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A Stereoconvergent Intramolecular Diels–Alder Cycloaddition Related to the Construction of the Decalin Core of *neo*-Clerodane Diterpenoids

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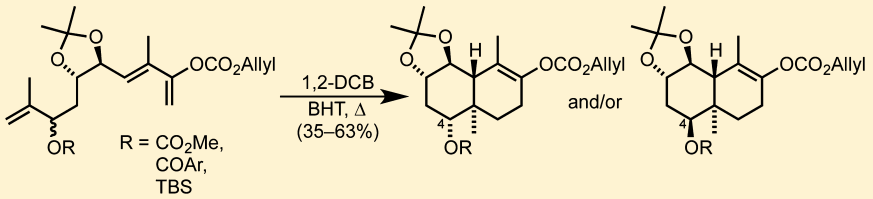
Supporting Information



ABSTRACT: Several examples of a highly specific, stereoconvergent intramolecular Diels–Alder cycloaddition that led to the *trans*-decalin core of *neo*-clerodane diterpenoids are described. The relative configuration adjacent to the dienophile, which led to C4 of the decalin system, as well as the electron-withdrawing effects of various substituents and conformational rigidity of the Diels–Alder precursors were explored.

INTRODUCTION

In recent years, chemists and biologists around the globe have shown interest in *neo*-clerodane diterpenoids[1] (NCDs, Figure 1). Much of the synthetic interest[2] stems from the unique

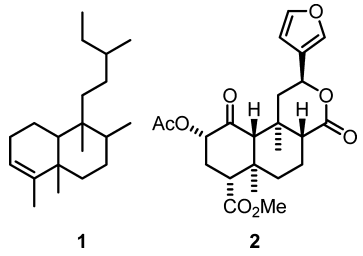
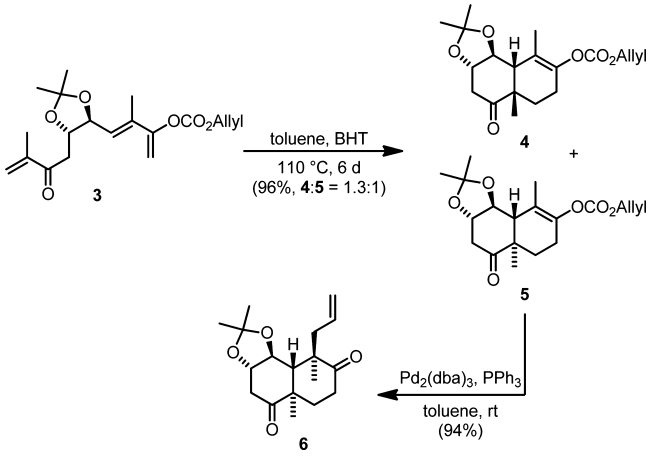


Figure 1. Carbon skeletons of *neo*-clerodane diterpenoids (**1**) and salvinorin A (**2**).

biological activity[3,4] of the selective and potent κ-opioid receptor agonist, salvinorin A (**2**),[5,6] which has led to several total syntheses[7−9] and is of interest to us as well.[10] Due to the inherent structural features of NCDs, including the position of stereogenic centers and the decalin core motif, there is no doubt that a Diels–Alder cycloaddition would prove to be a valuable tool in their construction.[1] Since its inception, the Diels–Alder reaction[11] has served as a powerful method for the synthesis of both large and small organic molecules.[12,13]

Previously, Burns and Forsyth[10] have shown that the decalin core of **2** could be prepared via an intramolecular Diels–Alder/Tsuji allylation (DATA) sequence. Since that account, the overall yield of the sequence has been improved via prolonged reaction times of the cycloaddition step (Scheme 1). Whereas

Scheme 1. Improvements in DATA Synthesis of Decalin Core of Salvinorin A



the original reaction gave complete lack of apparent endo versus exo selectivity, the prolonged reaction times had caused a slight shift in the product distribution where the undesired, *cis*-decalin **4** was now favored. This lack of selectivity in the cycloaddition reaction partly led to the exploration and determination of how the introduction of certain structural differences in **3** would affect the outcome of the intramolecular Diels–Alder reaction.

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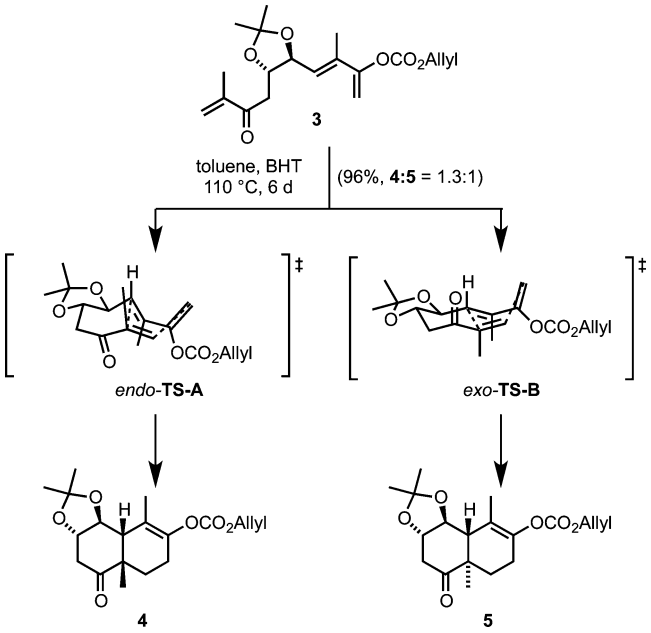
RESULTS AND DISCUSSION

To determine a plan of action with regard to the types of structural modifications necessary to improve the selectivity of the cycloaddition reaction, attention was turned toward the proposed transition states of the Diels–Alder reaction (Scheme 2). As previously noted,[10] it was likely that *cis*-decalin **4** arose

Scheme 2. Proposed Transition States in Formation of *cis*- and *trans*-Decalins 4 and 5[10]

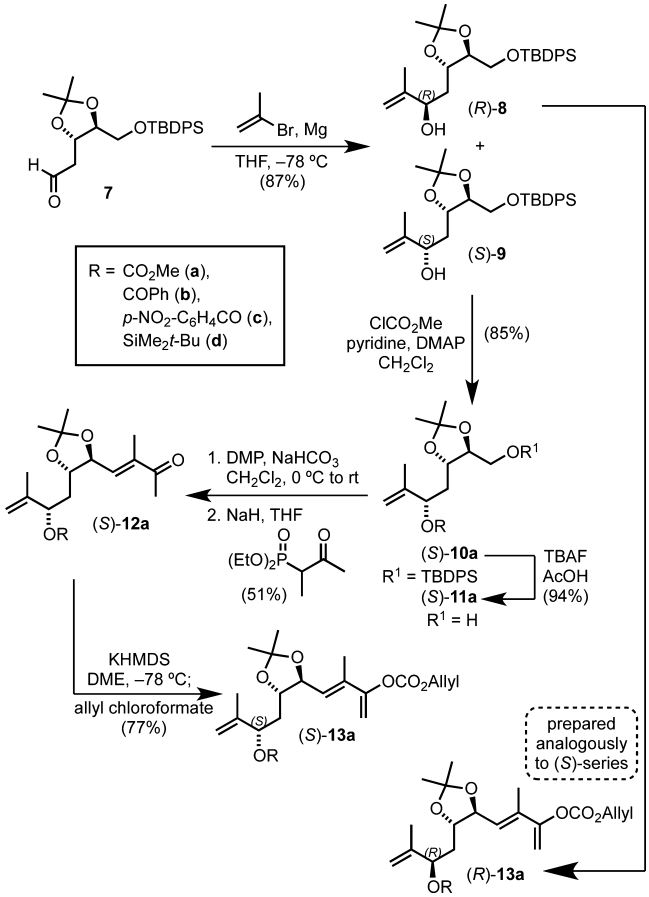


from a boatlike endo transition state A (*endo*-**TS-A**), whereas *trans*-decalin **5** was thought to originate from a chairlike exo transition state B (*exo*-**TS-B**). Apparently *endo*-**TS-A** and *exo*-**TS-B** have comparable energies, based on the product distribution, which offers an explanation of why *cis*-decalin **4** was not favored significantly over *trans*-decalin **5**. Therefore, it would be necessary to introduce structural adjustments to **3** that would guide the molecule into a transition state similar to *exo*-**TS-B** to produce a *trans*-decalin ring system.

Replacement of the dienophile enone carbonyl of **3** by introduction of a stereogenic center would ultimately allow us to determine whether configurational differences in the allylic position would affect the cycloaddition transition states and generate one product predominantly. Removal of the electron-withdrawing effect of the ketone moiety entirely would significantly reduce the reactivity toward annulation. Replacement of the ketone with an alternative electron-withdrawing group (EWG) at the allylic position would be necessary to preserve the reactivity of the molecule toward cycloaddition by retaining comparable energetics of the frontier molecular orbitals. Therefore, a methyl carbonate was initially chosen to replace the ketone functionality. It was envisioned that a methyl carbonate, a stronger EWG than a simple alcohol, would allow the cycloaddition to proceed without a drastic change in reaction conditions. This functional group manipulation would both permit a direct comparison of two diastereomeric compounds and determine whether the introduction of a specific epimer at the allylic sp^3 center would be advantageous in favoring an exo-cycloaddition.

Synthesis of the methyl carbonate substrates began with the addition of isopropenylmagnesium bromide to aldehyde **7** (Scheme 3), which was prepared from a derivative[14,15] of L-

Scheme 3. Synthesis of Diastereomeric Bis-carbonates (*S*)- and (*R*)-13a



(+)-tartaric acid. The secondary alcohols of unknown configuration were chromatographically separated, and the less polar isomer was converted into its corresponding (*S*)- and (*R*)-Mosher ester derivatives by use of (*S*)- and (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetic acids, respectively.[16,17] It was determined via advanced Mosher analysis[18] that the newly formed stereogenic center of the less polar isomer possessed the (*S*) absolute configuration. With the configurations of both isomeric alcohols established, each isomer was then functionalized analogously. Due to the similarities in chemical transformations, only the compounds that arose through the (*S*)-series will be discussed. Treatment of (*S*)-**9** with methyl chloroformate in the presence of pyridine and 4-dimethylaminopyridine (DMAP) afforded methyl carbonate (*S*)-**10a**, which was followed by the removal of the *tert*-butyldiphenylsilyl (TBDPS) group with a buffered solution of tetrabutylammonium fluoride (TBAF). Dess–Martin periodinane[19] facilitated the oxidation of primary alcohol (*S*)-**11a** to the corresponding aldehyde, which was directly transformed into enone (*S*)-**12a** via Horner–Wadsworth–Emmons (HWE) olefination with the conjugate base of diethyl (3-oxobutan-2-yl)phosphonate.[20] The Masamune modification[21] of the HWE reaction was used in an attempt to improve the yield of the olefination step. However, the use of anhydrous lithium chloride and diisopropylethylamine in acetonitrile only

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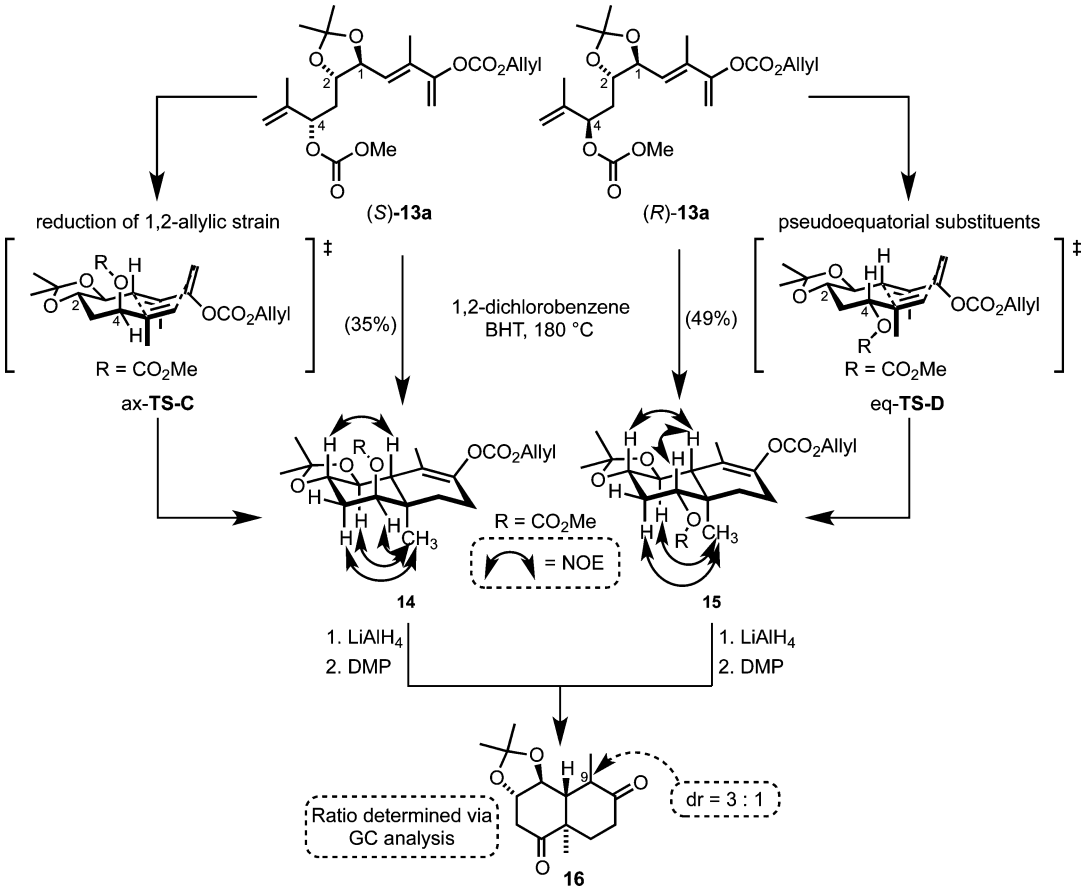
Scheme 4. Stereoconvergent IMDA Reaction of (*S*)- and (*R*)-13a



permitted isolation of (*S*)-**12a** in 46% yield. O-Acylation of the potassium enolate of (*S*)-**12a** with allyl chloroformate in dimethoxyethane (DME) completed the synthesis of bis-carbonate (*S*)-**13a** in suitable yield.

With bis-carbonates (*S*)- and (*R*)-**13a** in hand, focus turned toward the intramolecular Diels–Alder (IMDA) reactions of each isomer. As mentioned above, an electron-withdrawing carbonate was chosen to replace the ketone functionality on the dienophile to facilitate the cycloaddition; however, elevated temperatures were still required for annulation. In the event, separate heating of each allylic carbonate epimer (*S*)- and (*R*)-**13a** at 180 °C in 1,2-dichlorobenzene (DCB) in the presence of butylated hydroxytoluene (BHT) generated **14** and **15**, respectively. Each cycloadduct apparently bore the same *trans*-decalin stereochemistry and differed only in configuration at the original epimeric C4[22] centers (Scheme 4). This result was in favorable contrast to the original enone dienophile IMDA reaction that had shown little endo versus exo selectivity. The absolute configurations at C1 and C2 were known because the synthesis of **14** and **15** began from L-(+)-tartaric acid and the configurations at C4 were elucidated through advanced Mosher analysis. Consequently, two-dimensional NMR experiments (correlation and nuclear Overhauser effect spectroscopy, COSY and NOESY; Scheme 4) in combination with proton splitting and coupling constant data analyses indicated that the IMDA reaction of (*S*)- and (*R*)-**13a** led to the assembly of *trans*-decalin ring systems in both cases (**14** and **15**, respectively). Nevertheless, to further confirm these results, each cycloadduct was treated separately with lithium aluminum hydride to convert the bis-carbonates into secondary alcohols, which were subsequently oxidized to diastereomeric diones **16**, epimeric at the tertiary α-keto center C9. Gas chromatographic analysis of **16** derived from either **14** or **15** indicated the same 3:1 diastereomeric ratio. Therefore, with the combined chemical and spectral data, the complete stereochemistry of decalins **14** and **15** was assigned with confidence.

This stereoconvergent result was serendipitous, particularly in that the stereochemistry of the ring junction corresponded to that of *trans*-fused NCDs and **2**. To explain the stereospecificity of each IMDA reaction, transition states were proposed and examined for each transformation. Axial transition state C (ax-**TS-C**) and equatorial transition state D (eq-**TS-D**)[23] are most closely related to *exo*-**TS-B** in that they have been predicted to adopt chairlike conformations, versus boatlike conformations as proposed for *endo*-**TS-A**. The C4 methyl carbonate undoubtedly played a pivotal role in forcing the isopropenyl methyl group into a pseudoaxial position that ultimately led to the assembly of *trans*-decalin **14**. The fact that **14** is formed, instead of a *cis*-decalin, also suggests that the 1,2-allylic strain between the methyl carbonate and the isopropenyl methyl group would be more sterically demanding than the pseudo-1,3-diaxial interaction among the methyl groups of the [4 + 2] system. Similarly, the cycloaddition reaction of (*R*)-**13a** was also predicted to have occurred through a related transition state (eq-**TS-D**); the only difference was the opposite configuration at C4. As with ax-**TS-C**, the placement of the isopropenyl methyl substituent in a pseudoaxial orientation would also decrease the amount of 1,2-allylic strain in eq-**TS-D**, but in addition, the configuration at C4 also allowed the substituents among C1–C4 to possess a pseudoequatorial arrangement,

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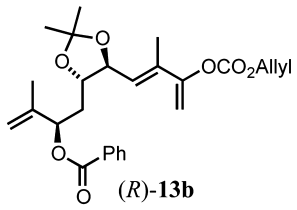
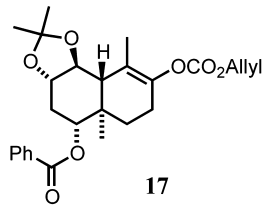
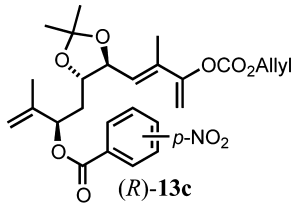
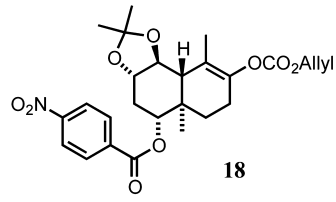
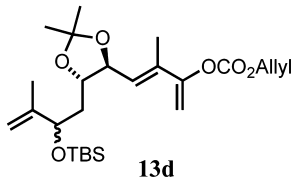
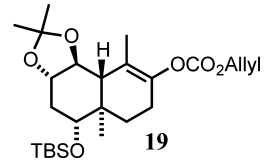
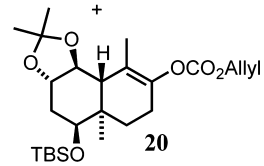
Table 1. Stereoconvergent Intramolecular Diels–Alder Cycloadditions[a]

entry	reactant(s)[a]	conditions[b]	product(s)	% yield
1	(*S*)-**13a**	180 °C, 72 h	**14**	35
2	(*R*)-**13a**	180 °C, 24 h	**15**	49
3	 (*R*)-**13b**	180 °C, 24 h	 **17**	52
4	 (*R*)-**13c**	180 °C, 24 h	 **18**	59
5[c]	 **13d**	225–250 °C 72 h	 **19** +  **20**	63

[a]Each substrate was prepared similarly from aldehyde **7**. [b]All reactions were conducted with 1,2-dichlorobenzene as the solvent and a substoichiometric amount of BHT as a radical inhibitor. [c]Reaction was performed in a sealed tube.

except the C5 methyl group. An increase in the reaction rate for cycloaddition of (*R*)-**13a** over (*S*)-**13a** was also observed. This is also likely due to the spatial arrangement of the C1–C4 substituents. Although both compounds produced *trans*-decalins, the higher-energy transition state ax-**TS-C** would be disfavored over eq-**TS-D** solely on the basis of the pseudoaxial carbonate moiety.

To improve the rate of the cyclization, the next logical step was to increase the electron-withdrawing power of the C4 substituent. Because the absolute configuration adjacent to the dienophile did not appear to affect the stereochemical outcome in the IMDA reaction, the kinetically favored (*R*)-series was explored further. The effect of aryl esters in place of the methyl carbonate substituents (Scheme 3 and Table 1, entries 3 and 4) were next examined.

The rates of cycloaddition of benzoyl esters (*R*)-**13b** and (*R*)-**13c** were similar to the previously observed cycloaddition of (*R*)-**13a**. The use of 1,2-DCB at 180 °C was still beneficial and the IMDA reactions of diastereomers (*R*)-**13b** and (*R*)-**13c** formed only the *trans*-decalin framework, but in higher yields than previously observed with (*R*)-**13a**. The *p*-nitrobenzoate of (*R*)-**13c** did not appreciably increase the rate of cyclization compared to (*R*)-**13b**. This observation suggests that the spatial arrangement of the C4 substituent and the ability of the acyclic Diels–Alder precursor to adopt the correct conformation had a greater influence on the rate than the inherent electron-withdrawing power of a given substituent. Each substituent at C4 studied thus far is electron-withdrawing. Attention was turned toward the epimeric mixture of silyl ethers **13d**, which allowed continued investigation of the effect of configuration at C4 with less electron-withdrawing substituents. Because the silyl ether was not able to lower the energy of the lowest unoccupied molecular orbital (LUMO) of the dienophile as effectively as a carbonate or ester, due to the diminution of electron-withdrawing power, higher temperatures were used to induce cyclization. The mixture of silyl ethers **13d** was reacted in a sealed tube at 225–250 °C for 72 h, which afforded *trans*-decalins **19** and **20** in 63% overall yield (Table 1, entry 5). By combining the results highlighted in Table 1, it was shown that the configuration at C4 does not affect the stereochemical outcome of decalin formation, but it does, along with the electron-withdrawing ability of the C4 substituent, have an effect on the reaction rate.

To more fully explore the reactivity of this IMDA reaction, we chose to investigate the rotational degrees of freedom of the Diels–Alder precursor. Each substrate to this point contained a cyclic isopropylidene moiety that conformationally restricts each molecule, whereas removal of the isopropylidene would allow further conformational freedom, which could effectively increase the reaction rate. It was desired to compare the

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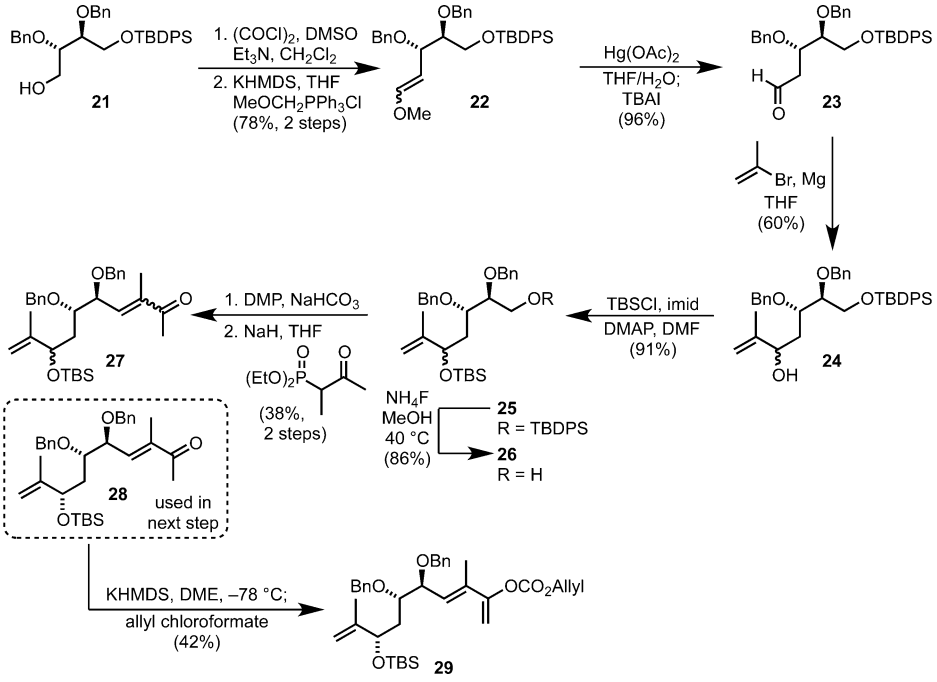
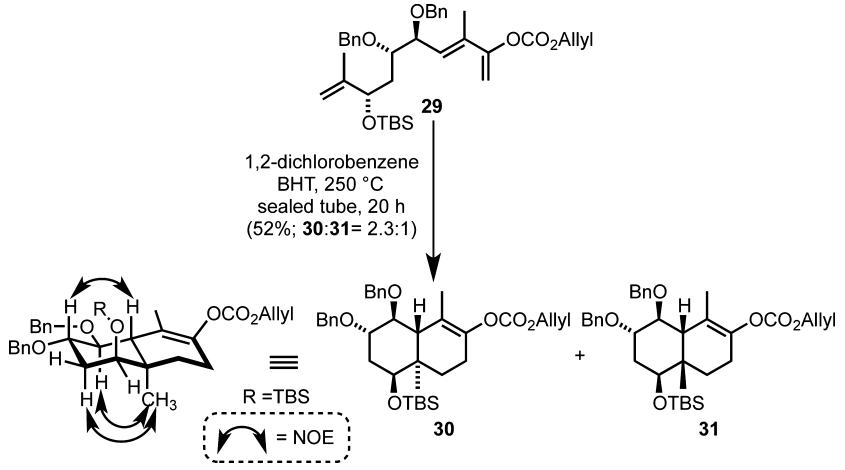
Scheme 5. Synthesis of Diels–Alder Precursor 29



Scheme 6. *trans*-Decalin-Selective IMDA Cycloaddition



reactivity of an acyclic protected C1–C2 vicinal diol with silyl ethers **13d**, as they were the most unreactive (Table 1, entry 5), and a large change in rate of cycloaddition of a different compound would be more evident. For this the isopropylidine moiety was replaced with two benzyl ethers while the *tert*-butyldimethylsilyl (TBS) ether was retained. Dibenzyl ether **29** was also synthesized from a L-(+)-tartaric acid derivative[24] in like manner to the isopropylidene substrates (Scheme 5).

Alcohol **21** was transformed into a mixture of methyl enol ethers **22** through a Swern oxidation/Wittig olefination sequence followed by the conversion to aldehyde **23** using mercuric acetate. The addition of isopropenylmagnesium bromide afforded **24**, at which point protecting group manipulations gave rise to alcohols **26**. The conversion of **26** to enone **27** revealed a complex mixture of diastereomers, which was not seen before with the HWE olefinations that yielded enones **12a–d**. However, enone **28** could be isolated from the mixture and was converted to **29** via O-acylation with the use of potassium bis(trimethylsilyl)amide and allyl chloroformate. At this point the configuration at C4 was unknown, but the Diels–Alder cycloaddition of **29** allowed the elucidation of the C4 stereocenter. When **29** was submitted to the same reaction conditions as **13d**, the cycloaddition was complete in 20 h, an almost 4-fold increase in rate (Scheme 6). However, this reaction was less efficient and stereoselective than had been seen previously, but it did still show *trans*-decalin selectivity. The cycloaddition of **29** gave a 40% yield of exo cycloaddition product **30** and a 12% yield of endo product **31**, compared to 63% combined yield of exo products **19** and **20** from the acetonide precursor **13d** (Table 1). This can be attributed to the acyclic vicinal diol benzyl ether protection array of **29** significantly lowering the energies, relative to those of the cyclic acetonide **13d**, of both endo and exo transition states, leading to **30** and **31** via conformational relaxation. The relative energetic difference between the endo and exo transition states is greater for the conformationally more rigid acetonide substrate **13d** than it is for the conformationally relaxed vicinal diol benzyl ether **29**.

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CONCLUSION

It has been demonstrated that the customization and tailoring of organic substrates indeed still has an important role in organic synthesis. It was determined here that either relative configuration at C4 would direct the construction of the *trans*-fused decalin motif, but it was advantageous to reduce the conformational freedom of the substrate through the use of a cyclic isopropylidene to observe complete *trans*-decalin formation in the cycloaddition. It was also realized that C4 substituents that occupy a pseudoequatorial position during the cycloaddition led to an increased rate of reaction. The increased rate of cycloaddition was even more apparent due to the greater electron-withdrawing power of the C4 substituent. In conclusion, the relative configuration adjacent to the dienophile, the conformational rigidity of the substrate, and the electron-withdrawing ability of the C4 substituent each played an integral part in the rate and stereoconvergence of the IMDA cycloadditions leading to functionalized decalin cores, which are prominent structural elements in a wide range of natural and biologically active compounds. The continued development of this chemistry will enable the synthesis of *neo*-clerodane diterpenoids (**1**), such as salvinorin A (**2**).

EXPERIMENTAL SECTION

General Methods. Unless otherwise stated, all oxygen- and moisture-sensitive reactions were performed under anhydrous conditions (oven-dried glassware sealed under a dry argon atmosphere). Solutions and solvents sensitive to moisture were transferred via standard syringe and cannula techniques. All commercial reagents were purchased as reagent grade and, unless otherwise noted, were used without further purification. All organic solvents were used dry: tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene were purified via a solvent purification system; triethylamine (Et_3N), diisopropylamine, and diisopropylethylamine (DIPEA) were distilled from CaH_2; dimethyl sulfoxide (DMSO) was stored over freshly activated 4 Å molecular sieves; and 1,2-dimethoxyethane (DME) was distilled from sodium benzophenone ketyl. Thin-layer chromatography was performed on glass-backed thin-layer chromatography (TLC) extra hard layer 60 Å, 250 μm, F-254 plates that were visualized via UV light (254 nm) or by *p*-anisaldehyde (PAA), phosphomolybdic acid (PMA), or ceric ammonium molybdate (CAM) stains and the column chromatographic separations were performed by use of silica gel (40−63 μm). Melting points were measured on a capillary melting point apparatus. Optical rotations were measured by a polarimeter at 589 nm with a sodium lamp and concentrations are reported in grams per 100 mL. Nuclear magnetic resonance (NMR) spectra were obtained for proton (^{1}H) and carbon (^{13}C) nuclei on 400 and 500 MHz spectrometers; residual solvent peak signals for $CDCl_3$ were set at 7.26 and 77.16 ppm in the ^{1}H and ^{13}C spectra, respectively. A Fourier transform infrared (FT-IR) spectrometer was used to record infrared spectra and absorptions are reported in reciprocal centimeters. High-resolution mass spectrometric data were obtained on a time-of-flight (TOF) electrospray ionization (ESI) mass spectrometer.

*Allyl {(3aS,5aS,9aR,9bS)-2,2,5a,9-Tetramethyl-5-oxo-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-d][1,3]dioxol-8-yl} Carbonate (**4**) and Allyl {(3aS,5aR,9aR,9bS)-2,2,5a,9-Tetramethyl-5-oxo-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-d][1,3]dioxol-8-yl} Carbonate (**5**).* Enol carbonate **3** (159.3 mg, 0.455 mmol) was dissolved in toluene (45 mL), and butylated hydroxytoluene (9.9 mg, 0.045 mmol) was added. The reaction mixture was warmed at 110 °C for 6 days before concentration under reduced pressure. The resulting residue was purified via flash chromatography on silica gel (10:1 hexanes/EtOAc, v/v) to afford *cis*-fused isomer **4** (44.6 mg, 28%) as a white solid and *trans*-fused isomer **5** (59.4 mg, 37%) as a colorless oil, as well as a mixture of the two isomers (49.2 mg, 31%, **4**:**5** = 7.5:1). Supplemental purification of the mixture via recrystallization from 95% ethanol facilitated the removal of **4** from **5**;

Spectral Data for cis-Fused Decalin 4 (Endo Product). R_f 0.42 (4:1 hexanes/EtOAc, v/v); mp 95−98 °C; $[\alpha]_D^{23}$ +23.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (dddd, *J* = 16.8, 10.4, 5.6, 5.6 Hz, 1H), 5.42−5.35 (m, 1H), 5.32−5.28 (m, 1H), 4.66 (d, *J* = 5.6 Hz, 2H), 3.72 (dd, *J* = 10.4, 9.2 Hz, 1H), 3.60 (ddd, *J* = 13.6, 8.8, 4.4 Hz, 1H), 2.89 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.72 (t, *J* = 14.4 Hz, 1H), 2.44−2.31 (m, 1H), 2.20 (dd, *J* = 17.2, 6.4 Hz, 1H), 2.09 (d, *J* = 10.4 Hz, 1H), 2.00 (ddd, *J* = 12.4, 12.4, 6.8 Hz, 1H), 1.75 (s, 3H), 1.46 (s, 3H), 1.44 (s, 3H), 1.41−1.36 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 209.1, 153.3, 142.4, 131.9, 121.8, 118.5, 111.0, 83.0, 77.0, 68.6, 47.9, 47.1, 42.8, 29.3, 27.3, 27.2, 23.3, 20.0, 16.2; IR (thin film) 2984, 2934, 1752, 1707, 1380, 1240 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{19}H_{26}NaO_6$ $[M + Na]^+$ calcd 373.1622, obsd 373.1617.

Spectral Data for trans-Fused Decalin 5 (Exo Product). R_f 0.44 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ +49.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (dddd, *J* = 17.2, 10.4, 6.0, 6.0 Hz, 1H), 5.38 (dddd, *J* = 17.2, 1.6, 1.6, 1.6 Hz, 1H), 5.29 (dddd, *J* = 10.4, 0.8, 0.8, 0.8 Hz, 1H), 4.66 (d, *J* = 5.6 Hz, 2H), 3.92 (dd, *J* = 11.2, 8.4 Hz, 1H), 3.50 (ddd, *J* = 13.4, 8.4, 5.2 Hz, 1H), 3.02 (t, *J* = 13.6 Hz, 1H), 2.81 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.57−2.50 (m, 1H), 2.33−2.24 (m, 2H), 2.00 (ddd, *J* = 14.0, 6.4, 2.8 Hz, 1H), 1.79−1.73 (m, 3H), 1.69−1.59 (m, 1H), 1.47 (s, 3H), 1.43 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 153.2, 142.3, 131.5, 120.7, 119.2, 111.0, 79.1, 77.4, 68.9, 47.8, 44.3, 41.6, 29.6, 27.12, 27.1, 24.0, 17.7, 14.0; IR (neat) 2987, 2936, 1751, 1718, 1376, 1239 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{19}H_{26}NaO_6$ $[M + Na]^+$ calcd 373.1622, obsd 373.1627.

*(3aS,5aR,9R,9aS,9bS)-9-Allyl-2,2,5a,9-tetramethylhexahydronaphtho[1,2-d][1,3]dioxole-5,8(5aH,9bH)-dione (**6**).* Tris(dibenzylideneacetone)dipalladium (12.5 mg, 13.7 μmol) and triphenylphosphine (35.9 mg, 0.137 mmol) were dissolved in toluene (13.7 mL) under an argon atmosphere and stirred at room temperature (rt) until the solution became yellow in color. Enol carbonate **5** (96.3 mg, 0.275 mmol) in toluene (1.3 mL) was added to the resultant solution via cannula, and the mixture was stirred for 1 h at rt. The solvent was removed in vacuo and the crude material was purified via flash chromatography on silica gel (6:1 hexanes/EtOAc, v/v) to afford **6** (79.3 mg, 94%); R_f 0.33 (4:1 hexanes/EtOAc, v/v); mp 69−70 °C; $[\alpha]_D^{23}$ −25.6 (*c* 0.515, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (dddd, *J* = 14.8, 9.6, 8.4, 6.4 Hz, 1H), 5.12−4.96 (m, 2H), 3.95 (dd, *J* = 11.6, 8.8 Hz, 1H), 3.60−3.50 (m, 1H), 2.92−2.82 (m, 2H), 2.54−2.40 (m, 4H), 2.28 (d, *J* = 11.6 Hz, 1H), 2.00−1.85 (m, 2H), 1.49 (s, 3H), 1.44 (s, 3H), 1.32 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.0, 209.1, 134.1, 119.6, 111.2, 77.8, 77.5, 50.3, 47.7, 45.9, 44.7, 42.5, 35.1, 30.6, 27.1, 27.0, 21.7, 19.7; IR (thin film) 2985, 2935, 1708, 1702, 1382, 1234, 1114 cm^{-1}; HRMS (ESI) for $C_{18}H_{26}NaO_4$ $[M + Na]^+$ calcd 329.1723, obsd 329.1732.

*(R)-1-[(4S,5S)-5-{[(tert-Butyldiphenylsilyl)oxy]methyl}-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-ol [(R)-**8**] and (S)-1-[(4S,5S)-5-{[(tert-Butyldiphenylsilyl)oxy]methyl}-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-ol [(S)-**9**].* Freshly prepared isopropenylmagnesium bromide (13.2 mL, 5.94 mmol, 0.45 M solution in THF) was added dropwise to a −78 °C solution of aldehyde **7** (1.22 g, 2.96 mmol) in THF (2 mL) over 2 h. After complete addition, the reaction mixture was warmed to rt and stirred an additional 1 h before a saturated solution of NH_4Cl (15 mL) was added. The mixture was partitioned between water (15 mL) and EtOAc (10 mL), and the layers were separated. The aqueous portion was extracted with EtOAc (3 × 30 mL) and the organic extracts were combined, dried ($MgSO_4$), and concentrated. Purification via flash chromatography on silica gel (9:1 to 7:1 hexanes/EtOAc, v/v) provided a diastereomeric mixture of alcohols (*R*)-**8** and (*S*)-**9** (1.18 g, 87%) as a colorless oil. In order to obtain spectral data for each isomer, an analytical sample was purified (8:1 hexanes/EtOAc, v/v) and the following data were collected. (Absolute configurations were determined via advanced Mosher ester analysis.)

*Spectral Data for (R)-**8**.* R_f 0.50 (7:1 hexanes/EtOAc, eluted three times); $[\alpha]_D^{23}$ −2.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.63 (m, 4H), 7.47−7.35 (m, 6H), 5.06−5.02 (m, 1H), 4.88−

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4.84 (m, 1H), 4.28 (dd, J = 9.6, 3.2 Hz, 1H), 4.12 (ddd, J = 9.6, 7.2, 2.4 Hz, 1H), 3.87−3.71 (m, 4H), 3.15 (br s, 1H), 1.93 (dt, J = 14.4, 3.2 Hz, 1H), 1.74 (s, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 135.74 (2C), 135.73 (2C), 133.20, 133.15, 130.00, 129.97, 127.9 (4C), 111.1, 109.5, 81.4, 79.0, 75.1, 64.1, 39.3, 27.4, 27.1, 27.0 (3C), 19.4, 18.1; IR (neat) 3485, 2930, 2857, 1428, 1379, 1246, 1216, 1112 cm^{-1}; HRMS (ESI) m/z for $C_{27}H_{38}NaO_4Si$ $[M + Na]^+$ calcd 477.2432, obsd 477.2434.

*Spectral Data for (S)-**9**.* R_f 0.59 (7:1 hexanes/EtOAc, eluted three times); $[\alpha]_D^{23}$ −14.6 (c 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.65 (m, 4H), 7.46−7.36 (m, 6H), 5.07−5.03 (m, 1H), 4.89 (s, 1H), 4.35−4.28 (br m, 1H), 4.23 (ddd, J = 8.4, 8.4, 3.2 Hz, 1H), 3.86−3.78 (m, 2H), 3.77−3.70 (m, 1H), 2.65 (d, J = 5.2 Hz, 1H), 1.98−1.90 (m, 1H), 1.85−1.77 (m, 1H), 1.73 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 135.79 (2C), 135.77 (2C), 133.3, 133.2, 130.0, 129.9, 127.89 (2C), 127.87 (2C), 110.7, 109.0, 80.8, 76.3, 72.8, 64.3, 37.8, 27.5, 27.1, 27.0 (3C), 19.4, 18.7; IR (neat) 3484, 2931, 2858, 1960, 1896, 1845, 1473, 1428, 1379, 1247, 1218, 1113 cm^{-1}; HRMS (ESI) m/z for $C_{27}H_{38}NaO_4Si$ $[M + Na]^+$ calcd 477.2432, obsd 477.2419.

*(R)-(S)-1-[(4S,5S)-5-{[(tert-Butyldiphenylsilyl)oxy]methyl}-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-yl-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(R)-Mosher Ester of (S)-**9**] and (S)-(S)-1-[(4S,5S)-5-{[(tert-Butyldiphenylsilyl)oxy]methyl}-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-yl-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate [(S)-Mosher Ester of (S)-**9**].* Dicyclohexylcarbodiimide (28.1 mg, 0.136 mmol) and DMAP (16.6 mg, 0.136 mmol) were added to a solution of (S)-**9** (20.0 mg, 0.044 mmol) and (R)-α-methoxy-α-trifluoromethylphenylacetic acid [(R)-MTPA-OH] (31.8 mg, 0.136 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred at rt for 4 days before it was filtered through a cotton plug to remove the solid byproducts, and the solvent was removed under reduced pressure. The residue was purified via flash chromatography on silica gel (20:1 hexanes/EtOAc, v/v) to yield the (R)-Mosher ester of (S)-**9** as a colorless oil (27.6 mg, 94%); R_f 0.23 (20:1 hexanes/EtOAc, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.61 (m, 4H), 7.55−7.51 (m, 2H), 7.45−7.39 (m, 3H), 7.38−7.33 (m, 6H), 5.57 (dd, J = 10.8, 2.8 Hz, 1H), 5.04 (s, 1H), 4.95 (t, J = 1.6 Hz, 1H), 4.02 (ddd, J = 10.0, 7.6, 2.4 Hz, 1H), 3.78 (dd, J = 10.0, 4.0 Hz, 1H), 3.74−3.68 (m, 1H), 3.63 (dd, J = 10.0, 6.0 Hz, 1H), 3.54 (d, J = 1.2 Hz, 3H), 2.19 (ddd, J = 14.4, 11.2, 2.4 Hz, 1H), 1.75 (ddd, J = 14.4, 10.4, 3.2 Hz, 1H), 1.66 (s, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.02 (s, 9H); HRMS (ESI) m/z for $C_{37}H_{45}F_3NaO_6Si$ $[M + Na]^+$ calcd 693.2830, obsd 693.2844.

In a similar fashion, the (S)-MTPA ester of (S)-**9** was prepared with (S)-MPTA-OH; R_f 0.16 (20:1 hexanes/EtOAc, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.61 (m, 4H), 7.55−7.50 (m, 2H), 7.45−7.32 (m, 9H), 5.64 (dd, J = 10.8, 2.8 Hz, 1H), 5.14 (s, 1H), 5.00 (t, J = 1.6 Hz, 1H), 3.75−3.70 (m, 1H), 3.69−3.62 (m, 2H), 3.53 (d, J = 1.2 Hz, 3H), 3.50 (dd, J = 10.4, 6.4 Hz, 1H), 2.18 (ddd, J = 13.2, 10.8, 2.0 Hz, 1H), 1.76−1.71 (m, 4H), 1.38 (s, 3H), 1.29 (s, 3H), 1.03 (s, 9H); HRMS (ESI) m/z for $C_{37}H_{45}F_3NaO_6Si$ $[M + Na]^+$ calcd 693.2830, obsd 693.2828.

*(S)-1-[(4S,5S)-5-{[(tert-Butyldiphenylsilyl)oxy]methyl}-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-yl Methyl Carbonate [(S)-**10a**].* Methyl chloroformate (1.36 mL, 17.6 mmol) was added dropwise over 2 h to a 0 °C solution of alcohol (S)-**9** (400 mg, 0.880 mmol), pyridine (2.14 mL, 26.4 mmol), and a catalytic amount of DMAP in CH_2Cl_2 (8.8 mL), and the mixture was stirred at rt for 18 h. The reaction mixture was cooled to 0 °C, additional methyl chloroformate (1.0 mL, 13.2 mmol) was added, and the mixture was stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl and the mixture was extracted with EtOAc (3 × 15 mL). The combined extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purification via flash chromatography on silica gel (20:1 hexanes/EtOAc, v/v) gave (S)-**10a** as a colorless oil (383.1 mg, 85%); R_f 0.19 (15:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −18.8 (c 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.69 (m, 4H), 7.47−7.38 (m, 6H), 5.27 (dd, J = 10.4, 2.4 Hz, 1H), 5.09 (s, 1H), 4.95 (t, J = 1.6 Hz, 1H), 4.14 (ddd, J = 9.6, 7.2, 2.0 Hz, 1H), 3.83−3.72 (m, 6H), 2.10 (ddd, J = 14.4, 10.4, 2.4 Hz, 1H), 1.83−1.75 (m, 4H), 1.40 (s, 3H), 1.39 (s, 3H), 1.90 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 143.4, 135.8 (2C), 135.75 (2C), 133.2, 133.1, 129.9, 129.8, 127.9 (2C), 127.8 (2C), 113.1, 109.0, 81.0, 78.5, 75.1, 64.1, 54.7, 37.7, 27.5, 27.0, 26.9 (3C), 19.3, 18.1; IR (neat) 3051, 2933, 2860, 1965, 1900, 1755, 1442, 1380, 1266, 1113, 1085 cm^{-1}; HRMS (ESI) m/z for $C_{29}H_{40}NaO_6Si$ $[M + Na]^+$ calcd 535.2486, obsd 535.2497.

*(S)-1-[(4S,5S)-5-(Hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-yl Methyl Carbonate [(S)-**11a**].* Silyl ether (S)-**10a** (138.5 mg, 0.270 mmol) was taken up in THF (2.7 mL), and a 1:1 equimolar mixture of TBAF/AcOH (0.85 mL, 0.810 mmol, 0.95 M solution in THF) was added. The reaction mixture was stirred at rt for 2 h before immediate concentration in vacuo. The resulting material was purified via flash chromatography on silica gel (4:1 to 1:1 hexanes/EtOAc, v/v) to give alcohol (S)-**11a** (69.8 mg, 94%) as a slightly opaque oil; R_f 0.10 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −42.5 (c 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (dd, J = 10.0, 3.2 Hz, 1H), 5.04 (m, 1H), 4.94−4.91 (m, 1H), 4.00−3.94 (m, 1H), 3.79−3.73 (m, 5H), 3.65−3.58 (m, 1H), 2.00 (br s, 1H), 1.95 (ddd, J = 14.4, 10.0, 3.2 Hz, 1H), 1.82 (ddd, J = 14.4, 8.8, 3.2 Hz, 1H), 1.75 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 143.1, 113.3, 109.3, 81.6, 78.5, 73.7, 62.0, 54.8, 37.5, 27.5, 27.2, 18.1; IR (neat) 3489, 2988, 1752, 1444, 1380, 1270 cm^{-1}; HRMS (ESI) m/z for $C_{13}H_{22}NaO_6$ $[M + Na]^+$ calcd 297.1309, obsd 297.1298.

*(S)-1-{(4S,5S)-2,2-Dimethyl-5-[(E)-2-methyl-3-oxobut-1-en-1-yl]-1,3-dioxolan-4-yl}-3-methylbut-3-en-2-yl Methyl Carbonate [(S)-**12a**].* Alcohol (S)-**11a** (96.4 mg, 0.351 mmol) was dissolved in CH_2Cl_2 (3.5 mL) and cooled to 0 °C. Sodium bicarbonate (442.7 mg, 5.27 mmol) was added, followed by Dess−Martin periodinane (223.5 mg, 0.527 mmol) and the reaction mixture was warmed to rt and stirred for 2.5 h. The reaction was quenched by the addition of saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$. The mixture was stirred vigorously for 20 min and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 15 mL), and the combined extracts were dried over $MgSO_4$ and concentrated. The residue was used in the next step with no further purification. A solution of 3-oxobutan-2-ylphosphonate (153.4 mg, 0.737 mmol) in THF (1.1 mL) was added to a slurry of NaH (28.1 mg, 0.702 mmol, 60% in oil) in THF (1.4 mL) at 0 °C, and the mixture was stirred for 1 h. Freshly prepared aldehyde in THF (1.1 mL) was introduced via cannula and the reaction mixture was warmed to rt and stirred for 14 h before being quenching with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined extracts were dried and concentrated in vacuo. Purification via flash chromatography on silica gel (6:1 hexanes/EtOAc, v/v) furnished enone (S)-**12a** (58.6 mg, 51% over two steps) as a colorless oil; $[\alpha]_D^{23}$ −11.6 (c 1.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45−6.40 (m, 1H), 5.17 (dd, J = 9.2, 4.0 Hz, 1H), 5.03 (s, 1H), 4.96−4.93 (m, 1H), 4.48 (dd, J = 8.0, 8.0 Hz, 1H), 3.89 (ddd, J = 8.4, 8.4, 4.4 Hz, 1H), 3.76 (s, 3H), 2.35 (s, 3H), 1.91−1.86 (m, 2H), 1.85 (d, J = 1.2 Hz, 3H), 1.75 (s, 3H), 1.45 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 155.1, 143.0, 141.4, 137.2, 113.5, 109.9, 78.3, 77.9, 77.3, 54.9, 36.2, 27.4, 27.2, 25.8, 18.1, 12.2; IR (neat) 2992, 2928, 1753, 1678, 1443, 1372, 1269, 1049 cm^{-1}; HRMS (ESI) m/z for $C_{17}H_{26}NaO_6$ $[M + Na]^+$ calcd 349.1622, obsd 349.1631.

*Dicarbonate (S)-**13a**.* Enone (S)-**12a** (58.6 mg, 0.180 mmol) in DME (0.6 mL) was added slowly to a −78 °C solution of potassium bis(trimethylsilyl)amide (KHMDS; 43.1 mg, 0.216 mmol) in DME (1.8 mL), and the mixture was stirred for 5 min prior to the introduction of neat allyl chloroformate (76.5 μL, 0.720 mmol). The reaction mixture was then warmed to 0 °C and stirred for 1 h before the addition of saturated aqueous NH_4Cl (3 mL). The mixture was extracted with EtOAc (3 × 5 mL), the combined organic extracts were dried over $MgSO_4$, and the volatiles were removed under reduced pressure. Purification via flash chromatography on silica gel (9:1 hexanes/EtOAc, v/v) yielded dicarbonate (S)-**13a** (56.6 mg, 77%) as a colorless oil; R_f 0.35 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −16.6 (c 1.18, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (dddd, J = 17.2, 10.4, 6.0, 6.0 Hz, 1H), 5.73 (d, J = 8.8 Hz, 1H), 5.40 (dd, J = 17.2, 1.2 Hz, 1H), 5.30 (dd, J = 10.4, 0.8 Hz, 1H), 5.20−5.12 (m, 2H), 5.05 (d, J = 2.0 Hz, 1H), 5.02 (s, 1H), 4.92 (m, 1H), 4.69 (m, 2H), 4.41 (dd, J =

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8.4, 8.4 Hz, 1H), 3.82−3.77 (m, 1H), 3.76 (s, 3H), 1.92 (d, J = 0.8 Hz, 3H), 1.89−1.79 (m, 2H), 1.74 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 153.9, 153.0, 143.0, 133.7, 131.4, 124.5, 119.4, 113.5, 109.2, 103.7, 78.3, 77.7, 77.3, 69.1, 54.8, 36.0, 27.4, 27.2, 18.1, 14.1; IR (neat) 1754, 1444, 1269, 1223 cm^{-1}; HRMS (ESI) m/z for $C_{21}H_{30}NaO_8$ [M + Na]$^+$ calcd 433.1833, obsd 433.1820.

*(R)-1-[(4S,5S)-5-{[(tert-Butyldiphenylsilyl)oxy]methyl}-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-yl Methyl Carbonate [(R)-**10a**].* Methyl chloroformate (1.3 mL, 17.1 mmol) was added dropwise over 2 h to a 0 °C solution of alcohol (*R*)-**8** (388.9 mg, 0.855 mmol), pyridine (2.1 mL, 25.7 mmol), and a catalytic amount of DMAP in CH_2Cl_2 (8.5 mL). The reaction mixture was stirred for 2 h at 0 °C, the reaction was quenched by addition of saturated aqueous NH_4Cl (5 mL), and the mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined extracts were dried over $MgSO_4$ and the volatiles were removed in vacuo. The material was purified via flash chromatography (20:1 to 10:1 hexanes/EtOAc, v/v) to afford methyl carbonate (*R*)-**10a** (369.1 mg, 84%) as a colorless oil; R_f 0.17 (15:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −7.2 (*c* 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.65 (m, 4H), 7.47−7.36 (m, 6H), 5.31 (dd, J = 7.2, 7.2 Hz, 1H), 5.13−5.11 (m, 1H), 5.04−5.01 (m, 1H), 4.02 (ddd, J = 7.2, 7.2, 4.4 Hz, 1H), 3.81−3.70 (m, 6H), 2.06−1.99 (m, 2H), 1.76 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 142.0, 135.7 (4C), 133.23, 133.2, 129.93, 129.9, 127.9 (2C), 127.8 (2C), 114.9, 109.0, 81.9, 79.5, 75.5, 64.1, 54.7, 36.3, 27.5, 27.0, 26.9 (3C), 19.3, 17.7; IR (neat) 3074, 2933, 2860, 1752, 1442, 1269, 1113, 1080 cm^{-1}; HRMS (ESI) m/z for $C_{29}H_{40}NaO_6Si$ [M + Na]$^+$ calcd 535.2486, obsd 535.2490.

*(R)-1-[(4S,5S)-5-(Hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-yl Methyl Carbonate [(R)-**11a**].* An equimolar (1:1) mixture of TBAF/AcOH in THF (0.38 mL, 0.360 mmol, 0.95 M solution in THF) was added to a rt solution of silyl ether (*R*)-**10a** (61.4 mg, 0.120 mmol) in THF (1.2 mL), and the mixture was stirred for 1.5 h. The mixture was concentrated under reduced pressure and the oil was purified via flash chromatography on silica gel (2:1 to 1:1 hexanes/EtOAc, v/v) to furnish alcohol (*R*)-**11a** (31.2 mg, 95%) as a slightly opaque oil; R_f 0.11 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −13.2 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (t, J = 6.8 Hz, 1H), 5.08 (m, 1H), 5.00−4.97 (m, 1H), 3.89 (ddd, J = 8.0, 8.0, 4.0 Hz, 1H), 3.82−3.74 (m, 5H), 3.65−3.58 (m, 1H), 2.04 (ddd, J = 14.0, 8.0, 6.8 Hz, 1H), 1.97 (br s, 1H), 1.89 (ddd, J = 14.4, 7.6, 4.0 Hz, 1H), 1.74 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 141.6, 114.8, 108.9, 81.2, 78.9, 73.7, 61.7, 54.7, 35.8, 27.3, 26.9, 17.6; IR (neat) 3512, 2988, 1752, 1444, 1381, 1271, 1069 cm^{-1}; HRMS (ESI) m/z for $C_{13}H_{22}NaO_6$ [M + Na]$^+$ calcd 297.1309, obsd 297.1310.

*(R)-1-{(4S,5S)-2,2-Dimethyl-5-[(E)-2-methyl-3-oxobut-1-en-1-yl]-1,3-dioxolan-4-yl}-3-methylbut-3-en-2-yl Methyl Carbonate [(R)-**12a**].* A solution of alcohol (*R*)-**11a** (182.5 mg, 0.665 mmol) in CH_2Cl_2 (6.6 mL) was cooled to 0 °C before addition of $NaHCO_3$ (838.4 mg, 9.98 mmol) and Dess−Martin periodinane (423.3 mg, 0.998 mmol). The cold bath was removed and the reaction mixture was stirred at rt for 3 h, after which saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ were added and the mixture was stirred vigorously for 30 min. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the organic extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude aldehyde was taken to the next step with no further purification. A solution of 3-oxobutan-2-ylphosphonate (291.5 mg, 1.40 mmol) in THF (2.0 mL) was added dropwise to a 0 °C slurry of sodium hydride (53.2 mg, 1.33 mmol, 60% in oil) in THF (2.7 mL). The reaction mixture stirred for 1 h at 0 °C and became transparent as all the NaH was consumed. A solution of freshly prepared aldehyde in THF (2.0 mL) was added via cannula and the cold bath was removed. The reaction mixture was stirred at rt for 14 h and then saturated aqueous NH_4Cl (10 mL) was added, followed by extraction with EtOAc (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. Purification via flash chromatography (6:1 hexanes/EtOAc, v/v) afforded enone (*R*)-**12a** (109.7 mg, 51% over two steps) as a colorless oil; R_f 0.29 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −10.4 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42−6.37 (m, 1H), 5.19 (app t, J = 7.2 Hz, 1H), 5.07−5.04 (m, 1H), 4.99−4.97 (m, 1H), 4.51 (app t, J = 8.4 Hz, 1H), 3.79−3.74 (m, 4H), 2.34 (s, 3H), 2.10−2.02 (m, 1H), 1.87 (d, J = 1.2 Hz, 3H), 1.82 (ddd, J = 11.2, 6.8, 4.0 Hz, 1H), 1.71 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 197.8, 155.4, 142.5, 141.1, 137.0, 114.6, 109.7, 78.6, 78.0, 77.8, 54.3, 35.1, 27.4, 27.1, 25.2, 17.7, 12.3; IR (neat) 2982, 2928, 1752, 1678, 1444, 1372, 1269, 1059 cm^{-1}; HRMS (ESI) m/z for $C_{17}H_{26}NaO_6$ [M + Na]$^+$ calcd 349.1622, obsd 349.1625.

*Dicarbonate (R)-**13a**.* Enone (*R*)-**12a** (50.0 mg, 0.153 mmol) in DME (1.5 mL) was added slowly to a −78 °C solution of KHMDS (36.7 mg, 0.184 mmol) in DME (0.5 mL) and stirred for 5 min prior to the introduction of neat allyl chloroformate (65.0 μL, 0.612 mmol). The reaction mixture was then warmed to 0 °C and stirred for 1 h before the addition of saturated aqueous NH_4Cl (5 mL). The mixture was extracted with EtOAc (3 × 10 mL), and the combined organic extracts were dried over $MgSO_4$ and the volatiles were removed under reduced pressure. Purification via flash chromatography on silica gel (9:1 hexanes/EtOAc, v/v) yielded dicarbonate (*R*)-**13a** (43.2 mg, 69%) in the form of a colorless oil; R_f 0.16 (9:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −18.5 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (dddd, J = 16.4, 10.4, 6.0, 6.0 Hz, 1H), 5.68 (d, J = 8.8 Hz, 1H), 5.39 (dd, J = 17.2, 1.6 Hz, 1H), 5.29 (dd, J = 10.4, 1.2 Hz, 1H), 5.20 (app t, J = 7.2 Hz, 1H), 5.14 (d, J = 2.4 Hz, 1H), 5.06 (s, 1H), 5.03 (d, J = 2.4 Hz, 1H), 4.99−4.95 (m, 1H), 4.67 (d, J = 6.0 Hz, 2H), 4.44 (dd, J = 8.8, 8.8 Hz, 1H), 3.75 (s, 3H), 3.63 (ddd, J = 8.4, 8.4, 3.6 Hz, 1H), 2.10−1.93 (m, 1H), 1.91 (d, J = 0.8 Hz, 3H), 1.80 (ddd, J = 14.0, 7.6, 3.6 Hz, 1H), 1.70 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 153.9, 153.0, 141.8, 133.5, 131.4, 124.4, 119.4, 115.1, 109.3, 103.7, 79.1, 77.6, 77.4, 69.1, 54.8, 34.4, 27.4, 27.1, 17.5, 14.1; IR (neat) 2986, 2928, 1762, 1752, 1270, 1224 cm^{-1}; HRMS (ESI) m/z for $C_{21}H_{30}NaO_8$ [M + Na]$^+$ calcd 433.1833, obsd 433.1827.

*(R)-1-[(4S,5S)-5-(Hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-yl Benzoate [(R)-**11b**].* A solution of alcohol (*R*)-**8** (389.1 mg, 0.856 mmol) in CH_2Cl_2 (8.5 mL) was cooled to 0 °C before the addition of benzoic anhydride (386.8 mg, 1.71 mmol), triethylamine (0.36 mL, 2.57 mmol), and a catalytic amount of DMAP. The reaction mixture was stirred for 24 h after warming to rt, and an additional portion of DMAP was added. The mixture was stirred an additional 2 days before a saturated solution of $NaHCO_3$ (15 mL) was added, followed by extraction with EtOAc (3 × 15 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. The resulting residue was taken up in THF (8.5 mL), and an equimolar (1:1) solution of TBAF/AcOH (2.7 mL, 2.57 mmol, 0.95 M) was added. The reaction mixture was stirred for 3 h at rt before being concentrated in vacuo. The resulting oil was purified via flash chromatography on silica gel (4:1 hexanes/EtOAc, v/v) to afford alcohol (*R*)-**11b** (222.4 mg, 81% over two steps) as a colorless oil; R_f 0.27 (2:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −24.8 (*c* 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−8.02 (m, 2H), 7.57−7.52 (m, 1H), 7.46−7.40 (m, 2H), 5.63 (dd, J = 6.8, 6.8 Hz, 1H), 5.12 (br s, 1H), 5.00−4.97 (m, 1H), 3.96 (ddd, J = 8.0, 8.0, 4.0 Hz, 1H), 3.83−3.76 (m, 2H), 3.67−3.62 (m, 1H), 2.28−2.24 (br s, 1H), 2.20−2.12 (m, 1H), 2.00 (ddd, J = 14.0, 6.8, 4.4 Hz, 1H), 1.81 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.4, 133.0, 130.5, 129.7 (2C), 128.5 (2C), 114.2, 109.0, 81.5, 75.5, 74.2, 62.0, 36.3, 27.4, 27.0, 18.1; IR (neat) 3441, 2986, 2934, 1720, 1602, 1452, 1379, 1314, 1272, 1097 cm^{-1}; HRMS (ESI) m/z for $C_{18}H_{24}NaO_5$ [M + Na]$^+$ calcd 343.1516, obsd 343.1514.

*(R)-1-{(4S,5S)-2,2-Dimethyl-5-[(E)-2-methyl-3-oxobut-1-en-1-yl]-1,3-dioxolan-4-yl}-3-methylbut-3-en-2-yl Benzoate [(R)-**12b**].* A solution of alcohol (*R*)-**11b** (432.8 mg, 1.35 mmol) in CH_2Cl_2 (13.5 mL) was cooled to 0 °C before addition of $NaHCO_3$ (1.71 g, 20.3 mmol) and Dess−Martin periodinane (861.0 mg, 2.03 mmol). The cold bath was removed and the reaction mixture was stirred at rt for 3 h, after which saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ were added and the mixture was stirred vigorously for 30 min. The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), and the organic extracts were combined, dried

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over $MgSO_4$, and concentrated under reduced pressure. The crude aldehyde was taken to the next step with no further purification. A solution of 3-oxobutan-2-ylphosphonate (618.3 mg, 1.35 mmol) in THF (4.2 mL) was added dropwise to a 0 °C slurry of sodium hydride (64.8 mg, 2.7 mmol, 60% in oil) in THF (5.4 mL). The reaction mixture stirred for 1 h at 0 °C before a solution of freshly prepared aldehyde in THF (4.2 mL) was added via cannula and the cold bath was removed. The reaction mixture was stirred at rt for 14 h and then saturated aqueous NH_4Cl (10 mL) was added, followed by extraction with EtOAc (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. Purification via flash chromatography (4:1 hexanes/EtOAc, v/v) afforded enone (*R*)-**12b** (163.6 mg, 33% over two steps) as a pale yellow oil; R_f 0.56 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −25.6 (*c* 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.15−8.00 (m, 2H), 7.58−7.52 (m, 1H), 7.46−7.40 (m, 2H), 6.41−6.36 (m, 1H), 5.56 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.10 (s, 1H), 5.00−4.96 (m, 1H), 4.52 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.84 (ddd, *J* = 8.0, 8.0, 4.0 Hz, 1H), 2.29 (s, 3H), 2.20 (ddd, *J* = 14.0, 8.0, 8.0 Hz, 1H), 1.92 (ddd, *J* = 14.0, 6.8, 4.4 Hz, 1H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.78 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 165.6, 142.3, 141.3, 137.2, 133.1, 130.5, 129.7 (2C), 128.5 (2C), 114.3, 109.8, 77.6 (2C), 75.3, 35.1, 27.3, 26.9, 25.7, 18.0, 12.3; IR (neat) 2985, 2934, 1719, 1676, 1271, 1113 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{22}H_{28}NaO_5$ $[M + Na]^+$ calcd 395.1829, obsd 395.1833.

*(R)-1-{(4S,5S)-5-[(E)-3-{[(Allyloxy)carbonyl]oxy}-2-methylbuta-1,3-dien-1-yl]-2,2-dimethyl-1,3-dioxolan-4-yl}-3-methylbut-3-en-2-yl Benzoate [(R)-**13b**].* Enone (*R*)-**12b** (163.0 mg, 0.438 mmol) in DME (2.0 mL) was added dropwise to a −78 °C solution of KHMDS (104.8 mg, 0.526 mmol) in DME (5.5 mL), and the mixture was stirred for 15 min prior to the introduction of neat allyl chloroformate (0.23 mL, 2.19 mmol). The reaction mixture was then warmed to −50 °C and stirred for 1 h before the addition of saturated aqueous NH_4Cl (5 mL). The mixture was extracted with EtOAc (3 × 10 mL), and the combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. Purification via flash chromatography on silica gel (8:1 hexanes/EtOAc, v/v) yielded enol carbonate (*R*)-**13b** (141.2 mg, 71%) as a colorless oil; R_f 0.45 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −37.5 (*c* 1.01, $CDCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.06−8.00 (m, 2H), 7.58−7.51 (m, 1H), 7.46−7.39 (m, 2H), 5.95 (dddd, *J* = 16.0, 10.4, 5.6, 5.6 Hz, 1H), 5.72 (d, *J* = 8.8 Hz, 1H), 5.61 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.43−5.35 (m, 1H), 5.33−5.27 (m, 1H), 5.14 (d, *J* = 2.4 Hz, 1H), 5.12 (s, 1H), 5.04 (d, *J* = 2.4 Hz, 1H), 5.00−4.97 (m, 1H), 4.69−4.64 (m, 2H), 4.44 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.72 (ddd, *J* = 8.4, 8.4, 3.2 Hz, 1H), 2.08 (ddd, *J* = 13.6, 8.4, 6.8 Hz, 1H), 1.95−1.92 (m, 1H), 1.91 (d, *J* = 0.8 Hz, 3H), 1.78 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 153.9, 153.0, 142.3, 133.7, 133.0, 131.4, 130.7, 129.7 (2C), 128.4 (2C), 124.4, 119.4, 114.5, 109.2, 103.7, 77.9, 77.5, 75.7, 69.1, 34.7, 27.4, 27.0, 17.9, 14.1; IR (neat) 2986, 2933, 1763, 1719, 1450, 1379, 1369, 1273, 1224, 1112, cm^{-1}; HRMS (ESI) *m*/*z* for $C_{26}H_{32}NaO_7$ $[M + Na]^+$ calcd 479.2040, obsd 479.2037.

*(R)-1-[(4S,5S)-5-(Hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-yl 4-Nitrobenzoate [(R)-**11c**].* A solution of alcohol (*R*)-**8** (1.20 g, 2.64 mmol) in CH_2Cl_2 (26.5 mL) was cooled to 0 °C before the addition of *p*-nitrobenzoyl chloride (1.47 g, 7.92 mmol), triethylamine (1.5 mL, 10.6 mmol), and a catalytic amount of DMAP. The reaction mixture was stirred for 18 h after warming to rt before saturated solution of $NaHCO_3$ (15 mL) was added, followed by extraction with EtOAc. The combined organic extracts were dried ($MgSO_4$) and concentrated. The resulting residue was dissolved in THF (26 mL) and an equimolar (1:1) solution of TBAF/AcOH (8.3 mL, 7.92 mmol, 0.95 M) was added. The reaction mixture was stirred for 14 h at rt before being concentrated in vacuo. The resulting oil was purified via flash chromatography on silica gel (4:1 hexanes/EtOAc, v/v) to afford alcohol (*R*)-**11c** (673.2 mg, 70% over two steps) as a colorless oil; R_f 0.30 (2:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −26.1 (*c* 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.29−8.25 (m, 2H), 8.22−8.17 (m, 2H), 5.67 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.13 (s, 1H), 5.03−5.00 (m, 1H), 3.95 (ddd, *J* = 8.4, 8.4, 3.6 Hz, 1H), 3.82−3.74 (m, 2H), 3.66−3.59 (m, 1H), 2.16−2.09 (m, 2H), 2.01 (ddd, *J* = 14.0, 6.8, 3.6 Hz, 1H), 1.81 (s, 3H), 1.36 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 150.6, 141.8, 136.1, 130.8 (2C), 123.6 (2C), 114.8, 109.1, 81.4, 76.9, 74.2, 61.8, 36.3, 27.4, 26.9, 18.0; IR (neat) 2985, 2935, 1716, 1527, 1274 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{18}H_{23}NaNO_7$ $[M + Na]^+$ calcd 388.1367, obsd 388.1363.

*(R)-1-{(4S,5S)-2,2-Dimethyl-5-[(E)-2-methyl-3-oxobut-1-en-1-yl]-1,3-dioxolan-4-yl}-3-methylbut-3-en-2-yl 4-Nitrobenzoate [(R)-**12c**].* A solution of alcohol (*R*)-**11c** (387.6 mg, 1.06 mmol) in CH_2Cl_2 (10.5 mL) was cooled to 0 °C before addition of $NaHCO_3$ (1.34 g, 15.9 mmol) and Dess−Martin periodinane (674.4 mg, 1.59 mmol). The cold bath was removed and the reaction mixture was stirred at rt for 3 h, after which saturated aqueous solutions of $NaHCO_3$ and $Na_2S_2O_3$ were added and the mixture was stirred vigorously for 30 min. The layers were separated, the aqueous layer was extracted with CH_2Cl_2, and the organic extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude aldehyde was taken to the next step with no further purification. A solution of 3-oxobutan-2-ylphosphonate (485.5 mg, 2.33 mmol) in THF (3.3 mL) was added dropwise to a 0 °C slurry of sodium hydride (84.8 mg, 2.12 mmol, 60% in oil) in THF (4.2 mL). The reaction mixture was stirred for 1 h at 0 °C before a solution of freshly prepared aldehyde in THF (3.3 mL) was added via cannula and the cold bath was removed. The reaction mixture was stirred at 14 h at rt before a solution of saturated aqueous NH_4Cl (10 mL) was added, followed by extraction with EtOAc (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent was removed in vacuo. Purification via flash chromatography (4:1 hexanes/EtOAc, v/v) afforded enone (*R*)-**12c** (168.5 mg, 38% over two steps) as a pale yellow oil; R_f 0.48 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −26.3 (*c* 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 2H), 6.43−6.37 (m, 1H), 5.62 (dd, *J* = 6.8, 6.8 Hz, 1H), 5.11 (s, 1H), 5.02−5.00 (m, 1H), 4.49 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.80 (ddd, *J* = 8.8, 8.8, 3.6 Hz, 1H), 2.32 (s, 3H), 2.21−2.12 (m, 1H), 1.91 (ddd, *J* = 14.0, 6.4, 3.6 Hz, 1H), 1.86 (d, *J* = 0.8 Hz, 3H), 1.78 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 163.8, 150.7, 141.7, 141.3, 137.0, 136.0, 130.8 (2C), 123.6 (2C), 115.1, 109.9, 77.9, 77.8, 76.7, 35.1, 27.3, 26.9, 25.8, 17.9, 12.3; IR (neat) 2985, 2933, 1724, 1676, 1528, 1273, 1101 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{22}H_{27}NaNO_7$ $[M + Na]^+$ calcd 440.1680, obsd 440.1682.

*(R)-1-{(4S,5S)-5-[(E)-3-{[(Allyloxy)carbonyl]oxy}-2-methylbuta-1,3-dien-1-yl]-2,2-dimethyl-1,3-dioxolan-4-yl}-3-methylbut-3-en-2-yl 4-Nitrobenzoate [(R)-**13c**].* Enone (*R*)-**12c** (164.4 mg, 0.394 mmol) in DME (2.0 mL) was added dropwise to a −78 °C solution of KHMDS (94.3 mg, 0.473 mmol) in DME (5.0 mL), and the mixture was stirred for 15 min prior to the introduction of neat allyl chloroformate (0.21 mL, 1.97 mmol). The reaction mixture was then warmed to −50 °C and stirred for 1 h before the addition of saturated aqueous NH_4Cl (5 mL). The mixture was extracted with EtOAc (3 × 10 mL) and the combined organic extracts were dried over $MgSO_4$ and concentrated. Purification via flash chromatography on silica gel (8:1 hexanes/EtOAc, v/v) gave enol carbonate (*R*)-**13c** (76.5 mg, 39%) as a colorless oil; R_f 0.45 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −37.0 (*c* 1.08, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 5.95 (dddd, *J* = 16.0, 10.8, 5.6, 5.6 Hz, 1H), 5.70 (d, *J* = 8.8 Hz, 1H), 5.63 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.43−5.36 (m, 1H), 5.33−5.27 (m, 1H), 5.15 (d, *J* = 2.4 Hz, 1H), 5.13 (s, 1H), 5.05 (d, *J* = 2.4 Hz, 1H), 5.03−5.00 (m, 1H), 4.68−4.62 (m, 2H), 4.42 (dd, *J* = 8.8, 8.8 Hz, 1H), 3.72 (ddd, *J* = 8.4, 8.4, 2.8 Hz, 1H), 2.09 (ddd, *J* = 14.0, 9.2, 7.6 Hz, 1H), 1.96−1.92 (m, 1H), 1.92 (d, *J* = 0.8 Hz, 3H), 1.79 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 153.8, 153.0, 150.6, 141.8, 136.2, 133.8, 131.3, 130.9 (2C), 124.2, 123.6 (2C), 119.4, 115.0, 109.4, 103.9, 78.0, 77.6, 77.0, 69.1, 34.8, 27.4, 27.0, 17.9, 14.1; IR (neat) 2985, 2933, 1763, 1726, 1527, 1350, 1273, 1224, 1116 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{26}H_{31}NaNO_9$ $[M + Na]^+$ calcd 524.1891, obsd 524.1892.

*tert-Butyl-{[(4S,5S)-5-{2-[(tert-butyldimethylsilyl)oxy]-3-methylbut-3-en-1-yl}-2,2-dimethyl-1,3-dioxolan-4-yl]methoxy}diphenylsilane (**10d**).* Imidazole (154.5 mg, 2.27 mmol) and a catalytic amount of DMAP were added to a solution of alcohols (*R*)-**8** and (*S*)-**9** (343.1 mg, 0.755 mmol, prepared from aldehyde **7**) in DMF (1 mL) at rt. The mixture was stirred until it was homogeneous, and TBSCl (170.3

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mg, 1.13 mmol) was added in one portion. The reaction mixture was stirred at rt for 14 h before it was partitioned between a solution of NH_4Cl (10 mL) and Et_2O (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The organic extracts were combined, dried over Na_2SO_4, and concentrated. The residue was purified via flash chromatography on silica gel (8:1 hexanes/EtOAc, v/v) to furnish silyl ethers **10d** (425.8 mg, 99%) as a colorless oil; R_f 0.61 (7:1 hexanes/EtOAc, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.66 (m, 8H), 7.47−7.35 (m, 12H), 4.97−4.94 (m, 1H), 4.93−4.90 (m, 1H), 4.86−4.82 (m, 1H), 4.78−4.75 (m, 1H), 4.38−4.31 (m, 2H), 4.26−4.19 (m, 1H), 3.95−3.88 (m, 1H), 3.83−3.62 (m, 6H), 1.94 (ddd, J = 13.6, 10.8, 2.0 Hz, 1H), 1.85−1.75 (m, 3H), 1.71 (s, 3H), 1.68 (s, 3H), 1.42 (s, 6H), 1.37 (s, 3H), 1.35 (s, 3H), 1.07 (s, 9H), 1.06 (s, 9H), 0.92 (s, 9H), 0.89 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 146.7, 135.82 (2C), 135.79 (2C), 135.77 (4C), 133.5, 133.4 (2C), 133.3, 129.9, 129.81 (2C), 129.79, 127.83 (6C), 127.8 (2C), 112.2, 110.6, 108.7, 108.6, 81.5, 81.1, 75.6, 75.5, 74.7, 73.5, 64.4, 64.0, 41.0, 39.9, 27.71, 27.66, 27.0 (2C), 26.95 (3C), 26.93 (3C), 26.03 (3C), 25.97 (3C), 19.4, 19.3, 18.4, 18.3, 17.2, 16.7, −4.57, −4.64, −4.9, −5.0; IR (neat) 2957, 2929, 2893, 2857, 1473, 1428, 1378, 1251, 1113 cm^{-1}; HRMS (ESI) m/z for $C_{33}H_{52}O_4NaSi_2$ $[M + Na]^+$ calcd 591.3296, obsd 591.3282.

*[(4S,5S)-5-{2-[(tert-Butyldimethylsilyl)oxy]-3-methylbut-3-en-1-yl}-2,2-dimethyl-1,3-dioxolan-4-yl]methanol (**11d**).* Silyl ether mixture **10d** (421.6 mg, 0.741 mmol) was taken up in a solution of 10% NaOH in MeOH (7.5 mL). The mixture was warmed at 65 °C for 2.5 h and then cooled to rt before a solution of NH_4Cl (10 mL) was added. The mixture was extracted with EtOAc (3 × 15 mL) and the organic extracts were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification via flash chromatography (8:1 hexanes/EtOAc, v/v) afforded a mixture of primary alcohols **11d** (224.9 mg, 92%) as a colorless oil; R_f 0.34 (4:1 hexanes/EtOAc, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94−4.92 (m, 1H), 4.92−4.90 (m, 1H), 4.84−4.81 (m, 1H), 4.77−4.74 (m, 1H), 4.30−4.24 (m, 2H), 4.06−3.98 (m, 1H), 3.82−3.71 (m, 5H), 3.70−3.64 (m, 1H), 3.63−3.54 (m, 2H), 2.19 (br s, 2H), 1.92−1.81 (m, 1H), 1.77−1.69 (m, 1H), 1.68 (s, 3H), 1.66 (s, 3H), 1.61−1.52 (m, 1H), 1.40 (s, 3H), 1.39 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.053 (s, 3H), 0.050 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 146.3, 112.2, 110.8, 108.8, 108.7, 81.8, 81.7, 74.4, 74.2, 73.6, 73.4, 62.1, 62.0, 40.4, 39.5, 27.6, 27.5, 27.11, 27.07, 25.9 (6C), 18.3 (2C), 17.3, 17.0, −4.6, −4.7, −5.0, −5.1; IR (neat) 3469, 2954, 2929, 2889, 2857, 1472, 1463, 1380, 1251, 1165 cm^{-1}; HRMS (ESI) m/z for $C_{17}H_{34}NaO_4Si$ $[M + Na]^+$ calcd 353.2119, obsd 353.2128.

*(E)-4-[(4S,5S)-5-{2-[(tert-Butyldimethylsilyl)oxy]-3-methylbut-3-en-1-yl}-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbut-3-en-2-one (**12d**).* A solution of DMSO (1.76 mL, 24.8 mmol) in CH_2Cl_2 (19.8 mL) was cooled to −78 °C before addition of oxalyl chloride (1.05 mL, 12.4 mmol) dropwise. The reaction mixture was stirred for 30 min at −78 °C, after which a solution of alcohols **11d** (2.05 g, 6.20 mmol) in CH_2Cl_2 (5 mL) was added dropwise and the mixture was stirred for 1 h. Triethylamine (6.91 mL, 49.6 mmol) was then added, the cold bath was removed, and the reaction mixture was warmed to rt and stirred for an additional 15 min. A saturated solution of NH_4Cl (20 mL) was then added to the reaction mixture and the layers were separated. The aqueous portion was extracted with EtOAc (3 × 50 mL). The combined extracts were dried over $MgSO_4$, filtered, and concentrated in vacuo to afford an aldehyde that was used directly in the next step. A suspension of NaH (297.7 mg, 7.44 mmol, 60% in oil) in THF (3.8 mL) was cooled to 0 °C, and a solution of diethyl 3-oxobutan-2-ylphosphonate (1.61 g, 7.75 mmol) in THF (7.1 mL) was added dropwise. The cloudy reaction mixture was stirred at 0 °C and became transparent (time required for complete consumption of base varied with different batches). Stirring continued at 0 °C for an additional 50 min before addition of a solution of the freshly prepared aldehyde in THF (7.1 mL) dropwise. The cold bath was removed, and the reaction mixture was warmed to rt and stirred for 36 h. The mixture was partitioned between a saturated solution of NH_4Cl (30 mL) and EtOAc (30 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The organic extracts were combined and dried ($MgSO_4$), and solvent was removed under reduced pressure. The resulting residue was purified via flash chromatography on silica gel (20:1 hexanes/EtOAc, v/v) to afford enones **12d** (1.70 g, 72% over 2 steps) as a pale yellow oil; R_f 0.39 (7:1 hexanes/EtOAc, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44−6.41 (m, 1H), 6.41−6.39 (m, 1H), 4.94−4.91 (m, 1H), 4.89−4.86 (m, 1H), 4.83−4.79 (m, 1H), 4.78−4.75 (m, 1H), 4.47 (t, J = 8.4 Hz, 1H), 4.41 (t, J = 8.4 Hz, 1H), 4.29−4.20 (m, 2H), 3.98−3.91 (m, 1H), 3.70 (ddd, J = 8.4, 8.4, 3.6 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 1.86 (d, J = 1.6 Hz, 3H), 1.83 (d, J = 1.2 Hz, 3H), 1.70−1.65 (m, 5H), 1.63 (s, 3H), 1.59 (dd, J = 7.2, 5.2 Hz, 2H), 1.45 (s, 3H), 1.44 (s, 6H), 1.40 (s, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.62, 199.56, 148.0, 146.5, 141.0, 140.9, 138.1, 137.1, 112.3, 111.0, 109.6, 109.5, 78.0, 77.92, 77.87, 77.4, 74.4, 73.3, 39.3, 38.5, 27.6, 27.5, 27.1, 27.0, 25.9 (6C), 25.79, 25.76, 18.34, 18.31, 17.3, 16.5, 12.3, 12.2, −4.5, −4.6, −5.0, −5.1; IR (neat) 2955, 2928, 2897, 2858, 1680, 1473, 1379, 1252, 1076 cm^{-1}; HRMS (ESI) for $C_{21}H_{38}NaO_4Si$ $[M + Na]^+$ calcd 405.2432, obsd 405.2433.

*Allyl {(E)-4-[(4S,5S)-5-{2-[(tert-Butyldimethylsilyl)oxy]-3-methylbut-3-en-1-yl}-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methylbuta-1,3-dien-2-yl} Carbonate (**13d**).* Potassium bis(trimethylsilyl)amide (71.0 mg, 0.365 mmol), obtained from a inert atmosphere glovebox, was taken up in DME (7 mL) and cooled to −78 °C, followed by the dropwise addition of enones **12d** (68.1 mg, 0.178 mmol) in DME (2 mL). The reaction mixture was warmed to −50 °C for 1 h and the solution became orange during that time period. The reaction mixture was again cooled to −78 °C, and neat allyl chloroformate (37.8 mL, 0.356 mmol) was added. The mixture was warmed to rt and stirred for 1 h before addition of a saturated solution of NH_4Cl (6 mL). The mixture was extracted with EtOAc (3 × 15 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified via flash chromatography on silica gel (15:1 hexanes/EtOAc, v/v) to yield enol carbonates **13d** (73.5 mg, 88%) as a colorless oil; R_f 0.57 (4:1 hexanes/EtOAc, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01−5.87 (m, 2H), 5.75−5.66 (m, 2H), 5.41−5.38 (m, 1H), 5.37−5.34 (m, 1H), 5.31−5.28 (m, 1H), 5.28−5.25 (m, 1H), 5.14−5.10 (m, 2H), 5.04−4.99 (m, 2H), 4.93−4.89 (m, 1H), 4.87−4.84 (m, 1H), 4.80−4.77 (m, 1H), 4.76−4.73 (m, 1H), 4.69−4.62 (m, 4H), 4.37 (t, J = 8.4 Hz, 1H), 4.32 (t, J = 8.4 Hz, 1H), 4.27−4.20 (m, 2H), 3.84 (ddd, J = 8.8, 8.8, 2.4 Hz, 1H), 3.55 (ddd, J = 8.8, 8.8, 3.2 Hz, 1H), 1.90 (d, J = 1.2 Hz, 3H), 1.88 (d, J = 1.2 Hz, 3H), 1.79−1.71 (m, 1H), 1.67 (s, 3H), 1.65−1.58 (m, 5H), 1.58−1.53 (m, 1H), 1.41 (s, 3H), 1.40 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H), 0.87 (s, 9H), 0.86 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H), 0.00 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 (2C), 152.97, 152.96, 148.2, 146.5, 133.3, 133.1, 131.4 (2C), 125.0, 124.8, 119.29, 119.26, 112.3, 110.8, 108.9, 108.8, 103.4 (2C), 78.1, 77.8, 77.7, 77.4, 74.7, 73.3, 68.98, 68.97, 39.2, 38.2, 27.6, 27.4, 27.1, 27.0, 25.92 (3C), 25.90 (3C), 18.29, 18.26, 17.3, 16.2, 14.1, 14.0, −4.6, −4.7, −5.0, −5.1; IR (neat) 2955, 2930, 2889, 2857, 1764, 1458, 1370, 1224 cm^{-1}; HRMS (ESI) for $C_{25}H_{42}NaO_6Si$ $[M + Na]^+$ calcd 489.2643, obsd 489.2596.

*Allyl {(3aS,5S,5aR,9aS,9bS)-5-[(methoxycarbonyl)oxy]-2,2,5a,9-Tetramethyl-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-d][1,3]-dioxol-8-yl} Dicarbonate (**14**).* Dicarbonate (*S*)-**13a** (56.6 mg, 0.138 mmol) and BHT (3.0 mg, 0.014 mmol) were dissolved in 1,2-dichlorobenzene (13.8 mL) and warmed at 180 °C for 3 days. The solvent was removed via low-pressure vacuum distillation. Purification of the residue via flash chromatography on silica gel (30:1 to 10:1 hexanes/EtOAc, v/v) afforded **14** (19.9 mg, 35%) as a pale yellow oil; R_f 0.31 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −10.9 (c 0.93, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (dddd, J = 16.4, 10.4, 6.0, 6.0 Hz, 1H), 5.42−5.35 (m, 1H), 5.32−5.27 (m, 1H), 4.76 (dd, J = 2.8, 2.8 Hz, 1H), 4.68−4.63 (m, 2H), 3.79 (s, 3H), 3.70 (ddd, J = 13.2, 8.8, 4.8 Hz, 1H), 3.53 (dd, J = 11.6, 8.8 Hz, 1H), 2.73−2.66 (m, 1H), 2.44−2.32 (m, 1H), 2.29 (ddd, J = 14.0, 4.4, 2.8 Hz, 1H), 2.24−2.15 (m, 1H), 2.11 (ddd, J = 13.6, 13.6, 3.2 Hz, 1H), 1.95−1.86 (m, 1H), 1.72 (s, 3H), 1.47−1.42 (m, 1H), 1.42 (s, 3H), 1.41 (s, 3H), 1.10 (s, 3H);

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^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 153.6, 142.1, 132.0, 122.3, 118.4, 109.4, 80.7, 78.4, 77.9, 68.5, 54.3, 43.8, 39.8, 31.6, 30.3, 27.2, 27.1, 24.5, 17.5, 14.5; IR (neat) 2984, 2956, 2929, 1751, 1273 cm^{-1}; HRMS (ESI) m/z for $C_{21}H_{30}NaO_8$ $[M + Na]^+$ calcd 433.1833, obsd 433.1837.

*Allyl {(3aS,5R,5aR,9aS,9bS)-5-[(methoxycarbonyl)oxy]-2,2,5a,9-Tetramethyl-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-d][1,3]-dioxol-8-yl} Dicarbonate (**15**).* Dicarbonate (*R*)-**13a** (43.1 mg, 0.105 mmol) and BHT (2.3 mg, 0.011 mmol) were dissolved in 1,2-dichlorobenzene (10.5 mL) and warmed at 180 °C for 2 days. The solvent was removed via low-pressure vacuum distillation. The residue was purified via flash chromatography on silica gel (30:1 to 10:1 hexanes/EtOAc, v/v), which afforded **15** (22.2 mg, 49%) as a waxy solid; R_f 0.35 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −25.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (dddd, *J* = 16.4, 10.8, 5.6, 5.6 Hz, 1H), 5.42−5.35 (m, 1H), 5.32−5.26 (m, 1H), 4.68−4.63 (m, 2H), 4.53 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.79 (s, 3H), 3.51 (dd, *J* = 11.2, 8.8 Hz, 1H), 3.43−3.35 (m, 1H), 2.43 (ddd, *J* = 11.2, 4.0, 4.0 Hz, 1H), 2.36−2.25 (m, 2H), 2.23−2.14 (m, 1H), 1.96 (app q, *J* = 11.6 Hz, 1H), 1.81 (dd, *J* = 13.2, 6.8 Hz, 1H), 1.71 (s, 3H), 1.51 (ddd, *J* = 12.0, 12.0, 7.2 Hz, 1H), 1.41 (s, 6H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 153.2, 142.3, 131.5, 121.2, 119.2, 110.3, 81.2, 78.4, 77.6, 68.9, 55.1, 45.6, 39.6, 33.3, 30.0, 27.1, 27.0, 23.9, 14.1, 12.9; IR (thin film) 2985, 2929, 1752, 1442, 1385, 1370, 1267, 1186, 1164, 1087, 1039, 1010, 978 cm^{-1}; HRMS (ESI) m/z for $C_{21}H_{30}NaO_8$ $[M + Na]^+$ calcd 433.1833, obsd 433.1825.

*(3aS,5R,5aR,9aS,9bS)-8-{[(Allyloxy)carbonyl]oxy}-2,2,5a,9-tetramethyl-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-d][1,3]dioxol-5-yl Benzoate (**17**).* Enol carbonate (*R*)-**13b** (74.7 mg, 0.164 mmol) and BHT (3.6 mg, 0.0164 mmol) were dissolved in 1,2-dichlorobenzene (16.4 mL) and warmed at 180 °C for 24 h. The solvent was removed via low-pressure vacuum distillation. Purification of the residue via flash chromatography on silica gel (8:1 hexanes/EtOAc, v/v) afforded **17** (38.8 mg, 52%) as a white, waxy solid; R_f 0.52 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −55.7 (*c* 1.07, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05−8.02 (m, 2H), 7.60−7.56 (m, 1H), 7.48−7.44 (m, 2H), 5.76 (dddd, *J* = 14.4, 8.4, 4.4, 4.4 Hz, 1H), 5.39 (dq, *J* = 14.0, 1.2 Hz, 1H), 5.29 (dq, *J* = 8.4, 0.8 Hz, 1H), 4.97 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.68−4.64 (m, 2H), 3.59 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.52−3.46 (m, 1H), 2.49 (ddd, *J* = 9.2, 3.2, 3.2 Hz, 1H), 2.44−2.39 (m, 1H), 1.74 (d, *J* = 0.8 Hz, 3H), 1.55 (ddd, *J* = 10.0, 10.0, 6.0 Hz, 1H), 1.43 (s, 3H), 1.428 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 153.2, 142.3, 133.3, 131.5, 130.2, 129.8 (2C), 128.6 (2C), 121.3, 119.1, 110.2, 78.6, 77.8, 77.4, 68.9, 45.8, 39.9, 33.6, 30.1, 27.1, 27.0, 24.0, 14.1, 13.3; IR (thin film) 2985, 2933, 2893, 1751, 1718, 1450, 1381, 1369, 1271, 1244, 1111 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{32}NaO_7$ $[M + Na]^+$ calcd 479.2040, obsd 479.2047.

*(3aS,5R,5aR,9aS,9bS)-8-{[(Allyloxy)carbonyl]oxy}-2,2,5a,9-tetramethyl-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-d][1,3]dioxol-5-yl 4-Nitrobenzoate (**18**).* Enol carbonate (*R*)-**13c** (75.9 mg, 0.151 mmol) and BHT (3.3 mg, 0.0151 mmol) were dissolved in 1,2-dichlorobenzene (15 mL) and warmed at 180 °C for 24 h. The solvent was removed via low-pressure vacuum distillation. Purification of the residue via flash chromatography on silica gel (8:1 hexanes/EtOAc, v/v) afforded **18** (45.0 mg, 59%) as a white foam; R_f 0.41 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ −54.7 (*c* 0.87, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.2 Hz, 2H), 8.20 (d, *J* = 6.8 Hz, 2H), 5.96 (dddd, *J* = 14.0, 8.4, 4.4, 4.4 Hz, 1H), 5.42−5.35 (m, 1H), 5.31−5.27 (m, 1H), 5.00 (dd, *J* = 9.2, 3.6 Hz, 1H), 4.68−4.65 (m, 2H), 3.59 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.49 (ddd, *J* = 10.0, 6.8, 3.2 Hz, 1H), 2.50 (ddd, *J* = 8.8, 3.2, 3.2 Hz, 1H), 2.45−2.40 (m, 1H), 2.37−2.28 (m, 1H), 2.22−2.15 (m, 1H), 2.05 (app q, *J* = 8.8 Hz, 1H), 1.76−1.71 (m, 4H), 1.60−1.55 (m, 1H), 1.434 (s, 3H), 1.43 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 153.2, 150.9, 142.2, 135.5, 131.5, 130.9 (2C), 123.8 (2C), 121.2, 119.2, 110.4, 78.6, 78.4, 77.7, 68.9, 45.8, 39.9, 33.6, 30.1, 27.1, 27.0, 24.0, 14.1, 13.4; IR (thin film) 2985, 2933, 1751, 1724, 1529, 1382, 1273, 1242, 1163, 1115 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{31}NaNO_9$ $[M + Na]^+$ calcd 524.1891, obsd 524.1888.

*Allyl {(3aS,5R,5aR,9aS,9bS)-5-[(tert-Butyldimethylsilyl)oxy]-2,2,5a,9-tetramethyl-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-d]-[1,3]dioxol-8-yl} Carbonate (**19**) and Allyl {(3aS,5S,5aR,9aS,9bS)-5-[(tert-Butyldimethylsilyl)oxy]-2,2,5a,9-tetramethyl-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-d][1,3]dioxol-8-yl} Carbonate (**20**).* Silyl ethers **13d** (76.4 mg, 164 μmol) and BHT (3.6 mg, 16.3 μmol) were dissolved in 1,2-dichlorobenzene (16.5 mL) and heated at 225−250 °C in a sealed tube for 3 days. The solvent was removed by vacuum distillation and the residue was purified via flash chromatography on silica gel (100:0 to 20:1 hexanes/EtOAc, v/v) to yield **19** (20.9 mg, 27.4%) as a off-white, waxy solid and **20** (11.5 mg, 15.0%) as a colorless oil, as well as a mixture containing both isomers (15.6 mg, 20.4%; **19**:**20** = 1:2).

*Spectral Data for **19**.* R_f 0.83 (15:1 hexanes/EtOAc, v/v, eluted five times); $[\alpha]_D^{23}$ −39.5 (*c* 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (dddd, *J* = 16.4, 10.8, 5.6, 5.6 Hz, 1H), 5.42−5.35 (m, 1H), 5.31−5.26 (m, 1H), 4.66 (d, *J* = 5.6 Hz, 2H), 3.50 (dd, *J* = 11.2, 8.4 Hz, 1H), 3.44 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.32 (ddd, *J* = 12.8, 8.8, 4.0 Hz, 1H), 2.37−2.25 (m, 1H), 2.25−2.12 (m, 3H), 1.95 (dd, *J* = 12.8, 6.8 Hz, 1H), 1.87 (app q, *J* = 12.0 Hz, 1H), 1.70 (s, 3H), 1.40 (s, 3H), 1.39 (s, 3H), 1.37−1.31 (m, 1H), 0.97 (s, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.4, 131.6, 121.6, 119.1, 109.7, 79.0, 78.0, 76.5, 68.8, 45.6, 41.1, 34.0, 33.8, 27.2, 27.1, 25.9 (3C), 24.3, 18.2, 14.1, 12.3, −3.9, −4.8; IR (thin film) 2953, 2929, 2858, 1752, 1239, 1151, 1104, 1074 cm^{-1}; HRMS (ESI) m/z for $C_{25}H_{42}NaO_6Si$ $[M + Na]^+$ calcd 489.2643, obsd 489.2644.

*Spectral Data for **20**.* R_f 0.70 (15:1 hexanes/EtOAc, v/v, eluted five times); $[\alpha]_D^{23}$ −9.90 (*c* 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ5.96 (dddd, *J* = 16.4, 10.8, 6.0, 6.0 Hz, 1H), 5.42−5.35 (m, 1H), 5.31−5.27 (m, 1H), 4.68−4.64 (m, 2H), 3.83 (ddd, *J* = 11.6, 8.8, 5.6 Hz, 1H), 3.63 (dd, *J* = 2.4, 2.4 Hz, 1H), 3.50 (dd, *J* = 11.6, 8.8 Hz, 1H), 2.70−2.64 (br m, 1H), 2.36−2.26 (m, 1H), 2.21−2.12 (m, 1H), 2.09−2.02 (m, 2H), 2.01−1.95 (m, 1H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.28−1.18 (m, 1H), 0.98 (s, 3H), 0.90 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 141.7, 131.7, 122.7, 119.1, 108.9, 78.5, 77.6, 75.9, 68.8, 42.7, 40.9, 32.7, 32.6, 27.2 (2C), 26.0 (3C), 24.6, 18.2, 17.8, 14.4, −4.4, −4.7; IR (neat) 2953, 2929, 2858, 1751, 1239, 1067, 833 cm^{-1}; HRMS (ESI) m/z for $C_{25}H_{42}NaO_6Si$ $[M + Na]^+$ calcd 489.2643, obsd 489.2650.

*{[(2S,3S)-2,3-Bis(benzyloxy)-5-methoxypent-4-en-1-yl]oxy}(tert-butyl)diphenylsilane (**22**).* Oxalyl chloride (3.13 mL, 37.0 mmol) was added dropwise to a solution of DMSO (5.25 mL, 74.0 mmol) in CH_2Cl_2 (60 mL) at −78 °C, and the reaction mixture was stirred for 15 min. Alcohol **21**[24] (10.0 g, 18.5 mmol) in CH_2Cl_2 (14.8 mL) was added dropwise and the mixture was stirred for 1 h at −78 °C, followed by the addition of triethylamine (20.6 mL, 148 mmol). The reaction mixture was warmed to rt and stirred for 15 min before saturated aqueous NH_4Cl (100 mL) was added. The resultant mixture was extracted with Et_2O (3 × 100 mL), and the combined organic extracts were washed with brine (100 mL), dried over $MgSO_4$, and concentrated with no further purification. Potassium bis(trimethylsilyl)amide (61.0 mL, 55.5 mmol, 0.91 M solution in THF) was added to a −78 °C slurry of methoxymethyltriphenylphosphonium chloride (25.4 g, 74.0 mmol) in THF (250 mL). The deep red slurry was stirred for 1 h at −78 °C before a solution of previously prepared crude aldehyde (9.96 g, 18.5 mmol) in THF (115 mL) was added dropwise. The reaction mixture was warmed to rt, stirred for 14 h, and then partitioned between Et_2O (200 mL) and H_2O (200 mL). The separated aqueous layer was extracted with Et_2O (3 × 200 mL), and the combined organic extracts were washed with brine (200 mL), dried over $MgSO_4$, and concentrated. Purification via flash chromatography on silica gel (20:1 hexanes/EtOAc, v/v) gave a diastereomeric mixture of enol ethers **22** (8.21 g, 78% over two steps) as a pale yellow oil; R_f 0.61 (4:1 hexanes/EtOAc, v/v) ^{1}H NMR (400 MHz, $CDCl_3$, major diastereomer) δ 7.75−7.69 (m, 4H), 7.48−7.27 (m, 16H), 6.50 (d, *J* = 12.8 Hz, 1H), 4.80−4.62 (m, 4H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.00−3.90 (m, 2H), 3.90−3.82 (m, 1H), 3.67−3.58 (m, 1H), 3.51 (s, 3H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of diastereomers) δ 151.2, 149.7, 139.3, 139.28, 139.1, 138.9, 135.8, 135.7, 133.9, 133.8, 133.7, 133.6, 129.7, 129.6, 128.33, 128.3, 128.2, 128.17, 128.13, 128.1, 127.9, 127.86, 127.8, 127.77, 127.7, 127.5, 127.4, 127.35, 127.2, 104.2, 99.8, 83.1, 82.8, 77.3, 73.7, 73.6, 72.2, 70.5,

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69.6, 64.4, 64.0, 60.5, 59.8, 55.9, 27.0, 26.9, 19.3; IR (neat) 3068, 2930, 2857, 1654, 1458, 1428, 1112, 1067 cm^{-1}; HRMS (ESI) m/z for $C_{36}H_{42}NaO_4Si$ $[M + Na]^+$ calcd 589.2745, obsd 589.2730.

*(3S,4S)-3,4-Bis(benzyloxy)-5-[(tert-butyldiphenylsilyl)oxy]-pentanal (**23**).* Mercuric acetate (6.54 g, 20.51 mmol) was added in one portion to enol ethers **22** (7.75 g, 13.76 mmol) in a THF/H_2O mixture (275 mL, 10:1) and stirred for 3 h at rt. Tetrabutylammonium iodide (22.7 g, 61.52 mmol) was added to the reaction mixture and it was stirred for an additional 2 h prior to the addition of saturated aqueous NH_4Cl (100 mL). The mixture was then extracted with EtOAc (3 × 150 mL), and the combined extracts were dried and concentrated. Purification via flash chromatography afforded **23** (7.23 g, 96%) as a viscous, yellow oil; R_f 0.50 (4:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ +5.9 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.67−9.65 (m, 1H), 7.71−7.66 (m, 4H), 7.47−7.20 (m, 16H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.55 (s, 2H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.23−4.17 (m, 1H), 3.93 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.83 (dd, *J* = 11.2, 6.0 Hz, 1H), 3.65−3.60 (m, 1H), 2.74−2.67 (m, 1H), 2.62−2.54 (m, 1H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 138.3, 138.1, 135.8 (4C), 133.4, 133.38, 129.93, 129.91, 128.5 (4C), 128.2 (2C), 128.1 (2C), 127.92 (2C), 127.9 (2C), 127.88 (2C), 80.3, 74.0, 73.0, 72.97, 63.1, 45.2, 27.0 (3C), 19.3; IR (neat) 2930, 2856, 1724, 1589, 1458, 1112 cm^{-1}; HRMS (ESI) m/z for $C_{36}H_{44}NaO_5Si$ $[M + CH_3OH + Na]^+$ calcd 607.2850, obsd 607.2851.

*(5S,6S)-5,6-Bis(benzyloxy)-7-[(tert-butyldiphenylsilyl)oxy]-2-methylhept-1-en-3-ol (**24**).* Freshly prepared isopropenylmagnesium bromide (42.4 mL, 21.2 mmol, 0.5 M solution in THF) was added to aldehyde **23** (5.84 g, 10.6 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C before being warmed to rt and quenched by the addition of a saturated solution of NH_4Cl (100 mL). The mixture was extracted with EtOAc (3 × 100 mL), and the combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Purification via flash chromatography on silica gel (10:1 hexanes/EtOAc, v/v) afforded **24** (3.80 g, 60%) as a diastereomeric mixture of alcohols in the form of a pale yellow oil.

Spectral Data for More Polar Isomer. R_f 0.39 (4:1 hexanes/EtOAc, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.67 (m, 4H), 7.46−7.22 (m, 16H), 4.91 (s, 1H), 4.81−4.74 (m, 2H), 4.63 (d, *J* = 2.8 Hz, 1H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.16−4.11 (br m, 1H), 3.96 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.89−3.80 (m, 2H), 3.75−3.71 (m, 1H), 3.02 (d, *J* = 1.2 Hz, 1H), 1.91 (ddd, *J* = 14.8, 4.0, 4.0 Hz, 1H), 1.68 (s, 3H), 1.65−1.60 (m, 1H), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 138.7, 138.0, 135.8 (4C), 133.51, 133.5, 129.9 (2C), 128.6 (2C), 128.5 (2C), 128.3 (2C), 128.0 (2C), 127.96, 127.9 (2C), 127.86 (2C), 127.8, 111.1, 80.7, 78.8, 74.9, 73.1, 72.9, 63.7, 35.9, 27.0 (3C), 19.4, 17.9; IR (neat) 3450, 3071, 2932, 2859, 1955, 1893, 1428, 1113 cm^{-1}; HRMS (ESI) m/z for $C_{38}H_{46}NaO_4Si$ $[M + Na]^+$ calcd 617.3058, obsd 617.3050.

*(7S,8S)-7,8-Bis(benzyloxy)-2,2,3,3,12,12-hexamethyl-11,11-diphenyl-5-(prop-1-en-2-yl)-4,10-dioxa-3,11-disilatridecane (**25**).* Imidazole (1.03 g, 15.1 mmol) and a catalytic amount of DMAP were added to a rt solution of alcohols **24** (3.00 g, 5.04 mmol) in DMF (8.4 mL). Upon complete solvation, TBSCl (1.14 g, 7.56 mmol) was added in one portion and the reaction mixture was stirred at rt for 12 h. Saturated aqueous NH_4Cl (10 mL) was added, and the mixture was extracted with EtOAc (3 × 25 mL). The combined organic extracts were dried and the solvent was evaporated under reduced pressure. Purification via flash chromatography on silica gel (8:1 hexanes/EtOAc, v/v) afforded **25** (3.24 g, 91%) as a diastereomeric mixture in the form of a colorless oil; R_f 0.56 (8:1 hexanes/EtOAc, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−7.66 (m, 8H), 7.46−7.20 (m, 32H), 4.87−4.85 (m, 1H), 4.77−4.69 (m, 4H), 4.66−4.47 (m, 6H), 4.45−4.39 (m, 1H), 4.24 (dd, *J* = 8.8, 3.2 Hz, 1H), 4.16 (dd, *J* = 7.6, 6.0 Hz, 1H), 3.96−3.79 (m, 5H), 3.78−3.63 (m, 2H), 3.57 (ddd, *J* = 8.4, 4.4, 4.4 Hz, 1H), 1.94−1.84 (m, 2H), 1.75−1.66 (m, 2H), 1.65 (s, 3H), 1.64 (s, 3H), 1.08 (s, 9H), 1.07 (s, 9H), 0.91 (s, 9H), 0.86 (s, 9H), 0.03 to −0.02 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 147.3, 139.09, 139.07, 139.0 (2C), 135.81 (6C), 135.78 (2C), 133.7 (2C), 133.67 (2C), 129.8 (4C), 128.39 (2C), 128.37 (4C), 128.3 (2C), 128.0 (6C), 127.9 (2C), 127.8 (6C), 127.7 (2C), 127.6, 127.57, 127.5, 127.48, 112.0, 111.3, 81.0, 80.9, 76.0, 75.9, 74.5, 74.1, 73.1, 73.0, 72.5, 72.4, 64.2, 63.8, 37.8, 36.7, 27.04 (3C), 27.02 (3C), 26.1 (3C), 26.0 (3C), 19.4, 19.3, 18.34, 18.3, 16.9, 16.6, −4.3, −4.6, −4.8, −4.9; IR (neat) 2954, 2928, 2886, 1251, 1112 cm^{-1}; HRMS (ESI) m/z for $C_{44}H_{60}NaO_4Si_2$ $[M + Na]^+$ calcd 731.3922, obsd 731.3892.

*(2S,3S)-2,3-Bis(benzyloxy)-5-[(tert-butyldimethylsilyl)oxy]-6-methylhept-6-en-1-ol (**26**).* Ammonium fluoride (183.0 mg, 4.94 mmol) was added to a solution of **25** (500 mg, 0.705 mmol) in methanol (14 mL). The reaction mixture was warmed at 40 °C for 2.5 days before being cooled to 0 °C and quenched by the addition of saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with EtOAc (3 × 25 mL), and the pooled extracts were dried and concentrated. Purification via flash chromatography on silica gel (8:1 hexanes/EtOAc, v/v) provided alcohol **26** (286.4 mg, 86%) as a diastereomeric mixture in the form of a colorless oil; R_f 0.15 (8:1 hexanes/EtOAc, v/v); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.28 (m, 20H), 4.91−4.89 (br m, 1H), 4.79−4.76 (br m, 2H), 4.72−4.68 (m, 2H), 4.67−4.55 (m, 6H), 4.50 (d, *J* = 11.6 Hz, 1H), 4.28 (dd, *J* = 8.8, 3.2 Hz, 1H), 4.20 (app t, *J* = 6.0 Hz, 1H), 3.91 (ddd, *J* = 9.2, 4.4, 2.4 Hz, 1H), 3.87−3.77 (m, 2H), 3.75−3.71 (m, 1H), 3.70−3.61 (m, 4H), 2.17 (br s, 1H), 2.13 (br s, 1H), 1.99−1.88 (m, 2H), 1.80−1.71 (m, 2H), 1.69 (s, 3H), 1.67 (s, 3H), 0.91 (s, 9H), 0.87 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 147.3, 138.5 (2C), 138.31, 138.3, 128.64 (2C), 128.6 (2C), 128.58 (2C), 128.5 (2C), 128.1 (2C), 128.06 (2C), 128.0 (2C), 127.97 (2C), 127.9 (2C), 127.8 (2C), 112.0, 111.4, 79.0, 78.9, 76.4, 76.2, 74.2, 74.1, 72.7, 72.6, 72.5, 72.3, 62.0 (2C), 37.4, 36.3, 26.1 (3C), 26.0 (3C), 18.32, 18.3, 17.0, 16.7, −4.3, −4.6, −4.9, −4.91; IR (neat) 3439, 2956, 2929, 2889, 2858, 1459, 1250, 1073 cm^{-1}; HRMS (ESI) for $C_{28}H_{42}NaO_4Si$ $[M + Na]^+$ calcd 493.2745, obsd 493.2758.

*(5S,6S,E)-5,6-Bis(benzyloxy)-8-[(tert-butyldimethylsilyl)oxy]-3,9-dimethyldeca-3,9-dien-2-one (**27**).* Alcohol mixture **26** (263.4 mg, 0.559 mmol) was dissolved in CH_2Cl_2 (5.6 mL) and cooled to 0 °C. Sodium bicarbonate (705.2 mg, 8.39 mmol) and Dess−Martin periodinane (356.0 mg, 0.839 mmol) were added sequentially and the cold bath was removed. The reaction mixture was stirred at rt for 2 h and then saturated solutions of $NaHCO_3$ (10 mL) and NaS_2O_3 (10 mL) were added. The mixture was stirred vigorously for 30 min, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the combined organic extracts were dried, and the solvent was evaporated. The corresponding aldehyde was taken to the next step with no further purification. A solution of 3-oxobutan-2-ylphosphonate (256.3 mg, 1.23 mmol) in THF (1.9 mL) was added to a cooled (0 °C) slurry of sodium hydride (44.8 mg, 1.12 mmol, 60% in oil) in THF (2.2 mL). After 1 h, a solution of aldehyde in THF (1.9 mL) was added via cannula, and the reaction mixture was warmed to rt and stirred for 14 h prior to the addition of saturated aqueous NH_4Cl (5 mL). The mixture was partitioned between water and EtOAc, and the layers were separated. The aqueous layer was extracted with EtOAc (3 × 20 mL), and the combined extracts were dried and concentrated. Purification via flash chromatography (9:1 hexanes/EtOAc) afforded **27** (111.6 mg, 38%) as a mixture of isomers in the form of a colorless oil. Enone **28** was obtained in 14% yield and spectral data are shown below. The relative configuration was determined after the Diels−Alder cycloaddition and COSY/NOESY analyses.

*Spectral Data for **28**.* R_f 0.30 (9:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ +1.55 (*c* 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.27 (m, 10H), 6.55−6.51 (m, 1H), 4.87−4.85 (m, 1H), 4.77−4.74 (m, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.63−4.57 (m, 2H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.32 (dd, *J* = 9.2, 5.2 Hz, 1H), 4.24 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.75 (ddd, *J* = 8.4, 4.8, 3.6 Hz, 1H), 2.29 (s, 3H), 1.85 (ddd, *J* = 14.0, 8.4, 3.6 Hz, 1H), 1.71 (d, *J* = 0.8 Hz, 3H), 1.69−1.66 (m, 1H), 1.65 (s, 3H), 0.90 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 147.9, 140.5, 140.2, 138.7, 138.1, 128.6 (2C), 128.5 (2C), 128.1 (2C), 128.0, 127.8 (2C), 127.7, 111.5, 78.4, 77.8, 73.8, 73.4, 71.5, 38.4, 26.0 (3C), 25.8, 18.3, 17.1, 12.1, −4.3, −4.9; IR (neat) 2950, 2930, 2855, 1677, 1458, 1251, 1072 cm^{-1}; HRMS (ESI) m/z for $C_{32}H_{46}NaO_4Si$ $[M + Na]^+$ calcd 545.3058, obsd 545.3059.

*Allyl {(5S,6S,8S,E)-5,6-Bis(benzyloxy)-8-[(tert-butyldimethylsilyl)-oxy]-3,9-dimethyldeca-1,3,9-trien-2-yl} Carbonate (**29**).* A solution

of enone **28** (40.7 mg, 77.9 μmol) in DME (0.8 mL) was added dropwise to a −78 °C solution of KHMDS (23.3 mg, 0.117 mmol) in DME (0.33 mL). The reaction mixture was stirred for 15 min at −78 °C before allyl chloroformate (33 μL, 0.31 mmol) was added in one portion, and stirring was continued for 1 h. Saturated aqueous NH_4Cl (3 mL) was added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined extracts were dried over $MgSO_4$ and the volatiles were removed in vacuo. Purification via flash chromatography (20:1 hexanes/EtOAc, v/v) provided enol carbonate **29** (19.9 mg, 42%) as a colorless oil; R_f 0.37 (8:1 hexanes/EtOAc, v/v); $[\alpha]_D^{23}$ +24.9 (*c* 0.995, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.27 (m, 10H), 5.93 (dddd, *J* = 16.0, 10.4, 5.6, 5.6 Hz, 1H), 5.83 (d, *J* = 9.6 Hz, 1H), 5.42−5.34 (m, 1H), 5.30−5.25 (m, 1H), 5.10 (d, *J* = 2.0 Hz, 1H), 5.03 (d, *J* = 2.4 Hz, 1H), 4.84 (br s, 1H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.74−4.71 (m, 1H), 4.66−4.61 (m, 2H), 4.59−4.53 (m, 2H), 4.33 (d, *J* = 11.6 Hz, 1H), 4.28−4.21 (m, 2H), 3.68 (ddd, *J* = 8.4, 5.2, 3.2 Hz, 1H), 1.81−1.78 (m, 1H), 1.77 (s, 3H), 1.64 (s, 3H), 1.64−1.55 (m, 1H), 0.89 (s, 9H), 0.01 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 153.3, 148.2, 139.2, 138.5, 132.2, 131.4, 128.4 (2C), 128.39 (2C), 128.1 (2C), 127.7 (2C), 127.67, 127.5, 127.0, 119.4, 111.3, 103.1, 78.9, 77.7, 73.9, 73.4, 70.5, 69.1, 38.7, 26.1 (3C), 18.3, 17.0, 14.2, −4.3, −4.9; IR (neat) 3068, 3029, 2951, 2928, 2857, 1870, 1845, 1762, 1225, 1072 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{36}H_{50}NaO_6Si$ $[M + Na]^+$ calcd 629.3269, obsd 629.3244.

*Allyl {(4aR,5S,7S,8S,8aS)-7,8-Bis(benzyloxy)-5-[(tert-butyldimethylsilyl)oxy]-1,4a-dimethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2-yl} Carbonate (**30**) and Allyl {(4aS,5S,7S,8S,8aS)-7,8-Bis(benzyloxy)-5-[(tert-butyldimethylsilyl)oxy]-1,4a-dimethyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-2-yl} Carbonate (**31**).* Dibenzyl ether **29** (19.6 mg, 32.3 μmol) and BHT (0.7 mg, 3.23 μmol) were dissolved in 1,2-dichlorobenzene (6 mL), and the mixture was heated at 250 °C in a sealed tube for 20 h. The solvent was removed by low-pressure vacuum distillation, and the residue was purified via flash chromatography on silica gel (20:1 hexanes/EtOAc, v/v) to afford **30** (5.2 mg, 27%) as a colorless oil and a mixture containing both **30** and **31** (4.9 mg, 25%; **30**:**31** = 1:1.7).

*Spectral Data for Major Isomer of **30** (trans).* $[\alpha]_D^{23}$ −18.0 (*c* 0.255, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.26 (m, 10H), 5.95 (dddd, *J* = 16.0, 10.4, 5.6, 5.6 Hz, 1H), 5.41−5.34 (m, 1H), 5.31−5.25 (m, 1H), 5.18 (d, *J* = 11.2 Hz, 1H), 4.67−4.63 (m, 2H), 4.59 (d, *J* = 11.2 Hz, 1H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.2 Hz, 1H), 3.97 (ddd, *J* = 12.0, 8.4, 5.2 Hz, 1H), 3.58 (dd, *J* = 11.2, 8.4 Hz, 1H), 3.49 (dd, *J* = 2.4, 2.4 Hz, 1H), 2.74−2.67 (br m, 1H), 2.35−2.25 (m, 1H), 2.22−2.14 (m, 1H), 2.09−1.96 (m, 2H), 1.90 (ddd, *J* = 13.6, 12.0, 2.4 Hz, 1H), 1.79 (d, *J* = 1.2 Hz, 3H), 1.17 (dd, *J* = 13.2, 6.4 Hz, 1H), 0.95 (s, 3H), 0.90 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 142.4, 139.4, 138.8, 131.7, 128.5 (2C), 128.4 (2C), 128.1 (2C), 127.7, 127.6 (2C), 127.3, 123.6, 119.0, 82.3, 80.9, 75.5, 73.2, 72.3, 68.7, 42.5, 39.9, 34.0, 32.1, 26.1 (3C), 24.5, 18.2, 17.5, 14.2, −4.3, −4.7; IR (neat) 3061, 3032, 2927, 2853, 1870, 1845, 1752, 1254, 1231, 1095 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{36}H_{50}NaO_6Si$ $[M + Na]^+$ calcd 629.3269, obsd 629.3269.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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