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Synthesis of Functionalised Optically Active Bicyclic and Angularly Fused Tricyclic Compounds from (*l*)-Menthone by Tin-Mediated Vinyl Radical Cyclization†

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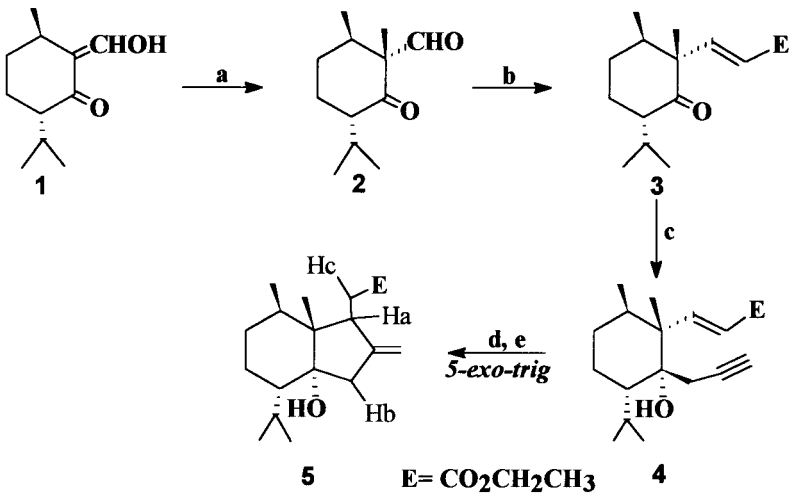
Abstract: Functionalised optically active bicyclo[4.3.0] system **5**, and angularly fused tricyclo [7.4.0.$0^{4,9}$] system **11** were synthesized from (*l*) - menthone propargyl derivative **4** and spiromenthone propargyl derivative **10** by tin- mediated radical cyclization.

Synthesis of bicyclic and angularly fused tricyclic systems is an area of immense interest in view of the presence of these frameworks in many naturally occurring compounds.[1] The formation of C-C bonds *via* radical reactions has been witnessed recently in tin-mediated intramolecular cyclization processes for the synthesis of several functionalised molecules with well defined stereochemistry.[2] As part of our ongoing research programme,[3] we became interested in employing a tin-mediated radical cyclization reaction for the construction of functionalised bicyclic and angularly fused tricyclic systems.

In this paper, we report the synthesis and tri-*n*-butyltin-mediated radical cyclization reaction of (*l*)-menthone propargyl derivative **4** and spiromenthone propargyl compound **10**. The synthesis of (*l*)-menthone propargyl derivative **4** and its radical cyclization reaction is outlined in Scheme 1.

2-Hydroxymethylene -(*l*)-menthone **1** was prepared from (*l*)-menthone[4] according to the literature procedure.[5] Compound **1** was methylated[6] at the 2-position with methyl iodide in presence of potassium-*t*-butoxide in *t*-butanol to yield 2-formyl-2-methyl-(*l*)-menthone **2** in 70% yield. The IR spectrum of **2** showed peaks at 1710 and 1690 cm^{-1} for cyclic carbonyl and formyl groups respectively. ^1H NMR of compound **2** showed a peak at δ 9.8, a singlet for formyl proton which confirms the structure **2**. Wittig olefination of compound **2** with (carbethoxymethylene) triphenylphosphorane in refluxing benzene for 8h under N_2 atmosphere

afforded the olefinated compound **3** in 75% yield. The ^{1}H NMR spectrum of compound **3** showed peaks at δ 7.2 and 5.6 two doublets of doublets for olefinic protons. Its mass spectrum showed a molecular ion peak at *m/e* 266(M^+).



Reagents and Conditions

a) *t*-BuO$^-$K$^+$/ *t*-BuOH, Methyl iodide, rt, N_2, 8h,70%, b) PPh_3=$CHCO_2CH_2CH_3$, PhH, N_2, Reflux, 12h, 75% ,c) Al/Hg, Propargyl bromide, N_2,THF, -78 °C, 3h, 90% d) 2.2 equiv. *n*-Bu_3SnH, AIBN, N_2, 80-85 °C, 5-10 min.80%e) 4 equiv. PPTS, CH_2Cl_2, rt, 48h, 100%

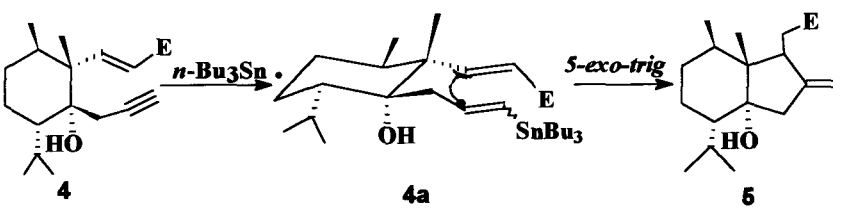
Scheme 1

Addition of a propargylaluminumsesquibromide solution to compound **3** at -78 °C under inert condition yielded propargyl compound **4** in 80% yield after silica gel column purification. Its ^{1}H NMR showed peaks at δ 2.0 a broad singlet for the -OH proton, a triplet at δ 2.1 for the acetylenic proton and at δ 2.4 a doublets of doublets for propargyl methylene unit. Mass spectrum of compound **4** showed a molecular ion peak at *m/z* 306 (M^+) and also gave satisfactory elemental analysis. The stereochemistry of compound **4** was assigned based on literature analogy.[3a,b]

Radical cyclization of compound **4** (Scheme 1) under neat and inert conditions with 1.2 equivalent of tri-*n*-butyltin hydride (TBTH) in the presence of a catalytic amount of azobisisobutyronitrile (AIBN) at 80-85 °C afforded the crude cyclised vinyl stannane. (The

reaction was exothermic and went to completion within 5- 10 min. . TLC showed the complete disappearance of starting material and formation of a less polar product and the IR spectrum of the crude vinyl stannane compound showed the disappearance of -C≡C-H absorptions at 3300 cm^{-1}). The crude vinyl stannane[7] thus obtained was subjected to protiodestannylation without further purification with pyridinium-*p*-toluenesulfonate (PPTS) in dichloromethane at room temperature for 48h. The destannylated compound **5** was purified by column chromatography(silica gel). The ^{1}H NMR of **5** showed two doublets of doublets for the exomethylene protons at δ 4.6 and 4.8, a doublets of doublets at δ 2.3 for the H_c proton, two doublets of doublets at δ 2.4 for the H_b proton, and a multiplet at δ 2.8 for the H_a proton. Its DEPT - 135 spectrum showed the presence of six CH_2, four methine and five methyl carbons. This is further evidence for the structure assigned for compound **5**. The mass spectrum of compound **5** showed a molecular ion peak at *m/z* 308 (M^+) and also gave satisfactory elemental analysis.

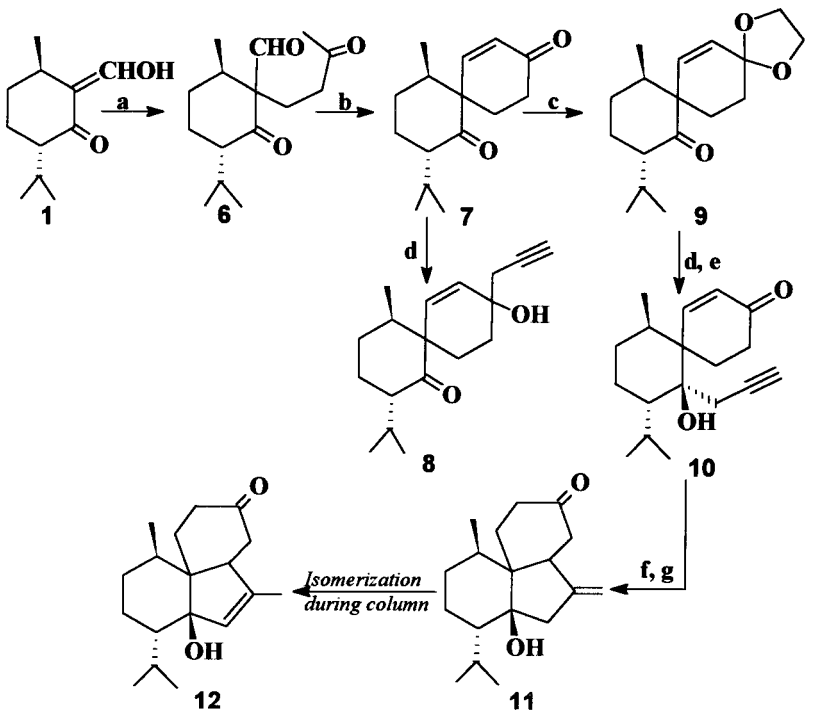
The formation of **5** from **4** by the addition of tin hydride in a 5-*exo*- *trig* fashion can be explained by the following Figure 1. Addition of tri-*n*-butyltin radical to the propargyl unit of compound **4** would give a vinyl radical intermediate **4a** which upon intramolecular radical addition to double bond gives compound **5**.



E= $CO_2CH_2CH_3$

Fig 1

The synthesis of spiromenthone propargyl compound **10** and its radical cyclization reaction is schematically represented in Scheme 2.



Reagents and Conditions

a) ref. 8, b)CH_3SO_3H, Benzene, Dean-Stark, 8h, 65%, c) Ethylene glycol, CPTS, benzene, Dean-Stark, reflux, 8h, 65%, d) Al/Hg, Propargyl bromide, N_2,THF, -78 °C, 3h, 90 %, e)10% HCl :THF (1:3), 24h, 98%, f) 1.2 equiv. *n*-Bu_3SnH, AIBN, N_2, 80-85 °C, 5-10 min.80%, g) 4 equiv. PPTS, CH_2Cl_2, rt, 48h, 100%

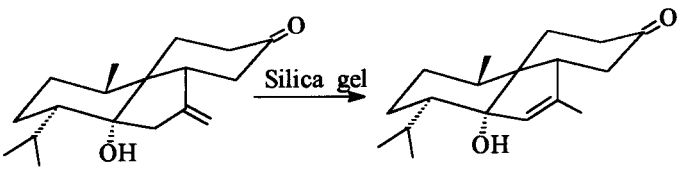
Scheme 2

2-Formyl-(*l*)-menthone[5] **1** was alkylated with methyl vinyl ketone (MVK) according to the literature procedure[8] to give **6** which upon cyclization using catalytic amount of methanesulfonic acid[9] gave the spirocyclic compound **7**.

The addition of 1.1 equiv. of propargylaluminiumsesquibromide solution to ketone **7** gave alcohol **8** in 75% yield. This mode of addition necessitated the protection of conjugated carbonyl group in **7** in order to get the desired product **10**. Selective ketalization of the enone carbonyl was achieved by means of the procedure described by Paquette and co-workers.[10] Ketal **9** was isolated in 65% yield after column chromatographic purification. Addition of a propargylaluminiumsesquibromide solution to ketone **9** gave the

carbinol, which was subjected without purification to deketalization. Alcohol **10** was isolated in 75% yield after column purification.

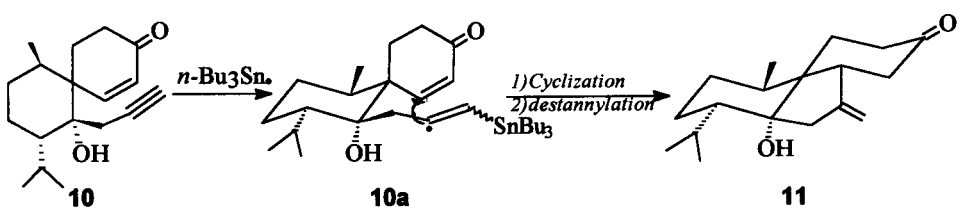
Radical cyclization of compound **10** (Scheme 2) with 1.2 equivalent of tri-*n*-butyltin hydride (TBTH) as described for compound **4** afforded **11.** The crude vinyl stannane[7] thus obtained was subjected to protiodestannylation without further purification with PPTS in dichloromethane at room temperature for 48h to yield compound **11**. Compound **11** was purified by column chromatography. The ^{1}H NMR of compound **11** showed a multiplet at δ 4.8-5.0 for exomethylene protons. Its DEPT - 135 spectrum showed the presence of seven CH_2, four methine and three methyl carbons. This is further evidence for the structure assigned for compound **11**. Its mass spectrum showed a molecular ion peak at *m/z* 276 (M^+) and also satisfactory elemental analysis. Apart from compound **11,** the isomerised compound **12** was also isolated in 20% yield. The isomerization is apparently taking place due to the acidic nature of silica gel (Figure 2). The structure of isomerised compound **12** was assigned based on spectral features (*see experimental*).



11 **12**

Fig 2

The formation of **11** from **10** by the addition of tin hydride in a 5-*exo*- *trig* fashion can be explained by the following Figure 3. Addition of tri-*n*-butyltin radical to the propargyl unit of compound **10** would give a radical intermediate **10a** which upon intramolecular radical addition to the vinyl double bond gives compound **11**.



10 **10a** **11**

Fig 3

Compounds like **5** can serve as a precursor for the synthesis of linearly fused triquinanes[11] while compounds like **11** and **12** can be used as precursors for the synthesis of triquinane derivatives.[12] In conclusion, we have expounded a general method of synthesis of functionalised optically active bicyclic and angularly fused tricyclic systems from (*l*)-menthone propargyl derivatives by tin-mediated radical cyclization. Further studies in this direction are underway.

EXPERIMENTAL

General Considerations

All melting points and boiling points are uncorrected. Specific rotations were recorded on a AUDOTOL II polarimeter. Infrared spectra were recorded on a Perkin-Elmer 598 spectrophotometer. ^{1}H NMR spectra were recorded either at 90 MHz on Varian EM-390 or at 200.1 MHz on BRUKER DPX 200 and ^{13}C NMR spectra were recorded at 50.3 MHz on a BRUKER DPX 200 spectrophotometer as indicated. Chemical shifts are reported in ppm(δ) with TMS as standard and coupling constants are expressed in Hertz. Mass spectra were recorded on a JEOL JMS-DX 303 HF mass spectrometer. Elemental analysis was performed using a Perkin-Elmer 240B elemental analyzer. Thin layer chromatograms (TLC) were developed on glass plates coated with silica gel-G (ACME) of 0.25mm thickness and visualized with iodine. Column chromatography was carried out with SiO_2 (ACME, 100-200 mesh) using hexane-ethyl acetate mixture as eluent. For an experiment glass ware was thoroughly dried in an air oven cooled and assembled under a stream of nitrogen. The organic extracts of crude products were dried over anhydrous $MgSO_4$. Solvents were reagent grade and were purified according to literature procedure.[13] Unless otherwise stated all reported compounds were homogeneous liquids. Tri-*n*-butyltin hydride (*n*-Bu_3SnH)[14] was prepared according to the literature procedure.

Methylation[6] of ketone 1 : *Synthesis of 2- methyl - 2 - formyl -(l)-menthone* 2

To a solution of potassium-*t*-butoxide in *t*-butanol [potassium (2g, 1 equiv.), *t*- butanol (100mL)] 2- formyl-(*l*)- menthone **1** (1 equiv.) in *t*- butanol (25mL) was added over a period of 15 min. at room temperature under a nitrogen atmosphere. Stirring was continued for an additional 15 min. and freshly distilled methyl iodide (2 equiv.) was added in one batch. After stirring for 6h, the precipitated KI was filtered off. Concentration of the filtrate under reduced pressure gave a colorless viscous liquid which upon vacuum distillation afforded the pure methylated product **2**.

***Data for compound* 2**

Yield : 70%; B.p: 131-133 °C /4.5 mm ; R_f : 0.3 (95:5, Hexane:EtOAc); IR (CCl_4) ν_{max} ,cm^{-1} : 1710 (carbonyl), 1690 (formyl carbonyl) ; ^1H NMR, (90 MHz, $CDCl_3$ / TMS) δ ppm : 1.1 (s, 3H, *methyl*), 1.2 (s, 3H,CH_3), 1.3 (s, 6H, -2CH_3), 1.3-2.3 (m, 7H, *methylenes & methines*), 9.8 (s, 1H, C*H*O); ^{13}C NMR(50.3 MHz, $CDCl_3$/TMS) ppm : δ 209.2, 191.5, 72.3, 72., 70.1, 42.7, 38.2, 33.6, 30.0, 25.9, 19.1, 16.2. ; Mass spectrum *(m/z)* : 196(M^+), 181,170, 167, 153, 78, 44.

Wittig olefination reaction of 2 : *Synthesis of 2-methyl- 2 (2' -carbethoxyvinyl) -(l) -menthone* 3

To a solution of 2-methyl-2-formyl derivative **2** (0.062 mol) in dry benzene (50 mL) was added (carbethoxymethylene)triphenylphosphorane (0.062 mol). The solution was refluxed for 8h under nitrogen atmosphere. The solution was cooled and the solvent was removed under reduced pressure to give a thick brown mass. Digestion of the mass with petroleum ether (10x25 mL) and concentration of the extract under reduced pressure afforded the olefinated compound **3**, which was purified by passing through a silica gel column using hexane-ethyl acetate as eluent.

***Data for compound* 3**

Yield : 70% ; $[\alpha]_{589}$ = + 12.35 ; R_f : 0.6(20:1, hexane:ethyl acetate) ; IR (CCl_4) $\nu_{max.}$ cm^{-1}: 1720(ester carbonyl), 1710(carbonyl), 1640(enone double bond) ; ^1H NMR,(90 MHz, $CDCl_3$ / TMS) δ ppm : 0.8(t, *J*= 7.33, 3H, $COOCH_2CH_3$), 1.0(s, 3H,CH_3), 1.2(s, 6H, *dimethyl* CH_3), 1.3(s, 3H,CH_3), 1.6-2.7 (m, 4H, *methylenes*), 1.8-2.2(m,3H, *methines*), 4.2(q, *J*=7.33, 2H, $COOCH_2CH_3$), 5.6(d, *J*=16.11,1H, H_8), 7.2(d, *J*=16.11, 1H, H_7); Mass spectrum *(m/z)* : 266(M^+) ; Analysis: $C_{16}H_{26}O_3$ requires: C, 68.55; H, 8.63%; Found : C, 68.53; H, 8.60%.

Procedure for spirocyclization of 6 : *Synthesis of 2α - isopropyl - 5β - methyl spiro [5.5] undec - 7 - ene - 1,9 - dione* 7

The diketoaldehyde **6** without further purification was dissolved in benzene (150 mL) and methanesulfonic acid (200 mg) was added. The solution was refluxed for 10h under nitrogen atmosphere using a Dean-Stark apparatus to remove water. The reaction mixture was cooled to room temperature. Sodium acetate (2g) was added and the solvent was removed in *vacuo*. The dark brown residue was taken up in dichloromethane (150 mL) and the solution was washed once with saturated sodiumhydrogencarbonate, water, brine and dried. Removal of the solvent gave a liquid residue **7**, which was purified by vacuum distillation.

***Data for compound* 7**

Yield : 65% ; $[\alpha]_{589}$ = + 21.68 ; R_f : 0.5(20:1, hexane:ethyl acetate) ; IR (CCl_4) $\nu_{max.}$ cm^{-1}:

1710 (carbonyl), 1680 (enone carbonyl), 1640 (enone double bond) ; ^{1}H NMR (90 MHz, $CDCl_3$/ TMS) , δ ppm :0.9 (s, 3H,CH_3), 1.1(s, 3H,CH_3), 1.3 (s, 3H,CH_3), 1.7-2.3 (m, 11H, *methylenes & methines*), 5.9 (d, *J*=16.11, 1H, H_8), 7.0 (d, *J*=16.11, 1H, H_7) ; ^{13}C NMR(50.3 MHz, $CDCl_3$/TMS) ppm : δ 208.2, 199.2, 126.3, 74.2, 71.6, 70.1, 44.2, 35.6, 30.2, 31.6, 29.3, 24.2, 24.0, 19.8, 16.4. ; Mass spectrum (*m/z*) : 234(M^+), 206, 191, 190, 180, 170, 78, 70, 44.

Selective ketalization[10] of the enone carbonyl of the (*l*) - menthone spirodione 7 : *Synthesis of* 9

Selective ketalization was achieved following the procedure described by Paquette[10] *et al.*,. A round bottomed flask was charged with the spirodione **7** (0.03 mol), collidinium-*p*-toluene sulfonate [CPTS (0.004 mol)], ethylene glycol (0. 045 mol) and benzene (125 mL). The reaction mixture was refluxed for 10h under nitrogen atmosphere using a Dean-Stark apparatus to remove water. The reaction mixture was cooled to room temperature and the solution was washed once with saturated sodiumhydrogencarbonate, water, brine and dried. Removal of the solvent under *vacuo* gave a liquid residue **9** which was purified by column chromatography (neutral alumina) using hexane : ethyl acetate (10:1) as eluent to yield the ketal **9**.

***Data for compound* 9**

Yield : 65% ; $[\alpha]_{589}$ = + 30.75 ; IR (CCl_4, ν_{max}) cm^{-1}: 1705 (cyclic carbonyl),1685 (enone carbonyl), 1620 (double bonds) ; ^{1}H NMR(200.1 MHz, $CDCl_3$/TMS) ppm : δ 0.9(s, 3H, CH_3), 1.0(s, 6H, *dimethyl*), 1.5-2.5(m, 11H, *methylenes and methines*), 3.9(m, 4H, O-CH_2-CH_2-O-), 5.9(d, 1H, H_8), 6.2(d, 1H, H_7); ^{3}C NMR(50.3 MHz, $CDCl_3$/TMS) ppm : δ 208.2, 126.3, 108.6, 74.2, 71.6, 70.1, 64.8, 64.3, 44.2, 35.6, 30.2, 31.6, 29.3, 24.2, 24.0, 19.8, 16.4. ; Mass spectrum, *m/z* : 278 (M^+), 265, 235, 234, 216, 170, 78, 70, 44.

General procedure for propargylation[3] of ketones 3 and 9 : *Synthesis of* 4 *and* 10

Aluminum amalgam was prepared from aluminum foil (0.036 mol, 3 equiv.) and mercuric chloride (10 mg, cat. amount) in THF (15mL) by vigorously stirring the mixture at room temperature for 1h under nitrogen atmosphere. A solution of propargyl bromide (0.036, 3 equiv.) in dry THF (25mL) was slowly added to a stirred suspension at such a rate so as to maintain a temperature of 30-40 °C, and after addition, stirring at 40 °C was continued until a dark gray solution was obtained (*Ca.* 1h). The propargylaluminiumsesquibromide solution thus obtained was added to a solution of the ketone (0.012mol) in dry ether (100mL) at -78 °C and the reaction mixture was stirred at that temperature for 3h, then poured into ice water and

extracted with ether (4x25mL). The combined ether extract was washed with brine, dried and concentrated. The residual liquid thus obtained was subjected to column chromatography over silica gel to afford pure propargylated compound.

***Data for compound* 4**

Yield : 80% ; $[\alpha]_{589}$ = + 18.25 ; IR(CCl_4, ν_{max}) cm^{-1}: 3510 (OH), 3300 (-C≡C-H), 2100(-C≡C-), 1720(ester carbonyl), 1640(double bond) ; ^1H NMR (200.1 MHz, $CDCl_3$/TMS) ppm : δ 0.8(t, 3H, $CO_2CH_2CH_3$), 1.0 (s, 3H, CH_3), 1.2(s, 6H, *dimethyl*), 1.3(s, 3H, CH_3), 1.6(m, 4H, *methylenes*), 1.8-1.9(m, 3H, *methines*), 2.0(br s, 1H, O*H*), 2.1(t, 1H, -C≡C-*H*), 2.4(dd, 2H, CH_2-C≡C-), 4.2(q, 2H, $CO_2CH_2CH_3$), 5.9(d,1H, H_8), 7.1(d, 1H, H_7) ; ^{13}C NMR(50.3 MHz, $CDCl_3$/TMS) ppm : δ 14.6, 16.6, 17.4, 20.8, 24.0, 27.4, 30.9, 37.7, 42.0, 46.5, 50.5, 52.5, 60.3, 60.7, 73.4, 81.2, 122.7, 151.0, 166.5 ; Mass spectrum, *m/z* : 306 (M^+) ; Elemental analysis: Calcd. for $C_{19}H_{30}O_3$: C, 74.47 , H, 9.87 %, Found C,74.40, H, 9.95 % .

***Data for compound* 10**

Yield : 75% ; $[\alpha]_{589}$ = + 37.18 ; IR(CCl_4, ν_{max}) cm^{-1}: 3505(OH), 3300 (-C≡C-H), 2100(-C≡C-) , 1685 (enone carbonyl), 1635(double bond) ; ^1H NMR (200.1 MHz, $CDCl_3$/TMS) ppm : δ 0.8(s, 9H, $3CH_3$), 1.1-1.4(m, 8H, *methylenes*), 1.5-1.8(m, 3H, *methines*), 2.1(m, 3H, -C≡C-*H*, CH_2-C≡C-), 2.7(br s, 1H, O*H*), 6.1(d,1H, H_8), 7.3(d, 1H, H_7) ; ^{13}C NMR(50.3 MHz, $CDCl_3$/TMS) ppm : δ 16.0, 19.1, 24.2, 26.3, 28.1, 30.6, 31.1, 33.4, 38.5, 43.9, 54.3, 69.8, 71.5, 80.5, 129.0, 152.2, 190.1 ; Mass spectrum *m/z* : 274 (M^+); Elemental analysis: Calcd. for $C_{18}H_{26}O_2$: C, 78.79 , H, 9.55 %, Found C, 78.70 , H, 9.50 %.

General procedure for radical cyclization of 4 and 10 : *Synthesis of* 5 *and* 11

A flame dried 100 mL round bottomed flask equipped with a magnetic stirring bar was flushed with analar nitrogen and the propargylated alcohol (0.0021 mol), tri-*n*-butyltin hydride (TBTH, 0.0022 mol, 1.2 equiv.) and azobisisobutyronitrile (AIBN, 0.001mol) were added. The entire assembly was lowered into an oil bath maintained at a temperature between 75-85 °C, and the mixture was stirred. After an induction period of less than 5 min. an exothermic reaction occurred which produced a small amount of gas and the reaction mixture was allowed to stir for an additional 10 min., at which point TLC showed the reaction to be essentially complete (also by IR). The unpurified vinylstannane thus obtained was subjected as such to protiodestannylation.

To the crude vinylstannane in methylene chloride (20 mL) was added pyridinium-*p*-toluene sulphonate (PPTS, 4 equiv.) and the reaction mixture was stirred at room temperature

for 48h at which time TLC analysis showed complete disappearance of the starting material and the formation of a less polar compound. The solvent was removed under reduced pressure, and the residue was extracted with hexane-ethyl acetate (2:3, 10x25 mL). The combined extracts were concentrated under reduced pressure, and the crude product was chromatographed over silica gel to give destannylated product.

***Data for compound* 5**

Yield : 80 % ; $[\alpha]_{589}$ = -3.10; IR(CCl_4, ν_{max}) cm^{-1}: 3505 (OH), 1720(ester carbonyl), 1650 (exomethylene) ; ^1H NMR (200.1 MHz, $CDCl_3$/TMS) ppm : δ 0.8(t, 3H, $CO_2CH_2CH_3$), 1.0 (s, 3H, CH_3), 1.2(s, 6H, *dimethyl*),1.3(s, 3H, CH_3), 1.4-2.0(m, 8H, *OH and methylenes*), 2.3(dd, 2H, H_c), 2.4(dd, 1H, H_b), 2.5(dd, 1H, H_b), 2.8(m, 1H, H_c), 4.2(q, 2H, $CO_2CH_2CH_3$), 4.6(d,1H, *exomethylene*), 4.8(d, 1H, *exomethylene*); ^{13}C NMR(50.3 MHz, $CDCl_3$/TMS) ppm : δ 13.5, 14.1, 16.4, 17.8, 19.1, 23.3, 26.7, 27.7, 37.0, 37.7, 39.6, 41.1, 42.5, 44.5, 60.2, 81.7, 107.7, 151.9, 173.5; Mass spectrum, *m/z* : 308 (M^+); Elemental analysis: Calcd. for $C_{19}H_{32}O_3$: C, 73.98 , H, 10.46 %, Found C,74.05 , H, 9.50 % .

***Data for compound* 11**

Yield : 60 % ; $[\alpha]_{589}$ = -7.14 ; IR(CCl_4, ν_{max}) cm^{-1}: 3510(OH), 1700 (carbonyl), 1640(double bond) ; ^1H NMR (200.1 MHz, $CDCl_3$/TMS) ppm : δ 0.8(s, 9H, $3CH_3$), 1.1-1.4(m, 13H, *methylenes*), 1.5-1.8(m, 3H, *methines*), 2.7(br s, 1H, *OH*), 5.1(d, 2H, *exomethylene protons*); ^{13}C NMR(50.3 MHz, $CDCl_3$/TMS) ppm : δ 211.6, 138.7, 125.6, 118.5, 70.4, 51.8, 43.6, 41.5, 37.5, 34.5, 30.9, 29.4, 28.1, 26.0, 21.5, 18.8, 16.5, 14.9. ; Mass spectrum, *m/z* : 276 (M^+) ; Elemental analysis: Calcd. for $C_{18}H_{28}O_2$: C, 78.21 , H, 10.21 %, Found C, 78.30 , H, 10.15 % .

***Data for compound* 12**

Yield : 20%; $[\alpha]_{589}$ = -7.85 ; IR(CCl_4, ν_{max}) cm^{-1}: 3510(OH), 1700 (carbonyl), 1625(double bond); ^1H NMR (200.1 MHz, $CDCl_3$/TMS) ppm : δ 0.8(s, 9H, $3CH_3$), 1.4(m, 3H, CH_3), 1.5-1.8(m, 13H, *methylenes and methines*), 2.7(br s, 1H, *OH*), 5.8(m, 1H, H_2); ^{13}C NMR(50.3 MHz, $CDCl_3$/TMS) ppm : δ 211.7, 137.6, 126.9, 118.5, 71.5, 55.5, 53.3, 52.1, 43.9, 41.7, 37.8, 34.8, 31.2, 28.4, 26.5, 21.9, 19.1, 15.3. ; Mass spectrum, *m/z* : 276 (M^+) ; Elemental analysis: Calcd. for $C_{18}H_{28}O_2$: C, 78.21 , H, 10.21 %, Found C, 78.30 , H, 10.15 % .

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