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Study of Metal and Acid Catalysed Deprotection of Propargyl Ethers of Alcohols via their Allenyl Ethers

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Abstract : A new method for the deprotection of prop-2-ynyl ethers **1b-9b** is described. Isomerisation of **1b-9b** to O-allenyl ethers **1d-9d** and deprotection by reaction with $Hg(OCOCF_3)_2$, aq.HCl, aq.CF_3CO_2H and best by use of a catalytic amount of OsO_4 is described to obtain the alcohols **1a-9a** in good yield. Application of this method for the deprotection of prop-2-enyl ethers **7c,8c,10c-13c** via their corresponding prop-1-enyl ethers **7e,8e,10e-13e** to obtain the corresponding alcohols **7a,8a,10a-13a** is also described.

Keywords : Alcohols; isomerisation; enol ethers; OsO_4.

Protection and deprotection of a hydroxy group is an important requirement in synthetic organic chemistry.[1] Among several protecting groups developed for this purpose, unsaturated ethers were considered because of their easy synthesis and facile metal mediated cleavage promoted due to the formation of π-allyl complex intermediates. As a result, cleavage of prop-2-enyl ethers has been reasonably well studied and recently reviewed.[2] The existing methodologies for the deprotection of prop-2-enyl ethers describe a two step reaction sequence involving first isomerisation to a prop-1-enyl ether by use of either a base (KO^tBu)[3] or $(Ph_3P)_3RhCl$[4] or {Ir(COD)$(PMePh_2)_2$]-PF_6[5] followed by hydrolysis with 0.1N HCl at 60°C or $HgCl_2$-HgO-H_2O[6] or I_2-H_2O.[7] Prop-2-enyl ethers have also been deprotected by use of Pd-C-MeOH-TsOH/$ClSO_3H$ at reflux,[8] SeO_2-HOAc at reflux,[9] $PdCl_2$-NaOAc-HOAc at 60°C,[10] $Pd(Ph_3P)_4$-HOAc at 60°C,[11] $SmCl_3$,[12] $AlCl_3$-N,N-dimethylaniline-$SnCl_4$,[13] NBS-CCl_4-NaOH,[14] Zirconacene,[15] $Pd(NH_3)_2Cl_2$[16] $NiCl_2$ (dppp)-DIBAL-H[17] and by a two step photochemical method.[18] Reaction of aromatic prop-2-enyl ethers with $PdCl_2$ has largely been described in the patented literature[19] and reported to undergo Claisen rearrangement, reaction with $PdCl_2(PhCN)_2$[20] has been reported to yield prop-1-enyl aromatic ethers under non-hydrolytic conditions due to isomerisation. Deprotection of aromatic prop-1-enyl ethers has been reported by Ogawa *et al* by reaction with $Pd(Ph_3P)_4$ THF at 25°C.[21] Formation of prop-2-enyl ethers of

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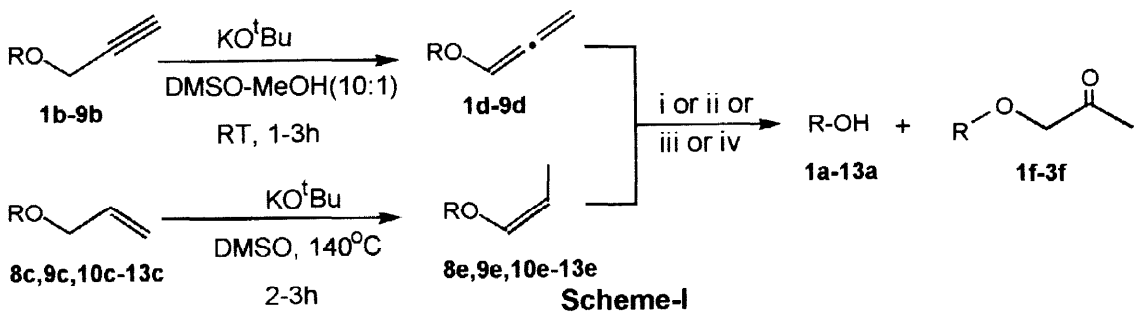
saccharide alcohols has been reported by use of $Pd_2(dba)_3$ and allylethyl carbonate with saccharide alcohols.[22] We have earlier described deprotection of prop-1-enyl and prop-2-enyl ethers under Wacker process conditions ($PdCl_2$-CuCl-O_2)[23] and have now initiated the study of deprotection of much less explored prop-2-ynyl ethers and esters.[24-26] Recently, Banerjee *et al*[27] have shown that *in-situ* generated low valent titanium (LVT) reagent deprotects prop-2-ynyl ethers without affecting prop-2-enyl ethers; however, carbonyl compounds have been reported to undergo McMurry reaction under these conditions.[28] Chandrasekharan *et al*[29] have reported that benzyltriethyl tetrathiomolybdate reagent cleaves prop-2-ynyl ethers efficiently. Dunach *et al*[30] have reported nickel-catalysed electrochemical deprotection of prop-2-ynyl esters and aryl ethers. In spite of these developments there exists enormous scope for finding efficient methods to deprotect prop-2-ynyl ethers.[31] Due to our interest in the area of carbohydrate chemistry where protection and deprotection strategies play an important role in synthesis, we initiated work to study the utility of prop-2-ynyl ethers for the protection of alcohols. We describe our detailed studies that cultiminated in the development of a new method for the deprotection of prop-2-ynyl and prop-2-enyl ethers of alcohols. Our protocol entails isomerisation of prop-2-ynyl ethers and prop-2-enyl ethers to the corresponding allenyl and prop-1-enyl ethers respectively, followed by cleavage under neutral and acidic reaction conditions to obtain the alcohols (Scheme-I).

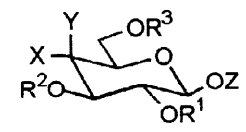


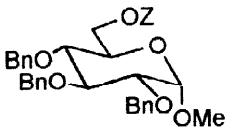
Scheme-I

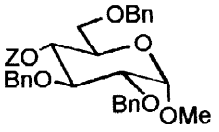
Reagents and conditions: i) Cat. $Hg(OCOCF_3)_2$ ii) 2N HCl iii) 5% aq. CF_3COOH iv) cat.OsO_4-NMO

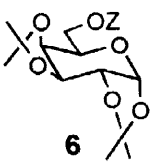
Accordingly, prop-2-ynyl ethers **1b-9b** possessing diverse protecting groups were severally reacted with KO^{t}Bu (2 mole equivalent) in DMSO-MeOH (10:1) at room temperature for 1-3 h to obtain their corresponding allenyl ethers **1d-9d** respectively in 65-94% yield[32] (Table-1). Formation of **1d-9d** was evident from the appearance of double bond protons of the allene between δ 6.6-7.0 (1H, t, J = 5.6 Hz) and δ 5.4-5.5 (2H, 2d) in the ^{1}H-NMR spectra and allene carbons at δ 91.0 (t), 121.5 (d) and 200.8 (s) in the ^{13}C-NMR spectra. In order to deprotect **1d-9d** to the corresponding alcohols several reaction conditions were tried (Table-2). Thus, reaction of allenyl substrates **1d-9d** containing protecting groups such as isopropylidene and cyclic ketal were reacted with catalytic amount of $Hg(OCOCF_3)_2$ (0.4 mole equivalent) (Table-2) in acetone-water (2:1) at 0°C to obtain the required alcohols **1a-3a** in low yield (58-67%) along with the undesired keto

products **1f-3f** (15-20%) respectively (Scheme-I) due to mercury catalysed hydration of allene[33] and **4a-9a** in good yield (77-87%); formation of keto by products was not









1) $R^1=R^2=R^3=$ Bn, X= OBn, Y= H

2) $R^1=R^2=R^3=$ Bn, X= H, Y= OBn

3) $R^1=R^2=R^3=$ Bn, X= 2,3,4,6-tetra-O-benzy-β-D-galactopyranosyl-, Y= H

1g) $R^1=R^2=R^3=$ OAc, X =OAc, Y= H

2g) $R^1=R^2=R^3=$ OAc, X = H, Y=OAc

3g) $R^1=R^2=R^3=$ OAc, X = 2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-, Y=H

4

5

6

a) Z= H

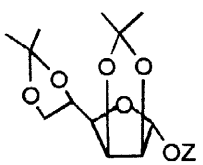
b) Z= $-CH_2C{\equiv}CH$

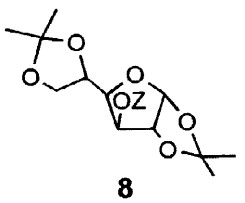
c) Z= $-CH_2CH{=}CH_2$

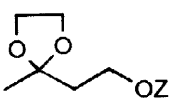
d) Z= $-CH{=}C{=}CH_2$

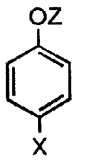
e) Z= $-CH{=}CH-CH_3$

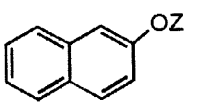
f) Z= $-CH_2COCH_3$











7

8

9

10) X = CH_3

11) X = $COCH_3$

12) X = Cl

13

Table 1. OsO_4-NMO catalysed deprotection of O-allenyl ethers **1d-9d** and enol ethers **7e,8e,10e-13e**

S.No	Propargyl ethers **1b-9b**		Allenyl ethers **1d-9d**		Allyl ethers **7c,8c,10c-13c**		Enol ethers **7e,8e,10e-13e**		Alcohols **1a-13a**	
		yield (time)		yield (time)		yield (time)		yield (time)		yield (time)
i	**1b**	89% (1 h)	**1d**	65% (0.5 h)	-	-	-	-	**1a**	95% (18 h)
ii	**2b**	82% (1 h)	**2d**	84% (1 h)	-	-	-	-	**2a**	95% (10 h)
iii	**3b**	78% (2 h)	**3d**	81% (1.5 h)	-	-	-	-	**3a**	97% (15 h)
iv	**4b**	69% (2.5 h)	**4d**	89% (1.5 h)	-	-	-	-	**4a**	94% (15 h)
v	**5b**	90% (3 h)	**5d**	87% (1.5 h)	-	-	-	-	**5a**	92% (16 h)
vi	**6b**	83% (2 h)	**6d**	84% (1 h)	-	-	-	-	**6a**	89% (17 h)
vii	**7b**	57% (3 h)	**7d**	85% (0.5 h)	-	-	-	-	**7a**	88% (12 h)
viii	-	-	-	-	**7c**	74% (2 h)	**7e**	71% (6 h)	**7a**	79% (45 h)
ix	**8b**	72% (2.5 h)	**8d**	90% (1 h)	-	-	-	-	**8a**	92% (22 h)
x	-	-	-	-	**8c**	78% (3 h)	**8e**	81% (8 h)	**8a**	82% (43 h)
xi	**9b**	89% (0.5 h)	**9d**	94% (0.5 h)	-	-	-	-	**9a**	90% (19 h)
xii	-	-	-	-	**10c**	92% (6 h)	**10e**	89% (9 h)	**10a**	87% (18 h)
xiii	-	-	-	-	**11c**	85% (6 h)	**11e**	88% (10 h)	**11a**	84% (21 h)
xiv	-	-	-	-	**12c**	76% (6 h)	**12e**	83% (9 h)	**12a**	88% (21 h)
xv	-	-	-	-	**13c**	88% (13 h)	**13e**	86% (7 h)	**13a**	92% (42 h)

observed. A similar reaction performed at room temperature (25°C) was essentially the same except that substrates **6d-9d** respectively indicated extensive decomposition due to

deprotection of acid labile isopropylidene and cyclic ketal protecting groups. Thus, anomeric allenyl glycosides **1d-3d** could not be deprotected in higher yields compared to the allenyl substituted pyranosides **4d-8d**. Such a difference in reactivity was also observed earlier while deprotecting allyl glycosides.[34] Hence in order to optimise reaction conditions for cleavage of anomeric allenyl glycosides **1d-3d** were reacted with various acidic reagents such as 2N HCl, 5% aqueous trifluoroacetic acid and p-TSA at room temperature to obtain the corresponding alcohols **1a-3a** in lower yields (52-68%) along with the undesired keto compounds **1f-3f** (18-20%) respectively (Table-2). However,

Table 2: Cleavage of allenyl ethers **1d-9d**

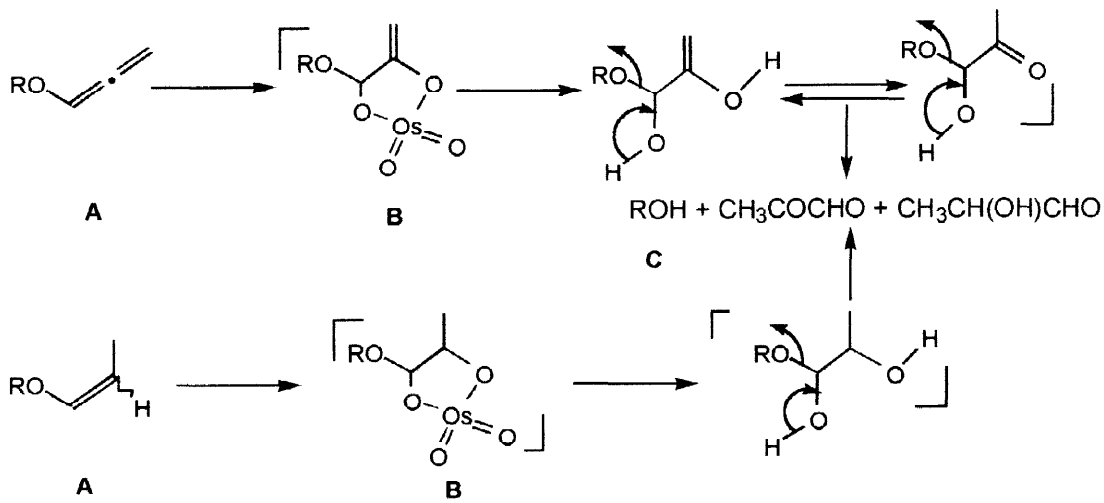
S.No	Allenyl ethers	Alcohols	%Yield (time in hours)		
			$Hg(OCOCF_3)_2$ (0.4 mole)	2N HCl	5% aq. TFA
i	**1d**	**1a**	62 (2 h)*	65 (1 h)*	62 (1 h)*
ii	**2d**	**2a**	67 (1 h)*	68 (2 h)*	58 (1.5 h)*
iii	**3d**	**3a**	58 (2 h)*	52 (1.5 h)*	65 (1.5 h)*
iv	**4d**	**4a**	84 (1 h)	76 (0.5 h)	75 (0.5 h)
v	**5d**	**5a**	77 (2.5 h)	77 (2.5 h)	73 (0.5 h)
vi	**6d**	**6a**	79 (3 h)	84 (0.5 h)	78 (1.5 h)
vii	**7d**	**7a**	80 (3 h)*	-	-
viii	**8d**	**8a**	87 (3 h)*	-	-
ix	**9d**	**9a**	82 (0.5 h)*	-	-

* and 15-20% of **1f-3f**

under the same reaction conditions **4d-9d** gave the corresponding alcohols **4a-6a** respectively in good yield (72-84%); formation of the corresponding keto compounds was not observed. Once again anomeric allenyl glycosides could not be deprotected in good yield. **7d-9d** under these reaction conditions gave rise to products resulting from the deprotection of 5,6-O-isopropylidene group and the cyclic ketal. We continued our investigations to find a superior reagent that does not lead to the formation of keto by products and is tolerant of acid labile isopropylidene protecting groups. This was best achieved by use of a catalytic amount of OsO_4 to obtain the alcohols in high yield. Thus, allenyl ethers **1d-9d** were reacted in acetone-water (4:1) containing a catalytic amount of OsO_4 (0.05 mole equivalent) and *N*-methyl morpholine *N*-oxide (NMO) (2 mole equivalent) at room temperature to obtain the corresponding alcohols **1a-9a** respectively in good yield (88-97%). Acid sensitive protecting groups such as isopropylidene (entries vi,vii,ix) and cyclic ketal (entry xi) remained unaffected under these reaction conditions (Table-1). Osmium tetroxide catalysed hydrolysis of allenyl ether can be rationalised by vicinal dihydroxylation of the electron rich enol ether of the allene (**A**) to form an acetal (**B**) followed by spontaneous cleavage to give the alcohol (**C**) (Scheme-II). Application of this methodology for the deprotection of phenyl prop-2-ynyl ethers could not applied due to problems encountered in base catalysed

isomerisation of phenyl prop-2-ynyl ethers to phenyl allenyl ethers. Reaction of **10b** and **13b** with 2 mole equivalent of KOtBu in DMSO-MeOH (10:1) at room temperature (2-4 h) led to the formation of allenyl ethers **10d** and **13d** in low yield (20-30%) and contained several other unidentified products.

Due to the use of prop-2-enyl protecting group specially in oligosaccharide chemistry[35] we looked into the applicability of OsO_4 catalysed deprotection of prop-2-enyl ethers of diverse substrates such as aromatic and cyclic functionalised sugar derivatives. Thus, **7c,8c,10c-13c** were isomerised with KOtBu in dry DMSO at 140°C for 6-10 h to their corresponding prop-1-enyl ethers **7e,8e,10e-13e** respectively[34] and reacted with a catalytic amount of OsO_4, *N*-methyl morpholine *N*-oxide at room temperature (18-45 h) to obtain the corresponding alcohols **7a,8a,10a-13a** respectively in good yields (79-92%) (Table-1). Alcohols were fully characterised by comparison of their physical data with that of authentic samples. Hydrolysis of prop-1-enyl ethers by OsO_4 can be rationalised analogous to hydrolysis of allenyl ethers. Dihydroxylation of the electron rich enol ether (**A**) with OsO_4 gives rise to acetal (**B**) which spontaneously forms alcohol (**C**) (Scheme-II). Acid labile isopropylidene protecting groups remained unaffected indicating the mildness of the reaction.



Scheme - II

In conclusion, a complementary mild method for the deprotection of prop-2-ynyl ethers and prop-2-enyl ethers has been developed involving isomerisation to the corresponding O-allenyl and prop-2-enyl ethers respectively followed by cleavage with OsO_4. This method is tolerant of acid sensitive protecting groups and useful for anomeric protected prop-2-ynyl and prop-2-enyl glycosides. Applicability of this method has been demonstrated on several aliphatic, aromatic and sugar derivatives.

Experimental

^{1}H-NMR spectra were measured with a Varian Gemini (200 MHz & 400 MHz) spectro-

meter, with tetramethylsilane as internal standard for solutions in deuteriochloroform. ^{13}C-NMR spectra were taken with a Varian Gemini (50 MHz) spectrometer with $CDCl_3$ as internal standard (δ_C 77.0) for solutions in deuteriochloroform. Optical rotations were measured with a JASCO DIP-370 instrument and $[\alpha]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were taken with a Perkin-Elmer 1310 spectrometer. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40°C in vacuo. Melting points were determined on a Fischer-John's melting point apparatus and are uncorrected. Chemical ionization mass spectra were taken on a VG 70-70H mass spectrometer using acetone as the CI reagent. LSIMS spectra were ran on a Micromass AUTOSPEC-M unit using Cs^+ ions as the primary beam for bombardment.

General procedure for the preparation of propargyl glycosides (1b-3b)

1g-3g[36] (1 mmol) were deacetylated in dry methanol (50 ml) containing a catalytic amount of sodium methoxide at room temperature for 4 h, neutralised by passing carbon dioxide gas and solvent removed to obtain **1h-3h** in quantitative yield (96-100%). To a solution of **1h-3h** in *N*,*N*-dimethylformamide (5 ml) was added hexane-washed NaH (4.8 mmol) at 0°C, stirred for 15 min. Benzyl bromide (4.4 mmol) was added to the above reaction mixture and stirred for 2 h at room temperature when t.l.c. [hexane : ethyl acetate] (6:1) indicated completion of the reaction, excess NaH was quenched with methanol (0.5 ml), diluted with water (200 ml), extracted into diethyl ether (2 x 100 ml). The organic phase was separated, washed with water, dried (Na_2SO_4), concentrated to obtain a residue which was purified by filtration on a bed of SiO_2 (60-120) by eluting with [hexane : ethyl acetate] (6:1) to obtain **1b-3b** (78-89% yield).

Preparation of *O*-propargyl ethers (4b-9b)

To a solution of alcohol **4a-9a** (1 mmol) in dry *N*,*N*-dimethylformamide (DMF) (1-2 ml) at 0°C was added hexane-washed NaH (1.2 mmol) and stirred for 15 min. Propargyl bromide (1.1 mmol) was added dropwise to the above reaction mixture, brought to room temperature and stirred for 0.5-1 h until t.l.c. indicated completion of the reaction from the appearence of a faster moving spot. The reaction mixture was quenched by addition of methanol (0.5 ml), diluted with water (350 ml), extracted into diethyl ether, dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to obtain the *O*-propargyl ethers **4b-9b** in 57-90% yield. Propargyl ethers **4b-9b** were purified by filtering on a bed of SiO_2 (60-120 mesh) by eluting with [hexane : ethyl acetate] (6:1) for characterisation.

Preparation of *O*-allyl ethers (7c and 8c)

To a solution of **7a** and **8a** (1 mmol) in dry *N*,*N*-dimethylformamide (4 ml) at 0°C was added hexane-washed NaH (1.2 mmol) at 0°C and stirred for 10 min. Allyl bromide (1.1 mmol) was added dropwise to the above reaction mixture and contents were brought to room temperature and stirred for 1-2 h until t.l.c. indicated completion of the reaction from the formation of a faster moving spot.

Reaction was quenched with methanol (0.5 ml), diluted with water (350 ml), extracted into

diethyl ether, dried (Na_2SO_4) and concentrated to obtain the title compounds **7c** and **8c** in 74-78% yield. They have been purified by filtration on a bed of SiO_2 (60-120) by eluting with [hexane : ethyl acetate] (10:1).

Preparation of *O*-allyl phenyl ethers (10c-13c)

To a solution of **10a-13a** (1 mmol) in acetone (10 ml) was added anhydrous K_2CO_3 (4 mmol) and allyl bromide (1.1 mmol). Reaction mixture was heated to reflux for 3 h, cooled to room temperature and filtered to remove K_2CO_3 and KBr; filtrate was concentrated to obtain a residue which was purified on a bed of SiO_2 (60-120), [hexane : ethyl acetate] (10:1) to obtain **10c-13c** as a syrup in 76-92% yield.

General procedure for isomerisation of *O*-propargyl ethers to allenyl ethers (1d-9d)

A solution of **1b-9b** (1 mmol) in dry DMSO-MeOH (10:1, 3 ml) and KO^{t}Bu (2 mmol) was stirred at room temperature for 1-3 h until t.l.c indicated completion of the reaction from the appearence of a faster moving spot. Reaction mixture was diluted with water (200 ml) and extracted into diethyl ether (200 ml). Organic phase was separated washed with water (100 ml), dried (Na_2SO_4) and concentrated on a rotary evaporator to obtain **1d-9d** in 76-94% yield after purification by filtration on a bed of SiO_2 (60-120 mesh) by eluting with [hexane : ethyl acetate] (8:1).

General procedure for isomerisation of *O*-allyl ethers to enol ethers (7e,8e,10e-13e)

To a solution of **7c,8c,10c-13c** (1 mmol) in dry DMSO (5 ml) was added KO^{t}Bu (0.5 mmol) and heated to 140°C for 2-3 h until t.l.c indicated completion of the reaction from the appearence of a slightly faster moving spot. Reaction mixture was cooled to room temperature, diluted with water (100 ml), extracted into diethyl ether, dried (Na_2SO_4) and concentrated to obtain **7e,8e,10e-13e** in 71-89% yield after purification by filtering on a bed of SiO_2 (60-120), by eluting with [hexane : ethyl acetate] (10:1).

General procedure for the deprotection of allenylethers (1d-9d) and enol ethers (7e,8e,10e-13e) with OsO_4-NMO in aqueous acetone.

To a homogeneous solution of allenyl ethers **1d-9d** and enol ethers **7e,8e,10e-13e** (1 mmol) in acetone:water (4:1, 4 ml) was added OsO_4 (0.05 mmol) and *N*-methyl morpholine *N*-oxide (2 mmol) and stirred for 10-45 h at room temperature. After completion of the reaction acetone was removed on a rotary evaporator, saturated aq.$NaHCO_3$ (10 ml) was added to the residue and stirred for an additional 30 min. Reaction mixture was diluted with water (100 ml) and extracted into ethyl acetate (2 x 50 ml). Organic phase was separated, dried (anhydrous Na_2SO_4) and concentrated on a rotary evaporator to obtain **1a-13a** in 79-97% yield and were fully characterised by comparison of their physical data with that of the authentic samples.

Prop-2-ynyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1b)

Deacetylation of **1g**[36] (7 g, 18 mmol) followed by benzylation gave **1b** (8.8 g, 89%) as a

crystalline solid, m.p. 80-82°C (hexane-dichloromethane); [Found : C, 76.72; H, 6.57. $C_{37}H_{38}O_6$ requires C, 76.79; H, 6.62%]; R_f (hexane/ethyl acetate) (6:1) 0.54; $[\alpha]_D$ -5.0 (c 1.0, $CHCl_3$); ν_{max} (KBr) 3260 cm^{-1} (C≡CH), 2118 cm^{-1} (C≡C); δ_H (200 MHz, $CDCl_3$) 7.5-7.05 (20H, m, Ph), 5.0–4.45 (9H, m, 4 x $OC\underline{H}_2Ph$, 1-H), 4.42 (2H, d, *J* 2.0 Hz, O-$C\underline{H}_2C$≡), 3.75-3.40 (6H, m, 2-6-H), 2.43 (1H, t, *J* 2.0 Hz, C≡C$\underline{H}$).

Allenyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (1d)

Reaction of **1b** (0.5 g, 0.86 mmol) with KO^{t}Bu (0.19 g, 1.73 mmol) in dry DMSO-MeOH (10:1, 4 ml) gave **1d** (0.38 g, 76%) as a syrup; [Found : C, 76.72; H, 6.57. $C_{37}H_{38}O_6$ requires C, 76.79; H, 6.62%]; R_f (hexane/ethyl acetate) (6:1) 0.55; $[\alpha]_D$ +5.0 (c 1.0, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.5-7.05 (20H, m, Ph), 6.76 (1H, t, *J* 6.4 Hz, O-C$\underline{H}$=), 5.44,5.42 (2H, 2d, *J* 6.4 Hz, C=C$\underline{H}_b$), 5.0–4.4 (9H, m, 4 x $OC\underline{H}_2Ph$, 1-H), 3.80-3.35 (6H, m, 2-6-H).

Prop-2-ynyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (2b)

Deacetylation of **2g**[36] (2 g, 5.18 mmol) followed by benzylation gave **2b** (2.41 g, 82%) as a crystalline solid, m.p. 89-90°C, (hexane/dichloromethane); [Found : C, 76.68; H, 6.54. $C_{37}H_{38}O_6$ requires C, 76.79; H, 6.62%]; R_f (hexane/ethyl acetate) (6:1) 0.52; $[\alpha]_D$ -21 (c 1.0, $CHCl_3$); ν_{max} (KBr) 3265 cm^{-1} (C≡CH), 2096 cm^{-1} (C≡C); δ_H (200 MHz, $CDCl_3$) 7.5-7.0 (20H, m, Ph), 5.0-4.3 (11H, m, 4 x $OC\underline{H}_2Ph$, O-$C\underline{H}_2C$≡,1-H), 3.92 - 3.40 (6H, m, 2-6-H), 2.4 (1H, t, *J* 2.0 Hz, C≡C$\underline{H}$).

Allenyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside (2d)

Reaction of **2b** (0.45 g, 0.78 mmol) with KO^{t}Bu (0.17 g, 1.55 mmol) in dry DMSO-MeOH (10:1, 3 ml) at room temperature gave **2d** (0.38 g, 84%) as a syrup; [Found : C, 76.75; H, 6.55. $C_{37}H_{38}O_6$ requires C, 76.79; H, 6.62%]; R_f (hexane/ethyl acetate) (6:1) 0.53; $[\alpha]_D$ +2.0 (c 1.0, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.5-7.1 (20H, m, Ph), 6.65 (1H, t, *J* 6.5 Hz, O-C$\underline{H}$=), 5.43,5.41 (2H, 2d, *J* 6.5 Hz, C=C$\underline{H}_2$), 5.1-4.35 (12H, m, 4 x $OC\underline{H}_2Ph$, 1-4-H), 4.0-3.4 (3H, m, 5,6-H).

Prop-2-ynyl 4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-2′,3′,6′-tri-*O*-benzyl-β-D-glucopyranoside (3b)

Deacetylation of **3g**[36] (2.3 g, 3.41 mmol) followed by benzylation gave **3b** (2.59 g, 78%) as a syrup; [Found : C, 75.98; H, 6.48. $C_{64}H_{66}O_{11}$ requires C, 76.02; H, 6.57%]; R_f (hexane/ethyl acetate) (5:1) 0.50; $[\alpha]_D$ +4.0 (c 1.0, $CHCl_3$); ν_{max} (neat) 3272 cm^{-1} (C≡CH), 2128 cm^{-1} (C≡C); δ_H (200 MHz, $CDCl_3$) 7.5-7.0 (35H, m, Ph), 5.1-4.15 (18H, m, 7 x $OC\underline{H}_2Ph$, O-$C\underline{H}_2C$≡, 1,1′-H), 4.1-3.3 (12H, m, 2-6-H, 2′-6′-H), 2.40 (1H, t, *J* 2.0 Hz, C≡C$\underline{H}$).

Allenyl 4-*O*-(2,3,4,6-tetra-*O*-β-D-galactopyranosyl)-2′,3′,6′-tri-*O*-benzyl-β-D-glucopyranoside (3d)

Reaction of **3b** (0.6 g, 0.59 mmol) with KO^{t}Bu (0.23 g, 2.07 mmol) in dry DMSO-MeOH (10:1, 3 ml) at room temperature gave **3d** (0.48 g, 81%) as a syrup; [Found : C, 75.92; H, 6.47. $C_{64}H_{66}O_{11}$ requires C, 76.02; H, 6.57%]; R_f (hexane/ethyl acetate) (5:1) 0.52; $[\alpha]_D$ +3.0 (c 1.0, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.5-7.0 (35H, m, Ph), 6.64 (1H, t, *J* 6.3 Hz, O-C$\underline{H}$=), 5.40,5.42 (2H, 2d, *J* 6.3 Hz, C=C$\underline{H}_b$), 5.2-4.15 (16H, m, 7 x $OC\underline{H}_2Ph$, 1,1′-H),

4.0-3.3 (12H, m, 2-6-H, 2′-6′-H).

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(prop-2-ynyl)-α-D-glucopyranoside (4b)

Reaction of **4a**[37] (0.5 g, 1.08 mmol) with propargyl bromide (0.14 g, 1.19 mmol) and NaH (0.06 g, 2.59 mmol) gave **4b** (0.48 g, 69%) as a syrup; [Found : C, 73.95; H, 6.77. $C_{31}H_{34}O_6$ requires C, 74.08; H, 6.82%]; R_f (hexane/ethyl acetate) (4:1) 0.49; $[\alpha]_D$ +15 (c 1.0, $CHCl_3$); ν_{max} (neat) 3268 cm^{-1} (C≡CH), 2122 cm^{-1} (C≡C); δ_H (200 MHz, $CDCl_3$) 7.45-7.1 (15H, m, Ph), 5.0-4.5 (7H, m, 3 x $OC\underline{H}_2Ph$, 1-H), 4.25 (2H, d, *J* 2.0 Hz, O-$C\underline{H}_2C$≡), 4.05-3.4 (6H, m, 2,6-H), 3.35 (3H, s, $OC\underline{H}_3$), 2.30 (1H, t, *J* 2.0 Hz, C≡C$\underline{H}$).

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(allenyl)-α-D-glucopyranoside (4d)

Reaction of **4b** (0.3 g, 0.59 mmol) with KO^{t}Bu (0.13 g, 1.19 mmol) in dry DMSO-MeOH (10:1, 3 ml) at room temperature gave **4d** (0.27 g, 89%) as a syrup; [Found : C, 73.95; H, 6.79. $C_{31}H_{34}O_6$ requires C, 74.08; H, 6.82%]; R_f (hexane/ethyl acetate) (4:1) 0.51; $[\alpha]_D$ +11 (c 1.0, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.5-7.2 (15H, m, Ph), 6.72 (1H, t, *J* 6.2 Hz, O-C$\underline{H}$=), 5.4,5.42 (2H, 2d, *J* 6.2 Hz, C=C$\underline{H}_2$), 5.0-4.5 (7H, m, 3 x $OC\underline{H}_2Ph$, 1-H), 4.05-3.4 (6H, m, 2-6-H), 3.35 (3H, s, $OC\underline{H}_3$).

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(prop-2-ynyl)-α-D-glucopyranoside (5b)

Reaction of **5a**[37] (0.5 g, 1.08 mmol) with propargyl bromide (0.14 g, 1.19 mmol) and NaH (0.06 g, 2.59 mmol) gave **5b** (0.49 g, 90%) as a syrup; [Found : C, 74.01; H, 6.77. $C_{31}H_{34}O_6$ requires C, 74.08; H, 6.82%]; R_f (hexane/ethyl acetate) (5:1) 0.46; $[\alpha]_D$ +17 (c 1.0, $CHCl_3$); ν_{max} (neat) 3268 cm^{-1} (C≡CH), 2126 cm^{-1} (C≡C); δ_H (200 MHz, $CDCl_3$) 7.5-7.1 (15H, m, Ph), 5.0-4.5 (7H, m, 3 x $OC\underline{H}_2Ph$, 1-H), 4.2 (2H, d, *J* 2.0 Hz, O-$C\underline{H}_2C$≡), 4.05-3.45 (6H, m, 2-6-H), 3.35 (3H, s, $OC\underline{H}_3$), 2.40 (1H, t, *J* 2.0 Hz, C≡C$\underline{H}$).

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(allenyl)-α-D-glucopyranoside(5d)

Reaction of **5b** (0.3 g, 0.6 mmol) with KO^{t}Bu (0.13 g, 1.2 mmol) in dry DMSO-MeOH (10:1, 2 ml) gave **5d** (0.26 g, 87%) as a syrup; [Found : C, 74.01; H, 6.79. $C_{31}H_{34}O_6$ requires C, 74.08; H, 6.82%]; R_f (hexane/ethyl acetate) (5:1) 0.48; $[\alpha]_D$ +33 (c 2.0, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.5-7.1 (15H, m, Ph), 6.7 (1H, t, *J* 6.3 Hz, O-C$\underline{H}$=), 5.34,5.36 (2H, 2d, *J* 6.3 Hz, C=C$\underline{H}_2$), 5.0-4.5 (7H, m, 3 x $OC\underline{H}_2Ph$, 1-H), 4.05-3.45 (6H, m, 2-6-H), 3.35 (3H, s, $OC\underline{H}_3$).

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(prop-2-ynyl)-α-D-galactopyranoside (6b)

Reaction of **6a**[38] (2 g, 7.69 mmol) with propargyl bromide (1 g, 8.46 mmol) and NaH (0.4 g, 16.92 mmol) gave **6b** (1.9 g, 83%) as a crystalline solid, m.p. 56-58°C, (hexane/dichloromethane); [Found : C, 60.32; H, 7.40. $C_{15}H_{22}O_6$ requires C, 60.38; H, 7.43%]; R_f (hexane/ethyl acetate) (8:1) 0.49; $[\alpha]_D$ -79 (c 1.0, $CHCl_3$); ν_{max} (KBr) 3274 cm^{-1} (C≡CH), 2126 cm^{-1} (C≡C); δ_H (200 MHz, $CDCl_3$) 5.45 (1H, d, $J_{1,2}$ 4.9 Hz, 1-H), 4.55 (1H, dd, $J_{2,3}$ 8.1 Hz, $J_{3,4}$ 2.0 Hz, 3-H), 4.3-4.2 (2H, m, 2,4-H), 4.15 (2H, d, *J* 2.0 Hz, O-$C\underline{H}_2C$≡), 3.95-3.85 (1H, m, 5-H), 3.7 (1H, dd, $J_{5,6'}$ 4.9 Hz, 6′-H), 3.55 (1H, dd, $J_{6,6'}$ 17.8 Hz, $J_{5,6}$ 6.7 Hz, 6-H), 2.35 (1H, t, *J* 2.0 Hz, C≡C$\underline{H}$), 1.45, 1.4, 1.3 x 2 (12H, 3s, 2 x $O_2C(C\underline{H}_3)_2$).

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(allenyl)-α-D-galactopyranoside (6d)

Reaction of **6b** (0.5 g, 1.67 mmol) with KO^{t}Bu (0.37 g, 3.35 mmol) in dry DMSO-MeOH (10:1, 4 ml) gave **6d** (0.42 g, 84%) as a syrup; [Found : C, 60.31; H, 7.38. $C_{15}H_{22}O_6$ requires C, 60.38; H, 7.43 %]; R_f (hexane/ethyl acetate) (8:1) 0.52; $[\alpha]_D$ -54 (c 2.3, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 6.8 (1H, t, *J* 6.4 Hz, O-C$\underline{H}$=), 5.50,5.47 (merged 1-H) (3H,

2d, $J_{1,2}$ 6.4 Hz, $J_{1',3'}$ 6.4 Hz, $J_{1',3''}$ 6.4 Hz, C=C$\underline{H}_2$, 1-H), 4.60 (1H, dd, $J_{2,3}$ 8.3 Hz, $J_{3,4}$ 2.3 Hz, 3-H), 4.4-4.2 (2H, m, 2,4-H), 4.05 (1H, m, 5-H), 3.75 (2H, d, $J_{5,6}$ 6.9 Hz, 6-H), 1.55, 1.45, 1.35 x 2 (12H, 3s, 2 x $O_2C(C\underline{H}_3)_2$); δ_C (50 MHz, $CDCl_3$) 200.8, 121.5, 109.3, 108.4, 96.2, 91.0, 70.9, 70.6, 70.4, 67.1, 65.8, 25.8, 24.8, 24.3.

2,3:5,6-Di-*O*-isopropylidene-1-*O*-(prop-2-ynyl)-α-D-mannofuranoside (7b)

Reaction of **7a** (1 g, 3.84 mmol) with propargyl bromide (0.5 g, 4.23 mmol) and NaH (0.18 g, 7.7 mmol) gave the title compound **7b** (0.66 g, 57%) after purification by column chromatography as a syrup; [Found : C, 60.31; H, 7.39. $C_{15}H_{22}O_6$ requires C, 60.38; H, 7.43%]; R_f (hexane/ethyl acetate) (8:1) 0.47; $[\alpha]_D$ +89 (c 1.5, $CHCl_3$); ν_{max} (KBr) 3262 cm^{-1} (C≡CH), 2098 cm^{-1} (C≡C); δ_H (200 MHz, $CDCl_3$) 5.50 (1H, s, 1-H), 4.75 (1H, dd, $J_{2,3}$ 6.8 Hz, $J_{3,4}$ 7.3 Hz, 3-H), 4.60 (1H, d, $J_{2,3}$ 6.8 Hz, 2-H), 4.45-4.30 (1H, m, 5-H), 4.2-3.85 (5H, m, O-C$\underline{H}_2$C≡, 4,6-H), 2.40 (1H, t, *J* 2.0 Hz, C≡C$\underline{H}$), 1.48, 1.45, 1.40, 1.35 (12H, 4s, 2 x $O_2C(C\underline{H}_3)_2$).

2,3:5,6-Di-*O*-isopropylidene-1-*O*-(allenyl)-α-D-mannofuranoside (7d)

Reaction of **7b** (0.6 g, 2.0 mmol) with KO^{t}Bu (0.45 g, 4.0 mmol) in dry DMSO-MeOH (10:1, 5 ml) gave **7d** (0.51 g, 85%) as a syrup; [Found : C, 60.32; H, 7.38. $C_{15}H_{22}O_6$ requires C, 60.38; H, 7.43 %]; R_f (hexane/ethyl acetate) (8:1) 0.49; $[\alpha]_D$ +81(c 1.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 6.66 (1H, dd, *J* 6.2 Hz, *J* 6.1 Hz, O-C$\underline{H}$=), 5.54,5.50 (2H, 2dd, $J_{1',3'}$ 6.2 Hz, $J_{1',3''}$ 6.1 Hz, $J_{3',3''}$ 3.2 Hz, C=C$\underline{H}_2$), 5.32 (1H, s, 1-H), 4.92 (1H, dd, 3-H), 4.80 (1H, d, $J_{2,3}$ 6.2 Hz, 2-H), 4.54-4.46 (1H, m, 5-H), 4.18 (2H, ddd, $J_{6,6'}$ 8.9 Hz, $J_{5,6}$ 6.6 Hz, $J_{5,6'}$ 4.3 Hz, 6-H), 4.08 (1H, dd, $J_{4,5}$ 8.2 Hz, $J_{3,4}$ 4.3 Hz, 4-H), 1.48, 1.45, 1.40, 1.35 (12H, 4s, 2 x $O_2C(C\underline{H}_3)_2$).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(allenyl)-α-D-glucopyranoside (8d)

Reaction of **8b**[39] (0.2 g, 0.67 mmol) with KO^{t}Bu (0.15 g, 1.34 mmol) in dry DMSO-MeOH (10:1, 2 ml) gave **8d** (0.18 g, 90%) as a syrup; [Found : C, 60.29; H, 7.39. $C_{15}H_{22}O_6$ requires C, 60.38; H, 7.43%]; R_f (hexane/ethyl acetate) (8:1) 0.35; $[\alpha]_D$ -2.0 (c 1.0, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 6.60 (1H, t, *J* 6.3 Hz, O-C$\underline{H}$=), 5.75 (1H, d, $J_{1,2}$ 3.6 Hz, 1-H), 5.52,5.50 (2H, 2d, *J* 6.3 Hz, C=C$\underline{H}_2$), 4.48 (1H, d, 2-H), 4.30-3.8 (5H, m, 3,6-H), 1.45, 1.35, 1.30, 1.25 (12H, 4s, 2 x $O_2C(C\underline{H}_3)_2$).

2-Methyl 2-(2′-propynyloxyethyl)-1,3-dioxolane (9b)

Reaction of **9a** (0.46 g, 3.48 mmol) with propargyl bromide (0.45 g, 3.83 mmol) and NaH (0.17 g, 6.96 mmol) in *N*,*N*-dimethylformamide gave **9b** (0.52 g, 89%) as a syrup; [Found : C, 63.44; H, 8.19. $C_9H_{14}O_3$ requires C, 63.50; H, 8.29%]; R_f (hexane/ethyl acetate) (5:1) 0.39; ν_{max} (neat) 3270 cm^{-1} (C≡CH), 2122 cm^{-1} (C≡C); δ_H (200 MHz, $CDCl_3$) 4.12 (2H, d, *J* 2.1 Hz, OC$\underline{H}_2$-C≡C), 3.98-3.84 (4H, m, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.6 (2H, t, *J* 6.1 Hz, -CH_2C$\underline{H}_2$-O), 2.37 (1H, t, *J* 2.1 Hz, C≡C$\underline{H}$), 1.94 (2H, t, *J* 6.1 Hz, -C$\underline{H}_2$-), 1.32 (3H, s, C$\underline{H}_3$).

2-Methyl 2-(1′,2′-propadienyloxyethyl)-1,3-dioxolane (9d)

Reaction of **9b** (0.32 g, 1.88 mmol) with KO^{t}Bu (0.42 g, 3.76 mmol) in dry DMSO-MeOH (10:1, 2 ml) at room temperature gave **9d** (0.3 g, 94%) as a syrup; [Found : C, 63.46; H, 8.21. $C_9H_{14}O_3$ requires C, 63.50; H, 8.29%]; R_f (hexane/ethyl acetate) (5:1) 0.42; δ_H (200 MHz, $CDCl_3$) 6.68 (1H, t, *J* 5.6 Hz, O-C$\underline{H}$=C), 5.42 (2H, 2d, *J* 5.6 Hz, C=C$\underline{H}_2$), 4.02-3.82 (4H, m, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.64 (2H, t, -CH_2C$\underline{H}_2$-O), 2.02 (2H, t, *J* 6.5 Hz, -C$\underline{H}_2$-), 1.35 (3H, s, C$\underline{H}_3$).

Allyl 4-methyl phenyl ether (10c)
Reaction of **10a** (2 g, 18.5 mmol) in acetone (20 ml) with allyl bromide (2.60 ml, 27.8 mmol) and K_2CO_3 (10.4 g, 88.8 mmol) gave **10c** (2.5 g, 92%) as a syrup; [Found : C, 80.98; H, 8.11. $C_{10}H_{12}O$ requires C, 81.04; H, 8.16%]; R_f (hexane/ethyl acetate) (10:1) 0.56; δ_H (200 MHz, $CDCl_3$) 7.1 (2H, d, *J* 9.2 Hz, Ph), 6.8 (2H, d, *J* 9.2 Hz, Ph), 6.2-6.0 (1H, m, -C<u>H</u>=C), 5.55-5.2 (2H, m, C=C<u>H</u>$_b$), 4.55 (2H, d, *J* 5.2 Hz, OC<u>H</u>$_2$-C=), 2.3 (3H, s, C<u>H</u>$_3$); M+ 148.

4-Methyl phenyl-(*E*)-1-propynyl ether (10e)
Reaction of **10c** (0.9 g, 6.1 mmol) with KO^{t}Bu (0.34 g, 3.0 mmol) in dry DMSO-MeOH (10:1, 2 ml) gave **10e** (0.8 g, 89%) as a syrup; [Found : C, 80.95; H, 8.12. $C_{10}H_{12}O$ requires C, 81.04; H, 8.16%]; R_f (hexane/ethyl acetate) (10:1) 0.57; δ_H (200 MHz, $CDCl_3$) 7.2-6.80 (4H, m, Ph), 6.35 (1H, m, O-C<u>H</u>=C), 4.8 (1H, m, C=C<u>H</u>-CH$_3$), 2.3 (3H, s, C<u>H</u>$_3$), 1.8-1.6 (3H, m, C<u>H</u>$_3$); M+ 148.

1-(4-Allyloxyphenyl)-1-ethanone (11c)
Reaction of **11a** (2 g, 14.7 mmol) in acetone (20 ml) with allyl bromide (2.15 ml, 22.0 mmol) and K_2CO_3 (8.2 g, 58.8 mmol) gave **11c** (2.2 g, 85%) yield as a syrup; [Found : C, 74.89; H, 6.82. $C_{11}H_{12}O_2$ requires C, 74.98; H, 6.86 %]; R_f (hexane/ethyl acetate) (10:1) 0.46; δ_H (200 MHz, $CDCl_3$) 7.9 (2H, d, *J* 9.2 Hz, Ph), 6.9 (2H, d, *J* 9.2 Hz, Ph), 6.2-5.9 (1H, m, -C<u>H</u>=C), 5.5-5.2 (2H, m, C=C<u>H</u>$_b$), 4.55 (2H, d, *J* 5.15 Hz, O-C<u>H</u>$_2$-C=), 2.5 (3H, s, C<u>H</u>$_3$); M+ 176.

1-[4-(*E*)-1-Propenyloxy]phenyl-1-ethanone (11e)
Reaction of **11c** (0.45 g, 2.55 mmol) with KO^{t}Bu (0.2 g, 1.28 mmol) in dry DMSO (10 ml) gave **11e** (0.4 g, 88%) as a syrup; [Found : C, 74.92; H, 6.82. $C_{11}H_{12}O_2$ requires C, 74.98; H, 6.86%]; R_f (hexane/ ethyl acetate) (10:1) 0.47; δ_H (200 MHz, $CDCl_3$) 7.9 (2H, d, *J* 9.0 Hz, Ph), 7.0 (2H, d, *J* 9.0 Hz, Ph), 6.5-5.5 (1H, m, O-C<u>H</u>=C), 4.95 (1H, m, C=C<u>H</u>-CH$_3$), 2.55 (3H, s, C<u>H</u>$_3$), 1.8-1.6 (3H, m, C<u>H</u>$_3$); M+ 176.

Allyl 4-chlorophenyl ether (12c)
Reaction of **12a** (2 g, 15.9 mmol) in acetone (20 ml) with allyl bromide (2.23 ml, 23.8 mmol) and K_2CO_3 (8.8 g, 63.5 mmol) gave **12c** (2.63 g, 76%) as a syrup; [Found : C, 64.01; H, 5.32. C_9H_9ClO requires C, 64.10; H, 5.37%]; R_f (hexane/ ethyl acetate) (10:1) 0.39; δ_H (200 MHz, $CDCl_3$) 7.25 (2H, d, *J* 9.0 Hz, Ph), 6.85 (2H, d, *J* 9.0 Hz, Ph), 6.2-5.9 (1H, m, -C<u>H</u>=C), 5.5-5.2 (2H, m, C=C<u>H</u>$_2$), 4.5 (2H, d, *J* 5.4 Hz, O-C<u>H</u>$_2$-C=); M+ 168.

4-Chlorophenyl-(*E*)-1-propenyl ether (12e)
Reaction of **12c** (0.9 g, 5.4 mmol) with KO^{t}Bu (0.3 g, 2.7 mmol) in dry DMSO (10 ml) gave **12e** (0.75 g, 83%) as a syrup; [Found : C, 64.04; H, 5.35. C_9H_9ClO requires C, 64.10; H, 5.37%]; R_f (hexane/ ethyl acetate) (10:1) 0.41; δ_H (200 MHz, $CDCl_3$) 7.35-7.15 (2H, m, Ph), 7.0-6.8 (2H, m, Ph), 6.4-6.25 (1H, m, OC<u>H</u>=C), 5.0-4.8 (1H, m, C=C<u>H</u>-CH$_3$), 1.8-1.60 (3H, m, C<u>H</u>$_3$); M+ 168.

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References and Notes

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