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Asymmetric Total Synthesis of Bioactive Natural Lipid Mycalol

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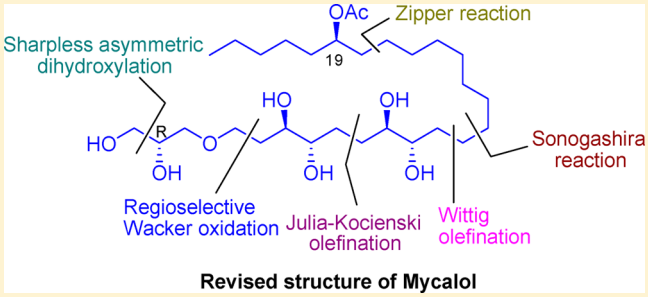
Supporting Information

ABSTRACT: A concise and convergent route for stereoselective total synthesis of promising anticancer natural lipid mycalol has been achieved using cheap and readily available L-arabinose as a chiral pool. The notable features of our synthesis comprised regioselective Wacker oxidation, Sharpless asymmetric dihydroxylation, Julia–Kocienski olefination, Wittig olefination, Zipper reaction, and Sonogashira reaction. Comparison of the spectroscopic data on a series of isomers supports the revised structure (*Org. Lett.* **2015**, 17, 1652) instead of the one originally proposed.



Revised structure of Mycalol

INTRODUCTION

Mycalol is a polyoxygenated monoalkyl glyceryl ether lipid that was first isolated by Fontana and co-workers from chloroform extract of the sponge *Mycale (Oxymycale) acerata Kirkpatrick 1907* collected in the coasts of Terra Nova Bay, Antarctica.[1] It exhibits promising and selective cytotoxic activity against human anaplastic thyroid carcinoma (ATC), the most aggressive human thyroid gland malignancy (IC_{50} against different human ATC-derived cell lines: FRO-HMGA1as = 7.3 μM, ACT1 = 4.5 μM, 8505c = 3.8 μM). It also shows moderate cytotoxicity to human colon solid tumor cell lines (IC_{50} = 10.9 μM).[1] The structure of mycalol was determined by a combination of spectroscopic methods (NMR, CD, mass) and by functional group derivatizations. Architecturally, mycalol possesses a C-27 linear skeleton embedded with nine oxygenated carbons and one ether linkage. There are seven hydroxy groups present in the molecule among which one remains in its acetylated form [Figure 1, proposed structure **1**[1] and revised structure **2**[2,3] (see abstract graphic)]. Statistical data[4] revealed that ATC is responsible for up to 40% of all deaths from thyroid cancer, and most anxiously, there is not a single clinical lead known to date[1] to combat against this malignancy. The discovery of mycalol may serve a significant role in deciphering cancer biology and as a lead compound for drug development. Mycalol was isolated in small yields from its natural source. Thus, the development of an efficient and scalable synthetic route is highly desirable to render it readily available for thorough biological investigations. As a part of our ongoing program[5] toward the synthesis of bioactive natural products, we envisaged the total synthesis of structurally intriguing and biologically potent natural lipid mycalol. Herein, we report a convergent stereoselective total synthesis of mycalol (Figure 1, both proposed and revised structure), which features the regioselective Wacker oxidation,[6] Sharpless asymmetric dihydroxylation,[7] Julia–Kocienski olefination,[8] Wittig olefination,[9] Zipper reaction,[10] and Sonogashira reaction[11] as the key steps. Spectroscopic data on the proposed synthesized structure of mycalol indicate discrepancies, suggesting that the proposed structure may be incorrect. To resolve these variations/deviations, we have also synthesized a total of 12 analogues of the proposed structure with eight diastereomers and four positional isomers. The results indicate that the observed data of mycalol is identical to that of a synthetic analogue that varies in the configuration of the C-2′ position (diastereomer) and position of the O-acetyl group (structural isomer). Our synthetic strategy is quite flexible, as demonstrated by the synthesis of a wide range of analogues. Our approach, as described above, uses a different set of key reactions than the recent report by Reddy and co-workers[3] in which they used Sharpless epoxidation, a low yielding cross metathesis and opening of chiral epoxide by alkyl Grignard as the pivotal steps to achieve both the proposed and revised structures of mycalol.

RESULTS AND DISCUSSION

Retrosynthetic analysis of the proposed structure of mycalol (**1**) is depicted in Scheme 1. It could be synthesized from the advanced stage of intermediates **3**(**a**–**d**) by hydrogenation followed by global deprotection of acetonides. Intermediates **3**(**a**–**d**) could be constructed further from the vinyl iodides **4**(**a**–**d**) and alkyne intermediate **5** using Sonogashira reaction[11] as one of the key coupling steps. Vinyl iodides **4**(**a**–**d**) could be accessed from compounds **6**(**a**,**b**) using Wittig olefination[9] as one of the pivotal steps. Next, Julia–Kocienski olefination[8] would disconnect compounds **6**(**a**,**b**) into two coupling partners **7** and **8**, which could be further synthesized from common precursor **9** derived from the chiral pool of L-arabinose.

Our synthetic endeavor began with preparation of known precursor **9** from L-arabinose following a reported procedure[12] (Scheme 2). Compound **9** was then protected as TBDPS ether

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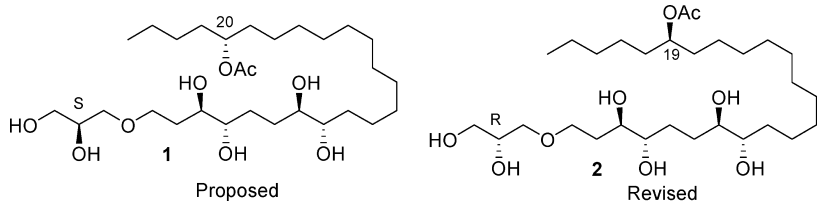
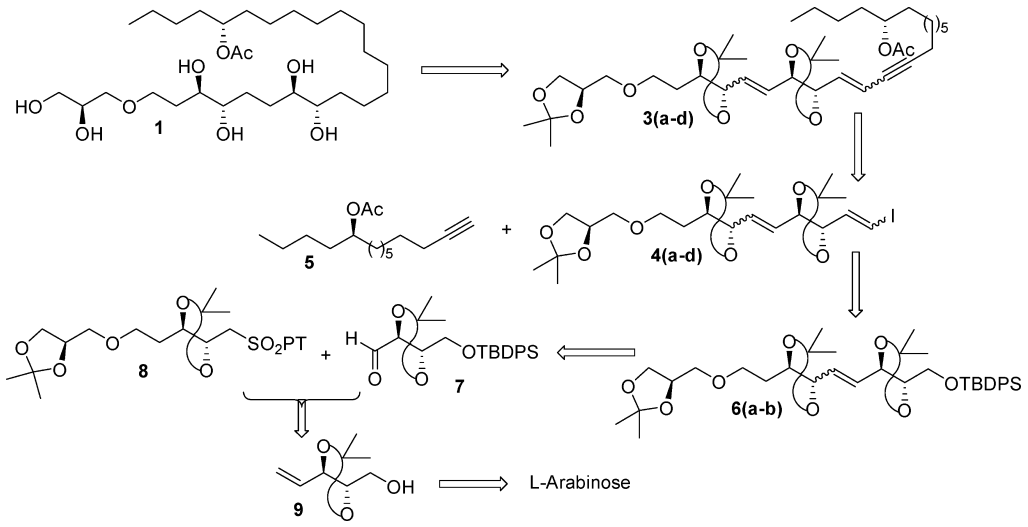
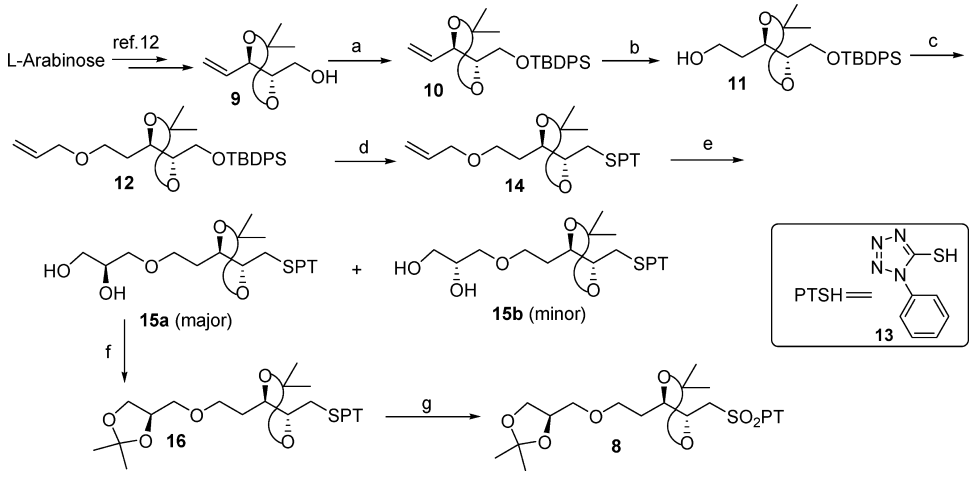


Figure 1. Chemical structure of mycalol.

Scheme 1. Retrosynthetic Analysis of the Proposed Structure of Mycalol (1)



Scheme 2. Synthesis of Glyceryl Ether Unit 8[a]



[a]Reagents and conditions: (a) TBDPSCl, imidazole, CH_2Cl_2, 0 °C to rt, 2 h, quantitative; (b) (i) $PdCl_2$, CuCl, DMF:H_2O (7:1), rt, 72 h; (ii) $NaBH_4$, MeOH, 0 °C, 30 min, 68% after two steps; (c) allyl bromide, NaH, TBAI, THF, 0 °C to rt, 2 h, 92%; (d) (i) TBAF, THF, 0 °C to rt, 30 min, 98%; (ii) **13**, DIAD, Ph_3P, THF, 0 °C to rt, 2 h, 88%; (e) AD-mix-β, $MeSO_2NH_2$, ^tBuOH:H_2O (1:1), 0 °C, 36 h, overall 90% (~69% isolable yield based on compound **15a**), (*dr* > 3.3:1); (f) 2,2-DMP, CSA, CH_2Cl_2, 0 °C to rt, 1 h, quantitative; (g) $(NH_4)_6Mo_7O_{24}.4H_2O$, 30% aqueous H_2O_2, EtOH, 0 °C to rt, 1.5 h, 85%.

using TBDPSCl in the presence of imidazole to achieve compound **10**. We have tried a number of hydroborylating reagents like 9-BBN and BH_3·THF at this stage in variable conditions to obtain compound **11**, but none of these were found to afford the desired compound even in moderate yields. This urged us to adopt a two-step reaction sequence as an alternative. Alkene **10** was first subjected to Wacker oxidation[6] using 10 mol % of $PdCl_2$ in the presence of CuCl to regioselectively produce the corresponding aldehyde, which concomitantly reduced with $NaBH_4$ to access alcohol **11** with good overall yield (68% over two steps). To construct the glyceryl ether moiety, we subjected alcohol **11** to a reaction with allyl bromide in the presence of NaH and a catalytic amount of TBAI to afford allyl ether **12**, which was further treated with TBAF to deprotect TBDPS ether and subsequently reacted with commercially available 1-phenyl-1H-tetrazole-5-thiol (PTSH, **13**) in the presence of DIAD/Ph_3P using Mitsunobu conditions[13] to achieve the synthesis of

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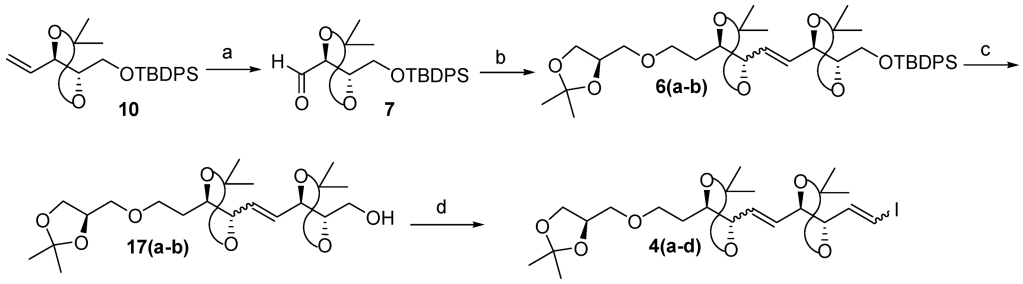
Scheme 3. Synthesis of Intermediates 4(a–d)[a]



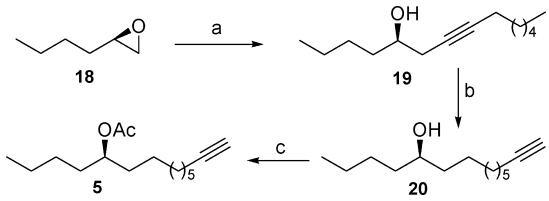
[a]Reagents and conditions: (a) OsO_4, NMO, $NaIO_4$, $NaHCO_3$, ^tBuOH:THF:H_2O (5:5:1), 0 °C to rt, 12 h, 90%; (b) **8**, NaHMDS, THF, −78 °C to rt, 1.5 h, 68%; (c) TBAF, THF, 0 °C to rt, 30 min, 97%; (d) (i) IBX, EtOAc, reflux, 2 h, quantitative; (ii) $Ph_3PCH_2I_2$, NaHMDS, −78 °C to rt, 4 h, 73% after two steps.

compound **14** in 86% yield over three steps. The terminal olefin of compound **14** was then dihydroxylated using AD-mix-β in the presence of $MeSO_2NH_2$ following the Sharpless asymmetric dihydroxylation protocol to get diols **15a** and **15b** (dr > 3.3:1, please see the HPLC analysis in Supporting Information) as major and minor isomers, respectively, with 90% overall yield.[7] Both of the diastereomers were separated cautiously using silica gel column chromatography. Our effort to reconfirm the absolute configuration of the newly generated secondary hydroxy center in major isomer **15a** by the modified Mosher method[14] was not successful at this stage due to the presence of several chemically similar protons in the recorded ^1H NMR spectrum. This precluded unambiguous determination of chemical shifts of the protons shielded or deshielded when the diol moiety of compound **15a** was converted to its corresponding (*R*) and (*S*)-Mosher esters, respectively. However, from the literature,[7] it can be anticipated that major compound **15a** is likely to be the appropriate isomer. Next, diol **15a** was treated with 2,2-dimethoxypropane (2,2-DMP) in the presence of camphorsulfonic acid (CSA) to afford compound **16** (Scheme 2), which was oxidized further using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in the presence of 30% H_2O_2[15] to result in sulfone **8** in 85% yield over two steps.

The synthesis of the intermediates **4(a–d)** is summarized in Scheme 3. Alkene **10** was first subjected to oxidative cleavage[16] in the presence of OsO_4, NMO, and $NaIO_4$ to produce aldehyde **7** and concomitantly reacted with sulfone **8** (Scheme 2) in the presence of NaHMDS following the Julia–Kocienski olefination protocol[8] to yield an inseparable mixture of alkenes **6(a,b)**, which further were reacted with TBAF to produce another inseparable mixture of alcohols **17(a,b)** in good overall yield (59% over three steps). Next, the mixture of alcohols **17(a,b)** was oxidized with IBX[17] to get the corresponding aldehydes, which were concomitantly subjected to a Wittig olefination[9] reaction in the presence of $Ph_3PCH_2I_2$ and NaHMDS to provide the mixture of compounds **4(a–d)** in 73% yield after two steps. We did not attempt to separate this mixture of geometrical isomers **4(a–d)** at this stage because the hydrogenation reaction at the prefinal stage of synthesis would logically convert them to a single saturated compound.

The synthesis of alkyne **5** is summarized in Scheme 4. Known epoxide **18**,[18] prepared from its racemic counterpart using the Jacobsen hydrolytic kinetic resolution protocol, was subjected to an epoxide ring opening reaction[19] with commercially available octyne in the presence of ^{n}BuLi and $BF_3\cdot Et_2O$ to afford compound **19** in 83% yield. The internal alkyne in compound **19** was next translocated to its terminal

Scheme 4. Synthesis of Alkyne 5[a]



[a]Reagents and conditions: (a) Octyne, ^{n}BuLi, $BF_3\cdot OEt_2$, THF, −78 to 0 °C, 30 min; then, −78 °C, 1.5 h, 83%; (b) KO^{t}Bu, ^{n}BuLi, 1,3-diaminopropane, THF, 0 °C to rt, 3 h, 73%; (c) Ac_2O, pyridine, 0 °C to rt, 30 min, quantitative.

position using Zipper conditions[10] (KO^{t}Bu/^{n}BuLi/1,3-diaminopropane) to achieve the synthesis of alkyne **20** in good yield. The free hydroxy of alkyne **20** was finally protected as acetate with Ac_2O/Py to produce the required alkyne intermediate **5** quantitatively.

The final synthetic endeavor for the proposed structure of mycalol (**1**) is outlined in Scheme 5. The advanced intermediates **4(a–d)** and alkyne **5** (Scheme 4) were next coupled together in the presence of $Pd[(Ph_3P)_2Cl_2]$/CuI/Et_3N following Sonogashira reaction conditions[11] to produce the mixture of intermediates **3(a–d)**, which finally was hydrogenated using 10% Pd/C to obtain single saturated product **21**. We have recorded both the ^1H and ^{13}C NMR spectrum of pure compound **21** in different solvents, including $CDCl_3$, d_6-benzene, and d_5-pyridine, and compared them with those delineated for the acetonide compound prepared by Fontana et al.[1] The ^1H NMR spectrum of synthesized compound **21** recorded either in $CDCl_3$, d_6-benzene, or d_5-pyridine was in agreement with the reported data, but there was a significant mismatch in the ^{13}C NMR spectrum when compared with the literature values.[1] The signals at δ 31.7 and 25.0 in the ^{13}C NMR spectrum of the acetonide derivative of isolated mycalol[1] were missing in the ^{13}C NMR spectrum (recorded in $CDCl_3$) of synthesized compound **21**. Additionally, minor mismatches were observed in the ^{13}C NMR signals of the aliphatic carbon centers bearing a hydroxy group (please see spectra and comparison Table 2 in the Supporting Information). As there was no specific rotation documented for that acetonide compound, we were unable to compare its specific rotation with the recorded data {observed $[\alpha]^{27}_D$ +3.2 (*c* 1.4, $CHCl_3$)} for compound **21**. However, compound **21** was finally subjected to a reaction with AcOH:H_2O (4:1) to afford compound **1** by global deprotection of the acetonides in good overall yield (Scheme 5). The spectral data, specifically the ^1H

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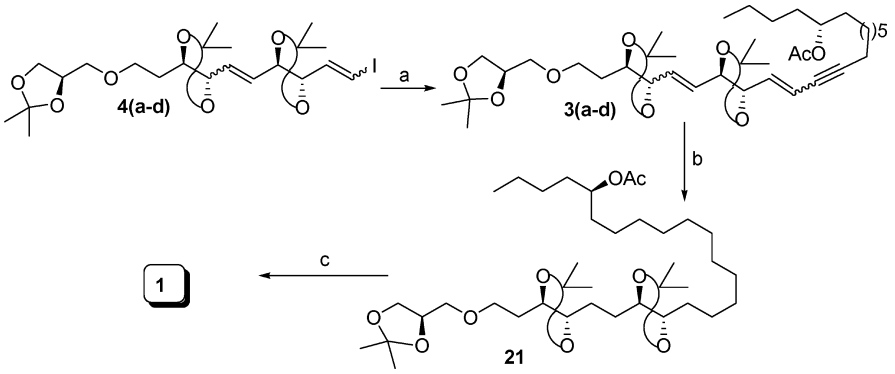
Scheme 5. Synthesis of the Reported Structure of Mycalol (1)[a]



[a]Reagents and conditions: (a) **5**, $Pd[(Ph_3P)_2Cl_2]$, CuI, Et_3N, rt, 4 h, 76%; (b) H_2, Pd/C (10%), EtOAc, rt, 12 h, 98%; (c) AcOH:H_2O(4:1), 0 °C to rt, 6 h, 97%.

NMR spectrum (recorded in d_5-pyridine) and HRMS, were in accordance with the reported values, but considerable mismatches (similar to the acetonide derivative) were observed when the ^{13}C NMR (recorded in d_5-pyridine) data was taken into consideration (please see spectra and comparison Table 1 in the Supporting Information). This result strongly suggests that the structures proposed for isolated mycalol may not be entirely accurate.

Next, we considered the possibility that the isolated mycalol is a diastereomer of the proposed structure. The configuration of the two vicinal diol units (C-3/C-4 and C-7/C-8, Figure 1, compound **1**) was assigned unambiguously as *erythro* by the isolation group. The ^{13}C NMR study of the synthesized acetonide derivative of isolated mycalol exhibited well-separated signals (27.1 and 25.9 ppm; 26.8 and 25.4 ppm) characteristic of the methyl acetals of dioxolane rings with a *cis* conformation.[1] Thus, the possibility of diastereomers with *threo* vicinal diol moieties has been discarded. The absolute configuration of the two *erythro* diol systems was assigned by the isolation group as *R*, *S*, *R*, and *S* for C-3, C-4, C-7, and C-8 centers, respectively, by the chiroptical approach using the 1′,2′-dibenzoate-3,4-dipivolyl and 1′,2′-dibenzoate-7,8-dipivolyl derivatives of mycalol.[1] The preparation, characterization, and chiroptical analysis of these compounds were really challenging and could be potential sources of complications. We thus planned to construct the possible diastereomers **22**–**24** (Figure 2), where the C-2′ center is in *S* configuration. The stereochemistry of the well-characterized C-20 center did not alter during the course of the synthesis.

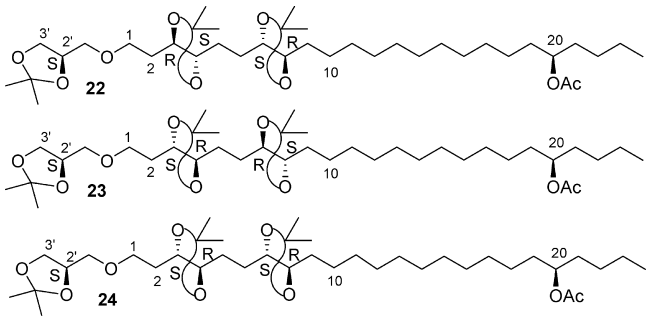


Figure 2. Diastereomers of compound **21** with the C-2′ center having *S* configuration.

The synthesis of intermediates from D-arabinose is described in Scheme 6. Similar chemistry as that developed for the synthesis of compound **21** was adopted. Alkene **25**, prepared from D-arabinose following a reported procedure,[12] was converted to TBDPS ether **26**. It was next subjected to regioselective Wacker oxidation[6] to obtain the corresponding aldehyde and concomitantly reduced to alcohol **27** using $NaBH_4$. Alcohol **27** was then treated with allyl bromide in the presence of NaH to access olefin ether **28**. Next, the TBDPS group was deprotected, and the resultant alcohol was reacted subsequently with PTSH (**13**) in Mitsunobu conditions to produce compound **29**, which finally was dihydroxylated[7] using AD-mix-β to obtain compounds **30a** and **30b** (dr > 3.3:1) as major and minor isomers, respectively, in good overall yield. Purified major isomer **30a** was then treated with 2,2-DMP to obtain acetonide **31** (Scheme 6) and finally oxidized[15] with H_2O_2 in the presence of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ to afford required sulfone **32** in 85% yield over two steps.

Synthesis of the advanced stage of intermediates for compounds **22**–**24** is summarized in Scheme 7. Alkene **26** was subjected to oxidative cleavage[16] using OsO_4/NMO and $NaIO_4$ to obtain aldehyde **33** and subsequently reacted with sulfone **8** (prepared from L-arabinose, Scheme 2) in the presence of NaHMDS following the Julia–Kocienski olefination protocol[8] to obtain an inseparable mixture of compounds **34**(**a**,**b**). The TBDPS group was next deprotected, and the mixture of the resulting alcohols was oxidized[17] to the corresponding aldehydes with IBX, which concomitantly reacted[9] with $Ph_3PCH_2I_2$ in the presence of NaHMDS to get a mixture of inseparable compounds **35**(**a**–**d**) in good overall yield (67%, in 3 steps). Similarly, sulfone **32** was separately subjected to the Julia–Kocienski olefination[8] with aldehydes **7** (prepared from L-arabinose, Scheme 3) and **33** (prepared from D-arabinose, Scheme 7) to obtain a mixture of compounds **36**(**a**,**b**) and **38**(**a**,**b**), respectively, which were finally transformed to their corresponding vinyl iodides **37**(**a**–**d**) and **39**(**a**–**d**), respectively, with good overall yield.

The final endeavor in the synthesis of compounds **22**–**24** is described in Scheme 8. Three sets of vinyl iodides **35**(**a**–**d**), **37**(**a**–**d**), and **39**(**a**–**d**) in hand were coupled separately with common alkyne **5** following the Sonogashira reaction conditions[11] to afford compounds **40**(**a**–**d**), **41**(**a**–**d**), and **42**(**a**–**d**), respectively, which were subsequently hydrogenated to produce the corresponding saturated compounds **22**, **23**, and **24**, respectively, in good overall yield (71–73% in two steps).

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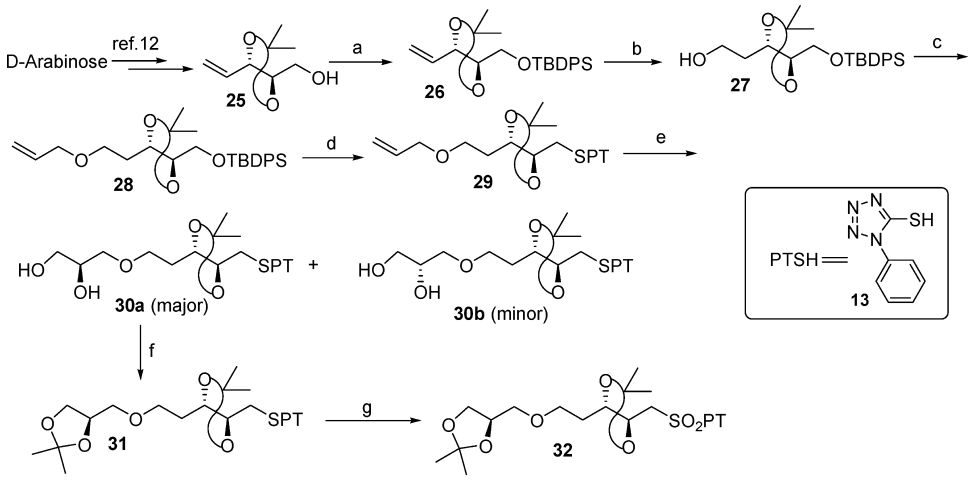
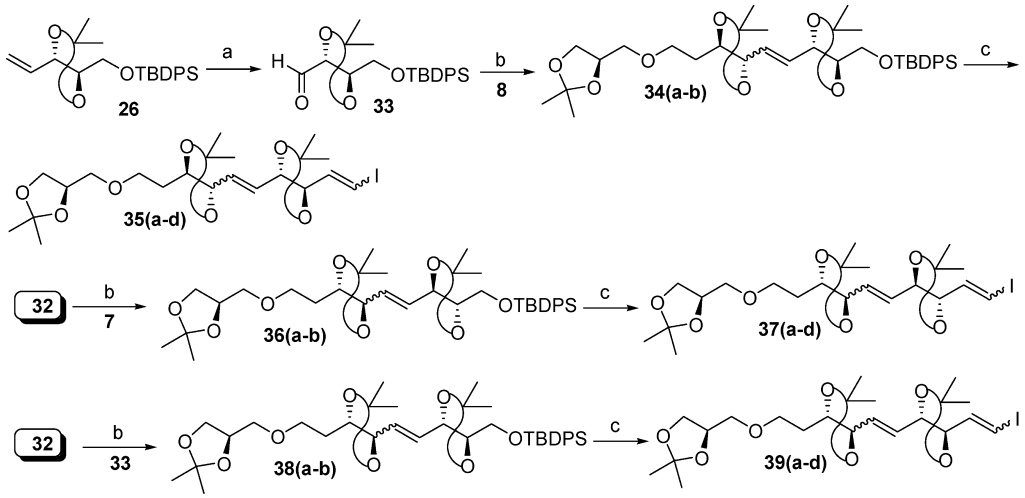
Scheme 6. Synthesis of Intermediates from D-Arabinose[a]



[a]Reagents and conditions: (a) TBDPSCl, imidazole, CH_2Cl_2, 0 °C to rt, 2 h, quantitative; (b) (i) $PdCl_2$, CuCl, DMF:H_2O (7:1), rt, 72 h; (ii) $NaBH_4$, MeOH, 0 °C, 30 min, 69% after two steps; (c) allyl bromide, NaH, TBAI, THF, 0 °C to rt, 2 h, 91%; (d) (i) TBAF, THF, 0 °C to rt, 30 min, 97%; (ii) **13**, DIAD, Ph_3P, THF, 0 °C to rt, 2 h, 88%; (e) AD-mix-β, $MeSO_2NH_2$, ^{t}BuOH:H_2O (1:1), 0 °C, 36 h, overall 90% (~69% isolatable yield based on compound **30a**), (dr > 3.3:1); (f) 2,2-DMP, CSA, CH_2Cl_2, 0 °C to rt, 1 h, quantitative; (g) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 30% aqueous H_2O_2, EtOH, 0 °C to rt, 1.5 h, 85%.

Scheme 7. Synthesis of the Advanced Stage of Intermediates for Compounds 22−24[a]



[a]Reagents and conditions: (a) OsO_4, NMO, $NaIO_4$, $NaHCO_3$, ^{t}BuOH:THF:H_2O (5:5:1), 0 °C to rt, 12 h, 90%; (b) **8** or **7** or **33** NaHMDS, THF, −78 °C to rt, 1.5 h, 68−71%; (c) (i) TBAF, THF, 0 °C to rt, 30 min, 93−97%; (ii) IBX, EtOAc, reflux, 2 h, quantitative; (iii) $Ph_3PCH_2I_2$, NaHMDS, −78 °C to rt, 4 h, 69−72%.

The ^{1}H NMR spectra of these compounds were in accordance with the reported data of the acetonide compound[1] prepared by Fontana et al. However, it was quite disappointing to see that the ^{13}C NMR data of compounds **22−24** deviated significantly from the reported values (please see spectra and comparison Table 2 in the Supporting Information).

Next, we were keen to see whether the variation of stereochemistry at the C-2′ center would provide any insight into the origin of the aberrant signals in the ^{13}C NMR data. Thus, we have synthesized all four possible diastereomers (**43−46**) of compound **21** (Figure 3) in which the C-2′ center is in the *R* configuration.

The synthesis of compounds **43−46** is summarized in Scheme 9. Compounds **15b** (Scheme 2) and **30b** (Scheme 6) were transformed separately to their corresponding sulfones **47** and **48**, respectively, following the same chemistry as described for the synthesis of compound **8** (Scheme 2). It is noteworthy that both compounds **15b** and **30b** were prepared on a larger scale (3.0 g, please see the Experimental Section) from corresponding olefins **14** (Scheme 2) and **29** (Scheme 6), respectively, using AD-mix-α with similar overall yield (~90%) and diastereoselectivity (dr >3.3:1, scheme not shown) as observed in the AD-mix-β reaction (Schemes 2 and 6). Next, sulfone **47** was converted separately to intermediates **49(a−d)** and **50(a−d)** by reacting with aldehydes **7** and **33**, respectively, following similar chemistry as developed above. Similarly, sulfone **48** transformed to compounds **51(a−d)** and **52(a−d)** using aldehydes **7** and **33**, respectively. All four sets of intermediates **49(a−d)**, **50(a−d)**, **51(a−d)**, and **52(a−d)** were coupled[11] with alkyne **5** separately and subsequently hydrogenated to obtain saturated compounds **43**, **44**, **45**, and **46**, respectively, in good overall yield (73−76% in two steps). Both

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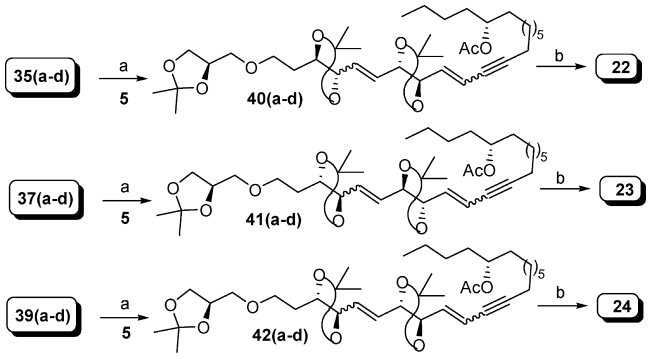
Scheme 8. Synthesis of Compounds 22−24[a]



[a]Reagents and conditions: (a) **5**, $Pd[(Ph_3P)_2Cl_2]$, CuI, Et_3N, rt, 4 h, 75−76%; (b) H_2, Pd/C (10%), EtOAc, rt, 12 h, 94−97%.

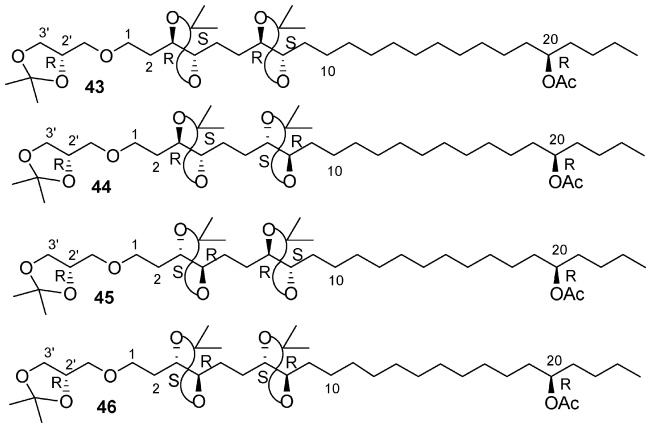


Figure 3. Diastereomers of compound **21** with the C-2′ center having *R* configuration.

^1H and ^{13}C NMR for all of these compounds were recorded and compared with those reported for the acetonide compound prepared by Fontana et al. The ^1H NMR data of compounds **43**−**46** were close to their reported values. It was observed that the ^{13}C NMR signals from the hydroxylated carbon centers of compounds **44**−**46** deviated significantly from the reported values. However, the corresponding signals from synthesized compound **43** were in much better agreement (please see spectra and comparison Table 3 in the Supporting Information). This result urged us to consider the possibility of other structural/positional isomers for the proposed structure of mycalol.

As the ^{13}C NMR data of compound **43** better matched the reported values for mycalol (except the resonances at 31.7 and 25.0 ppm) relative to the other synthesized diastereomers, we decided to synthesize its structural isomers by varying the position of hydroxy groups. To decide which functional group(s) should be varied, two issues were considered. First, the two methylene groups of protons positioned between the *erythro* vicinal diol moieties in the deuterated acetonide derivative of isolated mycalol prepared by Fontana et al. have different chemical shifts (δ 1.57 and 1.74)[1] despite being in an apparently similar chemical environment. Second, the integration of these protons in the presence of a number of other closely situated methylene groups of protons was arduous. Both of these facts tempted us to consider the possibility that there might be more than two methylene groups between the two *erythro* vicinal diol moieties. We thus designed two compounds, **53** and **54**, as shown in Figure 4, where the two *erythro* vicinal diol moieties are separated by three and four methylene groups, respectively. This would eventually generate two almost nonidentical environments (H_2-5/H_2-7 and H_2-6 for compound **53**; H_2-5/H_2-8 and H_2-6/H_2-7 for compound **54**) for those methylene protons flanked between the two vicinal diol units.

Synthesis of the advanced stage of intermediates for compounds **53** and **54** is outlined in Scheme 10. Alcohol **11** (Scheme 2) was oxidized[17] with IBX to get the corresponding aldehyde and subsequently subjected to Julia−Kocienski olefination[8] with sulfone **47** (Scheme 9) to afford a mixture of compounds **55**(**a**,**b**), which was finally converted to the compound mixture **56**(**a**−**d**) following the same chemistry as described for compound **21**. For the preparation of a higher homologue of alcohol **11**, aldehyde **7** (Scheme 3) was subjected to Wittig olefinations with $Ph_3P{=}CHCO_2Et$[20] to obtain the corresponding α,β-unsaturated ester, which was finally reduced with $LiBH_4$ to yield alcohol **57**. Next, this alcohol was transformed to an advanced stage of intermediates **59**(**a**−**d**) through intermediates **58**(**a**,**b**) following identical chemistry as that described above.

The syntheses of alkyne fragments for compounds **53** and **54** are depicted in Scheme 11. Following the identical chemistry of alkyne **5** (Scheme 4), we treated epoxide **18** separately with 1-heptyne and 1-hexyne to produce compounds **60a** and **60b**, respectively, which were further subjected to the Zipper reaction[10] to access corresponding alkynes **61a** and **61b**. Finally, the free hydroxy groups in both alkynes were protected separately as acetate to yield protected alkynes **62a** and **62b**, respectively.

The final endeavor in the synthesis of compounds **53** and **54** is described in Scheme 12. Following the same synthetic strategy as that developed for compound **21**, the mixture of compounds **56**(**a**−**d**) and **59**(**a**−**d**) were subjected to the Sonogashira reaction[11] with alkynes **62a** and **62b**, respectively, to yield the compound mixtures **63**(**a**−**d**) and **64**(**a**−**d**), respectively, which were finally hydrogenated to afford compounds **53** and **54**, respectively. Both the ^1H and ^{13}C NMR spectra of compounds **53** and **54** were recorded and compared with those data reported[1] for the acetonide compound synthesized by Fontana et al. Disappointingly, all of the spectra deviated significantly (please see the spectra and comparison in Table 4 in the Supporting Information) from the reported spectra, and no ^{13}C NMR signals at δ 31.7 and 25.0 were observed in either case. Thus, the possibility of the existence of more than two methylene groups between the two *erythro* vicinal diol moieties was discarded.

Finally, we considered the possibility that the position of the OAc group in the hydrophobic chain might be different in mycalol from its proposed structure. As has been reported that the terminal methyl group (C-24) has HMBC correlation with C-23, C-22, and C-21 methylene groups of protons, we planned to synthesize isomers where the OAc group is positioned elsewhere in the hydrophobic chain. As the ^{13}C NMR data of compound **43** was more compatible with the reported data (except the signals at 31.7 and 25.0 ppm), we prepared two of its structural isomers, **65** and **66** (Figure 5), where the OAc group is at the C-18 and C-19 position, respectively.

The syntheses of alkyne intermediates for compounds **65** and **66** are summarized in Scheme 13. Epoxides **67a** and **67b** prepared from their racemic counterparts using the Jacobsen hydrolytic kinetic resolution protocol were subjected to

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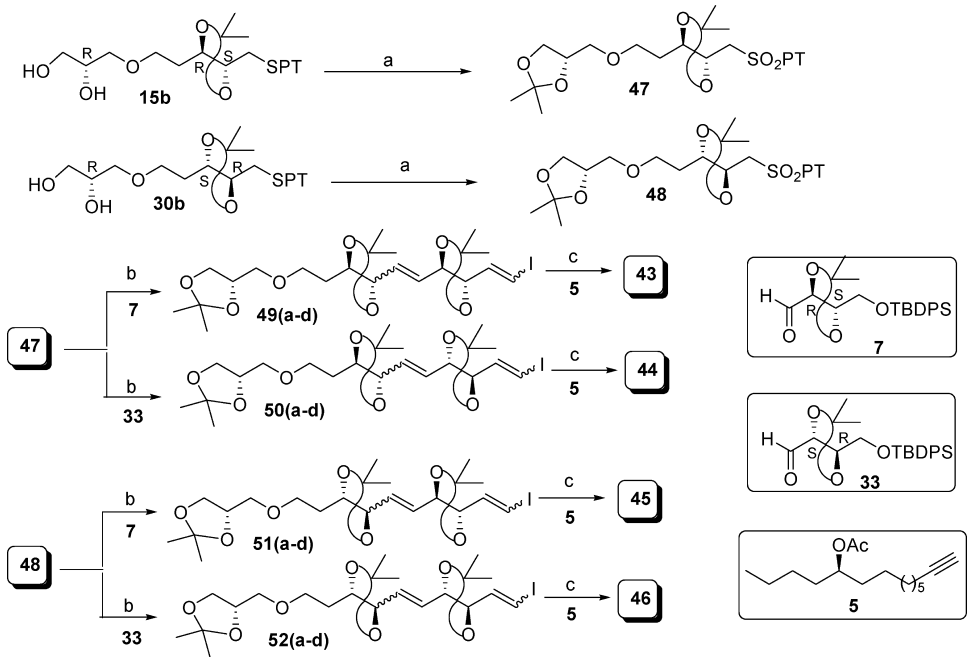
Scheme 9. Synthesis of Compounds 43−46[a]



[a]Reagents and conditions: (a) (i) 2,2-DMP, CSA, CH_2Cl_2, 0 °C to rt, 1 h, quantitative; (ii) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 30% aqueous H_2O_2, EtOH, 0 °C to rt, 1.5 h, 85%. (b) (i) **7** or **33**, NaHMDS, THF, −78 °C to rt, 1.5 h, 67−69%; (ii) TBAF, THF, 0 °C to rt, 30 min, 96−98%; (iii) IBX, EtOAc, reflux, 2 h, quantitative; (iv) $Ph_3PCH_2I_2$, NaHMDS, −78 °C to rt, 4 h, 73−76%; (c) (i) **5**, Pd[$(Ph_3P)_2Cl_2$], CuI, Et_3N, rt, 4 h, 75−79%; (ii) H_2, Pd/C (10%), EtOAc, rt, 12 h, 94−98%.

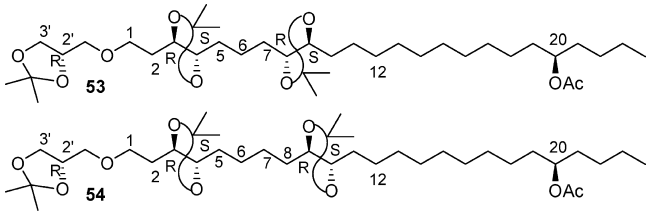
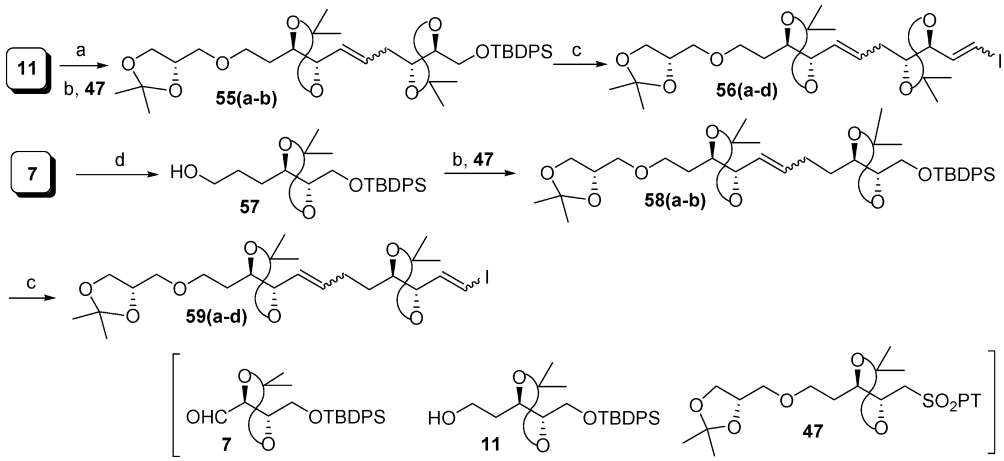


Figure 4. Positional isomers of compound **43**.

separate epoxide opening reactions with 1-hexyne and 1-heptyne to afford compounds **68a** and **68b**, respectively. Finally, both alkynes **68a** and **68b** were transformed to alkynes **70a** and **70b**, respectively, via the intermediate alkynes **69a** and **69b**, respectively, following the same chemistry as followed in the synthesis of alkyne **5**.

The final steps of the construction of compounds **65** and **66** are outlined in Scheme 14. The mixture of intermediates **49**(**a**−**d**) (Scheme 9) was coupled separately with alkynes **70a** and **70b**, respectively, following Sonogashira conditions[11] to achieve compounds **71**(**a**−**d**) and **72**(**a**−**d**), respectively, in good yields. Both these mixture of products were finally hydrogenated to get single saturated compounds **65** and **66**, respectively. The ^1H

Scheme 10. Synthesis of the Advanced Stage of Intermediates for Compounds 53 and 54[a]



[a]Reagents and conditions: (a) IBX, EtOAc, reflux, 2 h, quantitative; (b) **47**, NaHMDS, THF, −78 °C to rt, 1.5 h, 68−69%; (c) (i) TBAF, THF, 0 °C to rt, 30 min, 97−98%; (ii) IBX, EtOAc, reflux, 2 h, quantitative; (iii) $Ph_3PCH_2I_2$, NaHMDS, −78 °C to rt, 4 h, 74−76%; (d) (i) $Ph_3P{=}CHCO_2Et$, CH_2Cl_2, rt, 12 h, 98% (ii) $LiBH_4$, THF, 0 °C to rt, 12 h, 97%.

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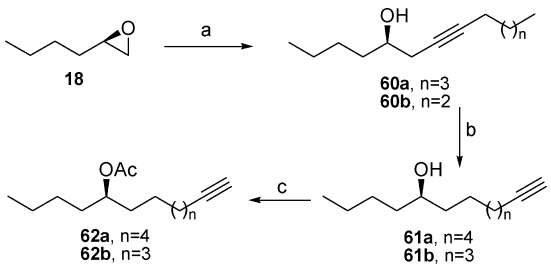
Scheme 11. Synthesis of Alkyne Intermediates for Compounds 53 and 54[a]



[a]Reagents and conditions: (a) 1-heptyne or 1-hexyne, ^{n}BuLi, BF_3·OEt_2, THF, −78 to 0 °C, 30 min; then, −78 °C, 1.5 h, 84−86%; (b) KO^{t}Bu, ^{n}BuLi, 1,3-diaminopropane, THF, 0 °C to rt, 3 h, 72−76%; (c) Ac_2O, pyridine, 0 °C to rt, 30 min, 98−99%.

and ^{13}C NMR spectra of both of these compounds were recorded, and it was observed that the ^{1}H NMR data of both compounds was compatible with the literature values.[1] Comparison of ^{13}C NMR data of both compounds **65** and **66** with the reported data (please see spectra and comparison Table 5 in the Supporting Information) confirmed unambiguously that compound **66** is the actual structure of the acetonide derivative of isolated mycalol reported by Fontana et al.

The final endeavor in the synthesis mycalol is depicted in Scheme 15. Prefinal compound **66** was finally subjected to AcOH:H_2O (4:1) for global deprotection of the acetonides to achieve compound **2** in very good yield. The spectral data and specific rotation [reported $[\alpha]^{20}_D$ +3.45 (*c* 0.1, MeOH); observed $[\alpha]^{22}_D$ +4.00 (*c* 0.4, MeOH)] of presently synthesized compound **2** were in good agreement with those[1] reported for the isolated natural product (for comparison of ^{1}H and ^{13}C NMR between isolated mycalol and synthetic mycalol, please see Table 6 in the Supporting Information), which unambiguously confirms the asymmetric total synthesis of isolated mycalol. While we engaged in resolving the differences between the NMR data of mycalol and that of synthesized compound **1** (i.e., its proposed structure, by synthesizing isomers in which both chiral centers and positions of functional groups were systematically varied), Reddy and co-workers[3] used elegant NMR techniques (HMBC at 700 MHz) to resolve the same problem and have arrived at the same conclusion (i.e., that the proposed structure of mycalol varies from its actual structure in the position of the OAc group and the chirality of the C-2′ center).

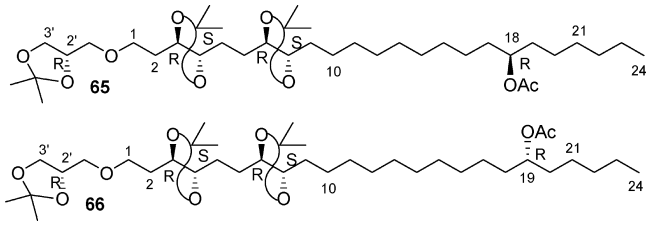
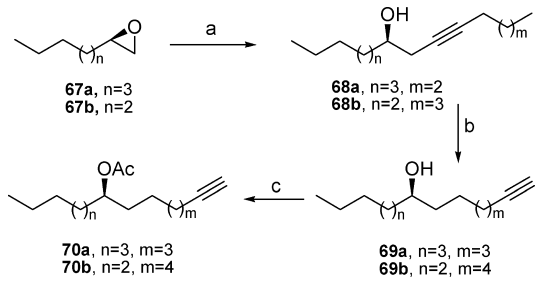


Figure 5. Other positional isomers of compound **43**.

Scheme 13. Synthesis of Alkyne Intermediates for Compounds 65 and 66[a]

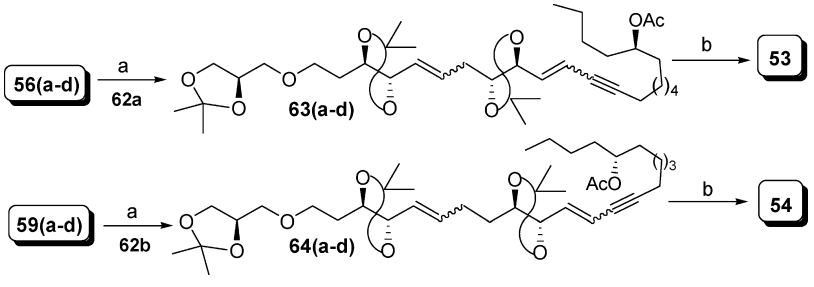


[a]Reagents and conditions: (a) 1-hexyne or 1-heptyne, ^{n}BuLi, BF_3·OEt_2, THF, −78 to 0 °C, 30 min then −78 °C, 1.5 h, 83−84%; (b) KO^{t}Bu, ^{n}BuLi, 1,3-diaminopropane, THF, 0 °C to rt, 3 h, 73−74%; (c) Ac_2O, pyridine, 0 °C to rt, 30 min, 98−99%.

CONCLUSION

In summary, we have developed a convergent and flexible synthetic strategy to accomplish the stereoselective total synthesis of biologically promising anticancer natural lipid mycalol from known precursor **9** with good overall yield [(16 linear steps with 10% for proposed structure (**1**) and 11.1% for revised/actual structure (**2**)]. Out of seven hydroxy groups, four have been installed from the chiral pool of L-arabinose. The key steps, including regioselective Wacker oxidation, Sharpless asymmetric dihydroxylation, Julia−Kocienski olefination, Wittig olefination, Zipper reaction, and Sonogashira reaction, have been employed logically to efficiently construct the complete architecture of mycalol. In our effort to resolve the differences in the NMR data of the isolated structure and the proposed synthesized structure, we have developed convenient synthetic strategies for several configurational and positional isomers of mycalol. The availability of a large number of isomers of the anticancer natural lipid mycalol (analogues) are ideally suited for developing structure−activity relationships, and their unique biological activities are currently under investigation.

Scheme 12. Synthesis of Compounds 53 and 54[a]



[a]Reagents and conditions: (a) **62a** or **62b**, Pd[$(Ph_3P)_2Cl_2$], CuI, Et_3N, rt, 4 h, 76−77%; (b) H_2, Pd/C (10%), EtOAc, rt, 12 h, 97−98%.

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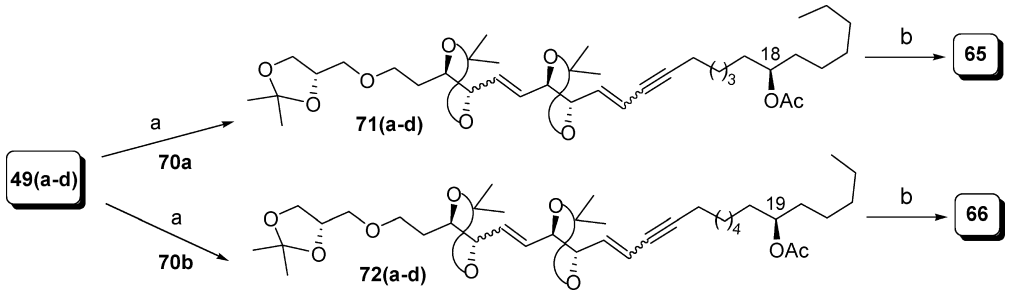
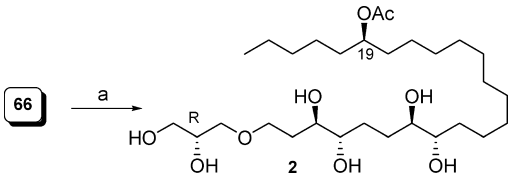
Scheme 14. Synthesis of Compounds 65 and 66[a]



[a]Reagents and conditions: (a) **70a** or **70b**, $Pd[(Ph_3P)_2Cl_2]$, CuI, Et_3N, rt, 4 h, 74−76%; (b) H_2, Pd/C (10%), EtOAc, rt, 12 h, 97−98%.

Scheme 15. Synthesis of the Revised Structure of Mycalol (2)[a]



[a]Reagents and conditions: (a) AcOH:H_2O (4:1), 0 °C to rt, 6 h, 98%.

EXPERIMENTAL SECTION

***tert*-Butyl(((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)methoxy)diphenylsilane (10).** To an ice cold solution of compound **9** (1.98 g, 12.50 mmol) in anhydrous CH_2Cl_2 (30 mL) under argon atmosphere were sequentially added imidazole (2.5 g, 37.50 mmol) and TBDPSCl (4.0 mL, 16.25 mmol). The reaction mixture was warmed to ambient temperature and stirred for another 2 h prior to quenching it with saturated aqueous NH_4Cl solution (10 mL). The resulting mixture was extracted with CH_2Cl_2 (30 mL), washed with water and brine, dried (Na_2SO_4), and concentrated under reduced pressure. Flash column chromatographic purification (SiO_2, 60−120 mesh, 2% EtOAc in hexane as eluant) of the resultant crude residue furnished pure TBDPS-protected compound **10** (4.95 g, quantitative) as a colorless liquid. R_f = 0.6 (5% EtOAc in hexane); $[\alpha]^{27}_D$ −6.5 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.65 (m, 4H), 7.43−7.35 (m, 6H), 5.99−5.88 (m, 1H), 5.36 (dt, *J* = 16.8, 1.5 Hz, 1H), 5.21 (dq, *J* = 10.2, 1.2 Hz, 1H), 4.65 (t, *J* = 6.6, 1H), 4.28 (q, $J_{1,2}$ = 6.6 Hz, 1H), 3.73−3.64 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.8, 134.8, 132.8, 128.8, 126.8, 117.2, 107.7, 77.9, 77.6, 61.9, 26.9, 25.9, 24.5, 18.4; IR (neat) ν_{max} 2931, 1215 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{32}O_3SiNa$ $[M + Na]^+$ 419.2018, found 419.2016.

2-((4*R*,5*S*)-5-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)ethanol (11). To a stirred solution of compound **10** (2 g, 5.04 mmol) in mixture of DMF (35 mL) and water (5 mL) at ambient temperature were added $PdCl_2$ (100 mg, 0.1 mmol, 10 mol %) and CuCl (740 mg, 7.47 mmol). The reaction mixture was stirred for 30 min prior to bubbling oxygen gas though it for 72 h at room temperature. The mixture was then filtered using a small pad of Celite and washed with EtOAc. The filtrate was washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo to afford the corresponding aldehyde as a yellowish liquid, which was used directly in the next reaction without further purification or characterization.

The crude aldehyde from the above step was taken in anhydrous MeOH (15 mL) under argon and cooled to 0 °C, and $NaBH_4$ (720 mg, 20.0 mmol) was cautiously added to it. The mixture was warmed slowly at room temperature and stirred for another 30 min. The reaction was then quenched with saturated aqueous NH_4Cl solution (5 mL), extracted with EtOAc (3 × 30 mL), washed with brine, dried over Na_2SO_4, and finally concentrated in vacuo. Purification of the resulting crude residue by column chromatography (SiO_2, 60−120 mesh, 20% EtOAc in hexane as eluant) afforded pure alcohol **11** (1.42 g, 68%) as a colorless oil. R_f = 0.4 (20% EtOAc in hexane); $[\alpha]^{30}_D$ +0.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68−7.61 (m, 4H), 7.47−7.35 (m, 6H), 4.41−4.35 (m, 1H), 4.26−4.19 (m,1H), 3.89−3.82 (m, 2H), 3.76−3.63 (m, 2H), 2.35 (br s, 1H), 1.93−1.86 (m, 2H), 1.37 (s, 3H), 1.33 (s, 3H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.7, 133.3, 133.2, 129.9, 127.9, 127.9, 108.3, 77.9, 62.6, 61.6, 31.6, 28.2, 26.9, 25.7, 19.3; IR (neat) ν_{max} 3446, 2929, 1112 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{34}O_4SiNa$ $[M + Na]^+$ 437.2124, found 437.2122.

(((4*S*,5*R*)-5-(2-(Allyloxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)(*tert*-butyl)diphenylsilane (12). To a stirred solution of alcohol **11** (1.5 g, 3.62 mmol) in anhydrous THF (10 mL) at 0 °C under argon was added NaH (174 mg, 60% dispersion in mineral oil, 4.34 mmol) portion wise. The reaction mixture was warmed to room temperature and stirred for 30 min. The mixture was cooled again to 0 °C, and allyl bromide (0.4 mL, 4.34 mmol) followed by TBAI (67 mg, 0.2 mmol) were added to it. The reaction mixture was warmed again to room temperature and stirred for another 1.5 h prior to quenching it with saturated aqueous NH_4Cl solution (3 mL). The resulting mixture was extracted with EtOAc (2 × 30 mL), washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the resultant crude residue by flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) provided allyl ether **12** (1.5 g, 92%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{28}_D$ +4.3 (*c* 1.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.65 (m, 4H), 7.45−7.34 (m, 6H), 5.96−5.87 (m, 1H), 5.27 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.17 (dq, *J* = 10.2, 1.8 Hz, 1H), 4.38−4.31 (m, 1H), 4.22−4.16 (m, 1H), 3.98 (dt, *J* = 2.7, 1.5 Hz, 2H), 3.77−3.56 (m, 4H), 1.99−1.96 (m, 1H), 1.86−1.81 (m, 1H), 1.37 (s, 3H), 1.33 (s, 3H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.8, 135.7, 135.1, 129.9, 127.8, 116.9, 108.0, 77.9, 74.5, 72.0, 67.6, 62.9, 29.8, 28.3, 27.0, 25.7, 19.3; IR (neat) ν_{max} 2931, 1587, 1109 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{27}H_{38}O_4SiNa$ $[M + Na]^+$ 477.2437, found 477.2439.

5-((((4*R*,5*R*)-5-(2-(Allyloxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)thio)-2-phenyl-2*H*-tetrazole (14). To a stirred solution of allyl ether **12** (1.45 g, 3.2 mmol) in anhydrous THF (10 mL) at 0 °C under argon was added TBAF (1 M in THF, 4.16 mL, 4.16 mmol). The reaction mixture was warmed to room temperature and stirred for 30 min prior to quenching it with saturated aqueous NH_4Cl solution (5 mL). The resultant mixture was extracted with EtOAc (2 × 30 mL), washed with water and brine, dried (Na_2SO_4), and concentrated under vacuum. Flash column chromatographic purification (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) of the resultant crude residue afforded the corresponding alcohol (995 mg, 98%) as a colorless oil. R_f = 0.4 (20% EtOAc in hexane); $[\alpha]^{27}_D$ −3.0 (*c* 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.95−5.82 (m, 1H), 5.26 (dq, *J* = 16.8, 1.5 Hz, 1H), 5.19 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.33−4.27 (m, 1H), 4.19−4.14 (m, 1H), 3.39 (dt, *J* = 5.7, 1.5 Hz, 2H), 3.79−3.49 (m, 4H), 2.27 (t, *J* = 5.4 Hz, 1H), 1.92−1.81 (m, 2H), 1.44 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.6, 117.4, 108.0, 78.1, 74.8, 72.2, 67.5, 61.8, 29.6, 28.3, 25.6; IR (neat) ν_{max} 3444, 2933 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{20}O_4Na$ $[M + Na]^+$ 239.1259, found 239.1256.

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To an ice cold solution of the above alcohol (650 mg, 3.0 mmol) in anhydrous THF (10 mL) under argon were sequentially added Ph_3P (870 mg, 3.3 mmol) and 1-phenyl-1*H*-tetrazole-5-thiol (**13**) (590 mg, 3.3 mmol). After stirring for 30 min at the same temperature, DIAD (0.65 mL, 3.3 mmol) was added in a dropwise manner. The mixture was warmed slowly to room temperature and stirred for 1.5 h prior to quenching it with brine (3 mL). The mixture was extracted with EtOAc (2 × 30 mL), washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Flash column chromatography (SiO_2, 100−200 mesh, 5% EtOAc in hexane as eluant) of the resultant crude residue afforded pure compound **14** (990 mg, 88%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); $[\alpha]^{30}_D$ −31.9 (*c* 0.91, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62−7.52 (m, 5H), 5.96−5.87 (m, 1H), 5.27 (dq, *J* = 16.5, 1.5 Hz, 1H), 5.18 (dq, *J* = 10.2, 1.5 Hz, 1H), 4.49−4.37 (m, 2H), 4.01 (dt, *J* = 2.7, 1.5 Hz, 2H), 3.73 (dd, *J* = 13.2, 3.0 Hz, 1H), 3.65−3.58 (m, 2H), 3.34 (dd, *J* = 12.9, 9.9 Hz, 1H), 1.97−1.88 (m, 2H), 1.45 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3, 134.8, 133.8, 130.3, 129.5, 123.9, 117.2, 108.8, 75.9, 75.2, 72.2, 67.1, 35.3, 29.9, 28.5, 25.8; IR (neat) ν_{max} 2927, 1217 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{24}N_4O_3SNa$ $[M + Na]^+$ 399.1467, found 399.1465.

5-((((4*R*,5*R*)-5-(2-((2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)thio)-2-phenyl-2*H*-tetrazole (16). AD mix-β (3.5 g, 1.4 g for 1 mmol of olefin) and $MeSO_2NH_2$ (475 mg, 5.0 mmol) were dissolved in a mixture of ^{t}BuOH (9 mL) and water (10 mL) and stirred for 30 min at room temperature. The reaction mixture was cooled to 0 °C, and compound **14** (990 mg, 2.5 mmol, dissolved in 1 mL ^{t}BuOH) was added to it. The mixture was stirred vigorously for 36 h at the same temperature and finally quenched with Na_2SO_3 (1.0 g). The resulting mixture was stirred for another 1 h and extracted with EtOAc (3 × 30 mL). The organic layer was washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo. Column chromatographic purification (SiO_2, 230−400 mesh, 50% EtOAc in hexane as eluant) of the resultant crude residue yielded the pure diols **15a** (709 mg, 69%) and **15b** (214 mg, 21%) as colorless oils.

Data for Compound 15a. R_f = 0.5 (60% EtOAc in hexane); $[\alpha]^{27}_D$ −10.3 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−7.53 (m, 5H), 4.93 (br s, 1H), 4.52−4.49 (m, 1H), 4.39−4.32 (m, 1H), 3.94−3.83 (m, 2H), 3.72−3.61 (m, 4H), 3.56−3.46 (m, 2H), 3.27−3.19 (m, 1H), 2.54 (br s, 1H), 2.04−1.95 (m, 2H), 1.44 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5, 133.7, 130.4, 130.0, 124.0, 108.6, 76.5, 75.9, 73.2, 70.7, 68.8, 64.2, 35.5, 29.5, 28.5, 25.8; IR (neat) ν_{max} 3409, 2927, 1218 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{26}N_4O_5SNa$ $[M + Na]^+$ 433.1522, found 433.1523.

Data for Compound 15b. R_f = 0.5 (60% EtOAc in hexane); $[\alpha]^{28}_D$ +4.9 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−7.52 (m, 5H), 4.53−4.45 (m, 1H), 4.38−4.31 (m, 1H), 4.00−3.79 (m, 2H), 3.74−3.58 (m, 4H), 3.55−3.47 (m, 2H), 3.27−3.19 (m, 1H), 2.00−1.92 (m, 2H), 1.43 (s, 3H), 1.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5, 133.6, 130.4, 129.9, 124.0, 108.6, 76.5, 75.9, 73.1, 70.7, 68.8, 64.1, 35.5, 29.5, 28.5, 25.7. IR (neat) ν_{max} 3421, 2920, 1216 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{26}N_4O_5SNa$ $[M + Na]^+$ 433.1522, found 433.1519.

To an ice cold solution of diol **15a** (700 mg, 1.7 mmol) in anhydrous CH_2Cl_2 (10 mL) under argon were sequentially added 2,2-DMP (0.63 mL, 5.1 mmol) and CSA (20 mg, 0.08 mmol). The reaction mixture was stirred for 1 h at room temperature prior to quenching it with Et_3N (1 mL). The mixture was concentrated and purified by flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as elutant) to obtain compound **16** (762 mg, quantitative) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); $[\alpha]^{27}_D$ −44.9 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62−7.53 (m, 5H), 4.47−4.43 (m, 1H), 4.40−4.36 (m, 1H), 4.31−4.26 (m, 1H), 4.08−4.03 (m, 1H), 3.75−3.57 (m, 4H), 3.56−3.44 (m, 2H), 3.31 (dd, *J* = 12.9, 10.2 Hz, 1H), 1.95−1.87 (m, 2H), 1.44 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 154.3, 133.8, 130.3, 129.9, 123.9, 109.6, 108.8, 75.9, 75.1, 74.8, 72.4, 68.5, 66.9, 35.3, 29.8, 28.5, 26.9, 25.8, 25.5; IR (neat) ν_{max} 2931, 1218 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{30}N_4O_5SNa$ $[M + Na]^+$ 473.1835, found 473.1837.

5-((((4*R*,5*R*)-5-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)sulfonyl)-2-phenyl-2*H*-tetrazole (8). To an ice cold solution of compound **16** (750 mg, 1.7 mmol) in EtOH (5 mL) were sequentially added $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (105 mg, 0.09 mmol) and 30% H_2O_2 (3 mL). The reaction mixture was warmed slowly to room temperature and stirred for another 1.5 h. The mixture was extracted with EtOAc (2 × 30 mL), washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. Flash column chromatography (SiO_2, 100−200 mesh, 20% EtOAc in hexane as eluant) of the resultant crude residue provided sulfone **8** (694 mg, 85%) as a colorless oil. R_f = 0.3 (30% EtOAc in hexane); $[\alpha]^{27}_D$ −66.3 (*c* 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.65−7.54 (m, 5H), 4.69−4.60 (m, 1H), 4.33 (q, $J_{1,2}$ = 6.6 Hz, 1H), 4.28−4.18 (m, 1H), 4.04−3.98 (m, 1H), 3.86−3.83 (m, 2H), 3.70−3.57 (m, 2H), 3.55−3.39 (m, 3H), 1.87−1.81 (m, 2H), 1.40 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4, 133.4, 131.5, 129.5, 126.0, 109.7, 109.4, 75.9, 74.6, 72.7, 72.7, 68.3, 66.8, 58.5, 29.8, 27.7, 26.9, 25.6, 25.4; IR (neat) ν_{max} 2926, 1219 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{30}N_4O_7SK$ $[M + K]^+$ 521.1472, found 521.1474.

(4*S*,5*S*)-5-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (7). To an ice cold solution of compound **10** (815 mg, 2.05 mmol) in a mixture of THF (3 mL), ^{t}BuOH (3 mL), and water (0.6 mL) were added OsO_4 (5% solution in ^{t}BuOH, 100 μL) and NMO (481 mg, 4.1 mmol), which was stirred for 30 min at the same temperature. $NaHCO_3$ (515 mg, 6.15 mmol) followed by $NaIO_4$ (875 mg, 4.1 mmol) was added to the mixture. The reaction mixture was warmed slowly to room temperature and stirred for another 11.5 h. The reaction mixture was then passed through a small pad of Celite and washed with EtOAc. The filtrate was washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo to give crude aldehyde **7** (740 mg, 90%) as a colorless liquid, which was taken directly to next reaction without further purification or characterization.

***tert*-Butyl(((4*S*,5*R*)-5-(2-(((*R*)-5-(2-(((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)diphenylsilane [6(a,b)].** Sulfone **8** (750 mg, 1.55 mmol) was dissolved in anhydrous THF (7 mL) under argon atmosphere and cooled to −78 °C. NaHMDS (1 M in THF, 1.6 mL, 1.6 mmol) was added and stirred for 5 min. A solution of aldehyde **7** (740 mg, 1.85 mmol, dissolved in 4 mL of THF) obtained from the previous step was cannulated into the reaction mixture and stirred for 30 min at the same temperature. The reaction mixture was warmed slowly to room temperature and stirring was continued for 1 h prior to quenching it with saturated aqueous NH_4Cl solution (3 mL). The mixture was extracted with EtOAc (2 × 30 mL), washed with water and brine, dried over Na_2SO_4, and finally concentrated in vacuo. Purification by flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) of the resultant crude residue provided an inseparable mixture of compounds **6**(**a**,**b**) (690 mg, 68%) as a colorless liquid. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.66 (m, 4H), 7.44−7.34 (m, 6H), 5.76 (q, $J_{1,2}$ = 8.4 Hz, 1H), 5.60−5.54 (m, 1H), 4.99 (t, *J* = 6.9 Hz, 1H), 4.91 (t, *J* = 7.5 Hz, 1H), 4.24−4.16 (m, 3H), 4.03−3.98 (m, 1H), 3.72−3.65 (m, 2H), 3.59−3.45 (m, 4H), 3.41−3.34 (m, 1H), 1.61−1.52 (m, 2H), 1.48−1.42 (m, 6H), 1.40 (s, 3H), 1.35−1.34 (m, 9H), 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.8 (135.8), 133.6 (133.5), 129.8, 129.6, 129.0, 127.8, 109.5, 108.9, 108.6, 79.2, 75.4 (75.3), 74.9 (74.8), 74.2, 73.4, 72.3 (72.2), 68.6 (68.6), 67.1, 63.5, 31.1, 29.8, 28.5, 27.9, 27.0 (26.9), 25.9, 25.6 (25.5), 19.4; IR (neat) ν_{max} 2931, 1215 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{37}H_{54}O_8SiNa$ $[M + Na]^+$ 677.3486, found 677.3488.

((4*S*,5*R*)-5-(2-((*R*)-5-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methanol [17(a,b)]. The inseparable mixture of compounds **6**(**a**,**b**) (450 mg, 0.68 mmol) was dissolved in anhydrous THF (4 mL) under argon and cooled to 0 °C. Then, TBAF (1 M in THF, 0.9 mL, 0.9 mmol) was added. The reaction was warmed to room temperature and stirred for another 30 min prior to

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quenching it with saturated aqueous NH_4Cl solution (3 mL). The resulting mixture was extracted with EtOAc (2 × 25 mL), washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo. Flash column chromatographic purification (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) of the resultant crude residue gave a mixture of alcohols **17**(**a**,**b**) (280 mg, 97%) as a colorless oil. R_f = 0.4 (40% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.72−5.61 (m, 2H), 5.06−5.00 (m, 1H), 4.95−4.91 (m, 1H), 4.30−4.18 (m, 3H), 4.07−4.02 (m, 1H), 3.76−3.69 (m, 1H), 3.67−3.52 (m, 4H), 3.51−3.41 (m, 2H), 2.29 (br s, 1H), 1.71−1.64 (m, 2H), 1.51 (s, 3H), 1.47 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H), 1.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 129.8 (129.7), 128.9 (128.9), 109.7, 109.1, 108.8, 78.9 (78.8), 75.5, 74.9 (74.8), 74.3, 73.4, 72.4 (72.0), 68.4, 66.8, 61.9, 31.3, 28.4, 28.1, 26.9 (26.9), 25.8, 25.5 (25.4); IR (neat) ν_{max} 3473, 2985, 1217 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{36}O_8Na$ $[M + Na]^+$ 439.2308, found 439.2306.

(*R*)-4-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)-ethyl)-5-(2-((4*R*,5*S*)-5-(2-iodovinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-2,2-dimethyl-1,3-dioxolane [4(a−d)]. To a stirred solution of alcohols **17**(**a**,**b**) (110 mg, 0.26 mmol) in EtOAc (3 mL) under argon was added IBX (110 mg, 0.4 mmol), which was then refluxed for 2 h. The reaction mixture was then cooled to room temperature, filtered through a small pad of Celite, and washed with EtOAc. The filtrate was concentrated in vacuo to afford the corresponding aldehyde as a yellowish liquid, which was used directly in the next reaction without further characterization.

To a suspension of $Ph_3PCH_2I_2$ [(iodomethyl)-triphenylphosphonium iodide] (420 mg, 0.8 mmol) in anhydrous THF (5 mL) at 0 °C under argon atmosphere was added NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) dropwise and stirred for 30 min at the same temperature. The resulting dark red solution was cooled to −78 °C, and the aldehyde from the above step (dissolved in anhydrous 3 mL of THF) was cannulated into it. After 30 min of stirring at −78 °C, the reaction mixture was warmed to room temperature and stirred for another 3 h. The reaction mixture was quenched with saturated aqueous NH_4Cl solution (3 mL) and extracted with EtOAc (2 × 25 mL), washed with water and brine, dried (Na_2SO_4), and concentrated in vacuo. Flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) of the resultant crude residue afforded an inseparable mixture of vinyl iodides **4**(**a**−**d**) (100 mg, 73%) as a colorless liquid. R_f = 0.5 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.51−6.47 (m, 1H), 6.29−6.24 (m, 1H), 5.64−5.53 (m, 2H), 5.07 (t, J = 6.9 Hz, 1H), 4.94−4.83 (m, 2H), 4.29−4.22 (m, 2H), 4.05 (q, $J_{1,2}$ = 6.3 Hz, 1H), 3.73−3.68 (m, 1H), 3.61−3.50 (m, 3H), 3.46−3.42 (m, 1H), 1.68−1.61 (m, 2H), 1.51 (s, 3H), 1.46 (s, 3H), 1.42−1.41 (m, 6H), 1.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 137.4, 137.3, 129.9, 129.1 (129.1), 109.8, 109.6 (109.5), 108.8, 85.8 (85.7), 81.4 (81.4), 75.7 (75.6), 74.9 (74.8), 73.9 (73.8), 72.3 (72.2), 68.8 (68.7), 67.0, 31.3, 29.8, 28.5, 28.2, 26.9, 25.9, 25.7, 25.6; IR (neat) ν_{max} 2924, 1217 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{35}IO_7Na$ $[M + Na]^+$ 561.1325, found 561.1323.

(*R*)-Tetradec-7-yn-5-ol (19). To a solution 1-octyne (0.75 mL, 5.0 mmol) in anhydrous THF (10 mL) at −78 °C under argon was added ^{n}BuLi (3 mL, 4.8 mmol, 1.6 M in hexane). The resulting mixture was stirred for 30 min at this temperature and then warmed slowly to 0 °C and stirred for another 1 h at the same temperature. The reaction was again cooled to −78 °C, and a solution of epoxide **18** (450 mg, 4.5 mmol, dissolved in 5 mL of anhydrous THF) followed by $BF_3{\cdot}Et_2O$ (freshly distilled, 0.6 mL, 4.8 mmol) were added to it. The reaction was quenched by saturated aqueous NH_4Cl solution (5 mL) and extracted with Et_2O (3 × 10 mL), washed with water and brine, dried (Na_2SO_4), and concentrated under vacuum. Flash column chromatographic purification (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) of the resultant crude residue provided pure alcohol **19** (785 mg, 83%) as a colorless liquid. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{28}_D$ −4.2 (c 1.38, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.67−3.66 (m, 1H), 2.41−2.36 (m, 1H), 2.28−2.23 (m, 1H), 2.17−2.14 (m, 2H), 1.99 (s,1H), 1.52−1.41 (m, 4H), 1.39−1.23 (m, 10H), 0.91−0.87 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 83.4, 76.2, 70.4, 36.1, 31.5, 29.1, 28.7, 27.9, 27.9, 22.8, 22.7, 18.9, 14.1, 14.1; IR (neat) ν_{max} 3373, 2929 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{27}O$ $[M + H]^+$ 211.2062, found 211.2054.

(*R*)-Tetradec-13-yn-5-ol (20). To a stirred solution of 1,3-diaminopropane (0.88 mL, 10.7 mmol) in anhydrous THF (7 mL) at 0 °C under argon was added ^{n}BuLi (5.34 mL, 8.56 mmol, 1.6 M in hexane). The resulting mixture was stirred for 30 min at the same temperature prior to the addition of ^{t}BuOK (960 mg, 8.56 mmol) in a portion wise manner. The resulting yellow solution was then warmed to room temperature and stirred for 30 min. The reaction mixture was cooled again to 0 °C, and the alcohol **19** (450 mg, 2.14 mmol, dissolved in 3 mL of anhydrous THF) was cannulated into it. The resulting red-brown color solution was slowly warmed to room temperature and stirred for another 2.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution (5 mL). The mixture was extracted with EtOAc (30 mL), washed with 5% HCl, saturated aqueous $NaHCO_3$ solution, water, and brine, dried (Na_2SO_4), and concentrated in vacuo. Purification by column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) of the resultant crude residue afforded alcohol **20** (330 mg, 73% yield) as a colorless liquid. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{27}_D$ −2.2 (c 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59−3.58 (m, 1H), 2.21−2.15 (m, 2H), 1.94 (t, J = 2.4 Hz, 1H), 1.55−1.26 (m, 18H), 0.91 (t, J = 1.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 84.8, 72.1, 68.2, 37.5, 37.3, 29.7, 29.2, 28.8, 28.6, 27.9, 25.7, 22.9, 18.5, 14.2; IR (neat) ν_{max} 3311, 2929, 2117 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{27}O$ $[M + H]^+$ 211.2062, found 211.2031.

(*R*)-Tetradec-13-yn-5-yl Acetate (5). To a solution of alcohol **20** (250 mg, 1.18 mmol) in anhydrous pyridine (2 mL) at 0 °C under argon was added Ac_2O (0.22 mL, 2.36 mmol). The reaction mixture was warmed slowly to room temperature and stirred for another 30 min. Pyridine was removed under reduced pressure. Purification by flash column chromatography (SiO_2, 60−120 mesh, 2% EtOAc in hexane as eluant) of the resultant crude residue afforded alkyne **5** as a colorless liquid (300 mg, quantitative). R_f = 0.9 (5% EtOAc in hexane); $[\alpha]^{28}_D$ +2.2 (c 1.95, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.87−4.82 (m, 1H), 2.18−2.15 (m, 2H), 2.02 (s, 3H), 1.92 (t, J = 2.5 Hz, 1H), 1.53−1.48 (m, 6H), 1.38−1.23 (m, 12H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 84.8, 74.5, 68.2, 34.2, 33.9, 29.5, 29.1, 28.8, 28.5, 27.6, 25.4, 22.7, 21.4, 18.5, 14.1; IR (neat) ν_{max} 3309, 2935, 2117, 1733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{28}O_2Na$ $[M + Na]^+$ 275.1987, found 275.1989.

16-((4*S*,5*R*)-5-(2-((*R*)-5-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadec-15-en-13-yn-5-yl Acetate [3(a−d)]. To a freshly dried and degassed Et_3N (1 mL) solution of vinyl iodides **4**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **5** (28 mg, 0.11 mmol) under argon at ambient temperature were successively added CuI (4 mg, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol). The resulting orange color suspension was stirred for another 4 h at the same temperature. Et_3N was removed under vacuo, and the resultant crude residue was purified by column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) to afford compounds **3**(**a**−**d**) as a colorless liquid (45 mg, 76%). R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.78−5.72 (m, 1H), 5.64−5.56 (m, 3H), 5.15 (q, $J_{1,2}$ = 6.6 Hz, 1H), 5.02 (t, J = 6.3 Hz, 1H), 4.91−4.81 (m, 2H), 4.29−4.18 (m, 2H), 4.05 (q, $J_{1,2}$ = 6.3 Hz, 1H), 3.75−3.69 (m, 1H), 3.63−3.49 (m, 3H), 3.45−3.40 (m, 1H), 2.35−2.29 (m, 2H), 2.03 (s, 3H), 1.67−1.61 (m, 2H), 1.54−1.46 (m, 10H), 1.41−1.34 (m, 14H), 1.28−1.22 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 136.7, 130.1, 129.2, 113.8, 109.5, 109.4, 108.6, 75.8, 75.7, 74.8, 74.8, 74.5, 73.8, 72.3, 67.1, 34.3, 33.9, 31.2, 29.8, 29.6, 29.2, 29.1, 28.9, 28.5, 28.3, 27.6, 26.9, 25.9, 25.7, 25.5, 25.5, 22.7, 21.4, 19.7, 14.1; IR (neat) ν_{max} 2929, 2217, 1732 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4290.

16-((4*S*,5*R*)-5-(2-((4*S*,5*R*)-5-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-5-yl Acetate (21).

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To a stirred solution of compounds **3**(**a**−**d**) (25 mg, 0.037 mmol) in EtOAc (1 mL) was added 10% Pd/C (4 mg) using a hydrogen balloon at room temperature and stirred for 12 h. The reaction mixture was filtered using a short pad of Celite and washed with EtOAc. The organic layers were concentrated in vacuum and purified by flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) to obtain pure saturated compound **21** (24 mg, 98%) as a colorless liquid. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{27}_D$ +3.2 (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.89−4.81 (m, 1H), 4.30−4.18 (m, 2H), 4.13−4.02 (m, 3H), 3.75−3.41 (m, 6H), 2.03 (s, 3H), 1.78−1.69 (m, 2H), 1.67−1.63 (m, 4H), 1.54−1.49 (m, 6H), 1.42 (s, 8H), 1.37−1.25 (m, 32H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 171.1, 109.6, 107.8, 107.5, 78.5, 78.4, 78.2, 74.9, 74.9, 74.6, 72.3, 68.8, 67.0, 34.3, 33.9, 30.3, 29.8, 29.7, 29.1, 28.7, 27.6, 27.3, 26.9, 26.5, 26.1, 261, 25.5, 25.5, 22.7, 21.4, 14.1; IR (neat) ν_{max} 2927, 1731 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4915.

(5*R*,17*S*,18*R*,21*S*,22*R*)-24-((*S*)-2,3-Dihydroxypropoxy)-17,18,21,22-tetrahydroxytetracosan-5-yl Acetate (1). Compound **21** (10 mg, 0.015 mmol) was dissolved in an AcOH:H_2O (4:1, 0.5 mL) mixture at 0 °C. The reaction mixture was warmed to room temperature and stirred for another 6 h. The mixture of AcOH and H_2O was removed under vacuum and purified by flash column chromatography (SiO_2, 60−120 mesh, 5% MeOH in CH_2Cl_2 as eluant) to afford pure compound **1** (8 mg, 97%) as a colorless liquid. R_f = 0.5 (10% MeOH in CH_2Cl_2); $[\alpha]^{21}_D$ +2.8 (*c* 0.44, MeOH); ^{1}H NMR (C_5D_5N, 300 MHz) δ 5.13−5.05 (m, 1H, merged in water peak, confirmed by HSQC NMR study), 4.40−4.33 (m, 1H), 4.23−4.17 (m, 1H), 4.15−4.04 (m, 3H), 4.02−3.98 (m, 3H), 3.95−3.83 (m, 3H), 2.59 (br d, *J* = 9.3 Hz, 2H), 2.43−2.29 (m, 2H), 2.18−2.09 (m, 5H), 2.02−1.95 (m, 1H), 1.88−1.85 (m, 2H), 1.61−1.53 (m, 5H), 1.32−1.22 (m, 20H), 0.83 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (C_5D_5N, 100 MHz) δ 170.7, 75.9, 75.3, 74.3, 73.7, 72.9, 71.9, 69.7, 64.7, 34.5, 34.2, 33.6, 30.6, 30.4, 30.3, 30.1, 29.9, 29.9, 29.9, 29.8, 27.8, 26.8, 25.7, 22.8, 21.1, 14.1; IR (neat) ν_{max} 3365, 2925, 1737 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{29}H_{58}O_9Na$ $[M + Na]^+$ 573.3979, found 573.3975.

***tert*-Butyl(((4*R*,5*S*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)-methoxy)diphenylsilane (26).** Following the same synthetic procedure used for compound **10**, alcohol **25** (4.0 g, 25.25 mmol) was converted to compound **26** using TBDPSCl (8.0 mL, 32.50 mmol) and imidazole (5.0 g, 75.0 mmol) in CH_2Cl_2 (60 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 2% EtOAc in hexane as eluant) afforded compound **26** (9.95 g, quantitative) as a colorless oil. R_f = 0.6 (5% EtOAc in hexane); $[\alpha]^{25}_D$ 8.2 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.67 (m, 4H), 7.46−7.35 (m, 6H), 6.00−5.88 (m, 1H), 5.39−5.20 (m, 2H), 4.66 (t, *J* = 6.6, 1H), 4.29 (q, $J_{1,2}$ = 6.3 Hz, 1H), 3.74−3.63 (m, 2H), 1.45 (s, 3H), 1.38 (s, 3H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.8, 134.8, 133.6 (133.5), 129.8, 127.8, 118.1, 108.7, 78.9, 78.6, 63.0, 27.9, 26.9, 25.5, 19.3; IR (neat) ν_{max} 2931, 1217 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{32}O_3SiNa$ $[M + Na]^+$ 419.2018, found 419.2014.

2-((4*S*,5*R*)-5-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)ethanol (27). Following the same synthetic procedure used for compound **11**, compound **26** (2.0 g, 5.04 mmol) was converted to compound **27** using $PdCl_2$ (100 mg, 0.1 mmol) and CuCl (740 mg, 7.47 mmol) in DMF:H_2O (7:1, 40 mL) followed by treatment of the resultant aldehyde with $NaBH_4$ (720 mg, 20.0 mmol) in MeOH (15 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 20% EtOAc in hexane as eluant) afforded compound **27** (1.45 g, 69%) as a colorless oil. R_f = 0.4 (20% EtOAc in hexane); $[\alpha]^{27}_D$ −2.3 (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68−7.65 (m, 4H), 7.46−7.36 (m, 6H), 4.41−4.36 (m, 1H), 4.26−4.21 (m,1H), 3.85−3.80 (m, 2H), 3.79−3.64 (m, 2H), 2.40 (br s, 1H), 1.93−1.87 (m, 2H), 1.37 (s, 3H), 1.34 (s, 3H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.7, 133.3, 133.2, 130.1, 129.9, 127.9, 127.9, 108.3, 77.8, 77.0, 62.6, 31.6, 28.2, 26.9, 25.6, 19.3; IR (neat) ν_{max} 3445, 2930, 1113 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{34}O_4SiNa$ $[M + Na]^+$ 437.2124, found 437.2120.

(((4*R*,5*S*)-5-(2-(Allyloxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)(*tert*-butyl)diphenylsilane (28). Following the same synthetic procedure used for compound **12**, compound **27** (1.5 g, 3.62 mmol) was converted to compound **28** using allyl bromide (0.4 mL, 4.34 mmol), NaH (174 mg, 4.34 mmol, 60% absorbed in oil), and TBAI (67 mg, 0.2 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **28** (1.48 g, 91%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{26}_D$ −2.0 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68−7.66 (m, 4H), 7.45−7.36 (m, 6H), 5.95−5.87 (m, 1H), 5.27 (dd, *J* = 12.9, 1.2 Hz, 1H), 5.17 (dd, *J* = 7.8, 0.6 Hz, 1H), 4.37−4.32 (m, 1H), 4.22−4.17 (m, 1H), 3.97 (t, *J* = 4.2 Hz, 2H), 3.77−3.54 (m, 4H), 2.01−1.97 (m, 1H), 1.85−1.79 (m, 1H), 1.37 (s, 3H), 1.33 (s, 3H), 1.06 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.8, 135.7, 135.1, 129.8, 127.8, 116.8, 108.0, 77.9, 74.5, 72.0, 67.6, 62.9, 29.8, 28.3, 27.2, 25.7, 19.3; IR (neat) ν_{max} 2930, 1587, 1110 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{27}H_{38}O_4SiNa$ $[M + Na]^+$ 477.2437, found 477.2436.

5-((((4*S*,5*S*)-5-(2-(Allyloxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)thio)-1-phenyl-1*H*-tetrazole (29). Following the same synthetic procedure used for compound **14**, compound **28** (1.5 g, 3.3 mmol) was converted to corresponding TBDPS deprotected alcohol using TBAF (1 M in THF, 4.0 mL, 3.95 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded a corresponding alcohol (692 mg, 97%) as a colorless oil. R_f = 0.4 (20% EtOAc in hexane); $[\alpha]^{28}_D$ +1.9 (*c* 1.1, $CHCl_3$); ^{1}NMR ($CDCl_3$, 300 MHz) δ 5.92−5.79 (m, 1H), 5.26 (dq, *J* = 16.8, 1.5 Hz, 1H), 5.19 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.29−4.23 (m, 1H), 4.17−4.11 (m, 1H), 3.94 (dt, *J* = 5.1, 1.5 Hz, 2H), 3.64−3.49 (m, 4H), 1.85−1.78 (m, 2H), 1.41 (s, 3H), 1.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 134.6, 117.2, 107.9, 78.0, 74.6, 72.1, 67.4, 61.6, 29.5, 28.2, 25.6; IR (neat) ν_{max} 3443, 2930 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{11}H_{20}O_4Na$ $[M + Na]^+$ 239.1259, found 239.1258.

This alcohol (650 mg, 3.0 mmol) was converted to compound **29** using compound **13** (641 mg, 3.6 mmol), DIAD (0.7 mL, 3.6 mmol), and Ph_3P (944 mg, 3.6 mmol) in THF (15 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 5% EtOAc in hexane as eluant) afforded compound **29** (1.04 g, 88%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); $[\alpha]^{25}_D$ +27.2 (*c* 1.3, $CHCl_3$); ^{1}NMR ($CDCl_3$, 300 MHz) δ 7.59−7.54 (m, 5H), 5.96−5.85 (m, 1H), 5.27 (dq, *J* = 16.5, 1.5 Hz, 1H), 5.18 (dd, *J* = 10.2, 1.5 Hz, 1H), 4.50−4.36 (m, 2H), 4.01 (dt, *J* = 2.7, 1.5 Hz, 2H), 3.73 (dd, *J* = 13.2, 3.0 Hz, 1H), 3.66−3.55 (m, 2H), 3.33 (dd, *J* = 12.9, 9.9 Hz, 1H), 1.97−1.88 (m, 2H), 1.45 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4, 134.8, 130.3, 129.9, 123.9, 117.2, 108.8, 75.9, 75.3, 72.2, 67.1, 35.3, 29.9, 28.5, 25.8; IR (neat) ν_{max} 2928, 1215 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{24}N_4O_3SNa$ $[M + Na]^+$ 399.1467, found 399.1466.

5-((((4*S*,5*S*)-5-(2-(((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)thio)-2-phenyl-2*H*-tetrazole (31). Following the same synthetic procedure used for compounds **15a** and **15b**, compound **29** (1.0 g, 2.55 mmol) was converted to compounds **30a** and **30b** using AD-mix-β (3.6 g, 1.4 g for 1 mmol of olefin) $MeSO_2NH_2$ (485 mg, 5.1 mmol) in ^{t}BuOH:H_2O (1:1, 20 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 50% EtOAc in hexane as eluant) afforded compounds **30a** (723 mg, 69%) and **30b** (219 mg, 21%) as a colorless oil.

Data for Compound 30a. R_f = 0.5 (60% EtOAc in hexane); $[\alpha]^{27}_D$ +3.2 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−7.54 (m, 5H), 4.55−4.67 (m, 1H), 4.39−4.32 (m, 1H), 3.96−3.81 (m, 2H), 3.72−3.64 (m, 4H), 3.57−3.54 (m, 2H), 3.23−3.17 (m, 1H), 2.00−1.98 (m, 2H), 1.44 (S, 3H), 1.35 (S, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4, 133.7, 130.4, 129.9, 124.0, 108.6, 76.5, 75.7, 73.1, 70.8, 68.8, 64.2, 35.5, 29.4, 28.5, 25.8; IR (neat) ν_{max} 3413, 2928, 1213 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{18}H_{26}N_4O_5SNa$ $[M + Na]^+$ 433.1522, found 433.1515.

Data for Compound 30b. R_f = 0.5 (60% EtOAc in hexane); $[\alpha]^{29}_D$ −15.6 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61−

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7.54 (m, 5H), 4.55−4.47 (m, 1H), 4.39−4.32 (m, 2H), 3.70−3.63 (m, 4H), 3.57−3.54 (m, 2H), 3.27−3.17 (m, 1H), 2.01−1.92 (m, 2H), 1.44 (s, 3H), 1.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.4, 133.7, 130.4, 129.9, 124.0, 108.6, 76.5, 75.9, 73.2, 70.6, 68.8, 64.2, 35.5, 29.5, 28.5, 25.8; IR (neat) ν_{max} 3410, 2926, 1209 cm^{-1}; HRMS (ESI) m/z calcd for $C_{18}H_{26}N_4O_5SNa$ $[M + Na]^+$ 433.1522, found 433.1521.

Following the same synthetic procedure used for compound **16**, compound **30a** (700 mg, 1.7 mmol) was converted to compound **31** using 2,2-DMP (0.63 mL, 5.1 mmol) and CSA (20 mg, 0.09 mmol) in CH_2Cl_2 (7 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **31** (762 mg, quantitative) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); $[\alpha]^{28}_D$ +43.2 (*c* 7.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58−7.49 (m, 1H), 4.46−4.39 (m, 1H), 4.36−4.29 (m, 1H), 4.27−4.23 (m, 1H), 4.05−3.99 (m, 1H), 3.72−3.64 (m, 4H), 3.63−3.41 (m, 2H), 3.29 (dd, J = 12.9, 10.2 Hz, 1H), 1.94−1.83 (m, 2H), 1.41 (s, 3H), 1.38 (s, 3H), 1.31−1.30 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 133.6, 130.2, 129.8, 123.8, 109.4, 108.6, 75.8, 75.1, 74.7, 72.2, 68.4, 66.8, 35.1, 29.6, 28.3, 26.8, 25.7, 25.4; IR (neat) ν_{max} 2932, 1218 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{30}N_4O_5SNa$ $[M + Na]^+$ 473.1835, found 473.1840.

5-((((4*S*,5*S*)-5-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-sulfonyl)-2-phenyl-2*H*-tetrazole (32). Following the same synthetic procedure used for sulfone **8**, compound **31** (500 mg, 1.1 mmol) was converted to sulfone **32** using $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (69 mg, 0.05 mmol) and 30% aqueous H_2O_2 (3 mL) in EtOH (5 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 20% EtOAc in hexane as eluant) afforded sulfone **32** (449 mg, 85%) as a colorless oil. R_f = 0.3 (30% EtOAc in hexane); $[\alpha]^{28}_D$ −2.4 (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.61−7.55 (m, 5H), 4.66−4.57 (m, 1H), 4.31 (q, J = 6.6 Hz, 1H), 4.24−4.16 (m, 1H), 4.02−3.96 (m, 1H), 3.84−3.81 (m, 2H), 3.68−3.58 (m, 2H), 3.55−3.47 (m, 1H), 3.45−3.39 (m, 2H), 1.85−1.79 (m, 2H), 1.37 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H), 1.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 133.3, 131.4, 129.4, 125.9, 109.5, 109.3, 75.9, 72.6, 72.4, 68.3, 66.7, 58.4, 29.7, 27.6, 26.9, 25.6, 25.3; IR (neat) ν_{max} 2926, 1210 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{30}N_4O_7SNa$ $[M + Na]^+$ 505.1733, found 505.1712.

***tert*-Butyl(((*R*)-5-(2-((4*S*,5*R*)-5-(2-(((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)diphenylsilane [34(a,b)].** Following the same synthetic procedure used for aldehyde **7**, compound **26** (396 mg, 1.0 mmol) was converted to aldehyde **33** (362 mg) using OsO_4 (5% solution in ^{t}BuOH, 50 μL), NMO (234 mg, 1.8 mmol), $NaIO_4$ (464 mg, 1.8 mmol), and $NaHCO_3$ (252 mg, 2.7 mmol) in ^{t}BuOH:THF:H_2O (5:5:1, 3.5 mL). The aldehyde was filtered through a silica gel column and taken for the next reaction without further characterization.

Following the same synthetic procedure used for compounds **6**(**a**,**b**), aldehyde **33** (362 mg, 0.92 mmol) and sulfone **8** (375 mg, 0.77 mmol) reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (4 mL) to obtain compounds **34**(**a**,**b**). Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded compounds **34**(**a**,**b**) (350 mg, 69%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68−7.65 (m, 4H), 7.42−7.37 (m, 6H), 5.94−5.87 (m, 1H), 5.78−5.71 (m, 1H), 4.68 (t, J = 6.3 Hz, 1H), 4.53 (t, J = 6.6 Hz, 1H), 4.27−4.21 (m, 3H), 4.06−4.01 (m, 1H), 3.73−3.66 (m, 2H), 3.64−3.58 (m, 1H), 3.54−3.47 (m, 3H), 3.42−3.37 (m, 1H), 1.65−1.63 (m, 2H), 1.44−1.42 (m, 9H), 1.36−1.33 (m, 9H), 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.8, 133.5 (133.4), 129.9 (129.8), 129.3, 129.0, 127.8, 109.6, 108.8, 108.4, 78.6, 78.4, 75.2, 75.1, 74.8, 72.3, 68.6, 67.0, 63.2, 31.2, 28.4, 27.8, 26.9, 25.8, 25.5 (25.5), 19.3; IR (neat) ν_{max} 2928, 1208 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{54}O_8SiNa$ $[M + Na]^+$ 677.3486, found 677.3496.

(4*R*,5*S*)-4-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)-ethyl)-5-(2-((*R*)-5-(2-iodovinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-vinyl)-2,2-dimethyl-1,3-dioxolane [35(a−d)]. Following the same synthetic procedure used for compounds **17**(**a**,**b**), the mixture of compounds **34**(**a**,**b**) (225 mg, 0.34 mmol) was converted to the corresponding alcohols using TBAF (1 M in THF, 0.5 mL, 0.5 mmol) in THF (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (140 mg, 97%) as a colorless oil. R_f = 0.4 (40% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.75−5.73 (m, 2H), 4.67−4.63 (m, 1H), 4.56−4.52 (m, 1H), 4.29−4.19 (m, 3H), 4.05−4.00 (m, 1H), 3.71−3.66 (m, 1H), 3.62−3.38 (m, 6H), 2.26 (s, 1H), 1.68 (q, $J_{1,2}$ = 6.0 Hz, 2H), 1.47 (s, 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.36−1.33 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 130.3 (130.2), 128.6 (128.5), 109.6 (109.5), 108.9, 108.4, 78.4, 75.3 (75.2), 74.8 (74.7), 72.2, 68.6, 66.8 (66.7), 62.1, 30.9, 29.8, 28.3, 27.9, 26.8, 25.7, 25.5 (25.4); IR (neat) ν_{max} 3476, 2970, 1219 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{36}O_8Na$ $[M + Na]^+$ 439.2308, found 439.2300.

Following the same synthetic procedure used for compounds **4**(**a**−**d**), the alcohols from the above step (100 mg, 0.23 mmol) were transformed to the corresponding aldehydes using IBX (110 mg, 0.4 mmol) in EtOAc (3 mL), which were further reacted with $Ph_3PCH_2I_2$ (420 mg, 0.8 mmol) in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (5 mL) to obtain compounds **35**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **35**(**a**−**d**) (95 mg, 69%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.46 (dd, J = 7.8, 1.2 Hz, 1H), 6.29 (t, J = 7.5 Hz, 1H), 5.77−5.69 (m, 1H), 5.66−5.56 (m, 1H), 4.89−4.85 (m, 1H), 4.79−4.75 (m, 1H), 4.54−4.49 (m, 1H), 4.31−4.24 (m, 2H), 4.05 (dd, J = 8.4, 6.3 Hz, 1H), 3.75−3.68 (m, 1H), 3.63−3.49 (m, 3H), 3.47−3.40 (m, 1H), 1.70−1.66 (m, 2H), 1.51 (s, 3H), 1.46 (s, 3H), 1.42−1.38 (m, 6H), 1.36−1.35 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.1, 130.1, 129.0, 109.6, 108.5, 84.9, 81.2, 78.5, 77.9, 75.2, 74.9, 72.3, 68.6, 66.9, 31.0, 28.4, 28.0, 26.9, 25.8, 25.6, 25.5; IR (neat) ν_{max} 2924, 1219 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{35}IO_7Na$ $[M + Na]^+$ 561.1325, found 561.1309.

***tert*-Butyl(((*S*)-5-(2-((4*R*,5*S*)-5-(2-(((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)diphenylsilane [36(a,b)].** Following the same synthetic procedure used for compounds **6**(**a**,**b**), aldehyde **7** (362 mg, 0.92 mmol) and sulfone **32** (375 mg, 0.77 mmol) reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (4 mL) to obtain compounds **36**(**a**,**b**). Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded compounds **36**(**a**,**b**) (350 mg, 68%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.66 (m, 4H), 7.44−7.34 (m, 6H), 5.77 (dd, J = 11.5, 8.4 Hz, 1H), 5.61−5.54 (m, 1H), 4.99 (t, J = 6.9 Hz, 1H), 4.26−4.17 (m, 3H), 4.04−3.98 (m, 1H), 3.73−3.66 (m, 2H), 3.60−3.45 (m, 4H), 3.41−3.37 (m, 1H), 1.61−1.56 (m, 2H), 1.46−1.45 (m, 6H), 1.41 (s, 3H), 1.36−1.34 (m, 9H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.7 (135.7), 133.4 (133.4), 129.8, 129.5, 128.9, 127.8, 109.5, 108.9, 108.5, 79.1, 75.3 (75.2), 74.8 (74.7), 74.1, 73.8, 72.2 (72.1), 68.5 (68.5), 66.9, 63.4, 31.0, 28.5, 27.8, 26.9 (26.9), 25.8, 25.5, 19.3; IR (neat) ν_{max} 2935, 1219 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{54}O_8SiNa$ $[M + Na]^+$ 677.3486, found 677.3478

(4*S*,5*R*)-4-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)-ethyl)-5-(2-((*S*)-5-(2-iodovinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-vinyl)-2,2-dimethyl-1,3-dioxolane [37(a−d)]. Following the same synthetic procedure used for compounds **17**(**a**,**b**), the mixture of compounds **36**(**a**,**b**) (250 mg, 0.34 mmol) was converted to the corresponding alcohols using TBAF (1 M in THF, 0.5 mL, 0.5 mmol) in THF (3 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (135 mg, 93%) as a colorless oil. R_f = 0.4 (40% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.77−5.76 (m, 2H), 4.69−4.66 (m, 1H), 4.58−4.54 (m, 1H),

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4.31−4.22 (m, 3H), 4.07−4.02 (m, 1H), 3.73−3.68 (m, 1H), 3.65−3.41 (m, 6H), 3.41 (q, J = 6.3 Hz, 2H), 1.29 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H), 1.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 130.4, 128.5, 109.7, 109.0, 108.5, 78.5, 78.5, 78.4, 75.3, 74.9, 72.3 (72.2), 68.7, 66.9 (66.8), 62.1, 30.9, 29.8, 28.3, 27.9, 26.9, 25.8, 25.5 (25.4); IR (neat) ν_{max} 3468, 2977, 1205 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{36}O_8Na$ [M + Na]$^+$ 439.2308, found 439.2301.

Following the same synthetic procedure used for compounds **4**(**a**−**d**), the alcohols from the above step (100 mg, 0.23 mmol) were transformed to the corresponding aldehydes using IBX (110 mg, 0.4 mmol) in EtOAc (3 mL) and were further reacted with $Ph_3PCH_2I_2$ (420 mg, 0.8 mmol) in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (5 mL) to obtain compounds **37**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **37**(**a**−**d**) (100 mg, 72%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.29 (t, J = 7.5 Hz, 2H), 5.77−5.57 (m, 3H), 4.90−4.85 (m, 1H), 4.79−4.72 (m, 1H), 4.59−4.49 (m, 1H), 4.33−4.24 (m, 2H), 4.07−4.03 (m, 1H), 3.75−3.69 (m, 1H), 3.67−3.47 (m, 3H), 3.45−3.42 (m, 1H), 1.72−1.64 (m, 2H), 1.51−1.49 (m, 3H), 1.46 (s, 3H), 1.42−1.41 (m, 6H), 1.36−1.35 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 138.1, 130.1, 129.0, 109.8, 109.6, 108.5, 84.3, 81.3, 78.6, 78.0, 75.2, 74.9, 74.8, 72.3, 68.7, 67.0 (67.9), 31.1, 29.8, 28.5 (28.4), 28.0, 26.9, 25.9 (25.8), 25.6; IR (neat) ν_{max} 2930, 1210 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{35}IO_7Na$ [M + Na]$^+$ 561.1325, found 561.1323.

***tert*-Butyl(((*R*)-5-(2-((4*R*,5*S*)-5-(2-(((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)vinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)diphenylsilane [38(a,b)].** Following the same synthetic procedure used for compounds **6**(**a**,**b**), aldehyde **33** (370 mg, 0.92 mmol) and sulfone **32** (375 mg, 0.77 mmol) reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (4 mL) to obtain compounds **38**(**a**,**b**). Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded compounds **38**(**a**,**b**) (360 mg, 73%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.66 (m, 4H), 7.42−7.35 (m, 6H), 5.77 (q, $J_{1,2}$ = 8.7 Hz, 1H), 5.58 (q, $J_{1,2}$ = 10.9 Hz, 1H), 4.99 (t, J = 7.5 Hz, 1H), 4.91(t, J = 7.5 Hz, 1H), 4.26−4.15 (m, 3H), 4.05−3.98 (m, 1H), 3.75−3.66 (m, 2H), 3.62−3.45 (m, 4H), 3.99−3.36 (m, 1H), 1.62−1.59 (m, 2H), 1.46−1.45 (m, 6H), 1.40 (s, 3H), 1.36−1.34 (m, 9H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.7 (135.7), 133.4 (133.4), 129.8, 129.5, 128.9, 127.8, 109.4, 108.8, 108.5, 79.1, 75.3, 74.7, 74.1, 73.3, 72.1, 68.5, 66.9, 63.4, 31.0, 28.5, 27.8, 26.9, 26.9, 25.8, 25.5, 25.5, 19.3; IR (neat) ν_{max} 2934, 1218 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{54}O_8SiNa$ [M + Na]$^+$ 677.3486, found 677.3464.

(4*S*,5*R*)-4-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)-ethyl)-5-(2-((*R*)-5-(2-iodovinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-vinyl)-2,2-dimethyl-1,3-dioxolane [39(a−d)]. Following same synthetic procedure used for compounds **17**(**a**,**b**), the mixture of compounds **38**(**a**,**b**) (250 mg, 0.34 mmol) was converted to the corresponding alcohols using TBAF (1 M in THF, 0.5 mL, 0.5 mmol) in THF (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (144 mg, 96%) as a colorless oil. R_f = 0.4 (40% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.70−5.59 (m, 2H), 5.04−4.99 (m, 1H), 4.91 (t, J = 6.9 Hz, 1H), 4.25−4.17 (m, 3H), 4.06−4.00 (m, 1H), 3.74−3.65 (m, 1H), 3.59−3.54 (m, 4H), 3.51−3.41 (m, 2H), 2.58 (s, 1H), 1.69−1.62 (m, 2H), 1.49 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H), 1.37−1.34 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 129.7, 128.9, 109.6, 109.1, 108.7, 78.8, 75.5, 74.9 (74.7), 74.2, 73.4, 71.9, 68.4, 66.9, 61.9, 31.2, 29.8, 28.4, 28.0, 26.9 (26.8), 25.7, 25.4 (25.4); IR (neat) ν_{max} 3460, 2988, 1217 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{36}O_8Na$ [M + Na]$^+$ 439.2308, found 439.2322.

Following the same synthetic procedure used for compounds **4**(**a**−**d**), the alcohols from the above step (100 mg, 0.23 mmol) were transformed to the corresponding aldehydes using IBX (110 mg, 0.4 mmol) in EtOAc (3 mL) and were further reacted with $Ph_3PCH_2I_2$ (420 mg, 0.8 mmol) in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (5 mL) to obtain compounds **39**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **39**(**a**−**d**) (98 mg, 71%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.51−6.47 (m, 1H), 6.29−6.24 (m, 1H), 5.64−5.53 (m, 2H), 5.07 (t, J = 6.9 Hz, 1H), 4.94−4.83 (m, 2H), 4.07−4.02 (m, 1H), 3.75−3.68 (m, 1H), 3.60−3.50 (m, 3H), 3.46−3.41 (m, 1H),1.64 (q, J = 6.9 Hz, 2H), 1.51 (s, 3H), 1.46 (s, 3H), 1.42−1.41 (m, 6H), 1.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 137.4, 129.9, 129.1, 109.8, 108.7, 85.7, 81.4, 75.7, 74.9 (74.8), 73.9, 73.7, 72.1, 68.8, 67.0, 31.3, 28.4, 29.8, 28.5, 26.9, 25.9, 25.7 (25.5); IR (neat) ν_{max} 2928, 1212 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{35}IO_7Na$ [M + Na]$^+$ 561.1325, found 561.1335.

(*R*)-16-((4*R*,5*S*)-5-(2-((4*S*,5*R*)-5-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-5-yl Acetate (22). Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **35**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **5** (28 mg, 0.11 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain compounds **40**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded compounds **40**(**a**−**d**) (44 mg, 75%) as a colorless liquid. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.78−5.59 (m, 4H), 5.19−5.14 (m, 1H), 4.87−4.83 (m, 1H), 4.71 (t, J = 6.0 Hz, 1H), 4.52 (t, J = 6.6 Hz, 1H), 4.29−4.23 (m, 2H), 4.05 (dd, J = 8.2, 6.6 Hz, 1H), 3.75−3.68 (m, 1H), 3.60−3.49 (m, 3H), 3.46−3.41 (m, 1H), 2.34−2.29 (m, 2H), 2.03 (s, 3H), 1.68−1.66 (m, 4H), 1.51−1.46 (m, 9H), 1.42−1.39 (m, 6H), 1.36−1.34 (m, 6H), 1.28−1.25 (m, 11H), 0.088 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 137.3, 135.4, 129.7, 129.5, 113.4, 109.6 (109.2), 108.4, 78.6 (78.5), 75.2 (75.2), 74.9, 74.8, 74.5, 72.3, 68.6, 66.9, 34.3, 33.9, 30.9, 29.8, 29.6, 29.2, 29.0, 28.8, 28.4, 28.2, 27.6, 26.9, 25.8, 25.7, 25.5, 25.5, 22.7, 21.4, 19.7, 14.1; IR (neat) ν_{max} 2927, 2223, 1730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ [M + Na]$^+$ 685.4292, found 685.4289.

Following the same synthetic procedure used for compound **21**, compounds **40**(**a**−**d**) (25 mg, 0.037 mmol) were hydrogenated to obtain compound **22** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **22** (23 mg, 94%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{27}_D$ +7.8 (c 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.89−4.81 (m, 1H), 4.28−4.18 (m, 2H), 4.11−4.03 (m, 4H), 3.75−3.69 (m, 1H), 3.66−3.51 (m, 3H), 3.48−3.41 (m, 1H), 2.03 (s, 3H), 1.78−1.72 (m, 4H), 1.52−1.48 (m, 6H), 1.42 (s, 9H), 1.36−1.33 (m, 10H), 1.29−1.25 (m, 23H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.6, 107.8, 107.6, 78.2, 74.9, 74.8, 72.3, 68.9, 66.9, 34.3, 33.9, 32.1, 30.2, 29.8, 29.8, 29.7, 28.7, 27.6, 26.9, 26.6, 26.5, 26.2, 26.1, 25.6, 25.5, 22.8, 21.4, 14.1; IR (neat) ν_{max} 2927, 1728 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ [M + Na]$^+$ 693.4918, found 693.4911.

(*R*)-16-((4*S*,5*R*)-5-(2-((4*R*,5*S*)-5-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-5-yl acetate (23). Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **37**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **5** (28 mg, 0.11 mmol) were coupled together using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain compounds **41**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded compounds **41**(**a**−**d**) (45 mg, 76%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ

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5.86−5.57 (m, 4H), 5.19−5.14 (m, 1H), 4.89−4.81 (m, 1H), 4.71 (t, J = 5.7 Hz, 1H), 4.55−4.50 (m, 1H), 4.31−4.21 (m, 2H), 4.07−4.02 (m, 1H), 3.75−3.68 (m, 1H), 3.65−3.49 (m, 3H), 3.46−3.39 (m, 1H), 2.34−2.24 (m, 2H), 2.03 (s, 3H), 1.70−1.64 (m, 2H), 1.58−1.46 (m, 15H), 1.42−1.25 (m, 33H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 137.3, 129.8, 129.4, 113.4, 109.6, 109.2, 108.4, 97.2, 78.7, 78.6, 78.5 (78.4), 77.6, 75.2, 74.9 (74.7), 74.5, 72.3, 68.7 (68.6), 67.0 (66.9), 34.3, 33.9, 30.9, 29.8, 29.6, 29.2, 29.0, 28.8, 28.4, 28.2, 27.6, 26.9, 25.8 (25.7), 25.6, 25.4, 22.7, 21.4, 19.7, 14.1; IR (neat) ν_{max} 2931, 2220, 1735 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4301.

Following the same synthetic procedure used for compound **21**, compounds **41(a−d)** (25 mg, 0.037 mmol) were hydrogenated to obtain compound **23** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **23** (23.4 mg, 96%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{28}_D$ +0.9 (c 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.89−4.81 (m, 1H), 4.30−4.18 (m, 2H), 4.13−4.02 (m, 4H), 3.75−3.69 (m, 1H), 3.65−3.51 (m, 3H), 3.47−3.41 (m, 1H), 2.03 (s, 3H), 1.78−1.63 (m, 6H), 1.54−1.47 (m, 6H), 1.42 (s, 8H), 1.37−1.25 (m, 32H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.6, 107.8, 107.6, 78.2, 77.6, 74.9, 74.8, 74.6, 72.3, 68.9, 66.9, 34.3, 33.9, 30.2, 29.8, 29.8, 29.7, 29.5, 28.7, 28.7, 27.6, 26.6, 26.2, 26.1, 25.6, 25.5, 22.8, 21.4, 14.1; IR (neat) ν_{max} 2928, 1730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4935.

(*R*)-16-((4*R*,5*S*)-5-(2-((4*R*,5*S*)-5-(2-(((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-5-yl Acetate (24). Following the same synthetic procedure used for compounds **3(a−d)**, compounds **39(a−d)** (50 mg, 0.09 mmol) and alkyne **5** (28 mg, 0.11 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain compounds **42(a−d)**. Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded compounds **42(a−d)** (44 mg, 75%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.78−5.72 (m, 1H), 5.64−5.53 (m, 3H), 5.18−5.13 (m, 1H), 5.04−4.99 (m, 1H), 4.90−4.83 (m, 2H), 4.27−4.14 (m, 2H), 4.07−4.02 (m, 1H), 3.75−3.69 (m, 1H), 3.61−3.49 (m, 3H), 3.45−3.38 (m, 1H), 2.82 (dt, J = 1.8 Hz, 2H), 2.03 (s, 3H), 1.67−1.61 (m, 2H), 1.51−1.45 (m, 12H), 1.42−1.39 (m, 7H), 1.35−1.34 (m, 7H), 1.28−1.25 (m, 12H), 0.088 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 136.7, 130.0, 139.1, 113.8, 109.5, 109.3, 108.6, 97.2, 76.4, 75.7, 74.8 (74.7), 74.5, 73.7, 72.2 (72.1), 68.9, 67.0, 34.3, 33.9, 31.2, 29.6, 29.2, 29.1, 28.8, 28.5, 28.3, 27.6, 26.9, 25.9, 25.6, 25.5, 22.7, 21.4, 19.7, 14.1; IR (neat) ν_{max} 2931, 2219, 1733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4289.

Following the same synthetic procedure used for compound **21**, compounds **42(a−d)** (25 mg, 0.037 mmol) were hydrogenated to obtain compound **24** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **24** (23.8 mg, 97%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{26}_D$ −3.9 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89−4.83 (m, 1H), 4.28−4.15 (m, 2H), 4.07−4.03 (m, 4H), 3.76−3.69 (m, 1H), 3.65−3.51 (m, 3H), 3.48−3.41 (m, 1H), 2.03 (s, 3H), 1.78−1.70 (m, 6H), 1.66−1.59 (m, 6H), 1.52−1.49 (m, 9H), 1.36−1.35 (m, 10H), 1.33−1.28 (m, 21H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.5, 107.8, 107.5, 78.5, 78.4, 78.2, 74.9, 74.6, 72.1, 68.8, 67.0, 34.3, 33.9, 30.3, 29.8, 29.8, 29.7, 29.7, 28.8, 28.7, 27.6, 27.3, 26.9, 26.5, 26.1, 25.6, 25.5, 22.8, 22.4, 14.1; IR (neat) ν_{max} 2925, 1727 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4923.

5-((((4*R*,5*R*)-5-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-sulfonyl)-2-phenyl-2*H*-tetrazole (47). Following the same procedure described above for the AD-mix-β reaction, compound **14** (3.0 g, 7.6 mmol) was transformed to **15a** as minor and **15b** as major isomers using AD-mix-α (10.7 g, 1.4 g for 1 mmol of olefin) and $MeSO_2NH_2$ (1.45 mg, 15.2 mmol) in ^{t}BuOH:H_2O (1:1, 60 mL) with good diastereoselectivity (**15a**:**15b** ∼ 1:3.3) and overall yield (90%). Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 50% EtOAc in hexane as eluant) afforded pure compound **15a** (653 mg, 21%) and **15b** (2.15 g, 69%) as a colorless oil.

Following the same synthetic procedure used for compound **16**, compound **15b** (2.0 g, 4.9 mmol) was converted to the corresponding acetonide using 2,2-DMP (1.2 mL, 9.8 mmol) and CSA (57 mg, 0.25 mmol) in CH_2Cl_2 (20 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding acetonide (2.2 g, quantitative) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); $[\alpha]^{27}_D$ +73.0 (c 1.35, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−7.53 (m, 5H), 4.49−4.43 (m, 1H), 4.39−4.33 (m, 1H), 4.31−4.24 (m, 1H), 3.75−3.63 (m, 4H), 3.57−3.48 (m, 2H), 3.35−3.28 (m, 1H), 1.99−1.85 (m, 2H), 1.44−1.41 (m, 6H), 1.35−1.34 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.3, 133.8, 130.3, 129.9, 123.9, 109.6, 108.8, 75.9, 75.2, 74.8, 72.3, 68.5, 66.9, 35.3, 29.7, 28.5, 26.9, 25.8, 25.5; IR (neat) ν_{max} 2930, 1213 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{30}N_4O_5SNa$ $[M + Na]^+$ 473.1835, found 473.1837.

Following the same synthetic procedure used for compound **8**, the acetonide (2.0 g, 4.5 mmol) from the step above was converted to compound **47** using $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (278 mg, 0.22 mmol) and 30% aqueous H_2O_2 (12 mL) in EtOH (20 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 20% EtOAc in hexane as eluant) afforded compound **47** (1.8 g, 85%) as a colorless oil. R_f = 0.3 (30% EtOAc in hexane); $[\alpha]^{28}_D$ +23.7 (c 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60−7.53 (m, 5H), 4.65−4.56 (m, 1H), 4.30 (q, J = 6.6 Hz, 1H), 4.23−4.15 (m, 1H), 4.01−3.95 (m, 2H), 3.82−3.79 (m, 2H), 3.68−3.59 (m, 2H), 3.58−3.46 (m, 1H), 3.44−3.39 (m, 2H), 1.83−1.78 (m, 2H), 1.38−1.36 (m, 3H), 1.29−1.27 (m, 3H), 1.23 (s, 3H), 1.18−1.17 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.1, 133.3, 131.4, 129.4, 125.9, 109.5, 109.3, 75.8, 72.5, 72.4, 68.2, 66.7, 58.4, 29.6, 27.6, 26.8, 25.5, 25.3; IR (neat) ν_{max} 2923, 1216 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{30}N_4O_7SNa$ $[M + Na]^+$ 505.1733, found 505.1730.

5-((((4*S*,5*S*)-5-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-sulfonyl)-2-phenyl-2*H*-tetrazole (48). Following the same procedure described above for the AD-mix-β reaction, compound **29** (1.0 g, 2.55 mmol) was transformed to **30a** as minor and **30b** as major isomers using AD-mix-α (3.6 g, 1.4 g for 1 mmol of olefin) and $MeSO_2NH_2$ (476 mg, 5.0 mmol) in ^{t}BuOH:H_2O (1:1, 20 mL) with good diastereoselectivity (**30a**:**30b** ∼ 1:3.3) and overall yield (90%). Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 50% EtOAc in hexane as eluant) afforded pure compound **30a** (220 mg, 21%) and **30b** (723 mg, 69%) as a colorless oil.

Following the same synthetic procedure used for compound **16**, compound **30b** (700 mg, 1.7 mmol) was converted to corresponding acetonide using 2,2-DMP (0.42 mL, 3.4 mmol) and CSA (20 mg, 0.085 mmol) in CH_2Cl_2 (7 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding acetonide (761 mg, quantitative) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); $[\alpha]^{27}_D$ −44.9 (c 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59−7.50 (m, 5H), 4.48−4.41 (m, 1H), 4.38−4.22 (m, 2H), 4.06−4.01 (m, 1H), 3.73−3.61 (m, 4H), 3.60−3.43 (m, 2H), 3.29 (dd, J = 12.9, 10.2 Hz, 1H), 1.95−1.81 (m, 2H), 1.42−1.39 (m, 6H), 1.33−1.32 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 133.7, 130.2, 129.9, 123.9, 109.5, 108.7, 75.9, 75.1, 74.7, 68.5, 66.8, 35.2, 29.7, 28.4, 26.9, 25.7, 25.5; IR (neat) ν_{max} 2933, 1217 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{30}N_4O_5SNa$ $[M + Na]^+$ 473.1835, found 473.1833.

Following the same synthetic procedure used for compound **8**, the acetonide (600 mg, 1.3 mmol) from the step above was converted to compound **48** using $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (83 mg, 0.06 mmol) and 30% aqueous H_2O_2 (3 mL) in EtOH (5 mL). Purification of the crude

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mixture using flash column chromatography (SiO_2, 100−200 mesh, 20% EtOAc in hexane as eluant) afforded compound **48** (530 mg, 85%) as a colorless oil. R_f = 0.3 (30% EtOAc in hexane); $[\alpha]^{28}_D$ −23.2 (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62−7.55 (m, 5H), 4.68−4.59 (m, 1H), 4.32 (q, *J* = 6.6 Hz, 1H), 4.25−4.18 (m, 1H), 4.03−3.97 (m, 1H), 3.85−3.82 (m, 2H), 3.69−3.32 (m, 2H), 3.60−3.49 (m, 1H), 3.47−3.38 (m, 2H), 1.86−1.79 (m, 2H), 1.39 (s, 3H), 1.31−1.29 (m, 3H), 1.25 (s, 3H), 1.21−1.19 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.2, 133.4, 131.4, 129.4, 125.9, 109.6, 109.4, 75.8, 74.6, 72.7, 72.6, 68.2, 66.8, 58.5, 29.7, 27.6, 26.9, 25.6, 25.3; IR (neat) ν_{max} 2930, 1217 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{30}N_4O_7SNa$ $[M + Na]^+$ 505.1733, found 505.1739.

(5*S*)-17-((4*S*,5*R*)-5-(2-((4*S*,5*R*)-5-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-4-methylheptadecan-5-yl Acetate (43). Following the same synthetic procedure used for compounds **6**(**a**,**b**), aldehyde **7** (370 mg, 0.92 mmol) and sulfone **47** (375 mg, 0.77 mmol) were reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (4 mL) to obtain the corresponding Julia−Kocienski products. Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding compounds (342 mg, 67%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.66 (m, 4H), 7.42−7.37 (m, 6H), 5.77 (dd, *J* = 11.4, 8.4 Hz, 1H), 5.61−5.55 (m, 1H), 5.00 (t, *J* = 7.5 Hz, 1H), 4.92 (t, *J* = 7.2 Hz, 1H), 4.25−4.18 (m, 3H), 4.04−3.99 (m, 1H), 3.73−3.66 (m, 2H), 3.60−3.46 (m, 4H), 3.42−3.35 (m, 1H), 1.62−1.56 (m, 2H), 1.47−1.45 (m, 6H), 1.41 (s, 3H), 1.36−1.34 (m, 9H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.8 (135.7), 133.4 (133.4), 129.8, 129.0, 127.8, 109.5, 108.9, 108.5, 79.1, 75.3 (75.2), 74.8 (74.7), 74.1, 73.3, 72.2 (72.1), 68.5, 66.9, 31.0, 28.5, 27.8, 26.9 (26.9), 25.8, 25.5 (25.5), 19.3; IR (neat) ν_{max} 2932, 1219 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{37}H_{54}O_8SiNa$ $[M + Na]^+$ 677.3486, found 677.3487.

Following the same synthetic procedure used for compounds **17**(**a**,**b**), compounds (225 mg, 0.34 mmol) from the step above were converted to their corresponding alcohols using TBAF (1 M in THF, 0.5 mL, 0.5 mmol) in THF (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (142 mg, 98%) as a colorless oil. R_f = 0.4 (40% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.71−5.59 (m, 1H), 5.05−4.99 (m, 1H), 4.92 (t, *J* = 6.6, Hz, 1H), 4.26−4.17 (m, 3H), 4.06−4.00 (m, 1H), 3.74−3.67 (m, 1H), 3.59−3.51 (m, 4H), 3.49−3.41 (m, 2H), 1.69−1.65 (m, 2H), 1.49 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.34 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 129.7, 128.9, 109.6, 109.1, 108.7, 78.8, 75.5, 74.9 (74.7), 74.2, 73.4, 71.9, 68.4, 66.7, 61.9, 31.2, 29.8, 28.4, 28.0, 26.9 (26.8), 25.8, 25.4, (25.4); IR (neat) ν_{max} 3467, 2987, 1210 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{36}O_8Na$ $[M + Na]^+$ 439.2308, found 439.2307.

Following the same synthetic procedure used for compounds **4**(**a**−**d**), the corresponding alcohols from the above step (110 mg, 0.26 mmol) were transformed to their corresponding aldehydes using IBX (110 mg, 0.4 mmol) in EtOAc (3 mL) and were further reacted with $Ph_3PCH_2I_2$ (420 mg, 0.8 mmol) in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (5 mL) to obtain compounds **49**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **49**(**a**−**d**) (99 mg, 73%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.51−6.47 (m, 1H), 6.30−6.24 (m, 1H), 5.64−5.33 (m, 2H), 5.09−5.05 (m, 1H), 4.94−4.83 (m, 2H), 4.28−4.19 (m, 2H), 4.05 (dd, *J* = 8.2, 6.6 Hz, 1H), 3.76−3.71 (m, 1H), 3.61−3.50 (m, 3H), 3.46−3.41 (m, 1H), 1.68−1.61 (m, 2H), 1.51 (s, 3H), 1.46 (s, 3H), 1.42−1.41 (m, 6H), 1.36 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 136.4, 128.9, 128.1, 108.8, 108.6 (108.5), 107.8, 84.7, 80.7, 74.7, 73.8, 72.9, 72.8, 71.1, 67.8, 66.0, 30.3, 28.8, 27.5, 27.2, 25.9, 24.8, 24.7 (24.5); IR (neat) ν_{max} 2932, 1215 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{35}IO_7Na$ $[M + Na]^+$ 561.1325, found 561.1331.

Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **49**(**a**−**d**) (25 mg, 0.045 mmol) and alkyne **5** (14 mg, 0.55 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (4 mg, 0.05 mmol) and CuI (2 mg, 0.01 mmol) in Et_3N (1 mL) to get corresponding Sonogashira-coupled products. Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding compounds (23 mg, 78%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.78−5.72 (m, 1H), 5.64−5.56 (m, 3H), 5.15 (dd, *J* = 8.7, 6.6 Hz, 1H), 5.04−5.00 (m, 1H), 4.91−4.83 (m, 2H), 4.27−4.14 (m, 2H), 4.05 (dd, *J* = 7.6, 6.6 Hz, 1H), 3.75−3.70 (m, 1H), 3.60−3.49 (m, 1H), 3.45−3.39 (m, 1H), 2.32 (td, *J* = 7.0, 1.8 Hz, 2H), 2.03 (s, 3H), 1.68−1.61 (m, 2H), 1.55−1.49 (m, 8H), 1.46 (s, 3H), 1.41−1.39 (m, 8H), 1.35−1.34 (m, 7H), 1.29−1.25 (m, 12H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 136.7, 130.1, 129.2, 113.8 (113.8), 109.5 (103.4), 108.6, 97.2, 75.8, 74.8 (74.8), 74.5, 73.8, 72.1, 68.9, 67.0, 34.3, 33.9, 31.2, 29.6, 29.2, 29.1, 28.9, 28.5, 28.3, 27.6, 26.9, 25.9, 25.7, 25.5 (25.5), 22.7, 21.4, 19.7, 14.1; IR (neat) ν_{max} 2932, 2219, 1729 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4307.

Following the same synthetic procedure used for compound **21**, the compounds (25 mg, 0.034 mmol) from the step above were hydrogenated to obtain compound **43** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **43** (24 mg, 98%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{27}_D$ +15.9 (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.89−4.81 (m, 1H), 4.28−4.18 (m, 2H), 4.07−4.03 (m, 4H), 3.75−3.69 (m, 1H), 3.65−3.51 (m, 3H), 3.48−3.43 (m, 1H), 2.03 (s, 3H), 1.82−1.59 (m, 5H), 1.52−1.48 (m, 6H), 1.45−1.42 (m, 9H), 1.36−1.33 (m, 10H), 1.29−1.25 (m, 22H), 0.88 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.5, 107.8, 107.6, 78.5, 78.3, 78.2, 74.8, 74.6, 74.5, 72.1, 68.8, 67.0, 34.3, 33.9, 29.8, 29.7, 29.7, 29.5, 28.7, 27.6, 26.9, 26.5, 26.1, 25.5, 22.8, 21.4, 14.1; IR (neat) ν_{max} 2926, 1728 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4917.

(*R*)-16-((4*R*,5*S*)-5-(2-((4*S*,5*R*)-5-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-5-yl Acetate (44). Following the same synthetic procedure used for compounds **6**(**a**,**b**), aldehyde **33** (370 mg, 0.92 mmol) and sulfone **47** (375 mg, 0.77 mmol) reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (7 mL) to obtain the mixture of corresponding Julia−Kocienski-coupled products. Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding Julia−Kocienski compounds (348 mg, 69%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.66 (m, 4H), 7.42−7.37 (m, 6H), 5.80−5.74 (m, 1H), 5.59 (t, *J* = 8.7 Hz, 1H), 5.03−4.89 (m, 2H), 4.27−4.18 (m, 3H), 4.04−3.99 (m, 1H), 3.73−3.66 (m, 2H), 3.60−3.46 (m, 4H), 3.42−3.37 (m, 1H), 1.64−1.55 (m, 2H), 1.47−1.45 (m, 3H), 1.36−1.34 (m, 6H), 1.26 (s, 6H), 1.05 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.8 (135.7), 133.5 (133.4), 129.8, 129.6 (129.5), 129.0, 127.8, 109.5, 108.9, 108.6, 97.2, 75.4 (75.3), 74.8 (74.7), 74.2, 73.3, 72.1, 68.6, 67.0, 63.4, 31.0, 28.5, 27.8, 26.9 (26.9), 25.8, 25.5 (25.5), 19.3; IR (neat) ν_{max} 2929, 1216 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{37}H_{54}O_8SiNa$ $[M + Na]^+$ 677.3486, found 677.3489.

Following the same synthetic procedure used for compounds **17**(**a**,**b**), the mixture of compounds (225 mg, 0.34 mmol) from the step above were converted to their corresponding alcohols using TBAF (1 M in THF, 0.5 mL, 0.5 mmol) in THF (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (140 mg, 97%) as a colorless oil. R_f = 0.4 (40% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.72−5.60

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(m, 1H), 5.06−5.00 (m, 1H), 4.93 (t, J = 6.9 Hz, 1H), 4.30−4.18 (m, 3H), 4.07−4.01 (m, 1H), 3.75−3.69 (m, 1H), 3.60−3.54 (m, 4H), 3.50−3.42 (m, 2H), 1.70−1.64 (m, 2H), 1.50 (s, 3H), 1.47 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H), 1.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 129.8 (129.7), 128.9 (128.9) 109.6, 109.1, 108.7, 78.8, 75.6 (75.5), 74.3 (74.3), 73.5, 72.0, 68.4, 66.8, 61.9, 31.3, 29.8, 28.4, 28.1, 26.9 (26.9), 25.8, 25.5 (25.4); IR (neat) ν_{max} 3469, 2977, 1210 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{36}O_8Na$ $[M + Na]^+$ 439.2308, found 439.2310.

Following the same procedure of synthesis used for compounds **4**(**a**−**d**), the corresponding alcohols from the step above (100 mg, 0.23 mmol) were transformed to the corresponding aldehydes using IBX (110 mg, 0.4 mmol) in EtOAc (2 mL) and were further reacted with $Ph_3PCH_2I_2$ (420 mg, 0.8 mmol) in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (5 mL) to get a mixture of compounds **50**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **50**(**a**−**d**) (95 mg, 69%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.51−6.47 (m, 1H), 6.29−6.24 (m, 1H), 5.64−5.53 (m, 2H), 5.09−5.05 (m, 1H), 4.94−4.83 (m, 2H), 4.30−4.19 (m, 2H), 4.07−4.02 (m, 1H), 3.75−3.68 (m, 1H), 3.63−3.53 (m, 3H), 3.52−3.39 (m, 1H), 1.64 (q, J = 6.9 Hz, 2H), 1.51 (s, 3H), 1.46 (s, 3H), 1.42−1.41 (m, 6H), 1.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 137.4, 129.3, 129.1, 109.9, 109.8, 108.8, 85.7, 81.4, 75.7 (75.6), 74.9 (74.8), 73.9 (73.8), 72.4, 72.2, 68.8, 67.0, 31.3, 29.8, 28.5, 28.2, 26.9, 25.9 (25.8), 25.7 (25.5); IR (neat) ν_{max} 2928, 1216 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{35}IO_7Na$ $[M + Na]^+$ 561.1325, found 561.1317.

Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **50**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **5** (28 mg, 0.11 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain a mixture of the corresponding Sonogashira products. Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding compounds (44.4 mg, 75%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.78−5.59 (m, 4H), 5.17 (t, J = 7.2 Hz, 1H), 4.85 (t, J = 6.0 Hz, 1H), 4.71 (t, J = 6.0 Hz, 1H), 4.53 (t, J = 6.3 Hz, 1H), 4.29−4.24 (m, 2H), 4.07−4.02 (m, 1H), 3.75−3.70 (m, 1H), 3.58−3.49 (m, 3H), 3.46−3.41 (m, 1H), 2.34−2.29 (m, 2H), 2.04 (s, 3H), 1.68 (q, J = 6.3 Hz, 2H), 1.51−1.46 (m, 10H), 1.42−1.40 (m, 6H), 1.36−1.35 (m, 6H), 1.29−1.25 (m, 14H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 137.4 (137.3), 113.5, 109.6 (109.5), 109.2, 108.4, 78.7, 78.5, 75.3, 74.8, 74.5, 72.1, 68.8, 66.9, 34.3, 33.9, 30.9, 29.8, 29.6, 29.2, 29.0, 28.8, 28.4, 28.2, 27.6, 25.8, 25.7, 25.6 (25.5), 22.7, 21.4, 14.4; IR (neat) ν_{max} 2924, 2216, 1734 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4297.

Following the same synthetic procedure used for compound **21**, the compounds (25 mg, 0.037 mmol) from the step above were hydrogenated to obtain compound **44** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **44** (23.8 mg, 97%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{26}_D$ −0.6 (c 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.90−4.82 (m, 1H), 4.30−4.16 (m, 2H), 4.11−4.03 (m, 4H), 3.75−3.65 (m, 1H), 3.63−3.59 (m, 2H), 3.57−3.51 (m, 1H), 3.48−3.41 (m, 1H), 2.04 (s, 3H), 1.79−1.68 (m, 4H), 1.54−1.48 (m, 6H), 1.42 (s, 8H), 1.37−1.36 (m, 4H), 1.33−1.25 (m, 30H), 0.89 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.5, 107.8, 107.6, 78.2, 75.0, 74.8, 74.6, 72.1, 68.9, 66.9, 34.3, 33.9, 32.1, 30.2, 29.9, 29.8, 29.7, 29.5, 28.7, 27.6, 26.9, 26.6, 26.5, 26.1, 25.6, 25.5, 22.8, 21.4, 14.1; IR (neat) ν_{max} 2933, 1736 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4922.

(*R*)-16-((4*S*,5*R*)-5-(2-((4*R*,5*S*)-5-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-5-yl Acetate (45). Following the same synthetic procedure used for compounds **6**(**a**,**b**), aldehyde **7** (370 mg, 0.92 mmol) and sulfone **48** (375 mg, 0.77 mmol) reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (4 mL) to get the mixture of corresponding Julia−Kocienski products. Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding compounds (349 mg, 69%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69−7.66 (m, 4H), 7.41−7.37 (m, 6H), 5.79−5.72 (m, 1H), 5.60−5.54 (m, 1H), 5.02−4.96 (m, 1H), 4.91 (t, J = 7.2 Hz, 1H), 4.29−4.15 (m, 3H), 4.03−4.98 (m, 1H), 3.72−3.65 (m, 2H), 3.62−3.45 (m, 4H), 3.41−3.34 (m, 1H), 1.59−1.53 (m, 2H), 1.46−1.44 (m, 3H), 1.40 (s, 3H), 1.35−1.34 (m, 6H), 1.04 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.7 (135.7), 133.4 (133.4), 129.8, 129.5 (129.5), 128.9, 127.8, 109.5, 108.9, 108.5, 79.1, 75.3 (75.2), 74.9 (74.7), 74.1, 73.3, 72.2 (72.1), 68.5 (68.5), 66.9, 63.4, 31.0, 28.5, 27.8, 26.9 (26.9), 25.8, 25.5, 19.3; IR (neat) ν_{max} 2930, 1215 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{54}O_8SiNa$ $[M + Na]^+$ 677.3486, found 677.3483.

Following the same synthetic procedure used for compounds **17**(**a**,**b**), the compounds (225 mg, 0.34 mmol) from the step above were converted to the corresponding alcohols using TBAF (1 M in THF, 0.5 mL, 0.5 mmol) in THF (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (140 mg, 97%) as a colorless oil. R_f = 0.4 (40% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.71−5.59 (m, 2H), 5.02 (t, J = 6.6 Hz, 1H), 4.92 (t, J = 6.6 Hz, 1H), 4.25−4.17 (m, 3H), 4.05−4.00 (m, 1H), 3.75−3.68 (m, 1H), 3.64−3.55 (m, 4H), 3.49−3.41 (m, 2H), 1.69−1.65 (m, 2H), 1.49−1.46 (m, 6H), 1.41−1.34 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 129.7, 128.9, 109.7 (109.6), 109.1, 108.8 (108.7), 78.9, 75.6 (75.5), 74.7, 74.2 (74.2), 73.4, 71.9, 68.4, 66.7, 61.9, 32.2, 29.8, 28.9, 28.0, 26.8, 25.8, 25.4; IR (neat) ν_{max} 3472, 2987, 1217 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{36}O_8Na$ $[M + Na]^+$ 439.2308, found 439.2305.

Following the same synthetic procedure used for compounds **4**(**a**−**d**), the alcohols from the step above (110 mg, 0.23 mmol) were transformed to the corresponding aldehydes using IBX (110 mg, 0.4 mmol) in EtOAc (3 mL) and were further reacted with $Ph_3PCH_2I_2$ (420 mg, 0.8 mmol) in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (5 mL) to obtain a mixture of compounds **51**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **51**(**a**−**d**) (103 mg, 75%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.41−6.37 (m,1H), 6.20−6.14 (m, 1H), 5.54−5.43 (m, 2H), 5.01−4.95 (m, 1H), 4.84−4.73 (m, 2H), 4.20−4.09 (m, 2H), 3.98−3.93 (m, 1H), 3.66−3.58 (m, 1H), 3.51−3.40 (m, 3H), 3.36−3.29 (m, 1H), 1.55 (q, J = 6.6 Hz, 2H), 1.41 (s, 3H), 1.36 (s, 3H), 1.32−1.31 (m, 6H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 137.4, 129.9, 129.1, 109.8, 109.5, 108.8, 85.7, 81.4, 75.7 (75.6), 74.9 (74.8), 73.9 (73.8), 72.1, 68.8 (68.7), 67.0, 31.3, 29.8, 28.5, 28.2, 26.9, 25.9, 25.7 (25.5); IR (neat) ν_{max} 2925, 1216 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{35}IO_7Na$ $[M + Na]^+$ 561.1325, found 561.1323.

Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **51**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **5** (28 mg, 0.11 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain a mixture of corresponding Sonogashira products. Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding compounds (47 mg, 79%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.80−5.72 (m, 1H), 5.18−5.13 (m, 1H), 5.05−5.00 (m, 1H), 4.95−4.81 (m, 2H), 4.29−4.14 (m, 2H), 4.07−4.02 (m, 1H), 3.75−3.69 (m, 1H), 3.64−3.44 (m, 3H), 3.45−3.38 (m, 1H), 2.34−2.29 (m, 2H), 2.03 (s, 3H), 1.68−1.61 (m, 2H), 1.55−1.46 (m, 10H), 1.41−1.40 (m, 6H), 1.36−1.34 (m, 6H), 1.29−1.25 (m, 14H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed

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minor diastereomeric peaks are given in parentheses) δ 171.1, 136.7, 130.1, 129.2, 113.8, 109.5, 109.4, 108.6, 97.2, 75.8, 74.8, 73.8, 72.1, 68.9, 67.1, 34.3, 33.9, 31.2, 29.8, 29.6, 29.2, 29.1, 28.9, 28.5, 28.3, 27.6, 26.9, 25.7, 25.5 (25.5), 22.7, 21.4, 19.7, 14.1; IR (neat) ν_{max} 2929, 2215, 1732 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4288.

Following the same synthetic procedure used for compound **21**, compounds (25 mg, 0.037 mmol) from the step above were hydrogenated to obtain compound **45** using 10 mol % Pd/C (5 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **45** (23 mg, 94%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{30}_D$ +1.5 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.89−4.81 (m, 1H), 4.29−4.15 (m, 2H), 4.07−4.03 (m, 4H), 3.76−3.69 (m, 1H), 3.63−3.48 (m, 3H), 3.48−3.41 (m, 1H), 2.03 (s, 3H), 1.78−1.63 (m, 5H), 1.52−1.42 (m, 15H), 1.36−1.25 (m, 32H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.5, 107.8, 107.5, 78.5, 78.4, 78.2, 75.0, 74.8, 74.6, 72.1, 68.9, 67.0, 34.3, 33.9, 30.3, 29.8, 29.8, 28.7, 27.6, 27.3, 27.2, 26.9, 26.1, 25.6, 25.5, 22.8, 21.4, 14.1; IR (neat) ν_{max} 2930, 1731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4917.

(*R*)-16-((4*R*,5*S*)-5-(2-((4*R*,5*S*)-5-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-5-yl Acetate (46). Following the same synthetic procedure used for compounds **6**(**a**,**b**), aldehyde **33** (370 mg, 0.92 mmol) and sulfone **48** (375 mg, 0.77 mmol) were reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (7 mL) to obtain a mixture of corresponding Julia−Kocienski products. Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding compounds (346 mg, 68%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68−7.66 (m, 4H), 7.44−7.35 (m, 6H), 5.78−5.73 (m, 1H) 5.59−5.54 (m, 1H), 4.99 (t, J = 5.7 Hz, 1H), 4.91(t, J = 6.3 Hz, 1H), 4.25−4.17 (m, 3H), 4.03−3.99 (m, 1H), 3.71−3.66 (m, 2H), 3.59−3.46 (m, 4H), 3.40−3.35 (m, 1H), 1.64−1.57 (m, 2H), 1.46−1.45 (m, 6H), 1.41−1.40 (m, 6H), 1.36−1.34 (m, 6H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.8 (135.8), 133.5, 129.8, 129.6, 129.0, 127.8, 109.6, 108.9, 108.6, 79.2, 75.3, 74.9, 74.2, 73.4, 72.2, 68.6, 67.0, 63.5, 31.1, 28.5, 27.9, 27.0, 25.9, 25.5, 19.4; IR (neat) ν_{max} 2937, 1218 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{54}O_8SiNa$ $[M + Na]^+$ 677.3486, found 677.3484.

Following the same synthetic procedure used for compounds **17**(**a**,**b**), the compounds (225 mg, 0.34 mmol) from the step above were converted to the corresponding alcohols using TBAF (1 M in THF, 0.5 mL, 0.5 mmol) in THF (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (137 mg, 96%) as a colorless oil. R_f = 0.4 (40% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.70−5.59 (m, 2H), 5.03−4.98 (m, 1H), 4.91(t, J = 6.9 Hz, 1H), 4.29−4.17 (m, 3H), 4.06−4.01 (m, 1H), 3.74−3.65 (m, 1H), 3.59−3.51 (m, 4H), 3.49−3.39 (m, 2H), 2.33 (s, 1H), 1.68−1.62 (m, 2H), 1.49 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 1.37 (s, 3H), 1.34 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 129.8 (129.7), 128.9 (128.9), 109.7, 109.1, 108.7, 78.8 (78.8), 75.5 (75.5), 74.9 (74.7), 74.2 (74.2), 73.4, 72.4, 68.4, 66.7, 61.9, 31.3, 29.8, 28.4, 28.0, 26.9 (26.8), 25.7, 25.4 (25.4); IR (neat) ν_{max} 3470, 2987, 1213 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{36}O_8Na$ $[M + Na]^+$ 439.2308, found 439.2315.

Following the same synthetic procedure used for compounds **4**(**a**−**d**), the alcohols from the step above (110 mg, 0.26 mmol) were transformed to the corresponding aldehydes using IBX (110 mg, 0.4 mmol) in EtOAc (3 mL) and were further reacted with $Ph_3PCH_2I_2$ (420 mg, 0.8 mmol) in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (5 mL) to obtain compounds **52**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **52**(**a**−**d**) (103 mg, 75%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.51−6.47 (m, 1H), 6.29−6.24 (m, 1H), 5.63−5.53 (m, 2H), 5.09−5.05 (m, 1H), 4.93−4.83 (m, 2H), 4.29−4.21 (m, 2H), 4.05 (dd, J = 8.1, 6.3 Hz, 1H), 3.75−3.68 (m, 1H), 3.62−3.49 (m, 3H), 3.46−3.39 (m, 1H), 1.67−1.61 (m, 2H), 1.51 (s, 3H), 1.46 (s, 3H), 1.41−1.40 (m, 6H), 1.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 137.4 (137.3), 129.9, 129.1 (129.1), 109.8, 109.6 (109.5), 108.4, 85.9 (85.7), 81.4, 75.7 (75.6), 74.9 (74.7), 73.9 (73.7), 72.3, 72.1, 68.8 (68.7), 67.0, 31.3, 28.5, 28.2, 26.9, 25.9, 25.7, 25.6; IR (neat) ν_{max} 2928, 1214 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{35}IO_7Na$ $[M + Na]^+$ 561.1325, found 561.1320.

Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **52**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **5** (28 mg, 0.11 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain a mixture of corresponding Sonogashira products. Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded the corresponding compounds (45 mg, 76%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.78−5.71 (m, 1H), 5.64−5.56 (m, 3H), 5.15 (dd, J = 8.7, 6.6 Hz, 1H), 5.02 (t, J = 6.6 Hz, 1H), 4.90−4.83 (m, 2H), 4.27−4.07 (m, 2H), 4.04 (dd, J = 8.1, 6.3 Hz, 1H), 3.75−3.68 (m, 1H), 3.61−3.49 (m, 3H), 3.45−3.38 (m, 1H), 2.32 (dt, J = 6.9, 1.8 Hz, 2H), 2.03 (s, 3H), 1.67−1.60 (m, 2H), 1.51−1.45 (m, 12H), 1.41−1.39 (m, 6H), 1.35−1.34 (m, 6H), 1.28−1.25 (m, 12H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 136.7 (136.7), 130.0, 129.2 (129.1), 113.8 (113.8), 109.5 (109.3), 108.6, 97.3, 76.4, 75.8 (75.7), 74.8 (74.7), 74.5, 73.7, 72.2 (72.1), 68.9, 67.1, 34.2, 33.9, 31.2, 29.6, 29.2, 29.1, 28.8, 28.5, 28.3, 27.6, 26.9, 25.8, 25.7, 25.5, 22.7, 21.4, 19.7, 14.1; IR (neat) ν_{max} 2933, 2218, 1731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4297.

Following the same synthetic procedure used for compound **21**, compounds (25 mg, 0.037 mmol) from the step above were hydrogenated to obtain compound **46** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **46** (23.5 mg, 96%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{26}_D$ −4.2 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.89−4.81 (m, 1H), 4.28−4.16 (m, 2H), 4.07−4.00 (m, 4H), 3.75−3.68 (m, 1H), 3.66−3.51 (m, 3H), 3.7−3.40 (m, 1H), 2.03 (s, 3H), 1.77−1.63 (m, 4H), 1.51−1.47 (m, 6H), 1.44−1.42 (m, 10H), 1.37−1.32 (m, 11H), 1.28−1.25 (m, 21H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.6, 107.7, 107.5, 78.5, 78.4, 78.2, 74.9, 74.9, 72.6, 68.8, 67.0, 34.3, 33.9, 30.3, 29.8, 29.8, 29.8, 29.7, 29.5, 28.8, 27.3, 26.9, 26.5, 26.1, 26.1, 25.6, 25.5, 22.7, 21.4, 14.1; IR (neat) ν_{max} 2925, 1728 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4915.

(4*R*,5*S*)-4-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)-ethyl)-5-(3-((*R*)-5-(2-iodovinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-prop-1-en-1-yl)-2,2-dimethyl-1,3-dioxolane [56(a−d)]. Following the same procedure as described before, compound **11**(362 mg, 0.9 mmol) was converted quantitatively to its corresponding aldehyde using IBX (504 mg, 1.8 mmol) in EtOAc (4 mL), which was taken for the next reaction without further characterization.

Following the same synthetic procedure used for compounds **6**(**a**,**b**), the aldehyde (370 mg, 0.9 mmol) from the step above and sulfone **47** (375 mg, 0.77 mmol) were reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (4 mL) to obtain compounds **55**(**a**,**b**). Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded compounds **55**(**a**,**b**) (350 mg, 68%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.68−7.64 (m, 4H), 7.46−7.35 (m, 6H), 5.80−5.72 (m, 1H), 5.57−5.50 (m, 1H), 4.87 (dd, J = 9.3, 6.3 Hz, 1H), 4.28−4.14 (m, 1H), 4.05−4.00 (m, 1H), 3.75−3.68 (m, 3H), 3.64−3.49 (m, 3H), 3.44−3.39 (m, 1H), 2.59−2.52 (m, 1H), 2.41−2.31 (m, 1H), 1.76−1.69 (m, 2H), 1.47 (s, 3H), 1.41 (s, 3H), 136−1.34 (m, 9H), 1.30 (s, 3H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor

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diastereomeric peaks are given in parentheses) δ 135.7 (135.7), 133.4, 133.3, 130.8, 129.9, 128.1 (127.9), 109.5, 108.3, 108.2, 76.9, 75.3, 74.8, 74.7, 73.9, 72.1, 68.9 (68.8), 67.1, 62.6, 30.9, 29.8, 28.5 (28.4), 28.2 (28.1), 27.0 (26.9), 25.8, 25.5 (25.5), 19.3; IR (neat) ν_{max} 2980, 1217 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{56}SiO_8Na$ $[M + Na]^+$ 691.3642, found 691.3640.

Following the same synthetic procedure used for compounds **17**(**a**,**b**), compounds **55**(**a**,**b**) (350 mg, 0.5 mmol) were converted to the corresponding alcohols using TBAF (1 M in THF, 0.6 mL, 0.6 mmol) in THF (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (209 mg, 97%) as a colorless oil. R_f = 0.5 (40% EtOAc in hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.82−5.64 (m, 1H), 5.58−5.52 (m, 1H), 4.90−4.85 (m, 1H), 4.29−4.14 (m, 4H), 4.04 (t, J = 7.2 Hz, 1H), 3.74−3.68 (m, 1H), 3.66−3.49 (m, 5H), 3.47−3.41 (m, 1H), 2.42−2.38 (m, 2H), 1.76−1.72 (m, 2H), 1.47 (s, 6H), 1.41 (s, 3H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 129.7, 128.2, 109.5, 108.4, 108.3, 77.7, 76.4, 75.3, 74.8, 73.9, 72.1, 68.8, 66.9 (66.9), 61.7, 30.8, 29.8, 28.5, 28.1, 26.9, 25.9, 25.5, 25.4; IR (neat) ν_{max} 3430, 2996, 1211 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{38}O_8Na$ $[M + Na]^+$ 453.2464, found 453.2462.

Following the same synthetic procedure used for compounds **4**(**a**−**d**), the alcohols from the step above (100 mg, 0.23 mmol) were transformed to the corresponding aldehydes using IBX (129 mg, 0.46 mmol) in EtOAc (2 mL) and were further reacted with $Ph_3PCH_2I_2$ (365 mg, 0.69 mmol) in the presence of NaHMDS ((1 M in THF, 0.7 mL, 0.7 mmol) in THF (5 mL) to obtain a mixture of compounds **56**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **56**(**a**−**d**) (94 mg, 74%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.53−6.49 (m, 1H), 6.36−6.30 (m, 1H), 4.87−4.81 (m, 2H), 4.31−4.22 (m, 3H), 4.07−4.02 (m, 1H), 3.74−3.68 (m, 1H), 3.60−3.46 (m, 3H), 3.45−3.41 (m, 1H), 2.27−2.21 (m, 2H), 1.75−1.71 (m, 2H), 1.47−1.16 (m, 6H), 1.41 (s, 3H), 1.37−1.36 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 137.9, 129.8, 128.1, 109.5, 109.1, 108.3, 85.2, 80.9, 75.3, 74.9 (74.8), 73.9, 72.4, 72.2, 68.8, 67.0, 30.9, 29.8, 29.1, 28.5, 28.1, 26.9, 25.9, 25.6; IR (neat) ν_{max} 2933, 1216 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{37}IO_7Na$ $[M + Na]^+$ 575.1482, found 575.1478.

(4*R*,5*S*)-4-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)-ethyl)-5-(4-((4*R*,5*S*)-5-(2-iodovinyl)-2,2-dimethyl-1,3-dioxolan-4-yl)but-1-en-1-yl)-2,2-dimethyl-1,3-dioxolane [59(a−d)]. To a stirred solution of aldehyde **7** (500 mg, 1.2 mmol) in anhydrous CH_2Cl_2 (5 mL) at 0 °C under argon was added $Ph_3P{=}CHCO_2Et$ (831 mg, 2.4 mmol). The reaction mixture was warmed to room temperature and stirred for 12 h. The mixture was concentrated in vacuo. Purification of the resultant crude residue by flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) provided corresponding α,β-unsaturated ester (550 mg, 98%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.66−7.62 (m, 4H), 7.43−7.35 (m, 6H), 7.13 (dd, J = 15.6, 5.4 Hz, 1H), 6.16 (dd, J = 15.6, 1.8 Hz, 1H), 4.88−4.84 (m, 1H), 4.34 (q, J = 6.6 Hz, 1H), 4.19 (q, J = 3.9 Hz, 2H), 3.63−3.61 (m, 2H), 1.44 (s, 3H), 1.34 (s, 3H), 1.29−1.24 (m, 3H), 1.03 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 166.1, 143.1, 135.8 (135.7), 133.2 (133.1), 129.9 (129.9), 127.9 (127.7), 122.7, 109.4, 78.3, 76.8, 62.6, 60.6, 27.7, 26.9 (26.8), 25.4, 19.3, 14.4; IR (neat) ν_{max} 2923, 2853, 1720 cm^{-1}; HRMS (ESI) m/z calcd for $C_{27}H_{36}O_5SiNa$ $[M + Na]^+$ 491.2230, found 491.2232.

To a stirred solution of the above ester (550 g, 1.2 mmol) in anhydrous THF (2 mL) and EtOH (2 mL) at 0 °C under argon was added $LiBH_4$ (104 mg, 4.8 mmol) portion wise. The reaction mixture was warmed to room temperature and stirred for 12 h. The mixture was cooled again to 0 °C prior to quenching it with saturated aqueous NH_4Cl solution (3 mL). The resulting mixture was extracted with EtOAc (2 × 30 mL), washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the resultant crude residue by flash column chromatography (SiO_2, 60−120 mesh, 11% EtOAc in hexane as eluant) provided alcohol **57** (504 mg, 98%) as a colorless oil. R_f = 0.4 (20% EtOAc in hexane); $[\alpha]^{28}_D$ +5.3 (c 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.68−7.65 (m, 4H), 7.44−7.36 (m, 6H), 4.21−4.16 (m, 2H), 3.73−3.63 (m, 4H), 1.77−1.68 (m, 2H), 1.62−1.58 (m, 2H), 1.38 (s, 3H), 1.35 (s, 3H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.8 (135.7), 133.5 (133.4), 129.9, 127.9, 108.1, 78.1, 77.8, 62.9, 62.8, 30.4, 28.2, 26.9, 26.3, 25.7, 19.3; IR (neat) ν_{max} 3443, 2929, 1115 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{36}O_4SiNa$ $[M + Na]^+$ 451.2281, found 451.2280.

Following the same oxidation procedure of compounds **17**(**a**,**b**), alcohol **57** (385 mg, 0.9 mmol) from the step above was converted to its corresponding aldehyde using IBX (504 mg, 1.8 mmol) in EtOAc (2 mL), which was taken for the next reaction without further characterization.

Following the same synthetic procedure used for compounds **6**(**a**,**b**), the aldehyde (384 mg, 0.9 mmol) from the step above and sulfone **47** (375 mg, 0.77 mmol) were reacted together in the presence of NaHMDS (1 M in THF, 0.8 mL, 0.8 mmol) in THF (4 mL) to obtain compounds **58**(**a**,**b**). Purification of the crude mixture using flash column chromatography (SiO_2, 230−400 mesh, 10% EtOAc in hexane as eluant) afforded compounds **58**(**a**,**b**) (363 mg, 69%) as a colorless oil. R_f = 0.5 (20% EtOAc in hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.68−7.65 (m, 4H), 7.40−7.36 (m, 6H), 5.64−5.58 (m, 1H), 5.51−5.43 (m, 1H), 4.96−4.89 (m, 1H), 4.28−4.19 (m, 2H), 4.18−4.12 (m, 2H), 4.07−4.02 (m, 1H), 3.75−3.65 (m, 3H), 3.63−3.51 (m, 3H), 3.46−3.40 (m, 1H), 2.42−2.29 (m, 1H), 2.24−2.03 (m, 1H), 1.72−1.63 (m, 4H), 1.42 (m, 3H), 1.36 (s, 9H), 1.32 (s, 3H), 1.26 (s, 3H), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 135.7 (135.7), 133.5 (133.3), 129.9, 129.5, 127.8 (127.8), 126.5 (126.3), 109.6 (109.5), 108.2 (108.1), 108.0 (107.9), 77.9 (77.8), 75.2 (75.1), 74.8 (74.7), 73.9, 72.3 (72.1), 68.8, 66.9, 62.8 (62.7), 31.1 (30.9), 29.8, 29.5 (29.2), 28.5 (28.4), 28.3, 26.9 (26.9), 25.9 (25.8), 25.7 (25.5), 19.3; IR (neat) ν_{max} 2985, 1215 cm^{-1}; HRMS (ESI) m/z calcd for $C_{39}H_{58}SiO_8Na$ $[M + Na]^+$ 705.3799, found 705.3797.

Following the same synthetic procedure used for compounds **17**(**a**,**b**), compounds **58**(**a**,**b**) (200 mg, 0.3 mmol) were converted to the corresponding alcohols using TBAF (1 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 30% EtOAc in hexane as eluant) afforded the corresponding alcohols (130 mg, 98%) as a colorless oil. R_f = 0.5 (40% EtOAc in hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.57−5.58 (m, 1H), 5.49−5.40 (m, 1H), 4.94−4.87 (m, 1H), 4.29−4.21 (m, 2H), 4.18−4.12 (m, 2H), 4.09−4.01 (m, 1H), 3.72−3.68 (m, 1H), 3.66−3.54 (m, 5H), 3.52−3.39 (m, 1H), 2.34−2.26 (m, 1H), 2.19−2.12 (m, 1H), 1.71−1.63 (m, 4H), 1.45 (s, 6H), 1.40 (s, 3H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 133.4, 126.9 (126.6), 109.6, 108.3, 108.2, 77.9 (77.9), 76.3, 75.0, 74.8 (74.7), 73.8, 72.3 (72.1), 68.8 (68.7), 66.9, 61.8 (61.7), 31.1 (30.9), 29.8, 29.4, 29.1, 28.6 (28.5), 28.3, 26.9, 25.8, 25.6 (25.5); IR (neat) ν_{max} 3456, 2990, 1216 cm^{-1}; HRMS (ESI) m/z calcd for $C_{23}H_{40}O_8Na$ $[M + Na]^+$ 467.2621, found 467.2632.

Following the same synthetic procedure used for compounds **4**(**a**−**d**), the alcohols from the step above (100 mg, 0.22 mmol) were transformed to the corresponding aldehydes using IBX (123 mg, 0.44 mmol) in EtOAc (2 mL) and were further reacted with $Ph_3PCH_2I_2$ (349 mg, 0.66 mmol) in the presence of NaHMDS (1 M in THF, 0.65 mL, 0.65 mmol) in THF (2 mL) to obtain compounds **59**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compounds **59**(**a**−**d**) (94 mg, 76%) as a colorless oil. R_f = 0.5 (10% EtOAc in hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.50−6.47 (m, 1H), 6.31−6.25 (m, 1H), 5.75−5.57 (m, 1H), 5.51−5.41 (m, 1H), 4.94−4.88 (m, 1H), 4.82−4.76 (m, 1H), 4.30−4.20 (m, 3H), 4.05 (t, J = 8.1 Hz, 1H); 3.74−3.68 (m, 1H), 3.62−3.50 (m, 3H), 3.46−3.40 (m, 1H), 2.28−2.21 (m, 1H), 2.13−2.08 (m, 1H), 2.06−1.94 (m, 1H), 1.71−1.54 (m, 4H), 1.47−1.46 (m, 3H), 1.42 (s, 3H), 1.37−1.36 (m, 6H), 1.25 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor

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diastereomeric peaks are given in parentheses) δ 138.0, 133.3, 126.6, 109.6 (109.5), 108.9 (108.9), 108.3 (108.2), 84.8, 81.0, 79.4, 75.2, 74.9 (74.8), 73.9, 72.4, 68.9, 68.8 (68.8), 67.0, 30.9, 30.2, 29.8, 28.5, 28.3, 26.9, 25.9, 25.7, 25.6; IR (neat) ν_{max} 2930, 1219 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{24}H_{39}IO_7Na$ $[M + Na]^+$ 589.1638, found 589.1635.

(*R*)-Tridec-12-yn-5-yl Acetate (62a). Following the same synthetic procedure used for compound **19**, epoxide **18** (450 mg, 4.5 mmol) was transformed to compound **60a** using 1-heptyne (0.66 mL, 5.0 mmol), ^{n}BuLi (3 mL, 4.8 mmol, 1.6 M in hexane), and $BF_3{\cdot}OEt_2$ (0.6 mL, 4.8 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **60a** (756 mg, 84%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{25}_D$ 1.2 (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.71−3.63 (m, 1H), 2.44−2.35 (m, 1H), 2.30−2.23 (m, 1H), 2.19−2.13 (m, 2H), 1.96 (s, 1H), 1.54−1.41 (m, 4H), 1.40−1.23 (m, 8H), 0.92−0.86 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.4, 76.2, 70.4, 36.1, 31.2, 28.8, 27.9, 27.9, 22.8, 22.3, 18.8, 14.1, 14.1; IR (neat) ν_{max} 3367, 2926 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{24}ONa$ $[M + Na]^+$ 219.1725, found 219.1723.

Following the same synthetic procedure used for compound **20**, compound **60a** (500 mg, 2.54 mmol) was transformed to compound **61a** using KO^{t}Bu (1.14 mg, 10.2 mmol), ^{n}BuLi (6.4 mL, 10.2 mmol), and 1,3-diaminopropane (1.04 mL, 12.7 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **61a** (358 mg, 72%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{29}_D$ +0.08 (*c* 9.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.58−3.52 (m, 1H), 2.19−1.93 (m, 2H), 1.92 (t, *J* = 2.7 Hz, 1H), 1.55−1.24 (m, 16H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 84.8, 72.1, 68.2, 37.5, 37.3, 29.3, 28.8, 28.5, 27.9, 25.6, 22.9, 18.5, 14.1; IR (neat) ν_{max} 3313, 2925, 2117 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{13}H_{24}ONa$ $[M + Na]^+$ 219.1725, found 219.1721.

Following the same synthetic procedure used for compound **5**, compound **61a** (300 mg, 1.52 mmol) was transformed to compound **62a** using Ac_2O (0.28 mL, 3.04 mmol) in pyridine (3 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 2% EtOAc in hexane as eluant) afforded compound **62a** (354 mg, 98%) as a colorless oil. R_f = 0.9 (5% EtOAc in hexane); $[\alpha]^{25}_D$ +0.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.88−4.80 (m, 1H), 2.19−2.13 (m, 2H), 2.02 (s, 3H), 1.92 (t, *J* = 2.7 Hz, 1H), 1.53−1.46 (m, 6H), 1.39−1.27 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.0, 84.7, 74.4, 68.2, 34.2, 33.9, 29.1, 28.7, 28.5, 27.6, 25.3, 22.7, 21.4, 18.5, 14.1; IR (neat) ν_{max} 3310, 2933, 2117, 1731 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{26}O_2Na$ $[M + Na]^+$ 261.1830, found 261.1826.

(*R*)-Dodec-11-yn-5-yl Acetate (62b). Following the same synthetic procedure used for compound **19**, epoxide **18** (450 mg, 4.5 mmol) was transformed to compound **60b** using 1-hexyne (0.57 mL, 5.0 mmol), ^{n}BuLi (3 mL, 4.8 mmol, 1.6 M in hexane), and $BF_3{\cdot}OEt_2$ (0.6 mL, 4.8 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **60b** (705 mg, 86%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{29}_D$ −9.2 (*c* 1.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.71−3.63 (m, 1H), 2.42−2.34 (m, 1H), 2.29−2.20 (m, 1H), 2.19−2.13 (m, 2H), 1.99 (s, 1H), 1.54−1.37 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.3, 76.2, 70.3, 36.0, 31.2, 27.9, 27.9, 22.8, 22.1, 18.5, 14.1, 13.7; IR (neat) ν_{max} 3370, 2925 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{22}ONa$ $[M + Na]^+$ 205.1568, found 205.1573.

Following the same synthetic procedure used for compound **20**, compound **60b** (500 mg, 2.74 mmol) was transformed to compound **61b** using KO^{t}Bu (1.23 g, 11.0 mmol), ^{n}BuLi (6.9 mL, 11.0 mmol, 1.6 M in hexane), and 1,3-diaminopropane (1.12 mL, 13.7 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **61b** (380 mg, 76%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{29}_D$ −3.2 (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.63−3.54 (m, 1H), 2.21−2.14 (m, 2H), 1.94−1.76 (m, 1H), 1.54−1.41 (m, 10H), 1.35−1.25 (m, 6H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 84.8, 72.0, 68.3, 37.4, 37.4, 28.9, 28.5, 27.9, 25.3, 22.9, 18.5, 14.1; IR (neat) ν_{max} 3309, 2927, 2113 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{12}H_{22}ONa$ $[M + Na]^+$ 205.1568, found 205.1565.

Following the same procedure of synthesis used for compound **5**, compound **61b** (200 mg, 1.1 mmol) was transformed to compound **62b** using Ac_2O (0.21 mL, 2.2 mmol) in pyridine (2 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 2% EtOAc in hexane as eluant) afforded compound **62b** (244 mg, 99%) as a colorless oil. R_f = 0.9 (5% EtOAc in hexane); $[\alpha]^{28}_D$ −0.3 (*c* 1.35, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.80−4.72 (m, 1H), 2.10−2.05 (m, 2H), 1.93 (s, 3H), 1.84−1.66 (m, 1H), 1.47−1.38 (m, 6H), 1.35−1.12 (m, 10H), 0.78 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 84.8, 74.4, 68.3, 34.1, 33.9, 28.7, 28.5, 29.6, 24.9, 22.7, 21.4, 18.5, 14.1; IR (neat) ν_{max} 3313, 2935, 2115, 1730 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{24}O_2Na$ $[M + Na]^+$ 247.1674, found 247.1672.

(*R*)-15-((4*S*,5*R*)-5-(3-((4*S*,5*R*)-5-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)propyl)-2,2-dimethyl-1,3-dioxolan-4-yl)pentadecan-5-yl Acetate (53). Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **56**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **62a** (25 mg, 0.1 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (0.7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain compounds **63**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded compounds **63**(**a**−**d**) (45 mg, 76%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.85−5.80 (m, 1H), 5.78−5.65 (m, 2H), 5.59−5.48 (m, 1H), 5.14−5.09 (m, 1H), 4.87−4.83 (m, 2H), 4.29−4.18 (m, 3H), 4.04 (dd, *J* = 8.1, 6.3 Hz, 1H), 3.74−3.68 (m, 1H), 3.62−3.50 (m, 3H), 3.46−3.41 (m, 1H), 2.35−2.21 (m, 4H), 2.04 (s, 3H), 1.72 (q, *J* = 6.6 Hz, 2H), 1.57−1.50 (m, 10H), 1.47−1.41 (m, 6H), 1.36−1.33 (m, 8H), 1.29−1.23 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 137.2, 130.2, 127.9, 113.6, 109.6, 108.7, 108.3, 97.1, 76.4, 75.3, 74.8, 74.5, 73.9, 72.2, 68.9, 67.1, 34.3, 33.9, 30.9, 29.8, 29.2, 28.9, 28.5 (28.5), 28.3, 29.6, 26.9, 25.9, 25.7 (25.6), 25.4, 22.8, 22.7, 21.4, 19.7, 14.1; IR (neat) ν_{max} 2930, 2218, 1729 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4289.

Following the same synthetic procedure used for compound **21**, compounds **63**(**a**−**d**) (25 mg, 0.038 mmol) were hydrogenated to obtain compound **53** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **53** (24.7 mg, 97%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{25}_D$ −0.6 (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.87−4.83 (m, 1H), 4.28−4.24 (m, 1H), 4.18−4.13 (m, 1H), 4.10−4.01 (m, 4H), 3.75−3.68 (m, 1H), 3.63−3.57 (m, 2H), 3.55−3.51 (m, 1H), 3.48−3.41 (m, 1H), 2.04 (s, 3H), 1.72−1.70 (m, 3H), 1.52−1.49 (m, 7H), 1.45−1.42 (m, 8H), 1.36 (s, 3H), 1.33−1.29 (m, 14H), 1.28−1.25 (m, 17H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.6, 107.7, 107.5, 78.2, 77.8, 77.8, 74.9, 74.8, 74.6, 72.2, 68.9, 66.9, 34.3, 33.9, 32.1, 30.3, 29.8, 29.7, 29.5, 28.7, 27.6, 26.9, 26.4, 26.2, 26.1, 25.6, 25.5, 22.8, 21.5, 14.1; IR (neat) ν_{max} 2928, 1728 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4915.

(*R*)-14-((4*S*,5*R*)-5-(4-((4*S*,5*R*)-5-(2-(((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)butyl)-2,2-dimethyl-1,3-dioxolan-4-yl)tetradecan-5-yl Acetate (54). Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **59**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **62b** (25 mg, 0.11 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain compounds **64**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded compounds **64**(**a**−**d**) (45.6 mg, 77%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.83−5.78 (m, 1H), 5.67−5.43 (m, 1H), 5.49−5.39 (m, 1H), 5.10−5.04 (m, 1H), 4.93−4.81 (m, 2H), 4.29−4.16 (m, 3H), 4.07−4.02 (m,

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1H), 3.74−3.68 (m, 1H), 3.64−3.50 (m, 3H), 3.46−3.43 (m, 1H), 2.34−2.29 (m, 2H), 2.27−2.09 (m, 2H), 2.03 (s, 3H), 1.73−1.65 (m, 2H), 1.59−1.53 (m, 8H), 1.50−1.46 (m, 5H), 1.42 (s, 3H), 1.39−1.36 (m, 10H), 1.33−1.25 (m, 8H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 137.4, 133.6, 126.5, 113.3, 109.6, 108.5, 108.2, 96.7, 77.8, 76.4 (76.4), 75.2 (75.1), 74.9 (74.8), 74.4, 73.9, 72.5 (72.2), 68.8, 67.0, 34.2, 34.0, 30.9, 30.3, 29.8, 28.9, 28.7, 28.5, 27.6, 26.9, 25.9, 25.6, 25.0, 24.4, 22.7, 21.4, 19.6, 14.1; IR (neat) ν_{max} 2932, 22183, 1730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ [M + Na]$^+$ 685.4292, found 685.4293.

Following the same synthetic procedure used for compound **21**, compounds **64**(**a**−**d**) (25 mg, 0.037 mmol) were hydrogenated to obtain compound **54** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **53** (24 mg, 98%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{28}_D$ +5.4 (c 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.89−4.81 (m, 1H), 4.31−4.25 (m, 1H), 4.23−4.11 (m, 1H), 4.09−3.99 (m, 4H), 3.75−3.68 (m, 1H), 3.66−3.51 (m, 3H), 3.48−3.41 (m, 1H), 2.03 (s, 3H), 1.73−1.66 (m, 3H), 1.54−1.44 (m, 10H), 1.42 (s, 9H), 1.36−1.25 (m, 30H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.6, 107.7, 107.4, 78.2, 78.1, 77.9, 74.9, 74.8, 74.6, 72.6, 68.8, 66.9, 34.3, 33.9, 30.3, 29.8, 29.7, 29.7, 28.8, 27.6, 26.9, 26.6, 26.4, 26.2, 25.8, 25.6, 25.5, 22.8, 21.4, 14.1; IR (neat) ν_{max} 2930, 1726 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ [M + Na]$^+$ 693.4918, found 693.4908.

(*R*)-Tetradec-13-yn-7-yl Acetate (70a). Following the same synthetic procedure used for compound **19**, epoxide **67a** (500 mg, 4.38 mmol) was transformed to compound **68a** using 1-heptyne (0.63 mL, 4.82 mmol), ^{n}BuLi (3.0 mL, 4.82 mmol, 1.6 M in hexane) and $BF_3{\cdot}OEt_2$ (0.65 mL, 5.3 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **68a** (775 mg, 84%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.72−3.64 (m, 1H), 2.44−2.36 (m, 1H), 2.22−2.14 (m, 2H), 1.52−1.38 (m, 4H), 1.37−1.25 (m, 10H), 0.93−0.86 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.4, 76.2, 70.4, 36.4, 31.9, 31.2, 29.8, 29.4, 27.9, 25.8, 22.7, 22.1, 18.6, 14.2; IR (neat) ν_{max} 3372, 2930 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{26}ONa$ [M + Na]$^+$ 233.1881, found 233.1880.

Following the same synthetic procedure used for compound **20**, compound **68a** (450 mg, 2.14 mmol) was transformed to compound **69a** using KO^{t}Bu (960 mg, 8.56 mmol), ^{n}BuLi (5.34 mL, 8.56 mmol, 1.6 M in hexane), and 1,3-diaminopropane (0.88 mL, 10.7 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **69a** (329 mg, 73%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{25}_D$ −0.13 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59−3.51 (m, 1H), 2.22−2.16 (m, 2H), 1.93 (t, J = 2.7 Hz, 1H), 1.56−1.49 (m, 2H), 1.47−1.39 (m, 8H), 1.38−1.28 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 84.8, 72.1, 68.3, 37.7, 37.4, 31.9, 19.5, 18.9, 28.6, 25.8, 25.3, 18.5, 14.2; IR (neat) ν_{max} 3310, 2927, 2115 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{26}ONa$ [M + Na]$^+$ 233.1881, found 233.1878.

Following the same synthetic procedure used for compounds **5**, compound **69a** (100 mg, 0.47 mmol) was transformed to compound **70a** using Ac_2O (0.09 mL, 0.94 mmol) in pyridine (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 2% EtOAc in hexane as eluant) afforded compound **70a** (117 mg, 98%) as a colorless oil. R_f = 0.9 (5% EtOAc in hexane); $[\alpha]^{25}_D$ +0.3 (c 4.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.88−4.80 (m, 1H), 2.19−2.13 (m, 2H), 2.02 (s, 3H), 1.91 (t, J = 2.4 Hz, 1H), 1.55−1.46 (m, 6H), 1.41−1.25 (m, 12H), 0.86 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.0, 84.6, 77.6, 77.2, 76.7, 74.4, 68.3, 34.2, 34.1, 31.8, 29.3, 28.7, 28.4, 25.4, 24.9, 22.7, 21.4, 18.4, 14.1; IR (neat) ν_{max} 3313, 2930, 2111, 1733 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{28}O_2Na$ [M + Na]$^+$ 275.1987, found 275.1986.

(*R*)-Tetradec-13-yn-6-yl Acetate (70b). Following the same synthetic procedure used for compound **19**, epoxide **67b** (500 mg, 3.9 mmol) was transformed to compound **68b** using 1-hexyne (0.54 mL, 4.7 mmol), ^{n}BuLi (3.0 mL, 4.7 mmol, 1.6 M in hexane), and $BF_3{\cdot}OEt_2$ (0.63 mL, 5.1 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **68b** (770 mg, 83%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.72−3.64 (m, 1H), 2.44−2.36 (m, 1H), 2.31−2.22 (m, 1H), 2.19−2.13 (m, 2H), 1.61−1.41 (m, 5H), 1.38−1.25 (m, 11H), 0.92−0.87 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 83.5, 76.2, 70.4, 36.3, 31.9, 31.2, 28.8, 27.9, 25.5, 22.7, 22.3, 18.9, 14.2, 14.1; IR (neat) ν_{max} 3365, 2925 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{26}ONa$ [M + Na]$^+$ 233.1881, found 233.1883.

Following the same synthetic procedure used for compound **20**, compound **68b** (450 mg, 2.14 mmol) was transformed to compound **69b** using KO^{t}Bu (960 mg, 8.56 mmol), ^{n}BuLi (5.34 mL, 8.56 mmol, 1.6 M in hexane), and 1,3-diaminopropane (0.88 mL, 10.7 mmol) in THF (10 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% EtOAc in hexane as eluant) afforded compound **69b** (334 mg, 74%) as a colorless oil. R_f = 0.7 (10% EtOAc in hexane); $[\alpha]^{25}_D$ −2.2 (c 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59−3.51 (m, 1H), 2.21−2.16 (m, 2H), 1.93 (t, J = 2.4 Hz, 1H), 1.53−1.48 (m, 1H), 1.44−1.39 (m, 6H), 1.37−1.29 (m, 10H), 0.91−0.87 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 84.8, 72.1, 68.2, 37.6, 37.5, 32.0, 29.8, 28.8, 28.5, 25.6, 25.5, 22.8, 18.5, 14.2; IR (neat) ν_{max} 3310, 2926, 2117 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_{26}ONa$ [M + Na]$^+$ 233.1881, found 233.1880.

Following the same synthetic procedure used for compound **5**, compound **69b** (100 mg, 0.47 mmol) was transformed to compound **70b** using Ac_2O (0.09 mL, 0.94 mmol) in pyridine (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 2% EtOAc in hexane as eluant) afforded compound **70b** (118 mg, 99%) as a colorless oil. R_f = 0.9 (5% EtOAc in hexane); $[\alpha]^{29}_D$ +0.1 (c 2.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.92−4.82 (m, 1H), 2.20−2.15 (m, 2H), 2.04 (s, 3H), 1.93 (t, J = 2.7 Hz, 1H), 1.56−1.47 (m, 6H), 1.33−1.22 (m, 12H), 0.90−0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 84.8, 74.5, 68.3, 34.2, 34.2, 31.9, 29.1, 28.7, 28.5, 25.3, 25.1, 22.7, 21.4, 18.5, 14.1; IR (neat) ν_{max} 3313, 2933, 2115, 1731 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{28}O_2Na$ [M + Na]$^+$ 275.1987, found 275.1986.

(*R*)-16-((4*S*,5*R*)-5-(2-((4*S*,5*R*)-5-(2-(((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-7-yl Acetate (65). Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **49**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **70a** (28 mg, 0.11 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain compounds **71**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded compounds **71**(**a**−**d**) (44 mg, 74%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.78−5.72 (m, 1H), 5.64−5.53 (m, 3H), 5.17−5.12 (m, 1H), 5.04−5.00 (m, 1H), 4.91−4.81 (m, 2H), 4.29−4.14 (m, 2H), 4.07−4.02 (m, 1H), 3.78−3.69 (m, 1H), 3.63−3.49 (m, 3H), 3.45−3.40 (m, 1H), 2.21 (dt, J = 6.9, 1.8 Hz, 2H), 2.03 (s, 3H), 1.67−1.62 (m, 2H), 1.53−1.45 (m, 10H), 1.41−1.40 (m, 7H), 1.35−1.34 (m, 7H), 1.26−1.25 (m, 12H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.0, 136.8, 130.0, 129.2, 113.8, 109.5, 109.4, 108.6, 97.0, 75.8, 75.7, 74.9, 74.5, 74.4, 73.8, 72.3 (72.1), 68.9, 67.1, 34.3, 34.2, 31.9, 31.2, 29.8, 29.3, 29.1, 28.8, 28.5, 28.3, 26.9, 25.9, 25.7 (25.6), 25.4, 25.1, 22.7, 21.4, 19.7, 14.2; IR (neat) ν_{max} 2930, 2216, 1732 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ [M + Na]$^+$ 685.4292, found 685.4290.

Following the same synthetic procedure used for compound **21**, compounds **71**(**a**−**d**) (20 mg, 0.03 mmol) were hydrogenated to obtain compound **65** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **65** (18.2 mg, 97%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{28}_D$ +3.8 (c 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz)

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δ 4.90−4.81 (m, 1H), 4.28−4.18 (m, 2H), 4.07−4.02 (m, 4H), 3.75−3.68 (m, 1H), 3.65−3.58 (m, 2H), 3.55−3.50 (m, 1H), 3.47−3.41 (m, 1H), 2.03 (s, 3H), 1.78−1.60 (m, 3H), 1.49−1.42 (m, 14H), 1.37−1.33 (m, 10H), 1.29−1.25 (m, 25H), 0.87 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.6, 107.8, 107.5, 78.5, 78.3, 78.2, 74.9, 74.8, 74.6, 72.3, 68.8, 67.0, 34.3, 31.9, 30.3, 29.8, 29.7, 29.3, 28.7, 27.3, 26.9, 26.5, 26.1, 25.9, 25.5, 25.4, 22.7, 21.4, 14.2; IR (neat) ν_{max} 2928, 1730 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4916.

(*R*)-16-((4*S*,5*R*)-5-(2-((4*S*,5*R*)-5-(2-(((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-ethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)hexadecan-6-yl Acetate (66). Following the same synthetic procedure used for compounds **3**(**a**−**d**), compounds **49**(**a**−**d**) (50 mg, 0.09 mmol) and alkyne **70b** (28 mg, 0.11 mmol) were coupled using $Pd(Ph_3P)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (4 mg, 0.02 mmol) in Et_3N (1 mL) to obtain compounds **72**(**a**−**d**). Purification of the crude mixture using flash column chromatography (SiO_2, 100−200 mesh, 10% EtOAc in hexane as eluant) afforded compounds **72**(**a**−**d**) (45 mg, 76%) as a colorless oil. R_f = 0.3 (20% EtOAc in hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.79−5.72 (m, 1H), 5.65−5.53 (m, 3H), 5.18−5.12 (m, 1H), 5.07−4.97 (m, 1H), 4.91−4.83 (m, 2H), 4.29−4.16 (m, 2H), 4.07−4.02 (m, 1H), 3.75−3.69 (m, 1H), 3.61−3.49 (m, 3H), 3.46−3.41 (m, 1H), 2.35−2.29 (m, 2H), 2.03 (s, 3H), 1.66−1.61 (m, 4H), 1.51−1.49 (m, 7H), 1.46 (s, 2H), 1.41−1.38 (m, 8H), 1.35−1.33 (m, 7H), 1.29−1.23 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, observed minor diastereomeric peaks are given in parentheses) δ 171.1, 136.8, 130.0, 129.2, 113.8, 109.5 (109.4), 108.7 (108.6), 97.1, 76.4, 75.8, 74.9, 74.8, 74.5 (74.4), 73.9, 72.1, 68.9, 67.0, 34.3, 34.2, 31.8, 31.2, 29.8, 29.1 (29.1), 28.8, 28.5, 28.3, 26.9, 25.9, 25.8, 25.5 (25.4), 25.1, 22.9, 21.4, 14.1; IR (neat) ν_{max} 2931, 2218, 1727 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{62}O_9Na$ $[M + Na]^+$ 685.4292, found 685.4290.

Following the same synthetic procedure used for compound **21**, compounds **72**(**a**−**d**) (20 mg, 0.03 mmol) were hydrogenated to obtain compound **66** using 10 mol % Pd/C (4 mg) in EtOAc (1 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 10% EtOAc in hexane as eluant) afforded compound **66** (19 mg, 98%) as a colorless oil. R_f = 0.35 (20% EtOAc in hexane); $[\alpha]^{25}_D$ +5.8 (c 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.89−4.81 (m, 1H), 4.28−4.19 (m, 2H), 4.07−4.02 (m, 4H), 3.75−3.69 (m, 1H), 3.63−3.59 (m, 2H), 3.56−3.51 (m, 1H), 3.47−3.42 (m, 1H), 2.03 (s, 3H), 1.75−1.64 (m, 6H), 1.49−1.48 (m, 6H), 1.45−1.39 (m, 9H), 1.36−1.33 (m, 11H), 1.29−1.25 (m, 20H), 0.89 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.1, 109.5, 107.8, 107.5, 78.5, 78.4, 78.2, 74.9, 74.8, 74.6, 72.1, 68.8, 67.0, 34.3, 34.2, 31.9, 30.3, 29.8, 29.7, 28.7, 27.2, 26.9, 26.5, 26.1, 25.6, 25.5, 25.1, 22.7, 21.4, 14.1; IR (neat) ν_{max} 2930, 1727 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{70}O_9Na$ $[M + Na]^+$ 693.4918, found 693.4916.

(6*R*,17*S*,18*R*,21*S*,22*R*)-24-((*R*)-2,3-dihydroxypropoxy)-17,18,21,22-tetrahydroxytetracosan-6-yl Acetate (2). Following the same synthetic procedure used for compound **1**, compound **66** (15 mg, 0.022 mmol) was transformed to compound **2** using AcOH:H_2O (4:1, 1.0 mL). Purification of the crude mixture using flash column chromatography (SiO_2, 60−120 mesh, 5% MeOH in CH_2Cl_2 as eluant) afforded compound **2** (12 mg, 98%) as a colorless oil. R_f = 0.5 (10% MeOH in CH_2Cl_2); $[\alpha]^{22}_D$ +4.00 (c 0.4, MeOH); ^{1}H NMR (C_5D_5N, 300 MHz) δ 5.13−5.05 (m, 1H, merged in water peak), 4.38 (m, 1H), 4.24−4.18 (m, 1H), 4.14−4.07 (m, 4H), 4.04−3.94 (m, 3H), 3.93−3.82 (m, 2H), 2.57 (bd, J = 9.3 Hz, 2H), 2.41−2.35 (m, 1H), 2.18−2.09 (m, 6H), 1.95−1.94 (m, 1H), 1.89−1.79 (m, 2H), 1.58−1.50 (m, 5H), 1.34−1.21 (m, 20H), 0.81 (t, J = 6.9 Hz, 3H); ^{13}C NMR (C_5D_5N, 75 MHz) δ 170.7, 75.9, 75.2, 74.2, 73.7, 72.9, 71.9, 69.6, 64.7, 34.5, 34.4, 33.6, 31.9, 30.6, 30.3, 30.0, 29.9, 29.8, 29.8, 26.7, 25.7, 25.3, 22.7, 21.1, 14.1; IR (neat) ν_{max} 3363, 2927, 1737 cm^{-1}; HRMS (ESI) m/z calcd for $C_{29}H_{58}O_9Na$ $[M + Na]^+$ 573.3979, found 573.3975.

■ ASSOCIATED CONTENT

Supporting Information

General experimental procedure, Tables (1−6) (data described in the text), HPLC analysis of the mixture of compounds **15a** and **15b**, copies of NMR (^{1}H and ^{13}C) and HRMS of representative compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00972.

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Notes

The authors declare no competing financial interest.

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