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Stoichiometric Reaction of Titanacyclopentadiene Compounds with Allylic Ethers: Regiochemistry of Methylenecyclohex-3-ene Formation

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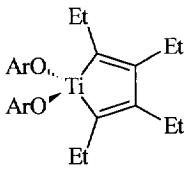
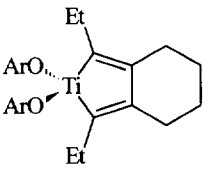
Abstract: The titanacyclopentadiene complexes $[(ArO)_2Ti(C_4Et_4)]$ (**1a**), $[(ArO)_2Ti(C_4Et_2(CH_2)_4)]$ (**1b**) and $[(ArO)_2Ti(C_4Bu^t_2H_2)]$ (**1c**) (ArO = 2,6-diphenylphenoxide) react with allylphenylether to produce new organometallic products containing cyclohexadiene-methyl and phenoxide ligands. Hydrolysis of these compounds leads to the formation of single regioisomers of substituted methylenecyclohex-3-ene along with two equivalents of 2,6-diphenylphenol and one equivalent of phenol. A reaction sequence involving initial (2+2+2) cycloaddition followed by cleavage of a phenyl ether bond is discussed.

INTRODUCTION

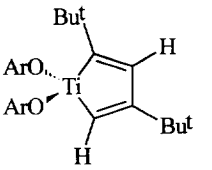
The last fifteen years have seen a dramatic evolution in the use of Group 4 metal organometallic compounds for carrying out both stoichiometric and catalytic organic transformations.[1,2] The majority of this work has focused on the metallocene dichloride's, $[Cp_2MCl_2]$ (M = Ti, Zr, Hf) as the metal reagent/precursor.[3] Our group is presently exploring the early transition metal organometallic chemistry that can be supported by sterically demanding aryloxide ligation.[4] Recently we have demonstrated that titanacyclopentadiene complexes such as **1a** ,**1b** and **1c**[5] (ArO = 2,6-diphenylphenoxide) can function as catalysts in the (2+2+2) cycloaddition of two equivalents of alkynes with simple olefins.[6]



1a



1b



1c

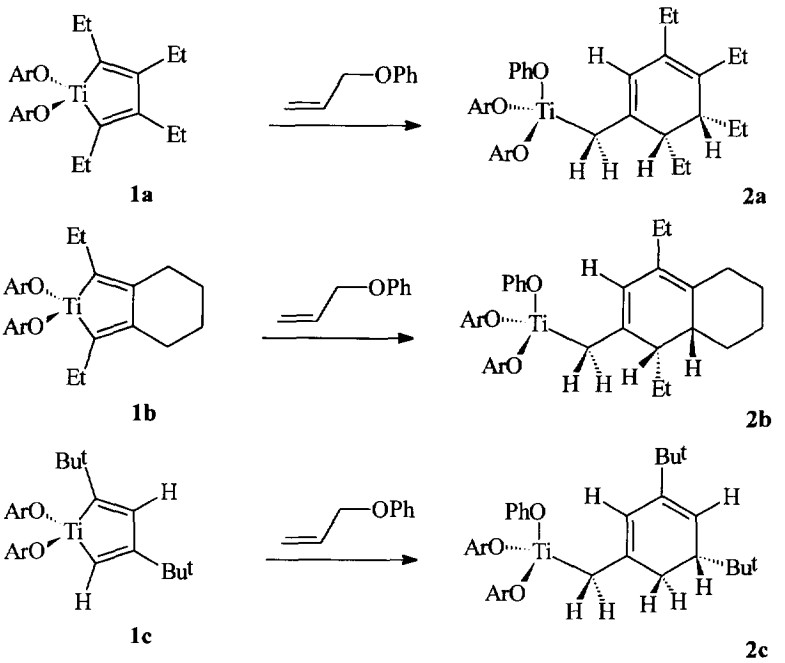
As an extension of this work we have examined the reaction of **1** with allylphenylether. These reactions are found to stoichiometrically yield methylenecyclohex-3-ene derivatives in a highly regioselective fashion.

RESULTS AND DISCUSSION

Synthesis and Characterization of Compounds.

The titanacyclopentadiene complexes **1** react slowly with allylphenylether in hydrocarbon solvents. The reactions can be readily monitored by ^{1}H NMR spectroscopy in C_6D_6 solvent. The resonance's due to **1a**, **1b** and **1c** are unshifted upon addition of the reagent, implying that a simple ether adduct is not formed. Over hours at 25°C the signals due to the substrates are replaced by a new set of signals and the reaction is complete in all cases after 20 hours. Removal of solvent and any excess ether reagent yields the new organo-titanium compounds **2**. These compounds were not purified but on the basis of their spectroscopic properties, compounds **2** are formulated as allyl-tris(phenoxides) of titanium as shown (**Scheme 1**).

Scheme 1



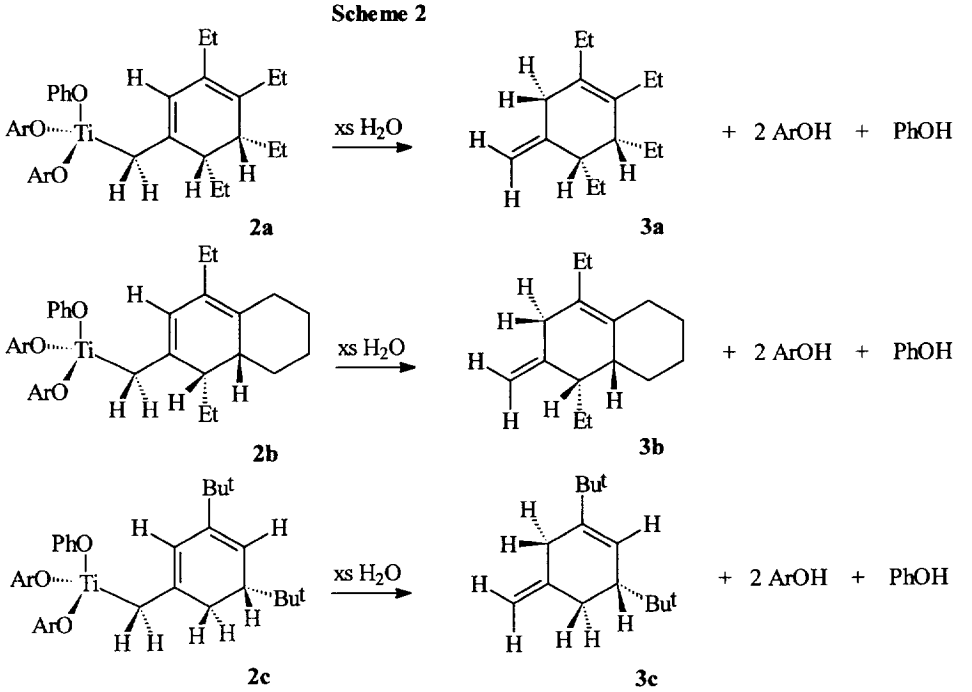
The ^{13}C NMR spectra of **2a** , **2b** and **2c** show the presence of three Ti-O-C(aryloxide) resonance's in the δ 160-170 ppm region of the spectrum. Two of these signals can be assigned to the two, non-equivalent 2,6-diphenylphenoxide ligands in **2** while the third is due to the new Ti-O-Ph group. This phenoxide ligand is also detected in the ^{1}H NMR spectrum where a well resolved multiplet for the ortho-protons is observed upfield of the normal aromatic region. The ^{1}H and ^{13}C NMR spectra also show the presence of the cyclohexadienyl-methyl group in **2**. Specifically, a slightly broad singlet is observed in the ^{1}H NMR for the single olefinic

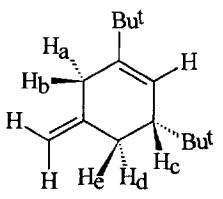
proton while a much broader singlet (**2a**) or AB pattern (**2b**) is observed for the diastereotopic methylene protons in the Ti-CH_2 group. The presence of this titanium-carbon bond is also evident by a peak at δ 94.8 ppm (**2a**) and 96.1 ppm (**2b**) in the ^{13}C NMR spectrum. This is a region typical for Ti-C(alkyl) groups containing aryloxide ancillary ligation.[4a] In compound **2c** two, non-equivalent olefin protons are observed in the ^1H NMR spectrum at δ 5.41 and 5.68 ppm. There is no spectroscopic evidence for the formulation of complexes **2** as being η^3-allyl species.

The *cis*-stereochemistry of the substituents shown in the cyclohexadiene rings of **2a** and **2b** (**Scheme 1**) is based upon results previously obtained in the catalytic coupling of alkynes with alpha olefins.[6] We have been unable to spectroscopically prove, however, this assigned stereochemistry for the single observed isomers of **2a** and **2b**.

The hydrolysis (H_2O) of benzene solutions of **2** leads to the formation of two equivalents of 2,6-diphenylphenol, one equivalent of phenol and one equivalent of organic products **3**. The gas chromatographic analysis of the crude hydrolysis mixture shows the presence of only one isomer for **3a** , **3b** and **3c**. The use of preparative thin layer chromatography allowed separation and purification of the compounds **3**. These products were identified on the basis of their spectroscopic properties as the methylenecyclohex-3-ene derivatives shown (**Scheme 2**).

Scheme 2





Particularly characteristic are the olefinic methylene protons at δ 4.81, 4.96 ppm (**3a**) , δ 4.71, 4.95 ppm (**3b**) and δ 4.86, 4.88 ppm (**3c**) in the ^{1}H NMR spectrum. The aliphatic region of the ^{1}H NMR spectrum of **3c** (**Figure 1**) shows proton H_c to be in a pseudo-axial environment (axial-axial coupling to H_c) consistent with the Bu^t substituent being pseudo-equatorial. The reaction of **2c** with D_2O leads to deuterium incorporation into both H_a and H_b (**Figure 1**; *vide-infra*). The resonance for the terminal methylene carbons appears at δ 106.8, 105.8 and 108.0ppm in the ^{13}C NMR spectrum for **3a**, **3b** and **3c** respectively.

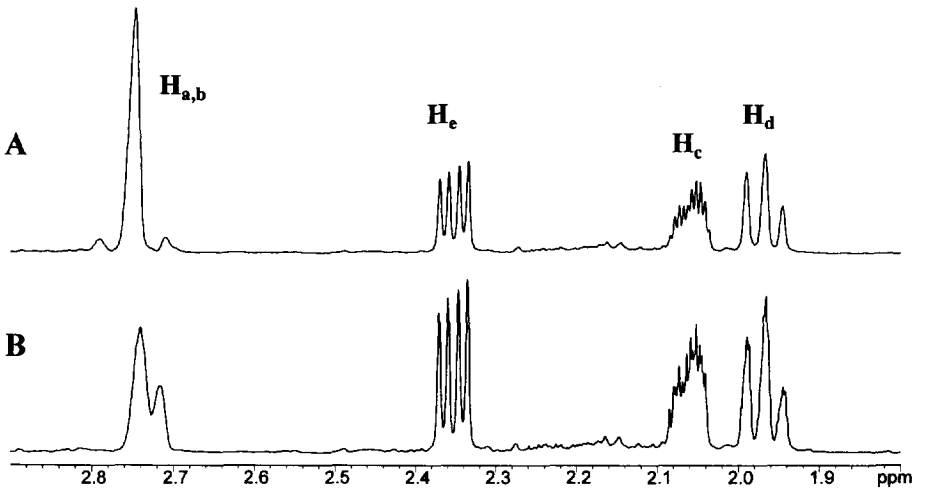
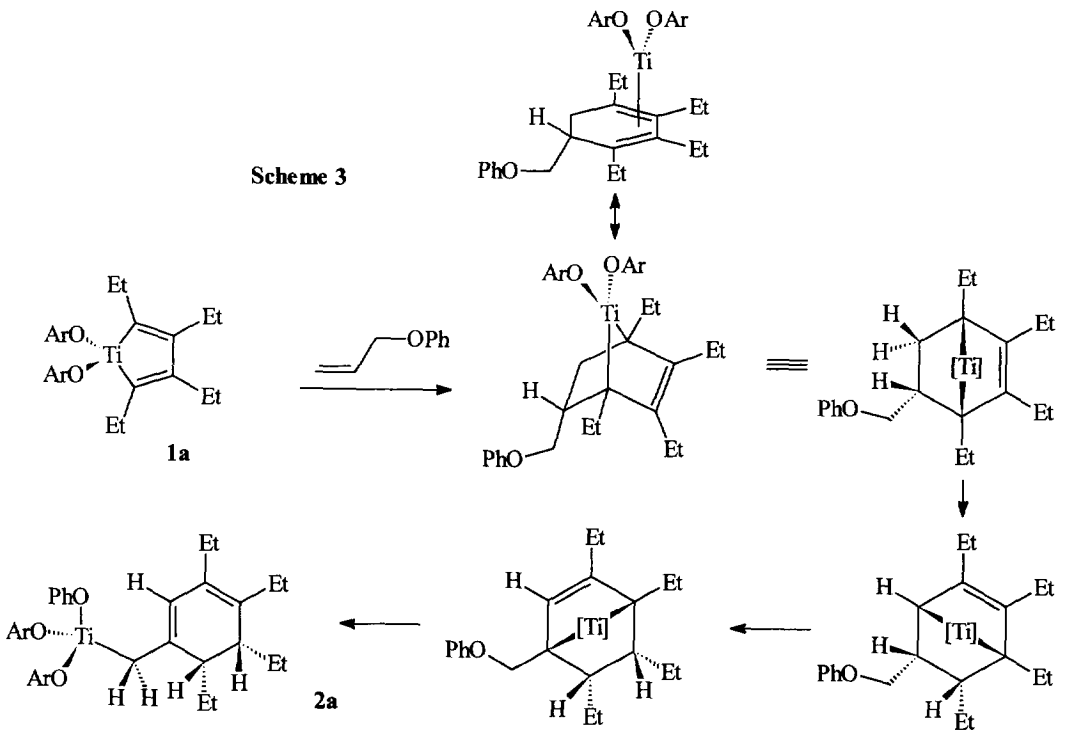


Figure 1. 500 MHz ^{1}H NMR spectra of the aliphatic region of compounds **3c** (A) and **3c-d$_1$** (B).

Mechanistic Discussion.

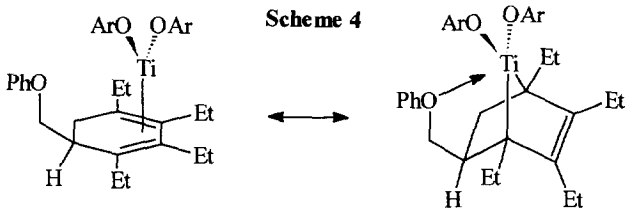
The work of Taguchi et.al. has shown that low valent zirconocene complexes have the ability to cleave allylphenylether to produce allylic zirconium reagents containing a phenoxide ancillary ligand.[7] It is highly doubtful that the products generated in this study are obtained via initial cleavage of the allyl-phenyl ether by **1**. Instead the most likely initial step involves addition of the olefinic portion of the ether to the titanacyclopentadiene. Previous work has shown that such reactions lead to intermediate 1,3-cyclohexadiene (metallanorbornene) complexes which undergo isomerization via a sequence of metal-mediated 1,5-hydrogen shifts.[6] The organometallic compounds **2a** and **2b** can be generated by two, sequential 1,5-hydrogen shifts followed by cleavage of the resulting allyl-ether bond (**Scheme 3**).

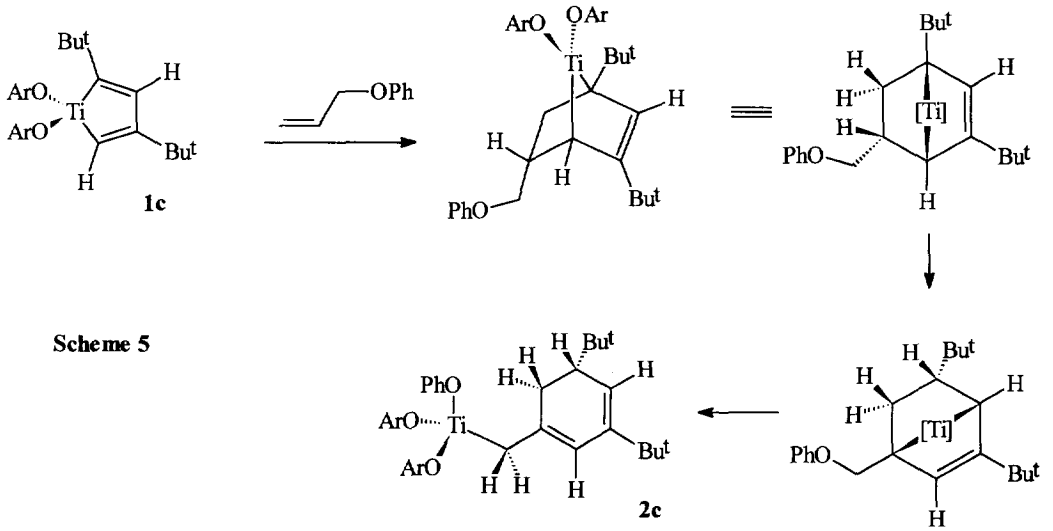
Scheme 3



The proposed stereochemistry of the initial intermediate (phenoxymethyl group *trans* to titanium) means that the ether group cannot approach the metal until after isomerization. The alternative, *cis* isomer has the potential to be stabilized by chelation, but cannot undergo metal mediated isomerization to the observed product (**Scheme 4**). The formation of **2c** from **1c** requires a regioselective initial addition of the olefin. followed by only one 1,5-shift from the initial intermediate prior to allyl-ether scission (**Scheme 5**) Two, sequential 1,5-shifts analogous to those in **Scheme 4** will also generate an identical product.

Scheme 4

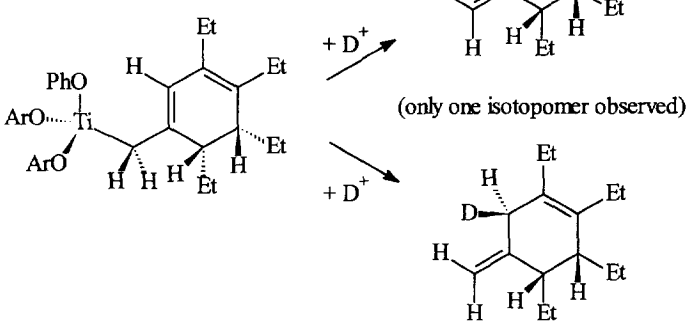




Scheme 5

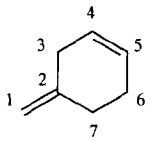
The hydrolysis of the allylic compounds **2** yields the methylenecyclohex-3-ene products **3**. The reaction can be readily rationalized in terms of electrophilic attack at the γ-position of the allylic group by the proton source. When the hydrolysis is carried out using D_2O, the products **3a-d$_1$**, and **3b-d$_1$** can be shown by ^{1}H NMR to contain deuterium in only one of the methylene ring positions, consistent with a highly stereospecific attack on the titanium allyl complex (**Scheme 6**). In contrast the product obtained from **2c**, **3c-d$_1$**, was found to contain proton intensity in both positions (**Figure 1**) indicating that the hydrolysis was not stereospecific in this case.

Scheme 6



Although the reactivity uncovered in this study leads to interesting organic products, the facile cleavage by titanium of the allyl-ether bond points to a possible limitation in the development of catalytic cycles using this metal and oxygenated substrates.

EXPERIMENTAL



General Procedures. All reactions were carried out under N_2 using either a Dri-Lab or standard Schlenk techniques. The reactions of **2** with D_2O were carried out in 5-mm J-Young Valve NMR tubes. ^1H and ^{13}C NMR spectra were recorded using a Varian 500MHz and 200MHz instrument. Mass spectral data was acquired through Purdue in-house facilities. Gas chromatography was performed on an HP 5890 Series II gas chromatograph.

Preparation of ***3a***. A sample of neat allylphenylether (0.017 g, 0.13 mmol) was added to $[(ArO)_2Ti(C_4Et_4)]$ **1a** (0.050 g, 0.071 mmol) in C_6D_6 (0.6 mL). The initial dark orange color of the reaction mixture became dark red over several hours. Solvent was removed in vacuo to give the red, intermediate product **2a**. Selected ^1H NMR data on **2a**: (C_6D_6, 30° C), δ 5.35 (s, olefin C*H*); 1.49 (s, Ti-CH_2); 0.68 (t), 0.72 (t), 0.86 (t), 1.00 (t, CH_2*Me*); 6.45 (m, ortho-*H*, Ti-OPh). The red product **2a** was hydrolyzed, and the colorless organic compound **3a** obtained by thin layer chromatography on silica gel using n-hexane as eluent. ^1H NMR (C_6D_6, 30° C) **3a**: δ 4.81 (d), 4.96 (d, H_2C=C, gem-^2J < 1 Hz); 2.81 (d), 2.72 (d, AB , ring CH_2, ^2J = 19.5 Hz); 2.18 (m), 1.26 (m, C*H*Et); 0.8-1.0 (m, CH_2*Me*); 1.25 (m), 1.38 (m), 1.61 (m), 1.77 (m), 1.85 (m), 1.94 (m), 2.18 (m), 2.22 (m, CH_2Me). ^{13}C NMR (C_6D_6, 30° C) **3a**: δ 106.8 (*C*-1); 148.7 (*C*-2); 39.1 (*C*-3); 131.3 (*C*-5); 137.3 (*C*-4); 44.0, 47.6 (*C*-6, 7); 22.1, 23.5, 25.4, 26.0 (*C*H_2Me); 13.0, 14.0, 14.1, 14.4 (CH_2*Me*). MS (EI) **3a**: 206(M^+, 20.7%), 178(15.9), 177(100), 149(22.4), 135(53.0), 121(35.7), 119(15.7), 109(10.8), 107(59.0), 105(13.7), 95(12.4), 93(54.5), 91(25.4), 83(10.2), 81(14.1), 79(32.6), 77(12.7), 71(10.7), 69(16.7), 67(15.1), 57(47.7), 55(39.7). MS(CI) **3a**: 207($(M+H)^+$, 100.0%), 205(10.8).

Preparation of ***3a-d$_1$***. To the crude product **2a** (0.1 mmol) in C_6D_6 (0.6 mL) was added an excess of D_2O (0.5 mmol) under N_2. The colorless organic product **3a-d$_1$** was obtained by thin layer chromatography. Selected ^1H NMR (C_6D_6, 30° C) **3a-d$_1$**: δ 2.71 (broad s, ring C*H*D). ^{13}C NMR (C_6D_6, 30° C) **3a-d$_1$**: 38.6 (t, ring *C*HD, J(^{13}C-D) = 19.0 Hz); MS (EI) **3a-d$_1$**: 207(M^+, 26.4%), 179(16.3), 178(100), 150(21.8), 136(37.9), 122(22.1), 121(10.4), 120(12.5), 108(34.0), 107(13.1), 94(27.0), 93(15.8), 92(11.7), 80(14.5), 79(10.5), 57(18.3), 55(21.1). MS (CI) **3a-d$_1$**: 208($(M+H)^+$, 100.0%), 207(11.9), 206(10.8).

Preparation of ***3b***. A similar procedure to that used in the preparation of **3a** was used except $[(ArO)_2Ti(C_8H_8Et_2)]$ **1b** (0.4 mmol) was reacted with allylphenylether (0.4 mmol) to give the intermediate product **2b** which was hydrolyzed to compound **3b**. Selected ^1H NMR data on **2b**: (C_6D_6, 30° C), δ 5.40 (s, olefin CH); 1.50, 1.55 (AB, Ti-CH2); 0.62 (t), 0.80 (t, CH_2*Me*); 6.48 (m, ortho-H, Ti-OPh). ^1H NMR (C_6D_6, 30° C) **3b**: δ 2.63 (d), 2.81 (d, AB , CCH_2CEt, ^2J = 18.0 Hz); 4.71 (m), 4.95 (broad s, H_2C=C); 0.8-1.0 (m, CH_2*Me*); 1.1-2.3 (CH_2Me, C*H*Et, ring CH_2). ^{13}C NMR (C_6D_6, 30° C) **3b**: δ 105.8 (*C*-1); 148.5 (*C*-2); 40.2 (*C*-3); 44.9, 46.3 (*C*-6, 7); 21.4, 26.2, 27.7, 29.2, 29.8, 31.3 (*C*H_2Me, ring CH_2); 12.7, 14.0 (CH_2*Me*). MS (EI) **3b**: 204(M^+, 28.1%), 203(19.2), 176(18.3), 175(100.0), 161(13.1), 147(18.2), 133(48.5), 119(27.9), 117(13.3), 107(17.3), 105(31.7), 93(17.9), 91(47.6), 81(15.3), 79(25.5), 77(16.8), 67(17.0), 57(16.4), 55(23.7), 53(11.4). MS (CI) **3b**: 205($(M+H)^+$, 100.0%). HRMS **3b**: Calcd. 204.1878, Found 204.1877.

Preparation of ***3b-d$_1$***. To the crude product **2b** (0.1 mmol) in C_6D_6 (0.6 mL) was added an excess of D_2O (0.5 mmol) under N_2. The colorless organic product **3b-d$_1$** was obtained by thin layer chromatography.. Selected ^1H NMR (C_6D_6, 30° C) **3b-d$_1$**: δ 2.60 (m, C*H*D). Selected ^{13}C NMR (C_6D_6, 30° C) **3b-d$_1$**: δ 39.8 (t, *C*HD, J(^{13}C-D) = 19.0 Hz); MS (EI) **3b-d$_1$**: 205(M^+, 25.1%), 177(16.4), 176(100.0), 148(14.2), 134(35.9), 133(11.3), 120(17.0), 119(11.9), 108(10.5), 106(20.4), 105(13.4), 92(26.7), 91(21.5), 80(11.0), 79(13.8), 77(10.0), 55(10.2). MS (CI) **3b-d$_1$**: 206($(M+H)^+$, 100.0%), 205(15.9), 204(17.1). HRMS (3b-d$_1$): Calcd. 205.1940, Found 205.1941.

Preparation of 3c. A similar procedure to that used in the preparation of **3a** was used except $[(ArO)_2Ti(C_4Bu^t_2H_2)]$ **1c** (0.4 mmol) was reacted with allylphenylether (0.4 mmol) to give the intermediate product **2c** which was hydrolyzed to compound **3c**. ^1H NMR (C_6D_6, 30° C) **3c** (assignments in **Fig. 1**): δ 5.66 (m); 4.88 (m); 2.76,2.78 (AB); 2.38 (dd, 10.6Hz, 4.3Hz); 2.03 (m); 1.97 (t, 11Hz); 0.91, 1.05 (s, C*Me*$_3$). ^{13}C NMR (C_6D_6, 30° C) **3c**: δ 108.0 (*C*-1); 147.8 (*C*-2); 33.9 (*C*-3); 146.2 (*C*-4); 120.6 (*C*-5); 48.7 (*C*-6); 34.2 (*C*-7); 33.9, 35.9 (*C*Me$_3$); 27.9, 29.7 (C*Me*$_3$). MS (CI) **3c**: 207 ((M+H)$^+$,100.0%). HRMS **3c**: Calcd. 206.2035, Found 206.2028.

Preparation of 3c-d$_1$. To the crude product **2c** (0.1 mmol) in C_6D_6 (0.6 mL) was added an excess of D_2O (0.5 mmol) under N_2. The colorless organic product **3c-d$_1$** was obtained by thin layer chromatography.. Selected ^1H NMR (C_6D_6, 30° C) **3c-d$_1$**: δ 2.76 (b, C*H*D). Selected ^{13}C NMR (C_6D_6, 30° C) **3c-d$_1$**: δ 33.5 (t, *C*HD, J(^{13}C-D) = 19.3 Hz). MS (CI) **3c-d$_1$**: 208((M+H)$^+$, 100.0%). HRMS (3b-d$_1$): Calcd. 205.1940, Found 205.1941.

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