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Desymmetrization of (*R*,*R*)-Hexa-1,5-diene-3,4-diol via Monofunctionalization and Rhodium-Catalyzed Allylic Substitution

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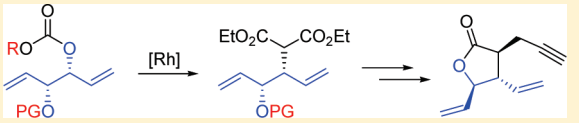
Supporting Information

ABSTRACT: A sequence of selective monoprotection and Rh-catalyzed enantioconservative allylic substitution is established as a desymmetrization strategy for C_2-symmetric hexa-1,5-diene-3,4-diol. A benzyl protecting group and ethyl carbonate as a leaving group emerged as the most useful combination with respect to reproducibility, stereoselectivity, and yield. A remarkable deviation from the normally observed regiospecificity of Rh-catalyzed allylic alkylations was observed for unprotected carbonates. In this case, a linear, rather than a branched alkylation product was obtained exclusively.



INTRODUCTION

Transition metal-catalyzed allylic alkylation reactions were for many years considered to be a domain of organopalladium chemistry.[1−4] Complexes of other metals, such as nickel,[2] molybdenum,[3] copper,[5] iridium,[6−8] iron,[9−11] or rhodium,[12] have attracted considerably less attention as precatalysts for this reaction, which is probably a consequence of the early observation that the reactivity of palladium exceeds that of rhodium, platinum, or ruthenium.[13] Against this background some drawbacks of Pd-catalyzed intermolecular allylic substitution reactions were accepted for quite some time. For instance, these reactions normally suffer from low selectivities, unless they proceed via symmetrical or electronically biased π-allyl complexes. This is attributed to the highly fluxional behavior of Pd-π-allyl complexes, which undergo rapid π-σ-π-rearrangement.[1] In contrast, Rhodium catalysts were as early as 1984 found to promote allylic substitution reactions with high regiospecificity.[14] Thus, secondary allylic carbonates yield predominantly branched substitution products, and primary allylic carbonates yield predominantly linear substitution products. Significant improvements of reactivity and selectivity were achieved over the past decade by Evans et al., who introduced phosphite-modified Wilkinson's catalyst for the regiospecific allylic alkylation.[15,16] Particularly important was the observation that the absolute configuration of an enantiopure secondary allylic carbonate is retained with this catalytic system,[17] which suggests the presence of a σ,π-coordinated enyl intermediate that undergoes a rather slow σ-π-σ-rearrangement.[12]

Over the past few years, we[18−23] and others[24−31] reported a number of examples for the successful application of the C_2-symmetric building block **1**[32] or *ent*-**1**[33] in stereoselective synthesis. Normally, a desymmetrization of **1** is required, which is in most cases achieved by selective monofunctionalization, e.g. protection, of one hydroxy group. Following the desymmetrization step, a selective secondary functionalization of the remaining hydroxy group or of one C−C double bond in **2** opens up a pathway to more complex structures. Our interest in this enantiopure building block was triggered by a study of directing effects exerted by polar functional groups, in particular allylic hydroxy groups, on the rate and selectivity of ring closing olefin (RCM) and enyne metathesis (RCEYM) reactions. For instance, we could demonstrate that dihydropyrans and dihydrofurans are selectively accessible from **1** in two or three steps, respectively, via ring size selective RCM[18,20] and ring size selective RCEYM[21] reactions. With a view toward the synthesis of other precursors for hydroxy group directed, ring size selective metathesis reactions, we became intrigued by the opportunity to combine a desymmetrization of **1** with a stereoconservative allylic substitution (Scheme 1).

Literature precedence for the use of **1** or its stereoisomers in allylic substitution reactions is scarce. An interesting example was published by Trost et al., who used a Pd-catalyzed allylic asymmetric alkylation of the cyclic carbonates derived from a mixture of **1**, *ent*-**1**, and *meso*-**1** to obtain enantiopure amino alcohols.[34,35] If **1** is desymmetrized by monoprotection, the remaining hydroxy group in **2** needs to be converted into a leaving group (LG). The steric demand of the protecting group (PG) and the leaving group in substrate **3** will most likely influence the formation of an assumed Rh-σ-π-enyl intermediate, and we therefore investigated different protecting and leaving groups (Scheme 2). A further complication might arise from the formation of Rh-chelate complexes by coordination of the remaining C−C double bond or the protected hydroxy group, which are both in close proximity to the Rh atom. In particular, coordination of the alkene is a possibility that must be taken into account, considering a recent report on the use of dienediol **1** as a chiral ligand for Rh-catalyzed conjugate addition reactions.[36] Formation of such a chelate will most likely disturb the regio- and stereochemical integrity of the Rh-σ-π-enyl intermediate and

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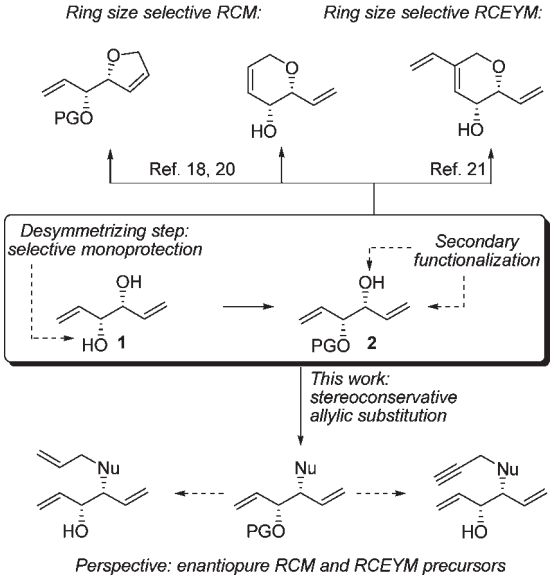
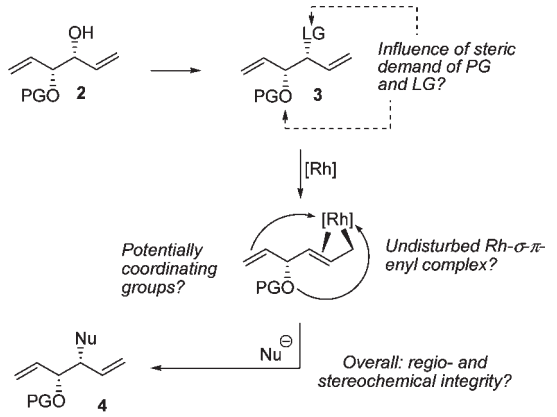
Scheme 1. Application of Diene 1 in Ring Size Selective RCM Reactions



Scheme 2. Mechanistic Considerations for the Envisaged Stereoconservative Allylic Substitution of Monoprotected Dienes 2



should therefore be detrimental to the overall regio- and stereospecificity of the allylic substitution. Even if the assumed Rh-σ-π-enyl intermediate undergoes a σ-π-σ-rearrangement only slowly in absolute terms, the overall result might still be unsatisfactory if the final nucleophilic attack is hampered by steric constraints, e.g. resulting from the protecting group.

The numerous imponderables described above and outlined in Scheme 2 prompted us to investigate stereoconservative Rh-catalyzed allylic alkylations of dienes **3** for a variety of protecting and leaving group combinations.

RESULTS AND DISCUSSION

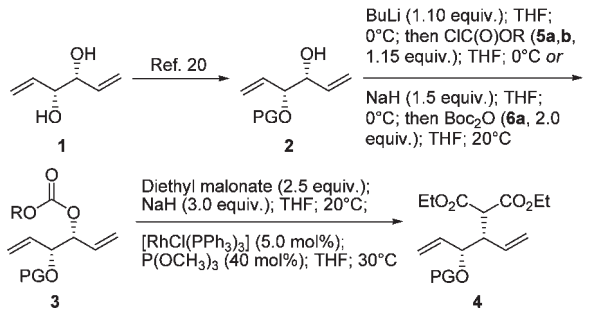
Two protecting groups with different steric demand were tested in this study. Monoprotected derivatives **2a** (PG = TBS) and **2b** (PG = Bn) were synthesized from **1** as described previously.[20] The remaining hydroxy group was converted into a carbonate, either by lithiation and reaction with methyl (**5a**) or ethyl chloroformate (**5b**), or by deprotonation with NaH and trapping with Boc_2O (**6a**). In this way, six precursors **3a**−**f** for the envisaged Rh-catalyzed allylic substitution were synthesized, which differ significantly in the steric demand of the side chain and at the reacting position. For the subsequent substitution reaction, Na-malonate was chosen as a nucleophile. The catalytic system tested for this transformation was trimethyl phosphite in combination with Wilkinson's catalyst (Scheme 3).

Table 1. Synthesis of Carbonates 3 and Results for Rh-Catalyzed Allylic Substitution[a]

entry	PG	2	reagent (R)	3 (yield)	4	dr	yield
1	TBS	**2a**	**5a** (Me)	**3a** (79%)	**4a**	3:1	n.d.[c]
2	TBS	**2a**	**5b** (Et)	**3b** (88%)	**4a**	5:1 to 10:1	56−83%
3	TBS	**2a**	**6a** (*t*-Bu)	**3c** (45%)	**4a**		—[b]
4	Bn	**2b**	**5a** (Me)	**3d** (86%)	**4b**	>8:1	47−71%
5	Bn	**2b**	**5b** (Et)	**3e** (58%)	**4b**	>10:1	58−63%
6	Bn	**2b**	**6a** (*t*-Bu)	**3f** (54%)	**4b**	1:1	79%

[a] See Scheme 3 for reagents and conditions. [b] Unreacted starting material was recovered in 88% yield. [c] Not determined. Complete conversion as judged from ^{1}H NMR spectrum of the crude mixture.

Scheme 3. Rh-Catalyzed Allylic Alkylation[a]



[a] See Table 1 for results.

We conclude from the results summarized in Table 1 that a sterically demanding protecting group such as TBS is less suitable for this reaction. In combination with leaving groups with low or intermediate steric demand results for the Rh-catalyzed substitution reaction were difficult to reproduce: for substrates **3a** and **3b** yields varied from 56% to 83%, and diastereomeric ratios in the range of 3:1 to 10:1 were observed (entries 1 and 2). Reproducibly, no reaction was observed for **3c**, which is sterically highly congested due to a combination of a TBS-protecting group and *tert*-butyl carbonate as a leaving group (entry 3). Significantly better results were obtained with a benzyl protecting group. In this series, both methyl and ethyl carbonates **3d**,**e** react in synthetically useful yields and selectivities. Results for **3e** appear to be slightly better, as the substitution product **4b** is generally formed in diastereomeric ratios better than 10:1 (entry 5). In contrast to the *tert*-butyl carbonate **3c** with a TBS-protecting group, the analogous benzyl protected derivative **3f** reacts with malonate in a substitution reaction; however, no diastereoselectivity was observed for this derivative (entry 6).

Currently, we do not fully understand why certain combinations of protecting group and leaving group (Table 1, entries 2 and 4) result, under apparently identical conditions, in a rather high spreading of conversion and isolated yield in the

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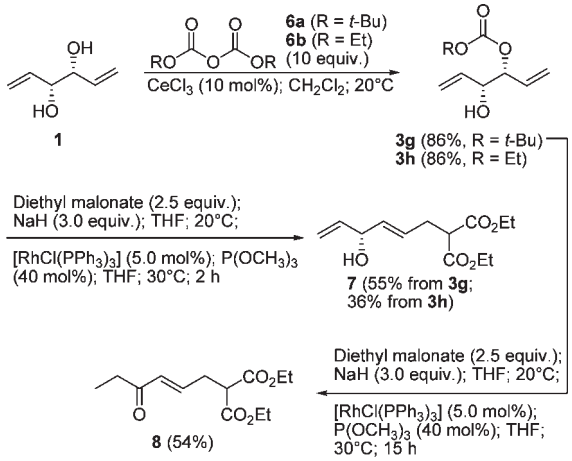
Scheme 4. Rh-Catalyzed Allylic Substitution with Unprotected Carbonates 3g,h

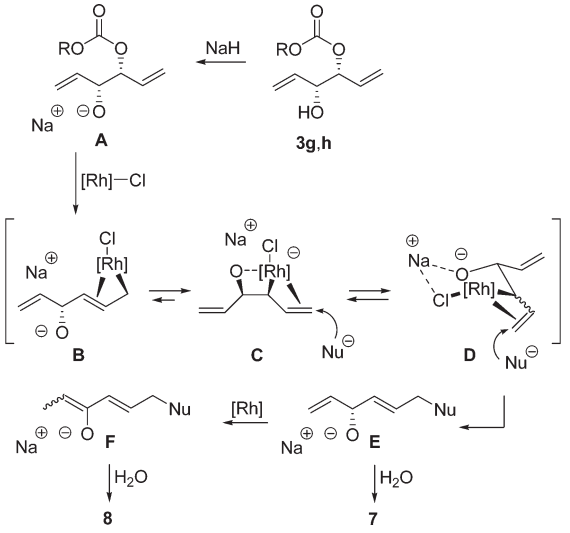


Rh-catalyzed allylic alkylation. It is, however, quite striking that high conversion seems to correlate with a lower diastereoselectivity. For these reasons, a combination of a benzyl protecting group and ethyl carbonate as a leaving group (substrate **3e**, entry 5) appears to be the best choice for synthetic purposes, because isolated yields of ca. 60% and diastereomeric ratios exceeding 10:1 are reliably obtained under these reaction conditions.

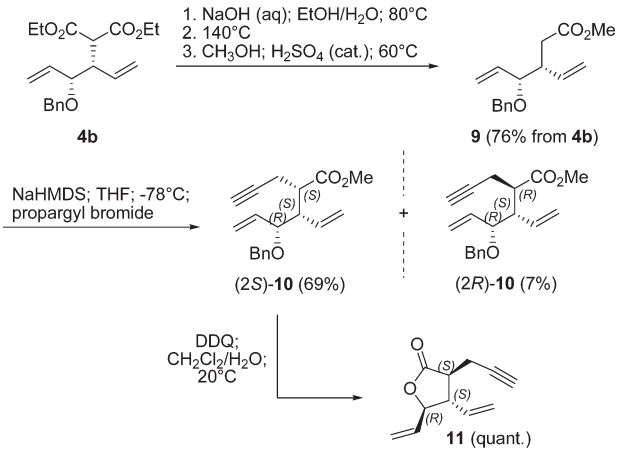
Polar functional groups, in particular protic groups, often exert a significant effect on the reactivity and selectivity of transition metal-catalyzed reactions.[37] Therefore, we also included the unprotected carbonates **3g**[19] and **3h** in this study. These were selectively synthesized from diol **1** and anhydrides **6a**,**b**, respectively, using Clarke's method.[38] We first tested *tert*-butyl carbonate **3g**, which was subjected to the previously established conditions of the Rh-catalyzed allylic substitution. After the standard reaction time of 15 h, only the ketone **8** could be isolated in 54% yield. We assume that **8** results from a γ-substitution and subsequent isomerization of the terminal allylic alcohol to an ethyl ketone. Therefore, the reaction time was reduced to 8 h, leading to a 1:1 mixture of γ-substitution product **7** and ketone **8**, which could be separated and isolated in 24% and 20% yield, respectively. If the reaction time was further reduced to 2 h, no isomerization product **8** was detected and allyl alcohol **7** was selectively obtained in 55% yield. Starting from ethyl carbonate **3h**, the same product was isolated, albeit in lower yield (Scheme 4).

A mechanistic rationale for this unusual regioselectivity is outlined in Scheme 5. Under the reaction conditions, the hydroxy group is rapidly deprotonated to the Na-alkoxide **A** by excess NaH. Oxidative addition gives the σ-π-enyl complex **B**, which might undergo a σ-π-σ-rearrangement to **C**, facilitated by coordination of the alkoxide to the Rh atom. Assuming that the chloro ligand remains bound to the Rh during the entire catalytic cycle, formation of a six-membered chelate complex **D**, in which a Na^+ ion interacts with the alkoxide and the Rh-chloro ligand simultaneously, would be an alternative scenario. Both organometallic intermediates **C** and **D** should preferrably undergo nucleophilic attack at the terminus, leading to an alkoxide **E** which, after hydrolytic workup, gives the observed product **7**. If the alkoxide is exposed to the Rh-catalyst for longer periods of time, it isomerizes slowly to the enolate **F**, which upon hydrolysis

Scheme 5. Mechanistic rationale for the γ-Selective Allylic Alkylation of 3g,h



Scheme 6. Diastereoselective Propargylation of a Na-Enolate Derived from 9



yields ketone **8** (Scheme 5). Remarkably, the Rh-catalyzed allylic substitution of **3g**,**h** proceeds to completion within 2 h, whereas benzyl- and TBS-protected carbonates **3a**—**f** require a reaction time of 15 h. Thus, the presence of an alkoxide does not only lead to an inverted regioselectivity, but also accelerates the reaction significantly.

To establish the relative configuration assigned to the substitution products **4** and to test further opportunities for their stereoselective functionalization, **4b** was converted to the ester **9** via saponification, decarboxylation, and esterification in 76% overall yield. In the following step, the possibility of a stereoselective α-alkylation was tested. It has previously been demonstrated that acyclic ester enolates with benzyloxy substituents in the proximity can be alkylated with high diastereoselectivity, presumably via formation of a chelate.[39] Upon treatment of **9** with NaHMDS and subsequent reaction of the resulting enolate with propargyl bromide, the α-propargylated ester **10** was obtained as a 10:1 mixture of two diastereomers. Gratifyingly, separation of the diastereomers was possible by column

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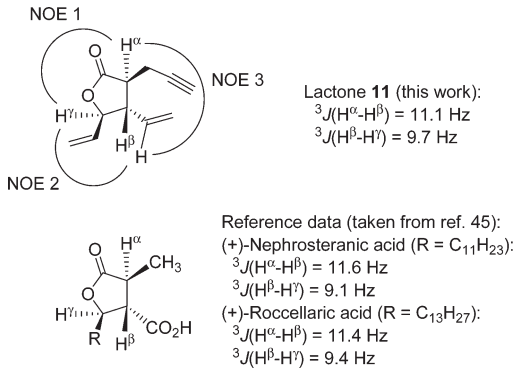
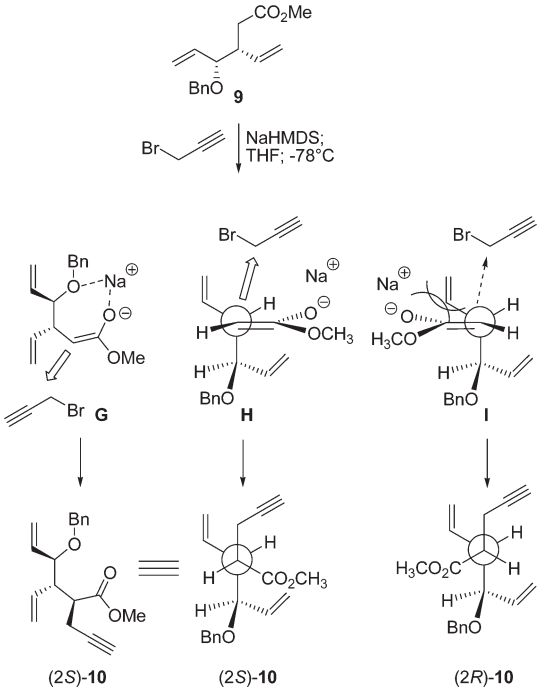


Figure 1. Assignment of relative configuration of lactone **11** by NMR methods and comparison with reference data.[45]

Scheme 7. Mechanistic Rationale for the Diastereoselective α-Alkylation of Ester 9



chromatography and enabled the isolation of (2*S*)-**10** in 69% and (2*R*)-**10** in 7% yield. Assignment of the relative configuration was achieved after debenzylation and cyclization to the more rigid lactone **11**. As a hydrogenative debenzylation catalyzed by Pd/C is obviously not an option, other methods were tested.[40] Lewis acids such as $TiCl_4$ or $Ti(O^iPr)_4$[41] resulted in the complete recovery of unreacted starting material (2*S*)-**10**, while BBr_3 led to extensive decomposition. Partial deprotection with formation of the desired lactone **11** was achieved by using DDQ under photoirradiation; however, conversion did not exceed 63%.[42] Quantitative and selective debenzylation with concomitant lactonization was eventually achieved with a large excess of DDQ in aqueous dichloromethane at ambient temperature.[43] Under these conditions, lactone **11** could be isolated in quantitative yield as a single isomer (Scheme 6).

Evidence for the assigned relative configuration of **11** came from one- and two-dimensional NMR experiments (Figure 1). Thus, nuclear Overhauser effects were observed between H^α and H^γ, and between the vinyl group at C^β and H^α and H^γ. In addition, we were able to determine the vicinal coupling constants $^3J(H^\alpha\text{—}H^\beta)$ = 11.1 Hz and $^3J(H^\beta\text{—}H^\gamma)$ = 9.7 Hz, and found that their values match those reported for the structurally related natural products nephrosteranic and rocellaric acid very well.[44,45]

The diastereoselectivity observed for the propargylation of the enolate derived from ester **9** may be rationalized assuming the formation of a seven-membered chelate **G**, which is preferentially alkylated from the less hindered *Si*-face (Scheme 7).

While the formation of such a chelate is not impossible, we believe that this scenario is less likely, because Na^+ has, compared to Li^+, a lower tendency to form sufficiently stable and rigid chelate complexes. Therefore, we propose an alternative explanation that is based on the minimization of allylic strain in the transition state.[46] If such a model is working in this case, transition state **H** should be favored over **I**, which would also result in a preferred attack of the enolate *Si*-face (Scheme 7).

CONCLUSION

Monoprotection in combination with enantioconservative Rh-catalyzed allylic substitution was established as a desymmetrization method for the enantiopure C_2-symmetric bisallylic alcohol **1**. This approach allows for further diastereoselective functionalization, e.g. enolate alkylation, which might become a useful route to olefin and enyne metathesis precursors. Another remarkable result of this study is the unusual γ-selectivity observed for the Rh-catalyzed allylic alkylation of a derivative with an unprotected hydroxy group adjacent to the leaving group.

EXPERIMENTAL SECTION

(3*R*,4*R*)-4-(*tert*-Butyldimethylsilyloxy)hexa-1,5-dien-3-ylmethyl Carbonate (3a). A solution of **2a** (2.00 g, 8.8 mmol) in dry and degassed THF (88 mL) was cooled to 0 °C. Butyllithium (1.6 M solution in hexanes, 9.7 mmol, 6.0 mL) was added and the reaction mixture was stirred for 10 min. Methyl chloroformate (**5a**, 10.6 mmol, 0.8 mL) was added and stirring was continued for 20 min. The reaction was then quenched by addition of a saturated aqueous solution of NH_4Cl. The aqueous phase was extracted with diethyl ether (3 × 20 mL) and the combined organic phases were dried with $MgSO_4$. Filtration, evaporation, and column chromatography on silica (hexanes/MTBE) gives **3a** (2.01 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86—5.73 (m, 2H), 5.36—5.16 (m, 4H), 5.02 (dddd, *J* = 6.6, 6.2, 1.2, 1.2 Hz, 1H), 4.20 (dddd, *J* = 6.6, 5.8, 1.3, 1.3v, 1H), 3.78 (s, 3H), 0.89 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 136.5, 132.4, 118.7, 117.1, 81.0, 74.5, 54.6, 25.7, 18.1, −4.6, −5.1; IR (neat) ν 3409 (bm), 2955 (s), 2932 (s), 2861 (m), 1749 (m), 1466 (m), 992 (m); LRMS (ESI) *m*/*z* 211 (8%), 285 (5%), 313 (70%), 341 (100%), 359 (50%); HRMS (ESI) calcd for $C_{14}H_{26}O_4NaSi$ 309.1498, found 309.1475; $[\alpha]^{27}_D$ 13.0 (*c* 0.79, CH_2Cl_2).

(3*R*,4*R*)-4-(*tert*-Butyldimethylsilyloxy)hexa-1,5-dien-3-ylethyl Carbonate (3b). The title compound was obtained from **2a** (200 mg, 0.9 mmol) and ethyl chloroformate (**5b**, 1.1 mmol, 103 μL) following the procedure given above for **3a**. Yield of **3b**: 231 mg (88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87—5.73 (m, 2H), 5.36—5.16 (m, 4H), 5.02 (dddd, *J* = 6.5, 6.5, 1.3, 1.3 Hz, 1H), 4.26—4.14 (m, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 136.4, 132.4, 118.6, 117.1, 80.7, 74.5, 63.9, 25.7, 18.2, 14.3, −4.6, −5.0; IR (neat) ν 2958 (w), 2930 (w), 2858 (w), 1750 (s), 1256 (s); LRMS (EI) *m*/*z* 147 (100%), 301 (M + H, 10%);

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HRMS (ESI) calcd for $C_{15}H_{28}O_4SiNa$ (M + Na) 323.1655, found 323.1676; $[\alpha]^{24}_D$ 29.7 (*c* 1.24, CH_2Cl_2).

***tert*-Butyl-(3*R*,4*R*)-4-(*tert*-butyldimethylsilyloxy)hexa-1,5-dien-3-yl Carbonate (3c).** A solution of **2a** (6.90 g, 30.2 mmol) in dry and degassed THF (150 mL) was cooled to 0 °C and NaH (60% dispersion in mineral oil, 1.81 g, 45.3 mmol) and Boc_2O (**6a**, 13.18 g, 60.4 mmol) were added. The reaction mixture was stirred at ambient temperature for 12 h and then quenched by addition of water. The aqueous phase was extracted with MTBE and the combined organic phases were washed with brine and then dried with $MgSO_4$. Filtration, evaporation, and column chromatography on silica gives **3c** (4.50 g, 45%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (ddd, *J* = 17.0, 10.5, 5.7 Hz, 1H), 5.77 (ddd, *J* = 17.0, 10.6, 6.3 Hz, 1H), 5.30 (ddd, *J* = 17.3, 1.4, 1.4 Hz, 1H), 5.28 (ddd, *J* = 17.1, 1.4, 1.4 Hz, 1H), 5.23 (ddd, *J* = 10.7, 1.3, 1.3 Hz, 1H), 5.18 (ddd, *J* = 10.4, 1.6, 1.6 Hz, 1H), 4.96 (ddm, *J* = 6.6, 6.5 Hz, 1H), 4.21 (ddm, *J* = 5.8, 5.8 Hz, 1H), 1.48 (s, 9H), 0.89 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 136.6, 132.8, 118.3, 116.9, 81.9, 80.0, 74.4, 27.9, 25.8, 18.2, −4.6, −4.9; IR (neat) ν 2957 (w), 2930 (w), 2887 (w), 2858 (w), 1742 (s), 1647 (w), 1473 (w), 1463 (w), 1369 (w), 1273 (s), 1252 (s), 1144 (s), 836 (s); LRMS (ESI) *m*/*z* 351 (M + Na, 80%), 329 (M + H, 10%), 295 (20%), 251 (20%), 211 (100%); HRMS (EI) calcd for $C_{17}H_{32}O_4Si$ (M) 328.2070, found 328.2087; $[\alpha]^{24}_D$ 37.9 (*c* 1.67, CH_2Cl_2). Anal. Calcd for $C_{17}H_{32}O_4Si$ (328.52): C, 62.2; H, 9.8. Found: C, 62.0; H, 10.1.

(3*R*,4*R*)-4-(Benzyloxy)hexa-1,5-dien-3-ylmethyl Carbonate (3d). The title compound was obtained from **2b** (200 mg, 1.0 mmol) and methyl chloroformate (**5a**, 1.2 mmol, 93 μL) following the procedure given above for **3a**. Yield of **3b**: 220 mg (86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.30 (m, 5H), 5.92−5.68 (m, 2H), 5.41−5.25 (m, 4H), 5.21 (dddd, *J* = 6.7, 6.7, 1.3, 1.3 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.92 (ddm, *J* = 7.5, 6.4 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 138.1, 133.9, 132.4, 128.3, 127.6, 127.5, 120.0, 119.0, 81.0, 79.5, 70.6, 54.7; IR (neat) ν 3030 (w), 2956 (w), 2864 (w), 1747 (s), 1441 (m), 1256 (s), 1070 (m), 1028 (w), 965 (m), 931 (m); LRMS (ESI) *m*/*z* 285 (M + Na, 100%), 263 (M + H, 20%), 227 (40%), 117 (50%); HRMS (ESI) calcd for $C_{15}H_{19}O_4$ (M + H) 263.1283, found 263.1262; $[\alpha]^{25}_D$ 8.7 (*c* 1.19, CH_2Cl_2). Anal. Calcd for $C_{15}H_{18}O_4$ (262.30): C, 68.7; H, 6.9. Found: C, 68.6; H, 6.9.

(3*R*,4*R*)-4-(Benzyloxy)hexa-1,5-dien-3-ylethyl Carbonate (3e). The title compound was obtained from **2b** (2.91 g, 14.3 mmol) and ethyl chloroformate (**5b**, 17.2 mmol, 1.6 mL) following the procedure given above for **3a**. Yield of **3e**: 2.30 g (58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.25 (m, 5H), 5.88 (ddd, *J* = 17.2, 10.6, 6.5 Hz, 1H), 5.77 (ddd, *J* = 18.3, 10.9, 7.5 Hz, 1H), 5.42−5.32 (m, 3H), 5.29 (ddd, *J* = 10.6, 1.3, 1.3 Hz, 1H), 5.22 (dddd, *J* = 6.5, 6.5, 1.2, 1.2 Hz, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.93 (dd, *J* = 7.4, 6.5 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.6, 138.2, 133.9, 132.5, 128.3, 127.6, 127.5, 120.0, 118.8, 81.0, 79.3, 70.6, 64.0, 14.2; IR (neat) ν 2983 (w), 2868 (w), 1744 (s), 1371 (m), 1250 (s), 1089 (m), 1071 (m), 991 (m); LRMS (EI) *m*/*z* 277 (M + H, 2%), 91 (100%); HRMS (EI) calcd for $C_{16}H_{20}O_4$ (M^+) 276.1362, found 276.1342; $[\alpha]^{28}_D$ +5.8 (*c* 0.87, CH_2Cl_2). Anal. Calcd for $C_{16}H_{20}O_4$ (276.33): C, 69.5; H, 7.3. Found: C, 69.2; H, 7.5.

(3*R*,4*R*)-4-(Benzyloxy)hexa-1,5-dien-3-yl-*tert*-butyl Carbonate (3f). The title compound was obtained from **2b** (2.00 g, 9.8 mmol) and Boc_2O (**6a**, 19.6 mmol, 4.5 mL) following the procedure given above for **3c**. Yield of **3e**: 1.60 g (54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37−7.25 (m, 5H), 5.85 (ddd, *J* = 17.2, 10.6, 6.4 Hz, 1H), 5.77 (dddd, *J* = 16.3, 11.3, 8.8, 7.4 Hz), 5.41−5.23 (m, 4H), 5.19 (dddd, *J* = 6.5, 6.5, 1.0, 1.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 3.92 (ddm, *J* = 7.3, 6.6 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 138.2, 134.0, 132.7, 128.2, 127.5, 127.4, 119.7, 118.4, 82.0, 81.2, 78.4, 70.6, 27.7; IR (neat) ν 2980 (w), 1741 (s), 1646 (w), 1455 (w), 1272 (s), 1252 (s), 1161 (m), 1122 (m), 1087 (m), 1071 (m), 929 (m), 697 (m); LRMS (EI) *m*/*z* 305 (M + H, 15%), 271 (35%), 169 (40%), 117 (100%), 91 (55%); HRMS (ESI) calcd for $C_{18}H_{25}O_4$ (M^+ + H) 305.1753, found 305.1741; $[\alpha]^{24}_D$ −41.0 (*c* 1.09, CH_2Cl_2). Anal. Calcd for $C_{18}H_{24}O_4$ (304.38): C, 71.0; H, 8.0. Found: C, 71.1; H, 7.9.

***tert*-Butyl-(3*R*,4*R*)-4-hydroxyhexa-1,5-dien-3-yl Carbonate (3g).** The title compound was obtained from **1** (5.00 g, 43.2 mmol) and Boc_2O (**6a**, 87.6 mmol, 19.7 g) following the previously published procedure.[19] Yield of **3g**: 8.00 g (85%). All analytical data match those previously reported in the literature.

Ethyl-(3*R*,4*R*)-4-hydroxyhexa-1,5-dien-3-yl Carbonate (3h). To a solution of **1** (500 mg, 4.4 mmol) in dichloromethane (44 mL) was added $CeCl_3$ (163 mg, 0.4 mmol, 10 mol %) and diethyl dicarbonate (**6b**, 1.3 mL, 8.8 mmol). The reaction mixture was stirred at ambient temperature for 12 h, diluted with ethyl acetate, and then washed with a saturated aqueous solution of Na_2CO_3, followed by water and brine. The organic phase was dried with $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography to give **3h** (704 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (ddd, *J* = 16.1, 9.2, 5.5 Hz, 1H), 5.81 (ddd, *J* = 17.2, 10.4, 6.7 Hz, 1H), 5.45−5.29 (m, 3H), 5.26 (dm, *J* = 10.5 Hz, 1H), 5.03 (ddm, *J* = 6.5, 6.4 Hz, 1H), 4.22 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 135.5, 132.3, 119.7, 117.6, 80.8, 73.7, 64.2, 14.2; IR (neat) ν 3469 (bw), 3087 (w), 2986 (w), 1744 (m), 1372 (m), 1250 (s), 991 (m), 928 (m); LRMS (EI) *m*/*z* 169 (15%), 130 (5%), 95 (8%), 71 (20%), 57 (100%); HRMS (ESI) calcd for $C_9H_{14}O_4$ (M^+) 186.0887, found 186.0905; $[\alpha]^{24}_D$ −25.0 (*c* 1.08, CH_2Cl_2). Anal. Calcd for $C_9H_{14}O_4$ (186.21): C, 58.1; H, 7.6. Found: C, 57.8; H, 7.6.

Diethyl 2-((3′*S*,4′*R*)-4′-(*tert*-Butyldimethylsilyloxy)hexa-1′,5′-dien-3′-yl)malonate (4a). The following procedure is representative for the synthesis of **4a**: To a suspension of Wilkinson's catalyst (79 mg, 0.1 mmol, 5 mol %) in dry and degassed THF (37 mL) was added $P(OMe)_3$ (80 μL, 0.7 mmol) and the mixture was stirred for 15 min at ambient temperature. In a separate flask, diethyl malonate (0.6 mL, 4.3 mmol) was dissolved in dry and degassed THF (6.0 mL) and NaH (60% dispersion in mineral oil, 204 mg, 5.1 mmol) was added to this solution. This solution was also stirred for 15 min at ambient temperature. The solution of the phosphite-modified Rh-catalyst was then transferred to the solution of the malonate via canula, and subsequently a solution of carbonate **3b** (500 mg, 1.7 mmol) in dry and degassed THF (6.0 mL) was slowly added to the malonate/catalyst mixture. The reaction mixture was warmed to 30 °C and stirred at this temperature for 15 h. The reaction was quenched by careful addition of water, the organic layer was separated, and the aqueous layer was extracted with MTBE. The combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography on silica to give **4a** (352 mg, 56%) as a 10:1 mixture of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93−5.26 (m, 2H), 5.18−4.99 (m, 4H), 4.25−4.06 (m, 5H), 3.73 (d, *J* = 7.1 Hz, 1H), 2.87 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 6H), 0.88 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 168.2, 139.1, 134.7, 118.8, 116.4, 74.6, 61.3, 61.0, 52.5, 50.8, 25.8, 18.1, 14.1, 14.0, −4.1, −5.0; IR (neat) ν 2930 (w), 2857 (w), 1732 (m), 1464 (w), 1369 (w), 1252 (m), 1078 (m), 836 (m); LRMS (EI) *m*/*z* 393 (M + Na, 15%), 371 (M + H, 5%), 239 (30%), 165 (100%); HRMS (ESI) calcd for $C_{19}H_{34}O_5NaSi$ (M + Na) 393.2073, found 393.2036; $[\alpha]^{23}_D$ −0.1 (*c* 0.80, CH_2Cl_2).

Diethyl 2-((3′*S*,4′*R*)-4′-(Benzyloxy)hexa-1′,5′-dien-3′-yl)-malonate (4b). The title compound was obtained from **3e** (3.00 g, 10.9 mmol), Wilkinson's catalyst (502 mg, 0.5 mmol, 5 mol %), $P(OMe)_3$ (0.5 mL, 4.3 mmol), and diethyl malonate (4.1 mL, 27.1 mmol) following the procedure given above for **4a**. The diastereomeric ratio of **4b** was 20:1. Yield of **4b**: 2.18 g (58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.27 (m, 5H), 5.84 (ddd, *J* = 16.7, 10.6, 9.8 Hz, 1H), 5.67 (ddd, *J* = 17.2, 10.3, 8.0

Hz, 1H), 5.30 (ddd, J = 10.3, 1.7, 0.5 Hz, 1H), 5.22 (ddd, J = 17.2, 1.7, 0.7 Hz, 1H), 5.15 − 5.05 (m, 2H), 4.56 (d, J = 11.5 Hz, 1H), 4.28 (d, J = 11.5 Hz, 1H), 4.15−4.00 (m, 4H), 3.88 (dd, J = 8.4, 8.3 Hz, 1H), 3.83 (d, J = 6.7 Hz, 1H), 3.03 (ddd, J = 9.1, 9.1, 6.7 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 168.2, 138.2, 136.5, 134.5, 128.2, 127.8, 127.4, 119.2, 119.2, 81.0, 70.5, 61.2, 61.0, 53.1, 49.1, 14.0, 14.0; IR (neat) ν 2982 (w), 1730 (s), 1443 (w), 1370 (w), 1262 (s), 1093 (m), 926 (m), 732 (s); LRMS (ESI) m/z 369 (M + Na, 5%), 347 (M + H, 10%), 279 (45%), 165 (100%); HRMS (ESI) calcd for $C_{20}H_{27}O_5$ (M + H) 347.1858, found 347.1839; $[\alpha]^{24}_D$ −11.4 (c 0.90, CH_2Cl_2).

(*R*,*E*)-Diethyl 2-(4′-Hydroxyhexa-2′,5′-dienyl)malonate (7). The title compound was obtained from **3g** (500 mg, 2.3 mmol), Wilkinson's catalyst (108 mg, 0.12 mmol, 5 mol %), $P(OMe)_3$ (55 μL, 0.47 mmol), and diethyl malonate (886 μL, 5.8 mmol) following the procedure given above for **4a**. The reaction was quenched after 2 h. Yield of **7** from **3g**: 328 mg (55%). Alternatively, compound **7** was obtained from **3h** (500 mg, 2.7 mmol), Wilkinson's catalyst (124 mg, 0.14 mmol, 5 mol %), $P(OMe)_3$ (63 μL, 0.50 mmol), and diethyl malonate (1.00 mL, 6.7 mmol) following the procedure given above for **4a**. The reaction was quenched after 2 h. Yield of **7** from **3h**: 248 mg (36%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (ddd, J = 17.2, 10.4, 5.8 Hz, 1H), 5.67 (ddd, J = 15.4, 6.3, 6.3 Hz, 1H); 5.58 (dd, J = 15.4, 5.4 Hz, 1H), 5.22 (dm, J = 17.2 Hz, 1H), 5.11 (dm, J = 10.4 Hz, 1H), 4.56 (m, 1H), 4.18 (q, J = 7.1 Hz, 4H), 3.39 (t, J = 7.5 Hz, 1H), 2.62 (dd, J = 7.5, 5.7 Hz, 2H), 1.78 (bs, 1H), 1.25 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 139.3, 134.2, 127.3, 115.0, 73.3, 61.4, 51.7, 31.3, 14.0; IR (neat) ν 3466 (bw), 2982 (m), 1727 (s), 1369 (m), 1223 (m), 1152 (s), 1030 (m); LRMS (ESI) m/z 279 (M^+ + Na, 22%), 165 (100%); HRMS (ESI) calcd for $C_{13}H_{21}O_5$ (M^+ + H) 257.1389, found 257.1370; $[\alpha]^{28}_D$ −3.6 (c 0.96, CH_2Cl_2). Anal. Calcd for $C_{13}H_{20}O_5$ (256.13): C, 60.9; H, 7.9. Found: C, 60.9; H, 7.7.

(*E*)-Diethyl 2-(4′-Oxohex-2′-enyl)malonate (8). The title compound was obtained from **3g** (500 mg, 2.3 mmol), Wilkinson's catalyst (108 mg, 0.12 mmol, 5 mol %), $P(OMe)_3$ (55 μL, 0.47 mmol), and diethyl malonate (886 μL, 5.8 mmol) following the procedure given above for **4a** (reaction time: 15 h). Yield of **8**: 320 mg (54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (dt, J = 15.8, 7.0 Hz, 1H), 6.12 (dm, J = 15.9 Hz, 1H), 4.17 (q, J = 6.8 Hz, 4H), 3.46 (t, J = 7.4 Hz, 1H), 2.75 (ddd, J = 7.1, 7.1, 1.0 Hz, 2H), 2.51 (q, J = 7.3 Hz, 2H), 1.23 (t, J = 7.1 Hz, 6H), 1.04 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 168.3, 141.3, 131.9, 61.6, 50.7, 33.4, 31.2, 14.0, 7.9; IR (neat) ν 2981 (m), 2940 (w), 1729 (s), 1675 (m), 1633 (m), 1369 (m), 1153 (s), 1030 (s); LRMS (ESI) m/z 279 (100%, M + Na), 257 (35%, M + H), 239 (10%); HRMS (EI) calcd for $C_{13}H_{20}O_5$ (M^+) 256.1311, found 256.1322.

(3*R*,4*R*)-Methyl 4-(Benzyloxy)-3-vinylhex-5-enoate (9). To a solution of **4b** (2.34 g, 6.7 mmol) in ethanol (14 mL) was added a solution of NaOH (944 mg, 23.6 mmol) in H_2O (3 mL). The reaction was heated to reflux and stirred at this temperatur for 3 h. All volatiles were removed in vacuo, and the residue was dissolved in ethyl acetate and diluted hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with diluted hydrochloric acid, saturated aqueous $NaHCO_3$ solution, and brine. It was then dried with $MgSO_4$, filtered, and evaporated. The residue was heated in substance to 140 °C and stirred at this temperature for 2 h. After cooling to ambient temperature, the residue was dissolved in methanol (30 mL) and a catalytic amount of concd H_2SO_4 (70 mg, 10 mol %) was added. The mixture was heated to reflux for 12 h, cooled to ambient temperature, and then evaporated. The residue was partitioned in water and ethyl acetate, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and brine, dried with $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography on silica to give **9** (1.33 g, 76% over three steps, based on **4b**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−7.27 (m, 5H), 5.81−5.62 (m, 2H), 5.31 (dm, J = 10.4 Hz, 1H), 5.23 (dm, J = 17.2 Hz, 1H), 5.08 (dm, J = 17.2 Hz, 1H), 5.06 (dm, J = 10.6 Hz, 1H), 4.60 (d, J = 11.9 Hz, 1H), 4.32 (d, J = 11.9 Hz, 1H), 3.68 (dd, J = 7.5, 7.2 Hz, 1H), 3.60 (s, 3H), 2.82 (m, 1H), 2.65 (dd, J = 15.3, 5.4 Hz, 1H), 2.33 (dd, J = 15.3, 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 138.4, 137.4, 136.5, 128.3, 127.7, 127.4, 118.7, 116.6, 82.5, 70.3, 51.4, 45.0, 35.6; IR (neat) ν 2950 (w), 1736 (s), 1641 (w), 1454 (w), 1251 (m), 1170 (m), 1066 (s), 920 (s), 697 (s); LRMS (ESI) m/z 283 (M^+ + Na, 100%), 261 (M^+ + H, 10%), 153 (5%); HRMS (EI) calcd for $C_{16}H_{20}O_3$ (M^+) 260.1412, found 260.1400; $[\alpha]^{23}_D$ −25.4 (c 0.86, CH_2Cl_2). Anal. Calcd for $C_{16}H_{20}O_3$ (260.33): C, 73.8; H, 7.7. Found: C, 73.6; H, 8.0.

Propargylation of 9. A solution of ester **9** (1.10 g, 4.2 mmol) in dry and degassed THF (42 mL) was cooled to −78 °C. NaHMDS (1.5 M solution in THF, 3.4 mL, 5.1 mmol) was added and the mixture was stirred at this temperature for 30 min. Propargyl bromide (80 wt % solution in toluene, 0.70 mL, 6.3 mmol) was added; the reaction mixture was then allowed to warm to ambient temperature and stirring was continued for 12 h. Water and MTBE were added to the reaction mixture, the organic layer was separated, and the aqueous layer was extracted with MTBE. The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography to give two diastereomers in a ratio of 10:1. The major diastereomer (2*S*)-**10** (870 mg, 69%) is more polar and was eluted in the second fraction, the minor diastereomer (2*R*)-**10** (86 mg, 7%) is less polar and was eluted first. Analytical data of **(2*S*,3*S*,4*R*)-methyl-4-(benzyloxy)-2-(prop-2-inyl)-3-vinylhex-5-enoate ((2*S*)-10)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.26 (m, 5H), 5.66 (ddd, J = 17.9, 10.3, 8.1 Hz, 1H), 5.47 (ddd, J = 16.9, 10.1, 6.9 Hz, 1H), 5.29 (dm, J = 10.3 Hz, 1H), 5.21 (dm, J = 17.1 Hz, 1H), 5.15 (dm, J = 10.3 Hz, 1H), 5.09 (dm, J = 17.1 Hz, 1H), 4.58 (d, J = 11.7 Hz, 1H), 4.32 (d, J = 11.7 Hz, 1H), 3.70 (dd, J = 7.7, 7.7 Hz, 1H), 3.55 (s, 3H), 2.85 (m, 1H), 2.75 (m, 1H), 2.43−2.35 (m, 2H), 1.96 (dd, J = 2.5, 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 138.1, 136.2, 134.4, 128.3, 127.9, 127.5, 119.6, 119.1, 81.8, 81.0, 70.2, 69.9, 51.6, 50.8, 46.0, 18.9; IR (neat) ν 3296 (bm), 2950 (w), 1734 (s), 1641 (w), 1454 (w), 1170 (m), 1066 (m), 923 (s), 732 (s); LRMS (ESI) m/z 321 (M^+ + Na, 100%); HRMS (EI) calcd for $C_{19}H_{22}O_3$ (M^+) 298.1569, found 298.1583; $[\alpha]^{30}_D$ − 20.0 (c 0.81, CH_2Cl_2). Anal. Calcd for $C_{19}H_{22}O_3$ (260.33): C, 76.5; H, 7.4. Found: C, 76.1; H, 7.4. Analytical data of **(2*R*,3*S*,4*R*)-methyl-4-(benzyloxy)-2-(prop-2-inyl)-3-vinylhex-5-enoate ((2*R*)-10)**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.25 (m, 5H), 5.67 (ddd, J = 17.4, 10.3, 8.0 Hz, 1H), 5.60 (ddd, J = 17.0, 10.2, 10.2 Hz, 1H), 5.29 (dm, J = 10.3 Hz, 1H), 5.22 (dm, J = 17.3 Hz, 1H), 5.15 (dm, J = 10.3 Hz, 1H), 5.12 (dm, J = 17.0 Hz, 1H), 4.59 (d, J = 11.3 Hz, 1H), 4.32 (d, J = 11.3 Hz, 1H), 3.82 (dd, J = 8.4, 8.4 Hz, 1H), 3.60 (s, 3H), 3.23 (ddd, J = 8.1, 7.4, 4.2 Hz, 1H), 2.64 (ddd, J = 9.4, 8.4, 4.2 Hz, 1H), 2.56 (ddd, J = 16.8, 7.4, 2.6 Hz, 1H), 2.33 (ddd, J = 16.8, 8.1, 2.6 Hz, 1H), 1.99 (dd, J = 2.6, 2.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 138.3, 137.1, 134.2, 128.3, 128.0, 127.5, 119.3, 118.7, 81.7, 81.0, 70.5, 69.9, 51.4, 50.8, 43.8, 19.7; $[\alpha]^{31}_D$ −41.5 (c 0.57, CH_2Cl_2).

(3*S*,4*S*,5*R*)-3-(Prop-2′-inyl)-4,5-divinyldihydrofuran-2(3*H*)-one (11). To a solution of (2*S*)-**10** (396 mg, 1.3 mmol) in dichloromethane (25 mL) was added water (0.5 mL) and DDQ (3.01 g, 13.27 mmol). The reaction mixture was stirred at ambient temperature for 12 h. It was then diluted with water, the organic layer was separated, and the aqueous layer was extracted with dichloromethane. The combined organic phases were washed with brine, dried with $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography to give lactone **11** (233 mg, 100%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.83 (ddd, J = 17.2, 10.5, 6.7 Hz, 1H), 5.69 (ddd, J = 17.3, 10.0, 8.3 Hz, 1H), 5.39 (ddd, J = 17.2, 1.1, 1.1 Hz, 1H), 5.31 (ddd, J = 10.5, 1.0, 1.0 Hz, 1H), 5.25 (ddd, J = 17.3, 1.1, 1.1 Hz, 1H), 5.24 (dm, J = 10.0 Hz, 1H), 4.51 (dddd, J = 9.7, 6.7,

1.0, 1.0 Hz, 1H), 2.89 (m, 1H), 2.73 (ddd, J = 17.1, 4.8, 2.6 Hz, 1H), 2.64 (ddd, J = 11.1, 4.8, 4.8 Hz, 1H), 2.50 (ddd, J = 17.1, 4.8, 2.7 Hz, 1H), 2.03 (dd, J = 2.7, 2.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.2, 133.4, 133.3, 120.1, 119.2, 82.6, 79.4, 71.3, 51.0, 44.9, 17.1; IR (neat) ν 3296 (bm), 3085 (w), 2987 (w), 2915 (w), 1770 (s), 1645 (w), 1426 (m), 1182 (s), 986 (s), 929 (s); LRMS (ESI) m/z 199 (M^+ + Na, 100%); HRMS (EI) calcd for $C_{11}H_{12}O_2$ (M^+) 176.0837, found 176.0822; $[\alpha]^{29}_D$ −59.9 (c 1.01, CH_2Cl_2).

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, analytical data, copies of ^{1}H and ^{13}C NMR spectra for all new compounds, and full NMR-signal assignment for **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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