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Total syntheses of *cis*-cyclopropane fatty acids: dihydromalvalic acid, dihydrosterculic acid, lactobacillic acid, and 9,10-methylenehexadecanoic acid[†]

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cis-Cyclopropane fatty acids (*cis*-CFAs) are widespread constituents of the seed oils of subtropical plants, membrane components of bacteria and protozoa, and the fats and phospholipids of animals. We describe a systematic approach to the synthesis of enantiomeric pairs of four *cis*-CFAs: *cis*-9,10-methylenehexa-decanoic acid, lactobacillic acid, dihydromalvalic acid, and dihydrosterculic acid. The approach commences with Rh₂(OAc)₄-catalyzed cyclopropenation of 1-octyne and 1-decyne, and hinges on the preparative scale chromatographic resolution of racemic 2-alkylcycloprop-2-ene-1-carboxylic acids using a homochiral Evan's auxiliary. Saturation of the individual diastereomeric *N*-cycloprop-2-ene-1-carbonylacyloxazolidines, followed by elaboration to alkylcyclopropylmethylsulfones, allowed Julia-Kocienski olefination with various ω -aldehyde-esters. Finally, saponification and diimide reduction afforded the individual *cis*-CFA enantiomers.

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Introduction

cis-Cyclopropane fatty acids (cis-CFAs) are widely distributed in microorganisms,¹ the seed oils of sub-tropical plants,² protozoa,³ and less commonly, within fats and phospholipids produced by animals.⁴ They are biosynthesized by methylenation of cis-unsaturated fatty acids (typically when esterified to phospholipid) with S-adenosylmethionine, catalyzed by CFA synthases.5 cis-CFAs are common components of bacterial membrane constituents, including phospholipids and glycolipids.¹ In bacteria, *cis*-CFA synthesis peaks in late exponential/ early stationary phase, and it has been speculated that this modification results in alteration of membrane fluidity that assists in adaptation to stationary phase.¹ Additionally, CFAs are chemically more stable against oxidative conditions than the unsaturated precursors, and may provide protective properties when incorporated into membrane components.¹ cis-CFA-containing natural products with notable biological activities include PHYLPA⁶ from the slime mold *Physarium polycephalum*, GL1⁷ from *Lactobacillus plantarum*, the maradolipids⁸

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from *Caenorhabditis elegans*, ornithine lipids from *Rhizobacterium tropici*,⁹ and a lysophosphatidylcholine from the marine sponge *Spirastrella abata*.¹⁰ Efforts to determine the structures and study the biological activity of these and other *cis*-CFA containing molecules would benefit from effective approaches to synthesize these molecules in enantiopure form.

Prominent cis-CFAs include those derived from: cis-palmitoleic acid (*cis*- Δ^9 C16:1), namely *cis*-9,10-methylenehexadecanoic acid;¹¹ 8Z-heptadecenoic acid (*cis*- Δ^8 C17:1), namely dihydromalvalic acid;¹² oleic acid (*cis*- Δ^9 C18:1), namely dihydrosterculic acid;¹³ and *cis*-vaccenic acid (*cis*- Δ^{11} C18:1), namely lactobacillic acid¹⁴ (Fig. 1). In nature, cis-9,10-methylenehexadecanoic acid occurs as the 9R,10S enantiomer in Esherichia coli¹⁵ and the 9S,10R isomer in the slime mold P. polycephalum.¹⁶ Lactobacillic acid exists as the 11R,12S isomer in L. plantarum,¹⁷ E. coli,¹⁵ and Brucella melitensis.¹⁸ Dihydrosterculic acid has been obtained as the 9R,10S isomer from the plant Litchi chinensis,19 and the 9S,10R isomer from L. plantarum.¹⁷ Interestingly, 9S,10R-dihydrosterculic acid cooccurs with 11R,12S-lactobacillic acid in L. plantarum, and there is evidence that the same cyclopropane synthase is involved in the biosynthesis of the two pseudoenantiomers.²⁰ To the best of our knowledge, the stereochemistry of naturallyoccurring dihydromalvalic acid has not been determined.

Several approaches to these enantioenriched and enantiopure *cis*-CFAs have been reported. Minnikin and co-workers reported the synthesis of both enantiopodes of enantiopure lactobacillic acid **4** by bidirectional elaboration of a homo-

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[†]Electronic supplementary information (ESI) available: Crystallographic information file for **14b**. Copies of ¹H and ¹³C NMR spectra of all new compounds. CCDC 1009686. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ob01863j



Fig. 1 Structures of cis-cyclopropane fatty acids 1-4 and their biogenic precursor unsaturated fatty acids.

chiral cyclopropane linchpin, which was derived from lipasemediated desymmetrization of cis-cyclopropane-1,2-dimethanol or by diastereoselective Simmons-Smith cyclopropanation of a p-mannitol-derived alkene.^{21,22} Kobayashi and co-workers reported a related approach to both enantiomers of cis-9,10methylenehexadecanoic acid 1 involving bidirectional Wittig extension of an enzymatically-derived homochiral cyclopropay-lactone.¹⁶ Manthorpe and co-workers have reported the synthesis of enantiopure 9R,10S-dihydrosterculic acid 3 with the key step involving the Corey-Chaykovsky cyclopropanation of a homochiral alkylidene bis(sulfoxide).²³ Corey and co-workers reported the synthesis of enantioenriched 9R,10S-dihydrosterculic acid 3 in 87% ee using an enantioselective cyclopropenation with a chiral Rh^{II}-catalyst.²⁴ Katsuki and co-workers reported the enantioselective synthesis of the methyl ester of cis-9R,10S-methylenehexadecanoic acid 1 in 98% ee using a chiral Ir^{III}-salen mediated cyclopropanation.²⁵ Herein we report a general approach to synthesize cis-CFAs in enantiopure forms using a diastereomeric resolution of cyclopropenecarboxamides, originally developed by the Fox group,²⁶ as a key enabling step, allowing the preparation of both enantiomers of the four CFAs 1-4.

Results and discussion

Our approach hinged on the identification of a practical entry point with one arm of the target fatty acid already installed in order to minimize the number of carbon–carbon bond forming reactions and thus total number of synthetic steps. Despite advances in enantioselective cyclopropenation²⁷ and cyclopropanation²⁸ reactions, the imperfect stereoselectivities of even the state-of-the-art methods and the complexity of catalyst synthesis dissuaded us from these approaches. Congruous with our goal to obtain enantiomeric pairs of *cis*-CFAs, our attention was drawn to the elegant work of Fox and coworkers, who reported the medium-scale chromatographic resolution of cycloprop-2-ene carboxylic acids derived from $Rh_2(OAc)_4$ -catalyzed cyclopropenation of terminal alkenes.²⁶ Computational approaches were used to identify chiral oxazolidinones as chromatographic resolving auxiliaries based on the pronounced differences in conformation between the diastereoisomers derived from racemic cyclopropene carboxamides.

Cyclopropenation of 1-octyne **5a** or 1-decyne **5b** with ethyl diazoacetate in toluene, catalyzed by $Rh_2(OAC)_4$,²⁹ afforded multigram quantities of the racemic cyclopropene esters **6a**³⁰ and **6b**,³⁰ respectively (Scheme 1). Saponification (KOH–MeOH) of these esters afforded the corresponding acids **7a**²⁶ and **7b**, respectively, which were converted to the *N*-acyloxazolidinones, by treatment with adamantoyl chloride and Et₃N (to generate the mixed anhydride), and then with (*S*)-4-benzyl-2oxazolidinone and LiCl.²⁶ As espoused by Fox, the use of adamantoyl chloride limits formation of unwanted *N*-acyloxazolidinone derived from reaction with the activating agent when pivalyl chloride is used;²⁶ our work is in concordance and also established the superiority of adamatoyl chloride over isobutylchloroformate. The diastereomers **8a** and **9a** (derived



Scheme 1 Synthesis and resolution of cyclopropenecarboxamides.

from 1-octyne) were readily resolved by flash chromatography, and the stereochemistry of the individual isomers was readily assigned by direct comparison with the data reported.²⁶ In the case of **8b** and **9b** (derived from 1-decyne), these isomers were also readily resolved by flash chromatography; however, the assignment of stereochemistry to each isomer had to await the identification of a crystalline derivative suitable for X-ray crystallographic analysis (*vide infra*).

It has been reported that reduction of cyclopropenes can be achieved with high stereoselectivity using either diimide³¹ or catalytic hydrogenation.^{24,32} In the latter case, H₂/Pd-C/ $CaCO_3^{24}$ is preferred to avoid unwanted cyclopropane ring cleavage that occurs when using H₂/Pd-C.³³ Surprisingly, we found that in all cases investigated, reductions of 8a or 8b using diimide (NH₂NH₂/CuSO₄, TsNHNH₂, KO₂CN=NCO₂K) or catalytic hydrogenation (H₂/Pd-C, H₂/Pd-C/CaCO₃) afforded significant quantities of trans cyclopropanes in amounts up to 10%. The trans-stereochemistry of the minor components obtained from reduction of 8a or 8b was identified on the basis of characteristic ¹H-¹H-coupling constants (*cis*-isomer: J_{cis} = 7.8, 8.6 Hz; J_{trans} = 5.6 Hz. trans-isomer: J_{cis} = 8.0 Hz; J_{trans} = 4.0, 4.6 Hz). Several sources of these compounds were considered, including possible isomerisation of the cyclopropene prior to reduction, loss of stereoselectivity arising from the presence of a chiral auxiliary, or imperfect stereoselectivity of reduction. To address the first point, if isomerisation of the cvcloprop-2-ene 8a to a cvcloprop-1-ene preceded reduction, the analogous reduction of the diastereoisomer 9a should yield the enantiomer; in fact, ¹H NMR analysis revealed that the two respective trans isomers were diastereoisomers. To address the second point, elaboration of 8a to $5-({[(1S)-2-hexy]})$ cvcloprop-2-en-1-vl]methyl}sulfonvl)-1-phenvl-1H-tetrazole and subsequent reduction also yielded similar amounts of the corresponding trans-isomer. We therefore conclude that the trans-isomer arises from intrinsic poor stereoselectivity in the reduction. We were unable to find a literature precedent for the formation of minor amounts of *trans*-cyclopropanes by reduction of similar systems, although we note that similar transformations by others are rarely quantitative.^{24,31} In practice, catalytic hydrogenation using H₂/Pd-C/CaCO₃ provided reproducible and satisfactory results, allowing acquisition of 10a, 10b, 14a and 14b in 70-75% yields (Schemes 2 and 3). In the case of 14b, single crystals were obtained that were suitable for X-ray analysis (Fig. 2), allowing the stereochemistry to be defined relative to the known (S) configuration of the 4-benzyloxazolidinone auxiliary, and allowing stereochemical assignment of the two diastereomers 8b and 9b (Scheme 1).

Reduction of the octyne-derived *N*-acyloxazolidinones **10a** and **14a** with LiBH₄ in MeOH–THF³⁴ afforded the volatile alcohols **11a** and **15a**, respectively, which were converted to the phenyltetrazole sulfides **12a** and **16a** (Schemes 2 and 3). Oxidation to the sulfones **13a** and **17a**, respectively, occurred smoothly upon treatment with ammonium molybdate/H₂O₂.³⁵ A similar sequence of reactions on the decyne-derived *N*-acyloxazolidinones **10b** (\rightarrow **11b** \rightarrow **12b**) and **14b** (\rightarrow **15b** \rightarrow **16b**), followed by oxidation, afforded **13b** and **17b**, respectively.



Scheme 2 Preparation of (2S,3R)-cyclopropane sulfones 13a and 13b.



Scheme 3 Preparation of (2R,3S)-cyclopropane sulfones 17a and 17b.



Fig. 2 ORTEP representation of the molecular structure of (2*R*,3*S*)cyclopropanecarboxamide **14b**, determined by single-crystal X-ray crystallography. Ellipsoids are at the 30% probability level.

The stage was now set for elongation of the fragments **13a**, **13b**, **17a** and **17b** to the full length fatty acids. We illustrate the general approach by the synthesis of (9S,10R)-1 (Scheme 4). Julia-Kocienski olefination of **18**³⁶ with octyne-derived sulfone **13a** in the presence of LiHMDS³⁷ yielded alkene **19** in 79% yield (*E*/*Z* ratio not determined). Saponification (aq. KOH) gave **20**,

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followed by diimide reduction afforded (9S,10R)-1.³⁸ In this reduction, we observed some formation of ring cleaved products when using TsNHNH₂ or KO₂CN=NCO₂K, which we attribute to high concentrations of highly reactive diimide formed by thermal decomposition of these reagents.³¹ By similar logic, **13a** and **21**³⁹ afforded (11*S*,12*R*)-4. Equivalent approaches using the combinations of **13b**, **17a** and **17b** with the appropriate ω -aldehyde esters **18**,³⁶ **21**³⁹ or **24**⁴⁰ afforded the remaining enantiopure *cis*-CFAs.

Conclusions

cis-CFAs are widespread constituents of many complex molecules however access to these compounds in enantiopure form has remained challenging. We report a general route to both enantiomers of four common *cis*-CFAs employing the practicable resolution method of Fox and co-workers and utilizing cyclopropenecarboxylates as synthetic intermediates. In several cases ((8S,9R)-2, (8R,9S)-2 and (9S,10R)-3) this work represents the first total synthesis of these *cis*-CFAs. The methods outlined in this report provide a practical means to not only access these *cis*-CFAs, but should be readily modified to allow the preparation of other straight chain *cis*-CFAs. This method thus stands as an efficient approach to acquire enantiomeric pairs of straight-chain *cis*-CFAs, which will be of particular utility in establishing the stereochemistry of natural materials by HPLC analysis.⁴¹

Experimental

General

Proton nuclear magnetic resonance spectra (¹H NMR, 400 MHz) and proton decoupled carbon nuclear magnetic resonance spectra (13C NMR, 100 MHz) were obtained in deuterochloroform, with residual protonated solvent as internal standard. Chemical shifts are followed by multiplicity, coupling constant(s) (*I*, Hz), integration and assignments where possible. Flash chromatography was carried out according to the procedure of Still et al.42 Analytical thin layer chromatography (t.l.c.) was conducted on aluminium-backed 2 mm thick silica gel 60 GF₂₅₄ and chromatograms were visualized with 20% w/w ceric ammonium molybdate in ethanol. High resolution mass spectra (HRMS) were obtained by ionizing samples using electron spray ionization (ESI) and a time of flight mass analyzer. Dry THF and CH₂Cl₂ was obtained by the method of Pangborn et al.43 Pet. spirits refers to petroleum ether, boiling range 40-60 °C. All other commercially available reagents were used as received. IR spectra were obtained as a thin film on a diamond-coated ZnSe attenuated total reflectance FT-IR spectrometer. The preparation of **6a**,³⁰ **6b**,³⁰ **7a**,²⁶ $8a^{26}$ and $9a^{26}$ have been reported previously.

2-Octylcycloprop-2-ene-1-carboxylic acid (7b). Aqueous KOH (8.5% w/v, 15 ml) was added to a solution of **6b** (1.80 g, 8.03 mmol) in methanol (15 ml) at 0 °C. The resulting mixture was stirred overnight at room temperature, concentrated to remove the methanol, acidified with conc. HCl to pH 1–3,

extracted with CH₂Cl₂, dried (MgSO₄), filtered and concentrated. Flash chromatography of the residue (EtOAc–pet. spirits–AcOH 20:79:1) afforded 7**b** as a colorless oil (1.35 g, 86%). ¹H NMR (CDCl₃, 400 MHz) δ 6.32 (1 H, m), 2.48–2.51 (2 H, m), 2.12 (1 H, d, *J* = 1.5 Hz), 1.56–1.60 (2 H, m), 1.24–1.36 (10 H, m), 0.88 (3 H, t, *J* = 6.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 181.7, 115.5, 93.6, 32.0, 29.4, 29.32, 29.30, 26.7, 25.1, 22.8, 19.4, 14.2; IR (neat) ν 2926, 2855, 1687, 1420, 1368, 1279, 1236 cm⁻¹; HRMS (ESI⁺) calcd for C₁₂H₂₀NaO₂ (M + Na)⁺ 219.1355. Found 219.1356.

(4S)-4-Benzyl-3-[(1S)-2-octylcycloprop-2-ene-1-carbonyl]oxazolidinone (8b) and (4S)-4-benzyl-3-[(1R)-2-octylcycloprop-2-ene-1-carbonyl]oxazolidinone (9b). A stirred solution of 7b (0.352 g, 1.78 mmol) in dry THF (80 ml) at -30 °C was sequentially treated with triethylamine (0.871 ml, 6.24 mmol) then adamantoyl chloride (0.375 g, 1.87 mmol). The mixture was stirred at -30 °C for 1 h, then lithium chloride (0.381 g, mmol), (S)-(-)-4-benzyl-2-oxazolidinone (0.351) 8.91 g, 1.96 mmol) and DMAP (0.021 g, 0.17 mmol) were added. The reaction mixture was gradually allowed to warm to room temperature and stirring was continued overnight. The solvent was evaporated and the residue was partitioned between Et₂O and water. The aqueous layer was extracted 3 times with Et₂O. The combined organic extracts were dried (MgSO₄), filtered and concentrated, and the residue purified by flash chromatography (8-15% EtOAc-hexanes). First to elute: 8b as a colorless oil (0.272 g, 42%), Rf 0.55 in 10% EtOAc-pet. spirits, run twice, $[\alpha]_{D}^{21}$ +103 (*c* 0.120, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.20-7.34 (5 H, m), 6.29 (1H, m), 4.63-4.68 (1 H, m), 4.15–4.23 (2 H, m), 3.46 (1 H, d, J = 1.6 Hz), 3.31 (1 H, dd, J = 10, 3.2 Hz,), 2.75 (1 H, dd, J = 9.6, 3.6 Hz), 2.48–2.54 (2 H, m), 1.58-1.62 (2 H, m), 1.27-1.38 (10 H, m), 0.88 (3 H, t, J = 6.8 Hz); 13 C NMR (CDCl₃, 100 MHz) δ 177.2, 154.1, 135.7, 129.6, 129.0, 127.4, 114.3, 92.3, 66.4, 55.8, 38.2, 32.0, 29.4, 29.32, 29.30, 26.9, 25.1, 22.8, 20.1, 14.2; IR (CH₂Cl₂) v 2927, 2856, 1778, 1686, 1455, 1368, 1275, 1260, 1078 cm⁻¹; HRMS (ESI^{+}) calcd for $C_{22}H_{29}NNaO_{3}$ $(M + Na)^{+}$ 378.2038. Found 378.2040.

Second to elute: **9b** as a semisolid (0.251 g, 40%), R_f 0.45 in 10% EtOAc-pet. spirits, run twice. $[\alpha]_D^{26}$ +43.1 (*c* 0.20, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.20–7.34 (5 H, m), 6.28 (1 H, m), 4.63–4.69 (1 H, m), 4.15–4.24 (2 H, m), 3.45 (1 H, d, *J* = 1.6 Hz), 3.29 (1 H, dd, *J* = 10, 3.2 Hz), 2.78 (1 H, dd, *J* = 9.6, 3.6 Hz), 2.52–2.56 (2 H, m), 1.55–1.64 (2 H, m), 1.26–1.40 (10 H, m), 0.87 (3 H, t, *J* = 6.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 177.1, 154.2, 135.7, 129.6, 129.0, 127.4, 114.1, 92.6, 66.5, 55.9, 38.2, 32.0, 29.4, 29.32, 29.30, 27.0, 25.1, 22.8, 20.2, 14.2; IR (CH₂Cl₂) ν 2927, 2855, 1779, 1687, 1454, 1369, 1275, 1260 cm⁻¹; HRMS (ESI⁺) calcd for C₂₂H₂₉NNaO₃ (M + Na)⁺ 378.2038. Found 378.2040.

General procedure for reduction of cyclopropenes

A solution of the cyclopropene in EtOAc (10 ml) was purged with hydrogen, and then 5% Pd/CaCO₃ (unreduced) (0.10 g per g of cyclopropene) was added. The suspension was stirred vigorously under H_2 for 2 h (until the catalyst changed color from brown to black). The reaction mixture was filtered through Celite and concentrated under reduced pressure to afford a residue.

General procedure for reductive cleavage of [cyclopropane-1-carbonyl]oxazolidinones

Methanol (1 eq.) was added to a stirred solution of [cyclopropane-1-carbonyl]oxazolidinone in dry THF (10 ml mmol⁻¹) at ice cold temperature followed by addition of LiBH₄ (4 eq.). The mixture was gradually warmed to room temperature and stirring was continued for further 4 h. The mixture was quenched with saturated aqueous NH₄Cl solution, extracted with Et₂O, dried (MgSO₄), filtered and concentrated at room temperature (at 600–800 mmHg pressure; caution, the cyclopropanecarbinols are volatile).

General procedure for Mitsunobu reactions

1-Phenyl-1*H*-tetrazole-5-thiol (1.2 eq.) was added to a stirred solution of cyclopropylmethanol in dry THF (10 ml) at 0 °C, followed by addition of PPh₃ (1.2 eq.) and powdered 4 Å molecular sieves (0.5 g). Stirring was continued for 10 min after which DIAD (1.2 eq.) was added. The reaction mixture was warmed to room temperature and stirring was continued overnight. The reaction mixture was filtered through Celite and concentrated under reduced pressure.

General procedure for molybdate oxidation of 1-phenyl-1*H*tetrazolylsulfides

Ammonium molybdate tetrahydrate (0.05 eq.) was dissolved in stages in 30% aq. H_2O_2 (24 eq.) and added slowly to a solution of 1-phenyl-1*H*-tetrazolylsulfide dissolved in a mixture of ethanol and THF (2:3, 30 ml per g of sulfide). After stirring at room temperature for 2 h, additional ammonium molybdate tetrahydrate (0.05 eq.) in 30% aq. H_2O_2 (24 eq.) was added and the mixture was stirred overnight. After partial concentration, the mixture was quenched with water and extracted with dichloromethane. The combined organic layers were dried (MgSO₄) and evaporated to dryness.

(4*S*)-4-Benzyl-3-[(1*S*,2*R*)-2-hexylcyclopropanecarbonyl]oxazolidin-2-one (10a). The general procedure for reduction of cyclopropenes conducted with 8a (0.702 g, 2.14 mmol), after flash chromatography (EtOAc-pet. spirits 1 : 9) afforded 10a as a colorless oil (0.540 g, 75%). $[\alpha]_D^{26}$ +87.6 (*c* 0.120, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.21–7.35 (5 H, m), 4.67–4.73 (1 H, m), 4.14–4.17 (2 H, m), 3.12–3.35 (1 H, dd, *J* = 10, 3.2 Hz), 3.08–3.14 (1H, m), 2.77 (1 H, dd, *J* = 10, 3.6 Hz), 1.25–1.55 (11 H, m), 1.21 (1 H, m), 1.14 (1 H, m), 0.86 (3 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 172.1, 154.0, 135.6, 129.6, 129.1, 127.4, 66.0, 55.6, 38.2, 32.0, 29.7, 29.1, 27.0, 24.7, 22.8, 19.1, 14.5, 14.2; IR (CH₂Cl₂) ν 2956, 2925, 2857, 1774, 1687, 1384, 1349, 1219 cm⁻¹; HRMS (ESI⁺) calcd for C₂₀H₂₈NO₃ (M + H)⁺ 330.2064. Found 330.2085.

(4*S*)-4-Benzyl-3-[(1*S*,2*R*)-2-octylcyclopropane-1-carbonyl]oxazolidin-2-one (10b). The general procedure for reduction of cyclopropenes conducted with 8b (1.00 g, 2.81 mmol), after flash chromatography (EtOAc-pet. spirits 1:9) afforded 10b as colorless oil (0.705 g, 70%). $[\alpha]_D^{20}$ +86 (*c* 0.155, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.21–7.35 (5 H, m), 4.68–4.74 (1 H, m), 4.14–4.17 (2 H, m), 3.31 (1 H, dd, *J* = 10, 3.2 Hz), 3.13 (1H, ddd, *J* = 5.6, 7.8, 8.6 Hz), 2.77 (1 H, dd, *J* = 9.6, 3.6 Hz), 1.21–1.57 (15 H, m), 1.21 (1 H, ddd, *J* = 4.2, 5.6, 6.6 Hz), 1.14 (1 H, ddd, *J* = 4.2, 5.6, 6.6 Hz), 0.87 (3 H, t, *J* = 6.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 172.1, 154.0, 135.6, 129.6, 129.1, 127.4, 66.0, 55.6, 38.2, 32.0, 29.7, 29.4, 29.4, 27.0, 24.7, 22.8, 19.1, 14.5, 14.3; IR (CH₂Cl₂) ν 2923, 2854, 1775, 1687, 1455, 1384, 1349, 1241, 1208 cm⁻¹; HRMS (ESI⁺) calcd for C₂₂H₃₁NNaO₃ (M + Na)⁺ 380.2196. Found 380.2207.

[(15,2*R*)-2-Hexylcyclopropyl]methanol (11a). The general procedure for reductive cleavage of [cyclopropane-1-carbonyl]-oxazolidinones conducted with 10a (0.550 g, 1.67 mmol), after flash chromatography (Et₂O–*n*-pentane 15 : 85) afforded 11a as a colorless oil (0.212 g, 80%). $[\alpha]_{D}^{26}$ –23.9 (*c* 0.105, CHCl₃) (lit.²² = -26.1). ¹H NMR (CDCl₃, 400 MHz) δ 3.55–3.67 (2 H, m), 1.19–1.45 (10 H, m), 1.06–1.12 (1 H, m), 0.83–0.90 (1 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.67–0.72 (1 H, m), -0.04 (1 H, q, *J* = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 63.5, 32.0, 30.3, 29.8, 29.3, 28.7, 22.8, 18.3, 16.3, 14.2, 9.6; IR (CH₂Cl₂) ν 3304, 3991, 2995, 2924, 2855, 1443, 1425, 1379 cm⁻¹; HRMS (ESI⁺) calcd for C₁₀H₂₀NaO (M + Na)⁺ 179.1406. Found 179.1407.

[(15,2*R*)-2-Octylcyclopropyl]methanol (11b). The general procedure for reductive cleavage of [cyclopropane-1-carbonyl]-oxazolidinones conducted with **10b** (0.501 g, 1.39 mmol), after flash chromatography (Et₂O-*n*-pentane 15 : 85) afforded **11b** as a colorless oil (0.220 g, 80%). ¹H NMR (CDCl₃, 400 MHz) δ 3.55–3.67 (2 H, m), 1.05–1.52 (15 H, m), 0.83–0.86 (1 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.67–0.73 (1 H, m), -0.03 (1 H, q, *J* = 4.8 Hz). HRMS (ESI⁺) calcd for C₁₂H₂₄NaO (M + Na)⁺ 207.1719. Found 207.1719.

5-({[(**1***S*,2*R*)-2-Hexylcyclopropyl]methyl}thio)-1-phenyl-1*H*-tetrazole (**12a**). The general procedure for Mitsunobu reactions conducted with **11a** (0.131 g, 0.832 mmol), after flash chromatography (EtOAc-hexane 1 : 9) afforded **12a** as a colorless oil (0.221 g, 84%). $[\alpha]_{D}^{22}$ -6.4 (*c* 0.135, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.53-7.62 (5 H, m), 3.47 (2 H, d, *J* = 8.0 Hz), 1.22-1.56 (11 H, m), 0.86-0.96 (1 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.79-0.85 (1 H, m), 0.07 (1 H, q, *J* = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 154.8, 134.0, 130.2, 129.9, 124.0, 35.2, 32.0, 30.1, 29.3, 28.6, 22.8, 18.1, 14.8, 14.2, 12.6; IR (CH₂Cl₂) ν 2954, 2924, 2854, 1499, 1409, 1384, 1219, 684 cm⁻¹; HRMS (ESI⁺) calcd for C₁₇H₂₅N₄S (M + H)⁺ 317.1794. Found 317.1795.

5-({[(1*S*,2*R*)-2-Octylcyclopropyl]methyl}thio)-1-phenyl-1*H*-tetrazole (12b). The general procedure for Mitsunobu reactions conducted with 11b (0.160 g, 0.818 mmol), after flash chromatography (EtOAc-hexane 1:9) afforded 12b as colorless oil (0.242 g, 80%). $[\alpha]_D^{24}$ –4.9 (*c* 0.47, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.52–7.62 (5 H, m), 3.48 (2 H, d, *J* = 7.6 Hz), 1.19–1.53 (15 H, m), 0.89–0.96 (1 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.79–0.85 (1 H, m), 0.07 (1 H, q, *J* = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 154.1, 134.1, 129.2, 128.9, 122.9, 34.2, 31.0, 29.2, 28.7, 28.6, 28.4, 27.6, 21.8, 17.1, 13.7, 13.2, 11.6; IR (CH₂Cl₂) ν 3016, 2970, 2925, 1743, 1366, 1216, 900 cm⁻¹;

HRMS (ESI⁺) calcd for $C_{19}H_{28}N_4NaS$ (M + Na)⁺ 367.1927. Found 367.1927.

5-({[(1*S*,2*R*)-2-Hexylcyclopropyl]methyl}sulfonyl)-1-phenyl-1*H*-tetrazole (13a). The general procedure for molybdate oxidation of 1-phenyl-1*H*-tetrazolylsulfides applied to **12a** (0.172 g, 0.537 mmol), after flash chromatography (EtOAc-pet. spirits 1:9) afforded **13a** as a colorless liquid (0.164 g, 86%). [α]_D²⁴ +36.3 (*c* 0.73, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.52–7.70 (5 H, m), 3.96 (1 H, dd, *J* = 5.6, 14.8 Hz), 3.55 (1 H, dd, *J* = 9.6, 14.8 Hz), 1.22–1.56 (11 H, m), 1.14–1.17 (1 H, m), 0.96–1.02 (1 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.24 (1 H, q, *J* = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 153.9, 133.2, 131.6, 129.8, 125.3, 57.3, 31.9, 29.7, 29.2, 22.8, 16.0, 14.2, 11.5, 8.1; IR (CH₂Cl₂) *ν* 2956, 2926, 2856, 1661, 1628, 1497, 1338, 1219, 1150, 686 cm⁻¹; HRMS (ESI⁺) calcd for C₁₇H₂₄N₄NaO₂S (M + Na)⁺ 371.1512. Found 371.1510.

5-({[(1*S*,2*R*)-2-Octylcyclopropyl]methyl}sulfonyl)-1-phenyl-1*H*tetrazole (13b). The general procedure for molybdate oxidation of 1-phenyl-1*H*-tetrazolylsulfides applied to 12b (0.131 g, 0.377 mmol), after flash chromatography (EtOAc-pet. spirits 1 : 9) afforded 13b as colorless liquid (0.125 g, 85%). $[\alpha]_D^{2+}$ +36.4 (*c* 0.73, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.60–7.70 (5 H, m), 3.96 (1 H, dd, *J* = 5.6, 14.8 Hz), 3.56 (1 H, dd, *J* = 9.2, 14.4 Hz), 1.22–1.47 (15 H, m), 1.26–1.19 (1 H, m), 0.98–1.02 (1 H, m), 0.87 (3 H, t, *J* = 6.8 Hz), 0.24 (1 H, q, *J* = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 153.9, 132.2, 131.6, 129.8, 125.2, 57.3, 32.0, 29.8, 29.7, 29.6, 29.4, 29.2, 22.8, 16.0, 14.3, 11.5, 8.2; IR (CH₂Cl₂) ν 3016, 2970, 1738, 1743, 1366, 1217, 1228, 1150, 771 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₂₈N₄NaSO₂ (M + Na)⁺ 399.1825. Found 399.1825.

(4*S*)-4-Benzyl-3-[(1*R*,2*S*)-2-hexylcyclopropane-1-carbonyl]oxazolidin-2-one (14a). The general procedure for reduction of cyclopropenes conducted with 9a (0.502 g, 0.152 mmol), after flash chromatography (EtOAc-pet. spirits 1:9) afforded 14a as a colorless oil (0.352 g, 71%). $[\alpha]_D^{20}$ +51 (*c* 0.155, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.22–7.35 (5 H, m), 4.63–4.69 (1 H, m), 4.13–4.20 (2 H, m), 3.26 (1 H, dd, *J* = 10, 3.2 Hz), 3.02–3.08 (1H, m), 2.63–2.69 (1 H, dd, *J* = 10, 3.2 Hz), 1.17–1.56 (11 H, m), 1.10–1.21 (1 H, m), 1.12–1.21 (1 H, m), 0.85 (3 H, t, *J* = 6.4 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 172.0, 154.0, 135.7, 129.5, 129.1, 127.4, 66.1, 56.0, 38.3, 32.0, 29.9, 29.2, 27.0, 24.8, 22.8, 19.1, 14.2; IR (CH₂Cl₂) ν 2955, 2923, 2856, 1775, 1686, 1404, 1349, 1219, 1192 cm⁻¹; HRMS (ESI⁺) calcd for C₂₀H₂₈NO₃ (M + H)⁺ 330.2064. Found 330.2063.

(4*S*)-4-Benzyl-3-[(1*R*,2*S*)-2-octylcyclopropane-1-carbonyl]oxazolidin-2-one (14b). The general procedure for reduction of cyclopropenes conducted with 9b (0.251 g, 0.703 mmol), after flash chromatography (EtOAc-pet. spirits 1:9) afforded 14b (0.18 g, 71%) as white solid, mp 62 °C; $[\alpha]_D^{25}$ +42.8 (*c* 0.47, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.21–7.35 (5 H, m), 4.63–4.69 (1 H, m), 4.13–4.20 (2 H, m), 3.32 (1 H, dd, *J* = 3.2, 13.2 Hz), 3.05 (1H, ddd, *J* = 5.6, 7.8, 8.6 Hz), 2.66 (1 H, dd, *J* = 10, 13.2 Hz), 1.17–1.56 (15H, m), 1.14 (1 H, ddd, *J* = 4.2, 7.8, 8.0 Hz), 1.10 (1 H, ddd, *J* = 4.2, 5.6, 6.6 Hz), 0.84 (3 H, t, *J* = 6.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 172.0, 154.0, 135.7, 129.56, 129.01, 127.4, 66.1, 56.0, 38.3, 32.0, 29.9, 29.8, 29.5, 29.4, 27.0, 24.8, 22.8, 19.1, 14.2, 14.2; IR $(CH_2Cl_2) \nu$ 2953, 2918, 2850, 1781, 1683, 1384, 1350, 1239, 1199 cm⁻¹; HRMS (ESI⁺) calcd for $C_{22}H_{31}NNaO_3 (M + Na)^+$ 380.2196. Found 380.2196.

[(1*R*,2*S*)-2-Hexylcyclopropyl]methanol (15a). The general procedure for reductive cleavage of [cyclopropane-1-carbonyl]-oxazolidinones conducted with 14a (0.705 g, 2.12 mmol), after flash chromatography (Et₂O-*n*-pentane 15:85) afforded 15a as a colorless oil (0.310 g, 80%). $[\alpha]_D^{25}$ +22.9 (*c* 0.251, CHCl₃) (lit.²² +23.1). ¹H NMR (CDCl₃, 400 MHz) δ 3.55–3.67 (2 H, m), 1.05–1.52 (15 H, m), 0.83–0.86 (1 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.67–0.73 (1 H, m), -0.04 (1 H, q, *J* = 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 63.5, 32.0, 30.3, 29.4, 28.7, 22.8, 18.3, 16.3, 14.3, 9.6; IR (CH₂Cl₂) ν 3307, 3291, 2924, 2855, 1442, 1424, 1219 cm⁻¹; HRMS (ESI⁺) calcd for C₁₀H₂₀NaO (M + Na)⁺ 179.1406. Found 179.1407.

[(1*R*,2*S*)-2-Octylcyclopropyl]methanol (15b). The general procedure for reductive cleavage of [cyclopropane-1-carbonyl]-oxazolidinones conducted with 14b (0.472 g, 0.89 mmol), after flash chromatography (Et₂O–*n*-pentane 2 : 8) afforded 15b as a colorless oil (0.205 g, 83%). ¹H NMR (CDCl₃, 400 MHz) δ 3.57–3.65 (2 H, m), 1.04–1.49 (15 H, m), 0.82–0.95 (1 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.67–0.73 (1 H, m), -0.03 (1 H, q, *J* = 5.6 Hz). HRMS (ESI⁺) calcd for C₁₂H₂₄NaO (M + Na)⁺ 207.1719.

5-({[[(1*R*,2*S*)-2-Hexylcyclopropyl]methyl}thio)-1-phenyl-1*H*-tetrazole (16a). The general procedure for Mitsunobu reactions conducted with 15a (0.332 g, 2.11 mmol), after flash chromatography (EtOAc-hexane 1:9) afforded 16a as a colorless oil (0.554 g, 82%). $[\alpha]_D^{20}$ +6 (*c* 0.155, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.53–7.61 (5 H, m), 3.47 (2 H, d, *J* = 8.0 Hz), 1.27–1.58 (11 H, m), 0.86–0.96 (1 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.79–0.83 (1 H, m), 0.07 (1 H, q, *J* = 5.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 154.8, 133.9, 130.2, 129.9, 124.0, 35.2, 32.0, 30.1, 29.3, 28.6, 22.8, 18.1, 14.8, 14.2, 12.6; IR (CH₂Cl₂) ν 2955, 2924, 2854, 1499, 1384, 1219, 684 cm⁻¹; HRMS (ESI⁺) calcd for C₁₇H₂₄N₄NaS (M + H)⁺ 317.1794. Found 317.1795.

5-({[(1*R*,2*S*)-2-Octylcyclopropyl]methyl}thio)-1-phenyl-1*H*-tetrazole (16b). The general procedure for Mitsunobu reactions conducted with 15b (0.201 g, 0.851 mmol), after flash chromatography (EtOAc-hexane 1:9) afforded 16b as colorless oil (0.272 g, 80%). $[\alpha]_{D}^{25}$ +4.2 (*c* 0.57, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.51–7.61 (5 H, m), 3.47 (2 H, d, *J* = 7.6 Hz), 1.19–1.57 (15 H, m), 0.91–0.96 (1 H, m), 0.88 (3 H, t, *J* = 6.4 Hz), 0.79–0.83 (1 H, m), 0.06 (1 H, q, *J* = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 154.8, 134.0, 130.2, 129.9, 124.0, 35.2, 32.0, 30.2, 29.8, 29.7, 29.5, 28.6, 22.8, 18.1, 14.8, 14.3, 12.6; IR (CH₂Cl₂) ν 3066, 2923, 2853, 1597, 1499, 1385, 1244, 1014, 758 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₂₉N₄S (M + H)⁺ 345.2107. Found 345.2113.

5-({[(1*R***,2***S***)-2-Hexylcyclopropyl]methyl}sulfonyl)-1-phenyl-1***H***tetrazole (17a). The general procedure for molybdate oxidation of 1-phenyl-1***H***-tetrazolylsulfides applied to 16a** (0.331 g, 1.04 mmol), after flash chromatography (EtOAc-pet. spirits 1:9) afforded **17a** as a colorless liquid (0.305 g, 83%). $[\alpha]_{D}^{21}$ -36.2 (*c* 0.095, CHCl₃), (lit.²⁵ -36.9). ¹H NMR (CDCl₃, 400 MHz) δ 7.58-7.70 (5 H, m), 3.96 (1 H, dd, *J* = 5.6, 14.4 Hz), 3.56 (1 H, dd, J = 9.2, 14.4 Hz), 1.14–1.45 (11 H, m), 0.97–1.02 (1 H, m), 0.89 (3 H, t, J = 6.4 Hz), 0.24 (1 H, q, J = 5.6 Hz), 0.07 (1 H, q, J = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 153.9, 133.2, 131.6, 129.8, 125.3, 57.3, 31.9, 29.7, 29.2, 22.8, 16.0, 14.2, 11.5, 8.1; IR (CH₂Cl₂) ν 3609, 2956, 2925, 2856, 1497, 1461, 1338, 1219, 1149, 770, 687 cm⁻¹; HRMS (ESI⁺) calcd for C₁₇H₂₄N₄NaO₂S (M + Na)⁺ 371.1512. Found 371.1512.

5-({[(1*R*,2*S*)-2-Octylcyclopropyl]methyl}sulfonyl)-1-phenyl-1*H*tetrazole (17b). The general procedure for molybdate oxidation of 1-phenyl-1*H*-tetrazolylsulfides applied to **16b** (0.232 g, 0.661 mmol), after flash chromatography (EtOAc-pet. spirits 1:9) afforded **17b** as colorless liquid (0.222 g, 88%). $[\alpha]_{D}^{26}$ -38.2 (*c* 0.13, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 7.60-7.70 (5 H, m), 3.96 (1 H, dd, *J* = 5.6, 14.8 Hz), 3.56 (1 H, dd, *J* = 9.2, 14.4 Hz), 1.22-1.47 (15 H, m), 1.26-1.19 (1 H, m), 0.98-1.02 (1 H, m), 0.87 (3 H, t, *J* = 6.8 Hz), 0.24 (1 H, q, *J* = 5.6 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 154.0, 133.3, 131.7, 129.9, 125.4, 57.3, 32.1, 29.9, 29.8, 29.7, 29.5, 29.3, 22.9, 16.1, 14.3, 11.6, 8.2; IR (CH₂Cl₂) ν 2924, 2854, 2361, 2359, 2320, 1738, 1743, 1366, 1217, 1228 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₂₉N₄SO₂ (M + H)⁺ 377.2006. Found 377.2018.

General procedure for Julia-Kocienski olefination

LiHDMS in THF (1 M, 1.2 eq.) was added to a solution of sulfone in dry THF (15 ml per g of sulfone) cooled to -78 °C. After stirring for 10 min, a solution of aldehyde (1.2 eq.) in dry THF (10 ml per g of aldehyde) was added at -78 °C. The reaction was gradually warmed to room temperature and stirring was continued overnight. The reaction mixture was quenched with sat. aq. ammonium chloride, extracted in 1:1 Et₂O-pet. spirits, washed with water, dried (MgSO₄) and concentrated.

General procedure for saponification

A solution of KOH (3 eq.) in H_2O (20 ml per g of ester) was added to a solution of ester in THF (2 ml per g of ester) and methanol (2 ml per g of ester) at 0 °C. The resulting mixture was gradually warmed to room temperature and stirring was continued overnight. The solvent was evaporated under reduced pressure, and the residue obtained was acidified with 0.5 M citric acid, extracted with Et₂O, dried (MgSO₄), filtered and concentrated.

General procedure for diimide reduction

Hydrazine monohydrate (1.60 ml) was added to a solution of alkene in ethanol (5 ml). Aliquots of a saturated aqueous solution of CuSO₄ (total amount 0.16 ml) were added daily for 5 d until ¹H-NMR analysis of an aliquot of the reaction mixture showed complete consumption of the starting material. The reaction mixture was quenched with 2 N HCl, extracted several times in Et₂O, dried (MgSO₄) and concentrated.

Methyl 8-[(1*S*,2*R*)-2-hexylcyclopropyl]oct-7-enoate (19). The general procedure for Julia–Kocienski olefination applied to 13a (0.305 g, 0.862 mmol) and methyl 7-oxaheptanoate (18)³⁶ (0.163 g, 1.03 mmol), after flash chromatography (EtOAc–pet. spirits 1:9) afforded 19 (0.191 g, 79%). $[\alpha]_{24}^{24}$ –34.9 (*c* 0.505, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.45–5.49 (0.7 H, m),

5.31–5.38 (0.3 H, m), 5.10–5.16 (0.7 H, m), 4.97–5.02 (0.3 H, m), 3.62 (3 H, s), 2.24–2.29 (2 H, m), 2.08–2.14 (0.6 H, m), 1.96 (1.4 H, q, J = 6.8 Hz), 1.55–1.64 (2 H, m), 1.20–1.39 (18 H, m), 0.72–0.88 (1.3 H, m), 0.84 (3 H, t, J = 6.8 Hz), 0.03–0.09 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 174.4, 130.2, 130.0, 129.9, 129.9, 51.6, 34.3, 34.2, 32.7, 32.0, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 29.0, 28.8, 27.5, 25.0, 22.8, 18.6, 18.5, 14.3, 14.3, 14.1, 12.5; IR (CH₂Cl₂) ν 2924, 2854, 1741, 1436, 1219 cm⁻¹; HRMS (ESI⁺) calcd for C₁₈H₃₃O₂ (M + H)⁺ 281.2475. Found 281.2494.

(9S,10R)-cis-Methylenehexadecanoic acid ((9S,10R)-1)

8-((1S,2R)-2-Hexylcyclopropyl)oct-7-enoic acid (20). The general procedure for saponification applied to 19 (0.102 g, 0.361 mmol) afforded crude 20 (0.081, 86%). $[\alpha]_{D}^{24}$ -36.8 (c 0.405, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.54–5.52 (0.7 H, m), 5.35-5.41 (0.3 H, m), 5.14-5.20 (0.7 H, m), 5.01-5.06 (0.3 H, m), 2.33-2.37 (2 H, m), 2.14-2.16 (0.6 H, m), 2.01 (1.4 H, q, J = 6.8 Hz), 1.59–1.69 (2 H, m), 1.59–1.69 (0.3 H, m), 1.20-1.43 (16.7 H, m), 0.76-0.94 (1.3 H, m), 0.88 (3 H, t, J = 6.8 Hz), 0.08-0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 179.2, 130.1, 130.0, 129.8, 34.0, 34.0, 32.6, 32.0, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 28.9, 28.7, 27.4, 24.8, 24.7, 22.8, 18.7, 18.6, 18.5, 14.3, 14.3, 14.1, 12.5; IR (CH₂Cl₂) v 2924, 2854, 1707, 1412, 1219 cm⁻¹; HRMS (ESI⁺) calcd for C₁₇H₃₁O₂ $(M + H)^+$ 267.2319. Found 267.2338.

(95,10*R*)-*cis-Methylenehexadecanoic* acid ((95,10*R*)-1). The general procedure for diimide reduction applied to **20** (0.079 g, 0.296 mmol), after flash chromatography (EtOAc–hexane 20:80) yielded (**95,10***R*)-**1** (0.073 g, 84%). $[\alpha]_{\rm D}^{25}$ –1.63 (*c* 0.23, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 2.35 (2 H, t, *J* = 6.7 Hz), 1.60–1.65 (2 H, m), 1.10–1.36 (20 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.61–0.67 (2 H, m), 0.53–0.58 (1 H, m), -0.33 (1 H, q, *J* = 5.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 179.7, 34.0, 31.9, 30.1, 30.1, 29.4, 29.3, 29.2, 29.0, 28.7, 28.6, 24.6, 22.7, 15.7, 15.7, 14.1, 10.1; IR (CH₂Cl₂) ν 2922, 2853, 1708, 1457, 1284, 1412 cm⁻¹; HRMS (ESI⁺) calcd for C₁₇H₃₃O₂ (M + H)⁺ 269.2475.

Methyl 10-((1S,2R)-2-hexylcyclopropyl)dec-9-enoate (22). The general procedure for Julia-Kocienski olefination applied to 13a (0.081 g, 0.23 mmol) and methyl 7-oxanonanoate $(21)^{39}$ (0.051 g, 0.28 mmol), after flash chromatography (EtOAc-pet. spirits 1:9) afforded 22 (0.061 g, 82%). $[\alpha]_{D}^{25}$ -32.3 (c 0.79, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.46–5.53 (0.7 H, m), 5.35-5.42 (0.3 H, m), 5.13-5.19 (0.7 H, m), 5.00-5.05 (0.3 H, m), 3.66 (3 H, s), 2.27-2.32 (2 H, m), 2.10-2.18 (0.6 H, m), 1.98 (1.4 H, q, J = 6.4 Hz), 1.59–1.63 (2 H, m), 1.26–1.41 (20 H, m), 0.75-1.07 (1.3 H, m), 0.87 (3 H, t, J = 6.8 Hz), 0.07-0.12 (0.7 H, m); 13 C NMR (CDCl₃, 100 MHz) δ 174.4, 130.1, 130.0, 129.9, 129.8, 51.5, 34.2, 32.6, 32.0, 29.9, 29.8, 29.72, 29.71, 29.52, 29.51, 29.4, 29.3, 28.7, 27.4, 24.9, 22.8, 18.6, 18.4, 14.2, 14.0, 12.5; IR (CH₂Cl₂) ν 2924, 2854, 1741, 1436, 1365, 1219 cm⁻¹; HRMS (ESI⁺) calcd for $C_{20}H_{37}O_2$ (M + H)⁺ 309.2788. Found 309.2809.

(11S,12R)-Lactobacillic acid ((11S,12R)-4)

10-((15,2R)-2-Hexylcyclopropyl)dec-9-enoic acid (23). The general procedure for saponification applied to 22 (0.052 g, 0.36 mmol) afforded crude 23 (0.042 g, 85%). $[\alpha]_{\rm D}^{25}$ -36.5

(c 0.40, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.46–5.53 (0.7 H, m), 5.36–5.42 (0.3 H, m), 5.13–5.19 (0.7 H, m), 5.00–5.05 (0.3 H, m), 2.32–2.37 (2 H, m), 2.10–2.16 (0.6 H, m), 1.99 (1.4 H, q, J = 6.4 Hz), 1.53–1.65 (2 H, m), 1.27–1.43 (21 H, m), 0.76–0.92 (1.3 H, m), 0.88 (3 H, t, J = 6.4 Hz), 0.08–0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 178.3, 130.4, 130.2, 129.8, 129.8, 33.9, 32.8, 32.0, 29.9, 29.8, 29.6, 29.4, 29.3, 29.21, 29.20, 29.1, 27.6, 24.9, 22.8, 18.6, 18.4, 14.3, 14.1, 12.5; IR (CH₂Cl₂) ν 2923, 2854, 1707, 1412, 1278, 1219, 959 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₃₅O₂ (M + H)⁺ 295.2632. Found 295.2656.

(11S,12R)-Lactobacillic acid ((11S,12R)-4). The general procedure for diimide reduction applied to 23 (0.042 g, 0.30 mmol), after flash chromatography (EtOAc-hexane 20 : 80) yielded (11S,12R)-4 (0.032 g, 86%). $[\alpha]_D^{26}$ –0.61 (*c* 0.25, CHCl₃), (lit.²² –0.31). ¹H NMR (CDCl₃, 400 MHz) δ 2.43 (2 H, t, *J* = 7.6 Hz), 1.62–1.68 (2 H, m), 1.25–1.37 (22 H, m), 1.10–1.17 (2 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.64–0.68 (2 H, m), 0.53–0.59 (1 H, m), -0.33 (1 H, q, *J* = 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 179.3, 34.0, 32.1, 30.4, 30.3, 29.9, 29.8, 29.6, 29.5, 29.4, 29.2, 28.94, 28.91, 24.8, 22.9, 15.92, 15.90, 14.3, 11.1; IR (CH₂Cl₂) ν 2923, 2854, 1740, 1365, 1217 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₃₇O₂ (M + H)⁺ 296.2788. Found 297.2786. The ¹H and ¹³C NMR data reported here differs from those previously reported.²²

Methyl 7-[(1S,2R)-2-octylcyclopropyl]hept-6-enoate (25). The general procedure for Julia-Kocienski olefination applied to **13b** (0.0821 g, 0.319 mmol) and methyl 6-oxohexanoate $(24)^{40}$ (0.055 g, 0.383 mmol) after flash chromatography (EtOAc-pet. spirits 1:9) afforded 25 (0.062 g, 80%). $\left[\alpha\right]_{D}^{24}$ -35.2 (c 0.21, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.54–5.52 (0.7 H, m), 5.35-5.41 (0.3 H, m), 5.15-5.21 (0.7 H, m), 5.02-5.07 (0.3 H, m), 3.66 (3 H, s), 2.28–2.34 (2 H, m), 2.16 (0.6 H, q, J = 7.2 Hz), 2.02 (1.4 H, q, J = 6.8 Hz), 1.59–1.71 (2 H, m), 1.16–1.44 (18 H, m), 0.76-0.94 (1.3 H, m), 0.88 (3 H, t, J = 6.4 Hz), 0.08-0.12 (0.7 H, m); 13 C NMR (CDCl₃, 100 MHz) δ 174.3, 130.3, 130.2, 129.7, 129.5, 51.6, 34.12, 34.10, 32.5, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 24.7, 24.6, 22.8, 18.6, 18.5, 18.4, 14.3, 12.5; IR (CH₂Cl₂) v 2992, 2924, 2854, 1742, 1457, 1436, 1200, 1168 cm⁻¹; HRMS (ESI⁺) calcd for $C_{19}H_{34}NaO_2$ (M + Na)⁺ 317.2451. Found 317.2451.

8S,9R-Dihydromalvalic acid ((8S,9R)-2)

7-[(1S,2R)-2-Octylcyclopropyl]hept-6-enoic acid (26). The general procedure for saponification applied to 25 (0.055 g, 0.17 mmol) afforded crude 26 (0.041 g, 85%). $\left[\alpha\right]_{\rm D}^{24}$ -31.7 $(c 0.14, \text{CHCl}_3)$. ¹H NMR $(\text{CDCl}_3, 400 \text{ MHz}) \delta 5.45-5.52 (0.7 \text{ H},$ m), 5.35-5.41 (0.3 H, m), 5.15-5.21 (0.7 H, m), 5.03-5.08 (0.3 H, m), 2.33–2.39 (2 H, m), 2.18 (0.6 H, q, J = 7.2 Hz), 2.03 (1.4 H, q, J = 7.2 Hz), 1.63–1.69 (2 H, m), 1.26–1.63 (18 H, m), 0.76-0.92 (1.3 H, m), 0.88 (3 H, t, J = 6.4 Hz), 0.09-0.13 (0.7 H, m); 13 C NMR (CDCl₃, 100 MHz) δ 177.7, 130.4, 130.3, 129.6, 129.4, 33.7, 33.6, 32.4, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.3, 27.2, 24.5, 24.3, 22.9, 18.7, 18.6, 18.5, 14.4, 14.3, 14.1, 12.6; IR (CH₂Cl₂) ν 2923, 2854, 1740, 1365, 1217 cm⁻¹; HRMS (ESI^{+}) calcd for $C_{18}H_{32}NaO_{2}$ $(M + Na)^{+}$ 303.2294. Found 303.2295.

8S,9R-Dihydromalvalic acid (8S,9R-2). The general procedure for diimide reduction applied to **26** (0.035 g, 0.13 mmol), after

flash chromatography (EtOAc–hexane 20 : 80) yielded (85,9*R*)-2 (0.026 g, 86%). $[\alpha]_D^{25}$ –0.77 (*c* 0.32, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 2.35 (2 H, t, *J* = 7.6 Hz), 1.62–1.66 (2 H, m), 1.27–1.38 (20 H, m), 1.12–1.14 (2 H, m), 0.88 (3 H, t, *J* = 7.2 Hz), 0.60–0.69 (2 H, m), 0.53–0.58 (1 H, m), -0.33 (1 H, q, *J* = 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 179.7, 34.1, 32.1, 30.4, 30.1, 29.8, 29.5, 29.4, 29.3, 289, 28.8, 24.9, 22.9, 15.9, 15.9, 14.3, 11.1; IR (CH₂Cl₂) ν 2970, 2924, 2854, 1738, 1456, 1366, 1228, 1217 cm⁻¹; HRMS (ESI⁺) calcd for C₁₈H₃₄NaO₂ (M + Na)⁺ 305.2451. Found 305.2451.

Methyl 8-[(1S,2R)-2-octylcyclopropyl]oct-7-enoate (27). The general procedure for Julia-Kocienski olefination applied to **13b** (0.102 g, 0.265 mmol) and methyl 7-oxoheptanoate $(18)^{36}$ (0.0512 g, 0.319 mmol) after flash chromatography (EtOAc-pet. spirits 1:9) afforded 27 (0.074 g, 78%). $[\alpha]_{D}^{26}$ -36.0 (c 0.45, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.54–5.53 (0.7 H, m), 5.36-5.42 (0.3 H, m), 5.14-5.20 (0.7 H, m), 5.01-5.06 (0.3 H, m), 3.66 (3 H, s), 2.28-2.33 (2 H, m), 2.12-2.17 (0.6 H, m), 1.98-3.04 (1.4 H, q, J = 6.4 Hz), 1.58-1.65 (2 H, m), 1.26-1.43 (19 H, m), 0.76-0.91 (2.3 H, m), 0.88 (3 H, t, J = 6.4 Hz),0.08–0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 174.4, 130.2, 130.02, 130.01, 129.9, 51.6, 34.2, 32.7, 32.1, 29.9, 29.84, 29.83, 29.7, 29.6, 29.52, 29.50, 29.3, 28.8, 25.0, 22.9, 18.6, 18.5, 14.32, 14.31, 12.5; IR (CH₂Cl₂) v 2970, 2923, 2854, 1740, 1436, 1365, 1217, 1228, 1204 cm⁻¹; HRMS (ESI⁺) calcd for $C_{20}H_{36}NaO_2 (M + Na)^+$ 331.2607. Found 331.2608.

(9S,10R)-Dihydrosterculic acid ((9S,10R)-3)

8-[(1S,2R)-2-Octylcyclopropyl]oct-7-enoic (28). The acid general procedure for saponification applied to 27 (0.071 g, 0.24 mmol) afforded crude 28 (0.052 g, 83%). $\left[\alpha\right]_{\rm D}^{26}$ -37.6 (c 0.21, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.54–5.53 (0.7 H, m), 5.36-5.42 (0.3 H, m), 5.14-5.20 (0.7 H, m), 5.01-5.06 (0.3 H, m), 3.66 (3 H, s), 2.28-2.33 (2 H, m), 2.12-2.17 (0.6 H, m), 1.98-3.04 (1.4 H, q, J = 6.4 Hz), 1.58-1.65 (2 H, m), 1.26-1.43 (17 H, m), 0.76-0.91 (2.3 H, m), 0.88 (3 H, t, J = 6.4 Hz), 0.08–0.12 (0.7 H, m); 13 C NMR (CDCl₃, 100 MHz) δ 177.7, 130.2, 130.1, 129.9, 33.8, 32.7, 32.2, 30.0, 29.92, 29.91, 29.8, 29.7, 29.6, 29.4, 28.9, 28.8, 27.5, 24.8, 24.8, 22.9, 18.71, 18.70, 18.5, 14.4, 14.4, 14.2, 12.6; IR (CH₂Cl₂) v 2970, 2924, 2854, 1713, 1455, 1365, 1228, 1217 cm⁻¹; HRMS (ESI⁺) calcd for $C_{19}H_{34}NaO_2 (M + Na)^+$ 317.2451. Found 317.2451.

(95,10*R*)-*Dihydrosterculic acid* ((95,10*R*)-3). The general procedure for diimide reduction applied to **28** (0.050 g, 0.17 mmol), after flash chromatography (EtOAc–hexane–AcOH 20:80:1) gave (**95,10***R*)-3 as a white solid (0.042 g, 80%). $[\alpha]_D^{24}$ –0.81 (*c* 0.295, CHCl₃). ¹H NMR (CDCl₃ + 1% TFA, 400 MHz) δ 2.43 (2 H, t, *J* = 7.6 Hz), 1.62–1.68 (2 H, m), 1.25–1.37 (22 H, m), 1.10–1.17 (2 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.64–0.68 (2 H, m), 0.53–0.59 (1 H, m), -0.33 (1 H, q, *J* = 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 178.7, 34.1, 32.1, 30.4, 30.3, 29.8, 29.6, 29.5, 29.4, 29.2, 28.9, 28.8, 24.9, 22.9, 15.9, 15.9, 14.3, 11.1; IR (CH₂Cl₂) ν 3016, 2970, 2925, 2854, 1738, 1436, 1366, 1229, 1217 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₃₆NaO₂ (M + Na)⁺ 319.2608. Found 319.2608.

Methyl 8-[(1R,2S)-2-hexylcyclopropyl]oct-7-enoate (29). The general procedure for Julia-Kocienski olefination applied to

17a (0.101 g, 0.520 mmol) and methyl 7-oxaheptanoate (18)³⁶ (0.091 g, 0.62 mmol), after flash chromatography (EtOAc-pet. spirits 1:9) afforded 29 (0.122 g, 83%). $[\alpha]_D^{22}$ +35.6 (*c* 0.190, CHCl₃) (lit.²⁵ +31.6). ¹H NMR (CDCl₃, 400 MHz) δ 5.45–5.52 (0.7 H, m), 5.35–5.41 (0.3 H, m), 5.13–5.19 (0.7 H, m), 5.01–5.06 (0.3 H, m), 3.66 (3 H, s), 2.28–2.33 (2 H, m), 2.12–2.17 (0.6 H, m), 2.01 (1.4 H, q, *J* = 6.8 Hz), 1.58–1.65 (2 H, m), 1.23–1.42 (18 H, m), 0.76–0.92 (1.3 H, m), 0.88 (3 H, t, *J* = 6.4 Hz), 0.06–0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 174.4, 130.1, 130.0, 129.9, 129.8, 51.5, 34.2, 32.6, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.9, 28.7, 27.4, 25.0, 24.9, 22.8, 18.5, 18.4, 14.3, 14.2, 14.1, 12.5; IR (CH₂Cl₂) ν 2989, 2924, 2855, 1741, 1543, 1437, 1219, 1168 cm⁻¹; HRMS (ESI⁺) calcd for C₁₈H₃₂NaO₂ (M + Na)⁺ 303.2294.

(9R,10S)-cis-Methylenehexadecanoic acid ((9R,10S)-1)

8-[(1R,2S)-2-Hexylcyclopropyl]oct-7-enoic acid (30). The general procedure for saponification applied to 29 (0.125 g, 0.446 mmol) afforded crude **30** (0.103 g, 87%). $\left[\alpha\right]_{D}^{23}$ +32.5 (c 0.34, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.45–5.52 (0.7 H, m), 5.35-5.41 (0.3 H, m), 5.14-5.20 (0.7 H, m), 5.01-5.06 (0.3 H, m), 2.32-2.37 (2 H, m), 2.13-2.17 (0.6 H, m), 2.00 (1.4 H, q, J = 6.8 Hz), 1.66–1.67 (1 H, m), 1.52–1.56 (1 H, m), 1.20-1.43 (16 H, m), 0.76-0.92 (1.3 H, m), 0.88 (3 H, t, J = 6.4 Hz), 0.08-0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 178.8, 130.1, 130.0, 129.8, 33.9, 33.9, 32.6, 32.0, 29.8, 29.7, 29.5, 29.4, 29.3, 29.3, 28.8, 28.6, 27.4, 24.7, 22.8, 18.6, 18.5, 18.4, 14.3, 14.2, 14.0, 12.5; IR (CH₂Cl₂) v 2923, 2854, 1708, 1456, 1412, 1219, 959 cm⁻¹; HRMS (ESI⁺) calcd for $C_{17}H_{31}O_2$ $(M + H)^+$ 267.2319. Found 267.2340.

(9R,10S)-cis-Methylenehexadecanoic acid ((9R,10S)-1). The general procedure for diimide reduction applied to **30** (0.08 g, 0.30 mmol), after flash chromatography (EtOAc-hexane 20:80) yielded (**9R,10S)**-1 (0.092 g, 89%). $[\alpha]_D^{20}$ +0.86 (c 0.155, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 2.35 (2 H, t, J = 7.6 Hz), 1.60–1.65 (2 H, m), 1.12–1.36 (20 H, m), 0.88 (3 H, t, J = 6.8 Hz), 0.64–0.67 (2 H, m), 0.53–0.58 (1 H, m), -0.33 (1 H, q, J = 5.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 178.6, 34.0 32.1, 30.3, 30.2, 29.8, 29.6, 29.5, 29.4, 29.2, 28.9, 28.8, 25.0, 22.8, 15.9, 15.8, 14.2, 11.1; IR (CH₂Cl₂) ν 2922, 2853, 1708, 1458, 1412, 1284, 937 cm⁻¹; HRMS (ESI⁺) calcd for C₁₇H₃₃O₂ (M + H)⁺ 269.2475. Found 269.2475.

Methyl 10-[(1*R*,2*S*)-2-hexylcyclopropyl]dec-9-enoate (31). The general procedure for Julia–Kocienski olefination applied to 17a (0.152 g, 0.431 mmol) and methyl 9-oxanonanoate (21)³⁹ (0.091 g, 0.52 mmol), after flash chromatography (EtOAc–pet. spirits 1:9) afforded 31 (0.115 g, 76%). [*α*]_D²⁴ +31.3 (*c* 0.35, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.46–5.53 (0.7 H, m), 5.35–5.41 (0.3 H, m), 5.13–5.19 (0.7 H, m), 5.00–5.05 (0.3 H, m), 3.66 (3 H, s), 2.27–2.31 (2 H, m), 2.10–2.15 (0.6 H, m), 1.98 (1.4 H, q, *J* = 6.8 Hz), 1.57–1.63 (2 H, m), 1.26–1.42 (20 H, m), 0.75–0.9 (1.3 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.08–0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 174.5, 130.5, 130.2, 129.8, 129.7, 51.5, 34.2, 32.8, 32.0, 29.8, 29.8, 29.7, 29.5, 29.33, 29.30, 29.24, 29.21, 29.0, 27.6, 2.1, 22.8, 18.6, 18.5, 18.4, 14.32, 14.31, 14.1, 12.5; IR (CH₂Cl₂) ν 2989, 2924, 2854, 1741, 1542, 1437,

1377, 1219, 1170, 673 cm $^{-1};$ HRMS (ESI $^{+})$ calcd for $C_{20}H_{36}NaO_2\left(M+Na\right)^{+}$ 331.2608. Found 331.2608.

(11R,12S)-Lactobacillic acid ((11R,12S)-4)

10-[(1R,2S)-2-Hexylcyclopropyl]dec-9-enoic (32). The acid general procedure for saponification applied to 31 (0.102 g, 0.324 mmol) afforded crude 32 (0.082 g, 84%). $\left[\alpha\right]_{D}^{23}$ +36.8 (c 0.3, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.46–5.53 (0.7 H, m), 5.36-5.42 (0.3 H, m), 5.13-5.19 (0.7 H, m), 5.00-5.05 (0.3 H, m), 2.32-2.36 (2 H, m), 2.10-2.16 (0.6 H, m), 1.99 (1.4 H, q, J = 6.8 Hz), 1.52–1.66 (2 H, m), 1.20–1.43 (20 H, m), 0.76-0.92 (1.3 H, m), 0.87 (3 H, t, J = 6.8 Hz), 0.08-0.12 (0.7 H, m); 13 C NMR (CDCl₃, 100 MHz) δ 178.9, 130.4, 130.1, 129.8, 129.7, 33.9, 32.8, 32.0, 29.9, 29.82, 29.80, 29.6, 29.4, 29.32, 29.30, 29.2, 29.1, 29.0, 27.6, 24.8, 22.8, 18.61, 18.60, 18.4, 14.3, 14.2, 14.0, 12.5; IR (CH₂Cl₂) v 2923, 2854, 1708, 1457, 1412, 1285, 959 cm⁻¹; HRMS (ESI⁺) calcd for $C_{19}H_{35}O_2$ (M + H)⁺ 295.2632. Found 295.2654.

(11*R*,12*S*)-Lactobacillic acid ((11*R*,12*S*)-4). The general procedure for diimide reduction applied to 32 (0.080 g, 0.27 mmol), after flash chromatography (EtOAc-hexane 20 : 80) yielded (11*R*,12*S*)-4 (0.062 g, 81%). $[\alpha]_{D}^{20}$ +0.94 (*c* 0.155, CHCl₃) (lit.²² +0.16; lit.⁴⁴ +0.25). ¹H NMR (CDCl₃, 400 MHz) δ 2.35 (2 H, t, *J* = 7.6 Hz), 1.61–1.65 (2 H, m), 1.25–1.37 (22 H, m), 1.10–1.17 (2 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.64–0.68 (2 H, m), 0.53–0.59 (1 H, m), -0.33 (1 H, q, *J* = 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 180.1, 34.2, 32.1, 30.4, 30.3, 29.9, 29.8, 29.6, 29.5, 29.4, 29.2, 28.9, 24.8, 22.9, 15.9, 15.9, 14.3, 11.1; IR (CH₂Cl₂) ν 2923, 2854, 1708, 1412, 1219 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₃₆O₂ (M + H)⁺ 297.2788. Found 297.2788. The ¹H and ¹³C NMR data reported here differs from those previously reported.²²

Methyl 7-[(1R,2S)-2-octylcyclopropyl]hept-6-enoate (33). The general procedure for Julia-Kocienski olefination applied to 17b (0.062 g, 0.15 mmol) and methyl 6-oxohexanoate $(24)^{40}$ (0.0412 g, 0.191 mmol) after flash chromatography (EtOAc-pet. spirits 1:9) afforded 33 (0.042 g, 87%). $\left[\alpha\right]_{D}^{24}$ +33.3 (c 0.25, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.54–5.52 (0.7 H, m), 5.35-5.41 (0.3 H, m), 5.15-5.21 (0.7 H, m), 5.00-5.07 (0.3 H, m), 3.66 (3 H, s), 2.28–2.34 (2 H, m), 2.13–2.17 (0.6 H, q, J = 7.2 Hz), 2.02 (1.4 H, q, J = 6.4 Hz), 1.59–1.71 (2 H, m), 1.21-1.46 (18 H, m), 0.76-0.92 (1.3 H, m), 0.88 (3 H, t, J = 6.4 Hz), 0.08-0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 174.4, 130.3, 130.2, 129.8, 129.5, 51.6, 34.1, 32.5, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.3, 24.6, 22.9, 18.6, 18.5, 14.3, 14.1, 12.6; IR (CH₂Cl₂) v 2923, 2854, 1742, 1436, 1365, 1219 cm⁻¹; HRMS (ESI⁺) calcd for $C_{19}H_{35}O_2$ (M + H)⁺ 295.2632. Found 295.2650.

(8R,9S)-Dihydromalvalic acid ((8R,9S)-2)

7-[(1R,2S)-2-Octylcyclopropyl]hept-6-enoic acid (34). The general procedure for saponification applied to 33 (0.042 g, 0.14 mmol) afforded crude 34 (0.029, 80%). $[\alpha]_{D}^{25}$ +32.9 (c 0.24, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.54–5.52 (0.7 H, m), 5.35–5.41 (0.3 H, m), 5.15–5.21 (0.7 H, m), 5.03–5.08 (0.3 H, m), 2.33–2.39 (2 H, m), 2.18 (0.6 H, q, *J* = 7.2 Hz), 2.03 (1.4 H, q, *J* = 7.2 Hz), 1.63–1.69 (2 H, m), 1.26–1.63 (16 H, m), 0.76–0.92 (1.3 H, m), 0.88 (3 H, t, *J* = 6.4 Hz), 0.09–0.13 (0.7 H,

m); ¹³C NMR (CDCl₃, 100 MHz) δ 177.7, 130.4, 130.3, 129.6, 129.4, 33.7, 33.6, 32.4, 32.1, 29.9, 29.84, 29.82, 29.7, 29.6, 29.5, 29.3, 27.2, 24.5, 24.3, 22.9, 18.7, 18.6, 18.5, 14.4, 14.3, 14.1, 12.6; IR (CH₂Cl₂) ν 2924, 2855, 1710, 1542, 1457, 1365, 1219 cm⁻¹; HRMS (ESI⁺) calcd for C₁₈H₃₃O₂ (M + H)⁺ 281.2475. Found 281.2494.

(8*R*,9*S*)-*Dihydromalvalic acid* ((8*R*,9*S*)-2). The general procedure for diimide reduction applied to 34 (0.021 g, 0.075 mmol), after flash chromatography (EtOAc-hexane 20:80) yielded (8*R*,9*S*)-2 as a colorless oil (0.015 g, 75%). $[\alpha]_D^{24}$ +0.61 (*c* 0.350, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 2.36 (2 H, t, *J* = 7.2 Hz), 1.63–1.66 (2 H, m), 1.25–1.37 (20 H, m), 1.10–1.14 (2 H, m), 0.88 (3 H, t, *J* = 7.2 Hz), 0.64–0.67 (2 H, m), 0.53–0.58 (1 H, m), -0.33 (1 H, q, *J* = 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 178.4, 33.9, 32.1, 30.4, 30.1, 29.8, 29.5, 29.4, 29.3, 28.9, 28.8, 24.9, 22.9, 15.92, 15.90, 14.3, 11.1; IR (CH₂Cl₂) ν 2922, 2854, 1708, 1458, 1366, 1284, 1217 cm⁻¹; HRMS (ESI⁺) calcd for C₁₈H₃₄NaO₂ (M + Na)⁺ 305.2451. Found 305.2451.

Methyl 8-[(1R,2S)-2-octylcyclopropyl]oct-7-enoate (35). The general procedure for Julia-Kocienski olefination applied to **17b** (0.130 g, 0.345 mmol) and methyl 7-oxoheptanoate $(18)^{36}$ (0.0651 g, 0.414 mmol) after flash chromatography (EtOAc-pet. spirits 1:9) afforded 35 (0.094 g, 85%) as a colorless oil. $[\alpha]_{D}^{24}$ +34.1 (c 0.36, CHCl₃). ¹H NMR (CDCl₃, 400 MHz) δ 5.45-5.52 (0.7 H, m), 5.35-5.41 (0.3 H, m), 5.13-5.19 (0.7 H, m), 5.01-5.06 (0.3 H, m), 3.66 (3 H, s), 2.28-2.33 (2 H, m), 2.12-2.15 (0.6 H, m), 2.00 (1.4 H, q, J = 6.8 Hz), 1.58-1.65 (2 H, m), 1.21-1.42 (18 H, m), 0.76-0.92 (2.3 H, m), 0.88 (3 H, t, J = 6.4 Hz), 0.08-0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 174.4, 130.2, 130.0, 129.9, 129.9, 51.6, 34.2, 32.7, 29.9, 29.84, 29.82, 29.7, 29.6, 29.51, 29.50, 29.3, 28.8, 25.0, 22.9, 18.6, 18.5, 14.3, 14.1, 12.5; IR $(CH_2Cl_2) \nu$ 2990, 2923, 2853, 1742, 1365, 1219 cm⁻¹; HRMS (ESI⁺) calcd for $C_{20}H_{37}O_2 (M + H)^+$ 309.2788. Found 309.2876.

8-[(1*R*,2*S*)-2-Octylcyclopropyl]octanoic acid (9*R*,10*S*-dihydrosterculic acid; 3)

8-[(1R,2S)-2-Octylcyclopropyl]oct-7-enoic (36). The acid general procedure for saponification applied to 35 (0.051 g, 0.17 mmol) afforded crude 36 (0.042 g, 81%) as a colorless oil. $[\alpha]_{D}^{26}$ +37.6 (c 0.24, CHCl₃) (lit.²⁴ +40). ¹H NMR (CDCl₃, 400 MHz) δ 5.45-5.53 (0.7 H, m), 5.36-5.41 (0.3 H, m), 5.14-5.20 (0.7 H, m), 5.01-5.06 (0.3 H, m), 2.33-2.38 (2 H, m), 2.15-2.17 (0.6 H, m), 2.01 (1.4 H, q, J = 6.4 Hz), 1.62-1.67 (2 H, m), 1.22–1.43 (19 H, m), 0.76–0.91 (2.3 H, m), 0.88 (3 H, t, J = 6.4 Hz), 0.07-0.12 (0.7 H, m); ¹³C NMR (CDCl₃, 100 MHz) δ 177.7, 130.2, 130.1, 129.9, 33.8, 32.7, 32.2, 30.0, 29.9, 29.9, 29.8, 29.7, 29.6, 29.4, 28.9, 28.8, 27.5, 24.84, 24.82, 22.9, 18.7, 18.7, 18.5, 14.42, 14.41, 14.2, 12.6; IR (CH₂Cl₂) v 2922, 2853, 2329, 1708, 1456, 1219 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₃₅O₂ $(M + H)^+$ 295.2632. Found 295.2522.

8-[(1R,2S)-2-Octylcyclopropyl]octanoic acid (9R,10S-dihydrosterculic acid; 3). The general procedure for diimide reduction applied to **36** (0.035 g, 0.17 mmol), after flash chromatography (EtOAc-hexane 20:80) yielded **9R,10S-3** as a semisolid (0.031 g, 86%). $[a]_{D}^{24}$ +0.95 (c 0.55, CHCl₃), (lit.²⁴ +0.92). ¹H NMR (CDCl₃, 400 MHz) δ 2.35 (2 H, t, J = 7.6 Hz), 1.62–1.65 (2 H, m), 1.25–1.36 (22 H, m), 1.12–1.16 (2 H, m), 0.88 (3 H, t, J = 6.8 Hz), 0.64–0.68 (2 H, m), 0.53–0.58 (1 H, m), –0.33 (1 H, q, J = 4.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 178.8, 33.9, 32.1, 30.4, 30.3, 29.8, 29.5, 29.4, 29.2, 28.9, 28.8, 24.9, 22.9, 15.92, 15.90, 14.3, 11.1; IR (CH₂Cl₂) ν 2924, 2854, 1711, 1456, 1219 cm⁻¹; HRMS (ESI⁺) calcd for C₁₉H₃₇O₂ (M + H)⁺ 297.2788. Found 297.2788.

X-ray crystallography

Intensity data were collected on an Oxford SuperNova CCD diffractometer using Cu-K α radiation (graphite crystal monochromator λ = 1.54184), the temperature during data collection was maintained at 130.0(1).

Crystal data for **14b**. $C_{22}H_{31}NO_3$, M = 357.48, T = 130.0(2) K, $\lambda = 1.5418$ Å, Monoclinic, space group *C2 a* = 32.485(3), *b* = 5.3094(4), *c* = 11.6620(7) Å, $\beta = 91.786(7)^{\circ}$, V = 2010.5(3) Å³, Z = 4, $D_c = 1.181$ Mg M⁻³ μ (Cu-K α) 0.613 mm⁻¹, *F*(000) = 776, crystal size 0.55 × 0.08 × 0.03 mm, 5781 reflections measured, 3169 independent reflections ($R_{int} = 0.067$) the final *R* was 0.0556 [$I > 2\sigma(I)$] and w*R*(F^2) was 0.1387 (all data), absolute structure parameter = 0.1(4), GOOF = 0.991. CCDC deposition: 1009686.

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