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Tributyltin Chloride-Sodium Cyanoborohydride Mediated Tandem Radical Cyclisation-Reductive Demethoxylation Sequence

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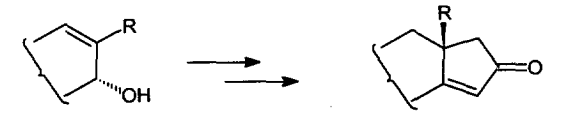
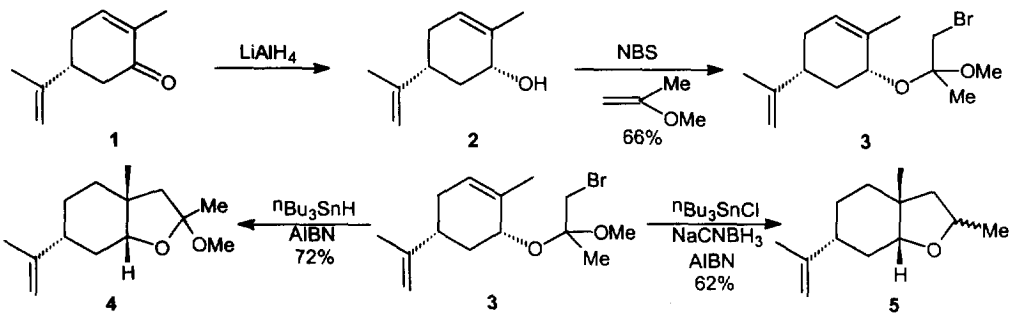
Abstract: Reaction of the bromoketals **3**, **7a-g** and **11** with tri-n-butyltin chloride and sodium cyanoborohydride in the presence of a catalytic amount of AIBN furnished the ethers **5**, **8a-g** and **13** via a tandem sequence comprising of a radical cyclisation reaction and tri-n-butylhalostannane and sodium cyanoborohydride mediated reductive demethoxylation of the resulting cyclic ketals. © 1997 Elsevier Science Ltd.

Nature builds polycyclic terpenes and steroids by way of a beautifully controlled series of enzymatic reactions triggered by carbonium ion intermediates. Some of the most attractive biosynthetic transformations are tandem or cascade reactions, which involve multi-reaction "one-pot" sequences where the first step creates the functionality to trigger the second one and so on. The novelty and efficiency of multistep reactions were a strong motivation for synthetic organic chemists to imitate the biosynthetic pathways. The processes occurring in the Nature have been successfully used as a guideline for the planning of organic synthesis. Tandem reactions are among the most powerful building tools available since they rapidly increase the complexity of a substrate starting from simple precursors. Important contributions to this area have been realised utilising cationic, anionic, radical, pericyclic and transition metal catalysed processes.[1] In recent years, several applications of tandem reactions to the synthesis of complex natural products have been reported using either the biogenetic like approach or tandem reactions specifically designed for their synthetic utility.[1] Accomplishment of two or more reactions of different nature, like a pericyclic reaction and a radical reaction; or a radical reaction and an ionic reaction, *etc.*, in a single operation is appealing from synthetic stand point of view. During our studies on the cyclopentenone annulation of allyl alcohols (eqn. 1) using a 5-*exo-trig* radical cyclisation reaction as the key step,[2] we have discovered a new tetrahydrofurannulation sequence *via* a tandem 5-*exo-trig* radical cyclisation reaction of an allyl methyl mixed ketal of α-bromoacetone followed by reductive demethoxylation of the resulting ketal (eqn. 2).[3] Herein, we describe the details of these investigations.



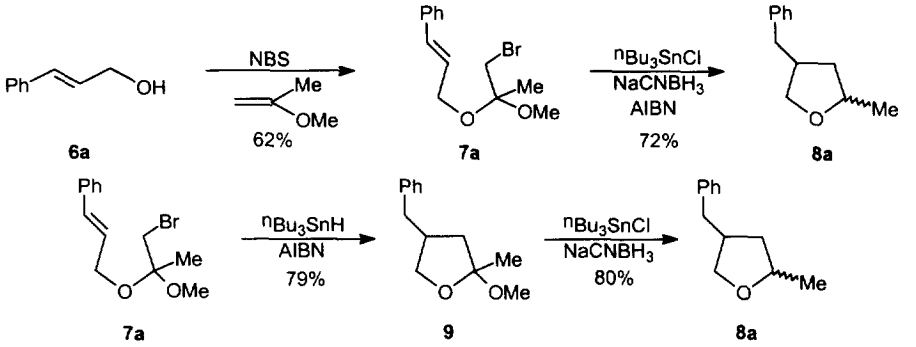
(eqn. 1)

(eqn. 2)



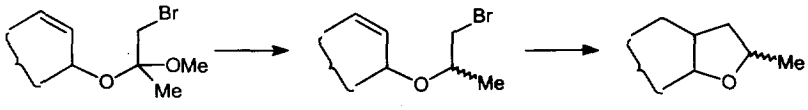
Regio- and stereoselective reduction of R-carvone (**1**) generated the allyl alcohol, carveol **2**.[4] Reaction of 2-methoxypropene with N-bromosuccinimide (NBS) in the presence of carveol (**2**) in methylene chloride at -50 °C furnished the radical precursor, bromoketal **3**, as a mixture of diastereomers in 66% yield. Radical cyclisation reaction of the bromoketal **3** with tri-n-butyltin hydride in the presence of a catalytic amount of azoisobutyronitrile (AIBN) under standard conditions furnished the 5-*exo* trig cyclised product **4**.[2] In contrast, employing a combination of a catalytic amount of tri-n-butyltin chloride and sodium cyanoborohydride for the *in situ* generation of tri-n-butyltin hydride[5] generated the demethoxylated product **5**. Thus, refluxing a 0.1 M solution of the bromoketal **3** in *tert*-butanol with 0.2 equivalents of tri-n-butyltin chloride and 2 equivalents of sodium cyanoborohydride in the presence of a catalytic amount of AIBN for 3 hours, furnished a 1:1 epimeric mixture of the tetrahydrofuran **5** in 62% yield, whose structure was deduced from its spectral data. In the high resolution mass spectrum of **5**, the molecular ion appeared at m/z 194.1647 ($C_{13}H_{22}O$). The ^1H and ^{13}C NMR spectra, with two sets of resonances (≈1:1), clearly revealed the presence of two epimeric compounds. The proton and carbon signals due to the methoxy group and the ring olefin moiety were absent in the NMR spectra. The ^1H NMR spectrum exhibited two singlets at δ 4.62 ($C{=}CH_2$) and 1.65 ($C{=}C{-}CH_3$) due to the isopropenyl group, a multiplet at 4.10-4.25 due to $OCHCH_3$, two doublet of doublets at 3.58 and 3.50, due to bridgehead O-CH, two doublets at 1.231 and 1.230 due to *sec*-methyl group and two singlets at 1.08 and 1.04 ppm due to *tert*-methyl group for the two epimers establishing the structure of the tetrahydrofuran **5** which was further confirmed by the ^{13}C NMR spectrum (see experimental). The formation of the product can be rationalised as follows: first a 5-*exo-trig* radical cyclisation reaction of the bromoketal **3** by the *in situ* generated catalytic tri-n-butyltin hydride furnishes the ketal **4**, which is followed by tri-n-butyltin bromide (by-product formed in the reaction) catalysed reductive demethoxylation of the ketal by the excess sodium cyanoborohydride present in the medium.

In order to establish the order of events in this tandem reaction process, the sequence was carried out with cinnamyl alcohol **6a** as the starting material. Thus, low temperature bromoketalisation reaction of cinnamyl alcohol **6a** in methylene chloride using NBS and 2-methoxypropene furnished the bromoketal **7a** in 62% yield. Refluxing a 0.1 M solution of the bromoketal **7a** in *tert*-butanol with 0.2 equivalents of tri-n-butyltin chloride and 2 equivalents of sodium cyanoborohydride in the presence of a catalytic amount of AIBN for 2.5 hours furnished a 2:1 epimeric mixture of 4-benzyl-2-methyltetrahydrofuran **8a** containing trace amounts of the mixed ketal **9**, in 72% yield. To establish that the radical cyclisation reaction precedes the reductive demethoxylation, the mixed ketal **9** was prepared *via* the radical cyclisation of the bromoketal **7a** using stoichiometric amount of

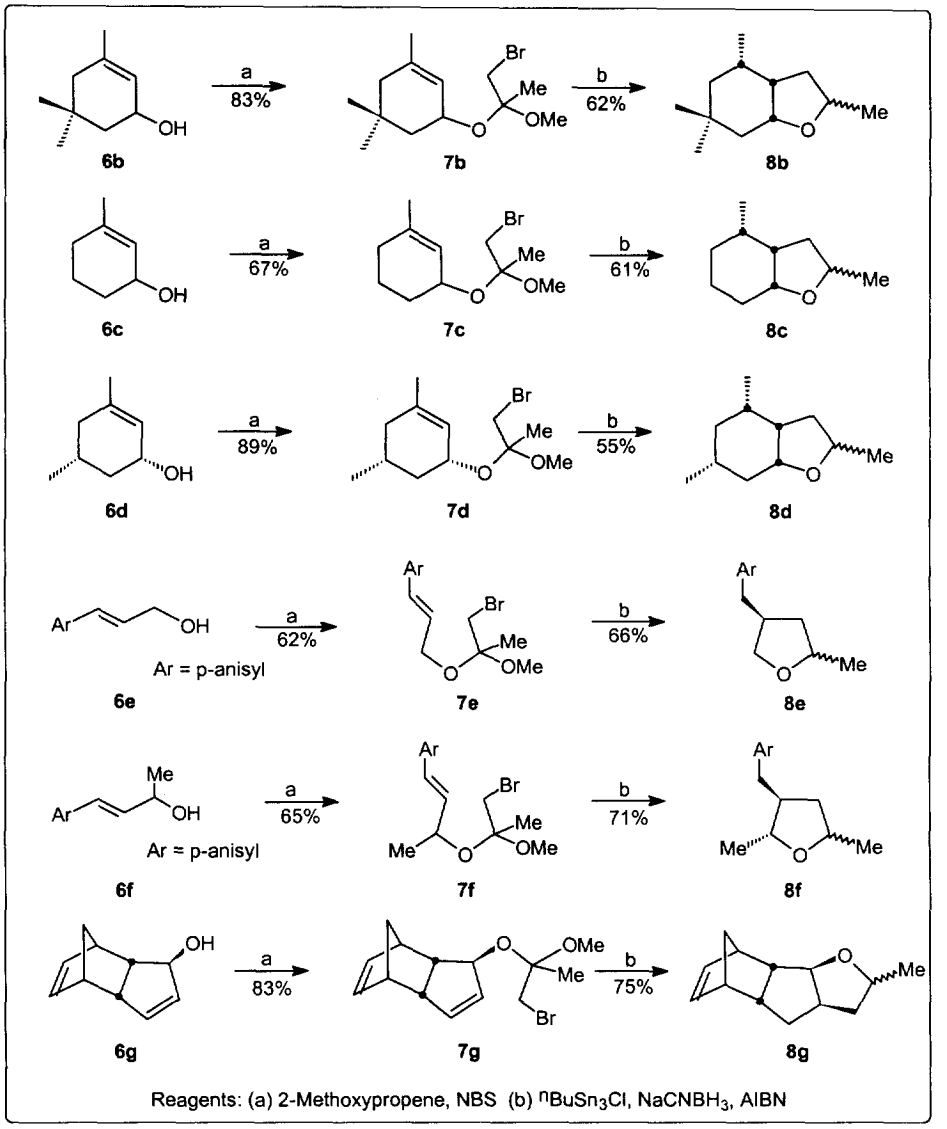


tri-n-butyltin hydride. Consequently, refluxing a 0.02 M benzene solution of the bromoketal **7a** using 1.1 equivalents of tri-n-butyltin hydride and a catalytic amount of AIBN for 2.5 hours furnished, quite expectedly, the 2-methoxytetrahydrofuran **9**, as a mixture of methoxy epimers, in 79% yield. Refluxing a solution of the ketal **9** in *tert*-butanol with 0.1 equivalents of tri-n-butyltin chloride and 2 equivalents of sodium cyanoborohydride in the presence of AIBN, furnished a 2:1 epimeric mixture of the tetrahydrofuran **8a**, in 80% yield. The epimeric ratio and the spectral data of the tetrahydrofuran **8a**, thus obtained, was identical in all respects with that obtained by the tandem sequence of the bromoketal **7a**. Quite expectedly, the ketal **9** furnished the cyclic ether **8a** even in the absence of AIBN using tri-n-butyltin chloride and sodium cyanoborohydride in *tert*-butanol, supporting the ionic nature of the reaction. In contrast, no reaction was observed when a catalytic amount of tri-n-butyltin hydride was employed in the place of tri-n-butyltin chloride, both in the presence as well as in the absence of AIBN, clearly establishing that tri-n-butyltin hydride did not catalyse the reductive demethoxylation reaction.

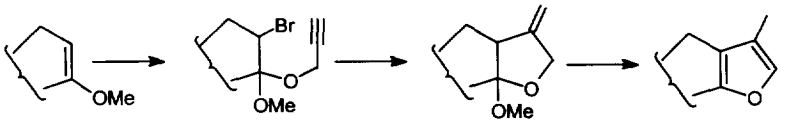
The generality of the tetrahydrofurannulation methodology *via* the tandem sequence was established by the conversion of alcohols **6b-g** into the tetrahydrofurans **8b-g** *via* the bromoketals **7b-g**. The starting allyl alcohols **6b-f** were obtained by low temperature $LiAlH_4$ reduction of the corresponding enones or esters and the allyl alcohol **6g** was obtained by selenium dioxide oxidation[6] of dicyclopentadiene. The bromoketalisation reaction of the allyl alcohols **6b-g** in methylene chloride using NBS and 2-methoxypropene at low temperature furnished the bromoketals **7b-g** in 62-83% yield. The tandem sequence was carried out by refluxing a 0.1 M solution of the bromoketals **6b-g** in *tert*-butanol with 0.2 equivalents of tri-n-butyltin chloride and 2 equivalents of sodium cyanoborohydride to furnish the tetrahydrofurans **8b-g**, as a mixture of epimers, whose structures rest secured from their spectral data. The tetrahydrofurans **8b-d** were obtained as a mixture of epimers varying between 5:1 and 10:1. This in turn established that the reductive demethoxylation reaction succeeds the radical cyclisation reaction in the tandem sequence, since, if the reductive demethoxylation process precedes the radical cyclisation reaction, one would anticipate the formation of a ≈1:1 epimeric mixture of tetrahydrofurans, as there will not be any stereoselectivity in the demethoxylation of acyclic ketals to bromoethers (eqn. 3).



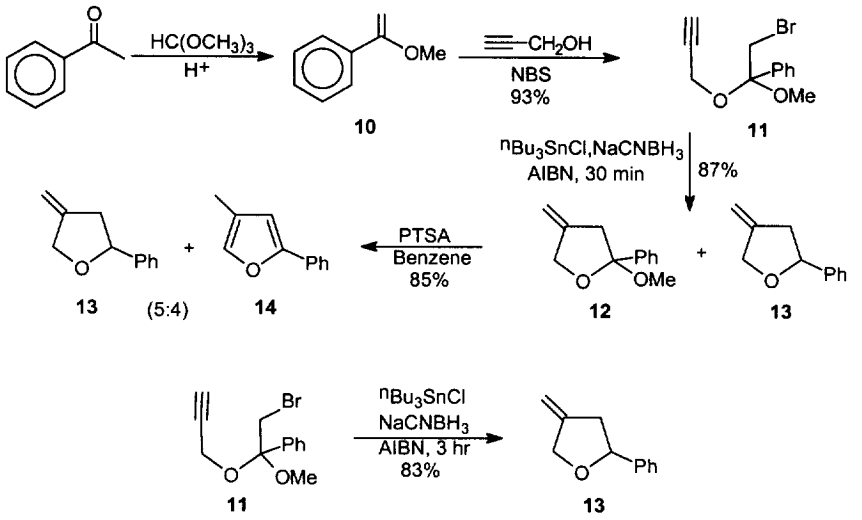
(eqn. 3)



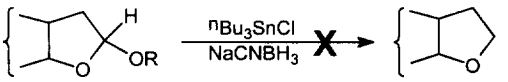
A furannulation methodology was reported,[7] earlier, starting from the enol ethers derived from ketones, employing a 5-*exo-dig* radical cyclisation reaction as the key step (eqn. 4). The overall yield of the furans from the bromoketals was found to be low when the radical cyclisation reaction was carried out for longer times using an *in situ* generated catalytic tri-n-butyltin hydride ($^{n}Bu_3SnCl$ and $NaCNBH_3$). Based on present investigations,



(eqn. 4)



it was felt that the partial reductive demethoxylation subsequent to the radical cyclisation may be responsible for the lower yields of the furans. Hence, the reaction was reinvestigated starting from the enol ether **10**[8] of acetophenone. Treatment of the enol ether **10** with NBS in a mixture of methylene chloride and propargyl alcohol at -50 °C furnished the bromoketal **11** in 93% yield. Refluxing a 0.2 M solution of the bromoketal **11** in *tert*-butanol using 0.15 equivalents of tri-n-butyltin chloride and 2 equivalents of sodium cyanoborohydride in the presence of a catalytic amount of AIBN for 30 minutes furnished a mixture of the mixed ketal **12** and the tetrahydrofuran **13**, in 87% yield, which on treatment with a catalytic amount of PTSA and purification on a silica gel column furnished the furan **14** (38%) and the tetrahydrofuran **13** (47%) confirming our hypothesis. When the radical cyclisation reaction of the bromoketal **11** was carried out for a longer period, *i.e.*, for 3 hours, only the tetrahydrofuran **13** was isolated in 83% yield, whose structure was established from its spectral data. It is worth noting that only in the case of methoxy ketals the reductive demethoxylation is observed leading to ethers (*ca.* eqn. 2), while no reductive cleavage was observed with the acetals (eqn. 5).



(eqn. 5)

In conclusion, we have described a tetrahydrofurannulation of allyl alcohols employing a tandem radical cyclisation of allyl methyl mixed ketal of α-bromoacetone followed by trialkylhalostannane-sodium cyanoborohydride mediated reductive demethoxylation of the resulting 2-methyl-2-methoxytetrahydrofurans. In turn, this sequence highlights the use of tri-n-butylhalostannanes as mild Lewis acids in the reductive demethoxylation of ketals,[9] and also points to the limitation of the use of a combination of tributyltin chloride and sodium cyanoborohydride for the *in situ* generation of catalytic tri-n-butyltin hydride[5] for carrying out radical mediated reactions.

Experimental Section

In ^1H and ^{13}C NMR spectra, chemical shifts (δ) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for ^1H) or the central line (77.1 ppm) of $CDCl_3$ (for ^{13}C). In ^{13}C NMR spectra, off-resonance multiplicities are given in parentheses. Dry benzene and *tert*-butanol were obtained by distillation over sodium. $^nBu_3SnH$, $^nBu_3SnCl$, $NaCNBH_3$, p-TSA, NBS, 2-methoxypropene and propargyl alcohol were obtained from Fluka and were used without further purification. AIBN was recrystallized from methanol and stored in dark.

(1R,5R)-2-Methyl-5-isopropenylcyclohex-2-en-1-yl 1-bromo-2-methoxyprop-2-yl ether (3): To a cold (-50 °C), magnetically stirred solution of the allyl alcohol **2** (500 mg, 3.2 mmol) and 2-methoxypropene (0.62 ml, 6.4 mmol) in CH_2Cl_2 (10 ml) was added a solution of NBS (570 mg, 3.2 mmol) in CH_2Cl_2 (20 ml) over a period of 15 min. The reaction mixture was allowed to warm up to room temperature over a period of 1.5 hr, and then diluted with CH_2Cl_2 (15 ml), washed with 2% aq. NaOH, water and brine, and dried (Na_2SO_4). Evaporation of the solvent and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished the bromoketal **3** (660 mg, 66%) as a colourless oil. IR (neat): ν_{max} 3060, 1635, 1070, 1030, 885 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 5.55 (1 H, br s, C=CH), 4.72 (2 H, s, $C=CH_2$), 4.38 (1 H, br s, O-CH), 3.57 and 3.39 (2 x d, *J*=6.3 Hz) & 3.47 (s) [2 H, CH_2-Br], 3.36 & 3.32 (3 H, s, O-CH_3), 1.80-2.45 (5 H, m), 1.74 (6 H, s, 2 x olefinic CH_3), 1.54 & 1.58 (3 H, s, *tert*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$, 1:1 mixture of diasteromers): δ 148.7 (s, *C*=CH_2), 135.0 (s, *C*=CH), 125.3 & 125.0 (d, C=*C*H), 109.0 (t, C=CH_2), 100.7 (s, O-C-O), 72.2 & 71.8 (d, O-CH), 50.0 & 49.0 (q, O-CH_3), 40.7 (d, C-5), 36.9 & 36.7 (t, CH_2-Br), 35.9 & 35.7 (t, C-6), 30.7 (t, C-4), 22.4 & 21.9 (q), 20.3 (q) and 19.9 (q) [3 x CH_3]. Mass: m/z 223 (M - Br, 1%), 191 (40), 153 and 155 [100, $BrCH_2C^+(OCH_3)CH_3$], 135 (100), 119 (60), 107 (100), 93 (100). HRMS: m/z For $C_{13}H_{19}O$ (M - Br,CH_3OH), Calcd.: 191.1436. Found: 191.1414.

(1R,4R,6R,8R) and (1R,4R,6R,8S)-1,8-Dimethyl-4-isopropenyl-7-oxabicyclo[4.3.0]nonanes (5): To a magnetically stirred solution of the bromoketal **3** (152 mg, 0.5 mmol) in *tert*-butanol (5 ml) was added $^nBu_3SnCl$ (0.02 ml, 0.074 mmol), $NaCNBH_3$ (63 mg, 1 mmol) and AIBN (catalytic) and refluxed for 2 hr. The reaction mixture was cooled, diluted with ether (10 ml), washed with 1% aqueous ammonia, water and brine, and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 1:1 epimeric mixture of the tetrahydrofuran **5** (54 mg, 62%) as a colourless oil. IR (neat): ν_{max} 3070, 1635, 1060, 880 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, 1:1 mixture of epimers): δ 4.62 (2 H, s, $C=CH_2$), 4.10-4.25 (1 H, m, O-C*H*-CH_3), 3.58 (dd, *J*=10.6 and 6.0 Hz) and 3.50 (dd, *J*=10.6 and 6.3 Hz) [1 H, bridgehead CH-O], 0.90-2.20 (9 H, m), 1.65 (3 H, s, olefinic CH_3), 1.231 (d, *J*=6.3 Hz) & 1.230 (d, *J*=5.48 Hz) [3 H, *sec*-CH_3], 1.08 & 1.04 (3 H, s, *tert*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 149.4 (s, *C*=CH_2), 108.4 (t, C=CH_2), 84.4 & 83.8 (d, bridgehead O-CH), 73.8 & 72.2 (d, O-*C*H-CH_3), 42.5 (t), 42.2 & 41.6 (d, C-4), 41.9 & 41.4 (s, bridgehead quaternary C), 37.9 & 33.2 (t), 34.5 (t), 27.0 (t), 30.4 & 28.5 (q), 23.6 & 23.0 (q) and 20.9 (q) [3 x *tert*-CH_3]. Mass: m/z 194 (M^+, 10%), 179 (40, M - CH_3), 136 (35), 135 (40), 134 (45), 125 (40), 109 (65), 107 (70), 93 (70), 41 (100). HRMS: m/z For $C_{13}H_{22}O$, Calcd.: 194.1671. Found: 194.1647.

E-3-Phenylprop-2-en-1-yl 1-bromo-2-methoxyprop-2-yl ether (7a): The bromoketalisation reaction of the cinnamyl alcohol (**6a**, 1 g, 7.5 mmol) at -50 °C with 2-methoxypropene (1.45 ml, 15.0 mmol) and NBS (1.6 g, 9.0 mmol) in CH_2Cl_2 (30 ml) for 1.5 hr and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished the bromoketal **7a** (1.31 g, 62%) as a colourless oil. IR (neat): ν_{max} 1590, 1070, 1040, 1030, 975, 735, 690 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 7.10-7.45 (5 H, m, aromatic H), 6.62 (1 H, d, *J*=16.2 Hz, Ar-C*H*=CH), 6.23 (1 H, t of d, *J*=16.2 and 5.4 Hz, Ar-CH=C*H*-), 4.14 (2 H, dd, *J*=5.4 and 1.2 Hz, allylic CH_2), 3.44 (2 H, s, CH_2-Br), 3.29 (3 H, s, O-CH_3), 1.52 (3 H, s, *tert*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 136.5 (s, C-1'), 128.3 (2 C, d, C-2'and 6'), 127.4 (d, C-4'), 126.2 (2 C, d, C-3'and 5'), 131.5 (d, Ar-*C*H=CH), 125.6 (d, Ar-CH=*C*H-CH_2), 99.9 (s, O-C-O), 61.8 (t, CH=CH-CH_2-O), 48.7 (q, O-CH_3), 34.9 (t, CH_2-Br), 21.2 (q, *tert*-CH_3). Mass: m/z 173 [(M - Br,CH_3OH), 3%], 151 and 153 [64, $CH_3OC^+(CH_3)CH_2Br$], 147 (35), 117 (100, Ph-CH=CH-CH_2^+), 115 (26), 91 (28, $C_7H_7^+$). HRMS: m/z For $C_{12}H_{13}O$ (M - CH_4BrO), Calcd.: 173.0966. Found: 173.0964.

(2α and 2β,4β)-4-benzyl-2-methoxy-2-methyltetrahydrofuran (9): The 5-*exo*-*trig* radical cyclisation reaction of the bromoketal **7a** (142 mg, 0.5 mmol) in benzene (28 ml) with $^nBu_3SnH$ (0.15 ml, 0.55 mmol) and a

catalytic amount of AIBN for 2.5 hr and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 2:1 epimeric mixture of the cyclic ketal **9** (81 mg, 79%) as an oil. IR (neat): ν_{max} 3020, 1600, 1065, 1025, 845, 750, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, 2:1 mixture of diastereomers): δ 7.29 (2 H, t, *J*=7.2 Hz) and 7.1-7.22 (3 H, m) [aromatic H], 3.96 & 3.94 (1 H, t, *J*=8.1 Hz) and 3.57 & 3.63 (1 H, t, *J*=8.4 Hz) [O-CH_2], 3.26 & 3.21 (3 H, s, O-CH_3), 2.60-2.80 (2 H, m, benzylic CH_2), 2.60 (1 H, septet, $J \approx$ 8.1 Hz, H-4), 1.99 & 2.13 (1 H, d of d, *J*=13.0 and 9.4 Hz) and 1.81 & 1.53 (1 H, dd, *J*=13.0 and 6.5 Hz) [H-3], 1.41 & 1.45 (3 H, s, CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$, 2:1 mixture of diastereomers): δ 140.8 (s'), 128.5 (2 C, d), 128.3 (2 C, d) and 126.0 (d) [aromatic C], 108.1 & 107.6 (s, O-C-O), 72.5 (t, O-CH_2), 48.2 (q, O-CH_3), 44.0 & 44.7 (d, C-4), 40.5 (t, benzylic CH_2), 39.6 (t, C-3), 21.9 & 21.3 (q, *tert*-CH_3). Mass: m/z 191 (M - CH_3, 3%), 174 (20, M - CH_3OH), 131 (20), 117 (25), 91 (65), 85 (25), 43 (100). HRMS: m/z For $C_{12}H_{15}O_2$ (M - CH_3), Calcd.: 191.1072. Found: 191.1056.

[(2α and 2β),4β]-4-Benzyl-2-methyltetrahydrofuran (8a): **From the bromoketal 7a:** The tandem radical cyclisation-demethoxylation reaction of the bromoketal **7a** (142 mg, 0.5 mmol) in *tert*-butanol (5 ml) with $^nBu_3SnCl$ (0.02 ml, 0.074 mmol), $NaCNBH_3$ (63 mg, 1 mmol) and a catalytic amount of AIBN for 2 hr and purification of the product on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 2:1 epimeric mixture of the tetrahydrofuran **8a** (63 mg, 72%) as an oil.

From the ketal 9: To a magnetically stirred solution of the cyclic ketal **9** (60 mg, 0.3 mmol) in *tert*-butanol (3 ml) was added $^nBu_3SnCl$ (0.01 ml, 0.037 mmol) and $NaCNBH_3$ (38 mg, 0.48 mmol), and refluxed for 2 hr. The reaction mixture was cooled, diluted with ether (7 ml) and washed with 1% aqueous ammonia, water and brine, and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 2:1 epimeric mixture of the demethoxylated product **8a** (41 mg, 80%) as a colourless oil. IR (neat): ν_{max} 3020, 1600, 1030, 745, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, 2:1 mixture of epimers): δ 7.1-7.4 (5 H, m, aromatic), 3.98 & 4.14 (1 H, m, O-CH), 4.0 & 3.83 (1 H, t, *J*=8.0 Hz, H-5a), 3.60 (dd, *J*=8.3 and 7.1 Hz) & 3.44 (dd, *J*=8.5 and 6.7 Hz) [H-5b], 2.50-2.80 (3 H, m, benzylic CH_2 and H-4), 1.55-2.2 (2 H, m, H-3), 1.28 & 1.22 (3 H, d, *J*=6.1 Hz, *sec*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$, 2:1 mixture of epimers): δ 140.9 (C-1'), 128.6 (2 C), 128.4 (2 C) and 126.0 (C-4') [aromatic C], 75.8 & 74.6 (O-CH), 72.7 & 73.1 (O-CH_2), 41.9 & 40.0, 40.6, 39.5 & 39.1, 21.4 & 21.1 (*sec*-CH_3). Mass: m/z 176 (M^+, 10%), 143 (15), 117 (40), 92 (90), 91 (100). HRMS: m/z For $C_{12}H_{16}O$, Calcd.: 176.1201. Found: 176.1197.

3,5,5-Trimethylcyclohex-2-en-1-yl 1-bromo-2-methoxyprop-2-yl ether 7b: The bromoketalisation reaction of the allyl alcohol **6b** (500 mg, 3.57 mmol) at -50 °C with 2-methoxypropene (0.68 ml, 7.14 mmol) and NBS (712 mg, 4.0 mmol) in CH_2Cl_2 (30 ml) for 1.5 hr and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished the bromoketal **7b** (865 mg, 83%) as a colourless oil. IR (neat): ν_{max} 1660, 1075, 1050, 1010, 995 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, 5:1 mixture of diastereomers): δ 5.34 (1 H, br s, olefinic H), 4.34 (1 H, br s, O-CH), 3.50 and 3.35 (2 x d, *J*=10 Hz) & 3.40 (s) [2 H, CH_2-Br], 3.30 & 3.26 (3 H, s, O-CH_3), 1.30-2.00 (4 H, m), 1.68 (3 H, s, olefinic CH_3), 1.52 & 1.38 (3 H, s, C*H*$_3$-C-OCH_3), 1.00 (3 H, s) and 0.91 (3 H, s) [CH_3-C-CH_3]. ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 136.3 & 135.5 (s, *C*=CH), 122.5 & 122.3 (d, C=*C*H), 100.5 (s, O-C-O), 67.1 & 71.8 (d, O-CH), 49.1 & 50.0 (q, O-CH_3), 43.9 & 44.2 (t, CH_2-Br), 43.7 & 43.5 (s, quaternary C), 42.3 & 35.8 (t, allylic CH_2), 31.4 (2 C, q and t, olefinic CH_3 and CH_2), 26.3 (q, *tert*-CH_3), 23.8 (q) and 22.4 (q) [*C*H$_3$-C-*C*H$_3$]. Mass: m/z 179 [(M - CH_3OH,Br), 22%], 151 & 153 (100, $BrCH_2C^+(OCH_3)CH_3$), 139 (22), 123 (90). HRMS: m/z For $C_{12}H_{19}O$ (M - CH_3OH,Br), Calcd.: 179.1436. Found: 179.1427.

[1β,2α,6β,(8α and 8β)]-2,4,4,8-Tetramethyl-7-oxabicyclo[4.3.0]nonanes (8b): The tandem radical cyclisation-demethoxylation reaction of the bromoketal **7b** (146 mg, 0.5 mmol) in *tert*-butanol (5 ml) with $^nBu_3SnCl$ (0.02 ml, 0.074 mmol), $NaCNBH_3$ (63 mg, 1 mmol) and a catalytic amount of AIBN for 2 hr and purification of the product on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 5:1 epimeric mixture of the tetrahydrofuran **8b** (56 mg, 62%) as an oil. IR (neat): ν_{max} 1360, 750 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, 5:1 mixture of epimers): δ 4.00-4.20 (2 H, m, 2 x O-CH), 2.30-2.45 (1 H, m), 1.94-2.08 (1 H, m), 1.30-1.64 (2 H, m), 1.28 & 1.21 (3 H, d, *J*=6.0 Hz, O-CHC*H*$_3$), 1.00-1.20 (4 H, m), 0.93 (3 H, d, *J*=6.8 Hz, C_2-CH_3), 0.90 (3 H, s) & 0.85 (3 H, s) [CH_3-C-CH_3]. ^{13}C NMR (22.5 MHz, $CDCl_3$, peaks due to the major isomer): δ 76.5 (bridgehead O-CH), 75.0 (O-*C*HCH$_3$), 44.4 (bridgehead CH), 43.8, 42.2, 33.1, 32.0, 31.6 (quaternary C), 27.2, 24.5, 23.2, 20.4. Mass: m/z 182 (M^+, 16%), 181 (20), 167 (40), 123 (85), 111 (100), 95 (35). HRMS: m/z For $C_{12}H_{21}O$ (M - 1), Calcd.: 181.1592. Found: 181.1596.

3-Methylcyclohex-2-en-1-yl 1-bromo-2-methoxyprop-2-yl ether (7c): The bromoketalisation reaction of the allyl alcohol **6c** (500 mg, 4.5 mmol) at -50 °C with 2-methoxypropene (0.85 ml, 9.0 mmol) and NBS (870 mg, 4.9 mmol) in CH_2Cl_2 (30 ml) for 1.5 hr and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished the bromoketal **7c** (790 mg, 67%) as a colourless oil. IR (neat): ν_{max} 1660, 1070, 1040, 1020, 965, 905 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, ≈1:1 mixture of diastereomers): δ 5.40 (1 H, br s, olefinic H), 4.28 (1 H, br s, O-CH), 3.59 and 3.42 (2 H, 2 x d, *J*=14 Hz, CH_2-Br), 3.30 (3 H, s, O-CH_3), 1.35-2.05 (6 H, m), 1.70 (3 H, s, olefinic CH_3), 1.52 (3 H, s, *tert*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$, ≈1:1 mixture of diastereomers): δ 137.4 & 137.1 (s, *C*=CH), 123.2 & 122.9 (d, C=*C*H), 99.7 (s, O-C-O), 65.5 (d, O-CH), 48.2 (q, O-CH_3), 35.1 (t, CH_2-Br), 29.7 (t) and 29.2 (t) [C-4 and 6], 23.1 (q) and 21.6 (q) [2 x CH_3], 19.2 & 19.0 (t, C-5). Mass: m/z 153 and 151 (100, M-$C_7H_{11}O$), 126 (15), 111 (30), 95 (100). HRMS: m/z For $C_{10}H_{15}O$ (M - CH_3OH,Br), Calcd.: 151.1123. Found: 151.1101.

[1β,2α,6β,(8α and 8β)]-2,8-Dimethyl-7-oxabicyclo[4.3.0]nonanes (8c): The tandem radical cyclisation-demethoxylation reaction of the bromoketal **7c** (132 mg, 0.5 mmol) in *tert*-butanol (5 ml) with $^nBu_3SnCl$ (0.02 ml, 0.074 mmol), $NaCNBH_3$ (63 mg, 1 mmol) and a catalytic amount of AIBN for 2 hr and purification of the product on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 10:1 epimeric mixture of the tetrahydrofuran **8c** (47 mg, 61%) as an oil. IR (neat): ν_{max} 1375, 1080 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$, 10:1 mixture of epimers, peaks due to the major isomer): δ 4.075 (1 H, quintets of d, *J*=10.2 and 5.9 Hz, H-2), 3.93 (1 H, t of d, *J*=9.1 and 6.9 Hz, H-1), 2.30-2.40 (1 H, m, bridgehead CH), 1.00-2.00 (9 H, m), 1.28 (3 H, d, *J*=6.1 Hz, C_2-CH_3), 0.93 (3 H, d, *J*=6.9 Hz, *sec*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$, peaks due to the major isomer): δ 78.1 and 75.2 [2 x O-CH], 45.3, 32.3, 31.4 (2 C), 29.0, 23.1 (2 C), 20.6. Mass: 154 (M^+, 0.3%), 110 (15), 111 (100, M - C_3H_7), 109 (21), 107 (58), 97 (24), 96 (42), 95 (100), 94 (30).

(1α,5α)-3,5-Dimethylcyclohex-2-en-1-yl 1-bromo-2-methoxyprop-2-yl ether (7d): The bromoketalisation reaction of the allyl alcohol **6d** (500 mg, 4.03 mmol) at -50 °C with 2-methoxypropene (0.85 ml, 9.0 mmol) and NBS (870 mg, 4.9 mmol) in CH_2Cl_2 (30 ml) for 1.5 hr and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished the bromoketal **7d** (990 mg, 89%) as a colourless oil. IR (neat): ν_{max} 1070, 1045, 1020, 995, 830, 685 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, peaks due to one diastereomer): δ 5.32 (1 H, br d, olefinic H), 4.38 (1 H, br s, O-CH), 3.30-3.60 (2 H, m, CH_2-Br), 3.32 (3 H, s, O-CH_3), 1.15-2.10 (5 H, m), 1.68 (3 H, s, olefinic CH_3), 1.52 (3 H, s, *tert*-CH_3), 0.97 (3 H, d, *J*=6.3 Hz, *sec*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$, mixture of diastereomers): δ 136.04 (s, *C*=CH),123.9 & 123.6 (d, C=*C*H), 99.4 (s, O-C-O), 67.9 & 67.2 (d, O-CH), 48.4 & 48.3 (q, O-CH_3), 39.2 & 38.9 (t, CH_2-Br), 38.2 (d and t, CH and CH_2), 35.1 (t, CH_2), 28.0 (q, olefinic CH_3), 22.9 (q, *tert*-CH_3), 22.0 (q, *sec*-CH_3). Mass: m/z 165 [(M^+ - Br,CH_3OH), 15%], 151 & 153 (100, $BrCH_2C^+(OCH_3)CH_3$), 125 (18), 109 (97, $C_8H_{13}^+$), 72 (62).

[1β,2α,4α,6β,(8α and 8β)]-2,4,8-Trimethyl-7-oxabicyclo[4.3.0]nonanes (8d): The tandem radical cyclisation-demethoxylation reaction of the bromoketal **7d** (138 mg, 0.5 mmol) in *tert*-butanol (5 ml) with $^nBu_3SnCl$ (0.02 ml, 0.074 mmol), $NaCNBH_3$ (63 mg, 1 mmol) and a catalytic amount of AIBN for 2 hr and purification of the product on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 5:1 epimeric mixture of the tetrahydrofuran **8d** (46 mg, 55%) as an oil. IR (neat): ν_{max} 1375, 1050 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, 5:1 mixture of epimers, peaks due to the major isomer): δ 3.80-4.20 (2 H, m, 2 x O-CH), 2.35 (1 H, q of d, *J*=12.7 and 6.5 Hz, bridgehead CH), 1.50-2.00 (2 H, m), 1.10-1.50 (6 H, m), 1.29 (3 H, d, *J*=6.1 Hz, O-CH*C*H_3), 0.94 (3 H, d, *J*=6.9 Hz) and 0.89 (3 H, d, *J*=6.4 Hz) [2 x *sec*-CH_3]. ^{13}C NMR (100 MHz, $CDCl_3$, peaks due to the major isomer): δ 78.2 (bridgehead O-CH), 75.3 (O-*C*HCH_3), 44.8 (bridgehead CH), 40.6, 38.1, 32.1, 31.2, 30.1, 23.4, 22.3 and 20.4 [3 x *sec*-CH_3].

E-3-(4'-Methoxyphenyl)prop-2-en-1-yl 1-bromo-2-methoxyprop-2-yl ether (7e): The bromoketalisation reaction of the allyl alcohol **6e** (500 mg, 3.4 mmol) at -50 °C with 2-methoxypropene (0.65 ml, 6.8 mmol) and NBS (730 mg, 4.08 mmol) in CH_2Cl_2 (30 ml) for 1.5 hr and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished the bromoketal **7e** (595 mg, 62%) as a colourless oil. IR (neat): ν_{max} 1610, 1515, 1075, 1040, 970, 840 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 7.34 and 6.84 (4 H, 2 x d, *J*=9.0 Hz, aromatic H), 6.60 (1 H, d, *J*=16.2 Hz, Ar-C*H*=CH), 6.14 (1 H, t of d, *J*=16.2 and 6.3 Hz, Ar-CH=C*H*), 4.10 (2 H, d, *J*=6.3 Hz, O-CH_2), 3.78 (3 H, s, Ar-O-CH_3), 3.47 (2 H, s, CH_2-Br), 3.24 (3 H, s, O-CH_3), 1.36 (3 H, s, *tert*-CH_3).

[(2α and 2β),4β]-4-(4'-Methoxybenzyl)-2-methyltetrahydrofurans (8e): The tandem radical cyclisation-demethoxylation reaction of the bromoketal **7e** (150 mg, 0.48 mmol) in *tert*-butanol (5 ml) with $^nBu_3SnCl$ (0.02

ml, 0.074 mmol), $NaCNBH_3$ (63 mg, 1 mmol) and a catalytic amount of AIBN for 3 hr and purification of the product on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 3:2 epimeric mixture of the tetrahydrofuran **8e** (65 mg, 66%) as an oil. IR (neat): ν_{max} 1610, 1510, 1035, 805, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 3:2 mixture of epimers): δ 7.01 and 6.76 (4 H, 2 x d, *J*=8.4 Hz, aromatic H), 3.89 & 4.06 (1 H, sextet, *J*=6.3 Hz, O-C*H*CH_3), 3.73 (3 H, s, O-CH_3), 3.60-3.80 (1 H, m) and 3.51 & 3.35 (1 H, t, *J*=7.6 Hz) [O-CH_2], 2.40-2.70 (4 H, m), 2.03 & 1.70 (2 H, quintet, *J*=6.2 Hz), 1.20 & 1.13 (3 H, d, *J*=6.1 Hz, *sec*-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$, 3:2 mixture of epimers): δ 157.4 (s), 132.5 (s), 129.3 (2 C, d), 113.4 (2 C, d), 76.1 & 74.5 (d, O-CH), 72.9 & 73.3 (t, O-CH_2), 55.2 (q, O-CH_3), 42.2 (d, CH), 41.3 & 41.0 (t, benzylic CH_2), 39.4 & 38.7 (t, CH_2), 21.4 & 21.2 (q, *sec*-CH_3). Mass: m/z 206 (M^+, 52%), 173 (6), 164 (12), 148 (15), 122 (50), 121 (100). HRMS: m/z For $C_{13}H_{18}O_2$, Calcd.: 206.1307. Found: 206.1307.

***E*-4-(4'-Methoxyphenyl)but-3-en-2-yl 1-bromo-2-methoxyprop-2-yl ether (7f):** The bromoketalisation reaction of the allyl alcohol **6f** (500 mg, 2.8 mmol) at -50 °C with 2-methoxypropene (0.6 ml, 6.3 mmol) and NBS (600 mg, 3.4 mmol) in CH_2Cl_2 (30 ml) for 1.5 hr and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 1:1 diastereomeric mixture of the bromoketal **7f** (600 mg, 65%) as a colourless oil. IR (neat): ν_{max} 1645, 1600, 1510, 1060, 1030, 960, 810 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 7.31 and 6.85 (4 H, 2 x d, J=9 Hz, aromatic H), 6.45 (1 H, d, J=16.2 Hz, Ar-C*H*=CH), 5.90-6.25 (1 H, m, Ar-CH=C*H*), 4.52 (1 H, quintet, J=6.4 Hz, O-CH), 3.82 (3 H, s, Ar-O-CH_3), 3.44 & 3.40 (2 H, s, CH_2-Br), 3.28 & 3.24 (3 H, s, O-CH_3), 1.54 & 1.48 (3 H, s, tert-CH_3), 1.33 (3 H, d, J=7.2 Hz, sec-CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 159.2 (s), 131.7 & 131.0 (d, Ar-C*H*=CH), 129.9 & 128.8 (d, Ar-CH=C*H*), 128.1 (s), 127.5 (2 C, d), 114.0 (2 C, d), 100.7 (s, O-C-O), 69.0 & 67.8 (d, O-CH), 55.3 (q, Ar-O-CH_3), 49.3 & 49.1 (q, O-CH_3), 36.5 & 35.8 (t, CH_2-Br), 25.8 & 25.3 (q, tert-CH_3), 23.1 & 22.5 (q, sec-CH_3). Mass: m/z 330 (M + 2) and 328 (M^+) [3%], 192 (62), 177 (52), 161 (100), 153 and 151 (27, $BrCH_2C^+(OCH_3)CH_3$),121 (20).

[2α,3β,(5α and 5β)]-2,5-Dimethyl-3-(4'-methoxybenzyl)tetrahydrofurans (8f): The tandem radical cyclisation-demethoxylation reaction of the bromoketal **7f** (164 mg, 0.5 mmol) in *tert*-butanol (5 ml) with $^nBu_3SnCl$ (0.02 ml, 0.074 mmol), $NaCNBH_3$ (63 mg, 1 mmol) and a catalytic amount of AIBN for 2.5 hr and purification of the product on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 1:1 epimeric mixture of the tetrahydrofuran **8f** (78 mg, 71%) as an oil. IR (neat): ν_{max} 1610, 1040 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$, ≈1:1 mixture of epimers): δ 7.10 and 6.80 (4 H, 2 x d, *J*=8.5 Hz, aromatic H), 3.4-4.4 (2 H, m, 2 x O-CH), 3.78 (3 H, s, O-CH_3), 2.42-2.70 (2 H, m, benzylic CH_2), 1.40-2.40 (3 H, m), 1.19 & 1.20 (3 H, d, *J*=6.2 Hz) and 1.14 (3 H, d, *J*=6.7 Hz) [2 x *sec*-CH_3]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 157.5, 132.5, 129.0 (2 C) and 113.5 (2 C) [aromatic C], 80.5 & 79.5 (C-2), 73.5 (C-5), 55.0 (Ar-O-CH_3), 49.6 & 47.5, 41.3 & 39.3, 37.9 & 37.7, 21.6 & 21.3 and 20.0 & 19.9 [2 x *sec*-CH_3]. Mass: m/z 220 (M^+, 31%), 162 (10), 147 (12), 135 (12), 122 (82), 121 (100, $CH_3OC_6H_4C^+H_2$), 112 (35), 99 (10). HRMS: m/z For $C_{14}H_{20}O_2$, Calcd.: 220.1464. Found: 220.1472.

Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-yl 1-bromo-2-methoxyprop-2-yl ether (7g): The bromoketalisation reaction of the allyl alcohol **6g** (500 mg, 3.4 mmol) at -50 °C with 2-methoxypropene (0.65 ml, 6.8 mmol) and NBS (730 mg, 4.08 mmol) in CH_2Cl_2 (30 ml) for 1.5 hr and purification of the product on a neutral alumina (5 g) column using ethyl acetate-hexane (1:40) as eluent furnished the bromoketal **7g** (845 mg, 83%) as a colourless oil. IR (neat): ν_{max} 3060, 1005, 770, 730 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, 1:1 mixture of diastereomers): δ 5.70-6.15 (3 H, m) and 5.42-5.70 (1 H, m) [olefinic H], 4.12 (1 H, s, O-CH), 3.30-3.60 (2 H, m, CH_2-Br), 3.30 & 3.26 (3 H, s, O-CH_3), 3.05 (1 H, br s), 2.50-2.95 (3 H, m), 1.61 and 1.40 (2 H, 2 x d, *J*=10.8 Hz, H-10), 1.58 (3 H, s, *tert*-CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 137.8, 135.3, 132.9 & 132.7 and 132.1 [olefinic C], 100.0 (O-C-O), 78.4 & 78.1 (O-CH), 54.4 & 51.8 (O-CH_3), 51.3 (C-10), 48.7 & 48.4 (O-CH_3), 44.5 (2 C), 35.7 & 35.4 (CH_2-Br), 22.4 & 22.0 (*tert*-CH_3). Mass: m/z 219 (M - Br, 2%), 151 and 153 [100, $BrCH_2C^+(OCH_3)CH_3$], 131 (80), 96 (100).

(5α and 5β)-(endo,anti,cis)-5-Methyl-4-oxatetracyclo[8.2.1.0^{2,9}.0^{3,7}]tridec-11-ene (8g): The tandem radical cyclisation-demethoxylation reaction of the bromoketal **7g** (302 mg, 1.0 mmol) in *tert*-butanol (8 ml) with $^nBu_3SnCl$ (0.04 ml, 0.15 mmol), $NaCNBH_3$ (126 mg, 2 mmol) and a catalytic amount of AIBN for 3 hr and purification of the product on a silica gel (4 g) column using ethyl acetate-hexane (1:40) as eluent furnished a 1:1 epimeric mixture of the tetrahydrofuran **8g** (143 mg, 75%) as an oil. IR (neat): ν_{max} 3070, 1080, 1030, 730 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$, 1:1 mixture of epimers): δ 5.40-6.00 (2 H, m, olefinic H), 3.10-4.60 (2 H, m, 2 x O-CH), 1.00-3.00 (11 H, m), 1.25 & 1.21 (3 H, d, *J*=6.3 Hz, *sec*-CH_3). Mass: m/z 190 (M^+, 45%), 189 (32),

132 (30), 131 (30), 122 (30), 123 (100), 97 (30), 95 (42), 91 (47). HRMS: m/z For $C_{13}H_{18}O$, Calcd.: 190.1358. Found: 190.1344.

3-[(2-Bromo-1-methoxy-1-phenyl)-ethoxy]-propyne (11): The bromoketalisation reaction of propargyl alcohol (0.66 ml, 11.2 mmol) at -50 °C with α-methoxystyrene (**10**, 500 mg, 3.73 mmol) and NBS (795 mg, 4.5 mmol) in CH_2Cl_2 (30 ml) for 1.5 hr and purification of the product on a neutral alumina (3 g) column using ethyl acetate-hexane (1:40) as eluent furnished the bromoketal **11** (930 mg, 93%) as a colourless oil.[6] IR (neat): ν_{max} 3300, 1500, 1075, 1040, 975, 770, 700 cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): δ 7.20-7.70 (5 H, m, aromatic H), 4.00 (2 H, t, *J*=3.0 Hz, O-CH_2), 3.75 and 3.51 (2 H, 2 x d, *J*=12.0 Hz, CH_2-Br), 3.37 (3 H, s, O-CH_3), 2.38 (1 H, t, *J*=3.0 Hz, C≡C-H).

4-Methyl-2-phenylfuran (14):

Step 1: Radical Cyclisation: The radical cyclisation reaction of the bromoketal **11** (268 mg, 1.0 mmol) in *tert*-butanol (5 ml) with $^nBu_3SnCl$ (0.04 ml, 0.15 mmol), $NaCNBH_3$ (126 mg, 2.0 mmol) and a catalytic amount of AIBN for 30 min and purification of the product on a silica gel (3 g) column using hexane as eluent furnished a 4:5 mixture of the mixed ketal **12** and the tetrahydrofuran **13** (150 mg, 87%) which was aromatised without further purification.

Step 2: Aromatisation: To a mixture of the ketal **12** and ether **13** (150 mg) in dry benzene (5 ml), obtained from the previous experiment, was added PTSA (catalytic, till the reaction mixture a dark colour) and magnetically stirred at room temperature for 25 min. The reaction mixture was diluted with ether (5 ml), washed with saturated aq. $NaHCO_3$ and brine, and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column furnished the furan **14**[7a] (60 mg, 38%) and the ether **13** (75 mg, 47%) as oils. **For the furan 14:**[7a] IR (neat): ν_{max} 1600, 1020, 915, 765, 690 cm^{-1}. ^1H NMR (80 MHz, $CDCl_3$): δ 7.00-7.70 (6 H, m, Ph and H-2), 6.42 (1 H, s, H-3), 2.01 (3 H, d, *J*=0.2 Hz, CH_3). **For the tetrahydrofuran 13:** IR (neat): ν_{max} 1500, 1460, 1280, 1055, 885, 755, 700 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 7.25-7.40 (5 H, m, aromatic), 5.04 (1 H, t, *J*=2.1 Hz) and 4.98 (1 H, t, *J*=2.1 Hz) [C=CH_2], 4.98 (1 H, t, *J*=6.8 Hz, O-CH), 4.60 (1 H, d, *J*=12.4 Hz) and 4.42 (1 H, t of d, *J*=12.4 and 1.4 Hz) [O-CH_2], 2.96 (1 H, dd, *J*=12.9 and 5.1 Hz) and 2.56 (1 H, dd, *J*=12.9 and 8.7 Hz) [allylic CH_2]. Mass: m/z 160 (M^+, 5%), 122 (30), 107 (22), 105 (100). HRMS: m/z For $C_{11}H_{12}O$, Calcd.: 160.0888. Found: 160.0889.

3-Methylene-5-phenyltetrahydrofuran (13): The tandem radical cyclisation-demethoxylation reaction of the bromoketal **11** (100 mg, 0.37 mmol) in *tert*-butanol (5 ml) with $^nBu_3SnCl$ (0.04 ml, 0.15 mmol), $NaCNBH_3$ (90 mg, 1.43 mmol) and a catalytic amount of AIBN for 3 hr and purification of the product on a silica gel (2 g) column using hexane as eluent furnished the tetrahydrofuran **13** (50 mg, 83%) as an oil.

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References

1. Ho, T.-L. *Tandem organic* reactions, Wiley, New York, 1992; Curran, D.P. *Comprehensive organic synthesis*, B.M. Trost and I. Fleming, Eds., Pergamon Press, New York, 1992, Vol. 4, pp.715; Posner, G.H. *Chem. Rev.*, **1986**, *86*, 831; Hoffmann, H.M.R. *Angew. Chem., Int. Ed. Engl.*, **1992**, *31*, 1332; Ihara, M.; Fukumoto, K. *Angew. Chem., Int. Ed. Engl.*, **1993**, *32*, 1010; Davies, H.M.L. *Tetrahedron*, **1993**, *49*, 5203; Bunce, R.A. *Tetrahedron*, **1995**, *51*, 13103.
2. Srikrishna, A.; Viswajanani, R.; Sattigeri, J.A. *J. Chem. Soc., Chem. Commun.*, **1995**, 469.
3. Preliminary communication, Srikrishna, A.; Viswajanani, R.; Yelamaggad, C.V. *Tetrahedron Lett.*, **1995**, *36*, 1127.
4. Garver, L.; van Eikeren, P.; Byrd, J.E. *J. Org. Chem.*, **1976**, *41*, 2773.
5. Stork, G.; Sher, P.M. *J. Am. Chem. Soc.*, **1986**, *108*, 303; Srikrishna, A. *J. Chem. Soc., Chem. Commun.*, **1987**, 587; Srikrishna, A.; Nagaraju, S.; Sharma, G.V.R. *J. Chem. Soc., Chem. Commun.*, **1993**, 285.
6. Woodward, R.B.; Katz, T.J. *Tetrahedron*, **1959**, *5*, 70.
7. (a) Srikrishna, A.; Pullaiah, K.C. *Tetrahedron Lett.*, **1987**, *28*, 5203. (b) Srikrishna, A.; Sundarababu, G. *Tetrahedron*, **1990**, *46*, 7901.
8. Wohl, R.A. *Synthesis*, **1974**, 38.
9. Srikrishna, A.; Viswajanani, R. *Synlett*, **1995**, 95.

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