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RUTHENIUM-CATALYZED ISOMERIZATION OF HOMOALLYLIC ALCOHOLS IN WATER

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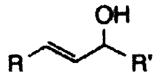
Summary: *Through the catalysis of $RuCl_2(PPh_3)_3$, the functional groups of homoallylic alcohols are repositioned to give allylic alcohols with controlled regioselectivity. The reaction proceeds most efficiently in an aqueous media. The selectivity in product formation is affected by the reaction temperature and the amount of the catalyst being used. A higher reaction temperature and the use of a smaller amount of the catalyst are preferable for the formation of allylic alcohols. The reaction process was postulated as a tandem olefin migration-allylic rearrangement. Under the same reaction conditions, the functional groups of allylic alcohols undergo allylic rearrangements.*

INTRODUCTION

Selective transposition of the functionalities of organic compounds provides an efficient access to molecules otherwise more complicated to synthesize. Isomerization of organic compounds through the catalytic activity of transition metals has been used in a variety of organic transformations, such as the isomerization of allylic alcohols to ketones.[1-16] Isomerization of organic compounds, as in the examples above, usually occurs with some attrition of the functionalities within the molecule. Examples of isomerizations where the functionalities are retained include the Brown's borane migration reaction,[17] transition-metal catalyzed olefin migrations,[18] and base-catalyzed alkyne migrations.[19] For the rearrangement of multi-functionalities, representative ones are the [3,3]-sigmatropic rearrangement[20] and the allylic ester rearrangement.[21-26] Re-positioning the functionalities of allylic alcohols (**1**) is a common process encountered in synthesis.[27-38] Such transformations often require multi-step reactions, or strong acids.[39] Recently, a rhenium complex was found to catalyze the 1,3-rearrangement of allylic alcohols.[40] The isomerization of the corresponding homoallylic or higher analogs (**2**) have not been studied previously. Recently, we reported that in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$[41] and in water, homoallylic alcohols undergo structural reorganization in which both the hydroxyl group and the olefin have been reshuffled.[42a] Under the same reaction conditions, allylic alcohols were also isomerizaed. Here we report the detailed study on this subject.



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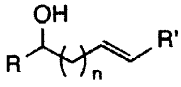

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RESULTS AND DISCUSSIONS

Homoallylic alcohols can be prepared by a variety of methods through allylation of carbonyl compounds.[43] More recently, Barbier-type allylation of carbonyl compounds has been developed in aqueous media with high yields by using several metals.[44-46] In the present study, homoallylic alcohols **3** were prepared using a literature procedure by reacting the corresponding carbonyl compounds with zinc powder and allyl bromide in a mixture of saturated aqueous ammonium chloride and THF.[44-46] In addition to homoallylic alcohols, a higher homolog **4** has also been prepared *via* the literature procedure,[47] with an attempt to effect a long range rearrangement.

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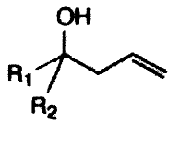

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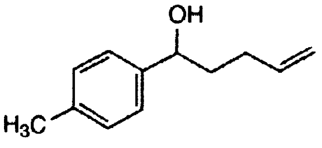

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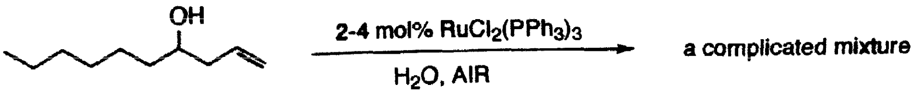
Isomerization of Homoallylic Alcohols

Previously, several transition metal complexes have been shown to catalyze the migration of terminal olefins into internal positions.[18] As a starting point, we chose $RuCl_2(PPh_3)_3$. The choice was made based on the fact that ruthenium complexes are compatible with water and air. Such properties of ruthenium complexes have been extensively explored by Grubbs in olefin metathesis reactions.[48] Previously, it has been shown that homoallylic alcohols form stable complexes with a ruthenium (II) salt in water that are inert toward olefin isomerizations.[1] We speculated that the attachment of triphenylphosphine to the metal center would alter its properties, effecting the desired isomerization. Subsequently, we examined the reaction of the alkyl homoallylic alcohol **5** in water catalyzed by $RuCl_2(PPh_3)_3$. When this compound was subjected to the ruthenium catalyst, a complicated mixture of several olefinic products was generated, which could not positively be identified (Eq. 1). While it is encouraging to observe the isomerization, the formation of a mixture of several olefinic alcohols demonstrated a lack of regio selectivity. In order to control the product formation, we would require to introduce, in the reaction substrate, a controlling element which will lock the location of the double bond. This lead us to investigate the isomerization of benzylic type homoallylic alcohols.

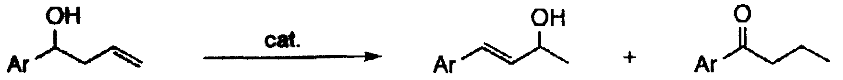


5

(1)

Stirring a mixture of the allyl benzyl alcohol **3a** with a catalytic amount of $RuCl_2(PPh_3)_3$ in water at 100°C for 3h led to compound **6a** together with a very small amount of ketone **7a**. Subsequently, a variety of conditions have been examined for their effect on the reaction. No reaction was observed when the same reaction was carried out in DMF, THF, DMSO, or toluene. Reactions in organic solvent lead either to no reaction or ether formations,[42b] in stead of isomerization. We have also carried out the same reaction by using aqueous 0.1N HCl (pH=1), $RuCl_3$ (pH=1), or aqueous saturated NH_4Cl as the reaction solvent, as well as using other transition metals, such as $FeCl_2$, $RhCl(PPh_3)_3$, $CoCl_2$ and $CuCl_2$, as catalysts for the reaction. The corresponding product, however, was not observed in any of these cases.

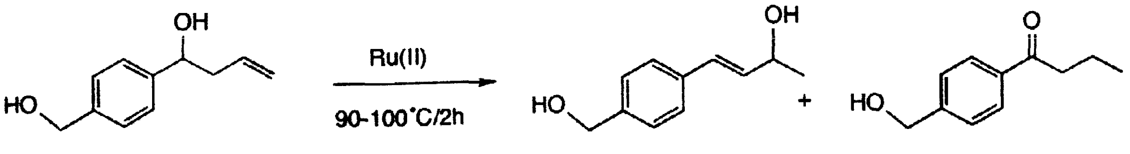
The unusual selectivity of this new process led us to investigate the reactivity of other homoallylic alcohols. Thus, a variety of homoallylic alcohols prepared previously were subjected to the ruthenium catalyzed process (Eq. 2). The experimental results are listed in Table 1. It was found that while the presence of various substituents on the aromatic ring does not affect the rate of the reaction significantly, their presence affected the amount of ketone product being formed. For example, while 1-phenyl-3-buten-1-ol gives a ratio of the allylic alcohol/ketone as 13:1 at 90-100°C with ca. 4 mol% catalyst present, other substrates provide a mixture of products with a ratio from 1.2 to 4.5. The reaction shows a marked dependence on the Ru(II)/substrate ratio. With each substrate being examined, decreasing the amount of the catalyst resulted in an increased selectivity in product formation. By cutting the amount of the catalyst in half, formation of the phenyl ketone **7**, also an isomerized product, has been sharply decreased or eliminated. A more extended study was carried out on 1-(4-methylphenyl)-3-buten-1-ol. By changing the amount of the catalyst from 2.2 to 4.5 to 7.0 to 10.0 mol%, a steady decrease of product selectivity was observed (from 12:1 to 1.2:1). In the last case, virtually a 1 to 1 mixture of the allylic alcohol and ketone was obtained. The ratio of product formations appears to be also dependent on the reaction temperature. A higher reaction temperature both increases the rate of the reaction and the selectivity in product formations. For example, no reaction has been observed with 1-phenyl-3-buten-1-ol (**3a**) at a temperature below 70°C, whereas the reaction occurs smoothly at 80-90°C to give the allylic alcohol and the ketone in 5.4:1 ratio. Increasing the reaction temperature to 90-100°C provides the same products in a 13:1 ratio. A bath temperature slightly above 100°C provides virtually a single product, with the ketone barely detectable in the crude reaction mixture by ^{1}H NMR. A similar relationship between the reaction temperature and the product ratio was observed with the methoxyl substituted compounds. Again, increasing the reaction temperature increases the product selectivity. On the other hand, 2-phenyl-4-penten-2-ol and 1-phenyl-3-buten-1-ol appeared inactive under the reaction conditions. While it is not clear what suppressed the reactivity of the phenol derivative, the lack of reaction of 2-phenyl-4-penten-2-ol could be attributed to increased steric crowdness, which hindered the ruthenium catalysis.



3 **6** **7**

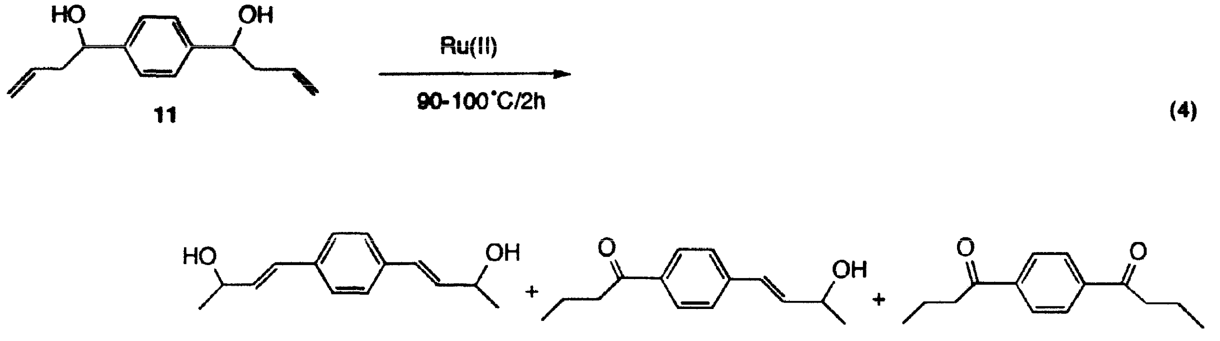
(2)

Other homoallylic alcohols were also investigated with the ruthenium catalyst under these reaction conditions. To study the compatibility of functional groups under the reaction conditions, two compounds (**8**, **11**) bearing additional hydroxyl groups were prepared. When compound **8** was subjected to the reaction, the corresponding isomerization product **9** was obtained together with the ketone isomer **10** (Eq. 3) A double reshuffling product **12** is the predominant product together with ketone formations (**13**, **14**) in the reaction of compound **11** (Eq. 4).



8 **9** **10**

(3)



11

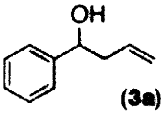
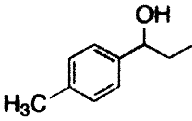
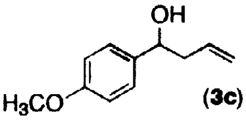
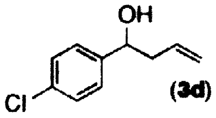
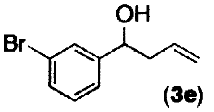
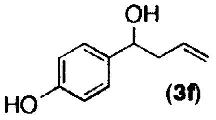
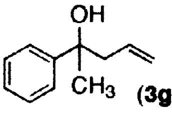
(4)

12 **13** **14**

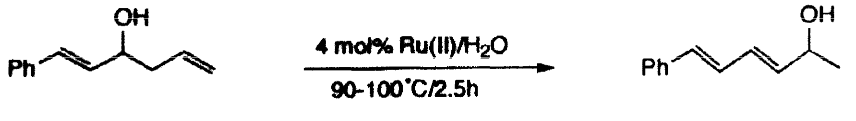
12: **13**: **14** = 4.2: 1: 1.2

In the case of compound **15**, where both an allylic and a homoallylic functional group are involved, the reaction occurs exclusively by rearrangement of the homoallylic group to give the conjugated dienol product **16** (Eq. 5). Attempts to effect long range isomerization with 1-phenyl-4-penten-1-ol (**4**) led to the migration of the double bond by only one carbon, forming compound **17** (Eq. 6). No further double bond migration was able to be effected.

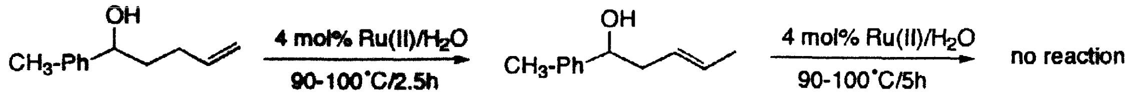
Table 1. Ruthenium Catalyzed Isomerization of Homoallylic Alcohols in Water

Entry	Homoallylic Alcohol (3)	Conditions (°C/hr)	Catalyst (mol%)	Conversion (%)	Alcohol/Ketone (6/7)		Isolated Yield (%)
1		60/7	4.0	no reaction			
2	 (3a)	80-90/2	4.0	63	(6a/7a)	5.4:1	
3		90-100/2.5	4.0	72	(6a/7a)	13:1	63
4		90-100/2.5	2.2	18	(6a/7a)	>20:1	
5		100-105/3	4.0	87	(6a/7a)	>20:1	
6	 (3b)	90-100/2	2.2	87	(6b/7b)	12:1	
7		90-100/2	4.5	94	(6b/7b)	4.5:1	75
8		90-100/2	7.0	90	(6b/7b)	1.7:1	
9		90-100/2	10.0	92	(6b/7b)	1.2:1	
10	 (3c)	70-80/6	4.5	82	(6c/7c)	1.4:1	
11		90-100/1.5	4.5	98	(6c/7c)	3.1:1	84
12		90-100/1.5	2.1	90	(6c/7c)	3.7:1	
13	 (3d)	90-100/1	2.2	82	(6d/7d)	4.1:1	
14		90-100/1	4.7	91	(6d/7d)	1.2:1	85
15	 (3e)	90-100/2	2.3	83	(6e/7e)	3.2:1	67
16		90-100/2	4.0	85	(6e/7e)	1.4:1	
17	 (3f)	90-100/2	4.0	no reaction			
18	 (3g)	90-100/2	4.0	no reaction			

Conversions were based on ^{1}H NMR measurement of the crude reaction mixtures. Yields and recovered starting materials were isolated ones after column chromatography on silica gel eluted with hexane/ethyl acetate. All reactions were carried out under an atmosphere of air with 4 to 5% mol of $RuCl_2(PPh_3)_3$.



15 16 (5)



4 17 (6)

Isomerization of Allyl Alcohols

For the isomerization of homoallyl alcohols, initially, a trace amount of acid generated from the catalyst was suspected as being responsible. However, the pH of the reaction medium shows a value between 5 and 6 both during and at the end of the reaction. As control experiments, we have carried out the same reactions by using aqueous 0.1N HCl (pH=1), $RuCl_3$ (pH=1), or aqueous saturated NH_4Cl as the reaction solvent, as well as using other transition metals, such as $FeCl_2$, $RhCl(PPh_3)_3$, $CoCl_2$ and $CuCl_2$. The corresponding product was not observed in any of these cases. A conjugated diene has also been suspected as being the reaction intermediate. Such a possibility was ruled out because the reaction of 1-phenyl-1,3-butadiene with the ruthenium catalyst did not generate any desired product under the same reaction conditions. A tentative mechanistic explanation is illustrated in Fig. 1. The ruthenium complex first coordinates to the olefin and transfers it from a terminal position to an internal position through the usual mechanism,[49, 50] providing an allylic alcohol. The allyl alcohol is then converted to either another allyl alcohol through C-O cleavage (route a) or a ketone through C-H cleavage (route b).

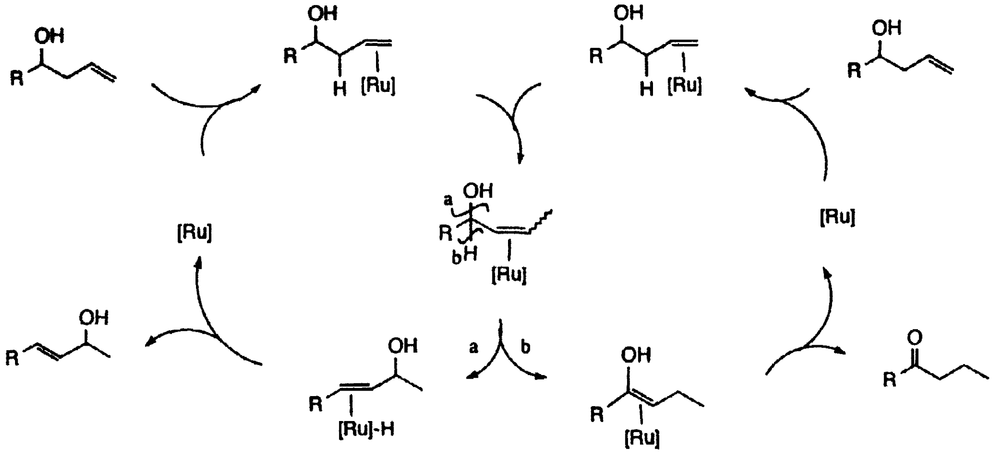
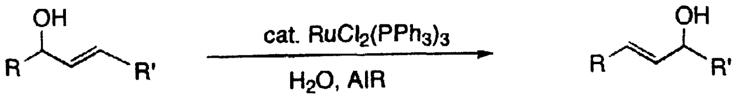


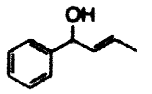
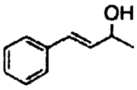
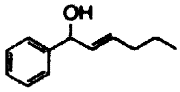
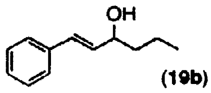
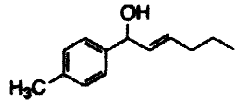
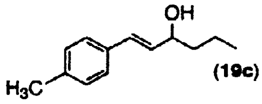
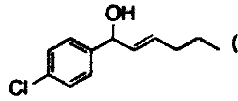
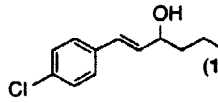
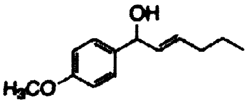
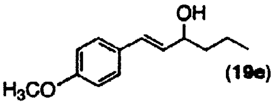
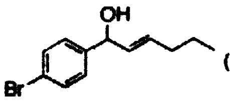
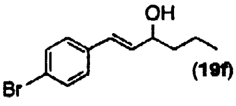
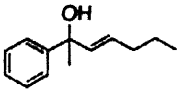
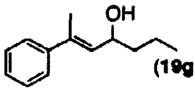
Fig. 1. Postulated catalytic cycle for the ruthenium catalyzed isomerization of homoallyl alcohols

Based on the postulated mechanism, the 1,3-rearrangement of allylic alcohols[40] should occur readily. Thus, a variety of other allylic alcohol compounds **18** were prepared from pentyne through a vinylalane addition to an aldehyde.[51] Under reaction conditions the same as or milder than those for the rearrangement of homoallylic alcohols, the allylic alcohols rearranged rapidly to the final products **19** in water (Eq. 7) (Table 2). These results indicate that the rate determining step of the reshuffling of homoallylic alcohols is the initial olefin migration.



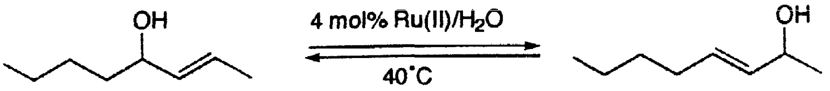
18 19 (7)

Table 2. Isomerization of Allylic Alcohols in Water

Entry	Allylic Alcohol	Conditions (catalyst/°C/hr)	Product	Yield (%)
1	 (18a)	45°C/2hr	 (6a)	89(99)
2		r.t./7hr		90(97)
3		r.t./2hr		90(97)
4		10% PPh$_3$/r.t./7hr/n.r.		n.r.
5		no catalyst/r.t./2.5hr/n.r.		n.r.
6		2% RuCl$_3$/r.t./2hr		(99)
7	 (18b)	45°C/2hr	 (19b)	70(78)
8		r.t./24hr		46(50)
9	 (18c)	45°C/3hr	 (19c)	70(79)
10		r.t./10hr		74(78)
11	 (18d)	80°C/3hr	 (19d)	65(73)
12		45°C/6h		(15)
13	 (18e)	45°C/3hr	 (19e)	95(99)
14		r.t./4hr		90(96)
15	 (18f)	80°C/9hr	 (19f)	72(78)
16		45°C/8hr		(<5)
17	 (18g)	45°C/2hr	 (19g)	70(71)
18		r.t./24hr		45(51)

Yields were isolated ones based on column chromatography on silica gel; ^{1}H NMR yield in parentheses. RuCl$_2$(PPh$_3$)$_3$ (2 mol%) was used as the catalyst in each case unless otherwise mentioned.

An internal allylic alcohol, where only aliphatic substituents are present, is also reactive. However, the reaction leads to the formation of an approximately 1:1 mixture of starting material **20** and the rearranged product **21**, which implies a lack of a controlling element (Eq. 8).



(8)

20 **21**

In conclusion, dichlorotris(triphenylphosphine)ruthenium (II) complex is an effective catalyst for effecting the repositioning of the functionalities of homoallylic alcohols and allylic alcohols in water. The reaction is compatible with air and is affected by the reaction temperature as well as the amount of catalyst being used.

EXPERIMENTAL SECTION

Air-sensitive reactions were generally conducted under a positive pressure of dry N_2 within glassware which had been flame-dried under a stream of dry N_2. Anhydrous solvents and reaction mixtures were transferred by oven-dried syringe or cannula. Zinc powder, ruthenium trichloride, cobalt chloride dichlorotris(tripehnylphosphine)ruthenium(II), cupric chloride, and ferrous chloride were used directly as received. Flash chromatography employed E. Merck silica gel (Kiesegel 60, 230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded from G.E. Omega 400 (400 MHz) instrument, with TMS as an internal standard. Infra-Red spectra were performed on FT-IR (Mattson Cygnus 100). Mass spectra and elemental analyses were performed at the Center of Instrumental Facility of Tulane University. Water was de-ionized before use.

Sample procedure for isomerization of homoallylic alcohols, formation of 4-(4-methylphenyl-3-buten-2-ol (6b):

A mixture of 1-(4-methylphenyl)-3-buten-1-ol **3b** (60 mg, 0.37 mmol) in water (3.5 mL) was stirred and heated to 80°C in an oil bath. At that temperature, $RuCl_2(PPh_3)_3$ (8 mg, 2.2 mol%) was added. The temperature of the oil bath was kept between 90-100°C, with efficient stirring. After 2hr, the reaction mixture was cooled to room temperature, extracted with ether, and dried over $MgSO_4$. After filtration and evaporation of solvent, the residue was separated by flash column chromatography on silica gel (with gradient eluent: hexane/ethyl acetate=15:1 to 10:1) to give the colorless liquids 4-(4-methylphenyl)-3-buten-2-ol (**6b**) (39 mg) and 1-(4-methylphenyl)-1-butanone (**7b**) (25 mg) (total yield, 75%), together with recovered starting material **3b** (6 mg, 10%). **6b**:[52] ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.12-7.27(m, 4H), 6.52(d, J=16.0 Hz, 1H), 6.18-6.22(dd, J=6.4, 16.0 Hz, 1H), 4.47(t, J=6.4 Hz, 1H), 1.70(bs, 1H), 2.33(s, 3H), 1.36(d, J=6.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 137.62, 133.98, 132.63, 129.47, 129.40, 126.48, 69.13, 23.43, 21.23. **7b**:[53] ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.25-7.85(m, 4H), 2.92(t, J=7.2 Hz, 2H), 2.40(s, 3H), 1.76(m, 2H), 0.99(t, J=7.6 Hz, 3H).

Formation of 4-phenyl-3-buten-2-ol (6a):

By the sample procedure as described above, isomerization of 1-phenyl-3-buten-1-ol (**3a**) (54 mg, 0.36 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (14 mg, 4.0 mol%) in water (4 mL) for 2.5hr at 90-100°C resulted in 75% conversion of the substrate. Flash column chromatography on silica gel (with gradient eluent: hexane/ethyl acetate =15:1 to 10:1) gave the colorless liquids 4-phenyl-3-buten-2-ol (**6a**) (32 mg) and 1-phenyl-1-butanone (**7a**) (2.4 mg) (total yield, 63%), together with recovered starting material (**3a**) (6.5 mg, 12%). **6a**:[54] ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.26-7.39(m, 5H), 6.56(d, J =15.6 Hz, 1H), 6.24-6.28(dd, J=6.4, 15.6 Hz, 1H), 4.50(t, J=6.4 Hz, 1H), 2.15(bs, 1H), 1.38(d, J=6.4 Hz, 3H). **7a**:[55] ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.95(d, J=1.6 Hz, 2H), 7.40(m, 3H), 2.95(t, J=7.2 Hz, 2H), 1.76(m, 2H), 1.00(t, J=7.6 Hz, 3H).

Formation of 4-(4-methoxyphenyl)-3-buten-2-ol (6c):

By the sample procedure as described above, isomerization of 1-(4-methoxyphenyl)-3-buten-1-ol (**3c**) (70 mg, 0.39 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (17 mg, 4.5 mol%) in water (4 mL) for 1.5hr at 90-100°C resulted in 98% conversion of the substrate. Flash column chromatography on silica gel (with gradient eluent: hexane/ethyl acetate=15:1 to 10:1) gave the colorless liquids 4-(4-methoxyphenyl)-3-buten-2-ol (**6c**) (44.5 mg) and 1-(4-methoxyphenyl)-1-butanone (**7c**) (14 mg) (total yield, 84%). **6c**:[56] ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 6.85-7.30(m, 4H), 6.50(d, J=15.6 Hz, 1H), 6.10-6.14(dd, J=6.4, 15.6 Hz, 1H), 4.46(q, J=6.4 Hz, 1H), 3.80(s, 3H), 1.65(bs, 1H), 1.35(d, J=6.4 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 159.23, 131.40, 129.41, 129.00, 127.63, 113.99, 69.12, 55.29, 23.46. **7c**:[57] ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 6.92-7.94(m, 4H), 3.86(s, 3H), 2.89(t, J=7.2 Hz, 2H), 1.75(m, 2H), 0.99(t, J=7.6 Hz, 3H).

Formation of 4-(4-chlorophenyl)-3-buten-2-ol (6d):

By the sample procedure as described above, isomerization of 1-(4-chlorophenyl)-3-buten-1-ol (**3d**) (70 mg, 0.38 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (17 mg, 4.5 mol%) in water (3 mL) for 1hr at 90-100°C resulted in 91% conversion of the substrate. Flash column chromatography on silica gel (with gradient eluent: hexane/ethyl acetate =15:1 to 10:1) gave the colorless liquids 4-(4-chlorophenyl)-3-buten-2-ol (**6d**) (32.5 mg) and 1-(4-chlorophenyl)-1-butanone (**7d**) (27 mg) (total yield, 84%). **6d:** [56] ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.27-7.29(m, 4H), 6.51(d, J=16.0 Hz, 1H), 6.20-6.24(dd, J=6.0, 16.0 Hz, 1H), 4.48(t, J =6.4 Hz, 1H), 1.76(bs, 1H), 1.36(d, J =6.4 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 135.20, 134.16, 133.21, 128.73, 128.11, 127.66, 68.77, 23.41. **7d:** [58] ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.42-7.89(m, J=8.4 Hz, 4H), 2.91(t, J=6.8 Hz, 3H), 1.75(m, 2H), 1.00(t, J=7.2 Hz, 3H).

Formation of 4-(3-bromophenyl)-3-buten-2-ol (6e):

By the sample procedure as described above, isomerization of 1-(3-bromophenyl)-3-buten-1-ol (**3e**) (70 mg, 0.31 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (6.7 mg, 2.3 mol%) in water (3.5 mL) for 2hr at 90-100°C resulted in 83% conversion of the substrate. Flash column chromatography on silica gel (with gradient eluent: hexane/ethyl acetate=15:1 to 10:1) gave the colorless liquids 4-(3-bromophenyl)-3-buten-2-ol (**6e**) (38 mg) and 1-(3-bromophenyl)-1-butanone (**7e**) (9 mg) (total yield, 84%), together with recovered starting material **3e** (9 mg, 13%). **6e:** IR(film): 3368, 1591, 1562, 1474, 1423, 1215, 1142, 1071, 964, 758, 683cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.52(t, J=1.6 Hz, 1H), 7.35(d, J=8.4 Hz, 1H), 7.28(d, J =7.6 Hz, 1H), 7.17(t, J =7.6 Hz, 1H), 6.50(d, J =15.6 Hz, 1H), 6.24-6.28(dd, J =6.0, 15.6 Hz, 1H), 4.49(q, J=6.4 Hz, 1H), 1.65(bs, 1H), 1.37(d, J =6.4 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 138.91, 135.10, 130.46, 130.09, 129.29, 127.82, 125.14, 122.76, 68.65, 23.40. HRMS: Calc'd for $C_{10}H_{11}OBr$ (M^+), 225.9990; Found, 225.9992. **7e:** IR(film): 1690, 1566, 1466, 1420, 1208, 787, 679cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 8.08(t, J=1.6 Hz, 1H), 7.87(d, J=7.6 Hz, 1H), 7.66(d, J=1.0 Hz, 1H), 7.33(t, J=7.6 Hz, 1H), 2.91(t, J=7.2 Hz, 2H), 1.75(m, 2H), 1.00(t, J =7.2 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$, ppm): δ 198.98, 138.81, 135.73, 131.14, 130.17, 126.56, 122.94, 40.56, 17.59, 13.82. HRMS: Calc'd for $C_{10}H_{11}OBr$ (M^+), 225.9990; Found, 225.9989.

Preparation of 1-(4-hydroxymethylphenyl)-3-buten-1-ol (8):

To a solution of allyl bromide (0.92 g, 7.6 mmol) in 4 mL of THF was added zinc powder (0.66 g, 10 mmol). The reaction mixture was stirred at room temperature for 30 min. The suspension was added in parts to the solution of terephthaldicarboxaldehyde (1.55 g, 11.6 mmol) in 12 mL of THF. The mixture was stirred at room temperature for 1.5 hr followed by quenching with saturated ammonium chloride aqueous solution. The reaction mixture was extracted with ether and dried over $MgSO_4$. Filtration followed by evaporation of the solvent gave a crude material. The mono-allylation product was isolated by flash chromatography on silica gel (gradient eluent: hexane/ethyl acetate=15:1 to 10:1) (yield 173 mg, 16%), and was directly used for the next step.

To a solution of the above mono-allylation product (110 mg, 0.6 mmol) in 8 mL of CH_3OH, $NaBH_4$ (45 mg, 1.2 mmol) was added slowly at room temperature. The reaction mixture was stirred for 3hr at room temperature, quenched with 10% HCl aqueous solution. Methanol was evaporated off; the reaction mixture was extracted with ether (3x10 mL). The ethereal solution was dried over $MgSO_4$ and filtered. Evaporation of the solvent gave a crude product which was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 5:1 to 2:1), to give compound **8** as a colorless liquid (70 mg, yield 61%). IR(film): 3372, 1642, 1514, 1420, 1217, 1041, 1009, 920, 756 cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.26(s, 4H), 5.71-5.81(m, 1H), 5.09-5.15(m, 2H), 4.67(t, J=6.4 Hz, 1H), 4.58(bs, 2H), 2.60(bs, 1H), 2.55(bs, 1H), 2.45(t, J =6.4 Hz, 2H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 143.21, 140.13, 134.41, 127.05, 126.03, 118.37, 73.10, 63.82, 43.73. MS(EI): 178(M+, 2.8), 137(100), 107(18), 91(31), 80(70). HRMS: Calc'd. for $C_{11}H_{14}O$ (M^+): 178.0994; Found, 178.0995.

Preparation of 1,4-(bis-1-hydroxy-3-buten-1-yl)benzene(11):

To a suspension of terephthaldicarboxaldehyde (0.8 g, 6 mmol) and allyl bromide (1.73 g, 14 mmol) in a mixture water/sat. aq. NH_4Cl/THF (5 mL/2 mL/ 2 mL) was added zinc powder (1.9 g, 16.8 mmol). The reaction mixture was stirred at room temperature for 4hr, extracted with ether, dried over $MgSO_4$, and filtered. Evaporation of the solvent gave a crude product which was purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 2:1), to give the title compound **11**[59] (202 mg, 16%). ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.34(s, 4H), 5.75-5.84(m, 2H), 5.14-5.19(m, 4H), 4.73(m, 2H), 2.47-2.54(m, 2H), 2.03(bs, 2H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ (143.18, 143.30), 134.39, 125.91, 118.58, (73.00, 73.04), 43.85. The data of ^{13}C NMR in paraphrase were assigned to one carbon of two isomers.

Isomerization of 1-(4-hydroxymethyl)phenyl-3-buten-1-ol (8), formation of 9, 10:

By the sample procedure as described for **6b**, isomerization of 1-(4-hydroxymethyl)phenyl-3-buten-1-ol (**8**) (58 mg, 0.325 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (12 mg, 2.3 mol%) in water (3 mL) for 3 hr at 90-100°C resulted in 91% conversion of the substrate. Flash column chromatography on silica gel (with gradient eluent: hexane/ethyl acetate =5:1 to 2:1) gave 4-(4-hydroxymethyl)phenyl-3-buten-2-ol (**9**) (26 mg) and 1-(4-hydroxymethyl)phenyl-1-butanone (**10**) (17 mg) (total yield, 74%). **9**: IR(film): 3356, 1696, 1603, 1456, 1418, 1364, 1215, 758cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.31-7.37(m, 4H), 6.56(d, J =15.6 Hz, 1H), 6.24-6.27(dd, J =6.4, 15.6 Hz, 1H), 4.67(bs, 2H), 4.49(p, J =6.4 Hz, 1H), 1.66(bs, 1H), 1.62(bs, 1H), 1.37(d, J =6.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 136.24, 133.70, 129.13, 127.38, 126.75, 69.02, 65.12, 23.43. HRMS: Calc'd. for $C_{11}H_{14}O$ (M^+): 178.0994; found, 178.1007. **10**: IR(film): 3421, 2961, 1681, 1608, 1460, 1215, 1040, 1002, 812 cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.45-7.95(m, 4H), 4.77(bs, 2H), 2.94(t, J =7.2 Hz, 2H), 1.76(m, 2H), 1.00(t, J =7.6 Hz, 3H). MS(EI): 176(6%), 147(35), 135(100), 89(17), 85(23), 50(26). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 200.29, 145,95, 136.25, 128.38, 126.64, 64.64, 40.58, 17.80, 13.91. HRMS: Calc'd. for $C_{11}H_{15}O$ (M+1): 179.1072; Found, 179.1034.

Isomerization of 1,4-(bis-1-hydroxy-3-buten-1-yl)benzene(11), formation of 12, 13, 14:

By the sample procedure as described for **6b**, isomerization of 1,4-(bis-1-hydroxy-3-buten-1-yl)benzene (**11**) (64 mg, 0.29 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (13 mg, 2.5 mol%) in water (3.5 mL) for 2 hr at 90-100°C resulted in quantitative conversion of the substrate. Flash column chromatography on silica gel (with gradient eluent: hexane/ethyl acetate=10:1 to 5:1 to 2:1) gave 1,4-(bis-3-hydroxy-1-buten-1-yl)benzene (**12**) (28 mg), 4-(4-butyrophenyl)-3-buten-2-ol (**13**) (15 mg), and 1,4-(bis-butyro)phenone (**14**) (12 mg) (total yield, 86%). **12**: IR(film): 3341, 1684, 1601, 1456, 1215, 1050, 9050, 739cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.33(s, 4H), 6.54(d, J =15.8 Hz, 2H), 6.24-6.27(dd, J =6.4, 15.8 Hz, 2H), 4.49(t, J =6.4 Hz, 2H), 1.60(bs, 2H), 1.37(d, J =4 Hz, 6H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 136.04, 133.47, 129.00, 126.69, 68.98, 23.41. MS(EI): 218(50%), 200(35), 182(59), 173(16), 167(29), 165(25), 160(66), 155(13), 145(32), 142(98), 128(59), 117(100), 91(21), 47(48). HRMS: Calc'd. for $C_{14}H_{18}O_2$ (M^+): 218.1307; found, 218.1299. **13**: IR(film): 3497, 1738, 1684, 1603, 1373, 1244, 1047, 914, 735 cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.44-7.91(m, 4H), 6.61(d, J =15.8 Hz, 1H), 6.36-6.40(dd, J=6.4, 15.8 Hz, 1H), 4.52(t, J=6.4 Hz, 1H), 2.93(t, J=7.6 Hz, 2H), 1.76(m, 2H), 1.64(bs, 1H), 1.38(d, J =6.4 Hz, 3H), 1.00(t, J =6.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 199.95, 141.20, 136.28, 135.98, 128.51, 128.24, 126.50, 68.71, 40.50, 23.39, 17.83, 13.91. HRMS: Calc'd. for $C_{14}H_{18}O_2$ (M^+): 218.1307; found, 218.1296. **14**:[60] ^1H NMR(400MHz, $CDCl_3$, ppm): δ 8.02(s, 4H), 2.97(t, J=7.6 Hz, 4H), 1.78(m, 4H), 1.01(t, J=7.2 Hz, 6H).

Isomerization of 1-phenyl-1,5-hexadien-3-ol (15):

By the sample procedure as described for **6b**, isomerization of 1-phenyl-1,5-hexadien-3-ol (**15**) (79 mg, 0.45 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (17 mg, 4.0 mol%) in water (4 mL) for 2.5 hr at 90-100°C resulted in 69% conversion of the substrate. Flash column chromatography on silica gel (with eluent:

hexane/ethyl acetate =10:1) gave (E, E)-6-phenyl-3,5-hexadien-2-ol (**16**) (39 mg, 61% based on recovered starting material) together with recovered **15** (15 mg, 19%). **16**:[61] ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.22-7.40(m, 5H), 6.74-6.78(dd, *J* =10.2, 15.6 Hz, 1H), 6.55(d, *J* =15.6 Hz, 1H), 6.35-6.40(dd, *J* =10.2, 15.4 Hz, 1H), 5.85-5.88(dd, *J* =6.8, 15.4 Hz, 1H), 4.42(t, *J* =6.4 Hz, 1H), 1.58(bs, 1H), 1.33(d, *J* =6.4 Hz, 3H).

Isomerization of 1-phenyl-4-penten-1-ol (4):

By the sample procedure as described for **6b**, isomerization of 1-(4-methylphenyl)-4-penten-1-ol (**4**) (55 mg, 0.31 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (12 mg, 4 mol%) in water (3 mL) for 5 hr at 90-100°C. Flash column chromatography on silica gel (with eluent: hexane/ethyl acetate =15:1) gave 1-(4-methylphenyl)-3-penten-1-ol (**17**)[62](31 mg, 55%).

Preparation of 1-phenyl-2-buten-1-ol (18a):

To a stirred solution of iodobenzene (2.04 g, 10 mmol) in THF (10 mL) at -78°C, n-BuLi (6.5 mL, 1.6M in hexane) was added slowly over 30 min. Then, a solution of crotonaldehyde (0.7 g, 10 mmol) in THF (10 mL) was added slowly into the above mixture at -78°C. The reaction mixture was stirred at -78°C for 30 min and at room temperature for another 30 min followed by quenching with saturated NH_4Cl aqueous solution. The mixture was extracted with ether (30x 4 mL), dried over Na_2SO_4, filtered, and evaporated in vacuo, giving 305 mg of a yellowish oil. Flash column chromatography on silica gel (eluent: hexane:ethyl acetate= 15:1) gave 1-phenyl-2-buten-1-ol (**18a**)[63] (290 mg, yield 20%). IR(film): 3373, 2863, 1673, 1602, 1492, 1426, 1087, 1012, 962, 750, 698 cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.25-7.40(m, 5H), 5.65-5.82(m, 2H), 5.15(d, *J* =6.4 Hz, 1H), 2.05(br, 1H), 1.72(d, *J* =5.6 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 143.35, 142.56, 133.60, 128.49, 127.51, 126.12, 75.22, 17.72 ppm.

Preparation of 1-phenyl-2-hexen-1-ol (18b):

A mixture of 1-pentyne (0.691 g, 10 mmol) and diiosobutyl aluminum hydride (7.5 mL, 1.5 N toluene solution, 11 mmol) in hexane (2 mL) was heated under N_2 at 45°C for 4h. Then, the mixture was cooled in ice bath followed by the addition of benzaldehyde (1.06 g, 10 mmol). After stirred for another 1h at room temperature, the reaction was quenched with 0.1 N aqueous HCl, extracted with ether (3x30 mL), washed with saturated sodium bicarbonate (3x30 mL) and water (3x30 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo.[51] Column chromatography on silica gel (eluent: hexane/ethyl acetate=15:1) gave 1-phenyl-2-hexen-1-ol (**18b**) (1.06 g, 60% yield). IR(film): 3360, 3100, 2872, 1670, 1602, 1493, 1451, 1010, 967, 750, 698 cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.20-7.40(m, 5H), 5.60-5.80(m, 2H), 5.14(d, *J* =6.4 Hz, 1H), 2.57(br, 1H), 2.00-2.10(m, 2H), 1.40-1.50(m, 2H), 0.94(t, *J* =7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 143.52, 132.51, 132.43, 128.44, 127.42, 126.24, 75.12, 34.30, 22.28, 13.77. HRMS: Calc'd for $C_{12}H_{16}O$ (M^+), 176.1201; Found, 176.1203.

Preparation of 1-(4-methylphenyl)-2-hexen-1-ol (18c):

By the same procedure as described for the preparation of compound **18b**, the title compound was obtained from 1-pentyne (0.691 g, 10 mmol), diiosobutyl aluminum hydride (7.5 mL, 1.5 N toluene solution, 11 mmol), and p-tolualdehyde (1.2 g, 10 mmol). Column chromatography on silica gel (eluent: hexane/ethyl acetate=15:1) gave 1-(4-methylphenyl)-2-hexen-1-ol (**18c**) (950 mg, 50% yield). IR(film): 3359, 1668, 1600, 1513, 1456, 1103, 1010, 967, 810cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.28(d, *J* =8 Hz, 2H), 7.18(d, *J* =8 Hz, 2H), 5.64-5.79(m, 2H), 5.11-5.13(m, 1H), 2.3 (br. 1H), 2.38(s, 3H), 2.02-2.09(m, 2H), 1.40-1.50(m, 2H), 0.95(t, *J* =7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 140.51, 137.17, 132.51, 132.34, 129.15, 126.11, 75.08, 34.27, 22.25, 21.13, 13.72. HRMS: Calc'd for $C_{13}H_{18}O$ (M^+), 190.1358; Found, 190.1356.

Preparation of 1-(4-chlorophenyl)-2-hexen-1-ol (18d):

By the same procedure as described for the preparation of compound **18b**, the title compound was obtained from 1-pentyne (0.691 g, 10 mmol), diiosobutyl aluminum hydride (7.5 mL, 1.5 N toluene solution, 11 mmol), and 4-chlorobenzaldehyde (1.4 g, 10 mmol). Column chromatography on silica gel (eluent: hexane/ethyl acetate=15:1) gave 1-(4-chloro-phenyl)-2-hexen-1-ol (**18d**) (1.2 g, 58% yield). IR(film): 3375, 2872, 1667, 1589, 1490, 1475, 1091, 1013, 968, 839cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm) δ 7.28-7.29(m, 4H), 5.70-5.77(m, 1H), 5.60(dd, J = 15.3, 6.7 Hz, 1H), 5.12(d, J =6.7 Hz, 1H), 2.00-2.07(m, 3H),1.36-1.43(m, 2H), 0.89(t, J =7.3 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 141.87, 133.03, 133.00, 132.11, 128.49, 127.56, 74.46, 34.22, 22.20, 13.70. HRMS: Calc'd for $C_{12}H_{15}OCl$ (M^+), 210.0811; Found, 254.0807.

Preparation of 1-(4-methoxyphenyl)-2-hexen-1-ol (18e):

By the same procedure as described for the preparation of compound **18b**, the title compound was obtained from 1-pentyne (0.691 g, 10 mmol), diiosobutyl aluminum hydride (7.5 mL, 1.5 N toluene solution, 11 mmol), and p-anisaldehyde (1.36 g, 10 mmol). Column chromatography on silica gel (eluent: hexane/ethyl acetate=15:1) gave 1-(4-methoxyphenyl)-2-hexen-1-ol (**18e**) (1.07 g, 52% yield). IR(film): 3405, 3031, 2871, 2835, 1666, 1610, 1585, 1512, 1464, 1250, 1174, 1036, 968, 830cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm) δ 7.27(d, J=8.8 Hz, 2H), 6.88(d, J=8.8 Hz, 2H), 5.61-5.75(m, 2H), 5.08(d, J=5.7 Hz, 1H), 3.78(s, 3H), 2.33(br, 1H), 1.98-2.05(m, 2H), 1.41(m, 2H), 0.90(t, J =7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 158.90, 135.78, 132.61, 132.03, 127.48, 113.79, 74.67, 55.25, 34.27, 22.28, 13.75. HRMS: Calc'd for $C_{13}H_{18}O_2$(M^+), 206.1307; Found, 206.1308.

Preparation of 1-(3-bromophenyl)-2-hexen-1-ol (18f):

By the same procedure as described for the preparation of compound **18b**, the title compound was obtained from 1-pentyne (0.691 g, 10 mmol), diiosobutyl aluminum hydride (7.5 mL, 1.5 N toluene solution, 11 mmol), and 3-bromobenzaldehyde (1.85 g, 10 mmol). Column chromatography on silica gel (eluent: hexane/ethyl acetate=15:1) gave 1-(3-bromophenyl)-2-hexen-1-ol (**18f**) (1.53 g, 60% yield). IR(film): 3347, 3043, 2871, 1683, 1609, 1569, 1474, 1426, 1010, 967, 882, 781, 696cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.49(s, 1H), 7.37(d, J =7.8 Hz, 1H), 7.23(d, J =7.8 Hz, 1H), 7.15-7.19(m, 1H), 5.67-5.74(m, 1H), 5.54(dd, J =15.2, 6.9 Hz, 1H), 5.03(d, J =6.9 Hz, 1H), 3.03(br, 1H), 1.98-2.03(m, 2H), 1.35-1.45(m, 2H), 0.90(t, J =7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 145.75, 133.24, 131.85, 130.36, 129.99, 129.25, 124.83, 122.51, 74.43, 34.25, 22.20, 13.79. HRMS: Calc'd for $C_{12}H_{15}OBr$ (M^+), 254.0306; Found, 254.0303.

Preparation of 2-phenyl-3-hepten-2-ol (18g):

By the same procedure as described for the preparation of compound **18b**, the title compound was obtained from 1-pentyne (0.691 g, 10 mmol), diiosobutyl aluminum hydride (7.5 mL, 1.5 N toluene solution, 11 mmol), and acetophenone (1.2 g, 10 mmol). Column chromatography on silica gel (eluent: hexane/ethyl acetate=15:1) gave 2-phenyl-3-hepten-2-ol (**18g**) (950 mg, 50% yield). IR(film): 3398, 1669, 1616, 1492, 1446, 1100, 972, 763, 686 cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm) δ 7.26-7.45(m, 5H), 5.79(d, J =15.7 Hz, 1H), 5.68(dt, J=15.7, 6.6 Hz, 1H), 2.02-2.08(m, 2H), 1.97(s, 1H), 1.64(s, 3H), 1.38-1.47(m, 2H), 0.91(t, J =7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 137.06, 128.95, 128.19, 128.13, 126.77, 125.22, 74.44, 34.30, 29.93, 22.39, 13.73. HRMS: Calc'd for $C_{13}H_{18}O$(M^+), 190.1358; Found, 190.1362.

Isomerization of 18a:

A mixture of 1-phenyl-2-buten-1-ol (74 mg, 0.5 mmol) (**18a**) and $RuCl_2(PPh)_3$ (9.58 mg, 0.01 mmol) in water (5 mL) was stirred at 45°C for 2hr. After cooled to room temperature, the reaction was extracted with ether (3x10 mL); the ether solution was washed with water (3x10 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo. The ^1H NMR spectrum showed 99% conversion of the starting material. Flash column chromatography on silica gel (eluent: hexane/ethyl acetate=15:1) gave 4-phenyl-3-buten-2-ol (**6a**) (65.8 mg, yield 89%).

Isomerization of 18b, formation of 1-phenyl-1-hexen-3-ol (19b):

By the same procedure as described for the isomerization of compound **18a**, isomerization of 1-phenyl-2-hexen-1-ol (**18b**) (88 mg, 0.5 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (9.58 mg, 0.01 mmol) in water (5 mL) for 2hr at 45°C resulted in 78% conversion of the substrate. Flash column chromatography on silica gel (eluent: hexane/ethyl acetate =15:1) gave 1-phenyl-1-hexen-3-ol (**19b**) (61.6 mg, yield 70%). IR(film): 3387, 3095, 2872, 1657, 1618, 1586, 1494, 1464, 1138, 1029, 980, 750, 696cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.07–7.24(m, 5H), 6.41(d.J=16.2 Hz, 1H), 6.07(dd, J=16.2, 6.9 Hz, 1H), 4.11-4.16(m, 1H), 1.63(br, 1H), 1.38-1.54(m, 2H), 1.20-1.36(m, 2H), 0.81(t, J=7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 136.75, 132.61, 130.20, 128.58, 127.61, 126.46, 72.86, 39.46, 18.69, 14.03. HRMS: Calc'd for $C_{12}H_{16}O$ (M^+), 176.1201; Found, 176.1200.

Isomerization of 18c, formation of 1-(4-methylphenyl)-1-hexen-3-ol (19c):

By the same procedure as described for the isomerization of compound **18a**, isomerization of 1-(4-methylphenyl)-2-hexen-1-ol (**18c**) (95 mg, 0.5 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (9.58 mg, 0.01 mmol) in water (5 mL) for 10hr at room temperature resulted in 78% conversion of the substrate. Flash column chromatography on silica gel (eluent: hexane/ethyl acetate =15:1) 1-(4-methylphenyl)-1-hexen-3-ol (**19c**) (70.3 mg, 74% yield). IR(film): 3366, 3100, 1445, 1660, 1606, 1514, 1456, 1006, 969, 800cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.28(d, J=7.6 Hz, 2H), 7.13(d, J=7.6 Hz, 2H), 6.53(d, J=16.2 Hz, 1H), 6.16(dd, J=16.2, 6.9 Hz, 1H), 4.24-4.27(m, 1H), 2.35(s, 3H), 1.75(s, 1H), 1.30-1.70(m, 4H), 0.95(t, J=7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 137.45, 133.95, 131.59, 130.17, 129.28, 126.37, 72.97, 39.48, 21.21, 18.80, 14.04. HRMS: Calc'd for $C_{13}H_{18}O$ (M^+), 190.1358; Found, 190.1358.

Isomerization of 18d, formation of 1-(4-chlorophenyl)-1-hexen-3-ol (19d):

By the same procedure as described for the isomerization of compound **18a**, isomerization of 1-(4-chlorophenyl)-2-hexen-1-ol (**18d**) (105.3 mg, 0.5 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (9.58 mg, 0.01 mmol) in water (5 mL) for 3hr at 80°C resulted in 73% conversion of the substrate. Flash column chromatography on silica gel (eluent: hexane/ethyl acetate =15:1) 1-(4-chlorophenyl)-1-hexen-3-ol (**19d**) (68.4 mg, 65% yield). IR(film): 3359, 2872, 1652, 1605, 1491, 1465, 1416, 1091, 1004, 967, 808cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.24-7.29(m, 4H), 6.50(d, J=15.7 Hz, 1H), 6.18(dd, J=15.7, 6.4 Hz, 1H), 4.24-4.29(m, 1H), 1.91(s, 1H), 1.37-1.64(m, 4H), 0.94(t, J=7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 135.26, 133.26, 133.16, 128.84, 128.71, 127.64, 72.65, 39.45, 18.67, 14.01. HRMS: Calc'd for $C_{12}H_{15}OCl$ (M^+), 210.0811; Found, 210.0813.

Isomerization of 18e, formation of 1-(4-methoxyphenyl)-1-hexen-3-ol (19e):

By the same procedure as described for the isomerization of compound **18a**, isomerization of 1-(p-methoxyphenyl)-2-hexen-1-ol (**18e**) (103 mg, 0.5 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (9.58 mg, 0.01 mmol) in water (5 mL) for 4hr at room temperature resulted in 96% conversion of the substrate. Flash column chromatography on silica gel (eluent: hexane/ethyl acetate =15:1) 1-(4-methoxyphenyl)-1-hexen-3-ol (**19e**) (92.2 mg, 89.5% yield). IR(film): 3400, 1651, 1607, 1584, 1511, 1465, 1251, 1174, 1032, 967, 815cm^{-1}. ^1H NMR(400MHz, $CDCl_3$, ppm): δ 7.28(d, J=8.3 Hz, 2H), 6.8(d, J=8.3 Hz, 2H), 6.47(d, J=15.7 Hz, 1H), 6.06(dd, J=15.7, 6.9 Hz, 1H), 4.18-4.25(m, 1H), 3.76(s, 3H), 2.47(s, 1H), 1.38-1.63(m, 4H), 0.93(t, J=7.85 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 159.15, 130.56, 129.67, 129.60, 127.63, 113.97, 72.92, 55.25, 39.54, 18.75, 14.06. HRMS: Calc'd for $C_{13}H_{18}O_2$ (M^+), 206.1307; Found, 206.1307.

Isomerization of 18f, formation of 1-(3-bromophenyl)-1-hexen-3-ol (19f):

By the same procedure as described for the isomerization of compound **18a**, isomerization of 1-(3-bromophenyl)-2-hexen-1-ol (**18f**) (127.5 mg, 0.5 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (9.58 mg, 0.01 mmol) in water (5 mL) for 9hr at 80°C resulted in 78% conversion of the substrate. Flash column chromatography on silica gel (eluent: hexane/ethyl acetate =15:1) gave 1-(3-bromophenyl)-1-hexen-3-ol (**19f**) (91.8 mg, 72% yield). IR(film): 3360, 3070, 1647, 1590, 1546, 1477, 1071, 970, 896, 790, 683cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm): δ 7.51(s, 1H), 7.35(d, J =7.8 Hz, 1H), 7.27(d, J =7.8 Hz, 1H), 7.16(m, 1H), 6.48(d, J =15.7 Hz, 1H), 6.23(dd, J =15.7, 6.4 Hz, 1H), 4.25-4.30(m, 1H), 1.89(br. 1H), 1.34-1.65(m, 4H), 0.94(t, J =7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm): δ 138.97, 134.21, 130.41, 130.09, 129.26, 128.55, 125.14, 122.76, 72.52, 39.43, 18.64, 14.01. HRMS: Calc'd for $C_{12}H_{15}OBr$ (M^+), 254.0306; Found, 254.0302.

Isomerization of 18g, formation of 2-phenyl-2-hepten-4-ol (E and Z) (19g):

By the same procedure as described for the isomerization of compound **18a**, isomerization of 2-phenyl-3-hepten-2-ol (**18g**) (95 mg, 0.5 mmol) under the catalysis of $RuCl_2(PPh_3)_3$ (9.58 mg, 0.01 mmol) in water (5 mL) for 2hr at 45°C resulted in 71% conversion of the substrate. Flash column chromatography on silica gel (eluent: hexane/ethyl acetate =15:1) gave 2-phenyl-2-hepten-4-ol (**19g**) as a mixture of E and Z isomers (66.5 mg, 70% yield, E: Z= 10: 2). IR(film): 3360, 1646, 1598, 1575, 1493, 1445, 1020, 850, 756, 697 cm^{-1}. ^{1}H NMR(400MHz, $CDCl_3$, ppm): (E-isomer): δ 7.18-7.42(m, 5H), 5.76(d, J =8.3 Hz, 1H), 4.53-4.59(m, 1H), 2.10(s, 3H), 1.20-1.78(m, 5H), 0.95(t, J =9.3 Hz, 3H). (Z-isomer): δ 7.18-7.42(m, 5H), 5.47(d, J =9.3 Hz, 1H), 4.05-4.11(m, 1H), 2.05(s, 3H), 1.20-1.78(m, 5H), 0.84(t, J =7.4 Hz, 3H). ^{13}C NMR(100MHz, $CDCl_3$, ppm) δ 143.01(Z–, 142.69), 141.36(Z–, 142.56), 139.58(Z–, 136.92), 131.01(Z–, 130.23), 128.27(Z–, 128.19), 127.26(Z–, 127.74), 125.83(Z–, 127.00), 68.81(Z–, 68.96), 39.85(Z–, 25.78), 18.69, 16.33, 14.13. HRMS: Calc'd for $C_{13}H_{18}O$ (M^+), 190.1358; Found, 190.1359.

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