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SYNTHESIS OF (9Z,15Z)-(11S,12S,13S)-11-HYDROXY-12,13-EPOXYOCTADECADIENOIC ACID : APPLICATION OF 'SHARPLESS KINETIC RESOLUTION' TO ALLYL PROPARGYL ALCOHOLS

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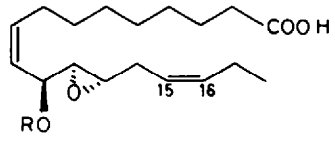
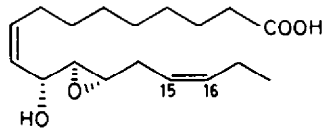
Abstract *Simple, concise first enantioselective total synthesis of* **1** *has been achieved. The route utilised is an attractive alternative to conventional synthetic methods employed in the synthesis of fatty acids, by using Sharpless kinetic resolution of allyl propargyl alcohols.*

One of the important class of compounds in biological systems is unsaturated oxygenated fatty acids. Several kinds of such fatty acids (**1-4**) have been isolated from cultivar variety of rice plants such as Fukuyuki by Kato et al[1], active against fungus causing rice blast disease. They are self-defensive substances produced by the affected plants for protection against the fungus, e.g. **1**. We wish to report first total synthesis of **1** by an unambiguous route from racemic allyl propargyl alcohols which also substantiates the recent CD studies by Kato[2] to establish its absolute configuration.





1 R = H

3 R = H, 15,16-dihydro

5 R = p-Br C_6H_4CO-

2

4 15,16-dihydro

The retrosynthetic analysis for **1** (Scheme 1) devised by us shows that allyl propargyl alcohol moiety (**7**) is well suited to generate the desired epoxy allyl alcohol system (**6**). The double bond can be conveniently epoxydised selectively in presence of triple bond which subsequently can be reduced to the requisite cis olefin. Accordingly, a study on Sharpless kinetic resolution[3,4] of racemic allyl propargyl alcohols was undertaken. The requisite allyl propargyl alcohols **8** and **9** were prepared easily by reacting 1-octynyl lithium with acrolein and trans-crotonaldehyde respectively. The asymmetric epoxidation was carried[5] out under conditions

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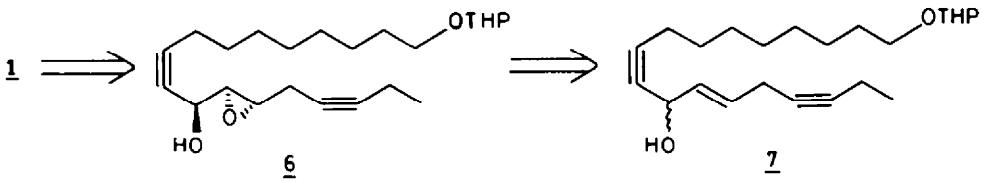
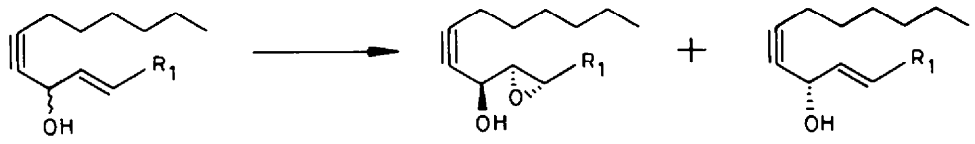
similar for secondary allylic alcohol (Scheme 2). The optical purity of recovered alcohols was determined[6] by studying ^{1}H NMR of their (-) MTPA-Mosher esters using Eu(fod)$_3$ shift reagent

Scheme 1

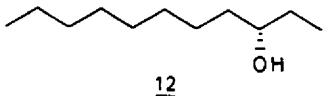


and the ee was found to be greater than 95%. The absolute stereochemistry of **8a** was established by reducing it to S(+)-undecan-3-ol (**12**)[7]. The diastereomeric excess of **10** and **11** was determined by ^{1}H NMR analysis and found to be 92:8 (erythro:threo) in both cases.

Scheme 2



Our studies revealed that the Sharpless kinetic resolution of allyl propargyl alcohols agrees with the predictions made by Sharpless[8] for alkyl allyl alcohols i.e. erythro selectivity with (+)DIPT and that R enantiomer has reacted faster with (+)DIPT leaving behind the S enantiomer, recovered alcohol **8a**, thereby affording kinetic resolution.



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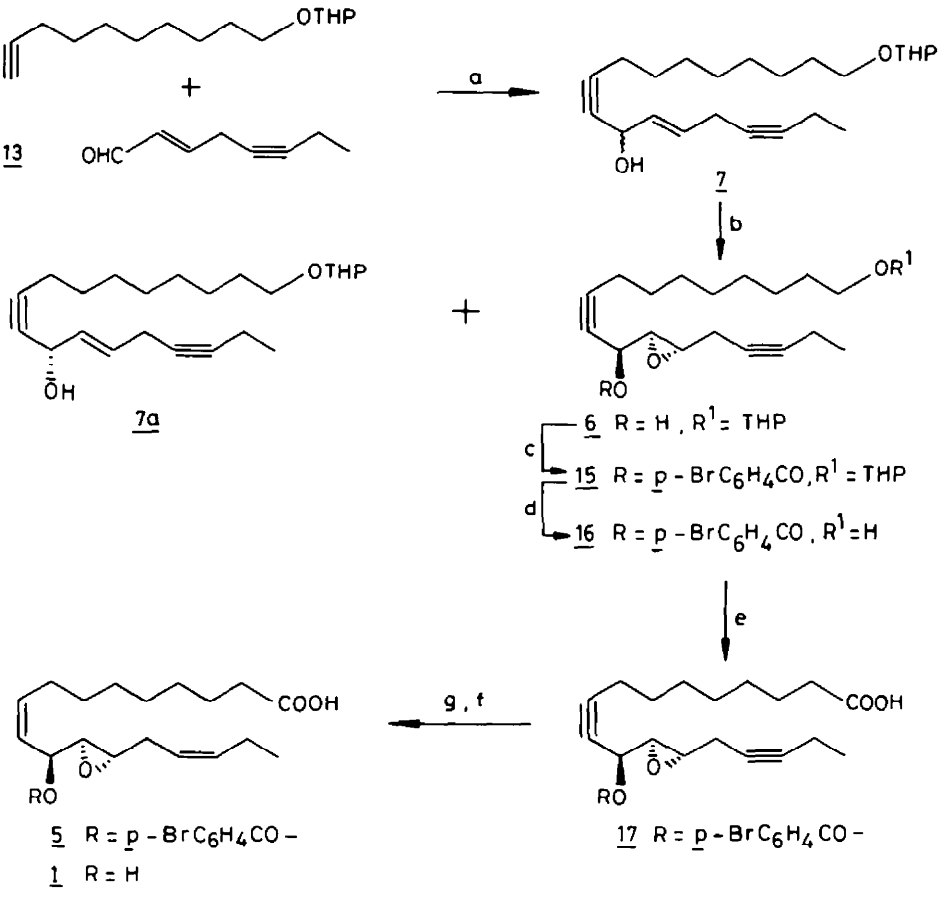
The favourable results of this study stimulated us to employ this approach for stereoselective synthesis of **1**. Thus, kinetic resolution of the desired fragment (**7**) would lead to isolation of the optically enriched epoxy alcohol **6** and allyl propargyl alcohol **7a** would be recovered in nearly optically pure form as delineated in Scheme 3. **7** was prepared by lithiation of 8-tetrahydropyranyloxy-1-decyne (**13**)[9] with n-BuLi and condensation of this anion with 2(E)-octen-5-yn-1-al (vide experimental) in good yield. Sharpless kinetic resolution was carried out by the stoichiometric method using 0.6 equivalent of TBHP and progress of the reaction was monitored[10] by

titrating unreacted TBHP. Reaction was quenched when nearly all (90%) TBHP was consumed. Chromatography led to isolation of **6** and **7a**. Subsequently, this unchanged allyl alcohol **7a** was

Scheme 3

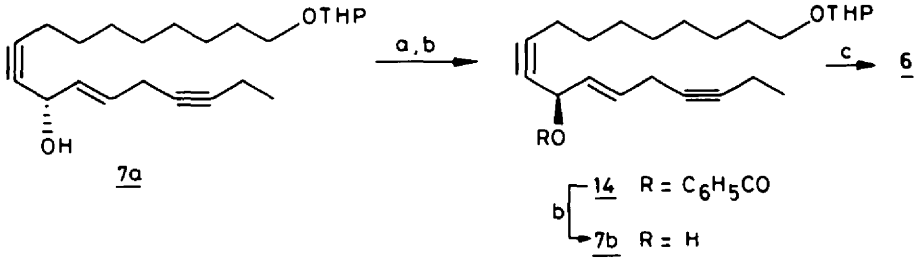


a) n-BuLi, THF, -78°C; **b)** TIP, (+)-DIPT, TBHP, CH_2Cl_2; **c)** p-BrC_6H_4COCl, Et_3N, DMAP; **d)** PPTS, EtOH; **e)** i. PCC, ii. $NaClO_2$, NaH_2PO_4, 2-Methyl-2-butene, t-BuOH; **f)** KOH, MeOH; **g)** Pd-$CaCO_3$, H_2

also converted to **6** as follows. The hydroxy group was inverted under Mitsunobu conditions[11] to give benzoate (**14**). This was hydrolysed by KOH/MeOH at room temperature to give **7b** which had desired stereochemistry. Sharpless epoxidation of **7b** yielded epoxy alcohol which was confirmed to be identical with **6** (Scheme 4). This strategy allowed us to make more amounts of **6** by avoiding wastage at the kinetic resolution stage.

The secondary alcohol in **6** was protected as p-bromobenzoate (**15**) with p-bromobenzoyl chloride, Et_3N, DMAP in CH_2Cl_2 at 0°C. This helped us in the correlation to evaluate optical purity which was reported by Kato et al. The THP ether was cleaved using PPTS/ethanol to

Scheme 4



a) DEAD, TPP, C_6H_5COOH ; b) KOH, MeOH ; c) TIP, (+)-DIPT, TBHP

give primary alcohol **16.** The tricky oxidation of **16** to acid **17** in presence of sensitive epoxide and acetylenic functionalities was effected in stepwise manner under mild conditions. Thus, **16** was first oxidised to aldehyde using PCC-CH_2Cl_2 and then to acid **17** using $NaClO_2$, NaH_2PO_4 and 2-methyl-2-butene in $tBuOH:H_2O$ (5:2) at ambient temperature.[12] Partial hydrogenation of acetylenic moiety in **17** over Lindlar's catalyst[13] gave **5** $[\alpha]_D$ -38.9° (c 0.59, $CHCl_3$), lit.[2] $[\alpha]_D$ -41.2° (c 0.13, $CHCl_3$). **5** on treatment with 0.25% methanolic KOH (2.2 eq) produced title compound **1** $[\alpha]_D$ +39.49° (c 0.79, $CHCl_3$).

The simplicity and versatility of this approach to unsaturated oxygenated fatty acid (**1**), should find numerous applications in the synthesis of members of this important class of biologically active compounds.

Acknowledgements

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EXPERIMENTAL

IR spectra were recorded on Perkin-Elmer 683 or 1310 spectrometers. ^1H NMR spectra were recorded on Varian FT-80A or Jeol PMX-90 or Bruker WH-300 spectrometers, using TMS as internal standard in $CDCl_3$ solution. Mass spectra were recorded on a Finnigan Mat 1210 double

focussing mass spectrometer operating at 70 eV using diret inlet system. Optical rotations were measured with a Jasco Dip 181 digital polarimeter.

1-Undecen-4-yn-3-ol(8)

To a stirred and cooled (-55°C) solution of n-octyne (3.1 g, 28 mmol) in dry ether (20 ml), n-BuLi (11.5 ml, 28 mmol, 2.44M solution in hexane) was added dropwise under nitrogen atmosphere. After 30 min. acrolein (1.56 g, 28 mmol) in ether (10 ml) was added and stirred for an additional 1.5 h. The reaction mixture was quenched with aq. NH_4Cl and the saturated aq. layer was extracted with ether. Combined ethereal extracts were washed with water, brine and dried (Na_2SO_4). The residue obtained after evaporation of solvent was purified by column chromatography (silica gel, pet.ether: EtOAc 14:1) to afford **8** (3.0 g) in 64% yield as an oil. ^1H NMR : δ 0.87 (dist. t, 3H), 4.65-4.95 (m, 1H), 5.14 (ddd, 1H), 5.40 (ddd, 1H), 5.86 (ddd, 1H). IR (Neat): 2240 and 3350 cm^{-1}. M^+ 166. $C_{11}H_{18}O$ requires C, 79.46; H, 10.92 and Found: C, 79.42; H, 10.63%.

(E)-2-Dodecen-5-yn-4-ol (9)

Compound **9** (2.07 g) was prepared as described above from crotonaldehyde (0.98 g) and 1-octyne (1.55 g) using n-BuLi (0.014 mol) in 82% yield as an oil. ^1H NMR : δ 0.87 (dist. t, 3H), 1.70 (dd, 3H), 4.65-4.85 (m, 1H), 5.56 (ddq, 1H), 5.78 (dq, 1H). IR (Neat): 3360, 2240, 965, M^+ 180; $C_{12}H_{20}O$ requires C, 79.94; H, 11.18 and FoundC, 79.94, H, 11.16%.

Epoxidation of 8 by Sharpless kinetic resolution method

To a cooled (-23°) dichloromethane (50 ml), were added sequentially titanium tetraisopropoxide (1.77 ml, 6 mmol), (+)DIPT (1.46 ml, 6 mmol) following **8** (0.83 g, 5 mmol) and TBHP (0.7 ml, 3 mmol, 4.25 M solution) after 10 min. The reaction mixture was stored at -10° and progress of the reaction was monitored by titrating the remaining TBHP. After 48 h, it was poured into precooled (-20°C) acetone (90 ml) containing water (3.1 ml) and allowed to warm to room temperature in 1 h and filtered. The filtrate was evaporated, residue taken in ether and treated with aq. 1N NaOH solution (18 ml) at 0°. After being stirred for 30 min organic layer was separated, washed with brine, dried (Na_2SO_4) and evaporated to give a clear oil, which was chromatographed (silica gel, 100-200 mesh, pet.ether:EtOAc 10:1) to afford 0.29 g and 0.31 g as fraction 1 and fraction 2 respectively.

Fraction 1: It was characterised as alcohol (**8a**) from ^1H NMR, IR and analysis $[\alpha]_D$ +26° (c 0.5, $CHCl_3$).

Fraction 2: It was characterised as **10.** ^1H NMR : δ 0.85 (dist.t, 3H), 3.05-3.25 (m, 1H), 4.5 (brs. 1H), IR (Neat): 2240 and 3430 cm^{-1}. $[\alpha]_D$ +22° (c 0.48, $CHCl_3$). $C_{11}H_{18}O_2$ requires C, 72.49; H, 9.96 and Found: C, 72.36; H, 9.89%.

(+)-(S)-Undecan-3-ol (12)

A mixture of **8a** (0.125 g, 0.75 mmol) and 5% Pd-C (0.125 g) in ethanol (10 mL) was subjected to hydrogenation under hydrogen at atmospheric pressure till 100.8 ml H_2 was absorbed. Usual workup gave **12** (0.05 g) in 38% yield as an oil. ^1H NMR :δ 0.9 (dist. t, 6H), 1.25 (brs. 16H), 3.3-3.6 (m, 1H). IR (Neat): 3340 cm^{-1}. $[\alpha]_D$ +5.6 (c 0.35, ethanol), lit.[7] $[\alpha]_D$ +6.2 (c 0.42,)].

Epoxidation of 9

Compound **9** (0.9 g) on epoxidation using TIP (1.48 ml) (-)-DIPT (1.46 ml) and TBHP (0.6 eq) gave **9a** $[\alpha]_D$ +30° (c 1.2, EtOH) and **11** $[\alpha]_D$ +2.55 (c, 2.2, EtOH). ^1H NMR : δ 0.9 (dt, 3H),

2.92 (dd, 1H), 3.15 (dq, 1H), 4.50 (bs, 1H). IR (Neat) : 3430, 2240 cm^{-1}. $C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27 and Found: C, 73.41; H, 10.25%.

(2E)-Octen-5-yn-1-al

2,5-Octadiyn-1-ol[14] (2.2 g, 18 mmol) in dry ether (25 ml) was added to a suspension of $LiAlH_4$ (0.342 g, 9.0 mmol) in ether (10 ml) at 0°C and the contents were stirred for 12 h at 25°. Excess hydrides were destroyed by slow addition of water (0.5 ml) at 0°C followed by the addition of saturated Na_2SO_4 solution (1.5 ml). The reaction mixture was filtered through celite, dried (Na_2SO_4) and concentrated to afford (3E)-octen-5-yn-1-ol (2 g) which was distilled b.p. 65-70° (bath)/1 mm to get pure liquid product (1.7 g). ^1H NMR : δ 1.1 (t, 3H), 2.6-2.8 (m, 2H), 4.1 (d, 2H), 5.5-6.0 (m, 2H). $C_8H_{12}O$ requires C, 77.37; H, 9.74 and Found: C, 77.30; H, 9.65%.

To a stirred suspension of PCC (2.9 g, 13.3 mmol) and celite (2 g) in CH_2Cl_2 (20 ml) was added a solution of (2E)-octen-5-yn-1-ol (1.5 g, 12 mmol) at room temperature. After a period of 20 min, the solvent was removed under reduced pressure and the residue (ca 5 ml) was diluted with ether (25 ml) and filtered through a pad of celite to afford (2E)-octen-5-yn-1-al (1.3 g) in 80% yield as an oil which was used as such for the next reaction because any attempt to purify the aldehyde resulted in more impure products.

1-[(Tetrahydro-2H-pyran-2-yl)oxy]-11-hydroxy-octadecadi-9,15-yn-12-ene (7)

A cooled (-78°) and stirred solution of 8-tetrahydropyranyloxy-9-decyne (**13**, 1.9 g, 7.9 mmol) in dry THF (20 ml) under N_2 atmosphere was treated with a 3.4M hexane solution of n-BuLi (2.31 ml, 7.9 mmol) dropwise. After 1.5 h, a solution of (2E)-octan-5-yn-1-ol (0.93 g, 7.62 mmol) in dry THF (10 ml), was added and the contents were allowed to stir at -78° for 30 min and at room temperature for 3 h. It was quenched with aq. NH_4Cl, organic layer separated, washed with brine, dried (Na_2SO_4) concentrated and purified (Silica gel, pet.ether-EtOAc 10:1) to result carbinol **7** (1.38 g) in 48% yield as an oil. ^1H NMR : δ 1.0 (t, 3H), 3.4-3.9 (m, 4H), 4.6 (m, 1H), 4.8 (m, 1H), 5.4-5.8 (m, 2H). IR (Neat): 2200 and 3300 cm^{-1}. $C_{23}H_{36}O_3$ requires C, 76.62; H, 10.07 and Found: C, 76.65; H, 10.02%.

1-[(Tetrahydro-2H-pyran-2-yl)oxy]-(11S,12S,13S)-11-hydroxy-12,13-epoxyoctadecadi-9,15-yne (6)

Compound **7** (1.3 g, 3.6 mmol) on kinetic resolution under Sharpless asymmetric epoxidation condition as described for alcohol **8**, gave recovered alcohol **7a** (0.48 g) and epoxy alcohol **6** (0.53 g, 40%). ^1H NMR : δ 1.0 (t, 3H), 2.6 (m, 2H), 3.2-3.9 (m, 6H), 4.6 (m, 2H). IR (Neat): 2200 and 3350 cm^{-1}. $C_{23}H_{36}O_4$ requires C, 73.36; H, 9.64 and Found C, 73.15; H, 9.56%.

The epoxy alcohol (**6**, 0.28 g) was also prepared from chirally enriched **7b** (0.3 g) using TIP (0.25 ml), (+)-DIPT (0.24l) and TBHP (0.15 ml) in 90% yield.

1-[(Tetrahydro-2H-pyran-2-yl)oxy]-(11S,12S,13S)-11-p-bromobenzoyloxy-12,13,epoxyoctadecadi-9,15-yne (15)

A stirred and cooled (0°) solution of **6** (0.55 g, 1.46 mmol) and triethyl amine (0.304 g, 2.17 mmol) in dry dichloromethane (10 ml) containing catalytic amount of DMAP was treated with p-bromo benzoyl chloride (0.32 g, 1.46 mmol). It was stirred at room temperature for 2 h and quenched by the addition of cold water. Organic layer was separated, washed with water, brine, dried (Na_2SO_4) and evaporated to give **15** (0.6 g) as an oil in 74% yield, after chromato-

graphic purification (silica gel, pet.ether:EtOAc 20:1). ^{1}H NMR : δ 1.0 (t, 3H), 2.6-2.8 (m, 2H); 3.2-3.4 (m, 2H), 3.4-3.9 (m, 4H), 4.6 (m, 1H), 5.8 (brs, 1H), 7.6 (d, 2H), 8.0 (d, 2H). IR (Neat): 1740 and 2200 cm^{-1}. $C_{30}H_{39}BrO_5$ requires C, 64.39; H, 7.02 and Found: C, 64.25; H, 6.98%.

(-)-(11S, 12S, 13S)-11-p-Bromobenzoyloxy-12,13-epoxyoctadecadi-9,15-yn-1-ol (16)

A solution of **15** (0.6 g, 1.07 mmol) in ethanol (6 ml) containing catalytic amount of PPTS was heated at reflux for 0.5 h. Ethanol was evaporated under reduced pressure and residue taken up in dichloromethane. Organic layer was washed with water, brine, dried (Na_2SO_4) evaporated and the residue obtained purified by column chromatography (silica gel, pet.ether:EtOAc 10:5) to afford **16** (0.4 g) in 80% yield. ^{1}H NMR :δ 1.0 (t, 3H), 2.4-2.8 (m, 2H), 3.2-3.4 (m, 2H), 3.6 (t, 2H), 5.8 (brs, 1H), 7.6 (d, 2H), 8.0 (d, 2H). IR(Neat): 1720 and 3300 cm^{-1} $[\alpha]_D$ -19.2° (c 0.26, $CHCl_3$). M^+ 276 (M^+-199) $C_{25}H_{31}BrO_4$ requires C, 63.15; H, 6.57 and Found: C, 63.10; H, 6.51%.

(-)-(11S,12S,13S)-11-p-Bromobenzoyloxy-12,13-epoxyoctadecadi-9,15-ynoic acid (17)

To a stirred mixture of PCC (0.25 g, 1.05 mmol), celite (0.25 g) and NaOAc (0.25 g) in dry dichloromethane (5 ml), a solution of **16** (0.25 g, 0.526 mmol) in dichloromethane (2 ml) was added. After 2 h, solvent was evaporated under reduced pressure residue treated with dry ether and filtered. The combined filtrates were dried (Na_2SO_4) and evaporated to give the aldehyde, which was used as such for the next reaction.

The above aldehyde was dissolved in t-BuOH (10 ml) and 2-methyl-2-butene was added. It was then treated with an aq. solution of sodium chlorite (0.28 g, 3.1 mmol) and sodium dihydrogen phosphate (0.28 g, 2.3 mmol) in water (3 ml) dropwise at 0°C. The reaction mixture was stirred at room temperature for 12 h and volatiles were removed at reduced pressure. The residue was diluted with $CHCl_3$ and acidified with dil.HCl to pH5. The separated organic phase was dried (Na_2SO_4), evaporated and purified by column chromatography (silica gel, pet.ether:EtOAc 7:3) to give acid **17** (0.13 g) in 52% yield as a syrup. ^{1}H NMR :δ 1.0 (t, 3H), 2.4-2.7 (m, 2H), 3.1-3.3 (m, 2H), 5.8 (brs, 1H), 7.4 (d, 2H), 8.0 (d, 2H). IR (Neat): 1720, 2200 and 3340 cm^{-1}. $[\alpha]_D$ -13.5° (c 0.7, $CHCl_3$), $C_{25}H_{29}BrO_5$ requires C, 61.35; H, 5.97 and Found: C, 61.32; H, 5.84%.

(-)-(9Z,15Z)-(11S,12S,13S)-11-p-Bromobenzoyloxy-12,13-epoxyoctadecadienoic acid (5)

A mixture of **17** (0.130 g, 0.265 mmol) and 50% Pd-$CaCO_3$ (0.01g) in ethanol (5 ml) was subjected to hydrogenation at atmospheric pressure till 11 ml of H_2 absorbed. The catalyst was filtered, solvent evaporated and residue filtered through a short column of silica gel (pet.ether: EtOAc 7:3) to result **5** (0.12g) in 92% yield. ^{1}H NMR :δ 1.0 (t, 3H), 2.4 (t, 2H), 2.84 (dd, 1H), 3.05 (dt, 1H), 5.2-5.66 (m, 2H), 5.8 (dd, 1H), 7.4 (d, 2H), 8.0 (d, 2H). IR (Neat) 1720 and 3340 cm^{-1}. $[\alpha]_D$ -38.9° (c 0.59, $CHCl_3$) lit.[2] $[\alpha]_D$ -41.2° (c 0.131, $CHCl_3$)]. $C_{25}H_{33}BrO_5$ requires C, 60.85; H, 6.74 and Found: C, 60.84; H, 6.7%.

(+)-(9Z,15Z)-(11S,12S,13S)-11-Hydroxy-12,13-epoxyoctadecadienoic acid (1)

Compound **5** (0.07 g, 0.141 mmol) in methanol (5 ml) was treated with 0.25% methanolic KOH (7.2 ml, 2.2 eq) at room temperature and stirred for 2 h. Methanol was removed, residue diluted with $CHCl_3$ and acidified with dil.HCl to pH4 at 0°. The organic layer was separated, washed with brine, dried (Na_2SO_4) and concentrated to give an oil which on chromatographic purification (silica gel, pet.ether:EtOAc 7:3) gave **1** (0.04 g) in 90% yield. ^{1}H NMR :δ 0.9 (t, 3H), 2.84 (dd, 1H), 3.05 (dt, 1H), 4.66 (dd, 1H), 5.2-5.5 (m, 4H). IR (Neat): 1720 and 3300 cm^{-1}. $[\alpha]_D$

+39.49° (c 0.79, $CHCl_3$). M^+ 310 $C_{18}H_{30}O_4$ requires C, 69.67; H, 9.67 and Found C, 69.65; H, 9.63%.

1-[(Tetrahydro-2H-pyran-2-yl)oxy]-(11S,12S,13S)-11-benzoyloxyoctadecadi-9,15-yn-12-ene (14)

The recovered alcohol (**7a**, 0.48 g, 1.33 mmol), benzoic acid (0.162 g, 1.33 mmol), triphenyl phosphine (0.349 g, 1.33 mmol) in anhydrous THF (15 ml) were stirred at 0° under N_2 atmosphere. A solution of diethylazodicarboxylate (DEAD) (0.205 ml, 1.30 mmol) on dry THF (2 ml) was added and the stirring continued for 3 h. THF was removed and residue filtered through a silica gel column (pet.ether:EtOAc 10:0.2) to give **14** (0.49 g) in 79% yield. ^1H NMR : δ 1.0 (t, 3H), 3.6-3.9 (m, 4H), 4.6 (m, 1H), 5.4-5.8 (m, 2H), 6.0 (m, 1H), 7.4-8.0 (m, 5H). IR (Neat): 1720 and 2200 cm^{-1}. $C_{30}H_{40}O_4$ requires C, 77.55; H, 8.68 and Found: C, 77.50; H, 8.59%.

1-[(Tetrahydro-2H-pyran-2-yl)oxy]-11(S)-hydroxy octadecadi-9,15-yn-12-ene (7b)

A solution of ester **19** (0.49 g, 1.05 mmol) in methanol (5 ml) was treated with 1N aq KOH (1 ml) at room temperature for 2 h. Methanol was removed, residue diluted with ether, washed with water, brine and dried (Na_2SO_4). Evaporation of solvent and purification of residue obtained by column chromatography (silica gel, pet.ether:EtOAc 9:1) to give **7b** (0.30 g) in 79% yield as a syrup.

References and Notes:

1. a) T. Kato, Y. Yamaguchi, S. Ohnuma, T. Uychara, T. Namai, M. Kodama and Y. Shibora, Chem. Lett. 577 (1986); b) J.S. Yadav and E.R. Reddy, J. Sci. Ind. Res., **48**, 38 (1981) and ref. cited therein.
2. T. Kato, Y. Yamaguchi, S. Ohnuma, T. Uychara, T. Namai, M. Kodama and Y. Shibora, J. Chem. Soc. Chem. Comm., 743 (1986).
3. V. S. Martin, S.C. Woodward, T. Katsuki, Y. Yamada, M. Ikeda and K.B. Sharpless, J. Am. Chem. Soc., **103**, 6237 (1981).
4. When this work was in progress K.C. Nicolaou has made use of asymmetric epoxidation on a similar substrate to prepare achiron for the synthesis of tetrahydrofuran moieties. However, its scope and generality has not been defined. See R.E. Dolle and K.C. Nicolaou, J. Am. Chem. Soc., **107**, 1691 (1985).
5. For preliminary publication see a) A.V. Rama Rao, A.P. Khrimian, P. Radhakirshna, P. Yadagiri and J.S. Yadav, Synth. Comm., **18**, 2325 (1988); b) A.V. Rama Rao, P. Radhakrishna and J.S. Yadav, Tetrahedron Lett., **30**, 1669 (1989).
6. G.R. Sullivan, J.A. Dale and M.S. Mosher, J. Org. Chem., **38**, 2143 (1974).
7. K. Mori, T. Nakada and T. Ebata, Tetrahedron, **37**, 1343 (1981).
8. K.B. Sharpless, S.C. Woodward and M.G. Finn, Pure and Appl. Chem., **55**, 1813 (1983).
9. A.V. Rama Rao, E. Rajarathnam Reddy, G.V.M. Sharma, P. Yadagiri and J.S. Yadav, Tetrahedron, **42**, 4523 (1986).
10. K.B. Sharpless and T.R. Veerhoeven, Aldrichimica Acta, **12**, 63 (1979).
11. O. Mitsunobu, Synthesis, 1 (1981).
12. B.S. Bal, W.E. Childers Jr. and H.W. Pinnick, Tetrahedron, **37**, 2029 (1981).
13. H. Lindlar and R. Dubuis, Org. Synth., **46**, 89 (1966).
14. L. Brandsma, "Preparative Acetylenic Chemistry" Elsevier, Amsterdam, p. 286 (1988).