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Stereoselectivity in (*Z*)-Vinylmetal Additions to the Dictyostatin C1–C9 β-Silyloxy Aldehyde

Andrea Ambrosi,[a] Luca Pignataro,[a] Chiara Zanato,[a] and Cesare Gennari*[a]

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(*Z*)-Vinyl iodides **6a**–**d** were synthesized in high yield with good diastereo- and enantioselectivity using a Marshall–Tamaru, Pd-catalyzed allenylzinc reaction as the key step. The addition of **6a**–**d** to the dictyostatin C1–C9 β-silyloxy aldehyde **5** was carried out through the vinyllithium and lithium vinylzincate routes. The lithium vinylzincate additions always proceeded in higher yields and gave fewer side products than the corresponding vinyllithium additions. The configuration of the newly created C9 stereocenter was assigned through Rychnovsky's acetonide ^{13}C NMR method. The diastereoselectivity in this particular type of (*Z*)-vinylmetal addition reaction appears to be controlled by a subtle balance between the intrinsic stereochemical preference of the β-silyloxy aldehyde (1,3-*anti*-selective) and that of the chiral lithium (*Z*)-vinylzincates. The latter becomes more influential with increasing stereochemical complexity, that is, passing from a stereodyad (**6a**,**6b**) to a stereotriad (**6c**,**6d**).

Introduction

1,3-Asymmetric induction in nucleophilic additions to β-oxy-substituted aldehydes is an important tool in stereoselective synthesis and has been widely exploited. Models for rationalizing the 1,3-stereoselectivity have been proposed by Cram,[1] Reetz,[2] and Evans,[3,4] who invoked steric hindrance, polar effects, and chelation as the ruling factors. In the case of β-silyloxy aldehydes and when the nucleophiles do not contain additional elements of stereocontrol (e.g. chiral auxiliaries, further stereocenters, etc.), reactions generally show a moderate to high preference for 1,3-*anti*-stereoselectivity. Sterically encumbering silyl groups usually favor a nonchelation pathway, which leads to the preferential formation of 1,3-*anti* addition products according to Evans's polar model.[3] Exceptionally, the use of aluminum Lewis acids provides chelation control by a boat-like model, which reinforces the 1,3-*anti* stereochemical outcome.[4]

We have recently reported the total synthesis of 9-*epi*-dictyostatin (**1**, Scheme 1) and 12,13-bis-*epi*-dictyostatin (**2**).[5,6] The key step of the synthetic sequence involved the addition of (*Z*)-vinyl iodides **3** and **4** to C1–C9 β-OTBS-substituted aldehyde **5**, which proceeded via the corresponding lithium vinylzincates.[7] Surprisingly, we observed a very high diastereoselectivity (≥95:5) for the 1,3-*syn* product (9*R*) when **3** was used.[8] This result disagrees with the models mentioned above and dramatically contradicts a literature precedent where an almost identical reaction was claimed to be 100% 1,3-*anti*-stereoselective.[9] On the other hand, addition of **4** to **5** showed a distinct preference (≥95:5) for the 1,3-*anti* diastereomer (9*S*).

Curran and co-workers have reported that the addition of several (*Z*)-vinyllithium compounds to similar aldehydes gave 1,3-*anti*/1,3-*syn* ratios ranging from 67:33 to 34:66.[10–12] Based on these results (Table 1), we concluded that the stereochemical course of this particular reaction is mainly dependent on the induction of the chiral (*Z*)-vinylmetal reagent rather than on the intrinsic preference of the C1–C9 β-OTBS-substituted aldehyde. In addition to the obvious relevance of the C12–C14 stereotriad (Table 1, Entry 6 vs. 7), it is worth noting that the 1,3-stereoselectivity was inverted as a result of remote, seemingly unimportant, structural variations in the vinyl iodide portion (Table 1, Entry 1 vs. 2 and Entry 3 vs. 4).

Results and Discussion

Wishing to delve deeper into the matter, we decided to investigate the addition of a set of model (*Z*)-vinyl iodides (**6a**–**d**) to aldehyde **5** (Figure 1). Models **6a** and **6b** possess a stereodyad that mimics the C10–C13 portion of vinyl iodides **3** and **4**, respectively. Models **6c** and **6d** contain a stereotriad that reproduces the C10–C14 portion of **3** and **4**.

Models **6a** and **6b** were prepared starting from phenylacetaldehyde (**7**, Scheme 2), which was subjected to a Marshall–Tamaru, Pd-catalyzed allenylzinc addition[13,14] with the enantiomeric mesylates of 3-butyn-2-ol. The (*R*)

[a] Università degli Studi di Milano,
Dipartimento di Chimica Organica e Industriale,
Centro Interdipartimentale C.I.S.I.,
Via G. Venezian 21, 20133 Milan, Italy
Fax: +39-02-50314072
E-mail: cesare.gennari@unimi.it

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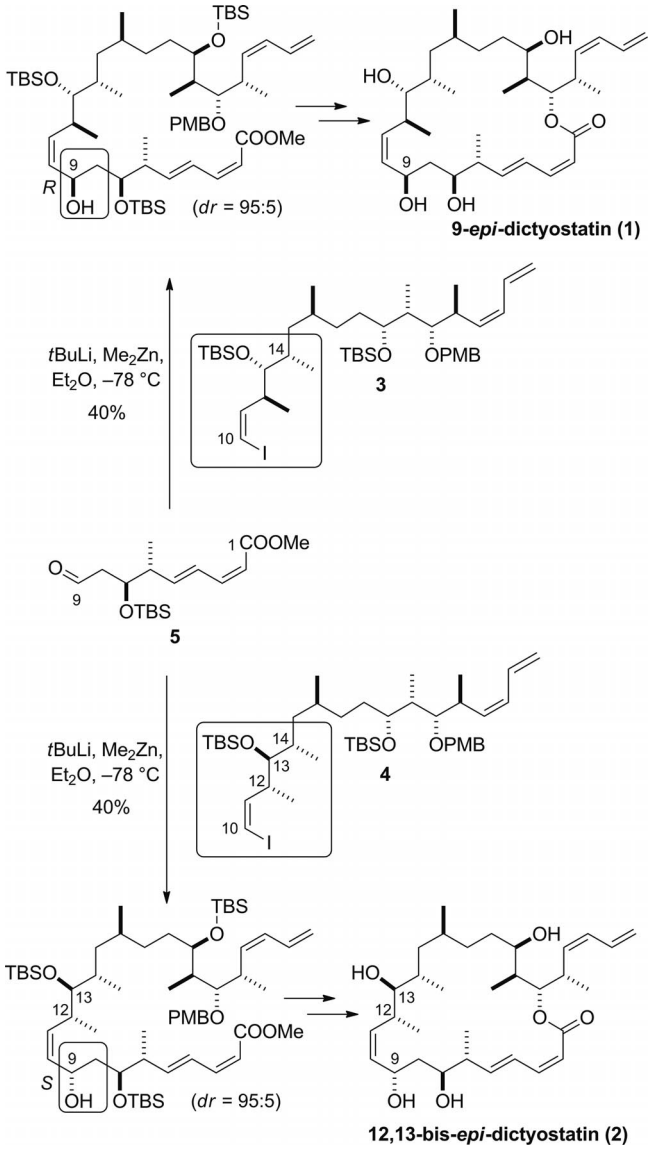
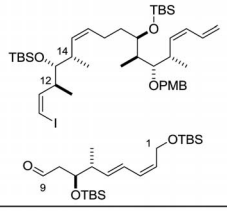
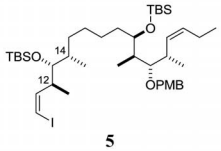
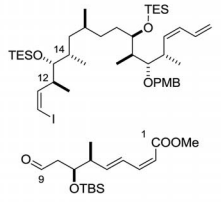
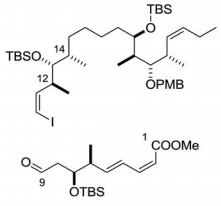
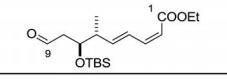
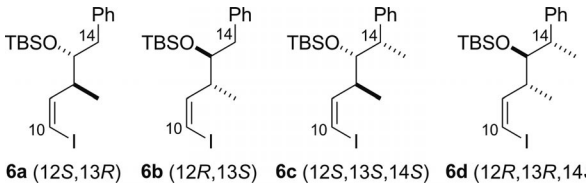


Scheme 1. Vinylzincate addition step in the total synthesis of **1** and **2**.

Table 1. Literature precedents.

Entry	Vinyl iodide, Aldehyde	Reagent	1,3-*anti*/ 1,3-*syn*	Yield [%]	Ref.
1		*t*BuLi	38:62	70	[10,11]
2	 **5**	*t*BuLi	67:33	36	[12]
3		*t*BuLi	34:66	_[a]	[11]
4		*t*BuLi	60:40	48	[12]
5	**3** 	*t*BuLi + Me_2Zn	100:0	35	[9]
6	**3** **5**	*t*BuLi + Me_2Zn	≤5:≥95	40	[5,6,8]
7	**4** **5**	*t*BuLi + Me_2Zn	≥95:≤5	40	[6]

[a] Not reported.



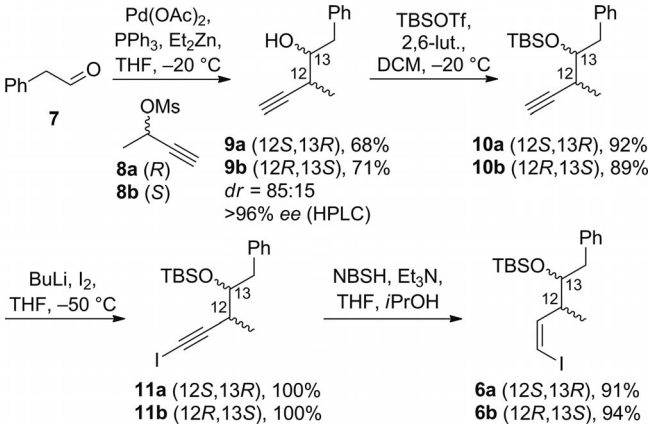
6a (12*S*,13*R*) **6b** (12*R*,13*S*) **6c** (12*S*,13*S*,14*S*) **6d** (12*R*,13*R*,14*S*)

Figure 1. Model (*Z*)-vinyl iodides **6a**–**d** (dictyostatin numbering).

enantiomer **8a** led to a mixture of stereoisomers (68% yield) with an 85:15 diastereomeric ratio (*dr*) in favor of the desired *anti* adduct **9a** (>96%*ee* by chiral HPLC), whereas the (*S*) enantiomer **8b** was used to access **9b** in a similar fashion.

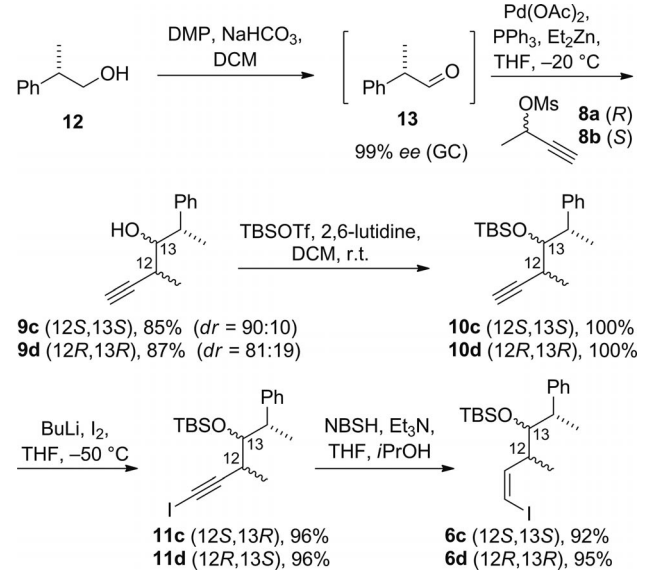
In both cases, the minor *syn* isomer was completely removed by flash chromatography during this and the following two steps. TBS protection (TBSOTf, 2,6-lutidine) of alcohols **9a** and **9b** afforded alkynes **10a** and **10b** (89–92%), which were lithiated (BuLi) and converted quantitatively into the corresponding alkynyl iodides **11a** and **11b**. Reduction of compounds **11** with diimide[15] provided **6a** and **6b** as single (*Z*)-diastereomers (91–94%).

The synthesis of **6c** and **6d** started from commercially available (*S*)-(–)-2-phenyl-1-propanol (**12**, Scheme 3). Dess–Martin oxidation[16] afforded the corresponding aldehyde **13** with no racemization (99%*ee* by chiral GC), which was not purified and directly subjected to Marshall–Tamaru, Pd-catalyzed allenylzinc addition.[13,14] Using the mesylate of (*R*)-3-butyn-2-ol (**8a**), a mixture of stereoisomers was accessed (85% yield), which contained 90% of the desired *anti*,*syn* product **9c**. The minor isomers (total 10%) were completely removed by chromatographic purification. The use of (*S*) mesylate **8b** led to an inseparable mixture of isomers (87% yield), which contained 81% of the desired



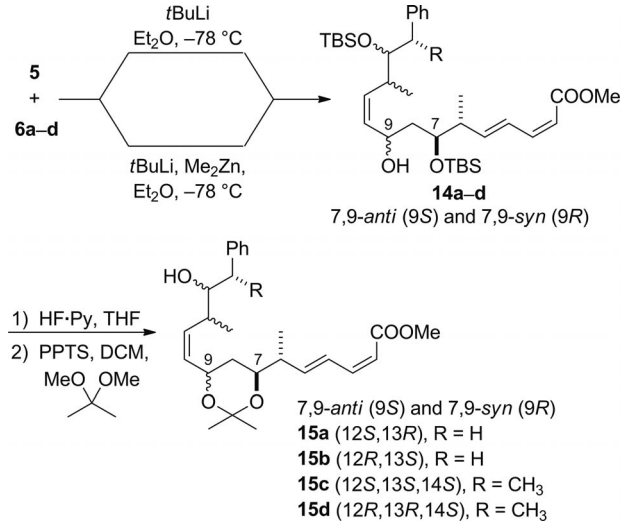
Scheme 2. Synthetic route to **6a** and **6b** (dictyostatin numbering).

anti,*anti* adduct **9d**. The synthetic sequence continued as described above [TBS protection (100%), iodination (96%), and diimide reduction (92–95%)] to give **6c** and **6d**. Removal of minor isomers (total 19%) formed in the Marshall–Tamaru step of the **d** series was possible only in the last stage of the sequence.



Scheme 3. Synthetic route to **6c** and **6d** (dictyostatin numbering).

With **6a**–**d** in hand, we examined their addition reactions to aldehyde **5**.[5,6,17] As mentioned above, Curran reported moderate diastereoselectivities in similar reactions when the nucleophilic species was a vinyllithium (Table 1, Entries 1–4). However, as conflictingly reported by Ramachandran (Table 1, Entry 5) and by us (Table 1, Entries 6 & 7), exceptional diastereoselectivities were observed when the nucleophile was a lithium vinylzincate. For this reason, each model **6a**–**d** was added to **5** as both a vinyllithium and a lithium vinylzincate, in order to assess the effect of the different coupling conditions on the stereochemical outcome (Scheme 4).



Scheme 4. Vinyllithium/lithium vinylzincate addition and acetonide synthesis (dictyostatin numbering).

The configuration of the newly created C9 stereocenter was assigned by Rychnovsky's acetonide ^{13}C NMR method.[18] For this purpose, both C9-epimers from each model [7,9-*anti* (9*S*) and 7,9-*syn* (9*R*) **14a**–**d**, eight products in total] were isolated, fully deprotected (HF·Py), and converted into the corresponding 7,9-*anti* (9*S*) and 7,9-*syn* (9*R*) acetonides **15a**–**d** (92–100%, two steps). Our experimental results are in complete agreement with Rychnovsky's rule,[19] and the stereochemistry at C9 was unambiguously assigned for all products (Table 2).

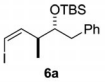
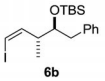
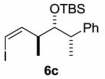
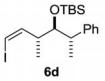
Table 2. Relevant ^{13}C NMR resonances in **15a**–**d**.

Compound	^{13}C NMR chemical shifts [ppm] Quaternary C	CH_3
15a 7,9-*anti* (9*S*)	100.5	25.0, 24.4
15a 7,9-*syn* (9*R*)	98.7	30.0, 19.5
15b 7,9-*anti* (9*S*)	100.5	25.1, 24.4
15b 7,9-*syn* (9*R*)	98.6	30.2, 19.7
15c 7,9-*anti* (9*S*)	100.4	24.8, 24.4
15c 7,9-*syn* (9*R*)	98.8	30.1, 19.7
15d 7,9-*anti* (9*S*)	100.5	24.9, 24.3
15d 7,9-*syn* (9*R*)	98.6	30.1, 19.5

On the basis of the C9 configuration assignment for **15a**–**d**, diastereomeric ratios of vinyllithium and lithium vinylzincate additions were determined (Table 3).

Lithium vinylzincate additions always proceeded in higher yields and gave fewer side products than the corresponding vinyllithium additions. Although the vinyllithium vs. vinylzincate stereochemical trend is difficult to rationalize, a relatively clear scenario emerges for the lithium vinylzincate additions (Table 3). The addition of the enantiomeric vinylzincates derived from **6a** and **6b** (simplified versions of **3** and **4**, respectively) to **5** appears to be guided by the preference of the aldehyde for the 1,3-*anti* (9*S*) product stereochemistry (vide infra). In the case of **6b** (Table 3, Entry 4) the two reactants are matched (1,3-*anti*/1,3-*syn* = 86:14), whereas with **6a** (Table 3, Entry 2) they are mis-

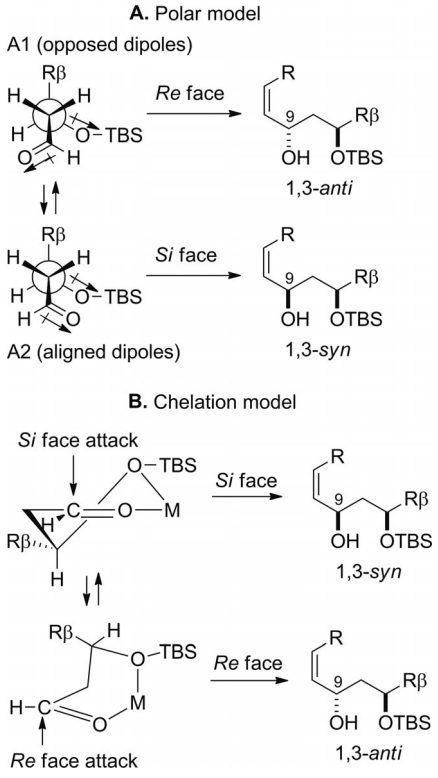
Table 3. Stereochemical outcome and yield of vinyllithium and lithium vinylzincate additions.

Entry	Vinyl iodide	Reagent	1,3-*anti*/1,3-*syn*[a]	Yield [%][a]
1	 **6a**	*t*BuLi	49:51	56
2		*t*BuLi + Me_2Zn	68:32	68
3	 **6b**	*t*BuLi	58:42	56
4		*t*BuLi + Me_2Zn	86:14	66
5	 **6c**	*t*BuLi	63:37	57
6		*t*BuLi + Me_2Zn	57:43	69
7	 **6d**	*t*BuLi	39:61	61
8		*t*BuLi + Me_2Zn	88:12	75

[a] Yields and diastereomeric ratios were determined from the crude reaction mixtures by ^1H NMR and/or ^{13}C NMR spectroscopy. Reactions were repeated three times to obtain statistically relevant ratios and yields.

matched (1,3-*anti*/1,3-*syn* = 68:32). These data suggest that the vinylzincate derived from **6b** must have a slight intrinsic preference for the 1,3-*anti* (9*S*) diastereomer, whereas **6a** would preferentially form the 1,3-*syn* (9*R*) product if the aldehyde control did not predominate. Passing from the stereodyads to the stereotriads (**6c** and **6d**), the preference of the vinylzincate appears to exert a stronger influence on the stereochemical outcome: the diastereoselectivity for the 1,3-*anti* (9*S*) product is enhanced in the matched case (1,3-*anti*/1,3-*syn* = 88:12 with **6d**, Table 3, Entry 8) and diminished in the mismatched case (1,3-*anti*/1,3-*syn* = 57:43 with **6c**, Table 3, Entry 6). Thus, for the lithium vinylzincate additions the following trend can be recognized: the influence on the diastereoselectivity of the intrinsic preference of the nucleophile increases with its stereochemical complexity. The results we obtained in the reaction of the vinylzincates derived from **3** and **4** with aldehyde **5** (Scheme 1, Table 1) are in full agreement with this trend. Indeed, the reaction of **4**, the most complex member of the matched series (**6b** → **6d** → **4**), is almost completely 1,3-*anti* (9*S*)-selective (Table 1, Entry 7), whereas vinyl iodide **3**, the extreme of the mismatched series (**6a** → **6c** → **3**), completely overthrows the preference of aldehyde **5**, yielding the 1,3-*syn* (9*R*) product as the major diastereomer (Table 1, Entry 6). From these data we conclude that the diastereoselectivity in this particular type of (*Z*)-vinylmetal addition reaction is the result of a subtle balance between the intrinsic stereochemical preferences of the nucleophile and the electrophile: although the preference of the chiral β-silyloxy aldehyde for the 1,3-*anti* diastereomer prevails with relatively simple chiral (*Z*)-vinylzincates, stereochemically more complex lithium (*Z*)-vinylzincates are able to control the stereochemical outcome, even overriding the aldehyde preference.

The preference of β-OTBS-substituted aldehydes for the 1,3-*anti* isomer is rationalized by the 1,3-asymmetric induction models that have been thoroughly investigated by Evans. Steric interactions in the aldehyde conformations are minimized when the β-alkyl substituent (Rβ) is oriented *anti* to the Cα-C=O bond as in the models A (Scheme 5). β-OTBS-Substituted aldehydes preferentially afford the 1,3-*anti* diastereomer according to the polar model A1, where the dipoles are opposed.[3] Although a chelate organization is unlikely for β-OTBS-substituted aldehydes in lithium-mediated additions,[20] the use of aluminum Lewis acids (Me_2AlCl or $MeAlCl_2$) provides exceptional chelation control via a boat-like transition state, which reinforces the 1,3-*anti* stereochemical outcome (model B, *Re* face attack).[4]



Scheme 5. 1,3-Asymmetric induction models.

The results obtained in this work (Table 3) and literature precedents (Table 1)[6,10,11,21] suggest that models A2 and/or B (*Si* face attack, half-chair-like transition state), which lead to the 1,3-*syn* diastereomer, can make a substantial impact in these addition reactions.

Conclusions

We have reported the addition of four (*Z*)-vinyl iodides (**6a**–**d**) to the dictyostatin C1–C9 β-silyloxy aldehyde **5** as both vinyllithium and lithium vinylzincate reagents. Lithium vinylzincate additions always proceeded in higher yields and gave fewer side products than the corresponding vinyllithium additions. Although the vinyllithium vs. vinylzincate stereochemical trend is difficult to rationalize, a relatively clear scenario emerged for the lithium vinylzincate

additions: the influence on the diastereoselectivity of the intrinsic preference of the nucleophile increases with its stereochemical complexity. It appears that, for the addition of structurally complex chiral (*Z*)-vinylmetals, the 1,3-asymmetric induction models have no predictive value as the stereochemical outcome is mainly dependent on the induction of the nucleophilic species rather than on the preference of the β-OTBS substituted aldehyde.

Experimental Section

General: ^{1}H (400.13 MHz) and ^{13}C (100.58 MHz) NMR spectra were recorded with a 400 MHz spectrometer. ^{1}H NMR chemical shifts are reported relative to TMS and the solvent resonance was employed as the internal standard ($CDCl_3$, δ = 7.26 ppm). ^{13}C NMR spectra were recorded with complete proton decoupling and the chemical shifts are reported relative to TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.0 ppm). Optical rotation values were measured with an automatic polarimeter with a 1-dm cell at the sodium D line. HRMS were measured with a Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometer equipped with ESI source. All reactions were carried out in oven- or flame-dried glassware under a nitrogen atmosphere unless stated otherwise. All commercially available reagents were used as received. All solvents were dried by standard procedures before use. Organic extracts were dried with anhydrous Na_2SO_4. Reactions were magnetically stirred and monitored by TLC with silica gel (60 F254 pre-coated glass plates, 0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp and/or staining with a ceric ammonium molybdate or *p*-anisaldehyde solution. Flash chromatography was performed with silica gel (60 Å, particle size 0.040–0.062 mm) according to the procedure of Still and coworkers.[22] Yields refer to chromatographically and spectroscopically pure compounds unless stated otherwise.

General Procedures for the Synthesis of 9, 10, 11, 6, 14, and 15

1. Marshall–Tamaru Reaction: Triphenylphosphane (recrystallized from ethanol prior to use, 0.05 equiv.), aldehyde **7** or **13**[23] (1 equiv.), and mesylbutynol **8**[6] (1.5 equiv.) were sequentially added to a cooled (–78 °C) solution of $Pd(OAc)_2$ (0.05 equiv.) in tetrahydrofuran (THF, aldehyde concentration: 0.10 M). Diethylzinc (1.0 M in hexane, 3 equiv.) was added over 15 min. After 10 min, the temperature was raised to –20 °C, and the reaction mixture was stirred overnight. The mixture was quenched with saturated aqueous NH_4Cl solution and extracted into Et_2O. The Et_2O layer was washed with brine, dried, and concentrated under vacuum. The residue was purified by flash column chromatography to afford **9** as a yellow oil.

2. TBS Protection: Freshly distilled 2,6-lutidine (4 equiv.) and TBSOTf (1.5 equiv.) were added to a stirred solution of **9** (1 equiv.) in CH_2Cl_2 (concentration of **9**: 0.04 M) at –20 °C (for **9a**, **9b**) or room temperature (for **9c**, **9d**). On completion of the reaction (1–2 h), the mixture was quenched with saturated aqueous NH_4Cl solution. The layers were separated, and the aqueous layer was extracted into CH_2Cl_2. The combined organic extracts were washed with brine, dried, and concentrated. Purification of the crude product by flash chromatography afforded **10** as a colorless oil.

3. Iodination: BuLi (1.6 M in hexane, 1.2 equiv.) was added dropwise over 5 min to a solution of **10** (1 equiv.) in THF (concentration of **10**: 2.0 M) at –50 °C. After 1 h, a solution of iodine (4.0 M, 1.7 equiv.) in THF was added. The mixture was stirred at –50 °C for 30 min then warmed to room temperature over 30 min. After quenching with saturated aqueous $Na_2S_2O_3$ and brine, the mixture was extracted into EtOAc and the combined organic layers were washed with brine. The organic phase was dried and concentrated under vacuum. The crude product was purified by flash chromatography to give **11** as a colorless oil.

4. Diimide Reduction: A solution of **11** (1 equiv.) in 1:1 THF/*i*PrOH (concentration of **11**: 0.22 M) at room temperature was treated with Et_3N (1.3 equiv.) and 2-nitrobenzenesulfonylhydrazide[24] (NBSH, 1.1 equiv.). After 24 h, additional Et_3N (0.6 equiv.) and NBSH (0.5 equiv.) were added, and the mixture was stirred for a further 24 h. The reaction was quenched with water and the mixture was extracted into EtOAc. The combined organic layers were washed with brine, dried, and concentrated. The crude product was purified by flash chromatography to give **6** as a colorless oil.

5a. Vinyllithium Addition: A solution of **6** (1 equiv.) in Et_2O (concentration of **6**: 0.095 M) was treated with *t*BuLi (1.6 M in pentane, 2.2 equiv.) at –78 °C under an argon atmosphere. After 30 min, a solution of **5** (1 equiv.), which had been azeotropically dried with toluene, in Et_2O (concentration of **5**: 0.20 M) was added dropwise and the mixture was stirred for 1.5 h at –78 °C. The reaction was quenched with saturated aqueous NH_4Cl, warmed to room temperature, and diluted with Et_2O. The phases were separated, and the aqueous layer was extracted into Et_2O. The combined organic extracts were washed with brine, dried, and concentrated under vacuum. The crude mixture was analyzed by ^{1}H and ^{13}C NMR spectroscopy to determine the *dr*, then purified by flash chromatography to give **14** as a yellow oil.

5b. Lithium Vinylzincate Addition: To a solution of *t*BuLi (1.6 M in pentane, 2.2 equiv.) in Et_2O (concentration of *t*BuLi: 0.75 M) at –78 °C under an argon atmosphere was added a solution of **6** (1 equiv.) in Et_2O (concentration of **6**: 0.30 M). After stirring for 30 min, dimethylzinc (2.0 M in toluene, 1.6 equiv.) was added dropwise, and the reaction mixture was stirred at –78 °C for a further 15 min. A solution of **5** (1 equiv.), which had been azeotropically dried with toluene, in Et_2O (concentration of **5**: 0.35 M) was added dropwise, and the mixture was stirred for 1.5 h at –78 °C. The reaction was quenched with saturated aqueous NH_4Cl solution, warmed to room temperature, and diluted with Et_2O. The phases were separated, and the aqueous layer was extracted into Et_2O. The combined organic extracts were washed with brine, dried, and concentrated under vacuum. The crude mixture was analyzed by ^{1}H and ^{13}C NMR spectroscopy to determine the *dr*, then purified by flash chromatography to give **14** as a yellow oil.

6. Deprotection and Synthesis of Acetonide: To a solution of **14** (1 equiv.) in THF (concentration of **14**: 0.009 M) kept at 0 °C in a plastic vial was added HF·Py (approximately 900 equiv.) dropwise over 2 min, and the solution was allowed to slowly warm to room temperature. The reaction was stirred for 24 h, cooled to 0 °C, diluted with EtOAc, and quenched with saturated aqueous $NaHCO_3$ solution. The layers were separated, and the aqueous layer was extracted into EtOAc. The combined organic extracts were dried, and the solvents were evaporated under vacuum. The crude mixture was purified by flash chromatography (1:1 hexane/EtOAc) to give the fully deprotected triol as a colorless oil, which was not characterized and directly converted into the corresponding acetonide. A small crystal of PPTS was added to a solution of the triol in 2,2-dimethoxypropane/CH_2Cl_2, 8:2 (concentration of triol: 0.015 M). The reaction mixture was stirred at room temperature for 1.5 h and quenched with saturated aqueous $NaHCO_3$ solution. The phases were separated and the aqueous layer was extracted into CH_2Cl_2. The combined organic extracts were dried and concentrated under

vacuum. The crude product was purified by flash chromatography to give **15** as a colorless oil.

(2*R*,3*S*)-3-Methyl-1-phenylpent-4-yn-2-ol (9a): Prepared by following General Procedure 1 from **7** and **8a**. Flash chromatography: 96:4 hexane/EtOAc. Yield: 510 mg (68%) of isomeric products, *dr* = 85:15 before chromatography, *dr* = 91:9 after chromatography, >96%*ee* by chiral HPLC. R_f = 0.52 (6:4 hexane/EtOAc). $[\alpha]_D^{29}$ = –34.5 (*c* = 0.32 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.22 (m, 5 H), 3.70 (ddd, *J* = 7.6, 5.8, 3.8 Hz, 1 H), 2.94 (dd, *J* = 13.6, 5.8 Hz, 1 H, AB system), 2.87 (dd, *J* = 13.6, 7.6 Hz, 1 H, AB system), 2.59 (m, 1 H), 2.21 (d, *J* = 2.4 Hz, 1 H), 1.60 (br. s, 1 H), 1.27 (d, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1 (C_0), 129.3 (CH), 128.5 (CH), 126.5 (CH), 84.8 (C_0), 75.1 (CH), 71.3 (CH), 41.7 (CH_2), 31.6 (CH), 17.4 (CH_3) ppm. HRMS (ESI): calcd. for $C_{12}H_{14}ONa$ $[M + Na]^+$ 197.09369; found 197.09400.

***tert*-Butyldimethyl[(2*R*,3*S*)-3-methyl-1-phenylpent-4-yn-2-yloxy]-silane (10a):** Prepared by following General Procedure 2. Flash chromatography: 96:4 hexane/CH_2Cl_2. Yield: 564 mg (92%) of isomeric products, *dr* = 91:9 before chromatography, *dr* = 99:1 after chromatography. R_f = 0.73 (8:2 hexane/EtOAc). $[\alpha]_D^{29}$ = –25.0 (*c* = 0.30 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.21 (m, 5 H), 3.88 (ddd, *J* = 8.2, 4.9, 3.6 Hz, 1 H), 3.08 (dd, *J* = 13.2, 4.9 Hz, 1 H, AB system), 2.72 (dd, *J* = 13.2, 8.0 Hz, 1 H), 2.60 (m, 1 H), 2.19 (d, *J* = 2.5 Hz, 1 H), 1.24 (d, *J* = 7.1 Hz, 3 H), 0.88 (s, 9 H), –0.03 (s, 3 H), –0.28 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4 (C_0), 129.8 (CH), 128.2 (CH), 126.1 (CH), 86.2 (C_0), 76.1 (CH), 70.2 (CH), 40.0 (CH_2), 31.7 (CH), 25.8 (CH_3), 18.0 (C_0), 15.3 (CH_3), –4.9 (CH_3), –5.1 (CH_3) ppm. HRMS (ESI): calcd. for $C_{18}H_{28}OSiNa$ $[M + Na]^+$ 311.18016; found 311.18037.

***tert*-Butyl[(2*R*,3*S*)-5-iodo-3-methyl-1-phenylpent-4-yn-2-yloxy]-dimethylsilane (11a):** Prepared by following General Procedure 3. Flash chromatography: 95:5 hexane/CH_2Cl_2. Yield: 711 mg (100%). R_f = 0.31 (9:1 hexane/CH_2Cl_2). $[\alpha]_D^{29}$ = –72.1 (*c* = 0.70 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.31 (m, 2 H), 7.26–7.22 (m, 3 H), 3.88 (m, 1 H), 3.04 (dd, *J* = 13.3, 4.8 Hz, 1 H, AB system), 2.78 (m, 1 H), 2.72 (dd, *J* = 13.3, 7.9 Hz, 1 H, AB system), 1.24 (d, *J* = 7.1 Hz, 3 H), 0.89 (s, 9 H), –0.02 (s, 3 H), –0.27 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2 (C_0), 129.8 (CH), 128.2 (CH), 126.2 (CH), 96.5 (C_0), 76.2 (CH), 40.2 (CH_2), 34.2 (CH), 25.8 (CH_3), 18.0 (C_0), 15.2 (CH_3), –4.9 (CH_3), –5.0 (C_0), –5.1 (CH_3) ppm. HRMS (ESI): calcd. for $C_{18}H_{27}OISiNa$ $[M + Na]^+$ 437.07681; found 437.07803.

***tert*-Butyl[(2*R*,3*S*,*Z*)-5-iodo-3-methyl-1-phenylpent-4-en-2-yloxy]-dimethylsilane (6a):** Prepared by following General Procedure 4. Flash chromatography: 99:1 hexane/CH_2Cl_2. Yield: 642 mg (91%). R_f = 0.36 (9:1 hexane/CH_2Cl_2). $[\alpha]_D^{29}$ = +53.2 (*c* = 0.43 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.26 (m, 2 H), 7.21–7.14 (m, 3 H), 6.37–6.28 (m, 2 H), 3.84 (td, *J* = 6.8, 2.6 Hz, 1 H), 2.71 (dd, *J* = 13.3, 6.6 Hz, 1 H, AB system), 2.62 (dd, *J* = 13.3, 7.0 Hz, 1 H, AB system), 2.55 (m, 1 H), 1.00 (d, *J* = 7.0 Hz, 3 H), 0.88 (s, 9 H), 0.05 (s, 3 H), 0.20 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7 (CH), 138.8 (C_0), 129.8 (CH), 128.3 (CH), 126.1 (CH), 82.5 (CH), 76.4 (CH), 43.7 (CH), 41.9 (CH_2), 25.9 (CH_3), 18.1 (C_0), 15.8 (CH_3), –4.5 (CH_3), –4.8 (CH_3) ppm. HRMS (ESI): calcd. for $C_{18}H_{29}OISiNa$ $[M + Na]^+$ 439.09246; found 439.09305.

(2*S*,3*R*)-3-Methyl-1-phenylpent-4-yn-2-ol (9b): Prepared by following General Procedure 1 from **7** and **8b**. Flash chromatography: 96:4 hexane/EtOAc. Yield: 324 mg (71%) of isomeric products, *dr* = 85:15 before chromatography, *dr* = 92:8 after chromatography, >96%*ee* by chiral HPLC. $[\alpha]_D^{30}$ = +38.2 (*c* = 0.31 $CHCl_3$); see **9a** for the NMR characterization data. HRMS (ESI): calcd. for $C_{12}H_{14}ONa$ $[M + Na]^+$ 197.09369; found 197.09391.

***tert*-Butyldimethyl[(2*S*,3*R*)-3-methyl-1-phenylpent-4-yn-2-yloxy]-silane (10b):** Prepared by following General Procedure 2. Flash chromatography: 95:5 hexane/CH_2Cl_2. Yield: 386 mg (89%) of isomeric products, *dr* = 92:8 before chromatography, *dr* = 99:1 after chromatography. $[\alpha]_D^{30}$ = +30.2 (*c* = 0.44 $CHCl_3$); see **10a** for the NMR characterization data. HRMS (ESI): calcd. for $C_{18}H_{28}OSiNa$ $[M + Na]^+$ 311.18016; found 311.18041.

***tert*-Butyl[(2*S*,3*R*)-5-iodo-3-methyl-1-phenylpent-4-yn-2-yloxy]dimethylsilane (11b):** Prepared by following General Procedure 3. Flash chromatography: 95:5 hexane/CH_2Cl_2. Yield: 432 mg (100%). $[\alpha]_D^{30}$ = +53.4 (*c* = 0.43 $CHCl_3$); see **11a** for the NMR characterization data. HRMS (ESI): calcd. for $C_{18}H_{27}OISiNa$ $[M + Na]^+$ 437.07681; found 437.07730.

***tert*-Butyl[(2*S*,3*R*,*Z*)-5-iodo-3-methyl-1-phenylpent-4-en-2-yloxy]-dimethylsilane (6b):** Prepared by following General Procedure 4. Flash chromatography: 99:1 hexane/CH_2Cl_2. Yield: 382 mg (94%). $[\alpha]_D^{30}$ = –63.5 (*c* = 0.53 $CHCl_3$); see **6a** for the NMR characterization data. HRMS (ESI): calcd. for $C_{18}H_{29}OISiNa$ $[M + Na]^+$ 439.09246; found 439.09311.

(2*S*,3*S*,4*S*)-4-Methyl-2-phenylhex-5-yn-3-ol (9c): Prepared by following General Procedure 1 from **13** and **8a**. Flash chromatography: 92:8 hexane/EtOAc. Yield: 276 mg (85%) of isomeric products, *dr* = 9:1 before chromatography, *dr* > 99:1 after chromatography. R_f = 0.36 (7:3 hexane/EtOAc). $[\alpha]_D^{30}$ = –82.8 (*c* = 0.35 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.22 (m, 5 H), 3.43 (dd, *J* = 9.2, 2.7 Hz, 1 H), 2.97 (m, 1 H), 2.36 (m, 1 H), 2.20 (d, *J* = 2.4 Hz, 1 H), 1.65 (br. s, 1 H), 1.42 (d, *J* = 7.0 Hz, 3 H), 1.21 (d, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.3 (C_0), 128.6 (CH), 127.5 (CH), 126.6 (CH), 84.5 (C_0), 79.2 (CH), 71.7 (CH), 45.0 (CH), 30.4 (CH), 18.4 (CH_3), 18.1 (CH_3) ppm. HRMS (ESI): calcd. for $C_{13}H_{16}ONa$ $[M + Na]^+$ 211.10934; found 211.10958.

***tert*-Butyldimethyl[(2*S*,3*S*,4*S*)-4-methyl-2-phenylhex-5-yn-3-yloxy]-silane (10c):** Prepared by following General Procedure 2. Flash chromatography: 95:5 hexane/EtOAc. Yield: 402 mg (100%). R_f = 0.79 (8:2 hexane/EtOAc). $[\alpha]_D^{30}$ = –24.8 (*c* = 0.60 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.17 (m, 5 H), 3.65 (dd, *J* = 7.8, 2.9 Hz, 1 H), 3.14 (m, 1 H), 2.38 (m, 1 H), 2.04 (d, *J* = 2.5 Hz, 1 H), 1.30 (d, *J* = 7.1 Hz, 3 H), 1.15 (d, *J* = 7.2 Hz, 3 H), 0.95 (s, 9 H), 0.07 (s, 3 H), 0.00 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.4 (C_0), 128.4 (CH), 127.8 (CH), 126.3 (CH), 85.9 (C_0), 79.7 (CH), 70.2 (CH), 44.1 (CH), 31.4 (CH), 26.1 (CH_3), 18.5 (C_0), 18.4 (CH_3), 18.2 (CH_3), –3.7 (CH_3) ppm. HRMS (ESI): calcd. for $C_{19}H_{30}OSiNa$ $[M + Na]^+$ 325.19581; found 325.19624.

***tert*-Butyl[(2*S*,3*R*,4*S*)-6-iodo-4-methyl-2-phenylhex-5-yn-3-yloxy]-dimethylsilane (11c):** Prepared by following General Procedure 3. Flash chromatography: 9:1 hexane/CH_2Cl_2. Yield: 536 mg (96%). R_f = 0.25 (95:5 hexane/CH_2Cl_2). $[\alpha]_D^{30}$ = –62.5 (*c* = 0.61 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 2 H), 7.26–7.21 (m, 3 H), 3.70 (dd, *J* = 7.5, 3.2 Hz, 1 H), 3.10 (m, 1 H), 2.62 (qd, *J* = 7.1, 3.3 Hz, 1 H), 1.33 (d, *J* = 7.0 Hz, 3 H), 1.19 (d, *J* = 7.2 Hz, 3 H), 0.98 (s, 9 H), 0.10 (s, 3 H), 0.00 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1 (C_0), 128.4 (CH), 127.9 (CH), 126.4 (CH), 96.4 (C_0), 79.9 (CH), 44.0 (CH), 33.8 (CH), 26.1 (CH), 18.4 (C_0), 18.1 (CH_3), 17.9 (CH_3), –3.8 (CH_3), –3.8 (CH_3), –5.2 (C_0) ppm. HRMS (ESI): calcd. for $C_{19}H_{29}OISiNa$ $[M + Na]^+$ 451.09246; found 451.09336.

***tert*-Butyl[(2*S*,3*S*,4*S*,*Z*)-6-iodo-4-methyl-2-phenylhex-5-en-3-yloxy]dimethylsilane (6c):** Prepared by following General Pro-

cedure 4. Flash chromatography: 100% hexane. Yield: 482 mg (92%). R_f = 0.49 (95:5 hexane/CH_2Cl_2). $[\alpha]_D^{30}$ = +103.6 (c = 0.79 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.26 (m, 2 H), 7.21–7.15 (m, 3 H), 6.18–6.14 (m, 1 H), 6.09 (d, J = 7.4 Hz, 1 H), 3.75 (dd, J = 8.3, 2.2 Hz, 1 H), 2.74 (m, 1 H), 2.42 (m, 1 H), 1.26 (d, J = 7.1 Hz, 3 H), 0.95 (s, 9 H), 0.94 (d, J = 7.8 Hz, 3 H), 0.11 (s, 3 H), 0.05 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7 (C_0), 142.6 (CH), 128.4 (CH), 128.2 (CH), 126.2 (CH), 81.9 (CH), 80.1 (CH), 44.8 (CH), 44.3 (CH), 26.2 (CH_3), 19.2 (CH_3), 18.5 (C_0), 17.1 (CH_3), –3.4 (CH_3), –3.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{19}H_{31}OISiNa$ [M + Na]$^+$ 453.10811; found 453.10849.

(2*S*,3*R*,4*R*)-4-Methyl-2-phenylhex-5-yn-3-ol (9d): Prepared by following General Procedure 1 from **13** and **8b**. Flash chromatography: 97:3 hexane/EtOAc. Yield: 221 mg (87%) of inseparable isomeric products, *dr* = 81:19. R_f = 0.45 (7:3 hexane/EtOAc). $[\alpha]_D^{30}$ = –29.6 (c = 0.29 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.34 (m, 5 H), 3.51 (dd, J = 8.0, 3.9 Hz, 1 H), 2.99 (m, 1 H), 2.74 (m, 1 H), 2.15 (d, J = 2.4 Hz, 1 H), 1.60 (br. s, 1 H), 1.31 (d, J = 7.0 Hz, 3 H), 1.31 (d, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4 (C_0), 128.6 (CH), 128.2 (CH), 126.7 (CH), 84.7 (C_0), 78.2 (CH), 70.8 (CH), 44.3 (CH), 29.9 (CH), 18.5 (CH_3), 18.1 (CH_3) ppm. HRMS (ESI): calcd. for $C_{13}H_{16}ONa$ [M + Na]$^+$ 211.10934; found 211.10942.

***tert*-Butyldimethyl[(2*S*,3*R*,4*R*)-4-methyl-2-phenylhex-5-yn-3-yl-oxy]silane (10d):** Prepared by following General Procedure 2. Flash chromatography: 95:5 hexane/EtOAc. Yield: 320 mg (100%) of inseparable isomeric products. R_f = 0.73 (8:2 hexane/EtOAc). $[\alpha]_D^{30}$ = –9.1 (c = 0.46 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.17 (m, 5 H), 3.75 (dd, J = 6.6, 3.7 Hz, 1 H), 3.04 (m, 1 H), 2.66 (m, 1 H), 2.09 (d, J = 2.6 Hz, 1 H), 1.32 (d, J = 7.2 Hz, 3 H), 1.06 (d, J = 7.2 Hz, 3 H), 0.84 (s, 9 H), –0.02 (s, 3 H), –0.40 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9 (C_0), 128.7 (CH), 128.1 (CH), 126.2 (CH), 86.6 (C_0), 78.8 (CH), 70.2 (CH), 44.4 (CH), 30.9 (CH), 26.0 (CH_3), 18.8 (CH_3), 18.2 (C_0), 16.8 (CH_3), –4.4 (CH_3), –5.0 (CH_3) ppm. HRMS (ESI): calcd. for $C_{19}H_{30}OSiNa$ [M + Na]$^+$ 325.19581; found 325.19631.

***tert*-Butyl[(2*S*,3*S*,4*R*)-6-iodo-4-methyl-2-phenylhex-5-yn-3-yloxy]-dimethylsilane (11d):** Prepared by following General Procedure 3. Flash chromatography: 9:1 hexane/CH_2Cl_2. Yield: 396 mg (96%) of inseparable isomeric products. R_f = 0.31 (95:5 hexane/CH_2Cl_2). $[\alpha]_D^{30}$ = +3.6 (c = 0.80 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.17 (m, 5 H), 3.75 (dd, J = 6.1, 4.2 Hz, 1 H), 3.00 (m, 1 H), 2.78 (qd, J = 7.1, 4.2 Hz, 1 H), 1.33 (d, J = 7.2 Hz, 3 H), 1.06 (d, J = 7.1 Hz, 3 H), 0.87 (s, 9 H), 0.01 (s, 3 H), –0.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5 (C_0), 128.7 (CH), 128.1 (CH), 126.2 (CH), 97.0 (C_0), 78.9 (CH), 44.2 (CH), 33.2 (CH), 26.0 (CH), 18.7 (CH_3), 18.2 (C_0), 16.8 (CH_3), –4.4 (CH_3), –4.8 (CH_3), –4.9 (C_0) ppm. HRMS (ESI): calcd. for $C_{19}H_{29}OISiNa$ [M + Na]$^+$ 451.09246; found 451.09312.

***tert*-Butyl[(2*S*,3*R*,4*R*,*Z*)-6-iodo-4-methyl-2-phenylhex-5-en-3-yloxy]-dimethylsilane (6d):** Prepared by following General Procedure 4. Flash chromatography: 100% hexane. Yield: 359 mg (95%) of isomeric products, *dr* = 81:19 before chromatography, *dr* > 99:1 after chromatography. R_f = 0.43 (95:5 hexane/CH_2Cl_2). $[\alpha]_D^{30}$ = –39.6 (c = 0.54 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.20 (m, 5 H), 6.47 (dd, J = 8.6, 7.5 Hz, 1 H), 6.19 (d, J = 7.3 Hz, 1 H), 3.80 (dd, J = 6.6, 2.0 Hz, 1 H), 2.83 (m, 1 H), 2.70 (m, 1 H), 1.25 (d, J = 7.2 Hz, 3 H), 0.93 (d, J = 7.1 Hz, 3 H), 0.90 (s, 9 H), 0.06 (s, 3 H), –0.34 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.7 (C_0), 143.3 (CH), 128.6 (CH), 128.2 (CH), 126.3 (CH), 81.2 (CH), 80.1 (CH), 45.9 (CH), 42.1 (CH), 26.1 (CH_3), 18.3 (C_0), 17.9 (CH_3), 16.9 (CH_3), –4.1 (CH_3), –4.8 (CH_3) ppm. HRMS (ESI): calcd. for $C_{19}H_{31}OISiNa$ [M + Na]$^+$ 453.10811; found 453.10794.

(2*Z*,4*E*,6*R*,7*S*,9*S*,10*Z*,12*S*,13*R*)-Methyl-7,13-bis(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,12-dimethyl-14-phenyltetradeca-2,4,10-trienoate [14a, 7,9-*anti* (9*S*)] and (2*Z*,4*E*,6*R*,7*S*,9*R*,10*Z*,12*S*,13*R*)-Methyl-7,13-bis(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,12-dimethyl-14-phenyltetradeca-2,4,10-trienoate [14a, 7,9-*syn* (9*R*)]: Prepared by following General Procedure 5a. Flash chromatography: 96:4 hexane/EtOAc. Yield: 60 mg (56% yield by ^1H NMR) of 9-epimeric products, *dr* [7,9-*anti* (9*S*)/7,9-*syn* (9*R*)] = 49:51. Data for **14a** 7,9-*anti* (9*S*): R_f = 0.17 (85:15 hexane/EtOAc). $[\alpha]_D^{30}$ = –1.5 (c = 0.24 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (dd, J = 15.4, 11.3 Hz, 1 H), 7.28–7.12 (m, 5 H), 6.56 (t, J = 11.3 Hz, 1 H), 6.04 (dd, J = 15.4, 7.5 Hz, 1 H), 5.66–5.60 (m, 2 H), 5.49 (dd, J = 10.9, 8.8 Hz, 1 H), 4.54 (dd, J = 13.3, 8.1 Hz, 1 H), 3.95 (dd, J = 10.6, 5.2 Hz, 1 H), 3.77 (m, 1 H), 3.75 (s, 3 H), 2.69 (d, J = 6.5 Hz, 2 H), 2.61 (m, 2 H), 1.88 (br. s, 1 H), 1.58 (m, 2 H), 1.05 (d, J = 6.8 Hz, 6 H), 0.88 (s, 9 H), 0.87 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H), 0.01 (s, 3 H), –0.31 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (C_0), 147.2 (CH), 145.4 (CH), 139.2 (C_0), 133.0 (CH), 132.8 (CH), 129.6 (CH), 128.2 (CH), 126.8 (CH), 126.1 (CH), 115.7 (CH), 77.0 (CH), 72.9 (CH), 64.6 (CH), 51.1 (CH_3), 42.7 (CH), 41.7 (CH_2), 40.0 (CH_2), 37.2 (CH), 25.9 (CH_3), 25.9 (CH_3), 18.3 (CH_3), 18.0 (C_0), 14.6 (CH_3), –4.4 (CH_3), –4.5 (CH_3), –5.0 (CH_3) ppm. HRMS (ESI): calcd. for $C_{35}H_{60}O_5Si_2Na$ [M + Na]$^+$ 639.38715; found 639.38838. Data for **14a** 7,9-*syn* (9*R*): R_f = 0.37 (85:15 hexane/EtOAc). $[\alpha]_D^{30}$ = +29.0 (c = 0.11 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.19 (m, 6 H), 6.51 (t, J = 11.3 Hz, 1 H), 5.94 (dd, J = 15.4, 7.9 Hz, 1 H), 5.59 (d, J = 11.3 Hz, 1 H), 5.54–5.42 (m, 2 H), 4.23 (t, J = 7.2 Hz, 1 H), 3.87–3.78 (m, 2 H), 3.72 (s, 3 H), 2.72 (d, J = 6.6 Hz, 2 H), 2.49 (m, 2 H), 1.65 (m, 1 H), 1.33 (m, 1 H), 1.07 (d, J = 6.8 Hz, 3 H), 0.90 (m, 3 H), 0.90 (s, 9 H), 0.87 (s, 9 H), 0.09 (s, 3 H), 0.07 (s, 3 H), 0.01 (s, 3 H), –0.21 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8 (C_0), 146.5 (CH), 145.3 (CH), 139.2 (C_0), 133.1 (CH), 132.7 (CH), 129.7 (CH), 128.2 (CH), 127.1 (CH), 126.1 (CH), 115.7 (CH), 76.7 (CH), 74.6 (CH), 66.5 (CH), 51.0 (CH_3), 42.3 (CH), 41.5 (CH_2), 40.6 (CH_2), 36.6 (CH), 25.9 (CH_3), 25.8 (CH_3), 18.1 (C_0), 17.9 (CH_3), 14.7 (CH_3), –4.3 (CH_3), –4.5 (CH_3), –4.8 (CH_3) ppm. HRMS (ESI): calcd. for $C_{35}H_{60}O_5Si_2Na$ [M + Na]$^+$ 639.38715; found 639.38801.

(*R*,2*Z*,4*E*)-Methyl-6-[(4*S*,6*S*)-6-{(3*S*,4*R*,*Z*)-4-hydroxy-3-methyl-5-phenylpent-1-enyl}-2,2-dimethyl-1,3-dioxan-4-yl]hepta-2,4-dienoate [15a, 7,9-*anti* (9*S*)]: Prepared by following General Procedure 6. Flash chromatography: 7:3 hexane/EtOAc. Yield: 14 mg (100%). R_f = 0.46 (1:1 hexane/EtOAc). $[\alpha]_D^{25}$ = –9.0 (c = 0.62 CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (dd, J = 15.4, 11.3 Hz, 1 H), 7.36–7.24 (m, 5 H), 6.62 (t, J = 11.3 Hz, 1 H), 6.13 (dd, J = 15.5, 7.6 Hz, 1 H), 5.64 (d, J = 11.3 Hz, 1 H), 5.59–5.55 (m, 2 H), 4.56 (dd, J = 15.0, 6.3 Hz, 1 H), 3.80–3.77 (m, 1 H), 3.74 (s, 3 H), 3.68 (m, 1 H), 2.87 (dd, J = 13.7, 3.5 Hz, 1 H, AB system), 2.67–2.63 (m, 2 H), 2.45 (m, 1 H), 1.79–1.63 (m, 3 H), 1.38 (s, 3 H), 1.37 (s, 3 H), 1.14 (d, J = 6.8 Hz, 3 H), 1.10 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1 (C_0), 147.0 (CH), 145.5 (CH), 138.6 (C_0), 134.2 (CH), 131.2 (CH), 129.4 (CH), 128.5 (CH), 126.9 (CH), 126.5 (CH), 115.6 (CH), 100.5 (C_0), 75.7 (CH), 69.7 (CH), 63.4 (CH), 51.1 (CH_3), 41.5 (CH), 41.1 (CH_2), 38.1 (CH), 36.5 (CH_2), 25.0 (CH_3), 24.4 (CH_3), 17.5 (CH_3), 15.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{26}H_{36}O_5Na$ [M + Na]$^+$ 451.24550; found 451.24566.

(*R*,4*E*)-Methyl-6-[(4*S*,6*R*)-6-{(3*S*,4*R*,*Z*)-4-hydroxy-3-methyl-5-phenylpent-1-enyl}-2,2-dimethyl-1,3-dioxan-4-yl]hepta-2,4-dienoate [15a, 7,9-*syn* (9*R*)]: Prepared by following General Procedure 6. Flash

chromatography: 8:2 hexane/EtOAc. Yield: 14 mg (92%). R_f = 0.51 (1:1 hexane/EtOAc). $[\alpha]_D^{25}$ = +33.0 (*c* = 0.57 CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (dd, *J* = 15.4, 11.3 Hz, 1 H), 7.30–7.18 (m, 5 H), 6.56 (t, *J* = 11.3 Hz, 1 H), 6.09 (dd, *J* = 15.5, 7.8 Hz, 1 H), 5.59 (d, *J* = 11.3 Hz, 1 H), 5.50–5.43 (m, 2 H), 4.50 (dd, *J* = 13.8, 5.5 Hz, 1 H), 3.75–3.73 (m, 1 H), 3.71 (s, 3 H), 3.59 (m, 1 H), 2.91 (dd, *J* = 13.9, 3.7 Hz, 1 H, AB system), 2.66 (dd, *J* = 13.9, 7.3 Hz, 1 H, AB system), 2.49 (m, 1 H), 2.38 (dd, *J* = 12.8, 6.7 Hz, 1 H), 2.32 (br. s, 1 H), 1.39–1.35 (m, 2 H), 1.34 (s, 3 H), 1.30 (s, 3 H), 1.05 (d, *J* = 6.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (C_0), 146.8 (CH), 145.5 (CH), 138.6 (C_0), 135.6 (CH), 131.4 (CH), 129.8 (CH), 128.3 (CH), 126.9 (CH), 126.2 (CH), 115.5 (CH), 98.7 (C_0), 75.0 (CH), 71.9 (CH), 65.2 (CH), 51.1 (CH_3), 41.8 (CH), 40.5 (CH_2), 37.8 (CH), 34.1 (CH_2), 30.0 (CH_3), 19.5 (CH_3), 17.7 (CH_3), 15.5 (CH_3) ppm. HRMS (ESI): calcd. for $C_{26}H_{36}O_5Na$ $[M + Na]^+$ 451.24550; found 451.24564.

(2*Z*,4*E*,6*R*,7*S*,9*S*,10*Z*,12*R*,13*S*)-Methyl-7,13-bis(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,12-dimethyl-14-phenyltetradeca-2,4,10-trienoate [14b, 7,9-*anti* (9*S*)] and (2*Z*,4*E*,6*R*,7*S*,9*R*,10*Z*,12*R*,13*S*)-Methyl-7,13-bis(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,12-dimethyl-14-phenyltetradeca-2,4,10-trienoate [14b, 7,9-*syn* (9*R*)]: Prepared by following General Procedure 5b. Flash chromatography: 96:4 hexane/EtOAc. Yield: 132 mg (66% yield by ^{1}H NMR) of a mixture of inseparable 9-epimeric products and unreacted **5**, *dr* [7,9-*anti* (9S)/7,9-*syn* (9*R*)] = 86:14. R_f = 0.32 (85:15 hexane/EtOAc). HRMS (ESI): calcd. for $C_{35}H_{60}O_5Si_2Na$ $[M + Na]^+$ 639.38715; found 639.38812.

(*R*,2*Z*,4*E*)-Methyl-6-[(4*S*,6*S*)-6-{(3*R*,4*S*,*Z*)-4-hydroxy-3-methyl-5-phenylpent-1-enyl}-2,2-dimethyl-1,3-dioxan-4-yl]hepta-2,4-dienoate [15b, 7,9-*anti* (9*S*)] and (*R*,4*E*)-Methyl-6-[(4*S*,6*R*)-6-{(3*R*,4*S*,*Z*)-4-hydroxy-3-methyl-5-phenylpent-1-enyl}-2,2-dimethyl-1,3-dioxan-4-yl]hepta-2,4-dienoate [15b, 7,9-*syn* (9*R*)]: Prepared by following General Procedure 6. Flash chromatography: 95:5 CH_2Cl_2/EtOAc. Yield: 69 mg (95%) of 9-epimeric products. Data for **15b** 7,9-*anti* (9*S*): R_f = 0.18 (95:5 CH_2Cl_2/EtOAc). $[\alpha]_D^{26}$ = –112.7 (*c* = 1.02 CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (dd, *J* = 15.4, 11.3 Hz, 1 H), 7.32–7.20 (m, 5 H), 6.56 (t, *J* = 11.3 Hz, 1 H), 6.09 (dd, *J* = 15.5, 7.7 Hz, 1 H), 5.61 (d, *J* = 11.3 Hz, 1 H), 5.56–5.47 (m, 2 H), 4.51 (dd, *J* = 15.5, 6.5 Hz, 1 H), 3.76 (m, 1 H), 3.72 (s, 3 H), 3.62 (m, 1 H), 2.89 (dd, *J* = 13.8, 3.5 Hz, 1 H, AB system), 2.65 (dd, *J* = 13.8, 8.3 Hz, 1 H, AB system), 2.55 (m, 1 H), 2.41 (m, 1 H), 2.12 (br. s, 1 H), 1.77–1.63 (m, 2 H), 1.33 (s, 3 H), 1.31 (s, 3 H), 1.08 (d, *J* = 5.8 Hz, 3 H), 1.06 (d, *J* = 6.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (C_0), 146.9 (CH), 145.5 (CH), 138.7 (C_0), 134.7 (CH), 131.4 (CH), 129.5 (CH), 128.3 (CH), 126.9 (CH), 126.2 (CH), 115.6 (CH), 100.5 (C_0), 75.3 (CH), 69.6 (CH), 63.2 (CH), 51.0 (CH_3), 41.6 (CH), 40.9 (CH_2), 37.9 (CH), 36.5 (CH_2), 25.1 (CH_3), 24.4 (CH_3), 17.7 (CH_3), 15.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{26}H_{36}O_5Na$ $[M + Na]^+$ 451.24550; found 451.24505. Data for **15b** 7,9-*syn* (9*R*): R_f = 0.10 (95:5 CH_2Cl_2/EtOAc). $[\alpha]_D^{26}$ = –31.4 (*c* = 0.70 CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (dd, *J* = 15.6, 11.4 Hz, 1 H), 7.35–7.24 (m, 5 H), 6.61 (t, *J* = 11.3 Hz, 1 H), 6.14 (dd, *J* = 15.5, 7.7 Hz, 1 H), 5.63 (d, *J* = 11.3 Hz, 1 H), 5.55–5.48 (m, 2 H), 4.58 (m, 1 H), 3.79 (m, 1 H), 3.74 (s, 3 H), 3.65 (m, 1 H), 2.90 (dd, *J* = 13.8, 3.4 Hz, 1 H, AB system), 2.69–2.61 (m, 2 H), 2.42 (m, 1 H), 1.71 (br. s, 1 H), 1.45 (s, 3 H), 1.41 (s, 3 H), 1.38–1.35 (m, 2 H), 1.13 (d, *J* = 6.7 Hz, 3 H), 1.09 (t, *J* = 6.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (C_0), 146.9 (CH), 145.6 (CH), 138.6 (C_0), 134.4 (CH), 131.6 (CH), 129.4 (CH), 128.5 (CH), 126.8 (CH), 126.5 (CH), 115.5 (CH), 98.6 (C_0), 75.6 (CH), 71.9 (CH), 65.6 (CH), 51.1 (CH_3), 41.9 (CH), 40.7 (CH_2), 38.2 (CH), 34.2 (CH_2), 30.2 (CH_3), 19.7 (CH_3), 17.3 (CH_3), 15.5 (CH_3) ppm. HRMS (ESI): calcd. for $C_{26}H_{36}O_5Na$ $[M + Na]^+$ 451.24550; found 451.24586.

(2*Z*,4*E*,6*R*,7*S*,9*S*,10*Z*,12*S*,13*S*,14*S*)-Methyl-7,13-bis(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,12-dimethyl-14-phenylpentadeca-2,4,10-trienoate [14c, 7,9-*anti* (9*S*)] and (2*Z*,4*E*,6*R*,7*S*,9*R*,10*Z*,12*S*,13*S*,14*S*)-Methyl-7,13-bis(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,12-dimethyl-14-phenylpentadeca-2,4,10-trienoate [14c, 7,9-*syn* (9*R*)]: Prepared by following General Procedure 5b. Flash chromatography: 96:4 hexane/EtOAc. Yield: 68 mg (69% yield by ^{1}H NMR) of 9-epimeric products, *dr* [7,9-*anti* (9*S*)/7,9-*syn* (9*R*)] = 57:43. Data for **14c** 7,9-*anti* (9*S*): R_f = 0.31 (85:15 hexane/EtOAc). $[\alpha]_D^{30}$ = +1.4 (*c* = 0.18 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 15.3, 11.3 Hz, 1 H), 7.26–7.09 (m, 5 H), 6.56 (t, *J* = 11.3 Hz, 1 H), 6.02 (dd, *J* = 15.5, 7.5 Hz, 1 H), 5.59 (m, 2 H), 5.32 (m, 1 H), 4.35 (dd, *J* = 13.1, 8.3 Hz, 1 H), 3.89 (dd, *J* = 10.4, 5.1 Hz, 1 H), 3.73 (s, 3 H), 3.67 (dd, *J* = 7.1, 3.2 Hz, 1 H), 2.79 (m, 1 H), 2.54 (m, 2 H), 1.91 (br. s, 1 H), 1.45 (m, 2 H), 1.24 (d, *J* = 7.1 Hz, 3 H), 1.02 (d, *J* = 6.8 Hz, 3 H), 1.01 (d, *J* = 7.0 Hz, 3 H), 0.92 (s, 9 H), 0.84 (s, 9 H), 0.05 (s, 6 H), 0.03 (s, 3 H), –0.14 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (C_0), 147.4 (CH), 145.4 (CH), 145.3 (C_0), 133.2 (CH), 132.2 (CH), 128.3 (CH), 127.8 (CH), 126.7 (CH), 126.2 (CH), 115.7 (CH), 80.7 (CH), 72.7 (CH), 64.5 (CH), 51.1 (CH_3), 44.2 (CH), 42.7 (CH), 39.7 (CH_2), 36.2 (CH), 26.3 (CH_3), 25.9 (CH_3), 20.1 (CH_3), 18.5 (C_0), 18.1 (CH_3), 18.0 (C_0), 14.6 (CH_3), –3.2 (CH_3), –4.0 (CH_3), –4.5 (CH_3), –4.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{36}H_{62}O_5Si_2Na$ $[M + Na]^+$ 653.40280; found 653.40322. Data for **14c** 7,9-*syn* (9*R*): R_f = 0.45 (85:15 hexane/EtOAc). $[\alpha]_D^{30}$ = +8.0 (*c* = 0.21 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.20 (m, 6 H), 6.49 (t, *J* = 11.3 Hz, 1 H), 5.94 (dd, *J* = 15.5, 8.3 Hz, 1 H), 5.57 (d, *J* = 11.3 Hz, 1 H), 5.46 (t, *J* = 10.6 Hz, 1 H), 5.30 (dd, *J* = 11.1, 8.4 Hz, 1 H), 3.84 (t, *J* = 7.9 Hz, 1 H), 3.78–3.69 (m, 2 H), 3.73 (s, 3 H), 2.78 (m, 1 H), 2.37 (m, 2 H), 1.86 (br. s, 1 H), 1.56 (m, 1 H), 1.25 (d, *J* = 7.0 Hz, 3 H), 1.24–1.21 (m, 1 H), 1.03 (d, *J* = 6.8 Hz, 3 H), 0.94 (s, 9 H), 0.89 (s, 9 H), 0.81 (d, *J* = 7.0 Hz, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.05 (s, 3 H), 0.00 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6 (C_0), 146.8 (CH), 145.7 (C_0), 145.5 (CH), 132.8 (CH), 131.9 (CH), 128.4 (CH), 128.1 (CH), 127.0 (CH), 126.2 (CH), 115.4 (CH), 80.5 (CH), 73.9 (CH), 65.8 (CH), 51.0 (CH_3), 45.0 (CH), 41.8 (CH), 41.3 (CH_2), 35.9 (CH), 26.3 (CH_3), 25.8 (CH_3), 20.0 (CH_3), 19.9 (CH_3), 18.5 (C_0), 18.0 (C_0), 15.7 (CH_3), –3.2 (CH_3), –3.6 (CH_3), –4.4 (CH_3), –4.4 (CH_3) ppm. HRMS (ESI): calcd. for $C_{36}H_{62}O_5Si_2Na$ $[M + Na]^+$ 653.40280; found 653.40313.

(*R*,2*Z*,4*E*)-Methyl-6-[(4*S*,6*S*)-6-{(3*S*,4*S*,5*S*,*Z*)-4-hydroxy-3-methyl-5-phenylhex-1-enyl}-2,2-dimethyl-1,3-dioxan-4-yl]hepta-2,4-dienoate [15c, 7,9-*anti* (9*S*)]: Prepared by following General Procedure 6. Flash chromatography: 8:2 hexane/EtOAc. Yield: 16 mg (98%). R_f = 0.48 (1:1 hexane/EtOAc). $[\alpha]_D^{26}$ = –45.1 (*c* = 0.71 CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (dd, *J* = 15.5, 11.3 Hz, 1 H), 7.30–7.16 (m, 5 H), 6.60 (t, *J* = 11.4 Hz, 1 H), 6.08 (dd, *J* = 15.5, 7.7 Hz, 1 H), 5.63 (d, *J* = 11.3 Hz, 1 H), 5.60–5.44 (m, 2 H), 4.21 (dd, *J* = 15.0, 8.5 Hz, 1 H), 3.73 (s, 3 H), 3.69 (m, 1 H), 3.52 (t, *J* = 5.9 Hz, 1 H), 2.80 (p, *J* = 6.9 Hz, 1 H), 2.50 (m, 1 H), 2.40 (m, 1 H), 1.68–1.54 (m, 3 H), 1.30 (d, *J* = 6.9 Hz, 3 H), 1.30 (s, 3 H), 1.23 (s, 3 H), 1.06 (d, *J* = 6.9 Hz, 3 H), 1.04 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (C_0), 147.1 (CH), 145.5 (CH), 144.8 (C_0), 134.5 (CH), 130.9 (CH), 128.4 (CH), 127.7 (CH), 126.9 (CH), 126.4 (CH), 115.6 (CH), 100.4 (C_0), 79.1 (CH), 69.7 (CH), 63.2 (CH), 51.1 (CH_3), 42.9 (CH), 41.4 (CH), 36.2 (CH_2), 35.7 (CH), 24.8 (CH_3), 24.4 (CH_3), 18.2 (CH_3), 16.2 (CH_3), 15.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{27}H_{38}O_5Na$ $[M + Na]^+$ 465.26115; found 465.26058.

(*R*,4*E*)-Methyl-6-[(4*S*,6*R*)-6-{(3*S*,4*S*,5*S*,*Z*)-4-hydroxy-3-methyl-5-phenylhex-1-enyl}-2,2-dimethyl-1,3-dioxan-4-yl]hepta-2,4-dienoate [15c, 7,9-*syn* (9*R*)]: Prepared by following General Procedure 6. Flash chromatography: 8:2 hexane/EtOAc. Yield: 19 mg (99%). R_f = 0.53 (1:1 hexane/EtOAc). $[\alpha]_D^{26}$ = +49.7 (*c* = 0.60 CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 15.5, 11.3 Hz, 1 H), 7.31–7.26 (m, 4 H), 7.21–7.17 (m, 1 H), 6.58 (t, *J* = 11.3 Hz, 1 H), 6.11 (dd, *J* = 15.5, 7.8 Hz, 1 H), 5.60 (d, *J* = 11.3 Hz, 1 H), 5.49–5.42 (m, 2 H), 4.47 (m, 1 H), 3.76 (m, 1 H), 3.72 (s, 3 H), 3.42 (t, *J* = 5.1 Hz, 1 H), 2.89 (m, 1 H), 2.52 (m, 1 H), 2.46 (br. s, 1 H), 2.39 (m, 1 H), 1.46 (s, 3 H), 1.41 (s, 3 H), 1.38–1.34 (m, 2 H), 1.28 (d, *J* = 7.0 Hz, 3 H), 1.07 (d, *J* = 6.9 Hz, 3 H), 1.01 (d, *J* = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (C_0), 146.8 (CH), 145.6 (CH), 145.6 (C_0), 135.4 (CH), 131.3 (CH), 128.2 (CH), 127.9 (CH), 126.8 (CH), 126.1 (CH), 115.5 (CH), 98.8 (C_0), 78.2 (CH), 71.9 (CH), 65.2 (CH), 51.1 (CH_3), 41.8 (CH), 36.4 (CH), 34.2 (CH_2), 30.1 (CH_3), 19.7 (CH_3), 18.2 (CH_3), 15.5 (CH_3), 14.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{27}H_{38}O_5Na$ $[M + Na]^+$ 465.26115; found 465.26127.

(2*Z*,4*E*,6*R*,7*S*,9*S*,10*Z*,12*R*,13*R*,14*S*)-Methyl-7,13-bis(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,12-dimethyl-14-phenylpentadeca-2,4,10-trienoate [14d, 7,9-*anti* (9*S*)] and (2*Z*,4*E*,6*R*,7*S*,9*R*,10*Z*,12*R*,13*R*,14*S*)-Methyl-7,13-bis(*tert*-butyldimethylsilyloxy)-9-hydroxy-6,12-dimethyl-14-phenylpentadeca-2,4,10-trienoate [14d, 7,9-*syn* (9*R*)]: Prepared by following General Procedure 5b. Flash chromatography: 96:4 hexane/EtOAc. Yield: 62 mg (75% yield by ^1H NMR) of 9-epimeric products, *dr* [7,9-*anti* (9*S*)/7,9-*syn* (9*R*)] = 88:12. Data for **14d** 7,9-*anti* (9*S*): R_f = 0.36 (85:15 hexane/EtOAc). $[\alpha]_D^{30}$ = –20.5 (*c* = 0.40 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (dd, *J* = 15.3, 11.4 Hz, 1 H), 7.29–7.17 (m, 5 H), 6.54 (t, *J* = 11.3 Hz, 1 H), 6.01 (dd, *J* = 15.4, 7.6 Hz, 1 H), 5.68–5.58 (m, 2 H), 5.35 (m, 1 H), 4.48 (t, *J* = 8.2 Hz, 1 H), 3.89 (m, 1 H), 3.73 (s, 3 H), 3.71 (m, 1 H), 2.87 (m, 1 H), 2.64 (m, 1 H), 2.54 (dd, *J* = 12.3, 6.4 Hz, 1 H), 1.80 (br. s, 1 H), 1.58–1.40 (m, 2 H), 1.25 (d, *J* = 6.9 Hz, 3 H), 1.02 (d, *J* = 6.8 Hz, 3 H), 0.88 (s, 9 H), 0.87 (s, 9 H), 0.85 (d, *J* = 7.1 Hz, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H), 0.02 (s, 3 H), –0.35 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (C_0), 147.2 (CH), 145.4 (CH), 144.9 (C_0), 133.2 (CH), 131.6 (CH), 128.5 (CH), 128.2 (CH), 126.8 (CH), 126.3 (CH), 115.6 (CH), 80.5 (CH), 72.6 (CH), 64.3 (CH), 51.1 (CH_3), 45.3 (CH), 42.9 (CH), 40.8 (CH_2), 35.3 (CH), 26.2 (CH_3), 25.8 (CH_3), 20.3 (CH_3), 18.4 (C_0), 18.0 (C_0), 17.2 (CH_3), 14.6 (CH_3), –3.9 (CH_3), –4.4 (CH_3), –4.5 (CH_3), –4.8 (CH_3) ppm. HRMS (ESI): calcd. for $C_{36}H_{62}O_5Si_2Na$ $[M + Na]^+$ 653.40280; found 653.40352. Data for **14d** 7,9-*syn* (9*R*): the product could not be completely separated from unreacted **5**. R_f = 0.40 (85:15 hexane/EtOAc). HRMS (ESI): calcd. for $C_{36}H_{62}O_5Si_2Na$ $[M + Na]^+$ 653.40280; found 653.40437.

(*R*,2*Z*,4*E*)-Methyl-6-[(4*S*,6*S*)-6-{(3*R*,4*R*,5*S*,*Z*)-4-hydroxy-3-methyl-5-phenylhex-1-enyl}-2,2-dimethyl-1,3-dioxan-4-yl]hepta-2,4-dienoate [15d, 7,9-*anti* (9*S*)]: Prepared by following General Procedure 6. Flash chromatography: 8:2 hexane/EtOAc. Yield: 19 mg (100%). R_f = 0.65 (1:1 hexane/EtOAc). $[\alpha]_D^{27}$ = –72.7 (*c* = 0.59 CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (dd, *J* = 15.5, 11.3 Hz, 1 H), 7.27–7.17 (m, 5 H), 6.52 (t, *J* = 11.4 Hz, 1 H), 6.04 (dd, *J* = 15.5, 7.7 Hz, 1 H), 5.58–5.43 (m, 3 H), 4.38 (dd, *J* = 15.3, 7.8 Hz, 1 H), 3.71–3.65 (m, 1 H), 3.69 (s, 3 H), 3.41 (t, *J* = 6.1 Hz, 1 H), 2.80 (m, 1 H), 2.47 (m, 1 H), 2.36 (m, 1 H), 1.77 (br. s, 1 H), 1.62 (m, 2 H), 1.27 (d, *J* = 7.0 Hz, 3 H), 1.27 (s, 3 H), 1.17 (s, 3 H), 1.02 (d, *J* = 6.8 Hz, 3 H), 1.00 (d, *J* = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (C_0), 146.9 (CH), 145.5 (CH), 143.4 (C_0), 134.5 (CH), 130.9 (CH), 128.6 (CH), 128.4 (CH), 126.8 (CH), 126.5 (CH), 115.5 (CH), 100.5 (C_0), 78.6 (CH), 69.6 (CH), 63.0 (CH), 51.1 (CH_3), 42.8 (CH), 41.5 (CH), 36.5 (CH_2), 35.7 (CH), 24.9 (CH_3), 24.3 (CH_3), 19.1 (CH_3), 18.2 (CH_3), 15.5 (CH_3) ppm. HRMS (ESI): calcd. for $C_{27}H_{38}O_5Na$ $[M + Na]^+$ 465.26115; found 465.26067.

(*R*,4*E*)-Methyl-6-[(4*S*,6*R*)-6-{(3*R*,4*R*,5*S*,*Z*)-4-hydroxy-3-methyl-5-phenylhex-1-enyl}-2,2-dimethyl-1,3-dioxan-4-yl]hepta-2,4-dienoate [15d, 7,9-*syn* (9*R*)]: Prepared by following General Procedure 6. Flash chromatography: 8:2 hexane/EtOAc. Yield: 3.0 mg (100%). R_f = 0.56 (1:1 hexane/EtOAc). $[\alpha]_D^{27}$ = –7.6 (*c* = 0.21 CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 15.5, 11.3 Hz, 1 H), 7.31–7.21 (m, 5 H), 6.58 (t, *J* = 11.3 Hz, 1 H), 6.11 (dd, *J* = 15.5, 7.8 Hz, 1 H), 5.61 (d, *J* = 11.3 Hz, 1 H), 5.54–5.43 (m, 2 H), 4.35 (dd, *J* = 13.7, 7.6 Hz, 1 H), 3.72 (s, 3 H), 3.66 (dt, *J* = 8.0, 5.2 Hz, 1 H), 3.45 (t, *J* = 6.0 Hz, 1 H), 2.83 (m, 1 H), 2.53 (m, 1 H), 2.38 (m, 1 H), 1.40 (s, 3 H), 1.33 (d, *J* = 6.7 Hz, 3 H), 1.33–1.28 (m, 2 H), 1.30 (s, 3 H), 1.08 (d, *J* = 6.7 Hz, 3 H), 1.07 (d, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (C_0), 146.9 (CH), 145.6 (CH), 143.1 (C_0), 134.0 (CH), 131.9 (CH), 128.6 (CH), 128.3 (CH), 126.8 (CH), 126.6 (CH), 115.5 (CH), 98.6 (C_0), 78.5 (CH), 71.9 (CH), 65.6 (CH), 51.1 (CH_3), 42.7 (CH), 41.9 (CH), 36.0 (CH), 34.2 (CH_2), 30.1 (CH_3), 19.5 (CH_3), 19.1 (CH_3), 18.0 (CH_3), 15.6 (CH_3) ppm. HRMS (ESI): calcd. for $C_{27}H_{38}O_5Na$ $[M + Na]^+$ 465.26115; found 465.26066.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of all new compounds; chiral HPLC and GC chromatograms and conditions.

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