+$; found: 453.2039.

1-methoxy-4-((((2R,E)-2-methyl-5-phenylhex-3-en-1-yl)oxy)-methyl)-benzene (**10**). To a dry schlenk flask containing a solution of SmI_2 in THF (0.1 M, 16.1 mL) at 0 °C was added DMPU (0.445 mL, 1.61 mmol) resulting in a dark purple solution which was stirred for 1 h. Compound **9** (0.100 g, 0.23 mmol) was then added and the solution was stirred for 1 h. The reaction was then quenched with aq. NH_4Cl (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gave **10** (0.051 g, 70%) as a colorless oil (d.r. 60:40).

R_f = 0.60 in 10:1 hexanes:EtOAc.

IR (ATR): 3080, 3057, 3025, 2957, 2926, 2850, 1948, 1877, 1804, 1730, 1611, 1511, 1452, 1360, 1245, 1087, 1035, 819, 757, 698 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.29 (t, *J* = 7.5 Hz, 4H), 7.20 (dd, *J* = 11.1, 2.3 Hz, 4H), 7.17 (t, *J* = 6.7 Hz, 2H) 6.87 (d, *J* = 8.5 Hz, 4H), 6.86 (d, *J* = 8.6 Hz, 4H), 5.63 (ddd, *J* = 15.5, 6.7, 1.3 Hz, 2H), 5.39 (ddd, *J* = 15.5, 7.1, 1.4 Hz, 2H), 4.42 (d, *J* = 6.53 Hz, 4H), 3.79 (s, 3H), 3.78 (s, 3H), 3.43 (p, *J* = 7.0 Hz, 2H), 3.32 (dd, *J* = 9.2, 6.2 Hz, 1H) 3.31 (dd, *J* = 9.1, 6.3 Hz, 1H) 3.24 (dd, *J* = 9.2, 6.2 Hz, 1H), 3.23 (dd *J* = 7.1, 4.0 Hz, 1H), 2.48 (hept, *J* = 6.7 Hz, 2H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H). 0.99 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.04, 134.62, 131.63, 129.13, 129.08, 128.30, 128.10, 127.18, 125.89, 113.70, 75.14, 72.50, 55.23, 42.20, 36.76, 21.48, 17.12.

HRMS (ES+): *m/z* [333.1830]$^+$ calcd for $C_{21}H_{26}O_2Na^+$ [M+Na]$^+$; found: 333.1836.

(2S,E)-1-hydroxy-2-methyl-5-phenylhex-4-en-3-yl benzoate (**12**). Prepared according to the general procedure for removal of a PMB group with DDQ using **9** (1.2 g, 2.78 mmol). Purification by flash chromatography on silica gave **12** (0.6 g, 70%) as a colorless oil.

R_f = 0.18 in 4:1 hexanes:EtOAc.

IR (ATR): 3420, 3060, 3032, 2964, 2922, 2880, 1714, 1450, 1268, 1110, 932, 711 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.07 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.42 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 5.95 (dd, *J* = 9.4, 8.1 Hz, 1H), 5.84 (dq, *J* = 9.4, 1.4 Hz, 1H), 3.68 (qd, *J* = 11.3, 4.6 Hz, 2H), 2.23 (d, *J* = 1.4 Hz, 3H), 2.15 (m, 1H), 1.10 (d, *J* = 7.0 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 166.48, 142.73, 140.69, 133.05, 130.20, 129.67, 128.38, 128.25, 127.54, 125.96, 124.33, 73.31, 64.09, 40.55, 16.88, 12.92.

HRMS (ES+): *m/z* [333.1467]$^+$ calcd for $C_{21}H_{26}O_2Na^+$ [M+Na]$^+$; found: 333.1472.

(2R,5R,E)-2-methyl-5-phenylhex-3-en-1-ol (**13**). Prepared according to the general procedure for $SmI_2(H_2O)_n$ reductions using compound **12** (0.025 g, 0.08 mmol). Purification by flash chromatography on silica gave **15** (0.0135 g, 90%) as a pale yellow oil.

R_f = 0.31 in 4:1 hexanes:EtOAc.

IR (ATR): 3360, 3083, 3061, 3025, 2961, 2925, 2871, 1950, 1876, 1803, 1716, 1601, 1492, 1415, 1373, 1272, 1029, 971, 760, 698 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.38 (t, *J*=4.7 Hz, 1H), 7.30 (t, *J*=6.9 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.74 (ddd, *J* = 15.5, 6.8, 1.1 Hz, 1H), 5.33 (ddd, *J* = 15.5, 7.9, 1.4 Hz, 1H), 3.47(m, 2H), 3.38 (dd, *J* =10.6, 8.1, 1H) 2.36 (hept, *J* = 7.0 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 146.04, 136.89, 131.00, 128.43, 127.07, 126.06, 67.35, 42.27, 39.66, 21.48, 16.60.

HRMS (ES+): *m/z* [190.1358]$^+$ calcd for $C_{13}H_{18}O^+$ [M]$^+$; found: 190.1358.

(S)-2-phenylpropanal (**15**). To a round bottom flask open to air containing **13**, **21**, **26**, or **39a** in DCM (0.1 M relative to substrate) at -78 °C, O_3 was bubbled into the solution until the reaction turned an electric blue color. The reaction was left at this temperature without stirring for 5 minutes and then nitrogen was bubbled though the reaction until the solution became colorless. The reaction was quenched with dimethyl sulfide (5 equiv.), warmed to room temperature, and stirred for 1 h. The reaction mixture was washed with brine (15 mL) and extracted with DCM (3 x 15mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Aldehyde **15** was then isolated by flash chromatography on silica (R_f = 0.63 in 4:1 Hex:EtOAc). NMR spectra for **15** matched that previously reported.[23]

Polarimetry value for (*S*)-**15** from **21**: $[\alpha]_D$ = +88.5 (*c* 0.4, $CHCl_3$); Lit for (*R*)-**15**: $[\alpha]_D$ = -88.6 (*c* 0.93, $CHCl_3$).[23]

(2R,E)-2-((4-methoxybenzyl)oxy)-5-phenylhex-4-en-3-ol (**17**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using aldehyde **16**[26] (0.500 g, 2.6 mmol). Purification by flash chromatography over silica gave **17** (0.688 g, 82%) as a colorless oil (d.r = 58:42).

R_f diastereomer$_\alpha$ = 0.30; R_f diastereomer$_\beta$ = 0.20 in 4:1 Hex:EtoAc.

IR (ATR): 3328, 3058, 3016, 2928, 1268, 1110, 932, 711 cm^{-1}.

Data for diastereomer α: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40 (dd, *J* = 8.6, 1.5 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.27 (t, *J* = 7.3, 1H) 6.90 (d, *J* = 8.7 Hz, 2H), 5.70 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.43 (d, *J* = 11.3 Hz 1H), 4.38 (dd, *J* = 8.9, 7.7 Hz, 1H), 3.82 (s, 3H), 3.50 (dq, *J* = 7.7, 6.2 Hz, 1H), 2.13 (d, *J* = 1.4 Hz, 3H), 1.20 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.32, 142.98, 139.81, 130.21, 129.48, 128.18, 127.30, 126.40, 125.88, 113.92, 78.64, 72.44, 70.91, 55.26, 16.90, 15.52.

HRMS (ES+): *m/z* [335.1623]$^+$ calcd for $C_{20}H_{24}O_3Na^+$ [M+Na]$^+$; found: 335.1612.

Data for diastereomer β: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40 (dd, *J* = 8.7, 1.4, 2H), 7.32 (t, *J* = 7.19 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.80 (dq, *J* = 8.4, 1.3 Hz, 1H), 4.62 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.62 (d, *J* = 11.7, 1H), 4.50 (d, *J* = 11.7, 1H), 3.81 (s, 3H), 3.66 (qd, *J* = 6.4, 3.5 Hz, 1H), 2.08 (d, *J* = 1.4 Hz, 3H), 1.20 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.26, 143.03, 138.24, 130.57, 129.53, 129.31, 128.23, 127.26, 126.55, 125.89, 113.88, 77.19, 70.92, 70.62, 55.31, 16.56, 14.42.

HRMS (ES+): *m/z* [335.1623]$^+$ calcd for $C_{20}H_{24}O_3Na^+$ [M+Na]$^+$; found: 335.1612.

(2R,E)-2-hydroxy-5-phenylhex-4-en-3-yl benzoate (**19**). Prepared according to the general benzoylation procedure using **17** (0.371 g, 1.18 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **19** (0.281 g, 80% over two steps) as a colorless oil.

R$_f$ = 0.24 in 4:1 Hex:EtoAc.

IR (ATR) 3450, 3062, 3031, 2976, 2929, 1712, 1600, 1583, 1450, 1266, 1110, 1025, 963, 909, 709 cm^{-1}.

Data for diastereomer α: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.07 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 8.1 Hz, 2H), 7.41 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.32 (t, *J* = 7.1 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 5.77 (m, 2H), 4.10 (p, *J* = 6.3 Hz, 1H), 2.29 (d, *J* = 1.2 Hz, 3H), 1.30 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 166.01, 142.54, 141.90, 133.09, 130.16, 129.66, 128.41, 128.27, 127.68, 125.96, 122.37, 69.74, 18.81, 17.07.

Data for diastereomer β: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.07 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 8.1 Hz, 2H), 7.43 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 5.91 (dq, *J* = 9.3, 1.3 Hz, 1H), 5.85 (dd, *J* = 9.3, 4.0 Hz, 1H), 4.15 (qd, *J* = 6.5, 4.1 Hz, 1H), 2.25 (d, *J* = 1.3 Hz, 3H), 1.31 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 165.94, 142.47, 142.03, 133.06, 130.15, 129.64, 128.39, 128.25, 127.66, 125.95, 122.37, 121.60, 76.73, 75.88, 69.59, 18.19, 16.90.

HRMS (ES+): *m/z* [319.1310]$^+$ calcd for $C_{19}H_{20}O_3Na^+$ [M+Na]$^+$; found: 319.1314.

(2R,E)-2-((4-methoxybenzyl)oxy)-5-methylnon-4-en-3-ol (**18**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using 1-hexyne (0.373 mL, 3.25 mmol) and aldehyde **16**[26] (0.500 g, 2.6 mmol). Purification by flash chromatography on silica gave **18** (0.441 g**,** 58%) as a colorless oil (d.r = 56:44).

R$_f$ diastereomer$_α$ = 0.38; R$_f$ diastereomer$_β$ = 0.34 in 4:1 Hex:EtoAc.

IR (ATR): 3420, 2980, 2928, 1614, 1570, 1265, 1110, 932, 886, 711 cm^{-1}.

Data for diastereomer α: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.29 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.13 (dq, *J* = 9.0, 1.3 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.42 (d, *J* = 11.3 Hz, 1H) 4.21 (dd, *J* = 9.0, 8.0 Hz, 1H), 3.82 (s, 3H), 3.39 (dq, *J* = 8.0, 6.2 Hz, 1H), 2.04 (t, *J* = 7.7 Hz, 2H), 1.71 (d, *J* = 1.4 Hz, 3H), 1.42 (m, 2H), 1.31 (h, *J* = 7.3 Hz, 2H), 1.13 (d, *J* = 6.2 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.22, 141.64, 130.31, 129.37, 123.08, 113.84, 78.91, 72.09, 70.80, 55.20, 39.38, 29.79, 22.29, 16.97, 15.36, 13.92.

Data for diastereomer β: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.27 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.20 (dq, *J* = 8.5, 1.3 Hz, 1H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.47 (d, *J* = 11.1 Hz, 1H) 4.46 (dd, *J* = 8.3, 3.9 Hz, 1H), 3.81 (s, 3H), 3.55 (qd, *J* = 6.4, 3.4 Hz, 1H), 2.01 (t, *J* = 7.0 Hz, 2H), 1.64 (d, *J* = 1.4 Hz, 3H), 1.39 (p, *J* = 7.5 Hz, 2H), 1.29 (m, 2H), 1.12 (d, *J* = 6.4 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.17, 140.08, 130.70, 129.20, 122.97, 113.81, 77.32, 70.50, 70.37, 55.28, 39.39, 29.91, 22.34, 16.66, 14.17, 13.97.

HRMS (ES+): *m/z* [315.1936]$^+$ calcd for $C_{18}H_{28}O_3Na^+$ [M+Na]$^+$; found: 315.1944.

(2R,E)-2-hydroxy-5-methylnon-4-en-3-yl benzoate (**20**). Prepared according to the general benzoylation procedure using **18** (0.431 g, 1.3 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **20** (0.344 g, 89%) as a colorless oil.

R$_f$ = 0.32 in 4:1 Hex:EtoAc.

IR (ATR) 3462, 3062, 2956, 2929, 2871, 1714, 1600, 1578, 1450, 1315, 1266, 1111, 1068, 962, 709 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.05 (dd, *J* = 8.5, 1.3 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 4H), 5.66 (dd, *J* = 9.2, 4.4 Hz, 1H), 5.57 (dd, *J* = 9.5, 7.2 Hz, 1H), 5.32 (dq, *J* = 9.2, 1.3 Hz, 1H), 5.20 (dq, *J* = 9.5, 1.3 Hz, 1H), 4.03 (qd, *J* = 6.3, 4.2 Hz, 1H), 3.97 (p, *J* = 6.6 Hz, 1H), 2.06 (t, *J* = 7.6 Hz, 2H), 2.04 (t, *J* = 7.3 Hz, 2H), 1.84 (d, *J* = 1.4 Hz, 3H), 1.81 (d, *J* = 1.4 Hz, 3H) 1.40 (m, 4H), 1.29 (p, *J* = 7.4 Hz, 4H), 1.24 (d, *J* = 6.5 Hz, 3H), 1.22 (d, *J* = 6.5 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 166.05, 165.96, 144.48, 144.07, 132.97, 132.95, 130.44, 130.42, 129.64, 129.63, 128.37, 119.36, 118.42, 76.80, 75.83, 69.74, 69.54, 39.50, 39.46, 29.86, 29.80, 22.32, 22.30, 18.73, 18.12, 17.20, 17.09, 13.94.

HRMS (ES+): *m/z* [319.1310]$^+$ calcd for $C_{19}H_{20}O_3Na^+$ [M+Na]$^+$; found: 319.1314.

(2R,5R,E)-5-phenylhex-3-en-2-ol (**21**). To a dry schlenk tube containing a solution of SmI_2 in THF (0.1 M, 7.0 mL, 7 equiv.) was added degassed nano-pure H_2O (2.5 mL, 1400 equiv.) turning the solution a deep red color. The solution was stirred for 5 min. before compound **19** (0.030 g, 0.10 mmol) was then added. After 30 min. the reaction was quenched with aq. $NaHCO_3$ (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gave **21** (0.011 g, 60%) as a colorless oil (d.r. 84:16).

R$_f$ = 0.30 in 4:1 Hex:EtoAc.

Data for the mixture of diastereomers: IR (ATR) 3462, 3062, 2956, 2929, 2871, 1714, 1600, 1578, 1450, 1315, 1266, 1111, 1068, 962, 709 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.18 (m, 3H), 5.82 (ddd, *J* = 15.4, 6.7, 1.1 Hz, 1H), 5.56 (ddd, *J* = 15.5, 6.6, 1.4 Hz, 1H), 4.30 (p, *J* = 6.4 Hz, 1H), 3.46 (p, *J* = 7.0, 6.4 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 3H), 1.28 (d, *J* = 6.4 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 145.56, 135.41, 132.87, 128.44, 127.16, 126.16, 68.87, 41.83, 23.42, 21.17.

HRMS (ES+): *m/z* [159.1174]$^+$ calcd for $C_{12}H_{15}$ [M-OH]$^+$; found: 159.1175.

(2R,5S,E)-5-methylnon-3-en-2-ol. (**22**). To a dry schlenk tube containing a solution of SmI_2 in THF (0.1 M, 7.7 mL, 7 equiv.) was added degassed nano-pure H_2O (2.75 mL, 1400 equiv.) turning the solution a deep red color. The solution was stirred for 5 min. before compound **20** (0.030 g, 0.11 mmol) was then added. After 30 min. the reaction was quenched with aq. $NaHCO_3$ (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gave **22** (0.010 g, 60%) as a colorless oil (d.r. 90:10).

R_f = 0.38 in 4:1 Hex:EtoAc.

Data for the mixture of diastereomers: IR (ATR) 3347, 2958, 2925, 2871, 2857, 1606, 1457, 1371, 1258, 1150, 1123, 1060, 969, 730 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 5.54 (dd, *J* = 15.4, 6.9 Hz, 1H), 5.48 (dd, *J* = 15.4, 6.0 Hz, 1H) 4.28 (p, *J* = 6.3 Hz, 1H), 2.11 (p, *J* = 6.6 Hz, 1H), 1.29 (m, 6H), 1.28 (d, *J* = 6.3 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR (CDCl$_3$, 126 MHz): δ = 136.99, 132.24, 69.03, 36.56, 36.14, 29.48, 23.49, 22.79, 20.40, 14.08.

HRMS (ES+): *m/z* [139.1487]$^+$ calcd for C$_{10}$H$_{19}$ [M-OH]$^+$; found: 139.1482.

(5S,E)-7-((4-methoxybenzyl)oxy)-5-methyl-2-phenylhept-2-en-4-ol (**24**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using (2*S*)-4-[[(1,1-dimethylethyl)dimethylsilyl]oxy]-2-methyl-butanal (**23**)[36] (0.29 g, 1.3 mmol). Purification by flash chromatography on silica gave **24** (0.288 g, 65%) as a colorless oil (d.r = 60:40).

R_f = 0.65 in 1:1 Hex:EtOAc.

IR (ATR) 3396, 3102, 3080, 3056, 3028, 2931, 2863, 1611, 1585, 1511, 1493, 1444, 1364, 1301, 1245, 1081, 1032, 909, 820, 757, 731, 696 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.42-7.38 (m, 4H), 7.32 (t, 7.32, *J* = 7.3 Hz, 4H) 7.27 (dd, *J* = 5.6, 2.1 Hz, 2H) 7.26 (dd, *J* = 7.0, 2.0 Hz, 2H), 7.25 (tt, *J* = 6.3, 1.3 Hz, 2H), 6.88 (d, *J* = 8.6, 2H), 6.87 (d, *J* = 8.6, 2H), 5.82 (dq, *J* = 8.7, 1.4 Hz, 1H), 5.77 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.47 (s, 2H) 4.47 (d, *J* = 11.5 Hz, 1H), 4.44 (d, 11.5 Hz, 1H), 4.43 (dd, = 9.1, 4.5 Hz, 1H), 4.30 (dd, *J* = 8.8, 6.9 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.63-3.56(m, 2H), 3.54-3.49 (m, 2H), 2.63 (br, OH), 2.40 (br, OH), 2.08 (d, 1.4 Hz, 3H) 2.07 (d, *J* = 1.4 Hz, 3H), 1.92-1.81 (m, 4H), 1.64 (sep, *J* = 6.7 Hz, 1H), 1.50 (sep, *J* = 6.6 Hz, 1H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 159.23, 143.31, 137.56, 137.26, 130.20, 129.55, 129.39, 129.37, 129.19, 128.20, 127.14, 125.90, 113.84, 113.83, 72.78, 72.77 72.71, 72.20, 68.36, 68.03, 55.28, 37.80, 37.56, 32.96, 32.77, 16.61, 16.51, 16.00, 15.21.

HRMS (ES+): *m/z* [363.1936]$^+$ calcd for C$_{22}$H$_{28}$O$_3$Na$^+$ [M+Na]$^+$; found: 363.1939.

(5S,E)-7-hydroxy-5-methyl-2-phenylhept-2-en-4-yl benzoate (**25**). Prepared according to the general benzoylation procedure using **24** (0.288 g, 0.85 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **25** (0.238 g, 86% 2-steps) as a colorless oil.

R_f = 0.15 in 4:1 Hex:EtOAc.

IR (ATR) 3047, 3059, 3031, 2967, 2931, 2877 1713, 1600, 1583, 1450, 1314, 1266, 1175, 1108, 1068, 909, 848, 731 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.40 (dt, *J* = 8.4, 1.5 Hz, 4H), 7.33 (tt, *J* = 8.3, 1.0, 4H), 7.27 (tt, *J* = 4.1, 1.3 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.80 (dq, *J* = 8.9, 1.5 Hz, 1H), 5.78 (dq, *J* = 9.0, 1.4 Hz, 1H), 4.44 (s, 2H), 4.43 (s, 2H), 4.38 (dd, *J* = 8.9, 5.7 Hz, 1H), 4.35 (dd, *J* = 8.9, 6.5 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.48-3.42 (m, 4H), 2.10 (d, *J* = 1.4 Hz, 3H), 2.09 (d, *J* = 1.4 Hz, 3H), 1.80-1.59 (m 10H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 166.33, 166.30, 143.26, 143.23, 140.64, 140.32, 133.21, 130.95, 129.96, 129.95, 128.71, 128.59, 127.82, 127.80, 126.33, 124.91, 124.56, 75.94, 75.78, 61.33, 61.24, 35.77, 35.74, 35.20, 34.97, 17.27, 17.18, 15.78, 15.61.

HRMS (ES+): *m/z* [347.1623]$^+$ calcd for C$_{21}$H$_{24}$O$_3$Na$^+$ [M+Na]$^+$; found: 347.1622.

(5S,E)-8-((4-methoxybenzyl)oxy)-5-methyl-2-phenyloct-2-en-4-ol (**29**). To a Schlenck flask containing ether (5.2 mL) and t-BuLi (1.7 M, 0.917 mL, 1.56 mL) at -78 ^{0}C was added vinyl iodide **27**[30] (0.190 g, 0.78 mmol) dropwise. The solution was stirred for 10 min at -78 ^{0}C before adding (2*S*)-5-[(4-methoxyphenyl)methoxy]-2-methyl-pentanal (**28**)[37] (0.123g, 0.520 mmol) was added dropwise, and the reaction was stirred for 1 hour at -78 ^{0}C. The reaction was quenched with aq. NH$_4$Cl (30 mL) and extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried over MgSO$_4$, and concentrated *in vacuo*. Purification by flash chromatography over silica gave **29** (0.097 g, 53%) as a colorless oil (d.r ~ 50:50).

R_f = 0.64 in 1:1 Hex:EtOAc.

IR (ATR) 3412, 3080, 3056, 3031, 2931, 2856, 1611, 1585, 1511, 1493, 1444, 1362, 1301, 1245, 1172, 1092, 1032, 821, 758, 735, 696 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.40 (dt, *J* = 8.4, 1.5 Hz, 4H), 7.33 (tt, *J* = 8.3, 1.0, 4H), 7.27 (tt, *J* = 4.1, 1.3 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.80 (dq, *J* = 8.9, 1.5 Hz, 1H), 5.78 (dq, *J* = 9.0, 1.4 Hz, 1H), 4.44 (s, 2H), 4.43 (s, 2H), 4.38 (dd, *J* = 8.9, 5.7 Hz, 1H), 4.35 (dd, *J* = 8.9, 6.5 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.48-3.42 (m, 4H), 2.10 (d, *J* = 1.4 Hz, 3H), 2.09 (d, *J* = 1.4 Hz, 3H), 1.80-1.59 (m 10H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 159.09, 143.17, 138.01, 137.65, 130.68, 129.38, 129.24, 129.22, 128.98, 128.24, 127.25, 127.22, 125.86, 113.75, 72.67, 72.65, 72.57, 72.55, 70.38, 70.32, 55.27, 39.51, 39.44, 28.96, 28.93, 27.53, 27.21, 16.59, 16.50, 14.97, 14.95.

HRMS (ES+): *m/z* [377.2093]$^+$ calcd for C$_{23}$H$_{30}$O$_3$Na$^+$ [M+Na]$^+$; found: 377.2094.

(5S,E)-8-hydroxy-5-methyl-2-phenyloct-2-en-4-yl benzoate (**30**). Prepared according to the general benzoylation procedure using **29** (0.097 g, 0.27 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **30** (0.065 g, 71%) as a colorless oil.

R_f = 0.13 in 4:1 hexanes:EtOAc.

IR (ATR) 3400, 3059, 3031, 2931, 2876, 1712, 1600, 1583, 1493, 1450, 1380, 1314, 1266, 1175, 1107, 1068, 1025, 908, 731 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 8.06 (dt, *J* = 8.4, 1.0 Hz, 4H), 7.55 (tq, *J* = 6.9, 1.3 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.40 (dt, *J* = 8.5, 1.5 Hz, 4H), 7.31 (tt, *J* = 7.38, 1.0 Hz, 4H), 7.26 (tq, *J* = 7.2 Hz, 1.3 Hz, 2H), 5.82 (m, 4H), 3.67 (tt, *J* = 6.5, 2.0 Hz, 4H), 2.24 (d, *J* = 1.0 Hz, 3H), 2.23 (s, 3H),2.04 (m, 1H), 1.97 (m, 1H) 1.77-1.54 (m, 8H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 165.97, 165.94, 142.93, 142.89, 140.14, 139.65, 132.79, 130.65, 129.57, 128.31, 128.20, 127.40, 127.38, 125.95, 125.94, 124.83, 124.27, 75.53, 75.45, 63.07, 63.06, 38.05, 37.56, 30.45, 30.17, 28.60, 28.56, 16.87, 16.78, 15.30, 15.05.

HRMS (ES+): *m/z* [361.1780]$^+$ calcd for C$_{22}$H$_{26}$O$_3$Na$^+$ [M+Na]$^+$; found: 361.1780.

(6S,E)-6-((tert-butyldimethylsilyl)oxy)-2-phenylhept-2-en-4-ol (**35**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using (*S*)-3-((tert-butyldimethylsilyl)oxy)butanal (**32**)[38] (0.231 g, 1.15 mmol). Purification by flash chromatography on silica gave **35** (0.234 g, 63%) as a colorless oil (d.r = 54:46).

R_f = 0.52 in 4:1 Hex:EtOAc.

IR (ATR): 3413, 3081, 3057, 3027, 2955, 2928, 2855, 1612, 1512, 1494, 1462, 1374, 1248, 1143, 1077, 1001, 834, 807, 774, 756, 731, 695 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.41 (d, *J* = 7.1 Hz, 4H), 7.31 (t, *J* = 7.4 Hz, 4H), 7.24 (t, *J* = 7.2 Hz 2H), 5.83 (dq, *J* = 8.6, 1.3 Hz, 1H), 5.79 (dq, *J* = 8.2, 1.4 Hz, 2H), 4.90 (dt, *J* = 8.9, 3.1 Hz, 1H) 4.72 (dt, *J* = 8.9, 3.1 Hz, 1H), 4.23 (pd, *J* = 6.2, 3.6 HZ 1H), 4.16 (dtd, *J* = 12.2, 6.1, 3.8 Hz, 1H), 3.35 (br, OH), 3.13 (br, OH), 2.10 (d, *J* = 1.4 Hz, 3H), 2.10 (d, *J* = 1.4 Hz, 3H), 1.83 (ddd, *J* = 9.1, 7.0, 3.4, Hz, 1H) 1.80 (ddd, *J* = 9.2, 5.2, 1.6, Hz, 1H) 1.63 (dddd, *J* = 14.3, 6.91, 3.8, 3.2 Hz, 1H) 1.60 (dddd, *J* = 14.3, 8.7, 6.2, 2.6 Hz, 1H) 1.28

(d, *J* = 6.3 Hz, 3H), 1.23 (d, *J* = 6.1 Hz, 3H), 0.93 (s, 18H), 0.14 (d, *J* = 9.1 Hz, 6H). 0.12 (d, *J* = 8.1 Hz, 6H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 143.24, 143.21, 136.54, 135.96, 131.13, 130.86, 128.33, 127.25, 127.22, 125.99, 125.94, 69.63, 68.69, 67.20, 66.06, 46.31, 45.03, 25.97, 24.71, 23.29, 18.11, 18.07, 16.52, 16.28, -3.66, -4.26, -4.65, -4.83.

HRMS (ES+): *m/z* $[343.2069]^+$ calcd for $C_{19}H_{32}O_2SiNa^+$ $[M+Na]^+$; found: 343.2065.

(6S,E)-6-hydroxy-2-phenylhept-2-en-4-yl benzoate (**38a**). Prepared according to the general benzoylation procedure using **35** (0.234g, 0.729 mmol). The crude product mixture was placed into a teflon reaction vessel containing THF (7.3 mL), cooled to 0 °C, and treated with HF·pyr (70 % HF, 0.400 mL, 12.064 mmol) and left to sit for 18 h at 4 °C without stirring. The reaction was quenched with aq. NaHCO$_3$ and extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over MgSO$_4$, and concentrated *in vacuo*. Purification by flash chromatography over silica gave **38a** (0.194 g, 86% over two steps) as a colorless oil.

R$_f$ diastereomer$_\alpha$ = 0.24; R$_f$ diastereomer$_\beta$ = 0.18 in 4:1 Hex:EtOAc)

IR (ATR): 3428, 3060, 3032, 1713, 1600, 1584, 1450, 1266, 1108, 1068, 1025, 934, 847, 731 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 8.06 (t, *J* = 9.2 Hz, 4H), 7.58 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.55 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 4H), 7.41 (d, *J* = 7.51 Hz, 4H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 (tt, *J* = 5.88, 1.3 Hz, 2H), 6.19 (dd, *J* = 8.8, 3.5 Hz, 1H), 6.10 (dt, *J* = 6.90 Hz, 1H) 5.90 (dq, *J* = 8.7, 1.4 Hz, 1H), 5.80 (dq, *J* = 9.2, 1.2 Hz, 1H), 3.97 (qd, *J* = 6.2, 1.4 Hz, 1H), 3.86 (qd, *J* = 6.2, 2.6 Hz, 1H), 2.26 (d, *J* = 1.2 Hz, 3H), 2.19 (t, *J* = 1.2 Hz, 3H), 2.13 (ddd, *J* =14.0, 8.3, 6.6, 1H), 1.99 (ddd, *J* = 13.3, 10.4, 2.6, 1H), 1.88 (ddd, *J* = 11.5, 7.3, 4.5 Hz, 1H), 1.80 (ddd, *J* = 13.7, 10.0, 3.3 Hz, 1H) 1.29 (d, *J* = 6.2 Hz, 3H), 1.24 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 167.10, 165.91, 142.66, 142.52, 139.76, 139.26, 133.20, 132.91, 130.52, 130.02, 129.79, 129.60, 128.42, 128.36, 128.30, 128.26, 127.59, 127.53, 125.96, 125.93, 125.87, 125.76, 70.75, 69.88, 65.46, 63.63, 45.08, 44.24, 24.14, 23.08, 16.66.

HRMS (ES+): *m/z* $[333.1467]^+$ calcd for $C_{20}H_{22}O_3Na^+$ $[M+Na]^+$; found: 333.1483.

(E)-7-((tert-butyldimethylsilyl)oxy)-6-methyl-2-phenylhept-2-en-4-ol (**36**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using 4-((tert-butyldimethylsilyl)oxy)-3-methylbutanal (**33**)[39] (0.500 g, 2.31 mmol). Purification by flash chromatography on silica gave **36** (0.658 g, 85%) as a colorless oil (d.r = 54:46).

R$_f$ = 0.51 in 4:1 Hex:EtOAc.

IR (ATR): 3347, 3082, 3058, 3028, 2954, 2927, 2855, 1598, 1495, 1471, 1462, 1387, 1360, 1250, 1153, 1089, 1028, 1005, 833, 774, 755, 694 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.43 (d, *J* = 7.8 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 4H), 7.26 (tq, *J* = 7.4, 1.3 Hz, 2H), 5.83 (tq, *J* = 8.5, 1.4 Hz, 2H), 4.72 (td, *J* = 7.3, 6.2, 1H), 4.64 (td, *J* = 8.8, 3.8 Hz, 1H), 3.60 (dd, *J* = 10, 4.7Hz, 1H) 3.58 (dd, 5.2, 9.9 Hz, 1H), 3.52 (dd, *J* = 9.9, 6.7 Hz 1H), 3.48 (dd, *J* = 10.0, 7.4 Hz, 1H), 3.25 (br, OH), 2.95 (br, OH), 2.12 (d, 1.4 Hz 6H), 1.89 (o, *J* = 6.6 Hz, 2H), 1.72 (ddd, *J* = 14.3, 9.2, 7.1 Hz, 1H), 1.66 (ddd, *J* = 7.2, 6.1, 3.6 Hz, 2H), 1.49 (ddd, *J* = 14.1, 5.9, 3.7 Hz, 1H), 0.98 (d, *J* = 6.8 Hz, 6H), 0.95 (s, 9H) 0.95 (s, 9H), 0.12 (d, *J* = 2.7 Hz, 6H), 0.11 (d, *J* = 2.2 Hz, 6H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 143.07, 143.05, 136.02, 135.69, 131.58, 131.19, 128.08, 126.97, 126.94, 125.74, 69.01, 68.39, 67.71, 66.58, 43.19, 42.31, 33.90, 32.30, 25.85, 18.26, 18.23, 17.76, 17.38, 16.14, -5.46, -5.51, -5.53.

HRMS (ES+): *m/z* $[357.2226]^+$ calcd for $C_{20}H_{34}O_2SiNa^+$ $[M+Na]^+$; found: 357.2222.

(E)-7-hydroxy-6-methyl-2-phenylhept-2-en-4-yl benzoate (**38b**). Prepared according to the general benzoylation procedure using **36** (0.250g, 0.747 mmol). The crude product mixture was placed into a teflon reaction vessel containing THF (7.4 mL), cooled to 0 °C, and treated with HF·pyr (70% HF, 0.400 mL, 12.064 mmol) and left to sit for 18 h at 4 °C without stirring. The reaction was quenched with aq. NaHCO$_3$ and extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over MgSO$_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gave **38b** (0.240 g, 99% over two steps) as a colorless oil.

R$_f$ = 0.18 in 4:1 Hex:EtOAc.

IR (ATR): 3429, 3065, 3032, 2962, 2919, 2877, 1712, 1600, 1583, 1450, 1314, 1267, 1108, 1069, 1025, 931, 711 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 8.05 (d, 8.0 Hz, 4H), 7.55 (tt, 7.5, 1.1 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 4H) 7.41 (dd, *J* = 7.6, 1.8 Hz, 4H), 7.32 (t, 7.2 Hz, 4H) 7.26 (tt, *J* = 7.3, 1.2 Hz, 2H), 6.06 (dt, *J* = 6.8, 9.1 Hz, 1H), 6.04 (dt, *J* = 8.7, 5.3 Hz, 1H), 5.81 (dq, *J* = 9.0, 1.3, 1H) 5.78 (dq, *J* = 9.2, 1.3 Hz, 1H) 3.57 (dd, *J* = 5.6, 1.8, 4H), 2.24 (d, *J* = 1.3 3H), 2.23 (d, *J* = 1.3 Hz, 3H), 1.98 (m, 2H), 1.94-1.78 (m, 4H), 1.05 (d, *J* = 6.7, 3H) 1.04 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 166.15, 166.10, 142.72, 142.69, 139.52, 138.98, 132.89, 132.87, 130.60, 130.53, 129.63, 129.62, 128.35, 128.26, 127.50, 127.47, 126.59, 126.35, 125.97, 125.96, 71.00, 70.58, 68.16, 68.02, 38.67, 32.47, 32.37, 17.17, 16.83, 16.71, 16.65.

HRMS (ES+): *m/z* $[347.1623]^+$ calcd for $C_{21}H_{24}O_3Na^+$ $[M+Na]^+$; found: 347.1619.

(E)-7-((4-methoxybenzyl)oxy)-2-phenyloct-2-en-4-ol (**37**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using 4-((4-methoxybenzyl)oxy)pentanal (**34**)[40] (0.300 g, 1.3 mmol). Purification by flash chromatography on silica gave **37** (0.254 g, 57%) as a colorless oil (d.r = 50:50).

R$_f$ = 0.61 in 4:1 Hex:EtOAc.

IR (ATR): 3395, 3080, 3056, 3030, 2930, 2861, 1611, 1585, 1512, 1493, 1443, 1374, 1337, 1301, 1172, 1032, 911, 821, 757, 733, 696 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.41 (d, *J* = 7.8 Hz, 4H), 7.33 (t, *J* = 7.3 Hz, 4H), 7.28 (dd, *J* = 8.8, 1.5 Hz, 4H) 7.26 (tt, *J* = 6.5, 1.2 Hz, 2H), 6.88 (dd, *J* = 8.6, 2.0 Hz, 4H), 5.78 (dq, *J* = 5.4, 1.4 Hz, 1H), 5.77 (dq *J* = 5.4, 1.4 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 4H), 4.40 (dd, *J* = 11.3, 2.4 Hz, 2H), 3.80 (s, 6H), 3.57 (hex, 5.9 Hz, 2H) 2.08 (d, *J* = 1.3 Hz, 3H) 2.08 (d, *J* = 1.3 Hz, 3H), 1.81-1.56 (m, 8H), 1.22 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 159.06, 142.97, 142.95, 136.80, 136.72, 130.86, 130.84, 129.26, 129.24, 128.18, 127.15, 125.78, 113.74, 74.44, 74.43, 70.02, 69.98, 68.96, 68.89, 55.22, 33.67, 33.58, 32.56, 32.51, 19.49, 19.47, 16.29, 16.27.

HRMS (ES+): *m/z* $[377.2093]^+$ calcd for $C_{23}H_{30}O_3Na^+$ $[M+Na]^+$; found: 377.2094.

(E)-7-hydroxy-2-phenyloct-2-en-4-yl benzoate (**38c**). Prepared according to the general benzoylation procedure using **37** (0.288 g, 0.845 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **38c** (0.180 g, 74% over two steps) as a colorless oil.

R$_f$ = 0.15 in 4:1 Hex:EtOAc.

IR (ATR): 3411, 3059, 3031, 2967, 2927, 2866, 1712, 1601, 1583, 1493, 1450, 1376, 1314, 1267, 1175, 1109, 1069, 1025, 710 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 8.06 (dd, *J* = 8.5, 1.3 Hz, 4H), 7.55 (tt, *J* = 7.4, 1.2 Hz, 2H), 7.44 (t, *J* = 8.0, 4H), 7.41 (dd, *J* = 7.6, 1.6 Hz, 4H), 7.32 (t, *J* = 7.8, 4H), 7.26 (tt, *J* = 7.2, 1.4 Hz, 2H), 5.95 (dt, *J* = 6.9, 6.7 Hz, 1H) 5.94 (dt, *J* = 6.9, 6.7 Hz, 1H), 5.81 (dq, *J* = 9.0, 1.3 Hz, 2H), 3.88 (hex, *J* = 6.5 Hz, 2H), 2.22 (d, *J* = 1.4 Hz, 3H), 2.21 (d, *J* = 1.3 Hz, 3H), 2.05 (qt, *J* = 6.94, 5.49, 1H), 1.95 (dt, *J* =6.8, 6.4 Hz, 1H) 1.93 (dt, *J* = 6.7, 6.5 Hz, 1H), 1.83 (qt, *J* = 6.0, 3.9 Hz, 1H), 1.63-1.54 (m, 4H), 1.23 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 166.08, 166.03, 142.72, 142.70, 139.39, 139.32, 133.63, 132.86, 132.85, 130.60, 130.17, 129.62, 128.48, 128.33, 128.25, 127.49, 127.47, 126.16, 126.14, 125.96, 72.28, 72.15, 67.93, 67.88, 34.70, 34.56, 31.42, 31.31, 23.70, 23.67, 16.71.

HRMS (ES+): *m/z* [361.1780]$^+$ calcd for $C_{22}H_{26}O_3Na^+$ [M+Na]$^+$; found: 361.1780.

(E)-5-(((4-methoxybenzyl)oxy)methyl)-6-methyl-2-phenylhept-2-en-4-ol (**45**) Prepared according to the general procedure for zirconium-catalyzed carboaluminations using 2-(((4-methoxybenzyl)oxy)methyl)-3-methylbutanal (**40**)[41] (0.346 g, 1.46 mmol). Purification by flash chromatography on silica gave **45** (0.392 g, 75%) as a colorless oil (d.r = 91:9).

R_f = 0.34 in 4:1 Hex:EtOAc.

IR (ATR): 3456, 3080, 3055, 3028, 2956, 2870, 1611, 1585, 1512, 1443, 1418, 1366, 1301, 1246, 1173, 1079, 1032, 987, 909, 819, 757, 732, 696 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.37 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.27 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.25 (tt, *J* = 7.3, 2.2 Hz, 1H), 6.89 (dt, *J* = 8.7, 2.1 Hz, 2H), 5.81 (dq, *J* = 8.5, 1.3 Hz, 1H), 4.72 (dt, *J* = 8.6, 5.8 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 3.81 (s, 3H), 3.79 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.68 (dd, *J* = 9.5, 5.7 Hz, 1H), 2.06 (d, *J* = 1.3 Hz, 3H), 2.04 (hex, *J* = 6.8 Hz, 1H), 1.47 (qd, *J* = 6.0, 3.0 Hz, 1H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.34, 143.20, 135.77, 131.06, 129.69, 129.47, 128.13, 126.98, 125.82, 113.86, 73.24, 70.87, 69.43, 55.25, 50.01, 26.35, 21.52, 19.25, 16.12.

HRMS (ES+): *m/z* [377.2093]$^+$ calcd for $C_{23}H_{30}O_3Na^+$ [M+Na]$^+$; found: 377.2076.

(E)-5-(hydroxymethyl)-6-methyl-2-phenylhept-2-en-4-yl benzoate (**50a**). Prepared according to the general benzoylation procedure using **45** (0.392 g, 1.11 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **50a** (0.281 g, 75% over two steps) as a colorless oil.

R_f = 0.50 in 4:1 Hex:EtOAc

IR (ATR): 3459, 3083, 3060, 3080, 2958, 2930, 2884, 1712, 1600, 1583, 1493, 1450, 1387, 1314, 1266, 1176, 1109, 1069, 1025, 920, 710 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.03 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.57 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.45 (tt, *J* = 7.9, 1.5 Hz, 2H), 7.41 (dd, *J* = 7.4, 1.5 Hz, 2H), 7.32 (t, *J* = 7.1 Hz, 2H), 7.27 (tt, *J* = 7.3, 1.3 Hz, 1H), 6.19 (dd, *J* = 9.3, 6.7 Hz, 1H), 5.90 (dq, *J* = 9.3, 1.3 Hz, 1H), 3.90 (dd, *J* = 4.5, 3.7 Hz, 2H), 2.26 (d, *J* = 1.4 Hz, 3H), 2.00 (hd, *J* = 6.9, 5.1 Hz, 1H), 1.79 (dtd, *J* = 6.7, 5.0, 4.1 Hz, 1H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 166.06, 142.67, 139.70, 133.07, 130.29, 129.57, 128.48, 128.26, 127.53, 125.95, 125.46, 73.06, 60.79, 51.30, 27.00, 21.42, 19.50, 16.69.

HRMS (ES+): *m/z* [361.1780]$^+$ calcd for $C_{22}H_{26}O_3Na^+$ [M+Na]$^+$; found: 361.1758.

(E)-5-(((4-methoxybenzyl)oxy)methyl)-6,6-dimethyl-2-phenylhept-2-en-4-ol (**46**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using 2-(((4-methoxybenzyl)oxy)methyl)-3,3-dimethylbutanal (**41**)[42] (0.387 g, 1.54 mmol). Purification by flash chromatography on silica gave **46** (0.175 g, 30%) as a colorless oil (d.r = 77:23).

R_f = 0.43 in 4:1 Hex:EtOAc

IR (ATR): 3445, 3080, 3056, 3027, 2954, 2868, 1611, 1586, 1512, 1493, 1464, 1443, 1363, 1301, 1246, 1206, 1075, 1034, 986, 819, 757, 696 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 (dd, *J* = 8.3, 1.7 Hz, 2H) 7.30 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.24 (tt, *J* = 6.0, 1.6 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.98 (dq, *J* = 8.3, 1.4 Hz, 1H), 4.89 (td, *J* = 8.3, 2.5 Hz, 1H), 4.46 (d, *J* = 11.4 Hz, 1H) 4.42 (d, *J* = 11.4 Hz, 1H), 3.83 (dd, *J* = 4.1, 1.5 Hz, 2H), 3.80 (s, 3H), 3.32 (d, *J* = 8.3 Hz, 1H), 2.05 (d, *J* = 1.3 Hz, 3H), 1.42 (td, *J* = 4.2, 2.6 Hz, 1H), 1.10 (s, 9H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.26, 143.33, 133.83, 132.89, 129.81, 129.45, 128.10, 126.85, 125.81, 113.81, 73.19, 69.71, 68.84, 55.23, 52.86, 33.39, 29.26, 15.95.

HRMS (ES+): *m/z* [391.2249]$^+$ calcd for $C_{24}H_{32}O_3Na^+$ [M+Na]$^+$; found: 391.2257.

(E)-5-(hydroxymethyl)-6,6-dimethyl-2-phenylhept-2-en-4-yl benzoate (**50b**). Prepared according to the general benzoylation procedure using **46** (0.144 g, 0.391 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **50b** (0.060 g, 42% over two steps) as a colorless oil.

R_f = 0.35 in 4:1 Hex:EtOAc.

IR (ATR): 3459, 3059, 3030, 2958, 2873, 1713, 1600, 1583, 1493, 1476, 1450, 1367, 1269, 1175, 1110, 1040, 910, 711 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.02 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.56 (tt, *J* = 7.0, 1.3 Hz, 1H), 7.45 (tt, *J* = 7.7, 1.5 Hz, 2H), 7.40 (dd, *J* = 7.0 Hz, 1.5 Hz, 2H), 7.30 (tt, *J* = 7.1, 1.5 Hz, 2H), 7.24 (tt, *J* = 7.1, 1.3 Hz, 1H), 6.33 (dd, *J* = 9.0, 2.2 Hz, 1H), 6.06 (dq, *J* = 9.0, 1.4 Hz, 1H), 4.18 (dd, *J* = 11.7, 6.1 Hz, 1H), 4.08 (dd, *J* = 11.7, 4.1 Hz, 1H), 2.27 (d, *J* = 1.4 Hz, 3H), 1.72 (ddd, *J* = 6.2, 4.1, 2.2 Hz, 1H) 1.08 (s, 9H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 165.60, 142.74, 137.24, 132.99, 130.44, 129.47, 128.47, 128.19, 127.33, 127.10, 125.93, 72.25, 60.94, 55.52, 33.20, 28.82, 16.51.

HRMS (ES+): *m/z* [375.1936]$^+$ calcd for $C_{23}H_{28}O_3Na^+$ [M+Na]$^+$; found: 375.1937.

(E)-1-((4-methoxybenzyl)oxy)-2,5-diphenylhex-4-en-3-ol (**47**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using 3-((4-methoxybenzyl)oxy)-2-phenylpropanal (**42**)[43] (0.113 g, 0.42 mmol). Purification by flash chromatography on silica gave **47** (0.097 g, 59%) as a colorless oil (d.r = 98:2).

R_f = 0.19 in 4:1 Hex:EtOAc

IR (ATR): 3419, 3082, 3059, 3028, 2999, 2915, 2858, 1611, 1585, 1512, 1493, 1452, 1362, 1301, 1246, 1173, 1076, 1030, 908, 819, 730, 697 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.35-7.27 (m, 2H), 7.26 (d, *J* = 8.7 Hz, 2H) 7.24-7.15 (m, 8H), 6.88 (d, *J* = 8.7, 2H), 5.60 (dq, *J* = 8.9, 1.4 Hz, 1H), 4.88 (td, 8.6, 3.0 Hz, 1H) 4.55 (d, *J* = 11.6 Hz, 1H), 4.51 (d, *J* = 11.6 Hz, 1H), 3.99 (dd, *J* = 9.4, 8.3 Hz, 1H), 3.88 (dd, *J* = 9.4, 4.7 Hz, 1H), 3.81 (s, 3H), 3.45 (d, *J* = 3.1 Hz, OH), 3.14 (td, *J* = 8.1, 4.6 Hz, 1H), 1.82 (d, *J* = 1.4 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.35, 143.37, 139.37, 137.61, 129.65, 129.44, 129.06, 128.65, 128.30, 128.03, 126.97, 126.89, 125.90, 113.89, 73.23, 73.11, 72.64, 55.28, 51.75, 16.40.

HRMS (ES+): *m/z* [411.1936]$^+$ calcd for $C_{26}H_{28}O_3Na^+$ [M+Na]$^+$; found: 411.1938.

(E)-1-hydroxy-2,5-diphenylhex-4-en-3-yl benzoate (**50c**). Prepared according to the general benzoylation procedure was using **47** (0.097 g, 0.249 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **50c** (0.065 g, 78% over two steps) as a colorless oil.

R_f = 0.37 in 4:1 Hex:EtOAc

IR (ATR): 3460, 3083, 3060, 3029, 2923, 1713, 1600, 1583, 1511, 1493, 1450, 1315, 1266, 1109, 1068, 1025, 907, 710 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.99 (dd, *J* = 8.3, 1.2, 2H), 7.49 (tt, 7.0, 1.2 Hz, 1H), 7.37 (tt, *J* = 7.9, 1.5 Hz, 2H), 7.25 (dd, *J* = 4.2, 1.0 Hz, 4H), 7.19-7.16 (m, 2H), 7.16-7.12 (m, 2H), 7.12-7.09 (m, 2H), 6.17 (t, *J* = 9.0 Hz, 1H), 5.56 (dq, *J* = 9.5, 1.4 Hz, 1H), 3.97 (d, *J* = 5.9 Hz, 2H), 3.26 (dt, *J* = 8.7, 5.9 Hz, 1H), 1.93 (d, *J* = 1.3 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 166.14, 142.79, 140.52, 138.28, 133.10, 130.13, 129.68, 129.05, 128.56, 128.41, 128.10, 127.38, 127.36, 125.92, 124.40, 72.63, 63.45, 53.03, 16.76.

HRMS (ES+): *m/z* [395.1623]$^+$ calcd for $C_{25}H_{24}O_3Na^+$ [M+Na]$^+$; found: 395.1610.

(E)-2-benzyl-1-((4-methoxybenzyl)oxy)-5-phenylhex-4-en-3-ol (**48**). To a Schlenck flask containing ether (3.5 mL) and *t*-BuLi (1.7 M, 0.905 mL, 1.54 mL) at -78 ^{0}C was added vinyl iodide **27**[30] (0.171 g, 0.702 mmol) dropwise. The solution was stirred for 10 min at -78 ^{0}C and 2-benzyl-3-((4-methoxybenzyl)oxy)propanal (**43**)[43] (0.100 g, 0.351 mmol) was then added dropwise. The reaction was stirred for 1 hour at -78 ^{0}C before being brought to room temperature for 30 min. The reaction was quenched with aq. NH_4Cl (30 mL) and extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography over silica gave **48** (0.051 g, 36%) as a colorless oil (d.r = 50:50).

R$_f$ = 0.22 in 4:1 Hex:EtOAc

IR (ATR): 3430, 3034, 2917, 2849, 1600, 1594, 1493, 1454, 1442, 1382, 1333, 1244, 1201, 1160, 1033, 968, 919, 836, 745, 687 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40-7.33 (m, 6H), 7.33-7.28 (m, 4H), 7.28-7.24 (m, 8H), 7.23-7.14 (m, 6H), 6.89 (d, *J* = 8.7 Hz, 4H), 5.89 (dq, *J* = 8.9, 1.4 Hz, 1H) 5.87 (dq, *J* = 8.6, 1.3 Hz, 1H), 4.75 (dd, *J* = 8.9, 3.8 Hz, 1H), 4.60 (t, *J* = 7.3 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 11.5 Hz, 2H), 4.36 (d, *J* = 11.5 Hz, 1H), 3.81 (s, 6H), 3.71 (dd, *J* = 9.4, 3.5 Hz, 1H), 3.51 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.48 (dd, *J* = 9.7, 4.2 Hz, 1H), 3.46 (dd, *J* = 9.4, 5.2 Hz, 1H), 3.26 (br, OH), 3.10 (br, OH), 2.93 (dd, *J* = 13.7, 5.8 Hz, 1H), 2.83 (dd, *J* = 13.7, 5.3 Hz, 1H), 2.70 (dd, *J* = 9.5, 3.5 Hz, 1H) 2.67 (dd, *J* = 9.5, 3.9 Hz, 1H), 2.27 (dtt, *J* = 9.7, 5.8, 4.1 Hz, 1H), 2.08 (d, *J* = 1.4 Hz, 3H), 2.05 (m, 1H), 2.02 (d, *J* = 1.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 159.30, 159.28, 143.17, 143.09, 140.33, 140.29, 137.46, 136.81, 130.04, 129.86, 129.81, 129.47, 129.43, 129.10, 129.07, 128.36, 128.32, 128.30, 128.18, 128.15, 127.15, 127.10, 125.97, 125.92, 125.86, 125.83, 113.82, 73.12, 73.10, 71.23, 71.22, 70.48, 70.12, 55.23, 46.39, 46.36, 34.74, 32.93, 16.48, 16.27.

HRMS (ES+): *m/z* [425.2093]$^+$ calcd for $C_{27}H_{30}O_3Na^+$ [M+Na]$^+$; found: 425.2112.

(E)-2-benzyl-1-hydroxy-5-phenylhex-4-en-3-yl benzoate (**50d**). Prepared according to the general benzoylation procedure was using **48** (0.102 g, 0.254 mmol). The general procedure for DDQ removal of the PMB was then performed on the crude benzoylation product mixture obtained. Purification by flash chromatography on silica gave **50d** (0.081 g, 82% over two steps) as a colorless oil.

R$_f$ = 0.32 in 4:1 Hex:EtOAc

IR (ATR): 3467, 3104, 3083, 3061, 3026, 2926, 1713, 1600, 1583, 1493, 1450, 1373, 1314, 1266, 1175, 1111, 1068, 1025, 909, 758, 733, 711 cm^{-1}.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.08 (dd, *J* = 8.2, 1.2 Hz, 2H), 8.06 (dd, *J* = 8.1, 1.2 Hz, 2H) 7.59 (m, 1H), 7.58 (m, 1H) 7.47 (t, *J* = 7.6 Hz, 4H), 7.44-7.40 (m, 2H), 7.40-7.32 (m, 6H), 7.32-7.27 (m, 6H), 7.26-7.19 (m, 6H), 6.23 (dd, *J* = 8.9, 4.8 Hz, 1H), 6.10 (dd, *J* = 9.4, 7.6 Hz, 1H), 5.97 (dq, *J* = 6.1, 1.3 Hz, 1H) 5.95 (dq, *J* = 6.5, 1.3 Hz, 1H), 3.71 (dd, *J* = 11.7, 3.5 Hz, 1H), 3.66 (dd, *J* = 11.5, 4.6 Hz, 1H), 3.61-3.55 (m, 2H), 3.05 (dd, *J* = 14.0, 4.9 Hz, 1H), 2.87 (dd, *J* = 13.6, 5.1 Hz, 1H), 2.80 (dd, *J* = 13.6, 9.8 Hz, 1H), 2.69 (dd, *J* = 14.0, 9.5 Hz, 1H), 2.39 (ddq, *J* = 9.6, 7.2, 4.8, 1H), 2.24 (m, 1H), 2.23 (d, *J* = 1.4 Hz, 3H), 2.21 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 166.46, 166.45, 142.66, 142.64, 140.96, 139.94, 139.92, 139.91, 133.14, 133.11, 130.16, 130.10, 129.71, 129.69, 129.19, 128.97, 128.53, 128.49, 128.43, 128.29, 128.26, 127.63, 127.54, 126.18, 125.99, 125.93, 124.47, 124.32, 72.31, 61.79, 60.15, 48.05, 47.63, 33.17, 33.04, 16.86, 16.72.

(E)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-phenylbut-2-en-1-ol (**49**). Prepared according to the general procedure for zirconium-catalyzed carboaluminations using (*R*)-2,2-dimethyl-1,3-dioxolane-4-carboxaldehyde (**44**) (0.500 g, 3.8 mmol). Purification by flash chromatography on silica gave **49** (0.586 g, 50%) as a colorless oil (d.r = 74:26).

R$_f$ = 0.66 in 1:1 Hex:EtOAc

IR (ATR): 3450, 3060, 3034, 2990, 2800, 1665, 1601, 1585, 1501, 1453, 1386, 1310, 1076, 853 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 2H), 7.27 (tt, *J* = 7.2, 1.4 Hz, 1H), 5.68 (dq, *J* = 8.5, 1.4 Hz, 1H), 4.73 (ddd, *J* = 8.4, 3.9, 2.9 Hz, 1H), 4.20 (td, *J* = 6.9, 4.1 Hz, 1H) 4.02 (dd, *J* = 8.2, 6.6 Hz, 1H), 4.00 (dd, 8.4, 8.2 Hz, 1H), 2.14 (d, *J* = 1.3 Hz, 3H), 1.48 (s, 3H), 1.39 (s, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 142.57, 139.96, 128.29, 127.55, 125.93, 125.89, 125.05, 109.28, 78.14, 68.35, 64.70, 26.45, 25.22, 16.78.

HRMS (ES+): *m/z* [271.1310]$^+$ calcd for $C_{15}H_{20}O_3Na^+$ [M+Na]$^+$; found: 271.1316.

(2R,E)-1,2-dihydroxy-5-phenylhex-4-en-3-yl benzoate (**50e**). Prepared according to the general benzoylation procedure was using **49** (0.45 g, 2.13 mmol). The crude product was then redissolved in methanol (8.5 mL) and p-toluenesulfonic acid (0.404 g, 2.128 mmol) was added. The reaction was stirred for 5 min. before quenching with aq. $NaHCO_3$ (10 mL) and extracting with DCM (3 x 10 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gave **50e** (0.223 g, 83%) as a colorless oil.

R$_f$ = 0.25 in 1:1 Hex:EtOAc

IR (ATR): 3389, 3061, 3032, 2926, 2881, 1712, 1600, 1583, 1493, 1450, 1382, 1265, 1176, 1111, 1068, 1025, 907, 710 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.08 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.59 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.47 (t, *J* = 8.1 Hz, 2H), 7.45 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.35 (t, *J* = 7.0 Hz, 2H), 7.30 (tt, *J* = 7.15, 1.4 Hz, 1H), 5.99 (dd, *J* = 9.3, 5.8 Hz, 1H), 5.94 (dq, *J* = 9.1, 1.3 Hz, 1H) 4.03 (td, *J* = 5.9, 3.2 Hz, 1H), 3.85 (dd, *J* = 11.7, 3.3 Hz, 1H), 3.76 (dd, *J* = 11.7, 6.1 Hz, 1H), 2.26 (d, *J* = 1.3 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 166.22, 142.54, 142.26, 133.30, 129.75, 128.45, 128.29, 127.80, 125.97, 121.93, 73.59, 72.10, 62.78, 16.95.

HRMS (ES+): *m/z* [335.1259]$^+$ calcd for $C_{19}H_{20}O_4Na^+$ [M+Na]$^+$; found: 335.1265.

2-isopropyl-5-phenylhex-3-en-1-ol (**51a**). Prepared according to the general procedure for SmI$_2$(H$_2$O)$_n$ reductions using **50a** (0.050 g, 0.147 mmol). Purification by flash chromatography on silica gave **51a** (0.026 g, 80%) as a colorless oil (d.r. 83:17).

R$_f$ = 0.37 in 4:1 Hex:EtOAc

IR (ATR): 3352, 3056, 2959, 2926, 2870, 1600, 1580, 1492, 1451, 1367, 1303, 1208, 1108, 1031, 908, 732, 699 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (dd, *J* = 6.6, 1.6 Hz, 2H), 7.20 (tt, *J* = 6.7, 1.3 Hz, 1H), 5.76 (ddd, *J* = 15.4, 6.7, 0.7 Hz, 1H), 5.28 (ddd, *J* = 15.4, 9.5, 1.4 Hz, 1H), 3.65 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.51 (p, *J* = 6.9 Hz, 1H), 3.41 (dd, *J* = 10.5, 9.0 Hz, 1H), 2.00 (tdd, *J* = 9.6, 6.9, 5.3 Hz, 1H), 1.67 (o, *J* = 6.7 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR (CDCl$_3$, 126 MHz): δ = 146.01, 139.51, 128.45, 128.05, 127.04, 126.06, 64.15, 52.46, 42.47, 28.89, 21.54, 20.86, 19.65.

HRMS (ES+): *m/z* [241.1568]$^+$ calcd for $C_{15}H_{22}ONa^+$ [M+Na]$^+$; found: 241.1558.

2-(tert-butyl)-5-phenylhex-3-en-1-ol (**51b**). Prepared according to the general procedure for SmI$_2$(H$_2$O)$_n$ reductions using **50b** (0.075 g, 0.212 mmol). Purification by flash chromatography on silica gave **51b** (0.027 g, 83%) as a colorless oil (d.r. 80:20).

R$_f$ = 0.33 in 4:1 Hex:EtOAc

IR (ATR): 3436, 3055, 2963, 2873, 1599, 1597, 1512, 1441, 1365, 1255, 1108, 1032, 909, 732 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.30 (t, *J* = 7.65 Hz, 2H), 7.23-7.17 (m, 3H), 5.78 (ddd, *J* = 15.3, 6.8, 0.6 Hz, 1H), 5.36 (ddd, *J* = 15.3, 9.9, 1.4 Hz, 1H), 3.74 (dd, *J* = 10.3, 3.8 Hz, 1H), 3.53 (p, *J* = 6.8 Hz, 1H), 3.36 (t, *J* = 10.3 Hz, 1H), 1.95 (td, *J* = 10.3, 4.0 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 3H), 0.91 (s, 9H).

Data for the major diastereomer: ^{13}C NMR (CDCl$_3$, 126 MHz): δ = 145.99, 140.50, 128.51, 127.52, 127.01, 126.12, 61.84, 56.49, 42.55, 32.07, 28.08, 21.54.

HRMS (ES+): *m/z* [255.1725]$^+$ calcd for $C_{16}H_{24}ONa^+$ [M+Na]$^+$; found: 255.1725.

2,5-diphenylhex-3-en-1-ol (**51c**). Prepared according to the general procedure for SmI$_2$(H$_2$O)$_n$ reductions using **50c** (0.066 g, 0.176 mmol). Purification by flash chromatography on silica gave **51c** (0.012 g, 27%) as a colorless oil (d.r. 73:27).

R$_f$ = 0.28 in 4:1 Hex:EtOAc

IR (ATR): 3427, 3026, 2924, 1601, 1492, 1451, 1271, 1031, 758 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.34 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26-7.17 (m, 6H), 5.82 (ddd, *J* = 15.6, 6.7, 0.88 Hz, 1H), 5.66 (ddd, *J* = 15.4, 8.0, 1.3 Hz, 1H), 3.87 (m, 1H), 3.77 (p, *J* = 8.15, 2H), 3.51 (q, *J* = 7.5 Hz, 1H). 1.36 (d, *J* = 7.1 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR (CDCl$_3$, 126 MHz): δ = 138.13, 128.73, 128.48, 127.90, 127.12, 126.83, 126.15, 66.51, 51.46, 42.38, 21.40.

HRMS (ES+): *m/z* [275.1412]$^+$ calcd for $C_{18}H_{20}ONa^+$ [M+Na]$^+$; found: 275.1412.

2-benzyl-5-phenylhex-3-en-1-ol (**51d**). Prepared according to the general procedure for SmI$_2$(H$_2$O)$_n$ reductions using **50d** (0.050 g, 0.147 mmol). Purification by flash chromatography on silica gave **51d** (0.030 g, 82%) as a colorless oil (d.r. 81:19).

R$_f$ = 0.37 in 4:1 Hex:EtOAc

IR (ATR): 3352, 3056, 3026, 2964, 2925, 2869, 1600, 1580, 1493, 1452, 1424, 1303, 1208, 1108, 1031, 973, 840, 800, 700 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = .29 (t, *J* = 7.1 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 2H) 7.21 (tt, *J* = 6.2, 2.1 Hz, 1H), 7.19-7.08 (m, 3H), 7.03 (d, *J* = 7.3 Hz, 2H), 5.64 (ddd, *J* = 15.5, 6.4, 0.8 Hz, 1H), 5.31 (ddd, *J* = 15.4, 8.4, 1.4 Hz, 1H), 3.61 (dd, *J* = 10.5, 4.9 Hz, 1H), 3.48 (dd, *J* = 10.5 Hz, 7.5 Hz, 1H), 3.42 (p, *J* = 6.5 Hz, 1H), 2.80 (dd, *J* = 13.1, 6.0 Hz, 1H), 2.60 (dd, *J* = 13.2 Hz, 8.4 Hz, 1H), 2.54 (dtd, *J* = 13.8 Hz, 7.8, 5.0 Hz, 1H), 1.28 (d, *J* = 7.1 Hz, 3H).

Data for the major diastereomer: ^{13}C NMR (CDCl$_3$, 126 MHz): δ = 145.83, 139.81, 138.48, 129.25, 129.00, 128.36, 128.23, 127.09, 126.01, 125.92, 65.44, 47.45, 42.14, 37.88, 21.31.

HRMS (ES+): *m/z* [289.1568]$^+$ calcd for $C_{19}H_{22}ONa^+$ [M+Na]$^+$; found: 289.1563.

(S)-4-benzyl-3-((S)-2-benzyl-4-((tert-butyldimethylsilyl)oxy)butanoyl)-oxazolidin-2-one (**53**). To a schlenk flask containing oxazolidinone **52**[26] (1.56 g, 4.14 mmol) in THF (20.73 mL) at -78 ^{0}C was added KHMDS (1 M in THF, 9.94 mL, 9.94 mmol) dropwise. The reaction was stirred at -78 ^{0}C for 1 hr before freshly distilled benzyl bromide (1.22 mL, 9.94 mmol) was added dropwise. The reaction was stirred for 12 hours at -78 ^{0}C before quenching with aq. NH$_4$Cl (40 mL) and extracting with EtOAc (3 x 20 mL). The combined organic extracts were dried over MgSO$_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gave **53** (1.01 g, 52%) as a colorless oil.

R$_f$ = 0.51 in 4:1 Hex:EtOAc

IR (ATR): 3087, 3064, 3028, 2953, 2927, 2855, 1778, 1697, 1603, 1496, 1384, 1348, 1248, 1205, 1098, 1029, 834, 775, 732, 699 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.28 (t, *J* = 7.4 Hz, 4H), 7.25 (d, *J* = 7.0 Hz, 2H), 7.19 (tt, *J* = 5.9, 2.0 Hz, 2H), 7.07 (d, *J* = 6.8 Hz, 2H) 4.61 (ddt, *J* = 9.7, 7.8, 3.1, 1H), 4.35 (ddd, *J* = 7.7, 4.6, 4.4 Hz, 1H) 4.09 (ddd, *J* = 8.6, 7.9, 0.8, 1H) 4.04, (dd, *J* = 9.0, 2.9 Hz, 1H), 3.65 (dd, *J* = 5.9, 1.2 Hz, 1H), 3.64 (d, *J* = 5.9 Hz, 1H), 3.07 (dd, *J* = 13.3, 7.8 Hz, 1H) 3.02 (dd, *J* = 13.5, 3.5 Hz, 1H) 2.80 (dd, *J* = 13.3, 7.5 Hz, 1H), 2.36 (dd, *J* = 13.5, 9.7 Hz, 1H) 2.05 (ddt, *J* = 13.6, 9.1, 6.5 Hz, 1H), 1.71 (dtd, *J* = 13.7, 5.8, 4.3 Hz 1H), 0.85 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 175.83, 152.99, 138.79, 135.42, 130.12, 129.44, 129.34, 128.87, 128.56, 128.47, 128.31, 127.18, 126.42, 65.66, 61.41, 55.12, 41.71, 39.15, 37.67, 34.55, 25.93, 25.85, 18.27, -5.49, -5.50.

HRMS (ES+): *m/z* [490.2390]$^+$ calcd for $C_{27}H_{37}NO_4SiNa^+$ [M+Na]$^+$; found: 490.2386.

(S)-2-benzyl-4-((tert-butyldimethylsilyl)oxy)butanal (**54**). To a schlenk flask containing DCM (100 mL) and **53** (1.014 g, 2.17 mmol) at -78 ^{0}C was added DIBAL-H (1.15 mL, 6.50 mmol) dropwise. The reaction was stirred at -78 ^{0}C for 4 hr. before being warmed to room temperature and quenched with 2M Rochelle's salt (100 mL) and stirred for 3 hours. The aqueous layer was extracted with DCM (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried over MgSO$_4$, and

concentrated *in vacuo*. Purification by flash chromatography on silica gave **54** (0.358 g, 56%) as a colorless oil.

R$_f$ = 0.74 in 4:1 Hex:EtOAc

IR (ATR): 3087, 3064, 3028, 2952, 2927, 2855, 2737, 2713, 1724, 1603, 1496, 1471, 1388, 1252, 1098, 1029, 987, 833, 809, 774, 730, 698cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = δ 9.71 (d, *J* = 2.1 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (tt, *J* = 6.7, 1.3 Hz, 1H), 7.17 (d, *J* = 6.7 Hz, 2H), 3.67 (ddd, *J* = 10.3, 6.9, 5.1 Hz, 1H), 3.62 (ddd, *J* = 10.3, 6.7, 5.2 Hz, 1H), 3.04 (dd, *J* = 13.4, 6.3 Hz, 1H), 2.77 (dddt, *J* = 12.0, 7.6, 4.1, 2.0 Hz, 1H), 2.71 (dd, *J* = 13.4, 7.7, 1H), 1.89 (dddd, *J* = 14.5, 7.9, 6.7, 5.1 Hz, 1H) 1.72 (dddd, *J* = 14.3, 6.8, 5.2, 4.4 Hz, 1H), 0.87 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 204.15, 138.87, 128.99, 128.50, 126.35, 60.48, 50.68, 34.69, 31.75, 25.86, 18.22, -5.51.

HRMS (ES+): *m/z* [315.1756]$^+$ calcd for C$_{17}$H$_{28}$O$_2$SiNa$^+$ [M+Na]$^+$; found: 315.1757.

(5S,E)-5-benzyl-7-((tert-butyldimethylsilyl)oxy)-2-phenylhept-2-en-4-ol (**55**). To a Schleck flask containing ether (12.0 mL) and t-BuLi (1.7 M, 2.82 mL, 4.8 mmol) at -78 ^{0}C was added vinyl iodide **27**[30] (0.190 g, 0.78 mmol) dropwise. The solution was stirred for 5 min at -78 ^{0}C, **54** (0.585g, 2.4 mmol) was then added dropwise, and the reaction was stirred for 1 hour at -78 ^{0}C. The reaction was quenched with aq. NH$_4$Cl (30 mL), and extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried over MgSO$_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gave **55** (0.394 g, 93%) as a colorless oil (d.r = 62:38).

R$_f$ = 0.44 in 4:1 Hex:EtOAc

IR (ATR): 3396, 3083, 3061, 3021, 2927, 2856, 1601, 1494, 1471, 1445, 1386, 1254, 1084, 1005, 908, 833, 775, 757, 730, 696, 664 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.42 (d, *J* = 7.5, 2H), 7.40 (d *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.32-7.23 (m, 10H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.17 (t, *J* = 8.2 Hz, 2H), 5.95 (dq, *J* = 8.8, 1.3 Hz, 1H), 5.89 (dq, J = 8.7, 1.4 Hz, 1H), 4.61 (dt, *J* = 8.8, 4.4 Hz, 1H), 4.42 (dt, *J* = 8.7, 5.4 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.62 – 3.56 (m, 2H), 3.55 (d, *J* = 5.2, OH), 3.49 (d, *J* = 5.3 Hz, OH), 2.89 (dd, *J* = 13.7, 6.0 Hz, 1H), 2.83 (dd, *J* = 13.9, 5.5 Hz, 1H), 2.54 (dd, *J* = 13.9, 9.3 Hz, 1H), 2.51 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.21 (oct, *J* = 4.7 Hz, 1H), 2.08 (d, *J* = 1.3 Hz, 3H), 2.04 (m, 1H), 2.01 (d, *J* = 1.3 Hz, 3H), 1.80 (m, 1H), 1.75 (dtd, *J* = 15.3, 7.9, 4.4 Hz, 1H), 1.66 (m, 1H), 1.55 (ddt, *J* = 9.0, 6.5, 4.3 Hz, 1H), 0.91 (s, 9H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 143.42, 143.35, 140.80, 140.78, 137.38, 136.93, 130.46, 129.13, 128.64, 128.33, 128.28, 128.17, 128.13, 127.09, 127.01, 125.89, 125.87, 125.84, 70.60, 70.53, 62.15, 61.21, 45.27, 45.24, 36.97, 36.87, 32.40, 31.98, 25.90, 25.89, 18.25, 16.59, 16.41, -5.43, -5.46, -5.48.

HRMS (ES+): *m/z* [433.2539]$^+$ calcd for C$_{26}$H$_{38}$O$_2$SiNa$^+$ [M+Na]$^+$; found: 433.2544.

(5S,E)-5-benzyl-7-hydroxy-2-phenylhept-2-en-4-yl benzoate (**56**). Prepared according to the general benzoylation procedure using **55** (0.394 g, 0.961 mmol). The crude product mixture was placed into a teflon reaction vessel containing THF (10 mL), cooled to 0 ^{o}C, and treated with HF·pyr (70% HF, 0.400 mL, 12.064 mmol) and left to sit for 18 h at 4 ^{o}C without stirring. The reaction was quenched with aq. NaHCO$_3$ (15 mL) and extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over MgSO$_4$, and concentrated *in vacuo*. Purification by flash chromatography over silica gave **56** (0.312 g, 81% over two steps) as a colorless oil.

R$_f$ = 0.63 in 1:1 Hex:EtOAc

IR (ATR): 3411, 3084, 3061, 3026, 2931, 2880, 1712, 1600, 1583, 1494, 1450, 1381, 1314, 1267, 1175, 1111, 1068, 1025, 907, 757, 730, 710, 696 cm^{-1}.

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 8.04 (d, *J* = 8.0 Hz, 4H), 7.57 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.56 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.39 (t, *J* = 7.0 Hz, 4H), 7.35-7.27 (m, 10H), 7.24-7.18 (m, 6H), 6.01 (dd, *J* = 9.1, 4.7 Hz, 1H), 5.94 (dd, *J* = 9.2, 4.3 Hz, 1H), 5.91 (dq, *J* = 9.2, 1.4 Hz, 1H), 5.90 (dq, *J* = 9.2, 1.4 Hz, 1H), 3.71 (t, *J* = 6.8 Hz, 4H), 2.98 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.97 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.70 (dd, *J* = 14.0, 8.5 Hz, 1H), 2.67 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.45 (dddd, *J* = 12.6, 8.4, 6.2, 4.9 Hz, 1H), 2.36 (dddd, *J* = 12.5, 8.2, 6.2, 4.6 Hz, 1H), 2.19 (d, *J* = 1.3 Hz, 3H), 2.12 (d, *J* = 1.2 Hz, 3H), 1.88 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.87 (dq, *J* = 13.0, 6.9 Hz, 1H), 1.76 (dq, *J* = 13.5, 6.5 Hz, 1H) 1.66 (dq, *J* = 13.2, 6.6 Hz, 1H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = 165.87, 142.82, 142.78, 140.52, 140.25, 140.13, 132.93, 132.92, 130.46, 129.61, 129.59, 129.10, 129.05, 128.50, 128.49, 128.38, 128.25, 128.23, 127.53, 127.49, 126.17, 125.97, 125.96, 124.23, 123.86, 73.88, 73.71, 61.17, 61.13, 42.22, 41.48, 37.08, 36.92, 32.94, 32.87, 16.86, 16.69.

HRMS (ES+): *m/z* [423.1936]$^+$ calcd for C$_{27}$H$_{28}$O$_3$Na$^+$ [M+Na]$^+$; found: 423.1933.

(3S,E)-3-benzyl-6-phenylhept-4-en-1-ol (**57**). Prepared according to the general procedure for SmI$_2$(H$_2$O)$_n$ reductions using **56** (0.312 g, 0.786 mmol). Purification by flash chromatography on silica gave **57** (0.13 g, 32%) as mixture of diastereomers (d.r. 74:26).

R$_f$ = 0.28 in 4:1 Hex:EtOAc

IR (ATR): 3084, 3056, 2928, 1600, 1583, 1494, 1450, 1381, 1068, 1025, 907, 757, 696 cm^{-1}.

Data for the major diastereomer: ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.40 (d, *J* = 4.5 Hz, 2H), 7.36 – 7.23 (m, 4H), 7.23 – 7.02 (m, 4H), 5.50 (dd, *J* = 15.7, 6.9 Hz, 1H), 5.28 (ddd, *J* = 15.6, 9.3, 1.5 Hz, 1H), 3.77 – 3.57 (m, 2H), 3.40 (m, 1H), 2.74 (dd, *J* = 13.3, 6.4 Hz, 1H), 2.63 (dd, *J* = 13.5, 8.4 Hz, 1H), 2.48 (m, 1H), 2.24 (t, *J* = 6.8 Hz, 1H), 1.75 (dtd, *J* = 14.0, 7.1, 3.9 Hz, 1H), 1.56 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (CDCl$_3$, 126 MHz): δ = ^{13}C NMR (126 MHz, CDCl$_3$) δ 146.08, 140.91, 140.34, 136.11, 132.10, 129.42, 129.40, 129.24, 128.59, 128.34, 128.31, 128.20, 128.15, 128.11, 127.69, 127.15, 127.13, 127.01, 126.63, 126.38, 125.95, 125.92, 125.84, 125.83, 125.67, 65.40, 61.45, 61.43, 61.13, 42.54, 42.46, 42.00, 41.98, 41.74, 40.77, 37.63, 37.48, 37.37, 36.68, 32.72, 21.29, 16.10.

HRMS (ES+): *m/z* [303.1725]$^+$ calcd for C$_{20}$H$_{24}$ONa$^+$ [M+Na]$^+$; found: 303.1725.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

NO (this text will be deleted prior to publication)

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(20) The reaction was also performed using DMPU and H$_2$O together and gave the same d.r. (75:25) as that obtained when using DMPU (Entry 1) or H$_2$O (Entry 5).

(21) Compound **6** was converted to a 1:1 mixture of diastereomers by oxidation with Dess-Martin periodinane followed by reduction with NaBH$_4$. See reference 13.

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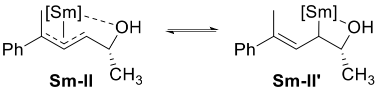
(32) Instead of an η3-complex, **Sm-II** could also be considered as the 4-membered chelate **Sm-II'**:



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