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Enantioselective total synthesis of decytospolide A and decytospolide B using an Achmatowicz reaction†

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Enantioselective syntheses of decytospolide A and decytospolide B are described here. The current synthesis highlights an Achmatowicz rearrangement of an optically active furanyl alcohol followed by reduction of the resulting dihydropyranone hemiacetal with $BF_3{\cdot}OEt_2$ and Et_3SiH to provide the saturated tetrahydropyranyl alcohol directly. This reduction was investigated with a variety of other Lewis acids. The synthesis also features Noyori asymmetric transfer hydrogenation and Friedel–Crafts acylation. Overall, the synthesis provides ready access to the natural products and may be useful in the preparation of bioactive derivatives.

Introduction

Functionalized tetrahydropyrans are important structural features present in many bioactive natural products.[1,2] Over the years, several methods have been developed for the synthesis of substituted tetrahydropyran rings.[3–5] However, there are limitations with respect to readily available starting materials, stereo- and regiochemical issues and lack of potential for incorporation of multiple substitutions within the tetrahydropyran ring system. Additionally, many of these transformations rely on transition metals such as a Pd-catalyzed decarboxylative allylation and an indium catalysed Prins cyclization.[6,7] The Achmatowicz reaction, an oxidative ring enlargement of a furanyl alcohol, has been developed into a very practical reaction with immense potential.[8,9] In recent years, the Achmatowicz reaction has been utilized in the synthesis of a variety of natural products.[10,11] We have utilized this reaction in the synthesis of a number of bioactive natural products containing functionalized tetrahydropyran rings.[10,12,13] In particular, the Achmatowicz reaction of furanyl alcohol **1** (Fig. 1) provides dihydropyranone hemiacetal **2** which upon reduction, typically with triethylsilane in the presence of trifluoroacetic acid (TFA) provided a variety of 2,6-disubstituted dihydropyranone derivatives **3**.[10,11] Such enones have been utilized in the synthesis of bioactive natural products, including the potent anticancer agent, herboxidiene **4**.[10,13]

Thus far, dihydropyranone hemiacetal reduction provides access to a range of enones under a variety of reaction conditions.[10,11] However, the potential for reduction of an Achmatowicz reaction product enone hemiacetal to a saturated tetrahydropyran derivative and further reduction to the alcohol functionality has been scarcely explored. For further development of the Achmatowicz reaction as well as its application, we sought to synthesize 2,6-disubstituted tetrahydropyranyl alcohols as exemplified by alcohol **5** using a silane in the presence

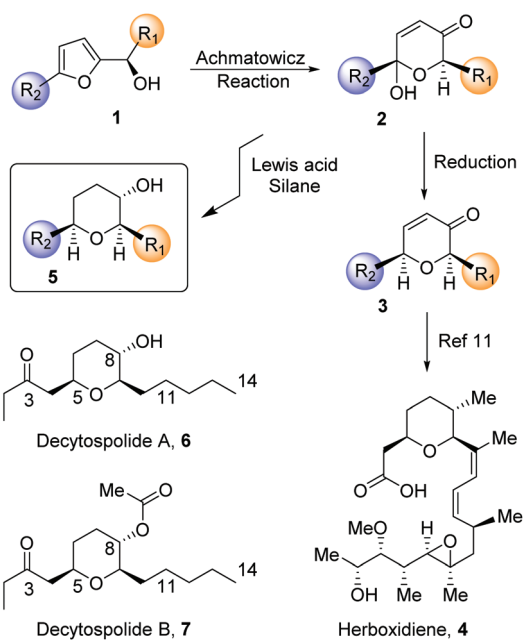

Fig. 1 Achmatowicz reaction and structures of the decytospolides.

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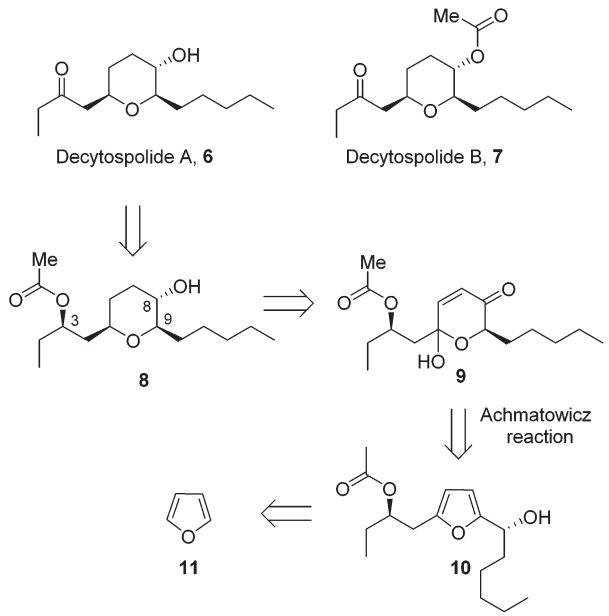
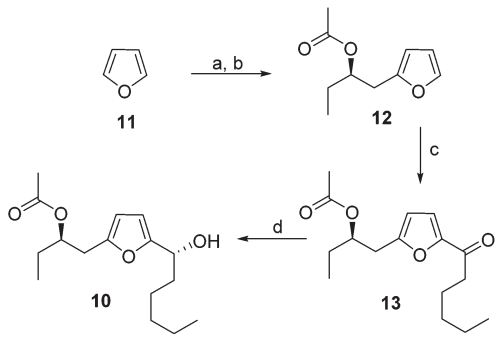
of a Lewis acid. There have been limited studies for this transformation.[14] This transformation would provide easy access to natural products containing substituted tetrahydropyran rings with three contiguous chiral centers. Such functionalized tetrahydropyran rings are imbedded in a variety of bioactive molecules, including decytospolides A (**6**) and B (7) and their derivatives.

The decytospolides contain three asymmetric centers surrounding a central tetrahydropyran ring flanked by two alkyl chains. Both natural products were recently isolated by Zhang and co-workers from the endophytic fungus, *Cytospora* sp. No ZW02, from *Ilex canariensis*, an evergreen shrub from the Canary Islands.[15] The chemical structure of both decytospolides was determined by extensive NMR studies and HRMS analysis. The absolute configuration was established through Mosher ester analysis.[15,16] Decytospolide B exhibited moderate cytotoxicity in A549 and QGY cancer cell lines with IC_{50} values of 14.8 and 46.8 μg mL^{-1}, respectively. Since decytospolide A did not show appreciable cytotoxicity, the acyl group in decytospolide B may be responsible for its moderate anticancer activity. There is potential for further improvement through modification of this acyl group. Several syntheses of these natural products have been reported.[6,7,17–19] We, however, planned to assemble the functionalized tetrahydropyran ring using the Achmatowicz reaction as the key step. Herein, we report our synthesis of decytospolides A and B using the Achmatowicz, Noyori reduction, and Friedel–Crafts reactions as the key steps. We particularly sought to synthesize 2,5,6-trisubstituted tetrahydropyran derivatives in a highly stereoselective manner in optically active form in a one-pot operation directly from the Achmatowicz product, the dihydropyranone hemiacetal.



Scheme 1 Retrosynthetic analysis of the decytospolides.



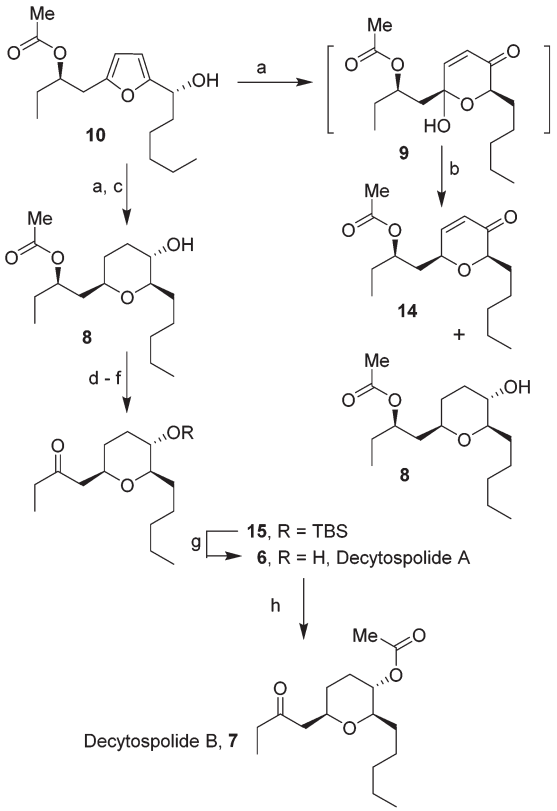
Scheme 2 Synthesis of alcohol **10**. Reagents and conditions: (a) (*R*)-1,2-Epoxybutane, *n*-BuLi, THF, 0 °C to 23 °C; (b) Ac_2O, Et_3N, DMAP, CH_2Cl_2, (84%, 2-steps); (c) $C_5H_{11}COCl$, $SnCl_4$, CH_2Cl_2, 0 °C (75%); (d) RuCl(mesitylene)[(*R*,*R*)-Ts-DPEN], (1 mol%), HCO_2H, Et_3N, CH_2Cl_2, 55° C (93%).

Results and discussion

Our synthetic strategies to decytospolides A and B is shown in Scheme 1. We planned to synthesize trisubstituted tetrahydropyran alcohol **8** in an optically active manner by reduction of dihydropyran hemiacetal **9** which would be obtained directly from furanyl alcohol **10** using an Achmatowicz rearrangement. We particularly planned to synthesize alcohol **8** stereoselectively from dihydropyran hemiacetal **9**.[10,11] Furan derivative **10** would be synthesized from furan **11** by a Friedel–Crafts acylation followed by asymmetric reduction.[20]

The synthesis of furanyl alcohol **10** in optically active form is shown in Scheme 2. Deprotonation of furan **11** with *n*-BuLi in THF at 0 °C to 23 °C followed by addition of commercially available (*R*)-butylene oxide furnished the corresponding alcohol through epoxide opening. The resulting alcohol was acetylated with acetic anhydride in the presence of Et_3N and DMAP to afford furan derivative **12** in 84% yield over two steps. We specifically planned to install the C3-acetoxy group with defined stereochemistry to avoid forming a mixture of diastereomers and provide easy access to C3 stereo-defined derivatives for biological evaluation. Furan derivative **12** underwent a Friedel–Crafts acylation by reaction with hexanoyl chloride in the presence of $SnCl_4$ at 0 °C for 30 min to provide ketone derivative **13** in 75% yield.[21] For enantioselective reduction of the ketone, we planned an asymmetric transfer hydrogenation reaction developed by Noyori and co-workers.[22,23] Therefore, reaction of **13** with a catalytic (1 mol%) amount of Noyori's catalyst, (*R*,*R*) RuCl(mesitylene)-Ts-DPEN, in the presence of Et_3N and formic acid in CH_2Cl_2 at 55 °C for 12 h, furnished alcohol **10** in 93% yield. The asymmetric reduction proceeded with high diastereoselectivity as alcohol **10** was isolated as the single product by ^1H- and ^{13}C-NMR analysis (diastereoselectivity >20 : 1).

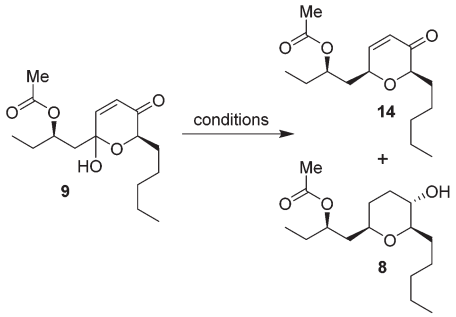
The synthesis of the decytospolides is shown in Scheme 3. Initially, the Achmatowicz reaction of **10** was carried out with a catalytic amount of $VO(acac)_2$ and ^tBuOOH; however, the reaction was sluggish.[24,25] Achmatowicz reaction with oxone in the



Scheme 3 Synthesis of the decytospolides. Reagents and conditions: (a) Oxone, KBr, $NaHCO_3$, THF/H_2O (4 : 1); (b) Et_3SiH, TFA, CH_2Cl_2, −45 °C to rt, (40%, **14**); (c) Et_3SiH, TFA, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −45 °C (47%, **8**); (d) TBSOTf, 2,6-lutidine, CH_2Cl_2, 0 °C to 23 °C; (e) K_2CO_3, MeOH; (f) DMP, $NaHCO_3$, CH_2Cl_2, 0 °C to 23 °C, (89%, 3-steps); (g) TBAF, THF, 23 °C (99%); (h) Ac_2O, pyr, DMAP, 23 °C, CH_2Cl_2 (99%).

presence of $NaHCO_3$ in a mixture (4 : 1) of THF and water at 23 °C for 30 min smoothly converted **10** to the corresponding dihydropyranone hemiacetal (**9**).[26] The resulting hemiacetal was initially subjected to reduction with Et_3SiH and TFA at −45 °C for 3 h. This resulted in a mixture of dihydropyranone **14** and a small amount of alcohol **8**. Further optimization of the reaction with an excess of $BF_3{\cdot}OEt_2$ at −45 °C for 3 h provided alcohol **8** as the exclusive product in 47% yield over 2-steps. The stereochemistry at C8 was determined by ^{1}H NMR coupling with the proton at C9, which has two J values (2.4 and 9 Hz). Having J = 9 Hz indicates a *trans* relationship between the protons at C8 and C9 and since the stereocenter at C9 was set by the Noyori reduction, the stereochemistry at C8 was assigned based on that. We then, investigated silane reduction of the dihydropyranone hemiacetal **9** in the presence of a number of other Lewis acids. The results are shown in Table 1. As can be seen, the use of $BF_3{\cdot}OEt_2$ and $SnCl_4$ as the Lewis acids provided alcohol **8** exclusively in 56% and 82% yield, respectively (entries 3 and 4). Reductions with Lewis acids $Sc(OTf)_3$ and $Cu(OTf)_2$ yielded only trace amounts of dihydropyranone **14**, while using $TiCl_4$ as the Lewis acid gave 14% of **14**.

Table 1 Reduction of the dihydropyranone hemiacetal **9** with various Lewis acids[a]

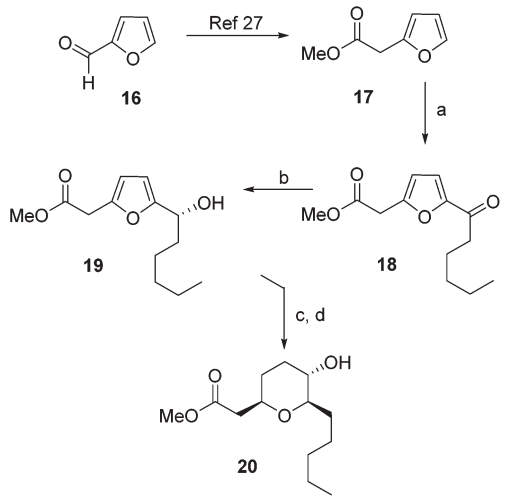


Entry	Lewis acid (equiv.)	Et_3SiH (equiv.)	Time	Yield for enone **14**	Yield for THP **8**
1	TFA [15]	5	24 h	40%	Trace
2	TFA [15]	5, then	4 h	None	47%
	$BF_3{\cdot}OEt_2$ [3]	5 more			
3	$BF_3{\cdot}OEt_2$ [6]	10	6 h	None	56%
4	$SnCl_4$ [6]	10	4 h	None	82%
5	$Cu(OTf)_2$ [6]	10	18 h	Trace	None
6	$TiCl_4$ [6]	10	18 h	14%	None
7	$Sc(OTf)_3$ [6]	10	18 h	Trace	None

[a] All reactions were carried out in CH_2Cl_2 at −45 °C.

To complete the synthesis of the decytospolides, alcohol **8** was protected as a TBS-ether with TBSOTf in the presence of 2,6-lutidine in CH_2Cl_2 at 0 °C to 23 °C for 12 h. The acetate was hydrolyzed with K_2CO_3 in MeOH at 23 °C to provide the corresponding alcohol. Oxidation of the resulting alcohol with Dess–Martin periodinane (DMP) in the presence of $NaHCO_3$ in CH_2Cl_2 furnished ketone **15** in 89% yield over 3-steps. Removal of the silyl ether was carried out with tetrabutylammonium fluoride (TBAF) in THF at 23 °C for 12 h to provide decytospolide A (**6**) {$[\alpha]_D^{23}$ +18.4 (*c* 0.45, $CHCl_3$)} in quantitative yield. Treatment of decytospolide A (**6**) with acetic anhydride in the presence of pyridine and DMAP in CH_2Cl_2 at 23 °C for 1.5 h furnished decytospolide B (**7**) {$[\alpha]_D^{23}$ +28.4 (*c* 0.75, $CHCl_3$)} in quantitative yield. The ^{1}H- and ^{13}C-NMR spectra of synthetic decytospolides are in complete agreement with the spectra reported for the natural decytospolide A {$[\alpha]_D^{20}$ +6.1 (*c* 0.08, $CHCl_3$)} and decytospolide B {$[\alpha]_D^{20}$ +26.6 (*c* 0.02, $CHCl_3$)}.[14]

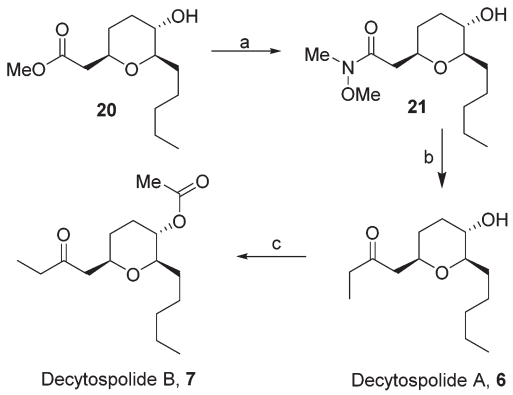
We also investigated an alternative route to the decytospolides in an effort to synthesize the saturated tetrahydropyranol directly following the Achmatowicz reaction. As shown in Scheme 4, commercially available furfural, was converted to furanyl methyl acetate **17** by a one-carbon homologation using a Jocic reaction as developed by Snowden and co-workers.[27,28] Methyl ester **17** is also commercially available. Methyl ester **17** was reacted with hexanoyl chloride in the presence of $SnCl_4$ as described above to provide furanyl-ketone **18** in 57% yield. Reduction of ketone **18** using Noyori's catalyst RuCl(mesitylene)[(*R*,*R*)-Ts-DPEN] (1 mol%) in the presence of Et_3N and formic acid at 50 °C for 12 h afforded optically active furanyl alcohol **19** in 83% yield and 99% *ee* determined by chiral



Scheme 4 Synthesis of alcohol **20**. Reagents and conditions: (a) $C_5H_{11}COCl$, $SnCl_4$, CH_2Cl_2, 0 °C (57%); (b) RuCl(mesitylene)[(*R*,*R*)-Ts-DPEN], (1 mol%), Et_3N, HCO_2H, CH_2Cl_2, 50 °C, 12 h (83%, 99% *ee*); (c) KBr, $NaHCO_3$, oxone, THF/H_2O (4 : 1), 0 °C to 23 °C, 3 h; (d) $BF_3{\cdot}OEt_2$, Et_3SiH, CH_2Cl_2, −40 °C, 16 h (58%, over 2-steps).

HPLC analysis (please see Experimental section for details).[20,21] Achmatowicz reaction of **19** with oxone at 23 °C for 30 min furnished the corresponding dihydropyranone hemiacetal which was subjected to reduction with excess Et_3SiH in the presence of $BF_3{\cdot}OEt_2$ at −40 °C for 16 h to provide saturated tetrahydropyranol derivative **20** as a single product by ^{1}H-NMR analysis. Presumably, the reduction of enone first provided the ketone which was reduced by Lewis acid chelation followed by axial delivery of hydride.

Tetrahydropyranol derivative **20** was readily converted to the decytospolides as shown in Scheme 5. Reaction of methyl ester **20** with NH(OMe)Me·HCl in the presence of *i*-PrMgCl in THF at −30 °C for 5 h provided Weinreb amide derivative **21**. Treatment of Weinreb amide **21** with EtMgBr in THF at 0 °C to 23 °C for 5 h afforded decytospolide A, **6** in 97% yield {$[\alpha]_D^{23}$ +7.8 (*c*, 1.33, $CHCl_3$)}. Acylation of **6** with acetic anhydride in the presence of pyridine and DMAP furnished decytospolide B, **7** {$[\alpha]_D^{23}$ +22.8 (*c*, 1.96, $CHCl_3$)} in 86% yield. The ^{1}H-NMR and ^{13}C-NMR spectra of these synthetic decytospolides are in complete agreement with reported spectra for the natural products.[14]



Scheme 5 Synthesis of decytospolides. Reagents and conditions: (a) NH(OMe)Me·HCl, *i*-PrMgCl, THF, −30 °C, 5 h (93%); (b) EtMgBr, THF, 0 °C to rt, 5 h (97%); (c) Ac_2O, pyridine, DMAP, CH_2Cl_2, 0 °C to 23 °C, 3 h (86%).

Conclusions

In summary, we have accomplished an enantioselective total synthesis of decytospolides A and B. The synthesis features an Achmatowicz rearrangement of an optically active furanyl alcohol which was obtained conveniently by use of the Friedel–Crafts reaction followed by a Noyori asymmetric transfer hydrogenation reaction as the key steps. The synthesis highlights a highly stereoselective reduction of the Achmatowicz product, a dihydropyranone hemiacetal to the saturated tetrahydropyranol derivative using $BF_3{\cdot}OEt_2$ and Et_3SiH. Reduction presumably proceeds through Lewis Acid chelation followed by delivery of an axial hydride. The current work will provide access to structural variants of these natural products for further studies. Further studies and applications are in progress in our laboratories.

Experimental section

Chemicals and reagents were purchased from commercial suppliers and used without further purification. Anhydrous solvents were obtained as follows: dichloromethane and toluene from calcium hydride, diethyl ether and tetrahydrofuran from sodium/benzophenone, and methanol from activated magnesium. All other solvents were reagent grade. All moisture-sensitive reactions were either carried out in flame- or oven-dried (120 °C) glassware under an argon atmosphere. TLC analysis was conducted using glass-backed thin-layer silica gel chromatography plates (60 Å, 250 μm thickness, F254 indicator). Column chromatography was performed using Silicycle 230–400 mesh, 60 Å pore diameter silica gel. ^{1}H and ^{13}C NMR spectra were recorded on either Bruker ARX400, Bruker DRX-500, Bruker AV500HD, or Bruker Avance-III-800 spectrometers. Chemical shift (δ values) are reported in parts per million and are referenced to the residual solvent signal ($CDCl_3$ ^{1}H singlet = 7.26, ^{13}C triplet = 77.16). Characteristic splitting patterns due to spin–spin coupling are identified as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, dq = doublet of quartets, brs = broad singlet, app = apparent. All coupling constants are measured in hertz (Hz). Optical rotations were recorded by a PerkinElmer 341 polarimeter. IR spectra were recorded on a PerkinElmer Spectrum Two FT-IR Spectrometer. LRMS and HRMS spectra were recorded at the Purdue University Department of Chemistry Mass Spectrometry Center. HPLC data was obtained on an Agilent 1290 Infinity II.

(*R*)-1-(Furan-2-yl)butan-2-yl acetate (12)

To furan (2.02 mL, 27.74 mmol) dissolved in THF (23 mL) at 0 °C was added *n*-BuLi (15.6 mL, 24.97 mmol) dropwise upon which a bright yellow color developed. After stirring for 1 h at this temperature, (*R*)-(+)-butylene oxide (1.21 mL, 13.87 mmol) was added and the reaction was slowly warmed to room temperature. After stirring for 12 h, the deep red solution was quenched with saturated NH_4Cl, extracted with EtOAc, washed with brine and dried over Na_2SO_4. Purification by column chromatography (10% EtOAc/hexanes) gave 1.69 g (87% yield) of the resulting furan alcohol as a yellow oil.

To (*R*)-furan alcohol (868 mg, 6.19 mmol) dissolved in CH_2Cl_2 (21 mL) at 0 °C was added acetic anhydride (1.2 mL, 12.4 mmol), Et_3N (1.3 mL, 9.3 mmol) and a few crystals of DMAP. The reaction was allowed to warm to room temperature. After 6 h, the reaction was quenched with saturated $NaHCO_3$, extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Purification by column chromatography (5% to 10% EtOAc/hexanes) afforded 1.1 g (97% yield) of acetate **12** as a clear oil $[\alpha]_D^{20}$ +19.6 (*c* 0.73, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (dd, J = 1.9, 0.9 Hz, 1H), 6.28 (dd, J = 3.2, 1.9 Hz, 1H), 6.05 (dd, J = 3.2, 0.9 Hz, 1H), 5.04 (m, 1H), 2.87 (d, J = 6.3 Hz, 2H), 2.02 (s, 3H), 1.65–1.55 (m, 2H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 151.9, 141.5, 110.4, 107.0, 73.8, 32.5, 26.7, 21.3, 9.7; FT-IR (neat) ν_{max} = 2965, 2925, 2852, 1738, 1507, 1461, 1436, 1376, 1239, 1012, 739 cm^{-1}.

(*R*)-1-(5-Hexanoylfuran-2-yl)butan-2-yl acetate (13)

Hexanoic acid (604 mg, 5.20 mmol) in an excess of thionyl chloride was refluxed overnight. The thionyl chloride was removed by distillation, strictly keeping the system under argon. The remaining hexanoyl chloride was used immediately for the subsequent reaction. To hexanoyl chloride (699 mg, 5.2 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added $SnCl_4$ (8.7 mL, 8.7 mmol, 1 M in CH_2Cl_2) dropwise. After stirring for 1 h at this temperature, acetate **12** (789 mg, 4.33 mmol) dissolved in CH_2Cl_2 (5 mL) was added to the reaction mixture *via* cannula and remained stirring at 0 °C. After 30 min, the red-brown solution was quenched with ice, extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Purification by column chromatography (10% to 20% EtOAc/hexanes) gave 909 mg (75% yield) of furan derivative **13** as a clear oil; $[\alpha]_D^{20}$ +16.2 (*c* 0.86, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.07 (d, J = 3.5 Hz, 1H), 6.21 (d, J = 3.5 Hz, 1H), 5.07 (quint, J = 6.4 Hz, 1H), 2.99–2.91 (m, 2H), 2.74 (t, J = 7.9 Hz, 2H), 2.02 (s, 3H), 1.72–1.66 (m, 2H), 1.65–1.59 (m, 2H), 1.34–1.31 (m, 4H), 0.92 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 189.4, 170.6, 157.0, 152.1, 118.3, 109.9, 73.2, 38.4, 32.8, 31.6, 26.9, 24.3, 22.6, 21.2, 14.0, 9.7; FT-IR (neat) ν_{max} = 2961, 2931, 2866, 1741, 1674, 1588, 1516, 1374, 1238, 1023 cm^{-1}.

(*R*)-1-(5-((*R*)-1-Hydroxyhexyl)furan-2-yl)butan-2-yl acetate (10)

To furan derivative **13** (280 mg, 1 mmol) in CH_2Cl_2 (5 mL) was sequentially added Et_3N (1.0 mL, 7.5 mmol), formic acid (0.28 mL, 7.5 mmol) and Noyori catalyst, (*R*,*R*) RuCl(mesitylene)-Ts-DPEN (6.2 mg, 0.01 mmol), and the reaction was set to reflux at 55 °C. After refluxing for 12 h, the orange solution was diluted with water, extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Purification by column chromatography (10% to 20% EtOAc/hexanes) provided 261 mg (93% yield) of alcohol **10** as a clear oil. This alcohol was obtained as a single diastereomer by ^{1}H NMR (ratio >20 : 1) $[\alpha]_D^{20}$ +13.5 (*c* 0.84, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.10 (d, J = 3.1 Hz, 1H), 5.97 (d, J = 3.1 Hz, 1H), 5.04 (m, 1H), 4.59 (q, J = 6.8 Hz, 1H), 2.88–2.80 (m, 2H), 2.01 (s, 3H), 1.92 (d, J = 5.2 Hz, 1H), 1.83–1.79 (m, 2H), 1.65–1.55 (m, 2H), 1.42 (m, 1H), 1.31–1.30 (m, 5H), 0.93–0.86 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 155.9, 151.3, 107.6, 106.7, 73.8, 68.0, 35.6, 32.6, 31.7, 26.8, 25.4, 22.7, 21.3, 14.2, 9.7; FT-IR (neat) ν_{max} = 3447, 2958, 2933, 2859, 1739, 1559, 1464, 1433, 1373, 1242, 1021, 964, 792 cm^{-1}; LRMS-ESI (+) m/z 305.1 $[M + Na]^+$.

(*R*)-1-((2*R*,5*S*,6*R*)-5-Hydroxy-6-pentyltetrahydro-2*H*-pyran-2-yl) butan-2-yl acetate (8)

To furanyl alcohol **10** (317 mg, 1.12 mmol) dissolved in THF (8 mL) and H_2O (2 mL) at 0 °C was added KBr (6.7 mg, 0.06 mmol), $NaHCO_3$ (47 mg, 0.56 mmol) and oxone (826 mg, 1.34 mmol) after which a light yellow color developed. After stirring at 0 °C for 30 min, the reaction was quenched with saturated $NaHCO_3$, extracted with EtOAc, washed with brine and dried over Na_2SO_4. The resulting crude hemiacetal **9** was used directly for the subsequent reaction.

To crude hemiacetal dissolved in CH_2Cl_2 (10 mL) at −45 °C was added Et_3SiH (0.89 mL, 5.6 mmol) and TFA (1.3 mL, 16.8 mmol) dropwise upon which a yellow color developed. The reaction was stirred at this temperature for 3 h, then was allowed to warm to room temperature. After stirring for 30 min at 23 °C, the reaction was cooled to 0 °C and additional Et_3SiH (0.895 mL, 5.6 mmol) was added followed by $BF_3{\cdot}OEt_2$ (0.415 mL, 3.36 mmol). After stirring for 30 min at 0 °C, the reaction was quenched slowly with satd. $NaHCO_3$ until the effervescence ceased. The reaction was extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Purification by column chromatography (10% to 30% EtOAc/hexanes) provided 151 mg (47% yield over two steps) of tetrahydropyran derivative **8** as a clear oil. It was obtained as a single diastereomer by ^{1}H NMR analysis (>20 : 1) $[\alpha]_D^{20}$ +2.7 (*c* 0.49, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.01 (m, 1H), 3.30–3.22 (m, 2H), 2.95 (td, J = 9.0, 2.4 Hz, 1H), 2.06 (m, 1H), 2.03 (s, 3H), 1.79 (m, 1H), 1.65–1.53 (m, 6H), 1.43–1.24 (m, 9H), 0.90–0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 170.7, 82.2, 74.1, 72.9, 70.9, 40.0, 33.3, 32.2, 32.1, 32.0, 31.8, 27.8, 25.0, 22.7, 21.3, 14.2, 9.5; FT-IR (neat) ν_{max} = 3451, 2929, 2859, 1739, 1718, 1461, 1436, 1373, 1242, 1080, 1056, 1024, 954 cm^{-1}; LRMS-ESI (+) m/z 287.1 $[M + H]^+$.

1-((2*R*,5*S*,6*R*)-5-((*tert*-Butyldimethylsilyl)oxy)-6-pentyltetrahydro-2*H*-pyran-2-yl)butan-2-one (15)

To tetrahydropyran derivative **8** (141 mg, 0.49 mmol) dissolved in CH_2Cl_2 (5 mL) at 0 °C was added 2,6-lutidine (0.23 mL, 1.97 mmol) and TBSOTf (0.34 mL, 1.48 mmol) and the reac-

tion was warmed to 23 °C. After stirring for 12 h, the reaction was quenched with saturated $NaHCO_3$, extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Purification by column chromatography (5% to 10% EtOAc/hexanes) gave 200 mg (quantitative) of the resulting silyl ether as a clear oil.

To the silyl ether (186 mg, 0.46 mmol) in MeOH (3 mL) at 0 °C was added K_2CO_3 (6.4 mg, 0.05 mmol) upon which a yellow color developed. The reaction was warmed to room temperature. After 12 h, the reaction was diluted with H_2O and EtOAc, extracted with EtOAc, washed with brine and dried over Na_2SO_4. Purification by column chromatography (5% to 20% EtOAc/hexanes) gave 155 mg (93% yield) of the resulting alcohol as a clear oil.

To the above alcohol (144 mg, 0.40 mmol) dissolved in CH_2Cl_2 (4 mL) at 0 °C was added $NaHCO_3$ (202 mg, 2.41 mmol) followed by DMP (341 mg, 0.8 mmol) and the reaction was warmed to room temperature. After 12 h, the reaction was quenched with a 1 : 1 mixture of saturated sodium thiosulfate and saturated $NaHCO_3$. The mixture was extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Purification by column chromatography (5% to 10% EtOAc/hexanes) gave 138 mg (96% yield) of ketone **15** as a clear oil $[\alpha]_D^{23}$ +32.0 (*c* 0.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.71 (m, 1H), 3.21 (m, 1H), 3.02 (m, 1H), 2.62 (dd, *J* = 14.9, 8.2 Hz, 1H), 2.53–2.41 (m, 2H), 2.36 (dd, *J* = 14.9, 4.7 Hz, 1H), 1.94 (m, 1H), 1.78–1.69 (m, 2H), 1.52–1.22 (m, 9H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.86 (s, 12H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.3, 82.5, 74.3, 71.4, 48.7, 37.2, 33.6, 32.2, 31.9, 31.5, 25.9, 25.1, 22.7, 18.1, 14.2, 7.6, −3.9, −4.6; FT-IR (neat) ν_{max} = 2954, 2929, 2855, 1721, 1464, 1376, 1253, 1105, 887, 837, 774 cm^{-1}; LRMS-ESI (+) *m*/*z* 357.3 $[M + H]^+$.

Decytospolide A (6)

To ketone **15** (126 mg, 0.35 mmol) dissolved in THF (4 mL) at 0 °C was added TBAF (0.71 mL, 0.71 mmol, 1 M in THF) and the reaction was warmed to 23 °C. After 12 h, the reaction was concentrated and purification by column chromatography (30% to 50% EtOAc/hexanes) provided 82 mg (96% yield) of decytospolide A (**6**) as a clear oil $[\alpha]_D^{23}$ +18.4 (*c* 0.45, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.72 (m, 1H), 3.24 (td, *J* = 9.8, 4.5 Hz, 1H), 3.01 (m, 1H), 2.64 (dd, *J* = 15.0, 8.1 Hz, 1H), 2.53–2.41 (m, 2H), 2.37 (dd, *J* = 15.0, 4.8 Hz, 1H), 2.06 (m, 1H), 1.81–1.69 (m, 2H), 1.54 (brs, 1H), 1.47–1.24 (m, 9H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.2, 82.3, 74.2, 70.6, 48.5, 37.2, 33.1, 32.1, 31.9, 31.4, 25.1, 22.7, 14.2, 7.6; FT-IR (neat) ν_{max} = 3447, 2929, 2859, 1714, 1457, 1376, 1077 cm^{-1}; LRMS-ESI (+) *m*/*z* 243.1 $[M + H]^+$; HRMS-ESI (+) *m*/*z* calc'd for $C_{14}H_{27}O_3$ $[M + H]^+$: 243.1955, found 243.1958.

Decytospolide B (7)

To decytospolide A (**6**) (73 mg, 0.30 mmol) dissolved in CH_2Cl_2 (3 mL) at 0 °C was added pyridine (73 μL, 0.9 mmol), acetic anhydride (85 μL, 0.9 mmol) and a few crystals of DMAP and the reaction was warmed to 23 °C. After 1.5 h, the reaction was diluted with H_2O, extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4. Purification by column chromatography (10% to 20% EtOAc/hexanes) provided 77 mg (89% yield) of decytospolide B (**7**) as a clear oil $[\alpha]_D^{20}$ +28.1 (*c* 0.75, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.43 (td, *J* = 10.0, 4.6 Hz, 1H), 3.75 (m, 1H), 3.21 (td, *J* = 9.1, 2.4 Hz, 1H), 2.66 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.52–2.40 (m, 2H), 2.36 (dd, *J* = 15.3, 4.9 Hz, 1H), 2.12 (m, 1H), 2.02 (s, 3H), 1.73 (m, 1H), 1.53–1.35 (m, 4H), 1.29–1.20 (m, 6H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 209.9, 170.4, 79.4, 74.3, 72.2, 48.3, 37.3, 32.0, 31.8, 30.9, 29.5, 24.9, 22.7, 21.3, 14.1, 7.6; FT-IR (neat) ν_{max} = 2933, 2859, 1739, 1714, 1457, 1373, 1235, 1080, 1042 cm^{-1}; LRMS-ESI (+) *m*/*z* 285.1 $[M + H]^+$; HRMS-ESI (+) *m*/*z* calc'd for $C_{16}H_{28}O_4Na$ $[M + Na]^+$: 307.1880, found 307.1884.

Methyl 2-(5-hexanoylfuran-2-yl)acetate (18)

Hexanoic acid (94 μL, 0.75 mmol) was dissolved in thionyl chloride (6 mL) and refluxed for 3 h. The excess thionyl chloride was distilled off to give the resulting hexanoyl chloride as a dark yellow oil. It was then dissolved in CH_2Cl_2 (6 mL) and cooled to 0 °C. $SnCl_4$ (1.13 mL, 1 M in CH_2Cl_2, 1.13 mmol) was then added slowly dropwise and the resulting solution stirred at 0 °C for 45 min. Methyl ester **17** (105.3 mg, 0.75 mmol) was dissolved in CH_2Cl_2 (2 mL) and the resulting solution was added slowly to the reaction over 10 min. The reaction was then stirred at 0 °C for 45 min before being quenched with ice. The biphasic mixture was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography (10% to 20% EtOAc/hexanes) to give ketone **18** (102 mg, 57%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (d, *J* = 3.5 Hz, 1H), 6.41 (d, *J* = 3.5 Hz, 1H), 3.77 (s, 2H), 3.74 (s, 3H), 2.84–2.66 (m, 2H), 1.70 (t, *J* = 7.4 Hz, 2H), 1.34 (h, *J* = 3.6 Hz, 4H), 0.90 (td, *J* = 7.1, 5.9, 3.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.3, 168.7, 152.1, 129.0 118.1, 110.7, 77.2, 76.9, 76.6, 52.4, 38.2, 34.0, 31.4, 24.1, 22.3, 13.8; ESI-API MS: [M + H] = 239.1; HRMS-ESI (+) *m*/*z* calc'd for $C_{13}H_{10}O_4$ $[M + H]^+$: 239.1280, found 239.1282.

Methyl (*R*)-2-(5-(1-hydroxyhexyl)furan-2-yl)acetate (19)

Ketone **18** (60.5 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (7 mL) and Et_3N (0.5 mL, 3.81 mmol) was added followed by HCO_2H (143 μL, 3.81 mmol). RuCl[(*R*,*R*)-TsDPEN](mesitylene) (3.9 mg, 0.006 mmol) was dissolved in CH_2Cl_2 (0.5 mL) and then added to the reaction. The reaction was then set to stir at 50 °C for 12 h before being quenched with H_2O. It was then extracted with CH_2Cl_2 and the combined organic layers washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography (10% to 30% EtOAc/hexanes) to give optically active alcohol **19** (50.3 mg, 83%) as a clear oil. $[\alpha]_D^{23}$ +2.9 (*c* 2.4, $CHCl_3$), $[\alpha]_D^{23}$ +7.9 (*c* 2.97, MeOH) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.15 (d, *J* = 0.9 Hz, 2H), 4.62 (t, *J* = 6.8 Hz, 1H), 3.71 (s, 3H), 3.66 (s, 2H), 1.98 (s, 1H), 1.88–1.74 (m, 2H), 1.43 (tdd, *J* = 10.0, 8.1, 7.5, 4.1 Hz, 1H), 1.36–1.22 (m, 5H), 0.88 (q, *J* = 4.9, 4.1 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 156.5, 146.8, 108.5, 106.6, 67.7, 52.2, 35.3, 33.8, 31.5, 25.1, 22.4, 13.9; ESI-API MS: [M + Na] = 263.1; HRMS-ESI (+) *m*/*z* calc'd for $C_{13}H_{20}O_4Na$ $[M + H]^+$: 263.1254, found 263.1256; 99% ee, determined by HPLC using Chiralpak IA3 and gradient of 0–10% isopropanol/hexanes (t_{major} = 25.7 min, t_{minor} = 24.8 min).

Methyl 2-((2*R*,5*S*,6*R*)-5-hydroxy-6-pentyltetrahydro-2*H*-pyran-2-yl)acetate (20)

Furanyl alcohol **19** (16.9 mg, 0.07 mmol) was dissolved in THF (2 mL) and H_2O (0.5 mL) and cooled to 0 °C. KBr (0.4 mg, 0.003 mmol), $NaHCO_3$ (2.9 mg, 0.03 mmol) and oxone (51.9 mg, 0.08 mmol) were then added and the reaction slowly warmed to 23 °C. After 3 h, it was quenched with saturated $NaHCO_3$ and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was used immediately for the next reaction.

The crude oil was dissolved in CH_2Cl_2 (3 mL) and Et_3SiH (112 μL, 0.7 mmol) was added. The reaction was then cooled to −40 °C and $BF_3{\cdot}OEt_2$ (52 μL, 0.42 mmol) was added slowly dropwise. The reaction was then stirred at −40 °C for 16 h before being warmed to 23 °C and stirred for an additional 1 h. It was then quenched with saturated NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography (20% to 30% EtOAc/hexanes) give tetrahydropyran derivative **20** (10.0 mg, 58%) as a clear oil. $[\alpha]_D^{23}$ +27.5 (*c* 2.57, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.80–3.69 (m, 1H), 3.67 (s, 3H), 3.27 (ddd, *J* = 10.4, 8.9, 4.6 Hz, 1H), 3.04 (td, *J* = 9.0, 2.4 Hz, 1H), 2.53 (dd, *J* = 14.9, 8.0 Hz, 1H), 2.40 (dd, *J* = 14.9, 5.4 Hz, 1H), 2.13–2.01 (m, 1H), 1.85–1.72 (m, 2H), 1.54–1.29 (m, 3H), 1.32–1.22 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 82.1, 73.8, 70.4, 51.5, 40.8, 32.7, 31.7, 31.6, 30.8, 24.8, 22.6, 13.9; ESI-API MS: [M + H] = 245.1, [M + Na] = 267.1; HRMS-ESI (+) *m*/*z* calc'd for $C_{13}H_{25}O_4$ $[M + H]^+$: 245.1747, found 245.1750.

2-((2*R*,5*S*,6*R*)-5-Hydroxy-6-pentyltetrahydro-2*H*-pyran-2-yl)-*N*-methoxy-*N*-methylacetamide (21)

To a solution of NH(OMe)Me·HCl (16.0 mg, 0.16 mmol) in dry THF (3 mL) and cooled to −30 °C, *i*-PrMgCl (450 μL, 0.45 mmol) was added slowly dropwise and the reaction stirred at −30 °C for 1 h. Methyl ester **20** (10 mg, 0.04 mmol) was dissolved in dry THF and then added slowly, dropwise to the reaction which was stirred at −30 °C for an additional 4 h before being quenched with saturated NH_4Cl. It was extracted with EtOAc and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography (50% to 80% EtOAc/hexanes) to give Weinreb amide **21** (10.4 mg, 93%) as a clear oil. $[\alpha]_D^{23}$ +7.8 (*c* 1.33, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 3.85–3.80 (m, 1H), 3.71 (d, *J* = 2.2 Hz, 3H), 3.32–3.27 (m, 1H), 3.20 (s, 3H), 3.09 (ddd, *J* = 8.9, 6.5, 2.5 Hz, 1H), 2.85 (d, *J* = 13.4 Hz, 1H), 2.43 (dd, *J* = 15.1, 6.3 Hz, 1H), 2.13–2.08 (m, 1H), 1.90–1.79 (m, 2H), 1.55–1.44 (m, 2H), 1.46–1.39 (m, 1H), 1.41–1.31 (m, 1H), 1.33–1.27 (m, 5H), 0.90 (td, *J* = 7.0, 2.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 82.2, 74.1, 70.6, 61.3, 37.9, 33.0, 32.0, 31.9, 31.2, 29.7, 25.0, 22.6, 14.1; ESI-API MS: [M + H] = 274.0, [M + Na] = 296.1.

Decytospolide A (6) *via* Weinreb amide 21

Weinreb amide **21** (10.4 mg, 0.038 mmol) was dissolved in dry THF (2 mL) and cooled to 0 °C. EtMgBr in THF solution (305 μL, 0.3 mmol) was added slowly dropwise and the reaction slowly warmed to 23 °C. It was stirred for 5 h, then quenched with saturated NH_4Cl and extracted with EtOAc. The combined organic layers were then washed with brine and dried over Na_2SO_4. The crude residue was purified by column chromatography (20% to 50% EtOAc/hexanes) to give decytospolide A, **6** (8.9 mg, 97%) as a clear oil. $[\alpha]_D^{23}$ = +7.8 (*c* 1.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (dddd, *J* = 10.2, 8.0, 4.8, 2.0 Hz, 1H), 3.25 (ddd, *J* = 10.6, 9.0, 4.6 Hz, 1H), 3.02 (td, *J* = 8.9, 2.5 Hz, 1H), 2.65 (dd, *J* = 15.0, 8.1 Hz, 1H), 2.58–2.29 (m, 3H), 2.07 (ddd, *J* = 12.0, 5.5, 2.8 Hz, 1H), 1.85–1.70 (m, 2H), 1.53–1.41 (m, 1H), 1.46 (s, 2H), 1.44–1.33 (m, 1H), 1.37–1.24 (m, 5H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.93–0.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 82.0, 74.0, 70.4, 48.2, 36.9, 32.8, 31.8, 31.7, 31.1, 24.9, 22.5, 13.9, 7.4; ESI-API MS: [M + H] = 243.1, [M + Na] = 265.1; HRMS-ESI (+) *m*/*z* calc'd for $C_{14}H_{27}O_3$ $[M + H]^+$: 243.1955, found 243.1958.

Decytospolide B (7) *via* Weinreb amide 21

Above synthetic decytospolide A (9.7 mg, 0.04 mmol) was dissolved in CH_2Cl_2 (3 mL) and cooled to 0 °C. Pyridine (10 μL, 0.12 mmol), Ac_2O (4 μL, 0.04 mmol) and a few crystals of DMAP were added and the reaction warmed to 23 °C. The reaction was stirred for 3 h before being quenched with water. It was extracted with CH_2Cl_2 and the combined organic layers washed with brine and dried over Na_2SO_4. The crude residue was purified by column chromatography (10 to 30% EtOAc/hexanes) to give **7** (9.8 mg, 86%) as a clear oil. $[\alpha]_D^{20}$ = +22.8 in $CHCl_3$ (*c* 1.96); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 (td, *J* = 10.0, 4.7 Hz, 1H), 3.76 (ddd, *J* = 10.9, 7.8, 4.9 Hz, 1H), 3.22 (td, *J* = 9.0, 2.6 Hz, 1H), 2.67 (dd, *J* = 15.2, 8.0 Hz, 1H), 2.58–2.33 (m, 3H), 2.13 (ddd, *J* = 11.3, 5.6, 3.3 Hz, 1H), 2.03 (s, 3H), 1.79–1.70 (m, 1H), 1.58–1.36 (m, 3H), 1.40–1.17 (m, 7H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 170.2, 79.2, 74.1, 71.9, 48.1, 37.1, 31.8, 31.6, 30.7, 29.2, 24.7, 22.5, 21.1, 13.9, 7.4; ESI-API MS: [M + H] = 285.1, [M + Na] = 307.2; HRMS-ESI (+) *m*/*z* calc'd for $C_{16}H_{28}O_4Na$ $[M + Na]^+$: 307.1880, found 307.1884.

Conflicts of interest

There are no conflicts to declare.

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