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FULL PAPER

Tandem IBX-Promoted Primary Alcohol Oxidation/Opening of Intermediate β,γ-Diolcarbonate Aldehydes to (*E*)-γ-Hydroxy-α,β-enals

Anupama Kumari,[a] Sachin P. Gholap[a] and Rodney A. Fernandes*[a]

Dedication ((optional))

Abstract: A tandem IBX-promoted oxidation of primary alcohol to aldehyde and opening of intermediate β,γ-diolcarbonate aldehyde to (*E*)-γ-hydroxy-α,β-enal has been developed. Remarkably, the carbonate opening delivered exclusively (*E*)-olefin and no over-oxidation of γ-hydroxy was observed. The method developed has been extended to complete the stereoselective total synthesis of both (*S*)- and (*R*)-coriolides and D-*xylo*- and D-*arabino*-C-20 guggultetrols.

Introduction

γ-Hydroxy-α,β-enals are a group of reactive aldehydes that have dose-dependent regulatory roles, as well as detrimental effects in various cell types and organs. Their origin and cellular functions are well documented.[1] These can act as Michael acceptors and are also involved in Schiff base formation with biological nucleophiles, which very well explains their bioactivity.[1] While γ-hydroxy-α,β-enals are the degradation products of lipid peroxidation, the major product is 4-hydroxy-2*E*-nonenal (HNE), which is involved in several biological processes, oxidative stress, regulation of mitochondrial uncoupling, etc.[2,3] Apart from this, the γ-hydroxy-α,β-enal moiety is formally present as skeletal unit in many natural products, for e.g. as vicinal diene-hydroxy unit in coriolide **1a**,[4a] and 4-hydroxy enoic ester moiety in patulolides **1b** and **1c**,[4b,c] aspicilin **1d**,[4d] cineromycin B **1e**,[4e] albocycline **1f**,[4f] and macrosphelides A **1g** and E **1h**,[4g,h] etc (Figure 1). Thus, this renders the γ-hydroxy-α,β-enal as a compelling moiety on both bioactivity and synthesis fronts.

The early synthesis of γ-hydroxy-α,β-enals has been described by Esterbauer *et al.*[5] and then by Erickson[6] using conventional routes. This was followed by the work of Grée *et al.*[7a] based on alkyl Grignard addition to fumaraldehyde monodimethyl acetal. A similar approach was used by Iriye and co-workers[7b] based on orthogonal functionalization of 2-butene-1,4-diol. Wittig reaction based approaches[8a,b] and opening of β,γ-epoxy aldehyde with NaOH or Et_3N with limited examples[9a-d] are also explored. Chakraborty *et al.* employed Swen oxidation, PDC, IBX or TPAP/NMO conditions for oxidative opening of epoxide **2** in the synthesis of γ-hydroxy-α,β-enals 3 (only four examples, Scheme 1A).[9d] The recent interesting report by Sasaki and Takeda[10] involved γ-p-toluenesulfonyl-α,β-epoxysilane **2′** as acrolein

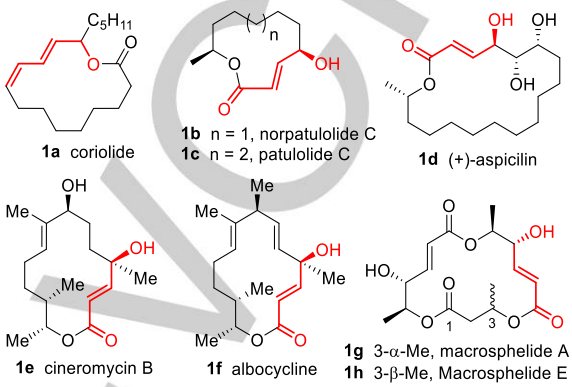
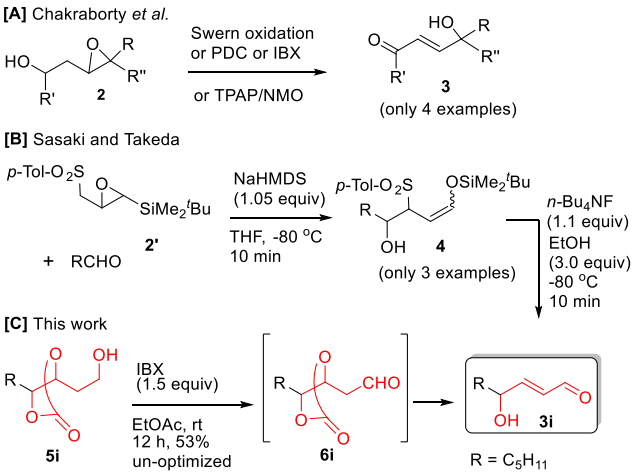


Figure 1. Natural Products with Formal γ-Hydroxy-α,β-enal Moiety

β-anion equivalent for a tandem base-promoted Brook-type epoxide opening, allylsilane-based aldehyde allylation and subsequent γ-*p*-toluenesulfonyl elimination, giving the γ-hydroxy-α,β-enals **3**, in one-pot manner (Scheme 1B). Our work reported herein, on preparing γ-hydroxy-α,β-enals was a serendipitous discovery. In the 2-iodoxybenzoic acid (IBX) oxidation of compound **5i** (R = C_5H_{11}) to get aldehyde **6i**, we observed exclusive formation of γ-hydroxy-α,β-enal **3i**, stereoselectively with (*E*)-olefin bond (Scheme 1C). The reaction involved IBX-promoted primary alcohol oxidation/opening of intermediate β,γ-diolcarbonate aldehyde providing stereoselectively (*E*)-γ-hydroxy-α,β-enal. IBX-mediated oxidation of saturated carbonyl compounds to α,β-unsaturated carbonyls has been developed by Nicolaou *et al.*[11] This method may not be applicable for γ-hydroxy-α,β-enals synthesis (γ-hydroxy being susceptible to oxidation). Our work compliments Takeda's approach and is simpler in terms of starting materials required and reagents involved. No over-oxidation of the γ-hydroxy group was observed. Hence we took up this reaction for further optimization and to study its scope and applications in natural product synthesis.



Scheme 1. Methods for the Synthesis of γ-Hydroxy-α,β-enals

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X-ray data and NMR spectra (PDF)

Accession Codes

CCDC 1882370 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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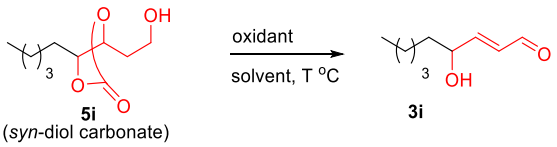
Results and Discussion

We chose compound **5i** to investigate various oxidants and to optimize the reaction conditions. In EtOAc, of the various oxidants investigated (Table 1, entries 1–6), IBX and Des-Martin periodinane (DMP) provided reasonable yields of **3i** (entries 1 and 2). $PhI(OAc)_2$ with TEMPO or oxone was not successful for this reaction (entries 5 and 6) and the substare **5i** was mostly recovered, in the latter case even after reflux. IBX (1.5 equiv) in different solvents (entries 7–13) was next examined and EtOAc (entry 1) was revealed as the best solvent. In 1,2-dichloroethane (DCE) solvent under reflux, trace of furan product was isolated, which may get formed through the hydroxy-enal cyclization. Increase in reaction temperature from room temperature to 60 °C increased the yield marginally (entry 1 v/s 14). Further use of additives such as NaOAc, pyridine, *p*-TsOH or DMSO at 60 °C did not improve the yield (entries 15–18). A reaction at reflux conditions improved the yield of **3i** to 81% (entry 19). An increase in amount of IBX (entries 20–22) showed best results with 2.0 equiv IBX providing **3i** in 94% yield in a 3 h reaction (entry 20). The higher loading of IBX over 2.0 equiv was not beneficial.

Table 1. Screening of Reaction Conditions.[a]

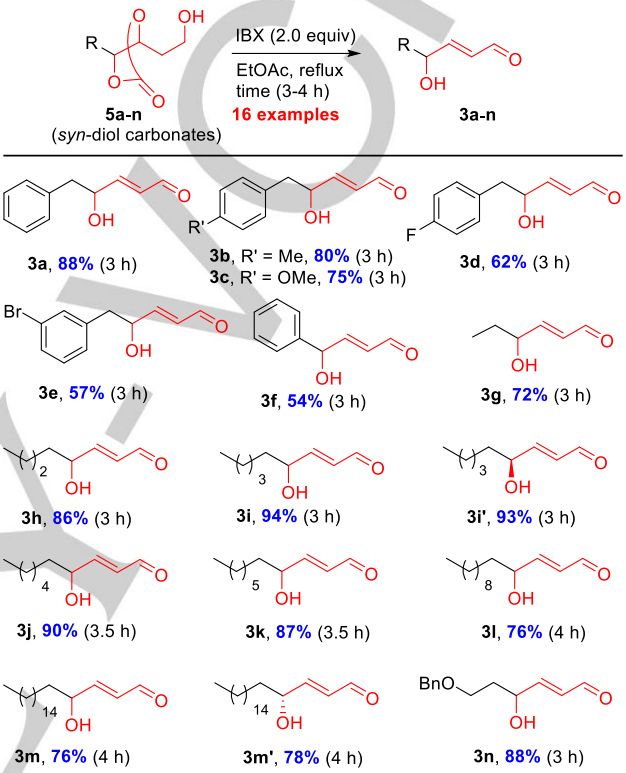


5i (*syn*-diol carbonate) **3i**

Entry	Oxidant (equiv)	Solvent	T (° C)	Time (h)	Yield[b] **3i** (%)
1	IBX (1.5)	EtOAc	rt	12	53
2	DMP (1.5)	EtOAc	rt	4	32
3	PDC (1.5)	EtOAc	rt	6	16
4	PCC (1.5)	EtOAc	rt	8	24
5	TEMPO (1.5)/ $PhI(OAc)_2$ (1.5)	EtOAc	rt	8	complex mixture
6	$PhI(OAc)_2$(1.5)/ Oxone(1.5)	EtOAc	rt-reflux	50	NR
7	IBX (1.5)	CH_2Cl_2	rt	12	36
8	IBX (1.5)	DCE	rt-reflux	30	15[c]
9	IBX (1.5)	THF	rt	13	40
10	IBX (1.5)	CH_3CN	rt	13	6
11	IBX (1.5)	DMSO	rt	15	5
12	IBX (1.5)	Benzene	rt	30	21
13	IBX (1.5)	Acetone	rt	20	NR
14	IBX (1.5)	EtOAc	60	14	59
15	IBX (1.5)/ NaOAc (1.0)	EtOAc	60	8	19
16	IBX (1.5)/ Pyr (1.0)	EtOAc	60	8	49
17	IBX (1.5)/ *p*-TsOH (1.0)	EtOAc	60	9	37
18	IBX (1.5)/ DMSO (1.0)	EtOAc	60	7	48
19	IBX (1.5)	EtOAc	reflux	8	81
20	IBX (2.0)	EtOAc	reflux	3	94
21	IBX (2.5)	EtOAc	reflux	3	94
22	IBX (3.0)	EtOAc	reflux	2.5	93

[a]Reaction conditions: **5i** (1.0 mmol), oxidant (1.5–3.0 equiv), solvent, rt–reflux, 2.5–30 h. [b]Isolated yield. [c]Traces of furan product observed. NR = No reaction, rt = room temperature

With the optimized conditions, the scope of this tandem oxidation of primary alcohol/subsequent opening of intermediate diol carbonate aldehyde was investigated. As shown in Scheme 2, the IBX-promoted reaction of various diolcarbonates **5a-n** with aliphatic or aryl groups delivered the γ-hydroxy-α,β-enals **3a-n** in good to excellent yields in 3-4 h reactions. A few chiral vicinal diol-carbonates **5i′** and **5m′** prepared through Sharpless asymmetric dihydroxylation, yielded the chiral γ-hydroxy-α,β-enals **3i′** and **3m′** in 93 and 78% yields, respectively with no loss in optical purity at the γ-hydroxy centre.



Scheme 2. Substrate Scope for γ-Hydroxy-α,β-unsaturated Aldehyde Synthesis. Reaction Conditions: **5a-n** (1.0 mmol), IBX (2.0 equiv), EtOAc, reflux, 3-4 h.

A selectivity reaction was investigated with acetonide group v/s the carbonate (Scheme 3). The reaction of 1,2-diol-acetonide compound (prepared from **7i**) with IBX (2.0 equiv) delivered the aldehyde **8i** with no opening of the acetonide moiety. In the carbonate case **5m**, a reaction quenched after 1 h showed the presence of starting material **5m** and the carbonate aldehyde **6m** in 1:1.5 ratio. The reaction for 3 h, with the complete consumption of **5m** showed the presence of product **3m** and the intermediate **6m** in 5:1 ratio. Further continuation of this reaction for another 1 h resulted in complete conversion to **3m**. Thus, the reaction involves first oxidation of primary hydroxy to the aldehyde followed by opening of the carbonate to give the enal **3m**. The reaction also requires the presence of the labile carbonate rather than the acetonide. The 1,2-diol carbonates used in this study were prepared by *cis*-dihydroxylation of (*E*)-olefins (see Experimental Section). The IBX-mediated reaction resulted exclusively in (*E*)-αβ-unsaturated aldehydes. To determine the stereospecificity of the reaction, we prepared the *anti*-diol carbonate **5i″** (through *cis*-dihydroxylation of *cis*-olefin) and subjected to IBX oxidation (Scheme 3). This resulted in the same product, (*E*)-αβ-unsaturated aldehyde **3i** in 80% yield. Thus, the reaction is not stereospecific with regards to relative stereochemistry of the diol carbonate and the geometry of olefin formed in the enal.

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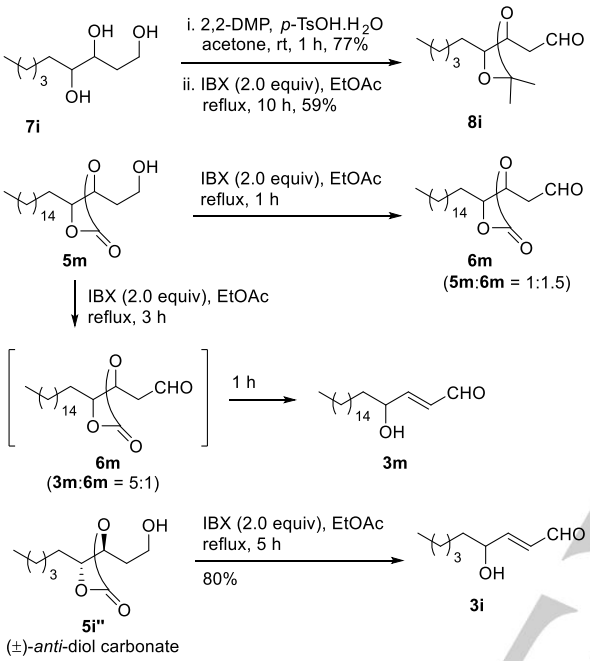
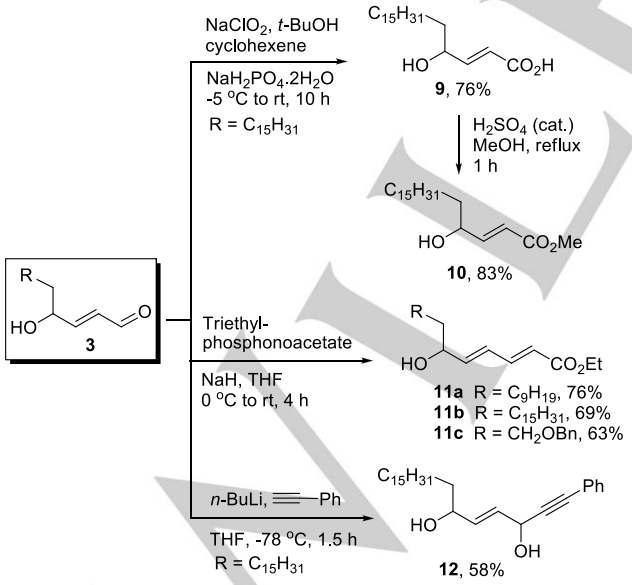
We further considered the synthetic modifications of the γ-hydroxy-α,β-enal compounds (Scheme 4). Pinnick oxidation of aldehyde group of **3m** delivered the corresponding γ-hydroxy-α,β-unsaturated acid **9** in 76% yield. Further esterification of **9** gave the γ-hydroxy-β,γ-unsaturated ester **10** in 83% yield. Homologation of enals **3l**, **3m** and **3n** with the ylide from triethylphosphonoacetate gave the dienoates **11a**, **11b** and **11c**, respectively in 63-76% yields. Addition of lithiated phenylacetylene to enal **3m** furnished the skipped ene-yne alcohol **12** in 58% yield, with no conjugate addition being observed.

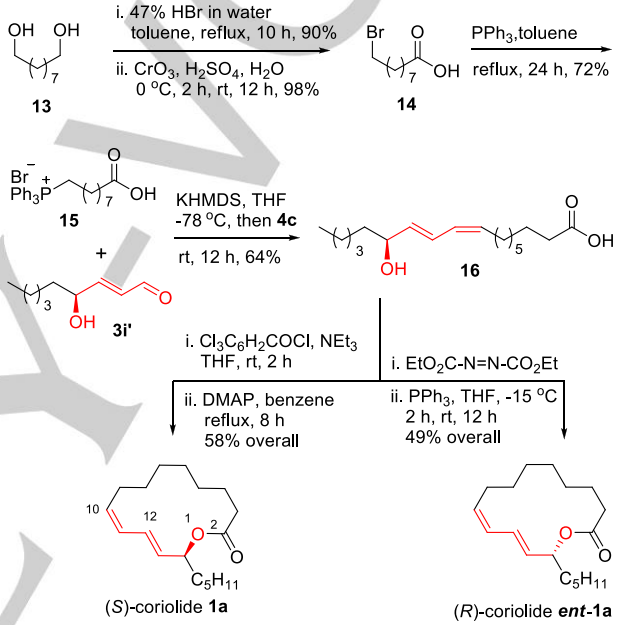


Scheme 3. Selectivity Experiments and Stepwise Formation of **3m**



Scheme 4. Synthetic Modifications of γ-Hydroxy-α,β-enals

The application of a synthetic methodology toward the synthesis of natural products is an important validation of its synthetic potential and usefulness. Thus, the developed reaction was also utilized in the total synthesis of both enantiomers of coriolide. It is a major component in the scent gland extracts of the male long wing tropical butterflies, *Heliconius pachinus.*[4a,12] It was also isolated from the seed oil of *Monninae marginata* (polygalaceae), a plant native to Uruguay.[13] A few syntheses of coriolide are reported in the literature.[12,14] Our synthesis started from 1,9-nonanediol **13**, which on monobromination (90%) and further oxidation of the remaining hydroxy group delivered the carboxylic acid **14** in 98% yield (Scheme 5). The phosphonium salt **15** was prepared from bromo acid **14** in 72% yield. This was converted into its ylide using KHMDS and reacted with the (*S*)-γ-hydroxy-α,β-enal **3i'** at –78 °C to provide stereoselectively the *Z*,*E*-diene acid **16** in 64% yield. The latter on macrolactonization by the Yamaguchi method[15] afforded (*S*)-coriolide **1a** in 58% yield.[14b] On the other hand, inversion-cyclization of **16** under Mitsunobu's conditions[16] delivered (*R*)-coriolide ***ent*-1a**.[14b]



Scheme 5. Total Synthesis of (*S*)-and (*R*)-Coriolides

Further, the total synthesis of D-*xylo*- and D-*arabino*-C20 guggultetrols was undertaken. These are long chain aliphatic 1,2,3,4-tetrols, with the former as major naturally occurring lipid isolated from the gum resin of the tree *Commiphora mukul*, known as guggul.[17] It has been used in Ayurveda, the ancient Indian medicinal system for the treatment of inflammation, rheumatoid arthritis, obesity, and disorders of lipid metabolism besides several other ailments.[18] The C18 and C20 guggultetrols have been synthesized before by various methods.[19] Our synthesis of C20 guggultetrol is shown in Scheme 6. The reduction of the aldehyde group in compound **3m'** with DIBAL-H gave the ene-diol **17** in 80% yield. This was converted into its diacetate **18** (85% yield) and then subjected to asymmetric dihydroxylation using $(DHQ)_2$-PHAL ligand to afford the diol diacetate **19**, which without further purification was converted into its tetraacetate as a diastereomer mixture (dr = 9:1). The mixture was separated by column chromatography to furnish the D-*xylo*-C20 guggultetrol tetraacetate **20a**[20] in 70% overall yield. The minor diastereomer D-*arabino*-C20 guggultetrol **20b** was obtained in 8% yield. While compound **17** could be subjected directly for dihydroxylation, the tetrol product purification was hampered due to its high polarity and resulted in lower yields of the tetraacetate in the subsequent reaction. The stepwise conversion, first into the diacetate and then dihydroxylation resulted in better overall yields and diastereomeric ratio.

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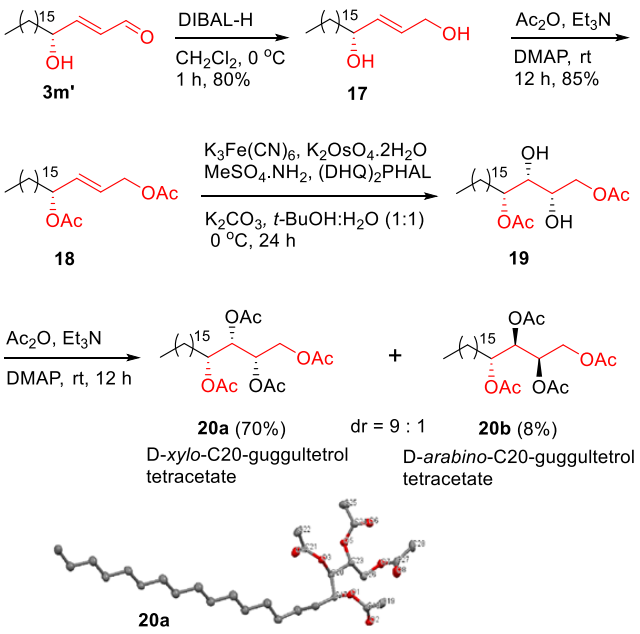


Scheme 6. Total Synthesis of D-*xylo*- and D-*arabino*-C20 Guggultetrol Tetraacetates

Conclusions

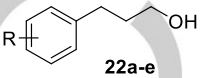
In summary, in this paper we have executed an interesting chemistry of IBX promoted primary alcohol oxidation to aldehyde and the subsequent opening of the intermediate β,γ-diolcarbonate aldehyde to give stereoselectively the (*E*)-γ-hydroxy-α,β-enals. These are important compounds for their inherent bioactivity and also as useful synthons in natural products synthesis. This has been demonstrated by completing the total synthesis of both enantiomers of coriolide and the C20 D-*xylo*- and D-*arabino*-guggultetrol tetraacetates.

Experimental Section

General information. Solvents were dried by using standard procedures. Thin-layer chromatography was performed on EM 250 Kieselgel 60 F254 silica gel plates. The spots were visualized by staining with $KMnO_4$ or by using a UV lamp. ^{1}H-NMR and ^{13}C-NMR were recorded with a spectrometer operating at 400 or 500 and 100 or 125 MHz for proton and carbon nuclei, respectively. The chemical shifts are based on the TMS peak at δ = 0.00 pm for proton NMR and the $CDCl_3$ peak at δ = 77.00 ppm (t) for carbon NMR. For other deuterated solvents the standard chemical shifts were considered. IR spectra were obtained on an FT-IR spectrometer. Optical rotations were measured using sodium D-line (589 nm). HRMS (ESI-TOF) spectra were recorded using positive electrospray ionization by the TOF method. The enantiomeric excess was determined by the HPLC method using Chiralpak OD-H or AD-H columns at wavelength 230 nm.

General Procedure for the Synthesis of Alcohols (22a-e). To a stirred solution of malonic acid (2.71 g, 26.0 mmol, 1.3 equiv) in pyridine (4 mL) was added piperidine (0.2 mL, 2.0 mmol, 0.1 equiv) and then aryl aldehyde **21a-e** (20 mmol) drop wise under N_2 atmosphere. The resulting mixture was stirred for 6 h at 85 °C, when TLC indicated the disappearance of the starting material. The mixture was cooled to room temperature and neutralized with 10% aq. HCl (5 mL) to give a white solid that was filtered and washed with cold water. Recrystallization from aqueous EtOH (1:1) afforded (*E*)-3-(aryl)-acrylic acids, which were used directly for the next reaction.

To a suspension of $LiAlH_4$ (1.52 g, 40.0 mmol, 2.0 equiv) in THF (60 mL) under N_2 atmosphere at 0 °C was added the solution of above (*E*)-3-(aryl)-acrylic acids in THF (15 mL) dropwise. The resulting mixture was stirred at reflux for 6-8 h. The mixture was then cooled to room temperature and quenched with saturated aq. Na_2SO_4 solution (15 mL) at 0 °C. Then EtOAc (100 mL) was added and the mixture stirred for 1 h. It was then filtered through a sintered glass funnel and the filtrate was concentrated. The residue was purified by a silica gel column chromatography using petroleum ether/EtOAc (3:1) as eluent to give the corresponding alcohols **22a-e** in 44-58% overall yields over two steps.



22a-e

3-Phenylpropan-1-ol (***22a***).[21] Colourless oil (1.362 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.65 (br s, 1H, *OH*), 1.88–1.93 (m, 2H), 2.72 (t, *J* = 7.9 Hz, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 7.18–7.22 (m, 3H), 7.28–7.31 (m, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 32.0, 34.2, 62.2, 125.8, 128.36, 128.4, 141.8 ppm.IR ($CHCl_3$): υ_{max} = 3361, 3084, 3062, 3026, 2937, 2863, 1603, 1583, 1496, 1454, 1266, 1218, 1154, 1059, 1032, 918, 805, 753, 699, 668, 574 cm^{-1}.

3-(p-Tolyl)propan-1-ol (***22b***).[21] Colourless oil (1.683 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.61 (br s, 1H, *OH*), 1.87–1.90 (m, 2H), 2.33 (s, 3H), 2.68 (t, *J* = 7.7 Hz, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 7.10 (s, 4H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 21.0, 31.6, 34.3, 62.3, 128.3, 129.1, 135.3, 138.7 ppm. IR ($CHCl_3$): υ_{max} = 3351, 3018, 2927, 2862, 1515, 1452, 1266, 1160, 1112, 1046, 911, 837, 805, 781, 756, 669, 561 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{10}H_{14}ONa$ 173.0937; Found 173.0935.

3-(4-Methoxyphenyl)propan-1-ol (***22c***).[21] Colourless oil (1.928 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82–1.89 (m, 2H), 2.58 (br s, 1H, *OH*), 2.65 (t, *J* = 7.6 Hz, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 3.79 (s, 3H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.0, 34.3, 55.1, 61.9, 113.6, 129.2, 133.8, 157.6 ppm. IR ($CHCl_3$): υ_{max} = 3389, 2994, 2939, 1612, 1584, 1513, 1465, 1372, 1299, 1247, 1178, 1111, 1038, 912, 832, 814, 748, 701, 638, 563, 522 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{10}H_{14}O_2Na$ 189.0886; Found 189.0888.

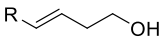
3-(4-Fluorophenyl)propan-1-ol (***22d***).[22] Colourless oil (1.357 g, 44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (br s, 1H, *OH*), 1.83–1.89 (m, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 6.94–6.99 (m, 2H), 7.12–7.17 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 31.2, 34.3, 62.0, 115.08 (d, *J* = 20.9 Hz), 129.70 (d, *J* = 7.9 Hz), 137.34 (d, *J* = 3.1 Hz), 161.30 (d, *J* = 242.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −117.73 ppm. IR ($CHCl_3$): υ_{max} = 3343, 2932, 2868, 1664, 1511, 1450, 1273, 1222, 1158, 1094, 1041, 912, 822, 760, 552 cm^{-1}.

3-(3-Bromophenyl)propan-1-ol (***22e***).[23] Colourless oil (2.151 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.75 (br s, 1H, *OH*), 1.87–1.93 (m, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 3.68 (t, *J* = 6.5 Hz, 2H), 7.20–7.22 (m, 2H), 7.28–7.32 (m, 2H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 32.0, 34.2, 62.2, 125.8, 126.9, 128.4, 129.9, 131.4, 141.8 ppm. IR ($CHCl_3$): υ_{max} = 3344, 2928, 2854, 1664, 1535, 1454, 1278, 1149, 1085, 946, 758, 700 cm^{-1}.

General Procedure for the Synthesis of Homoallyl Alcohols (23a-n). Oxalyl chloride (1.523 g, 12.0 mmol, 1.5 equiv) was gradually added to a solution of DMSO (1.875 g, 24.0 mmol, 3.0 equiv) in CH_2Cl_2 (25 mL) at –78 °C over a period of 2 min. After stirring for 15 min, a solution of alcohol **22a-n** (8.0 mmol) in CH_2Cl_2 (5 mL) was added and the reaction mixture stirred for 45 min. A solution of NEt_3 (4.5 mL, 32.0 mmol, 4.0 equiv) in CH_2Cl_2 (3 mL) was added and the reaction mixture stirred for 30 min and then gradually warmed to room temperature over 1 h. After addition of water (20 mL), the organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with water, brine, dried (Na_2SO_4) and concentrated to give the crude aldehyde, which was used directly in the next reaction.

To the solution of above aldehyde in DMSO (30 mL) was added sequentially malonic acid (1.665 g, 16.0 mmol, 2.0 equiv) and piperidinium acetate (34.8 mg, 0.24 mmol, 0.03 equiv). The mixture was stirred vigorously at 100 °C for 6-12 h and then cooled to room temperature. EtOAc (30 mL) was added and the organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and filtered through a plug of silica gel. The filtrate was concentrated and the residue was used in the next reaction.

To a slurry of $LiAlH_4$ (0.607 g, 16.0 mmol, 2.0 equiv) in dry THF (50 mL) at 0 °C was added dropwise a solution of the above acid in THF (20 mL). The reaction mixture was refluxed for 14 h and then quenched with saturated aq. Na_2SO_4 solution (15 mL) at 0 °C. Then EtOAc (80 mL) was added and the mixture stirred for 1 h. The mixture was filtered through a sintered glass funnel and the filtrate was concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (3:1) as eluent to give the corresponding alcohols **23a-n**.



23a-n

(E)-5-Phenylpent-3-en-1-ol ***(23a)***.[24] Pale yellow oil (0.856 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (q, *J* = 6.0 Hz, 2H), 3.37 (d, *J* = 6.7 Hz, 2H), 3.66 (t, *J* = 6.3 Hz, 2H), 5.49 (tdt, *J* = 14.5, 6.9, 1.4 Hz, 1H), 5.73 (dtt, *J* = 14.5, 6.7, 1.3 Hz, 1H), 7.18–7.22 (m, 3H), 7.28–7.32 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 35.8, 39.0, 61.9, 125.9, 127.4, 128.35, 128.4, 132.3, 140.4 ppm. IR($CHCl_3$): υ_{max} = 3408, 2952, 1654, 1636, 1219, 1104, 1042, 855, 822, 775 cm^{-1}. LRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{14}ONa$ 185.0936; Found 185.1049.

(E)-5-(p-Tolyl)pent-3-en-1-ol ***(23b)***. Colourless oil (0.902 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.64 (br s, 1H, *OH*), 2.28–2.32 (m, 5H), 3.32 (d, *J* = 6.7 Hz, 2H), 3.65 (t, *J* = 6.3 Hz, 2H), 5.50 (dtt, *J* = 14.8, 6.9, 1.5 Hz, 1H), 5.73 (dtt, *J* = 14.4, 6.8, 1.3 Hz, 1H), 7.06–7.11 (m, 4H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 21.0, 35.9, 38.7, 62.0, 127.1, 128.3, 129.1, 132.8, 135.5, 137.4 ppm. IR ($CHCl_3$): υ_{max} = 3399, 3092, 3020, 3002, 2924, 2858, 1619, 1514, 1432, 1378, 1258, 1182, 1109, 1045, 969, 806, 618, 552 cm^{-1}. LRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{16}ONa$ 199.1093; Found 199.0438.

(E)-5-(4-Methoxyphenyl)pent-3-en-1-ol ***(23c)***. Pale yellow oil (0.969 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58 (br s, 1H, *OH*), 2.30 (q, *J* = 6.5 Hz, 2H), 3.30 (d, *J* = 6.7, 2H), 3.65 (t, *J* = 6.3 Hz, 2H), 3.79 (s, 3H), 5.46 (dtt, *J* = 14.7, 6.9, 1.4 Hz, 1H), 5.70 (dtt, *J* = 14.4, 6.8, 1.3 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 35.9, 38.2, 55.3, 62.0, 113.8, 127.1, 129.4, 132.5, 132.9, 157.9 ppm. IR ($CHCl_3$) υ_{max} = 3392, 3030, 2996, 2932, 2835, 1611, 1511, 1440, 1300, 1245, 1176,1108, 1036, 969, 817, 708, 638, 563, 513 cm^{-1}. LRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{16}O_2Na$ 215.1042; Found 215.0425.

(E)-5-(4-Fluorophenyl)pent-3-en-1-ol ***(23d)***. Colourless oil (1.081 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (q, *J* = 7.0 Hz, 2H), 3.35 (dd, *J* = 11.7, 6.7 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 5.48 (dtt, *J* = 14.5, 6.8, 1.3 Hz, 1H), 5.66–5.76 (m 1H), 6.95–6.99 (m, 1H), 7.11–7.21 (m, 2H), 7.28–7.31 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 35.9, 38.2, 62.0, 115.15 (d, *J* = 21.1 Hz), 127.7, 129.7, 129.82 (d, *J* = 7.8 Hz), 132.2, 136.10 (d, *J* = 3.1 Hz), 161.4 (d, *J* = 243.4 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ –117.5 ppm. IR ($CHCl_3$): υ_{max} = 3343, 2931, 1660, 1510, 1453, 1222, 1158, 968, 909, 826, 759, 669 cm^{-1}. LRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{13}FONa$ 203.0842; Found 203.0536.

(E)-5-(3-Bromophenyl)pent-3-en-1-ol ***(23e)***. Colourless oil (1.543 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (q, *J* = 6.1 Hz, 2H), 3.37 (d, *J* = 6.7 Hz, 2H), 3.66 (t, *J* = 6.3 Hz, 2H), 5.49 (dtt, *J* = 14.9, 6.7, 1.4 Hz, 1H), 5.73 (dtt, *J* = 14.4, 6.8, 1.4 Hz, 1H), 7.18–7.22 (m, 2H), 7.28–7.32 (m, 2H) ppm.$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 35.9, 39.1, 62.0, 126.0, 127.4, 128.4, 128.44, 132.5, 140.5 ppm. IR ($CHCl_3$): υ_{max} = 3352, 2931, 2878, 1665, 1535, 1453, 1240, 1159, 1046, 769 cm^{-1}. LRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{13}BrONa$ 265.0022; Found 265.0888.

(E)-4-Phenylbut-3-en-1-ol ***(23f)***. Pale yellow oil (0.901 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.79 (br s, 1H, *OH*), 2.49 (q, *J* = 6.2 Hz, 2H), 3.76 (t, *J* = 6.3 Hz, 2H), 6.21 (dt, *J* = 15.9, 7.2 Hz, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 7.21–7.24 (m, 1H), 7.29–7.32 (m, 2H), 7.36–7.38 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 36.4, 62.0, 126.0, 126.3, 127.2, 128.5, 132.8, 137.2 ppm. IR ($CHCl_3$) υ_{max} = 3399, 3025, 2922, 2850, 1656, 1493, 1449, 1377, 1046, 966, 693, 668 cm^{-1}. LRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{12}ONa$ 171.0780; Found 171.0729.

(E)-Hex-3-en-1-ol ***(23g)***.[25] Colourless oil (0.553 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.99–2.07 (m, 2H), 2.23–2.28 (m, 2H), 3.61 (t, *J* = 6.3 Hz, 2H), 5.36 (dtt, *J* = 14.6, 6.9, 1.4 Hz, 1H), 5.59 (dtt, *J* = 14.1, 6.3, 1.2 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.7, 25.6, 35.9, 62.0, 124.7, 135.8 ppm. IR ($CHCl_3$): υ_{max} = 3393, 2952, 2925, 2854, 1654, 1464, 1374, 1266, 1048, 911, 802, 764 cm^{-1}.

(E)-Oct-3-en-1-ol ***(23h)***.[26] Pale yellow oil (0.667 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.23–1.36 (m, 4H), 1.99–2.03 (m, 2H), 2.25 (q, *J* = 6.1 Hz, 2H), 3.61 (t, *J* = 6.3 Hz, 2H), 5.36 (dtt, *J* = 14.8, 6.9, 1.3 Hz, 1H), 5.54 (dtt, *J* = 14.5, 6.8, 1.2 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.9, 22.2, 31.6, 32.3, 36.0, 62.0, 125.7, 134.3 ppm. IR ($CHCl_3$): υ_{max} = 3368, 2957, 2927, 2873, 2857, 1653, 1466, 1378, 1266, 1049, 969, 911, 738, 706, 541, 472 cm^{-1}.

(E)-Non-3-en-1-ol ***(23i)***.[26] Pale yellow oil (0.774 g, 68%).^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.24–1.38 (m, 6H), 2.00 (q, *J* = 7.0 Hz, 2H), 2.25 (q, *J* = 6.1 Hz, 2H), 3.62 (t, *J* = 6.3 Hz, 2H), 5.37 (dtt, *J* = 14.6, 6.9, 1.3 Hz, 1H), 5.55 (dtt, *J* = 14.5, 6.7, 1.2 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 29.1, 31.4, 32.6, 36.0, 62.0, 125.6, 134.5 ppm. IR ($CHCl_3$): υ_{max} = 3365, 2956, 2927, 2857, 1668, 1542, 1467, 1376, 1171, 1127, 1049, 969 cm^{-1}. LRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_9H_{18}OK$ 181.0989; Found 181.1087.

(E)-Dec-3-en-1-ol ***(23j)***.[26] Pale yellow oil (0.788 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.26–1.36 (m, 8H), 2.06 (q, *J* = 6.9 Hz, 2H), 2.26 (q, *J* = 6.2 Hz, 2H), 3.62 (t, *J* = 6.2 Hz, 2H), 5.36 (dtt, *J* = 14.6, 6.9, 1.2 Hz, 1H), 5.54 (dtt, *J* = 14.5, 6.6, 1.1 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 28.8, 29.4, 31.7, 32.7, 36.0, 62.0, 125.6, 134.4 ppm. IR ($CHCl_3$): υ_{max} = 3367, 2952, 2925, 2854, 1465, 1378, 1176, 1049, 967 cm^{-1}.

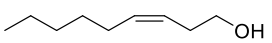
(E)-Undec-3-en-1-ol ***(23k)***.[26] Pale yellow oil (0.844 g, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.26–1.36 (m, 10H), 2.00 (q, *J* = 6.9 Hz, 2H), 2.25 (q, *J* = 6.2 Hz, 2H), 3.61 (t, *J* = 6.3 Hz, 2H), 5.36 (dtt, *J* = 14.7, 7.0, 1.2 Hz, 1H), 5.54 (dtt, *J* = 15.2 6.7, 1.5 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 22.6, 27.3, 29.1, 29.4, 31.8, 32.6, 36.0, 62.0, 125.6, 134.4 ppm. IR ($CHCl_3$): υ_{max} = 3363, 2952, 2929, 2854, 1629, 1465, 1377, 1259, 1177, 1047, 968, 887, 758, 722, 668 cm^{-1}.

(E)-Tetradec-3-en-1-ol ***(23l)***. Pale yellow oil (1.0 g, 59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.25–1.36 (m, 16H), 2.00 (q, *J* = 7.1 Hz, 2H), 2.25 (q, *J* = 6.4 Hz, 2H), 3.61 (t, *J* = 6.3 Hz, 2H), 5.36 (dt, *J* = 14.7, 6.9 Hz, 1H), 5.54 (dt, *J* = 14.7, 6.7 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 27.4, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 32.7, 36.0, 62.0, 125.6, 134.4 ppm. IR ($CHCl_3$): υ_{max} = 3411, 2924, 2853, 1466, 1378, 1264, 1178, 1047, 970, 909, 743, 705 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{28}ONa$ 235.2032; Found 235.2027.

(E)-Icos-3-en-1-ol ***(23m)***. White semisolid (1.73 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.25–1.36 (m, 28H), 2.00 (q, *J* = 7.0 Hz, 2H), 2.26 (q, *J* = 6.3 Hz, 2H), 3.62 (q, *J* = 6.3 Hz, 2H), 5.36 (dtt, *J* = 14.6, 6.9, 1.3 Hz, 1H), 5.54 (dtt, *J* = 14.6, 6.7, 1.2 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 29.2, 29.4, 29.48, 29.5, 29.6, 29.7, 31.9, 32.7, 36.0, 62.0, 125.6, 134.4 ppm. IR ($CHCl_3$) υ_{max} = 3429, 3052, 2925, 2854, 1466, 1378, 1264, 1183, 1047, 970, 909, 742, 706 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{40}ONa$ 319.2971; Found 319.2971.

(E)-6-(Benzyloxy)hex-3-en-1-ol ***(23n)***. Pale yellow oil (1.106 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (q, *J* = 6.3 Hz, 2H), 2.35 (q, *J* = 6.7 Hz, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 3.61 (t, *J* = 6.3 Hz, 2H), 4.51 (s, 2H), 5.47 (dt, *J* = 14.1, 6.6Hz, 1H), 5.56 (dt, *J* = 14.4, 6.3 Hz, 1H), 7.28–7.36 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 33.1, 36.0, 61.8, 69.7, 72.8, 127.5, 127.6, 128.1, 128.3, 130.0, 138.3 ppm. IR ($CHCl_3$): υ_{max} = 3398, 2929, 2859, 1605, 1448, 1356, 1097, 1048, 973 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{18}O_2Na$ 229.1199; Found 229.1172.

(Z)-Non-3-en-1-ol ***(23i")***. Was prepared following literature procedure.[27]



23i"

General Procedure for the Synthesis of Diol Carbonates (5a-n). To a mixture of $K_3[Fe(CN)_6]$ (3.951 g, 12.0 mmol, 3.0 equiv), K_2CO_3 (1.658 g, 12.0 mmol, 3.0 equiv) and few drops of pyridine or $(DHQD)_2PHAL$ or $(DHQ)_2PHAL$ (31.2 mg, 0.04 mmol, 1.0 mol%) in *t*-BuOH–H_2O (1:1, 20 mL) cooled at 0 °C was added $K_2OsO_4 \cdot 2H_2O$ (5.9 mg, 0.016 mmol, 0.4 mol%) followed by methanesulfonamide (380.5 mg, 4.0 mmol, 1.0 equiv). After stirring for 5 min at 0 °C, the olefin **23a-n** (4.0 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 24 h and then quenched with solid Na_2SO_3 (0.4 g). The stirring was continued for an additional 45 min and the solution extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. Silica gel column chromatography of the crude product using petroleum ether/EtOAc (2:3) as eluent gave the triol as a colourless oil, which was used for the next reaction.

To the solution of above triol in CH_2Cl_2 (40 mL) was added pyridine (1.3 mL, 16.0 mmol, 4.0 equiv) under N_2 atmosphere. The reaction mixture was stirred for 5-10 min and then triphosgene (1.19 g, 4.0 mmol, 1.0 equiv) was

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added under N_2 atmosphere and stirring was maintained at room temperature for 40 min. The reaction was quenched with saturated aq. NH_4Cl (2 mL). The phases were separated and the organic layer was diluted with EtOAc (30 mL), washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to afford **5a-n**.

4-Benzyl-5-(2-hydroxyethyl)-1,3-dioxolan-2-one ***(5a)****.* Colourless semisolid (0.435 g, 49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68–1.76 (m, 1H), 1.83–1.91 (m, 1H), 2.00 (br s, 1H, *OH*), 3.00 (dd, *J* = 14.2, 6.0 Hz, 1H), 3.11 (dd, *J* = 14.1, 6.2 Hz, 1H), 3.70 (t, *J* = 6.6 Hz, 2H), 4.55–4.63 (m, 2H), 7.22–7.24 (m, 2H), 7.28–7.35 (m, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 35.9, 39.2, 57.9, 78.8, 82.1, 127.4, 128.9, 129.4, 134.1, 154.4 ppm. IR ($CHCl_3$): υ_{max} = 3432, 2919, 2850, 1788, 1631, 1453, 1381, 1266, 1169, 1055, 755, 701, 465 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{12}H_{14}O_4Na$ 245.0784; Found 245.0786.

4-(2-Hydroxyethyl)-5-(4-methylbenzyl)-1,3-dioxolan-2-one ***(5b)****.* Colourless semisolid (0.482 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68–1.76 (m, 1H), 1.83–1.90 (m, 1H), 2.33 (s, 3H), 2.95 (dd, *J* = 14.3, 5.6 Hz, 1H), 3.07 (dd, *J* = 14.3, 5.7 Hz, 1H), 3.69–3.72 (m, 2H), 4.53–4.60 (m, 2H), 7.09–7.15 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 21.0, 36.0, 38.8, 58.0, 78.7, 82.2, 129.3, 129.6, 131.0, 137.2, 154.4 ppm. IR ($CHCl_3$): υ_{max} = 3433, 2923, 1796, 1639, 1516, 1383, 1169, 1057, 808, 774, 697, 618, 526, 489 cm^{-1}. LRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{13}H_{16}O_4Na$ 259.0940; Found 259.0568.

4-(2-Hydroxyethyl)-5-(4-methoxybenzyl)-1,3-dioxolan-2-one ***(5c)****.* Colourless semisolid (0.484 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70–1.77 (m, 1H), 1.84–1.92 (m, 1H), 2.95 (dd, *J* = 14.3, 5.7 Hz, 1H), 3.06 (dd, *J* = 14.8, 5.7 Hz, 1H), 3.71–3.74 (m, 2H), 3.79 (s, 3H), 4.54–4.57 (m, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 36.0, 38.4, 55.3, 58.1, 78.6, 82.2, 114.3, 126.0, 130.5, 154.3, 159.0 ppm. IR ($CHCl_3$): υ_{max} = 3479, 2936, 2838, 1791, 1612, 1514, 1442, 1383, 1331, 1302, 1249, 1178, 1112, 1031, 904, 822, 774, 696, 617, 527 cm^{-1}. LRMS (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd for $C_{13}H_{16}O_5Na$ 275.0889; Found 275.0433.

4-(4-Fluorobenzyl)-5-(2-hydroxyethyl)-1,3-dioxoan-2-one ***(5d)****.* Pale yellow semisolid (0.490 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74–1.82 (m, 1H), 1.87–1.95 (m, 1H), 2.98–3.09 (m, 2H), 3.73–3.77 (m, 2H), 4.53–4.61 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 7.18–7.22 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 35.9, 38.4, 58.0, 78.7, 82.0, 115.76 (d, *J* = 21.4, Hz), 130.0 (d, *J* = 3.4, Hz), 131.0 (d, *J* = 8.0, Hz), 154.2, 162.2 (d, *J* = 247.9, Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ –114.87 ppm. IR ($CHCl_3$): υ_{max} = 3378, 2931, 1796, 1663, 1511, 1455, 1384, 1337, 1279, 1221, 1159, 1054, 826, 771 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{12}H_{13}FO_4Na$ 263.0690; Found 263.0690.

4-(3-Bromobenzyl)-5-(2-hydroxyethyl)-1,3-dioxoan-2-one ***(5e)****.* Colourless semisolid (0.650 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68–1.77 (m, 1H), 1.83–1.91 (m, 1H), 2.16 (br s, 1H, *OH*), 3.00 (dd, *J* = 14.4, 5.4 Hz, 1H), 3.10 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.69 (t, *J* = 5.8 Hz, 2H), 4.54–4.63 (m, 2H), 7.22–7.35 (m, 4H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 35.9, 39.2, 57.9, 78.8, 82.1, 127.4, 128.6, 128.8, 129.3, 129.4, 134.2, 154.4 ppm. IR ($CHCl_3$): υ_{max} = 3414, 2927, 2888, 1795, 1660, 1546, 1497, 1455, 1384, 1242, 1215, 1166, 1058, 756, 701 cm^{-1}. LRMS (ESI-TOF) *m/z:* [M + Na]$^+$ Calcd for $C_{12}H_{13}BrO_4Na$ 303.0050; Found 303.1249.

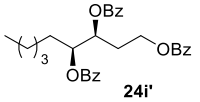
4-(2-Hydroxyethyl)-5-phenyl-1,3-dioxolan-2-one ***(5f)****.* Pale yellow oil (0.566 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.05 (q, *J* = 6.0 Hz, 2H), 2.80 (br s, 1H, *OH*), 3.76–3.86 (m, 2H), 4.72 (q, *J* = 6.5 Hz, 1H), 5.33 (d, *J* = 7.6 Hz 1H), 7.34–7.42 (m, 5H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 35.3, 57.9, 81.7, 83.3, 126.1, 129.1, 129.7, 135.2, 154.5 ppm. IR ($CHCl_3$): υ_{max} = 3433, 3020, 2918, 2849, 1805, 1498, 1458, 1376, 1353, 1279, 1186, 1159, 1069, 1050, 1027, 973, 699, 667, 626, 588, 496 cm^{-1}. LRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_{12}O_4Na$ 231.0627; Found 231.0729.

5-Ethyl-4-(2-hydroxyethyl)-1,3-dioxolan-2-one ***(5g)****.* Colourless oil (0.333 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (t, *J* = 7.4 Hz, 3H), 1.72–1.79 (m, 2H), 1.89–1.96 (m, 2H), 2.57 (br s, 1H, *OH*), 3.79 (t, *J* = 6.5 Hz, 2H), 4.31 (q, *J* = 6.3 Hz, 1H), 4.47–4.52 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 8.7, 26.5, 36.2, 57.9, 79.1, 83.3, 154.8 ppm. IR ($CHCl_3$): υ_{max} = 3432, 2969, 2925, 2854, 1794, 1551, 1464, 1377, 1264, 1185, 1055, 910, 775, 734 cm^{-1}. LRMS (ESI-TOF) *m/z*: [M + K]$^+$ Calcd for $C_7H_{12}O_4K$ 199.0367; Found 199.0581.

4-(2-Hydroxyethyl)-5-butyl-1,3-dioxolan-2-one ***(5h)****.* Pale yellow oil (0.496 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 6.7 Hz, 3H), 1.34–1.45 (m, 4H), 1.66–1.77 (m, 2H), 1.90–1.96 (m, 2H), 3.81 (t, *J* = 5.3 Hz, 2H), 4.32–4.37 (m, 1H), 4.46–4.51 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 13.7, 22.2, 26.6, 33.1, 36.1, 58.0, 79.4, 82.3, 154.8 ppm. IR ($CHCl_3$): υ_{max} = 3434, 2959, 2931, 2871, 1797, 1556, 1466, 1381, 1264, 1215, 1181, 1057, 914, 776, 754 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_9H_{16}O_4Na$ 211.0941; Found 211.0959.

(4S,5S)-4-(2-Hydroxyethyl)-5-pentyl-1,3-dioxolan-2-one ***(5i')****.* Prepared using $(DHQ)_2$-PHAL ligand in asymmetric dihydroxylation. Pale yellow oil (0.501 g, 62%). $[\alpha]_D^{25}$ = –32.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, 3H), 1.29–1.49 (m, 6H), 1.63–1.75 (m, 2H), 1.90–1.96 (m, 2H), 2.53 (br s, 1H, *OH*), 3.81 (t, *J* = 5.5 Hz, 2H), 4.32–4.37 (m, 1H), 4.46–4.51 (m, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 13.8, 22.3, 24.2, 31.2, 33.4, 36.1, 58.0, 79.5, 82.3, 154.8 ppm. IR ($CHCl_3$): υ_{max} = 3458, 2955, 2932, 2864, 1801, 1654, 1552, 1464, 1381, 1175, 1061, 773, 668 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{10}H_{18}O_4Na$ 225.1097; Found 225.1099. Following a similar procedure, racemic **5i** was prepared from **24i** using catalytic pyridine instead of $(DHQ)_2$-PHAL ligand, followed by preparation of the carbonate. Analytical data is same as **5i'**. The enantiomeric excess was determined by converting the triol **7i'** obtained after asymmetric dihydroxylation of **23i** into its tribenzoate **24i'** as described below.

(3S,4S)-Nonane-1,3,4-triyl tribenzoate ***(24i')****.* To a stirred solution of (3*S*,4*S*)-nonane-1,3,4-triol **7i'** (25 mg, 0.142 mmol) in pyridine (1.5 mL) was added benzoyl chloride (0.17 mL, 1.43 mmol, 10.0 equiv) at 0 °C. The reaction mixture was stirred for 12 h and then quenched with ice water. The solution was extracted with $CHCl_3$ (2 × 10 mL). The combined organic layers were concentrated and the residue purified by silica gel coloumn chromatography using petroleum ether/EtOAc (19:1) to give the tribenzoate **24i'** as colourless semisolid (59 mg, 85%).



24i'

$[\alpha]_D^{25}$ = –0.8 (*c* = 0.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81–0.85 (m, 3H), 1.26–1.38 (m, 4H), 1.39–1.43 (m, 2H), 1.78–1.79 (m, 2H), 2.24–2.27 (m, 2H), 4.36–4.42 (m, 1H), 4.46–4.54 (m, 1H), 5.46–5.50 (m, 1H), 5.65–5.69 (m, 1H), 7.36–7.45 (m, 6H), 7.50–7.57 (m, 3H), 7.98–8.07 (m, 6H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 13.9, 22.4, 24.9, 30.4, 30.7, 31.5, 61.2, 71.6, 74.6, 128.3, 128.4, 129.6, 129.66, 129.7, 129.8, 129.9, 132.9, 133.06, 133.1, 165.9, 166.1, 166.4 ppm. IR ($CHCl_3$): υ_{max} = 3063, 3032, 2955, 2928, 2857, 1720, 1602, 1584, 1491, 1451, 1378, 1314, 1268, 1176, 1108, 1070, 1026, 1001, 937, 913, 850, 803, 757, 711, 687, 617 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{30}H_{32}O_6Na$ 511.2091; Found 511.2090. The racemic tribenzoate was prepared following similar procedure. HPLC analysis: Chiralpak OD-H coloumn, hexane-*i*PrOH = 92:8, flow rate = 0.7 mL/min, t_{major} = 9.90 min, 100% *ee*.

4-(2-Hydroxyethyl)-5-hexyl-1,3-dioxolan-2-one ***(5j)****.* Pale yellow oil (0.450 g, 52%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 6.4 Hz, 3H), 1.26–1.50 (m, 8H), 1.69–1.73 (m, 2H), 1.95–2.01 (m, 2H), 3.85 (t, *J* = 4.9 Hz, 2H), 4.33–4.37 (m, 1H), 4.47–4.51 (m, 1H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.0, 22.4, 24.5, 28.8, 31.5, 33.5, 36.1, 58.2, 79.4, 82.2, 154.6 ppm. IR ($CHCl_3$): υ_{max} = 3433, 2952, 2928, 2857, 1796, 1464,1380, 1268, 1213, 1174, 1057, 903, 692, 666 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{11}H_{20}O_4Na$ 239.1254; Found 239.1257.

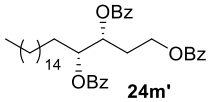
4-(2-Hydroxyethyl)-5-heptyl-1,3-dioxolan-2-one ***(5k)****.* Pale yellow oil (0.442 g, 48%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.24–1.49 (m, 8H), 1.66–1.78 (m, 4H), 1.92–1.99 (m, 2H), 3.83–3.85 (m, 2H), 4.33–4.37 (m, 1H), 4.46–4.50 (m, 1H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.0, 22.6, 24.6, 29.0, 29.1, 31.6, 33.5, 36.1, 58.2, 79.4, 82.2, 154.6 ppm. IR ($CHCl_3$): υ_{max} = 3485, 3018, 2926, 2855, 1801, 1655, 1465, 1379, 1349, 1180, 1056, 893, 695, 667, 620, 520, 488 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{12}H_{22}O_4Na$ 253.1410; Found 253.1412.

4-(2-Hydroxyethyl)-5-decyl-1,3-dioxolan-2-one ***(5l)****.* Pale yellow oil (0.534 g, 49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.25–1.48 (m, 16H), 1.67–1.73 (m, 2H), 1.91–1.97 (m, 2H), 3.83 (t, *J* = 5.9 Hz, 2H), 4.34 (q, *J* = 6.6 Hz, 1H), 4.48 (q, *J* = 6.6 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 14.1, 22.6, 24.6, 29.1, 29.25, 29.3, 29.4, 29.5, 31.8, 33.5, 36.1, 58.1, 79.4, 82.2, 154.6 ppm. IR ($CHCl_3$): υ_{max} = 3482, 3018, 2925, 2855, 1794, 1561, 1465, 1379, 1344, 1181, 1058, 889, 760, 694, 667, 620, 536 cm^{-1}. HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ Calcd for $C_{15}H_{28}O_4Na$ 295.1880, Found 295.1876.

(3R,4R)-4-(2-Hydroxyethyl)-5-hexadecyl-1,3-dioxolan-2-one ***(5m')****.* Prepared using $(DHQD)_2$-PHAL ligand in asymmetric dihydroxylation. White solid (0.813 g, 57%), m.p. = 48–50 °C. $[\alpha]_D^{25}$ = +15.4 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.24–1.48 (m, 26H),

1.65–1.77 (m, 4H), 1.92–1.98 (m, 2H), 3.83–3.85 (m, 2H), 4.31–4.37 (m, 1H), 4.46–4.50 (m, 1H) ppm.$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 24.6, 29.2, 29.3, 29.5, 29.56, 29.6, 29.63, 29.7, 31.9, 33.5, 36.1, 58.2, 79.4, 82.2, 154.7 ppm. IR ($CHCl_3$): υ_{max} = 3396, 2918, 2852, 1778, 1760, 1471, 1378, 1051, 771 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{40}O_4Na$ 379.2819; Found 379.2814. Following a similar procedure, racemic **5m** was prepared from **23m** using catalytic pyridine instead of $(DHQD)_2$-PHAL, followed by preparation of the carbonate. Analytical data is same as **5m′**. The enantiomeric excess was determined by converting the triol **7m′** obtained after asymmetric dihydroxylation of **23m** into its tribenzoate **24m′** as described below.

*(3R,4R)-Icosane-1,3,4-triyl tribenzoate (**24m′**).* The tribenzoate **24m′** was prepared from **7m′** by a similar procedure as described for **24i′** to afford **24m′** as white semisolid (85%).

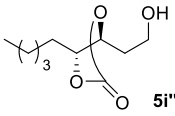


24m'

$[\alpha]_D^{25}$ = +16.3 (*c* = 2.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20–1.30 (m, 26H), 1.37–1.48 (m, 2H), 1.76–1.81 (m, 2H), 2.25 (q, *J* = 6.3 Hz, 2H), 4.36–4.42 (m, 1H), 4.46–4.52 (m, 1H), 5.46–5.50 (m, 1H), 5.65–5.69 (m, 1H), 7.36–7.45 (m, 6H), 7.50–7.57 (m, 3H), 7.98–8.07 (m, 6H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 25.2, 29.3, 29.4, 29.45, 29.5, 29.7, 30.4, 30.8, 31.9, 61.2, 71.6, 74.6, 128.3, 128.4, 129.56, 129.67, 129.7, 129.8, 129.9, 132.9, 133.05, 133.1, 165.9, 166.1, 166.4 ppm. IR ($CHCl_3$): υ_{max} = 2925, 2853, 1723, 1695, 1603, 1585, 1492, 1452, 1315, 1269, 1179, 1111, 1070, 1027, 802, 759, 711, 686, 547 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{41}H_{54}O_6Na$ 665.3813; Found 665.3804. The racemic tribenzoate was prepared following similar procedure. HPLC analysis: Chiralpak AD-H coloumn, hexane-*i*PrOH = 97:3, flow rate = 0.5 mL/min, t_{major} = 8.88 min, 100% *ee*.

*4-(2-Benzyloxyethyl)-5-(2-hydroxyethyl)-1,3-dioxolan-2-one (**5n**).* Colourless semisolid (0.543 g, 51%). ^1H NMR (500 MHz, $CDCl_3$): δ 1.88–1.92 (m, 2H), 2.02–2.03 (m, 2H), 3.62 (t, *J* = 5.8 Hz, 2H), 3.70–3.74 (m, 2H), 4.49–4.52 (m, 2H), 4.55–4.59 (m, 2H), 7.29–7.37 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 33.6, 35.9, 57.9, 65.3, 73.3, 79.6, 79.7, 127.76, 127.8, 128.4, 137.6, 154.6 ppm. IR ($CHCl_3$): υ_{max} = 3427, 2924, 2871, 1798, 1369, 1178, 1072, 750, 700 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_5Na$ 289.1046; Found 289.1047.

*(±)-anti-4-(2-Hydroxyethyl)-5-pentyl-1,3-dioxolan-2-one (**5i″**).*



5i''

cis-Dihydroxylation of (*Z*)-non-3-en-1-ol (**23i″**, 142 mg, 1.0 mmol) and subsequent carbonate preparation by following similar procedure as described for **5i** produced **5i″** (103 mg, 51%) as pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.26–1.44 (m, 6H), 1.53–1.57 (m, 2H), 1.84–1.93 (m, 2H), 3.79–3.88 (m, 2H), 4.67–4.70 (m, 1H), 4.88–4.93 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 13.9, 22.4, 25.2, 29.1, 31.3, 31.4, 58.5, 76.8, 79.9, 154.6 ppm. IR ($CHCl_3$): υ_{max} = 3471, 3020, 2917, 2850, 1778, 1757, 1469, 1378, 1310, 1178, 1051, 997, 959, 924, 912, 876, 848, 715, 666, 624 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{18}O_4Na$ 225.1097; Found 225.1096.

General Procedure for the Synthesis of Enals (3a-n). To a stirred solution of **5a-n** (1.0 mmol) in EtOAc (5 mL) was added IBX (0.56 g, 2.0 mmol, 2.0 equiv) under N_2 atmosphere. The resulting suspension was refluxed for 3-4 h (TLC monitoring). The reaction was cooled to room temperature and filtered through a sintered glass funnel. The filter cake was washed with EtOAc (3 × 2 mL) and the combined filtrates were concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:2) as eluent to afford **3a-n** (54–94%).

*(E)-4-Hydroxy-5-phenylpent-2-enal (**3a**).* Pale yellow oil (155 mg, 88%). ^1H NMR (500 MHz, $CDCl_3$): δ 2.35 (br s, 1H, *OH*), 2.87 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.96 (dd, *J* = 13.7, 5.3 Hz, 1H), 4.62–4.66 (m, 1H), 6.31 (ddd, *J* = 15.7, 7.9, 1.6 Hz, 1H), 6.85 (dd, *J* = 15.7, 4.3 Hz, 1H), 7.22–7.24 (m, 2H), 7.27–7.28 (m, 1H), 7.32–7.35 (m, 2H), 9.54 (d, *J* = 7.9 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 43.0, 71.7, 127.1, 128.7, 129.4, 130.9, 136.4, 157.8, 193.6 ppm. IR($CHCl_3$): υ_{max} = 3426, 2925, 2851, 2361, 1686, 1636, 1450, 1138, 1095, 1020, 976, 773, 701, 464 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{13}O_2$ 177.0910; Found 177.0913.

*(E)-4-Hydroxy-5-(p-tolyl)pent-2-enal (**3b**).* Pale yellow oil (152 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.82 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.94 (dd, *J* = 13.6, 5.2 Hz, 1H), 4.59–4.65 (m, 1H), 6.32 (ddd, *J* = 15.7, 7.9, 1.7 Hz, 1H), 6.85 (dd, *J* = 15.7, 4.3 Hz, 1H), 7.10–7.16 (m, 4H), 9.56 (d, *J* = 7.9 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.0, 42.6, 71.8, 129.3, 129.5, 130.9, 133.1, 136.8, 157.6, 193.5 ppm. IR ($CHCl_3$): υ_{max} = 3434, 2921, 2857, 1686, 1515, 1438, 1263, 1136, 1090, 1022, 978, 911, 866, 803, 752, 735, 672, 529, 507 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{12}H_{14}O_2K$ 229.0625; Found 229.0623.

*(E)-4-Hydroxy-5-(4-methoxyphenyl)pent-2-enal (**3c**).* Pale yellow oil (155 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$): δ 2.80 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.94 (dd, *J* = 13.8, 5.2 Hz, 1H), 3.80 (s, 3H), 4.59–4.64 (m, 1H), 6.33 (ddd, *J* = 15.6, 7.9, 1.6 Hz, 1H), 6.84 (dd, *J* = 15.7, 4.4 Hz, 1H), 6.87–6.89 (m, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 9.57 (d, *J* = 7.8, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 42.2, 55.3, 71.9, 114.3, 128.1, 130.4, 131.0, 157.5, 158.8, 193.4 ppm. IR ($CHCl_3$): υ_{max} = 3436, 2916, 2836, 1687, 1612, 1513, 1464, 1441, 1399, 1301, 1248, 1178, 1136, 1110, 1090, 1033, 981, 827, 735, 672, 600, 527 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{14}O_3Na$ 229.0835; Found 229.0839.

*(E)-5-(4-Fluorophenyl)-4-hydroxypent-2-enal (**3d**).* Pale yellow oil (120 mg, 62%). ^1H NMR (500 MHz, $CDCl_3$): δ 2.84 (dd, *J* = 13.8, 8.2 Hz, 1H), 2.96 (dd, *J* = 13.8, 5.1 Hz, 1H), 4.61–4.65 (m, 1H), 6.32 (ddd, *J* = 15.7, 7.7, 1.7 Hz, 1H), 6.83 (dd, *J* = 15.7, 4.4 Hz, 1H), 7.01–7.05 (m, 2H), 7.18–7.21 (m, 2H), 9.58 (d, *J* = 7.8 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 42.2, 71.7, 115.65 (d, *J* = 21.2 Hz), 130.9 (d, *J* = 7.7 Hz), 131.2, 132.0 (d, *J* = 2.9 Hz), 156.9, 162.0 (d, *J* = 245.5 Hz), 193.2 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ –115.5 ppm.IR ($CHCl_3$) υ_{max} = 3425, 2924, 2847, 1685, 1601, 1510, 1222, 1159, 1138, 1101, 1016, 979, 913, 830, 758, 736, 534 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{11}H_{11}FO_2K$ 233.0375; Found 233.0372.

*(E)-5-(3-Bromophenyl)-4-hydroxypent-2-enal (**3e**).* Pale yellow oil (0.145 g, 57%). ^1H NMR (500 MHz, $CDCl_3$): δ 2.09 (br s, 1H, *OH*), 2.86 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.98 (dd, *J* = 13.6, 5.3 Hz, 1H), 4.63–4.67 (m, 1H), 6.32 (ddd, *J* = 15.7, 7.9, 1.7 Hz, 1H), 6.85 (dd, *J* = 15.7, 4.4 Hz, 1H), 7.22–7.36 (m, 4H), 9.56 (d, *J* = 7.8 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 43.1, 71.7, 127.1, 128.3, 128.7, 128.8, 129.4, 131.0, 136.3, 157.4, 193.4 ppm. IR ($CHCl_3$): υ_{max} = 3435, 3029, 2926, 2849, 1686, 1639, 1605, 1495, 1454, 1138, 1094, 1027, 981, 912, 751, 702, 521 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{11}H_{11}BrO_2K$ 292.9574; Found 292.9586.

*(E)-4-Hydroxy-4-phenylbut-2-enal (**3f**).* Colourless oil (87.6 mg, 54%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.48 (dd, *J* = 4.5, 1.6 Hz, 1H), 6.43 (ddd, *J* = 15.6, 7.8, 1.7 Hz, 1H), 6.91 (dd, *J* = 15.6, 4.6 Hz, 1H), 7.32–7.42 (m, 5H), 9.57 (d, *J* = 7.9 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 73.6, 126.6, 128.7, 129.0, 130.3, 140.4, 157.0, 193.6 ppm. IR($CHCl_3$): υ_{max} = 3430, 2921, 2852, 1686, 1136, 1093, 1010, 978, 912, 738, 702 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{10}H_{10}O_2K$ 201.0312; Found 201.0312.

*(E)-4-Hydroxyhex-2-enal (**3g**).* Colourless oil (82.2 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.0 (t, *J* = 7.5 Hz, 3H), 1.61–1.73 (m, 2H), 1.89 (br s, 1H, *OH*), 4.36–4.41 (m, 1H), 6.31 (ddd, *J* = 15.7, 7.8, 1.5 Hz, 1H), 6.82 (dd, *J* = 15.7, 4.7 Hz, 1H), 9.59 (d, *J* = 7.8 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.4, 29.5, 72.3, 130.9, 158.5, 193.5 ppm. IR ($CHCl_3$): υ_{max} = 3433, 2955, 2924, 2853, 1685, 1559, 1463, 1377, 1261, 1086, 1041, 1024, 980, 859, 801, 762, 671, 540 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_6H_{10}O_2Na$ 137.0573; Found 137.0568.

*(E)-4-Hydroxyoct-2-enal (**3h**).* Colourless oil (122.3 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.32–1.46 (m, 4H), 1.57–1.66 (m, 2H), 2.05 (br s, 1H, *OH*), 4.42 (q, *J* = 5.3 Hz, 1H), 6.30 (ddd, *J* = 15.7, 7.8, 1.3 Hz, 2H), 6.82 (dd, *J* = 15.7, 4.7 Hz, 1H), 9.57 (d, *J* = 7.8 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.9, 22.5, 27.3, 36.2, 71.1, 130.6, 159.1, 193.7 ppm. IR ($CHCl_3$): υ_{max} = 3429, 2955, 2927, 2856, 1689, 1505, 1465, 1378, 1261, 1124, 1095, 1022, 978, 801, 761 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_8H_{15}O_2$ 143.1067; Found 143.1061.

*(S,E)-4-Hydroxynon-2-enal (**3i′**).*[28] Colourless oil (145.4 mg, 93%). $[\alpha]_D^{25}$ = +43.8 (*c* = 0.6, $CHCl_3$), lit.[28] $[\alpha]_D^{25}$ = +48.0 (c = 0.69, $CHCl_3$).^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.28–1.47 (m, 6H), 1.59–1.66 (m, 2H), 1.89 (br s, 1H, *OH*), 4.43 (q, *J* = 5.6 Hz, 1H), 6.30 (ddd, *J* = 15.7, 7.9, 1.3 Hz, 1H), 6.82 (dd, *J* = 15.7, 4.7 Hz, 1H), 9.58 (d, *J* = 7.9 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.0, 22.5, 24.8, 31.6, 36.4, 71.1, 103.6, 159.0, 193.6 ppm. IR ($CHCl_3$): υ_{max} = 3429, 2955, 2930, 2858, 1692, 1635, 1466, 1380, 1312, 1260, 1219, 1185, 1125, 1023, 973, 909, 797,

10.1002/asia.201900421

758, 699, 595 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_9H_{16}O_2K$ 193.0782; Found 193.0778.

Following a similar procedure, racemic **3i** (94%) was prepared from **5i**. Analytical data is same as **3i′**. Aslo *anti*-diol carbonate **5i″** on oxidation with IBX (2.0 equiv) produced **3i** in 80% yield.

*(E)-4-Hydroxydec-2-enal (**3j**):* Pale yellow oil (153 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.29–1.45 (m, 8H), 1.60–1.66 (m, 2H), 1.75 (br s, 1H, *OH*), 4.43 (q, *J* = 5.6 Hz, 1H), 6.31 (ddd, *J* = 15.7, 7.9, 0.9 Hz, 1H), 6.82 (dd, *J* = 15.7, 4.7 Hz, 1H), 9.58 (d, *J* = 7.8 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 25.1, 29.1, 31.6, 36.5, 71.1, 130.6, 159.2, 193.7 ppm. IR ($CHCl_3$): υ_{max} = 3436, 2952, 2930, 2856, 2733, 1691, 1682, 1639, 1467, 1288, 1146, 1126, 1076, 976, 757, 724 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{10}H_{18}O_2K$ 209.0938; Found 209.0943.

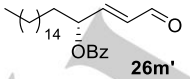
*(E)-4-Hydroxyundec-2-enal (**3k**).* Pale yellow oil (160 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.25–1.46 (m, 10H), 1.59–1.69 (m, 2H), 4.41–4.46 (m, 1H), 6.31 (ddd, *J* = 15.7, 7.8, 1.6 Hz, 1H), 6.82 (dd, *J* = 15.7, 4.7 Hz, 1H), 9.58 (d, *J* = 7.8 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0, 22.6, 25.2, 29.1, 29.3, 31.7, 36.5, 71.1, 130.6, 159.2, 193.7 ppm. IR ($CHCl_3$): υ_{max} = 3434, 2952, 2927, 2855, 1693, 1639, 1466, 1378, 1144, 1125, 1078, 975, 760, 577 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{11}H_{20}O_2K$ 223.1095; Found 223.1092.

*(E)-4-Hydroxytetradec-2-enal (**3l**).* Pale yellow oil (172 mg, 76%). ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.25–1.46 (m, 16H), 1.59–1.65 (m, 2H), 1.85 (br s, 1H, *OH*), 4.42 (q, *J* = 5.6 Hz, 1H), 6.30 (ddd, *J* = 15.7, 7.9, 1.2 Hz, 1H), 6.82 (dd, *J* = 15.6, 4.7 Hz, 1H), 9.57 (d, *J* = 7.9 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 25.2, 29.3, 29.4, 29.46, 29.5, 29.6, 31.9, 36.5, 71.1, 130.6, 159.9, 193.6 ppm. IR ($CHCl_3$): υ_{max} = 3433, 2927, 2855, 1693, 1467, 1378. 1272, 1035, 978, 925, 823, 763, 617, 556, 469 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{26}O_2Na$ 249.1825; Found 249.1823.

*(R,E)-4-Hydroxyicos-2-enal (**3m′**).* White solid (242 mg, 78%), m.p. = 55 °C. $[\alpha]_D^{25}$ = –9.5 (*c* = 1.85, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.25–1.48 (m, 28H), 1.60–1.66 (m, 2H), 1.71 (br s, 1H, *OH*), 4.41–4.45 (m, 1H), 6.30 (ddd, *J* = 15.7, 7.9, 1.5 Hz, 1H), 6.82 (dd, *J* = 15.6, 4.7 Hz, 1H), 9.58 (d, *J* = 7.8 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 25.2, 29.4, 29.44, 29.5, 29.6, 29.63, 29.66, 29.7, 31.9, 36.5, 71.2, 130.7, 158.9, 193.6 ppm. IR ($CHCl_3$): υ_{max} = 3454, 2923, 2852, 1742, 1685, 1600, 1527, 1488, 1463, 1437, 1378, 1347, 1268, 1247, 1225, 1164, 1082, 1016, 852, 712, 669, 534 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{38}O_2Na$ 333.2764; Found 333.2765.

Following a similar procedure, racemic **3m** (76%) was prepared from **5m**. Analytical data is same as **3m′**. The enantiomeric excess of **3m′** was determined by converting it into its benzoate derivative **26m′** as described below.

*(R,E)-1-oxoicos-2-en-4-yl benzoate (**26m′**):* To a stirred solution of (*R,E*)-4-Hydroxyicos-2-enal **3m′** (20 mg, 0.064 mmol) in pyridine (1.5 mL) was added benzoyl chloride (0.074 mL, 0.64 mmol, 10.0 equiv) at 0 °C. The reaction mixture was stirred for 12 h and then quenched with ice water. The solution was extracted with $CHCl_3$ (2 × 10 mL). The combined organic layers were concentrated and the residue purified by silica gel coloumn chromatography using petroleum ether/EtOAc (19:1) as eluent to give the tribenzoate **26m′** as colourless semisolid (20 mg, 80%).

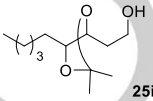


26m'

$[\alpha]_D^{25}$ = –20.0 (*c* = 0.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.20–1.35 (m, 26H), 1.40–1.47 (m, 2H), 1.83–1.90 (m, 2H), 5.74–5.80 (m, 1H), 6.29 (ddd, *J* = 15.8, 7.7, 1.6 Hz, 1H), 6.85 (dd, *J* = 15.8, 4.6 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.60 (tt, *J* = 7.5, 1.2 Hz, 1H), 8.07 (d, *J* = 7.1 Hz, 2H), 9.59 (d, *J* = 7.7 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 25.0, 29.3, 29.34, 29.4, 29.5, 29.6, 29.7, 31.9, 33.8, 72.8, 128.5, 129.6, 129.7, 131.5, 133.4, 154.1, 165.6, 193.0 ppm. IR ($CHCl_3$): υ_{max} = 3792, 3701, 3434, 2928, 2857, 2413, 2304, 1720, 1586, 1461, 1272, 1108, 986, 837, 793, 713, 639 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{27}H_{42}O_3K$ 453.2766; Found 437.2758. The racemic benzoate was prepared following similar procedure. HPLC analysis: Chiralpak AD-H coloumn, hexane-*i*PrOH = 93:7, flow rate = 1 mL/min, t_{major} = 6.39 min, 100% *ee*.

*(E)-6-(Benzyloxy)-4-hydroxyhex-2-enal (**3n**).* Pale yellow oil (194 mg, 88%). ^1H NMR (500 MHz, $CDCl_3$): δ 1.82–1.89 (m, 1H), 1.95–2.01 (m, 1H), 3.65–3.74 (m, 2H), 4.50 (d, *J* = 1.2 Hz, 2H), 4.61–4.65 (m, 1H), 6.34 (ddd, *J* = 15.6, 7.9, 1.7 Hz, 1H), 6.79 (dd, *J* = 15.6, 4.2 Hz, 1H), 7.27–7.36 (m, 5H), 9.54 (d, *J* = 7.9, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 35.3, 67.9, 70.1, 73.3, 127.7, 127.9, 128.4, 130.6, 137.3, 158.7, 193.6 ppm. IR ($CHCl_3$): υ_{max} = 3451, 2921, 2863, 1685, 1636, 1367, 1249, 1114, 977, 910, 738, 700, 609, 464 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_3Na$ 243.0992; Found 243.0986.

*3,4-Isopropylidinedioxy-nonanol (**25i**).* To a stirred solution of triol **7i** (30 mg, 0.170 mmol) in acetone (3 mL) was added *p*-TsOH·H_2O (1 mg, catalytic) followed by 2,2-dimethoxypropane (19.5 mg, 0.187 mmol, 1.1 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 1 h under N_2 atmosphere and then quenched with 2 drops of saturated aq. $NaHCO_3$ and stirred for additional 5 min. The solvents were removed and the residue purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to afford **25i** (28.5 mg, 77%) as colorless oil.



25i

^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 6.3 Hz, 3H), 1.28–1.45 (m, 6H), 1.38 (s, 6H), 1.51–1.52 (m, 2H), 1.72–1.75 (m, 1H), 1.82–1.84 (m, 1H), 2.16 (br s, 1H, *OH*), 3.66–3.67 (m, 1H), 3.74–3.77 (m, 1H), 3.81 (t, *J* = 4.9 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 25.8, 27.2, 27.3, 31.9, 32.5, 34.8, 60.9, 80.2, 81.0, 108.4 ppm. IR ($CHCl_3$): υ_{max} = 3441, 2955, 2926, 2855, 1632, 1463, 1378, 1242, 1166, 1054, 876, 761, 722 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{24}O_3Na$ 239.1618; Found 239.1614.

*3,4-Isopropylidinedioxy-nonanal (**8i**).* Reaction of compound **25i** (25 mg, 0.115 mmol) with IBX (64.4 mg, 0.230 mmol, 2.0 equiv) following similar procedure as described for **3a-n** for 10 h gave **8i** (14.6 mg, 59%) as pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.28–1.39 (m, 4H), 1.38, 1.40 (2s, 6H), 1.48–1.55 (m, 4H), 2.62–2.63 (m, 2H), 3.68 (q, *J* = 7.4 Hz, 1H), 4.07 (q, *J* = 7.5 Hz, 1H), 9.82 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.0, 22.5, 25.7, 27.1, 27.2, 31.9, 32.3, 46.5, 75.5, 80.7, 108.8, 200.2 ppm. IR ($CHCl_3$): υ_{max} = 3440, 2956, 2928, 2856, 2728, 1729, 1629, 1460, 1241, 1167, 1090, 1031, 988, 911, 874, 735, 511 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_3Na$ 237.1461; Found 237.1464.

The IBX oxidation of compound **5m** after 1 h showed the presence of **5m** and **6m** in 1:1.5 ratio. The ^1H NMR of the crude reaction mixture (after concentration) showed characteristic peaks for **6m** at δ = 2.90 (dd, *J* = 18.4, 6.8 Hz, 1H) and 3.10 (dd, *J* = 18.5, 6.0 Hz, 1H) ppm. These correspond to the α-hydrogens of compound **6m** (See SI for the spectra). In a 3 h reaction of **5m**, we found the presence of **6m** in minor amount and the corresponding peaks (as above) completely disappeared after another 1 h of reaction giving the final product **3m**.

*(E)-4-Hydroxyicos-2-enoic acid (**9**).* To a solution of aldehyde **3m** (0.05 g, 0.16 mmol) and cyclohexene (39.4 mg, 0.48 mmol, 3.0 equiv) in *t*-BuOH (0.5 mL) was added sodium chlorite (14.5 mg, 0.16 mmol, 1.0 equiv) in NaH_2PO_4 (1 mL, pH 3.5 buffer) dropwise at –5 °C. The resulting colourless solution was stirred for 10 h at room temperature. Then the mixture was basified with 6 N NaOH (pH 10), and *t*-BuOH was removed at reduced pressure. The residue was dissolved in water and extracted with hexane (2 × 10 mL). The hexane layer was discarded and the aqueous layer was acidified (6 N HCl, pH 3) and extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (1:1) to give **9** (40 mg, 76%) as white solid, m.p. = 55–60 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.15–1.45 (m, 28H), 1.52–1.64 (m, 2H), 4.34 (q, *J* = 5.3 Hz, 1H), 6.05 (dd, *J* = 15.7, 1.3 Hz, 1H), 7.05 (dd, *J* = 15.6, 4.7 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 25.2, 29.3, 29.4, 29.5, 29.55, 29.6, 29.64, 29.7, 31.9, 36.5, 71.1, 119.2, 152.8, 170.9 ppm. IR ($CHCl_3$): υ_{max} = 3475, 2914, 2848, 1676, 1644, 1471, 1286, 1202, 1141, 1078, 976, 893, 741, 710 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{38}O_3Na$ 349.2713; Found 349.2717.

*Methyl (E)-4-hydroxyicos-2-enoate (**10**).* The α,β-unsaturated acid **9** (35 mg, 0.107 mmol) was treated with a solution of concentrated sulphuric acid (1 drop) in methanol (2 mL) and refluxed for one hour. The solution was cooled to room temperature and concentrated in vacuo. Et_2O (1 mL) was added and the organic layer was washed with 5% aqueous solution of $NaHCO_3$ followed by brine, dried (Na_2SO_4) and concentrated. The crude compound was purified by silica gel coloumn chromatography using petroleum ether/EtOAc (7:3) as eluent to give the ester **10** (30.2 mg, 83%) as light brown solid, m.p. = 48–52 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 0.87

(t, *J* = 7.0 Hz, 3H), 1.24–1.46 (m, 28H), 1.54–1.60 (m, 2H), 1.89 (br s, 1H, *OH*), 3.73 (s, 3H), 4.29 (q, *J* = 5.6 Hz, 1H), 6.03 (dd, *J* = 15.7, 1.2 Hz, 1H), 6.95 (dd, *J* = 15.7, 4.9 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 25.2, 29.3, 29.4, 29.5, 29.54, 29.6, 29.7, 31.9, 36.6, 51.6, 71.1, 119.6, 150.6, 167.0 ppm. IR ($CHCl_3$): υ_{max} = 3361, 3244, 2918, 2847, 1726, 1662, 1464, 1430, 1325, 1274, 1191, 1178, 1137, 980, 909, 734 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{40}O_3Na$ 363.2870; Found 363.2869.

General Procedure for the Synthesis of Diene Esters (11a-c). To a stirred solution of triethylphosphonoacetate (33.6 mg, 0.15 mmol, 1.5 equiv) in dry THF (3 mL) at 0 °C was added NaH (3.6 mg, 0.15 mmol, 1.5 equiv). The reaction mixture was stirred for 0.5 h at room temperature and then cooled to 0 °C and the aldehyde **3** (0.1 mmol) in THF (1 mL) was added dropwise. The reaction mixture was stirred for 4 h from 0 °C to room temperature (monitored through TLC). The reaction mixture was then quenched with saturated aqueous NH_4Cl solution (1 mL). The solution was extracted with EtOAc (3 × 5 mL) and the combined organic layers were washed with H_2O, brine, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel coloumn chromatography using petroleum ether/EtOAc (4:1) as eluent to afford the diene esters **11a-c** (63-76%).

*Ethyl (2E,4E)-6-hydroxyhexadeca-2,4-dienoate (**11a**).* Pale yellow oil (22.5 mg, 76%). ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.7 Hz, 3H), 1.25–1.30 (m, 19H), 1.54–1.58 (m, 2H), 4.18–4.26 (m, 3H), 5.29 (s, 1H, *OH*), 5.88 (d, *J* = 15.3 Hz, 1H), 6.11 (dd, *J* = 15.3, 5.9 Hz, 1H), 6.33–6.38 (m, 1H), 7.24–7.29 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 14.3, 22.7, 25.2, 29.3, 29.48, 29.5, 29.54, 29.6, 31.9, 37.1, 60.3, 72.0, 121.5, 127.4, 143.8, 144.9, 167.0 ppm. IR ($CHCl_3$): υ_{max} = 3372, 3237, 2953, 2919, 2849, 1714, 1641, 1617, 1463, 1366, 1306, 1261, 1233, 1179, 1139, 1093, 1068, 1039, 1000, 955, 921, 868, 825, 721, 656 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{32}O_3Na$ 319.2244; Found 319.2247.

*Ethyl (2E,4E)-6-hydroxydocosa-2,4-dienoate (**11b**).* White semisolid (26.3 mg, 69%). ^1H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.25–1.33 (m, 32H), 1.54–1.58 (m, 2H), 4.17–4.26 (m, 3H), 5.89 (d, *J* = 15.4 Hz, 1H), 6.11 (dd, *J* = 15.3, 5.9 Hz, 1H), 6.33–6.39 (m, 1H), 7.25–7.28 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 24.7, 25.3, 29.1, 29.2, 29.3, 29.4, 29.5, 29.53, 29.6, 29.64, 29.7, 31.9, 33.7, 37.1, 60.4, 72.0, 121.5, 127.4, 143.8, 144.9, 167.0 ppm. IR ($CHCl_3$): υ_{max} = 2922, 2851, 1714, 1644, 1608, 1466, 1374, 1302, 1259, 1181, 1139, 1042, 995, 910, 735 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{44}O_3Na$ 403.3183; Found 403.3179.

*Ethyl (2E,4E)-8-(benzyloxy)-6-hydroxyocta-2,4-dienoate (**11c**).* Pale yellow oil (18.3 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (t, *J* = 7.1 Hz, 3H), 1.78–1.94 (m, 2H), 3.62–3.73 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.46–4.49 (m, 1H), 4.51 (s, 2H), 5.87 (d, *J* = 15.3 Hz, 1H), 6.09 (dd, *J* = 15.2, 5.2 Hz, 1H), 6.37–6.44 (m, 1H), 7.23–7.26 (m, 1H), 7.29–7.37 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.3, 36.0, 60.3, 68.3, 70.9, 73.4, 121.3, 127.2, 127.7, 127.9, 128.5, 137.6, 143.9, 144.3, 167.0 ppm. IR ($CHCl_3$): υ_{max} = 3306, 2933, 2877, 1667, 1532, 1452, 1412, 1278, 1239, 1150, 1097, 947, 762, 665 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{22}O_4Na$ 313.1410; Found 313.1413.

*(E)-1-Phenyldocos-4-en-1-yne-3,6-diol (**12**).* To a stirred solution of phenylacetylene (36.2 mg, 0.354 mmol, 2.2 equiv) in dry THF (1 mL) was added *n*-BuLi (0.22 mL, 1.6 M solution in THF, 2.2 equiv) at –78 °C. The reaction mixture was stirred for 15 min and then aldehyde **3m** (50 mg, 0.161 mmol) in THF (1 mL) was added dropwise and stirred for additional 1.5 h. After completion of reaction, it was quenched with saturated aqueous NH_4Cl (few drops) and the solution was concentrated. The residue was purified by silica gel coloumn chromatography using petroleum ether/EtOAc (4:1) as eluent to afford the diol **12** (38.5 mg, 58%) as white semisolid. ^1H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.25–1.34 (m, 28H), 1.51–1.59 (m, 2H), 4.19 (q, *J* = 6.4 Hz, 1H), 5.12 (d, *J* = 5.4 Hz, 1H), 5.89 (ddd, *J* = 15.4, 5.5, 0.9 Hz, 1H), 5.98–6.03 (m, 1H), 7.29–7.33 (m, 3H), 7.44–7.46 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 25.4, 29.4, 29.5, 29.58, 29.6, 29.65, 29.7, 31.9, 37.1, 62.8, 71.9, 86.3, 87.9, 122.3, 128.3, 128.6, 129.2, 131.7, 135.7 ppm. IR ($CHCl_3$): υ_{max} = 3286, 2920, 2849, 1790, 1652, 1466, 1266, 1137, 1078, 970, 917, 818, 723, 686, 564, 529 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{44}O_2Na$ 435.3234; Found 435.3233.

*9-Bromononanol (**27**).*[29] To a solution of nonane-1,9-diol **13** (0.5 g, 3.12 mmol) in toluene (15 mL) was added aqueous HBr (48%, 0.360 mL, 3.12 mmol, 1.0 equiv) dropwise with stirring. The mixture was refluxed for 10 h and then cooled to room temperature and washed with dilute aqueous NaOH and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to afford 9-bromononanol **27** (0.627 g, 90%) as a colourless oil.

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^1H NMR (400 MHz, $CDCl_3$): δ 1.31 (m, 8H), 1.40–1.43 (m, 2H), 1.53–1.59 (m, 2H), 1.85 (quintet, *J* = 7.2 Hz, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 25.7, 28.1, 28.7, 29.3, 29.4, 32.7, 32.8, 34.0, 63.0 ppm. IR ($CHCl_3$): υ_{max} = 3390, 2930, 2855, 1659, 1464, 1437, 1264, 1247, 1220, 1057, 758 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_9H_{19}BrOK$ 261.0251; Found 261.0248.

*9-Bromononanoic acid (**14**).*[29] A solution of CrO_3 (238 mg, 2.386 mmol, 1.5 equiv) in water (1.0 mL) was cooled to 0 °C and conc H_2SO_4 (0.17 mL, 3.18 mmol, 2.0 equiv), was added cautiously followed by water (0.5 mL). After 5 min, a solution of 9-bromononanol **27** (355 mg, 1.591 mmol) in acetone (2 mL) was added dropwise. The reaction mixture was stirred for 2 h at 0 °C before warming to room temperature and then stirred for 12 h. Et_2O (5.0 mL) and H_2O (5.0 mL) were added and the aq. layer was extracted with Et_2O (3 × 2 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) as eluent to afford the acid **14** (370 mg, 98%) as colourless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 1.32–1.37 (m, 6H), 1.39–1.45 (m, 2H), 1.62 (quint., *J* = 7.1 Hz, 2H), 1.84 (quint., *J* = 7.0 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 24.6, 28.0, 28.5, 28.9, 29.0, 32.7, 33.9, 34.0, 180.2 ppm. IR ($CHCl_3$): υ_{max} = 3420, 2932, 2852, 1702, 1464, 1434, 1410, 1302, 1204, 1098, 937, 760, 721, 648, 542. cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{17}BrO_2Na$ 259.0304; Found 259.0304.

Preparation of Wittig Salt (15).[29] 9-Bromononanoic acid **14** (230 mg, 0.970 mmol) and triphenylphosphine (254 mg, 0.970 mmol, 1.0 equiv) were dissolved in toluene (10 mL). This mixture was heated to reflux for 24 h. On cooling, the upper layer was decanted and the lower layer was dissolved in CH_2Cl_2 and concentrated in vacuo. The resulting brown viscous solid was washed with boiling EtOAc, and a white viscous solid **15** (349 mg, 72%) was collected by filtration and dried in vacuo.

*(S,9Z,11E)-13-Hydroxyoctadeca-9,11-dienoic acid (**16**).* To a slurry of Wittig salt **15** (0.831 g, 1.664 mmol, 2.0 equiv) in THF (5 mL), stirred at –78 °C was added KHMDS (3.33 mL, 1 M solution in toluene, 3.33 mmol, 4.0 equiv) dropwise. The mixture was warmed to room temperature over 2 h before re-cooling to –78 °C. To this was added the aldehyde **3i'** (130 mg, 0.832 mmol) in THF (3 mL) dropwise and the mixture stirred for 12 h at room temperature. EtOAc (5 mL) and 1 M HCl (5 mL) were added and the aq. layer was separated. This was further extracted with EtOAc (2 × 10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (7:3) as eluent to give **16** (157.8 mg, 64%) as colourless oil. $[\alpha]_D^{25}$ = +6.3 (*c* = 0.6, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.25–1.39 (m, 14H), 1.46–1.64 (m, 4H), 2.14–2.19 (m, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 4.16 (q, *J* = 6.7 Hz, 1H), 5.39–5.46 (m, 1H), 5.65 (dd, *J* = 15.2, 6.8 Hz, 1H) 5.96 (t, *J* = 10.9 Hz, 1H), 6.48 (dd, *J* = 15.2, 11.2 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.0, 22.6, 24.6, 25.1, 25.8, 27.6, 28.8, 28.82, 29.3, 31.7, 33.9, 37.2, 72.9, 125.8, 127.8, 132.8, 135.7, 179.0 ppm. IR ($CHCl_3$): υ_{max} = 3429, 2928, 2855, 1724, 1713, 1590, 1449, 1402, 1380, 1242, 1220, 1047, 1024, 948, 770. cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{32}O_3Na$ 319.2244; Found 319.2243.

*(S,10Z,12E)-14-Pentyloxacyclotetradeca-10,12-dien-2-one, (S)-coriolide (**1a**).*[12,14b] A mixture of acid **16** (50 mg, 0.169 mmol) and Et_3N (18.8 mg, 0.186 mmol, 1.1 equiv) in dry THF (3 mL) was stirred for 10 min at room temperature and then 2,4,6-tri-chlorobenzoyl chloride (41.2 mg, 0.169 mmol, 1.0 equiv) was added under N_2 atmosphere. After stirring for 2 h at room temperature, the resulting precipitate was filtered and washed with a small amount of THF (1 mL). The filtrate was diluted with benzene (90 mL) and slowly added to a refluxing solution of 4-dimethylaminopyridine (DMAP) (124 mg, 1.014 mmol, 6.0 equiv) in benzene (22 mL) over a period of 8 h with dropping condenser. The reaction mixture was washed successively with a saturated aq. citric acid solution, water, and aq. $NaHCO_3$, dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9.5:0.5) as eluent to afford **1a** (27.3 mg, 58%) as colourless oil. $[\alpha]_D^{25}$ = +31.9 (*c* = 0.5, hexane), lit.[14b] $[\alpha]_D^{25}$ = +33.0 (*c* = 2.82, hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.25–1.36 (m, 14H), 1.56–1.63 (m, 4H), 1.83–1.92 (m, 2H), 2.35–2.41 (m, 1H), 2.53–2.61 (m, 1H), 5.41–5.45 (m,

1H), 5.48–5.55 (m, 1H), 5.72 (dd, *J* = 15.4, 3.8 Hz, 1H), 6.03 (t, *J* = 10.8 Hz, 1H), 6.46–6.54 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.0, 22.5, 24.8, 24.9, 25.1, 25.4, 26.3, 26.7, 27.0, 31.6, 33.0, 35.1, 72.3, 123.8, 128.3, 131.2, 132.0, 172.9 ppm. IR ($CHCl_3$): υ_{max} = 2929, 2856, 1739, 1464, 1373, 1261, 1180, 1156, 1094, 1024, 949, 804, 545. cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{30}O_2Na$ 301.2138; Found 301.2134.

*(R,10Z,12E)-14-Pentyloxacyclotetradeca-10,12-dien-2-one, (R)-coriolide (**ent-1a**).*[14b] To a stirred solution of diethyl azodicarboxylate (60 mg, 0.202 mmol, 2.0 equiv) and acid **16** (30 mg, 0.101 mmol) in dry CH_2Cl_2 (3 mL) at −15 °C was added triphenylphosphine (53 mg, 0.202 mmol, 2.0 equiv) under vigorous stirring. The reaction mixture was stirred for 2 h and then at room temperature for 12 h and the precipitate formed was removed by filtration. The filtrate was concentrated and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (9.5:0.5) as eluent to give ***ent*-1a** (13.8 mg, 49%) as colorless oil. $[\alpha]_D^{25}$ = –30.7 (*c* = 0.5, hexane), lit.[14b] $[\alpha]_D^{25}$ = –31.9 (*c* = 1.73, hexane). Spectral data is same as **1a**.

*(R,E)-Icos-2-ene-1,4-diol (**17**).* To stirred solution of **3m′** (125 mg, 0.402 mmol) in dry CH_2Cl_2 (10 mL) was added DIBAL-H (0.58 mL, 1.75 M solution in toluene, 1.006 mmol, 2.5 equiv) dropwise under N_2 atmosphere at 0 °C. The mixture was stirred for 1 h and then quenched with saturated aq. solution of sodium-potassium tartrate (5 mL) and further stirred for 3 h until two separate layers were formed. The aqueous layer was extracted with CH_2Cl_2 (3 × 4 mL) and the combined organic layers were dried (Na_2SO_4)and concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (3:2) as eluent to afford **17** (100 mg, 80%) as white solid, m.p. = 76 °C. $[\alpha]_D^{25}$ = –4.6 (*c* = 0.2, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.25–1.41 (m, 28H), 1.47–1.57 (m, 2H), 4.11–4.13 (m, 1H), 4.16 (d, *J* = 5.2 Hz, 2H), 5.72–5.76 (m, 1H), 5.81–5.86 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 22.7, 25.4, 29.4, 29.5, 29.58, 29.6, 29.65, 29.66, 29.7, 31.9, 37.3, 63.0, 72.3, 129.7, 134.6 ppm. IR ($CHCl_3$): υ_{max} = 3285, 2916, 2849, 1685, 1463, 1315, 1273, 1071, 1025, 912, 770 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{40}O_2Na$ 335.2921; Found 335.2921.

*(R,E)-Icos-2-ene-1,4-diyl diacetate (**18**).* To a stirred solution of **17** (50 mg, 0.160 mmol) in CH_2Cl_2 (3 mL) was sequentially added DMAP (2 mg, catalytic), anhydrous Et_3N (65 mg, 0.64 mmol, 4.0 equiv) and Ac_2O (49 mg, 0.48 mmol, 3.0 equiv) under N_2 atmosphere at room temperature. The mixture was stirred for 12 h and concentrated. The residue was purified by silica gel coloumn chromatography using petroleum ether/EtOAc (5:1) as eluent to give **18** (53.9 mg, 85%) as white semisolid. $[\alpha]_D^{25}$ = –5.00 (*c* = 0.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.24–1.39 (m, 28H), 1.52–1.62 (m, 2H), 2.05 (s, 3H), 2.07 (s, 3H), 4.55 (d, *J* = 5.3 Hz, 2H), 5.24 (q, *J* = 6.5 Hz, 1H), 5.66–5.80 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 20.9, 21.2, 22.7, 25.1, 29.3, 29.47, 29.5, 29.6, 29.7, 31.9, 34.2, 64.1, 73.7, 126.3, 132.6, 170.3, 170.7 ppm. IR ($CHCl_3$): υ_{max} = 2959, 2927, 2858, 1713, 1466, 1417, 1380, 1290, 1219, 1171, 1080, 1028, 969, 931, 760, 705, 671, 627 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + K]^+$ Calcd for $C_{24}H_{44}O_4K$ 435.2871; Found 435.2871.

*(2S,3S,4R)-Icosane-1,2,3,4-tetrayl tetraacetate, D-xylo-C20-guggultetrol (**20a**)*[19f] *and (2R,3R,4R)-Icosane-1,2,3,4-tetrayl tetraacetate, D-arabino-C20-guggultetrol (**20b**).* To a mixture of $K_3[Fe(CN)_6]$ (183.7 mg, 0.558 mmol, 3.0 equiv), K_2CO_3 (77.1 mg, 0.558 mmol, 3.0 equiv), $(DHQ)_2PHAL$ (2.2 mg, 0.0028 mmol, 1.5 mol%) in *t*-BuOH-H_2O (1:1, 1 mL) cooled at 0 °C was added $K_2OsO_4.2H_2O$ (0.8 mg, 0.00188 mmol, 1.0 mol%) followed by methanesulfonamide (18.6 mg, 0.186 mmol, 1.0 equiv). After stirring for 5 min at 0 °C, the olefin **18** (74 mg, 0.186 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 24 h and then quenched with solid Na_2SO_3 (60 mg). The stirring was continued for an additional 45 min and the solution extracted with EtOAc (5 × 2 mL). The combined organic layers were washed with water, brine, dried (Na_2SO_4) and concentrated. The colourless semisolid **19** (72 mg) was used for the next reaction.

To a stirred solution of **19** (72 mg) in dry CH_2Cl_2 (3 mL) was added sequentially DMAP (2 mg, catalytic), anhydrous Et_3N (75.3 mg, 0.744 mmol, 4.0 equiv) and Ac_2O (57 mg, 0.558 mmol, 3.0 equiv) under N_2 atmosphere at room temperature. The mixture was stirred for 12 h and then concentrated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc (4:1) to give the mixture of **20a** and **20b** (79 mg, dr = 9:1)). The mixture was separated by flash column chromatograpgy using petroleum ether/EtOAc (5:1) to give **20a** (67 mg, 70%) and then **20b** (7.6 mg, 8**%**) as white solids.

Data for 20a. M.p. = 44–48 °C. $[\alpha]_D^{25}$ = +1.1 (*c* = 1.15, $CHCl_3$), lit.[19f] $[\alpha]_D^{25}$ = +0.99 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.23–1.32 (m, 28H), 1.50–1.53 (m, 2H), 2.04, 2.07, 2.07, 2.09 (4s, 12H), 3.97 (dd, *J* = 12.0, 5.4 Hz, 1H), 4.36 (dd, *J* = 11.8, 3.7 Hz, 1H), 5.07 (q, *J* = 6.4 Hz, 1H), 5.23–5.27 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 14.1, 20.56, 20.6, 20.7, 20.9, 22.7, 24.9, 29.2, 29.3, 29.4, 29.5, 29.6, 29.63, 30.6, 31.9, 62.0, 69.6, 71.3, 71.4, 169.96, 170.0, 170.3, 170.4 ppm. IR ($CHCl_3$): υ_{max} = 3021, 2926, 2855, 1746, 1456, 1435, 1373, 1047, 1030, 959, 669 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{50}O_8Na$ 537.3398; Found 537.3396. For crystal structure see supporting information.

Data for 20b. M.p. 50–54 °C. $[\alpha]_D^{25}$ = –0.87 (*c* = 0.35, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.24–1.39 (m, 28H), 1.51–1.53 (m, 2H), 2.03, 2.05, 2.07, 2.11 (4s, 12H), 3.96 (dd, *J* = 11.7, 6.9 Hz, 1H), 4.23 (dd, *J* = 11.6, 5.0 Hz, 1H), 5.03 (q, *J* = 6.7 Hz, 1H), 5.22 (dd, *J* = 7.1, 3.3 Hz, 1H), 5.32–5.36 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.67, 20.7, 20.8, 20.9, 22.7, 25.0, 29.4, 29.42, 29.44, 29.5, 29.6, 29.66, 29.7, 30.4, 31.9, 62.1, 68.3, 70.3, 71.3, 170.0, 170.2, 170.24, 170.5 ppm. IR ($CHCl_3$): υ_{max} = 2924, 2853, 1751, 1465, 1437, 1371, 1219, 1049, 958, 890, 855, 819, 756, 721, 665, 651, 629, 602, 570 cm^{-1}. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{50}O_8Na$ 537.3398; Found 537.3396.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Oxidation • tandem reaction • enal • coriolide • guggultetrol

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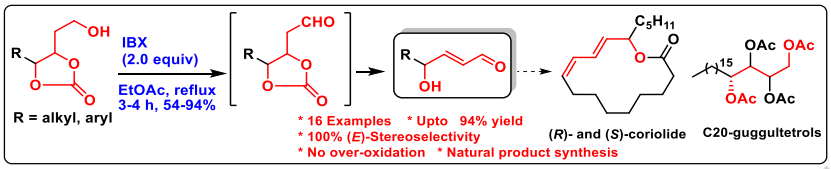
FULL PAPER

*Anupama Kumari, Sachin P. Gholap and Rodney A. Fernandes**

Page No. – Page No.

Tandem IBX-Promoted Primary Alcohol Oxidation/Opening of Intermediate β,γ-Diolcarbonate Aldehydes to (*E*)-γ-Hydroxy-α,β-enals



A tandem IBX-promoted oxidation of primary alcohol to aldehyde, opening of intermediate β,γ-diolcarbonate aldehyde to (*E*)-γ-hydroxy-α,β-enal has been developed with application to the stereoselective total synthesis of both (S)- and (R)-coriolides and D-xylo- and D-arabino-C-20-guggultetrols