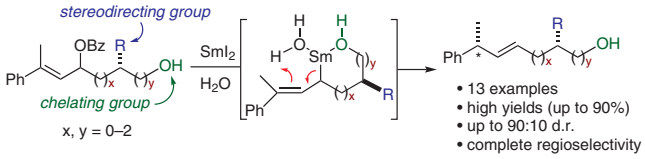
Synthesis T. F. Stockdale et al. Paper

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
oneilg@wwu.edu



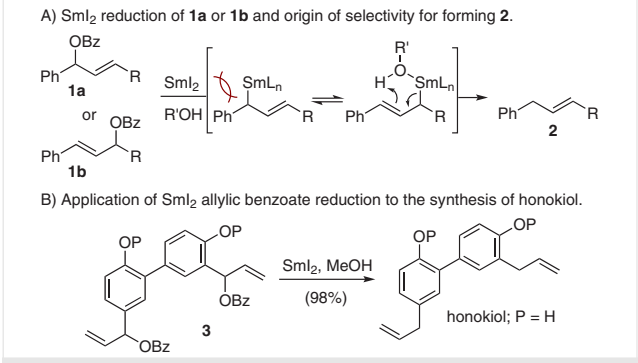
Received: 31.12.2019
Accepted after revision: 28.01.2020
Published online: 20.02.2020
DOI: 10.1055/s-0039-1690826; Art ID: ss-2019-n0518-op

Abstract $SmI_2(H_2O)_n$ reductions of allylic benzoates adjacent to a trisubstituted alkene occur in high yields 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]

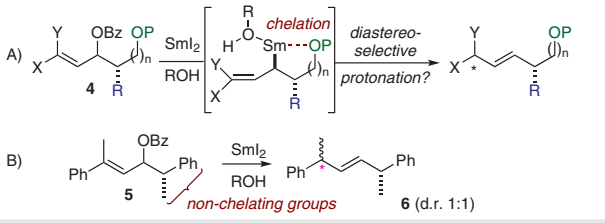
Our group became interested in the use of SmI_2 for the reduction of acyloxysulfones as part of a masked-alkene metathesis protocol.[11] More recently we reported that allylic benzoates **1a** or **1b** can be reduced with SmI_2 in the presence of an alcohol additive (R'OH),[12] converging to the corresponding 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]



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

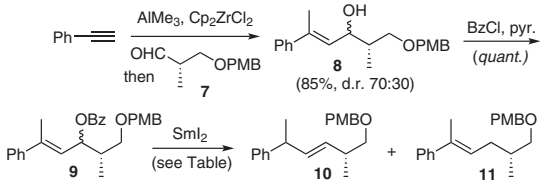
Applied to trisubstituted alkene-containing substrates, we recognized that the reaction would generate a new stereocenter (*), and became interested in finding ways to develop this reaction as a new strategy for stereoselective synthesis (Scheme 2).[14] We hypothesized that incorporation of a Lewis basic chelating element (e.g., OP) and stereo-

directing 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).

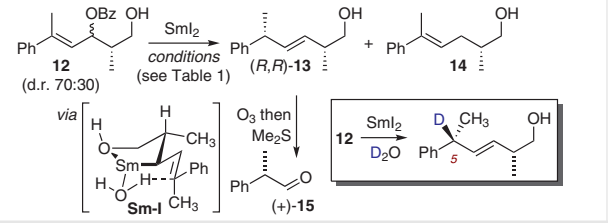


Entry	Additive[a]	**10**:**11**[b]	**10** d.r.[b]
1	DMPU	1.3:1	60:40
2	*t*-BuOH	3:1	69:31
3	MeOH	3:1	60:40
4	H_2O	5:1	50:50

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 equiv (entry 8) vs 75:25 for 1400 equiv (entry 6)], 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 equiv (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**

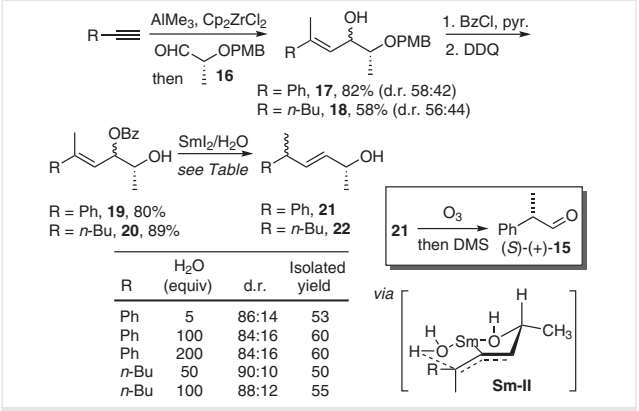
Table 1 Additive Effects on SmI_2 Reductions of Compound **12** (ref. Scheme 4)

Entry	Additive[a]	**13**:**14**[b]	d.r.[b] of **13**
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

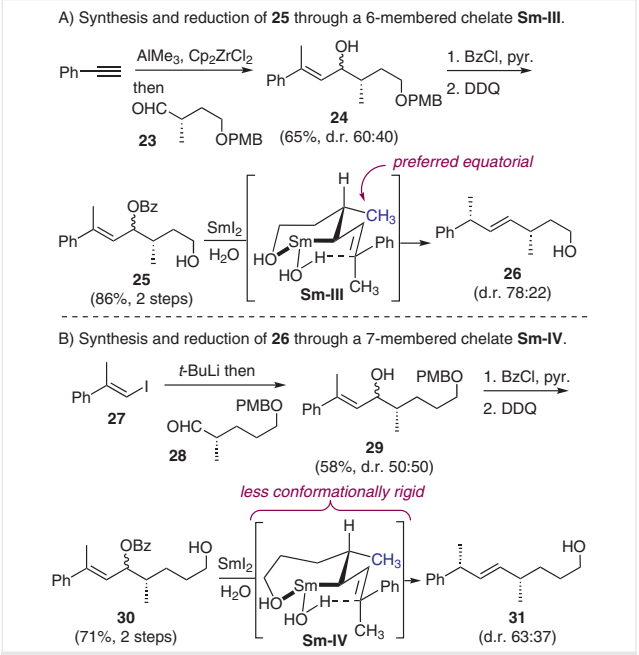
[a] Reactions were performed by adding the additive (16 equiv DMPU or 1400 equiv ROH) to SmI_2 (7 equiv) followed by the substrate and stirring for 30 min.
[b] Determined by ^1H NMR spectroscopy.
[c] Compound **14** was not detected by NMR spectroscopy.
[d] Performed at 0 °C.
[e] Compound **12** was 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 equiv H_2O relative to SmI_2, r.t.) 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 β-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]

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



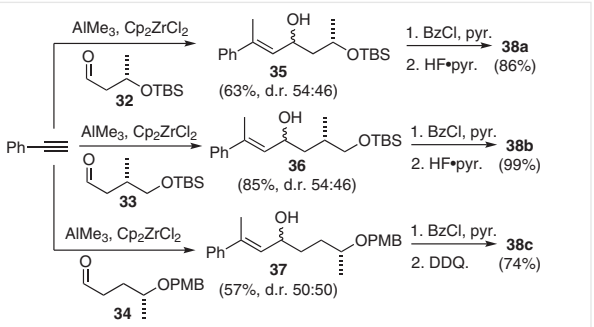
Scheme 5 Synthesis and elimination of lactate-derived compounds **21** and **22**



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**.

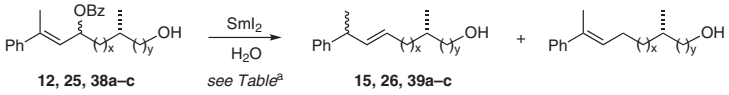
organosamarium ring chelate **Sm-IV** would be less stable and/or less conformationally rigid than 5- and 6-membered chelate substrates.[28] Indeed, the reaction of **30** with $SmI_2(H_2O)_n$ gave **31** with not only a lower diastereomeric ratio (63:37), but was accompanied by large amounts of what 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.

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** (Table 2, 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.

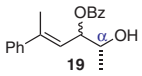
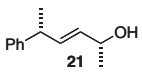
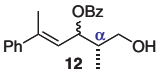
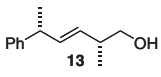
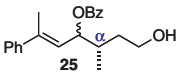
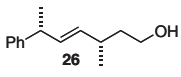
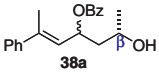
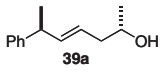
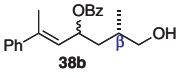
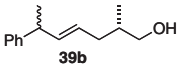
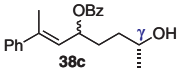
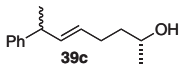


Scheme 7 Synthesis of additional elimination substrates **37a–c** containing differing methyl stereocenter positioning

Table 2 Comparison of Chelation Size and Methyl Stereocenter Position on Regio- and Diastereoselectivity for $SmI_2(H_2O)_n$ Allylic Benzoate Reductions[a]

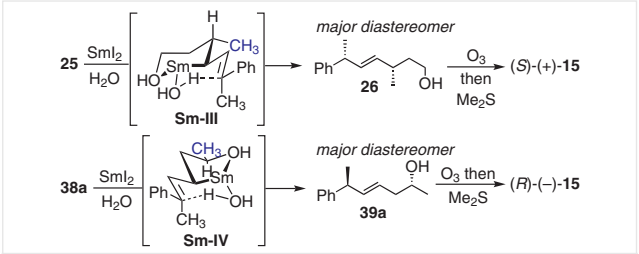


12, 25, 38a–c — 15, 26, 39a–c

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

[a] All reactions were preformed using 105 equiv of H_2O and 7 equiv of SmI_2 in degassed THF at r.t. under N_2.
[b] Determined by ^1H NMR and GC-FID analysis.
[c] Identical results were obtained when the reaction was performed under argon.

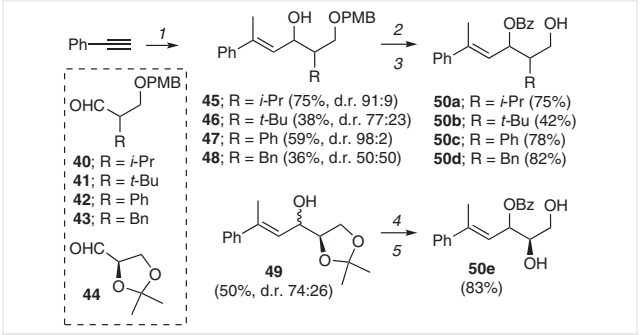
Ozonolysis of the product mixtures obtained from the reductions of compounds **25** and **38a** produced oppositely enantioenriched mixtures of aldehyde **15**. From **25** we obtained primarily *S*-(+)-**15** whereas **38a** gave primarily the *R*-(–)-enantiomer.[23] Both results are consistent with 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

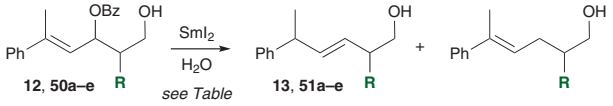
We also prepared a series of compounds **50a–e** in order to examine the effect of stereodirecting group identity in these reactions (Scheme 9, Table 3). It was hypothesized that larger groups might impart better diastereoselectivities based on, for instance, larger energy differences between axial and 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.

Based on 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 2 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 it 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 gel. 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.



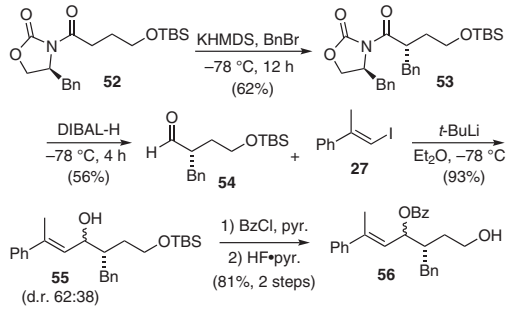
Scheme 9 *Reagents and conditions*: (1) $AlMe_3$, Cp_2ZrCl_2, then **40**, **41**, **42**, **43**, or **44**; (2) BzCl, pyridine; (3) DDQ; (4) BzCl, pyridine; (5) pTSA, MeOH.

Table 3 Stereodirecting Group Identity Effects on Regio- and Diastereoselectivity for $SmI_2(H_2O)_n$ Allylic Benzoate Reductions[a]



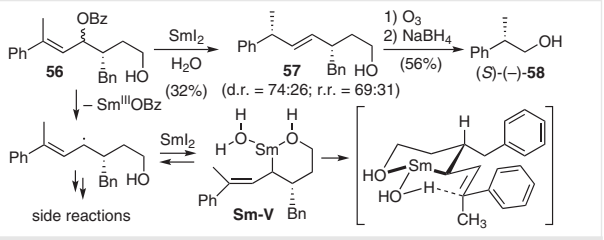
Entry	R	d.r.[b]	r.r.[b]	Yield (%)[c]
1	Me (**12**)	75:25	98:2	90
2	*i*-Pr (**50a**)	83:17	93:7	80
3	*t*-Bu (**50b**)	80:20	95:5	73
4	Ph (**50c**)	73:27	100:0	25
5	Bn (**50d**)	81:19	96:4	82
6	OH (**50e**)	–	–	0

[a] All reductions were performed at r.t. using 7 equiv of SmI_2 and 105 equiv of H_2O.
[b] Determined by ^1H NMR analysis.
[c] Isolated yield.



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 11). 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 diastereo- 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 diastereo- 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 (3*S*,6*R*). 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 trisubstituted 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 β-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, which 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.

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 Al_2O_3 under N_2 immediately prior to use. SmI_2 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 gel 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 hertz (Hz). The solvent signals were used as references ($CDCl_3$: δ_c = 77.0; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26). MS (EI): Bruker MaXis Impact mass spectrometer. Spectral data listed are for stereoisomeric mixtures unless specifically labelled to the contrary.

Zirconium-Catalyzed Carboalumination; General Procedure

To a Schlenk tube filled with DCM (0.3 M relative to alkyne) and Cp_2ZrCl_2 (0.1 equiv) at –20 °C was added $AlMe_3$ (2.0 equiv) dropwise resulting in a yellow solution, which was stirred for 10 min. Deionized H_2O (1.0 equiv) 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 r.t. for 10 min and then cooled to 0 °C. Phenylacetylene (1.0 equiv) was added dropwise and the solution was stirred for 40 min at 0 °C. The aldehyde (0.8 equiv) was then added dropwise and the mixture was stirred for 1 h at 0 °C. The reaction was quenched slowly with cold H_2O and then aq HCl, and extracted with DCM (3 ×). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo.

Benzoylation of Alcohols; General Procedure

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 °C followed by the addition of benzoyl chloride (1.2 equiv). The reaction was allowed to warm to r.t. for 15 h., before quenching with aq $NaHCO_3$ and extracting with DCM (3 ×). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo.

DDQ Removal of a PMB; General Procedure

Substrate was added to a round-bottomed flask containing a 50:50 mixture of DCM:pH 7 buffer (0.1 M relative to substrate). The reaction mixture was cooled to 0 °C and stirred vigorously at which time DDQ (3 equiv) was added portionwise over 30 min. The reaction was stirred vigorously for 1 h and then quenched with aq NaOH (1.0 M) and extracted with DCM (3 ×). The combined organic extracts were washed with brine (2 ×), dried ($MgSO_4$), and concentrated in vacuo.

$SmI_2(H_2O)_n$ Reductions; General Procedure

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 to 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 (3 ×). The combined organic extracts were dried ($MgSO_4$), 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 gel gave **5** (0.64 g, 90%) as a colorless oil (d.r. = 80:20); R_f = 0.52 (4:1 hexanes:EtOAc).

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

Major Diastereomer

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

^{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.

(2*S*,*E*)-1-[(4-Methoxybenzyl)oxy]-2-methyl-5-phenylhex-4-en-3-ol (8)

Prepared according to the general Zr-catalyzed carboalumination procedure using aldehyde **7**[17] (1.0 g, 4.7 mmol). Purification by flash chromatography on silica gel gave **8** (1.31 g, 85%) as a colorless oil (d.r. = 70:30); R_f = 0.65 (1:1 hexanes:EtOAc).

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

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

(2*S*,*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 gel gave **9** (1.72 g, quant.) as a colorless oil; R_f = 0.48 (4:1 hexanes:EtOAc).

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

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

^{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-({[(2*R*,*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 × 20 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gel gave **10** (0.051 g, 70%) as a colorless oil (d.r. = 60:40); R_f = 0.60 (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}.

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

^{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.

(2*S*,*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 gel gave **12** (0.6 g, 70%) as a colorless oil; R_f = 0.18 (4:1 hexanes:EtOAc).

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

Major Diastereomer

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

^{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.

(2*R*,5*R*,*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 gel gave **15** (0.0135 g, 90%) as a pale yellow oil; R_f = 0.31 (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}.

Major Diastereomer

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

^{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-bottomed 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 mixture turned to an electric blue color. The reaction was left at this temperature without stirring for 5 min and then N_2 was bubbled though the reaction until the solution became colorless. The reaction was quenched with Me_2S (5 equiv), warmed to r.t., and stirred for 1 h. The reaction mixture was washed with brine (15 mL) and extracted with DCM (3 × 15mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Aldehyde **15** was then isolated by flash chromatography on silica gel; R_f = 0.63 (4:1 hexanes:EtOAc). NMR spectra for **15** matched with that previously reported.[23]

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

(2*R*,*E*)-2-[(4-Methoxybenzyl)oxy]-5-phenylhex-4-en-3-ol (17)

Prepared according to the general procedure for Zr-catalyzed carboaluminations using aldehyde **16**[26] (0.500 g, 2.6 mmol). Purification by flash chromatography over silica gel 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 (4:1 hexanes:EtOAc).

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

Diastereomer α

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

^{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.

Diastereomer β

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

^{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.

(2*R*,*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 gel gave **19** (0.281 g, 80% over two steps) as a colorless oil; R_f = 0.24 (4:1 hexanes:EtOAc).

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

Diastereomer α

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

^{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.

Diastereomer β

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.07 (dd, *J* = 8.3, 1.2 Hz, 2 H), 7.57 (t, *J* = 7.3 Hz, 1 H), 7.45 (t, *J* = 8.1 Hz, 2 H), 7.43 (dd, *J* = 8.4, 1.3 Hz, 1 H), 7.33

(t, *J* = 7.1 Hz, 2 H), 7.28 (t, *J* = 7.3 Hz, 1 H), 5.91 (dq, *J* = 9.3, 1.3 Hz, 1 H), 5.85 (dd, *J* = 9.3, 4.0 Hz, 1 H), 4.15 (qd, *J* = 6.5, 4.1 Hz, 1 H), 2.25 (d, *J* = 1.3 Hz, 3 H), 1.31 (d, *J* = 6.4 Hz, 3 H).

^{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.

(2*R*,*E*)-2-[(4-Methoxybenzyl)oxy]-5-methylnon-4-en-3-ol (18)

Prepared according to the general procedure for Zr-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 gel gave **18** (0.441 g, 58%) as a colorless oil (d.r. = 56:44); R_f (diastereomer$_\alpha$) = 0.38; R_f (diastereomer$_\beta$) = 0.34 (4:1 hexanes:EtOAc).

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

Diastereomer α

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

^{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.

Diastereomer β

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

^{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.

(2*R*,*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 gel gave **20** (0.344 g, 89%) as a colorless oil; R_f = 0.32 (4:1 hexanes: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, 4 H), 7.55 (t, *J* = 7.4 Hz, 2 H), 7.44 (t, *J* = 7.7 Hz, 4 H), 5.66 (dd, *J* = 9.2, 4.4 Hz, 1 H), 5.57 (dd, *J* = 9.5, 7.2 Hz, 1 H), 5.32 (dq, *J* = 9.2, 1.3 Hz, 1 H), 5.20 (dq, *J* = 9.5, 1.3 Hz, 1 H), 4.03 (qd, *J* = 6.3, 4.2 Hz, 1 H), 3.97 (pent, *J* = 6.6 Hz, 1 H), 2.06 (t, *J* = 7.6 Hz, 2 H), 2.04 (t, *J* = 7.3 Hz, 2 H), 1.84 (d, *J* = 1.4 Hz, 3 H), 1.81 (d, *J* = 1.4 Hz, 3 H), 1.40 (m, 4 H), 1.29 (pent, *J* = 7.4 Hz, 4 H), 1.24 (d, *J* = 6.5 Hz, 3 H), 1.22 (d, *J* = 6.5 Hz, 3 H), 0.89 (t, *J* = 7.3 Hz, 3 H), 0.88 (t, *J* = 7.3 Hz, 3 H).

^{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.

(2*R*,5*R*,*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 to 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 × 15 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gel gave **21** (0.011 g, 60%) as a colorless oil (d.r. = 84:16); R_f = 0.30 (4:1 hexanes:EtOAc).

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

Major Diastereomer

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

^{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.

(2*R*,5*S*,*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 to a deep red color. The solution was stirred for 5 min before compound **20** (0.030 g, 0.11 mmol) was added. After 30 min, the reaction was quenched with aq $NaHCO_3$ (15 mL) and extracted with EtOAc (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gel gave **22** (0.010 g, 60%) as a colorless oil (d.r. = 90:10); R_f = 0.38 (4:1 hexanes:EtOAc).

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

Major Diastereomer

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.54 (dd, *J* = 15.4, 6.9 Hz, 1 H), 5.48 (dd, *J* = 15.4, 6.0 Hz, 1 H), 4.28 (pent, *J* = 6.3 Hz, 1 H), 2.11 (pent, *J* = 6.6 Hz, 1 H), 1.29 (m, 6 H), 1.28 (d, *J* = 6.3 Hz, 3 H), 0.99 (d, *J* = 6.8 Hz, 3 H), 0.90 (t, *J* = 7.0 Hz, 3 H).

^{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.

(5*S*,*E*)-7-[(4-Methoxybenzyl)oxy]-5-methyl-2-phenylhept-2-en-4-ol (24)

Prepared according to the general procedure for Zr-catalyzed carboaluminations using (2*S*)-4-{[(1,1-dimethylethyl)dimethylsilyl]oxy}-2-methylbutanal (**23**;[36] 0.29 g, 1.3 mmol). Purification by flash

chromatography on silica gel gave **24** (0.288 g, 65%) as a colorless oil (d.r. = 60:40); R_f = 0.65 (1:1 hexanes: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}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.42–7.38 (m, 4 H), 7.32 (t, 7.32, *J* = 7.3 Hz, 4 H), 7.27 (dd, *J* = 5.6, 2.1 Hz, 2 H), 7.26 (dd, *J* = 7.0, 2.0 Hz, 2 H), 7.25 (tt, *J* = 6.3, 1.3 Hz, 2 H), 6.88 (d, *J* = 8.6 Hz, 2 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 5.82 (dq, *J* = 8.7, 1.4 Hz, 1 H), 5.77 (dq, *J* = 8.9, 1.4 Hz, 1 H), 4.47 (s, 2 H), 4.47 (d, *J* = 11.5 Hz, 1 H), 4.44 (d, *J* = 11.5 Hz, 1 H), 4.43 (dd, *J* = 9.1, 4.5 Hz, 1 H), 4.30 (dd, *J* = 8.8, 6.9 Hz, 1 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.63–3.56 (m, 2 H), 3.54–3.49 (m, 2 H), 2.63 (br, OH), 2.40 (br, OH), 2.08 (d, *J* = 1.4 Hz, 3 H), 2.07 (d, *J* = 1.4 Hz, 3 H), 1.92–1.81 (m, 4 H), 1.64 (sept, *J* = 6.7 Hz, 1 H), 1.50 (sept, *J* = 6.6 Hz, 1 H), 0.98 (d, *J* = 6.5 Hz, 3 H), 0.93 (d, *J* = 6.8 Hz, 3 H).

^{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 $C_{22}H_{28}O_3Na^+$ [M + Na]$^+$; found: 363.1939.

(5*S*,*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 gel gave **25** (0.238 g, 86% over two steps) as a colorless oil; R_f = 0.15 (4:1 hexanes:EtOAc).

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

Major Diastereomer

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.40 (dt, *J* = 8.4, 1.5 Hz, 4 H), 7.33 (tt, *J* = 8.3, 1.0 Hz, 4 H), 7.27 (tt, *J* = 4.1, 1.3 Hz, 2 H), 7.24 (d, *J* = 8.5 Hz, 4 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 6.85 (d, *J* = 8.6 Hz, 2 H), 5.80 (dq, *J* = 8.9, 1.5 Hz, 1 H), 5.78 (dq, *J* = 9.0, 1.4 Hz, 1 H), 4.44 (s, 2 H), 4.43 (s, 2 H), 4.38 (dd, *J* = 8.9, 5.7 Hz, 1 H), 4.35 (dd, *J* = 8.9, 6.5 Hz, 1 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.48–3.42 (m, 4 H), 2.10 (d, *J* = 1.4 Hz, 3 H), 2.09 (d, *J* = 1.4 Hz, 3 H), 1.80–1.59 (m 10 H), 1.00 (d, *J* = 6.7 Hz, 3 H), 0.93 (d, *J* = 6.7 Hz, 3 H).

^{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 $C_{21}H_{24}O_3Na^+$ [M + Na]$^+$; found: 347.1622.

(5*S*,*E*)-8-[(4-Methoxybenzyl)oxy]-5-methyl-2-phenyloct-2-en-4-ol (29)

To a Schlenk flask containing Et_2O (5.2 mL) and *t*-BuLi (1.7 M, 0.917 mL, 1.56 mL) at –78 °C was added vinyl iodide **27**[30] (0.190 g, 0.78 mmol) dropwise. The solution was stirred for 10 min at –78 °C before adding (2*S*)-5-[(4-methoxyphenyl)methoxy]-2-methylpentanal (**28**;[37] 0.123g, 0.520 mmol) dropwise, and the reaction mixture was stirred for 1 h at –78 °C. The reaction was quenched with aq NH_4Cl (30 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography over silica gel gave **29** (0.097 g, 58%) as a colorless oil (d.r. = ~50:50); R_f = 0.64 (1:1 hexanes: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}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.40 (dt, *J* = 8.4, 1.5 Hz, 4 H), 7.33 (tt, *J* = 8.3, 1.0 Hz, 4 H), 7.27 (tt, *J* = 4.1, 1.3 Hz, 2 H), 7.24 (d, *J* = 8.5 Hz, 4 H), 6.87 (d, *J* = 8.6 Hz, 2 H), 6.85 (d, *J* = 8.6 Hz, 2 H), 5.80 (dq, *J* = 8.9, 1.5 Hz, 1 H), 5.78 (dq, *J* = 9.0, 1.4 Hz, 1 H), 4.44 (s, 2 H), 4.43 (s, 2 H), 4.38 (dd, *J* = 8.9, 5.7 Hz, 1 H), 4.35 (dd, *J* = 8.9, 6.5 Hz, 1 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.48–3.42 (m, 4 H), 2.10 (d, *J* = 1.4 Hz, 3 H), 2.09 (d, *J* = 1.4 Hz, 3 H), 1.80–1.59 (m 10 H), 1.00 (d, *J* = 6.7 Hz, 3 H), 0.93 (d, *J* = 6.7 Hz, 3 H).

^{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 $C_{23}H_{30}O_3Na^+$ [M + Na]$^+$; found: 377.2094.

(5*S*,*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 gel gave **30** (0.065 g, 71%) as a colorless oil; R_f = 0.13 (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}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 8.06 (dt, *J* = 8.4, 1.0 Hz, 4 H), 7.55 (tq, *J* = 6.9, 1.3 Hz, 2 H), 7.44 (t, *J* = 7.6 Hz, 4 H), 7.40 (dt, *J* = 8.5, 1.5 Hz, 4 H), 7.31 (tt, *J* = 7.38, 1.0 Hz, 4 H), 7.26 (tq, *J* = 7.2, 1.3 Hz, 2 H), 5.82 (m, 4 H), 3.67 (tt, *J* = 6.5, 2.0 Hz, 4 H), 2.24 (d, *J* = 1.0 Hz, 3 H), 2.23 (s, 3 H), 2.04 (m, 1 H), 1.97 (m, 1 H), 1.77–1.54 (m, 8 H), 1.12 (d, *J* = 6.9 Hz, 3 H), 1.09 (d, *J* = 6.8 Hz, 3 H).

^{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 $C_{22}H_{26}O_3Na^+$ [M + Na]$^+$; found: 361.1780.

(6*S*,*E*)-6-[(*tert*-Butyldimethylsilyl)oxy]-2-phenylhept-2-en-4-ol (35)

Prepared according to the general procedure for Zr-catalyzed carboaluminations using (*S*)-3-[(*tert*-butyldimethylsilyl)oxy]butanal (**32**;[38] 0.231 g, 1.15 mmol). Purification by flash chromatography on silica gel gave **35** (0.234 g, 63%) as a colorless oil (d.r. = 54:46); R_f = 0.52 (4:1 hexanes: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}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.41 (d, *J* = 7.1 Hz, 4 H), 7.31 (t, *J* = 7.4 Hz, 4 H), 7.24 (t, *J* = 7.2 Hz 2 H), 5.83 (dq, *J* = 8.6, 1.3 Hz, 1 H), 5.79 (dq, *J* = 8.2, 1.4 Hz, 2 H), 4.90 (dt, *J* = 8.9, 3.1 Hz, 1 H), 4.72 (dt, *J* = 8.9, 3.1 Hz, 1 H), 4.23 (pentd, *J* = 6.2, 3.6 Hz, 1 H), 4.16 (dtd, *J* = 12.2, 6.1, 3.8 Hz, 1 H), 3.35 (br, OH), 3.13 (br, OH), 2.10 (d, *J* = 1.4 Hz, 3 H), 2.10 (d, *J* = 1.4 Hz, 3 H), 1.83 (ddd, *J* = 9.1, 7.0, 3.4 Hz, 1 H), 1.80 (ddd, *J* = 9.2, 5.2, 1.6 Hz, 1 H), 1.63 (dddd, *J* = 14.3, 6.91, 3.8, 3.2 Hz, 1 H), 1.60 (dddd, *J* = 14.3, 8.7, 6.2, 2.6 Hz, 1 H), 1.28 (d, *J* = 6.3 Hz, 3 H), 1.23 (d, *J* = 6.1 Hz, 3 H), 0.93 (s, 18 H), 0.14 (d, *J* = 9.1 Hz, 6 H), 0.12 (d, *J* = 8.1 Hz, 6 H).

^{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.

(6*S*,*E*)-6-Hydroxy-2-phenylhept-2-en-4-yl Benzoate (38a)

Prepared according to the general benzoylation procedure using **35** (0.234 g, 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 × 10 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography over silica gel 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 (4:1 hexanes: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, 4 H), 7.58 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.55 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 4 H), 7.41 (d, *J* = 7.51 Hz, 4 H), 7.33 (t, *J* = 7.2 Hz, 2 H), 7.32 (t, *J* = 7.5 Hz, 2 H), 7.27 (tt, *J* = 5.88, 1.3 Hz, 2 H), 6.19 (dd, *J* = 8.8, 3.5 Hz, 1 H), 6.10 (dt, *J* = 6.90 Hz, 1 H), 5.90 (dq, *J* = 8.7, 1.4 Hz, 1 H), 5.80 (dq, *J* = 9.2, 1.2 Hz, 1 H), 3.97 (qd, *J* = 6.2, 1.4 Hz, 1 H), 3.86 (qd, *J* = 6.2, 2.6 Hz, 1 H), 2.26 (d, *J* = 1.2 Hz, 3 H), 2.19 (t, *J* = 1.2 Hz, 3 H), 2.13 (ddd, *J* =14.0, 8.3, 6.6 Hz, 1 H), 1.99 (ddd, *J* = 13.3, 10.4, 2.6 Hz, 1 H), 1.88 (ddd, *J* = 11.5, 7.3, 4.5 Hz, 1 H), 1.80 (ddd, *J* = 13.7, 10.0, 3.3 Hz, 1 H), 1.29 (d, *J* = 6.2 Hz, 3 H), 1.24 (d, *J* = 6.2 Hz, 3 H).

^{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 Zr-catalyzed carboaluminations using 4-[(*tert*-butyldimethylsilyl)oxy]-3-methylbutanal (**33**;[39] 0.500 g, 2.31 mmol). Purification by flash chromatography on silica gel gave **36** (0.658 g, 85%) as a colorless oil (d.r. = 54:46); R_f = 0.51 (4:1 hexanes: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, 4 H), 7.33 (t, *J* = 7.4 Hz, 4 H), 7.26 (tq, *J* = 7.4, 1.3 Hz, 2 H), 5.83 (tq, *J* = 8.5, 1.4 Hz, 2 H), 4.72 (td, *J* = 7.3, 6.2 Hz, 1 H), 4.64 (td, *J* = 8.8, 3.8 Hz, 1 H), 3.60 (dd, *J* = 10, 4.7 Hz, 1 H), 3.58 (dd, 5.2, 9.9 Hz, 1 H), 3.52 (dd, *J* = 9.9, 6.7 Hz, 1 H), 3.48 (dd, *J* = 10.0, 7.4 Hz, 1 H), 3.25 (br, OH), 2.95 (br, OH), 2.12 (d, *J* = 1.4 Hz, 6 H), 1.89 (octet, *J* = 6.6 Hz, 2 H), 1.72 (ddd, *J* = 14.3, 9.2, 7.1 Hz, 1 H), 1.66 (ddd, *J* = 7.2, 6.1, 3.6 Hz, 2 H), 1.49 (ddd, *J* = 14.1, 5.9, 3.7 Hz, 1 H), 0.98 (d, *J* = 6.8 Hz, 6 H), 0.95 (s, 9 H), 0.95 (s, 9 H), 0.12 (d, *J* = 2.7 Hz, 6 H), 0.11 (d, *J* = 2.2 Hz, 6 H).

^{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 × 10 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gel gave **38b** (0.240 g, 99% over two steps) as a colorless oil; R_f = 0.18 (4:1 hexanes: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, 4 H), 7.55 (tt, 7.5, 1.1 Hz, 2 H), 7.44 (t, *J* = 7.8 Hz, 4 H), 7.41 (dd, *J* = 7.6, 1.8 Hz, 4 H), 7.32 (t, 7.2 Hz, 4 H), 7.26 (tt, *J* = 7.3, 1.2 Hz, 2 H), 6.06 (dt, *J* = 6.8, 9.1 Hz, 1 H), 6.04 (dt, *J* = 8.7, 5.3 Hz, 1 H), 5.81 (dq, *J* = 9.0, 1.3 Hz, 1 H), 5.78 (dq, *J* = 9.2, 1.3 Hz, 1 H), 3.57 (dd, *J* = 5.6, 1.8 Hz, 4 H), 2.24 (d, *J* = 1.3 Hz, 3 H), 2.23 (d, *J* = 1.3 Hz, 3 H), 1.98 (m, 2 H), 1.94–1.78 (m, 4 H), 1.05 (d, *J* = 6.7 Hz, 3 H), 1.04 (d, *J* = 6.4 Hz, 3 H).

^{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 Zr-catalyzed carboaluminations using 4-[(4-methoxybenzyl)oxy]pentanal (**34**;[40] 0.300 g, 1.3 mmol). Purification by flash chromatography on silica gel gave **37** (0.254 g, 57%) as a colorless oil (d.r. = 50:50); R_f = 0.61 (4:1 hexanes: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, 4 H), 7.33 (t, *J* = 7.3 Hz, 4 H), 7.28 (dd, *J* = 8.8, 1.5 Hz, 4 H), 7.26 (tt, *J* = 6.5, 1.2 Hz, 2 H), 6.88 (dd, *J* = 8.6, 2.0 Hz, 4 H), 5.78 (dq, *J* = 5.4, 1.4 Hz, 1 H), 5.77 (dq *J* = 5.4, 1.4 Hz, 1 H), 4.54 (d, *J* = 11.5 Hz, 4 H), 4.40 (dd, *J* = 11.3, 2.4 Hz, 2 H), 3.80 (s, 6 H), 3.57 (hex, 5.9 Hz, 2 H), 2.08 (d, *J* = 1.3 Hz, 3 H), 2.08 (d, *J* = 1.3 Hz, 3 H), 1.81–1.56 (m, 8 H), 1.22 (d, *J* = 6.2 Hz, 6 H).

^{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 gel gave **38c** (0.180 g, 74% over two steps) as a colorless oil; R_f = 0.15 (4:1 hexanes:EtOAc).

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

^1H NMR ($CDCl_3$, 500 MHz): δ = 8.06 (dd, *J* = 8.5, 1.3 Hz, 4 H), 7.55 (tt, *J* = 7.4, 1.2 Hz, 2 H), 7.44 (t, *J* = 8.0 Hz, 4 H), 7.41 (dd, *J* = 7.6, 1.6 Hz, 4 H), 7.32 (t, *J* = 7.8 Hz, 4 H), 7.26 (tt, *J* = 7.2, 1.4 Hz, 2 H), 5.95 (dt, *J* = 6.9, 6.7 Hz, 1 H), 5.94 (dt, *J* = 6.9, 6.7 Hz, 1 H), 5.81 (dq, *J* = 9.0, 1.3 Hz, 2 H), 3.88 (hex, *J* = 6.5 Hz, 2 H), 2.22 (d, *J* = 1.4 Hz, 3 H), 2.21 (d, *J* = 1.3 Hz, 3 H), 2.05 (qt, *J* = 6.94, 5.49 Hz, 1 H), 1.95 (dt, *J* = 6.8, 6.4 Hz, 1 H), 1.93 (dt, *J* = 6.7, 6.5 Hz, 1 H), 1.83 (qt, *J* = 6.0, 3.9 Hz, 1 H), 1.63–1.54 (m, 4 H), 1.23 (d, *J* = 6.3 Hz, 6 H).

^{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 Zr-catalyzed carboaluminations using 2-{[(4-methoxybenzyl)oxy]methyl}-3-methylbutanal (**40**;[41] 0.346 g, 1.46 mmol). Purification by flash chromatography on silica gel gave **45** (0.392 g, 75%) as a colorless oil (d.r. = 91:9); R_f = 0.34 (4:1 hexanes: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}.

Major Diastereomer

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

^{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 gel gave **50a** (0.281 g, 75% over two steps) as a colorless oil; R_f = 0.50 (4:1 hexanes: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}.

Major Diastereomer

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

^{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 Zr-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 gel gave **46** (0.175 g, 38%) as a colorless oil (d.r. = 77:23); R_f = 0.43 (4:1 hexanes: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}.

Major Diastereomer

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

^{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 gel gave **50b** (0.060 g, 42% over two steps) as a colorless oil; R_f = 0.35 (4:1 hexanes:EtOAc).

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

Major Diastereomer

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

^{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 Zr-catalyzed carboaluminations using 3-[(4-methoxybenzyl)oxy]-2-phenylpropanal

(**42**;[43] (0.113 g, 0.42 mmol). Purification by flash chromatography on silica gel gave **47** (0.097 g, 59%) as a colorless oil (d.r. = 98:2); R_f = 0.19 (4:1 hexanes: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}.

Major Diastereomer

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

^{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 gel gave **50c** (0.065 g, 78% over two steps) as a colorless oil; R_f = 0.37 (4:1 hexanes:EtOAc).

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

Major Diastereomer

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

^{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 Schlenk flask containing Et_2O (3.5 mL) and *t*-BuLi (1.7 M, 0.905 mL, 1.54 mL) at –78 °C was added vinyl iodide **27**[30] (0.171 g, 0.702 mmol) dropwise. The solution was stirred for 10 min at –78 °C and 2-benzyl-3-[(4-methoxybenzyl)oxy]propanal (**43**;[43] 0.100 g, 0.351 mmol) was then added dropwise. The reaction mixture was stirred for 1 h at –78 °C before being brought to r.t. for 30 min. The reaction was quenched with aq NH_4Cl (30 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography over silica gel gave **48** (0.051 g, 36%) as a colorless oil (d.r. = 50:50); R_f = 0.22 (4:1 hexanes: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}.

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

^{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 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 gel gave **50d** (0.081 g, 82% over two steps) as a colorless oil; R_f = 0.32 (4:1 hexanes: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}.

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

^{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 Zr-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 gel gave **49** (0.586 g, 50%) as a colorless oil (d.r. = 74:26); R_f = 0.66 (1:1 hexanes:EtOAc).

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

Major Diastereomer

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

^{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.

(2*R*,*E*)-1,2-Dihydroxy-5-phenylhex-4-en-3-yl Benzoate (50e)

Prepared according to the general benzoylation procedure using **49** (0.45 g, 2.13 mmol). The crude product was then redissolved in MeOH (8.5 mL) and pTSA (0.404 g, 2.128 mmol) was added. The reaction mixture was stirred for 5 min before quenching with aq $NaHCO_3$ (10 mL) and extracting with DCM (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gel gave **50e** (0.223 g, 83%) as a colorless oil; R_f = 0.25 (1:1 hexanes:EtOAc).

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

Major Diastereomer

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

^{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 $SmI_2(H_2O)_n$ reductions using **50a** (0.050 g, 0.147 mmol). Purification by flash chromatography on silica gel gave **51a** (0.026 g, 80%) as a colorless oil (d.r. = 83:17); R_f = 0.37 (4:1 hexanes:EtOAc).

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

Major Diastereomer

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.31 (t, *J* = 7.5 Hz, 2 H), 7.22 (dd, *J* = 6.6, 1.6 Hz, 2 H), 7.20 (tt, *J* = 6.7, 1.3 Hz, 1 H), 5.76 (ddd, *J* = 15.4, 6.7, 0.7 Hz, 1 H), 5.28 (ddd, *J* = 15.4, 9.5, 1.4 Hz, 1 H), 3.65 (dd, *J* = 10.5, 5.0 Hz, 1 H), 3.51 (pent, *J* = 6.9 Hz, 1 H), 3.41 (dd, *J* = 10.5, 9.0 Hz, 1 H), 2.00 (tdd, *J* = 9.6, 6.9, 5.3 Hz, 1 H), 1.67 (octet, *J* = 6.7 Hz, 1 H), 1.38 (d, *J* = 7.0 Hz, 3 H), 0.93 (d, *J* = 6.8 Hz, 3 H), 0.89 (d, *J* = 6.8 Hz, 3 H).

^{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 $SmI_2(H_2O)_n$ reductions using **50b** (0.075 g, 0.212 mmol). Purification by flash chromatography on silica gel gave **51b** (0.027 g, 73%) as a colorless oil (d.r. = 80:20); R_f = 0.33 (4:1 hexanes:EtOAc).

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

Major Diastereomer

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.30 (t, *J* = 7.65 Hz, 2 H), 7.23–7.17 (m, 3 H), 5.78 (ddd, *J* = 15.3, 6.8, 0.6 Hz, 1 H), 5.36 (ddd, *J* = 15.3, 9.9, 1.4 Hz, 1 H), 3.74 (dd, *J* = 10.3, 3.8 Hz, 1 H), 3.53 (pent, *J* = 6.8 Hz, 1 H), 3.36 (t, *J* = 10.3 Hz, 1 H), 1.95 (td, *J* = 10.3, 4.0 Hz, 1 H), 1.38 (d, *J* = 7.0 Hz, 3 H), 0.91 (s, 9 H).

^{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 $SmI_2(H_2O)_n$ reductions using **50c** (0.066 g, 0.176 mmol). Purification by flash chromatography on silica gel gave **51c** (0.012 g, 25%) as a colorless oil (d.r. = 73:27); R_f = 0.28 (4:1 hexanes:EtOAc).

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

Major Diastereomer

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.34 (t, *J* = 7.6 Hz, 2 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 7.26–7.17 (m, 6 H), 5.82 (ddd, *J* = 15.6, 6.7, 0.88 Hz, 1 H), 5.66 (ddd, *J* = 15.4, 8.0, 1.3 Hz, 1 H), 3.87 (m, 1 H), 3.77 (pent, *J* = 8.15 Hz, 2 H), 3.51 (q, *J* = 7.5 Hz, 1 H). 1.36 (d, *J* = 7.1 Hz, 3 H).

^{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 $SmI_2(H_2O)_n$ reductions using **50d** (0.050 g, 0.147 mmol). Purification by flash chromatography on silica gel gave **51d** (0.030 g, 82%) as a colorless oil (d.r. = 81:19); R_f = 0.37 (4:1 hexanes:EtOAc).

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

Major Diastereomer

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.29 (t, *J* = 7.1 Hz, 2 H), 7.24 (t, *J* = 7.7 Hz, 2 H), 7.21 (tt, *J* = 6.2, 2.1 Hz, 1 H), 7.19–7.08 (m, 3 H), 7.03 (d, *J* = 7.3 Hz, 2 H), 5.64 (ddd, *J* = 15.5, 6.4, 0.8 Hz, 1 H), 5.31 (ddd, *J* = 15.4, 8.4, 1.4 Hz, 1 H), 3.61 (dd, *J* = 10.5, 4.9 Hz, 1 H), 3.48 (dd, *J* = 10.5, 7.5 Hz, 1 H), 3.42 (pent, *J* = 6.5 Hz, 1 H), 2.80 (dd, *J* = 13.1, 6.0 Hz, 1 H), 2.60 (dd, *J* = 13.2, 8.4 Hz, 1 H), 2.54 (dtd, *J* = 13.8, 7.8, 5.0 Hz, 1 H), 1.28 (d, *J* = 7.1 Hz, 3 H).

^{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 °C was added KHMDS (1 M in THF, 9.94 mL, 9.94 mmol) dropwise. The reaction mixture was stirred at –78 °C for 1 h before freshly distilled benzyl bromide (1.22 mL, 9.94 mmol) was added dropwise. The mixture was stirred for 12 h at –78 °C before quenching with aq NH_4Cl (40 mL) and extracting with EtOAc (3 × 20

mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gel gave **53** (1.01 g, 62%) as a colorless oil; R_f = 0.51 (4:1 hexanes: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}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.28 (t, *J* = 7.4 Hz, 4 H), 7.25 (d, *J* = 7.0 Hz, 2 H), 7.19 (tt, *J* = 5.9, 2.0 Hz, 2 H), 7.07 (d, *J* = 6.8 Hz, 2 H), 4.61 (ddt, *J* = 9.7, 7.8, 3.1 Hz, 1 H), 4.35 (ddd, *J* = 7.7, 4.6, 4.4 Hz, 1 H), 4.09 (ddd, *J* = 8.6, 7.9, 0.8 Hz, 1 H), 4.04, (dd, *J* = 9.0, 2.9 Hz, 1 H), 3.65 (dd, *J* = 5.9, 1.2 Hz, 1 H), 3.64 (d, *J* = 5.9 Hz, 1 H), 3.07 (dd, *J* = 13.3, 7.8 Hz, 1 H), 3.02 (dd, *J* = 13.5, 3.5 Hz, 1 H), 2.80 (dd, *J* = 13.3, 7.5 Hz, 1 H), 2.36 (dd, *J* = 13.5, 9.7 Hz, 1 H), 2.05 (ddt, *J* = 13.6, 9.1, 6.5 Hz, 1 H), 1.71 (dtd, *J* = 13.7, 5.8, 4.3 Hz 1 H), 0.85 (s, 9 H), –0.01 (s, 3 H), –0.02 (s, 3 H).

^{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 °C was added DIBAL-H (1.15 mL, 6.50 mmol) dropwise. The reaction mixture was stirred at –78 °C for 4 h before being warmed to r.t. and quenched with 2 M Rochelle's salt (100 mL) and stirred for 3 h. The aqueous layer was extracted with DCM (3 × 50 mL). The combined organic extracts were washed with brine (50 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gel gave **54** (0.358 g, 56%) as a colorless oil; R_f = 0.74 (4:1 hexanes:EtOAc).

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

^1H NMR ($CDCl_3$, 500 MHz): δ = δ 9.71 (d, *J* = 2.1 Hz, 1 H), 7.29 (t, *J* = 7.6 Hz, 2 H), 7.20 (tt, *J* = 6.7, 1.3 Hz, 1 H), 7.17 (d, *J* = 6.7 Hz, 2 H), 3.67 (ddd, *J* = 10.3, 6.9, 5.1 Hz, 1 H), 3.62 (ddd, *J* = 10.3, 6.7, 5.2 Hz, 1 H), 3.04 (dd, *J* = 13.4, 6.3 Hz, 1 H), 2.77 (dddt, *J* = 12.0, 7.6, 4.1, 2.0 Hz, 1 H), 2.71 (dd, *J* = 13.4, 7.7 Hz, 1 H), 1.89 (dddd, *J* = 14.5, 7.9, 6.7, 5.1 Hz, 1 H) 1.72 (dddd, *J* = 14.3, 6.8, 5.2, 4.4 Hz, 1 H), 0.87 (s, 9 H), 0.03 (s, 3 H), 0.02 (s, 3 H).

^{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 $C_{17}H_{28}O_2SiNa^+$ [M + Na]$^+$; found: 315.1757.

(5*S*,*E*)-5-Benzyl-7-[(*tert*-butyldimethylsilyl)oxy]-2-phenylhept-2-en-4-ol (55)

To a Schlenk flask containing Et_2O (12.0 mL) and *t*-BuLi (1.7 M, 2.82 mL, 4.8 mmol) at –78 °C was added vinyl iodide **27**[30] (0.190 g, 0.78 mmol) dropwise. The solution was stirred for 5 min at –78 °C, **54** (0.585g, 2.4 mmol) was then added dropwise, and the reaction was stirred for 1 h at –78 °C. The reaction was quenched with aq NH_4Cl (30 mL), and extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gel gave **55** (0.394 g, 93%) as a colorless oil (d.r. = 62:38); R_f = 0.44 (4:1 hexanes: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}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.42 (d, *J* = 7.5 Hz, 2 H), 7.40 (d *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 7.3 Hz, 2 H), 7.32–7.23 (m, 10 H), 7.19 (d, *J* = 8.1 Hz, 2 H), 7.17 (t, *J* = 8.2 Hz, 2 H), 5.95 (dq, *J* = 8.8, 1.3 Hz, 1 H), 5.89 (dq, *J* = 8.7, 1.4 Hz, 1 H), 4.61 (dt, *J* = 8.8, 4.4 Hz, 1 H), 4.42 (dt, *J* = 8.7, 5.4 Hz, 1 H), 3.80–3.73 (m, 2 H), 3.62–3.56 (m, 2 H), 3.55 (d, *J* = 5.2 Hz, OH), 3.49 (d, *J* = 5.3 Hz, OH), 2.89 (dd, *J* = 13.7, 6.0 Hz, 1 H), 2.83 (dd, *J* = 13.9, 5.5 Hz, 1 H), 2.54 (dd, *J* = 13.9, 9.3 Hz, 1 H), 2.51 (dd, *J* = 13.7, 9.3 Hz, 1 H), 2.21 (octet, *J* = 4.7 Hz, 1 H), 2.08 (d, *J* = 1.3 Hz, 3 H), 2.04 (m, 1 H), 2.01 (d, *J* = 1.3 Hz, 3 H), 1.80 (m, 1 H), 1.75 (dtd, *J* = 15.3, 7.9, 4.4 Hz, 1 H), 1.66 (m, 1 H), 1.55 (ddt, *J* = 9.0, 6.5, 4.3 Hz, 1 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.09 (s, 3 H), 0.08 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H).

^{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 $C_{26}H_{38}O_2SiNa^+$ [M + Na]$^+$; found: 433.2544.

(5*S*,*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 °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 $NaHCO_3$ (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography over silica gel gave **56** (0.312 g, 81% over two steps) as a colorless oil; R_f = 0.63 (1:1 hexanes: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}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 8.04 (d, *J* = 8.0 Hz, 4 H), 7.57 (tt, *J* = 7.5, 1.3 Hz, 1 H), 7.56 (tt, *J* = 7.4, 1.4 Hz, 1 H), 7.45 (t, *J* = 7.7 Hz, 4 H), 7.39 (t, *J* = 7.0 Hz, 4 H), 7.35–7.27 (m, 10 H), 7.24–7.18 (m, 6 H), 6.01 (dd, *J* = 9.1, 4.7 Hz, 1 H), 5.94 (dd, *J* = 9.2, 4.3 Hz, 1 H), 5.91 (dq, *J* = 9.2, 1.4 Hz, 1 H), 5.90 (dq, *J* = 9.2, 1.4 Hz, 1 H), 3.71 (t, *J* = 6.8 Hz, 4 H), 2.98 (dd, *J* = 14.0, 5.8 Hz, 1 H), 2.97 (dd, *J* = 13.7, 6.3 Hz, 1 H), 2.70 (dd, *J* = 14.0, 8.5 Hz, 1 H), 2.67 (dd, *J* = 13.7, 8.2 Hz, 1 H), 2.45 (dddd, *J* = 12.6, 8.4, 6.2, 4.9 Hz, 1 H), 2.36 (dddd, *J* = 12.5, 8.2, 6.2, 4.6 Hz, 1 H), 2.19 (d, *J* = 1.3 Hz, 3 H), 2.12 (d, *J* = 1.2 Hz, 3 H), 1.88 (dq, *J* = 13.6, 6.8 Hz, 1 H), 1.87 (dq, *J* = 13.0, 6.9 Hz, 1 H), 1.76 (dq, *J* = 13.5, 6.5 Hz, 1 H) 1.66 (dq, *J* = 13.2, 6.6 Hz, 1 H).

^{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 $C_{27}H_{28}O_3Na^+$ [M + Na]$^+$; found: 423.1933.

(3*S*,*E*)-3-Benzyl-6-phenylhept-4-en-1-ol (57)

Prepared according to the general procedure for $SmI_2(H_2O)_n$ reductions using **56** (0.312 g, 0.786 mmol). Purification by flash chromatography on silica gel gave **57** (0.13 g, 32%) as mixture of diastereomers (d.r. = 74:26), R_f = 0.28 (4:1 hexanes:EtOAc).

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

Major Diastereomer

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.40 (d, *J* = 4.5 Hz, 2 H), 7.36–7.23 (m, 4 H), 7.23–7.02 (m, 4 H), 5.50 (dd, *J* = 15.7, 6.9 Hz, 1 H), 5.28 (ddd, *J* = 15.6, 9.3, 1.5 Hz, 1 H), 3.77–3.57 (m, 2 H), 3.40 (m, 1 H), 2.74 (dd, *J* = 13.3, 6.4 Hz, 1 H), 2.63 (dd, *J* = 13.5, 8.4 Hz, 1 H), 2.48 (m, 1 H), 2.24 (t, *J* = 6.8 Hz, 1 H), 1.75 (dtd, *J* = 14.0, 7.1, 3.9 Hz, 1 H), 1.56 (m, 1 H), 1.27 (d, *J* = 7.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 126 MHz): 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.

Funding Information

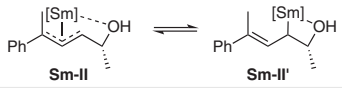
National Science Foundation (CHE-1760918)

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690826.

References

(1) (a) Namy, J. L.; Girard, P.; Kagan, H. B. *New J. Chem.* **1977**, *1*, 5. (b) Kagan, H. B. *Tetrahedron* **2003**, *59*, 10351.
(2) (a) Nicolaou, K. C.; Ellery, S. P.; Chen, J. S. *Angew. Chem. Int. Ed.* **2009**, *48*, 7140. (b) Edmonds, D. J.; Johnston, D.; Procter, D. J. *Chem. Rev.* **2004**, *104*, 3371. (c) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 843. (d) Szostak, M.; Spain, M.; Parmar, D.; Procter, D. J. *Chem. Soc. Rev.* **2013**, *42*, 9155. (e) Procter, D. J.; Flowers, R. A. II.; Skrydstrup, T. *Organic Synthesis using Samarium Diiodide*; RSC Publishing: Cambridge, **2010**. (f) Plesniak, M. P.; Huang, H-M.; Procter, D. J. *Nat. Rev. Chem.* **2017**, *1*, 0077.
(3) (a) Enemærke, R. J.; Daasbjerg, K.; Skrydstrup, T. *Chem. Commun.* **1999**, 343. (b) Miller, R. S.; Sealy, J. M.; Shabangi, M.; Kuhlman, M. L.; Fuchs, J. R.; Flowers, R. A. II. *J. Am. Chem. Soc.* **2000**, *122*, 7718. (c) Dahlén, A.; Hilmersson, G. *Eur. J. Inorg. Chem.* **2004**, 3393. (d) Sadasivam, D. V.; Teprovich, J. A.; Procter, D. J.; Flowers, R. A. II. *Org. Lett.* **2010**, *12*, 4140.
(4) (a) Hutton, T. K.; Muir, K. W.; Procter, D. J. *Org. Lett.* **2003**, *5*, 4811. (b) Chopade, P. R.; Prasad, E.; Flowers, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 44. (c) Teprovich, J. A. Jr.; Balili, M. N.; Pintauer, T.; Flowers, R. A. II. *Angew. Chem. Int. Ed.* **2007**, *46*, 8160. (d) Amiel-Levy, M.; Hoz, S. *J. Am. Chem. Soc.* **2009**, *131*, 8280.
(5) (a) Curran, D. P.; Hasegawa, E. *J. Org. Chem.* **1993**, *58*, 5008. (b) Szostak, M.; Spain, M.; Parmar, D.; Procter, D. J. *Chem. Commun.* **2012**, *48*, 330. (c) Szostak, M.; Spain, M.; Procter, D. J. *J. Am. Chem. Soc.* **2014**, *136*, 8459.
(6) (a) Yasuko, K.; Tadahiro, K. *Chem. Lett.* **1993**, *22*, 1495. (b) Szostak, M.; Spain, M.; Procter, D. J. *Nat. Protoc.* **2012**, *7*, 970. (c) Szostak, M.; Spain, M.; Eberhart, A. J.; Procter, D. J. *J. Am. Chem. Soc.* **2014**, *136*, 2268. (d) Huang, H-M.; Procter, D. J. *J. Am. Chem. Soc.* **2016**, *138*, 7770.
(7) Berndt, M.; Hölemann, A.; Niermann, A.; Bentz, C.; Zimmer, R.; Reissig, H-U. *Eur. J. Org. Chem.* **2012**, 18093.
(8) Prasad, E.; Flowers, R. A. II. *J. Am. Chem. Soc.* **2005**, *127*, 1299.
(9) Chopade, P. R.; Prasad, E.; Flowers, R. A. II. *J. Am. Chem. Soc.* **2004**, *126*, 44.
(10) (a) Chciuk, T. V.; Anderson, W. R.; Flowers, R. A. II. *J. Am. Chem. Soc.* **2016**, *138*, 8738. (b) Chciuk, T. V.; Anderson, W. R.; Flowers, R. A. II. *J. Am. Chem. Soc.* **2018**, *140*, 15342. (c) Chciuk, T. V.; Flowers, R. A. II. *J. Am. Chem. Soc.* **2015**, *137*, 11526. (d) Kolmar, S. S.; Mayer, J. M. *J. Am. Chem. Soc.* **2017**, *139*, 10687.
(11) (a) O'Neil, G. W.; Moser, D. J.; Volz, E. O. *Tetrahedron Lett.* **2009**, *50*, 7355. (b) Volz, E. O.; O'Neil, G. W. *J. Org. Chem.* **2011**, *76*, 8428.
(12) Schaefer, S. L.; Roberts, C. L.; Volz, E. O.; Grasso, M. R.; O'Neil, G. W. *Tetrahedron Lett.* **2013**, *54*, 6125.
(13) Wright, A. M.; O'Neil, G. W. *Tetrahedron Lett.* **2016**, *57*, 3441.
(14) Stockdale, T. F.; O'Neil, G. W. *Synlett* **2017**, *28*, 2267.
(15) (a) Farran, H.; Hoz, S. *Org. Lett.* **2008**, *10*, 4875. (b) Maity, S.; Flowers, R. A. II.; Hoz, S. *Chem. Eur. J.* **2017**, *23*, 17070.
(16) Wipf, P.; Lim, S. *Angew. Chem. Int. Ed.* **1993**, *32*, 1068.
(17) Mulzer, J.; Mantoulidis, A.; Öhler, E. *J. Org. Chem.* **2000**, *65*, 7456.
(18) (a) Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748. (b) Reetz, M. T. *Acc. Chem. Res.* **1993**, *26*, 462.
(19) Keck, G. E.; Wager, C. A. *Org. Lett.* **2000**, *2*, 2307.
(20) The reaction was also performed using DMPU and H_2O together and gave the same d.r. (75:25) as that obtained when using DMPU (Table 1, entry 1) or H_2O (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.
(22) (a) Banik, B. K.; Venkatraman, M. S.; Banik, I.; Basu, M. K. *Tetrahedron Lett.* **2004**, *45*, 4737. (b) Banik, B. K.; Banik, I.; Aounallah, N.; Castillo, M. *Tetrahedron Lett.* **2005**, *46*, 7065. (c) Williams, D. B. G.; Caddy, J.; Blann, K.; Grove, J. J. C.; Holzapfel, C. W. *Synthesis* **2009**, 2009. (d) Gómez, A. M.; Uriel, C.; Company, M. D.; López, J. C. *Eur. J. Org. Chem.* **2011**, 7116. (e) Powell, J. R.; Dixon, S.; Light, M. E.; Kilburn, J. D. *Tetrahedron Lett.* **2009**, *50*, 3564. (f) Ankner, T.; Hilmersson, G. *Tetrahedron Lett.* **2007**, *48*, 5707.
(23) Corey, E. J.; Hannon, F. J.; Boaz, N. W. *Tetrahedron* **1989**, *45*, 545.
(24) Eleil, E. L.; Pillar, C. *J. Am. Chem. Soc.* **1955**, *77*, 3600.
(25) Prasad, E.; Flowers, R. A. II. *J. Am. Chem. Soc.* **2002**, *124*, 6357.
(26) Yu, W.; Zhang, Y.; Jin, Z. *Org. Lett.* **2001**, *3*, 1447.
(27) Bied, C.; Kagan, H. B. *Tetrahedron* **1992**, *48*, 3877.
(28) Hancock, R. D. *J. Chem. Educ.* **1992**, *69*, 615.
(29) Bajpai, R.; Yang, F.; Curran, D. P. *Tetrahedron Lett.* **2007**, *48*, 7965.
(30) Mousseau, J. J.; Bull, J. A.; Charette, A. B. *Angew. Chem. Int. Ed.* **2010**, *49*, 1115.
(31) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.
(32) Instead of an η^3-complex, **Sm-II** could also be considered as the 4-membered chelate **Sm-II'** (Scheme 12).



Scheme 12

(33) Kiyotsuka, Y.; Acharya, H. P.; Katayama, Y.; Hyodo, T.; Kobayashi, Y. *Org. Lett.* **2008**, *10*, 1719.
(34) Szostak, M.; Spain, M.; Procter, D. J. *J. Org. Chem.* **2012**, *77*, 3049.
(35) Spino, C.; Granger, M.-C.; Tremblay, M.-C. *Org. Lett.* **2002**, *4*, 4735.
(36) Fuerst, R.; Lentch, C.; Rinner, U. *Synthesis* **2014**, *46*, 357.

(37) Tanaka-Yanuma, A.; Watanabe, S.; Ogawa, K.; Watanabe, S.; Aoki, N.; Ogura, T.; Usuki, T. *Tetrahedron Lett.* **2015**, *56*, 6777.
(38) Fernandes, R. A.; Mulay, S. V. *J. Org. Chem.* **2010**, *75*, 7029.
(39) Udagawa, S.; Satoshi, S.; Takemura, T.; Sato, M.; Arai, T.; Nitta, A.; Takumi, A.; Kawai, K.; Iwamura, T.; Okazaki, S.; Takahashi, T.; Kaino, M. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 1617.
(40) Sanaboina, C.; Chidara, S.; Jana, S.; Eppakayala, L. *Tetrahedron Lett.* **2016**, *57*, 1767.
(41) Angle, S. R.; Bernier, D. S.; Chann, K.; Jones, D. E.; Kim, M.; Neitzel, M. L.; White, S. L. *Tetrahedron Lett.* **1998**, *39*, 8195.
(42) Mydock, L. K.; Spilling, C. D.; Demchenko, A. V. *C. R. Chim.* **2011**, *14*, 301.
(43) Yadav, J. S.; Nanda, S. *Tetrahedron: Asymmetry* **2001**, *12*, 3223.