Tetrahedron 68 (2012) 4805–4812

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Gold-catalyzed intramolecular hydroalkoxylation/cyclization of conjugated dienyl alcohols

B. Chandrasekhar, Jae-Sang Ryu *

Center for Cell Signaling & Drug Discovery Research, College of Pharmacy and Division of Life & Pharmaceutical Sciences, Ewha Womans University, 11-1 Daehyun-Dong, Seodaemun-Gu, Seoul 120-750, Republic of Korea

ARTICLE INFO

Article history:
Received 4 February 2012
Received in revised form 29 March 2012
Accepted 30 March 2012
Available online 9 April 2012

Dedicated to Professor Young-Ger Suh on his 60th birthday

Keywords:
Hydroalkoxylation
Conjugated diene
Alcohol
Gold
Cyclization

ABSTRACT

Catalytic intramolecular additions of hydroxyl groups to tethered conjugated dienes are described. The reactions proceed smoothly at 60 °C in the presence of 5 mol % of $(PPh_3)AuCl/AgOTf$ as a catalyst. A broad range of structurally diverse conjugated dienes produce substituted tetrahydrofurans and tetrahydropyrans in good yields. This reaction represents an atom-economic route to construct five- and six-membered cyclic ethers.

1. Introduction

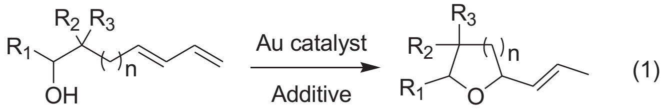
Oxygen heterocycles[1] are widespread structural motifs found in a diverse array of bioactive natural products. Despite the biological relevance of these motifs, the traditional synthetic methods for oxygen heterocycles are limited. Therefore, the development of new, efficient synthetic methodologies for C–O bond formation is of fundamental interest to modern organic chemists. In this context, direct addition of O–H bond to non-activated C–C multiple bonds, so-called hydroalkoxylation,[2] offers in principle a straightforward, atom-economical process for the C–O bond formation. However, the relatively high bond enthalpies of most O–H σ-bonds and the modest reactivity of electron-rich olefins with nucleophiles make it elusive.[3] Recently, transition-metal-catalyzed intramolecular insertion of the O–H bond of an alcohol across the tethered C–C multiple bonds has emerged as an attractive method to overcome these inherent problems. Specifically, the various transition-metal-catalyzed intramolecular hydroalkoxylations of alkenes, alkynes, and allenes have been well documented for Au,[4] Ag,[5] Cu,[6] Pt,[7] Pd,[8] Al,[9] and Ln[3,10] catalysts. Nevertheless, the relatively low reactivity of alkenes and the intrinsic chirality of 1,3-disubstituted allenes have prompted chemists to search for new hydroalkoxylation/hydroamination substrates.[11] From this perspective, conjugated dienes are attractive precursors for the intramolecular hydroalkoxylations. Compared to alkenes, alkynes and allenes, only a few examples of intramolecular hydroalkoxylation of conjugated dienes are known. Yeh and co-workers reported both $CeCl_3 \cdot 7H_2O$–NaI-catalyzed intramolecular hydroalkoxylation of 7-hydroxy-1,3-dienes,[12] and Pd-catalyzed intramolecular hydroalkoxylation/cross-coupling of 7-hydroxy-1,3-dienes and aryl bromides,[13] while Duñach and co-workers reported $Al(OTf)_3$-catalyzed intramolecular hydroalkoxylation of conjugated dienyl alcohols that was applied to the synthesis of rose oxide.[14]

Over the last decade, gold catalysts have been extensively studied due to their superior catalytic activity in various organic transformations.[15] In particular, gold-catalyzed intramolecular hydroalkoxylation has attracted considerable attention as an effective approach toward cyclic ethers. In our ongoing efforts to develop catalytic intramolecular hydroalkoxylation of unsaturated alcohols,[16] we herein report for the first time the gold-catalyzed intramolecular hydroalkoxylation of conjugated dienyl alcohols [Eq. 1].

---

* Corresponding author. Tel.: +82 2 3277 3008; fax: +82 2 3277 2851; e-mail address: ryuj@ewha.ac.kr (J.-S. Ryu).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2012.03.120

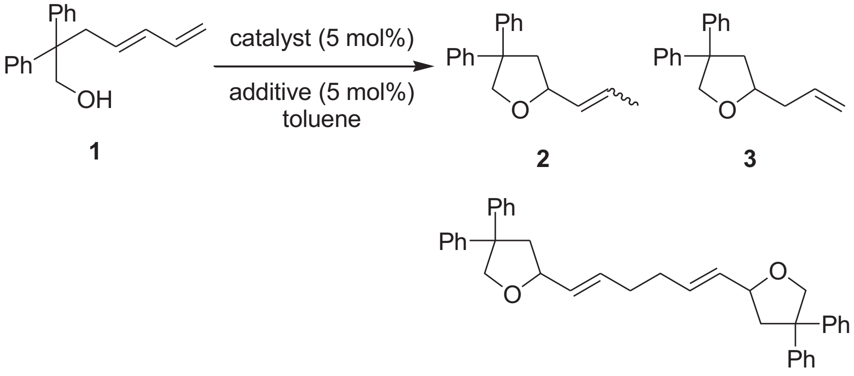


R_1, R_2, R_3 = H, alkyl, aryl
n = 1, 2

2. Results and discussion

To assess the feasibility of gold-catalyzed intramolecular hydroalkoxylation of conjugated dienes, we began to investigate the cycloisomerization of 2,2-diphenyl-hepta-(4*E*,6)-dien-1-ol (**1**) in the presence of various combinations of gold catalysts and silver salts: [(IPr)AuCl] (IPr=*N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), (PPh_3)AuCl, AuCl, $AuCl_3$, along with AgOTf, AgOTs, $AgSbF_6$, $AgBF_4$ or $AgNO_3$ (Table 1). To our delight, Au–Ag catalyst systems were effective in cycloisomerization and produced the corresponding cyclic ethers except for [(IPr)AuCl]/$AgBF_4$, (PPh_3)AuCl/$AgBF_4$, and AuCl/$AgNO_3$ (Table 1, entries 4, 9, and 15). In most cases, the gold-catalyzed intramolecular hydroalkoxylation afforded the 5-*exo* 1,4-addition product **2** as the sole product, which was derived from addition of the oxygen and proton across the conjugated diene system through 5-*exo-trig* cyclization. However, upon treatment with [(IPr)AuCl]/AgOTs, [(IPr)AuCl]/$AgNO_3$, (PPh_3)AuCl/AgOTs or (PPh_3)AuCl/$AgNO_3$, the formation of 5-*exo* 1,2-addition product **3** was also observed (entries 2, 5, 7, and 10).

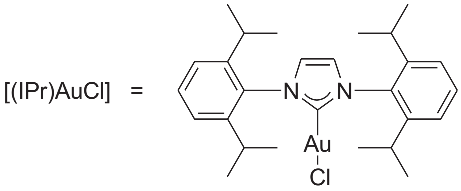
Table 1
Intramolecular hydroalkoxylation of conjugated dienyl alcohol **1**[a]



1 **2** **3** **4**

Entry	Catalyst	Additive	Temp (°C)	Time (h)	Yield[b] (%)		
					2 (*E*/*Z*)	**3**	**4**
1	[(IPr)AuCl]	AgOTf	60	4	50 (11:1)	0	0
2	[(IPr)AuCl]	AgOTs	60	24	38 (6:1)	19	0
3	[(IPr)AuCl]	$AgSbF_6$	60	144	65 (3:1)	0	0
4	[(IPr)AuCl]	$AgBF_4$	60	72	0	0	0
5	[(IPr)AuCl]	$AgNO_3$	60	144	49 (1:1)	30	0
6	(PPh_3)AuCl	AgOTf	60	12	85 (10:1)	0	0
7	(PPh_3)AuCl	AgOTs	60	120	40 (1:1)	10	0
8	(PPh_3)AuCl	$AgSbF_6$	60	12	65 (10:1)	0	0
9	(PPh_3)AuCl	$AgBF_4$	60	24	0	0	0
10	(PPh_3)AuCl	$AgNO_3$	60	120	10 (1:1)	20	0
11	AuCl	AgOTf	rt	48	31 (*E* only)	0	0
12	AuCl	AgOTs	60	72	53 (*E* only)	0	0
13	AuCl	$AgSbF_6$	rt	48	36 (*E* only)	0	0
14	AuCl	$AgBF_4$	60	72	28 (*E* only)	0	0
15	AuCl	$AgNO_3$	60	72	0	0	0
16	$AuCl_3$	AgOTf	rt	36	68 (*E* only)	0	4
17	$AuCl_3$	AgOTs	60	24	80 (*E* only)	0	8
18	$AuCl_3$	$AgSbF_6$	rt	12	83 (*E* only)	0	8
19	$AuCl_3$	$AgBF_4$	rt	36	10 (*E* only)	0	0
20	$AuCl_3$	$AgNO_3$	60	48	10 (*E* only)	0	8
21	$AuCl_3$	—	60	24	25 (*E* only)	0	20
22	(PPh_3)AuCl	—	60	12	0	0	0
23	—	AgOTf	60	12	0	0	0

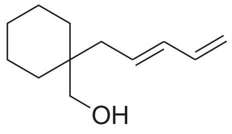
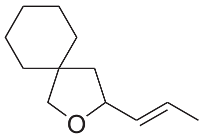
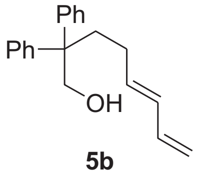
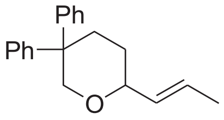
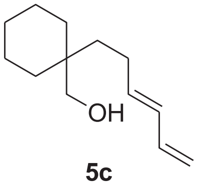
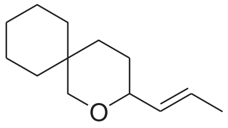
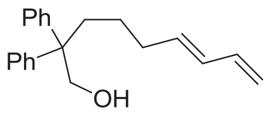
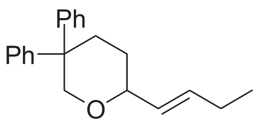
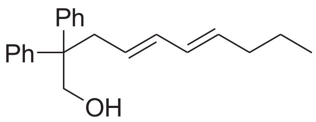
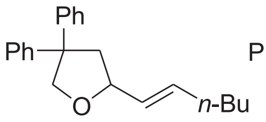
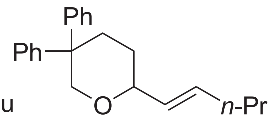
[a] Reaction condition: **1** (0.2 mmol), Au-catalyst (5 mol %), Ag salt (5 mol %), toluene (1 mL).
[b] Isolated yields.



Among the catalysts screened, the best result was obtained from a combination of 5 mol % of (Ph$_3$P)AuCl and 5 mol % of AgOTf in toluene at 60 °C, which produced only **2** in 85% yield (*E*/*Z*=10:1, entry 6). The obtained 5-*exo* 1,4-addition product **2** was an inseparable *E*/*Z* mixture and the ratio was measured by NMR. In the meantime, AuCl/Ag salts or AuCl$_3$/Ag salts exclusively produced the *E* isomer (entries 11–14, 16–21). In our attempts to develop an effective catalytic system, we screened Au(III) catalysts as well. Interestingly, when conjugated dienyl alcohol **1** was treated with the combination of AuCl$_3$ and Ag salts, the dimeric compound **4** was delivered as a minor product in low yield (entries 16–18, 20). The yield of the dimerization product **4** could be increased up to 20% when the reaction was carried out only in the presence of AuCl$_3$ (entry 21). Au(I)/Au(III)-catalyzed alkyne dimerizations have sometimes been reported but Au(I)/Au(III)-catalyzed alkene dimerizations are rare.[15b,d] In contrast to Au/Ag catalyst systems, neither (PPh$_3$)AuCl nor AgOTf by themselves effectively promoted the reaction (entries 22 and 23). These intramolecular hydroalkoxylation reactions failed to give the desired products at 60 °C.

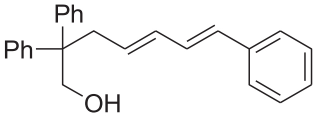
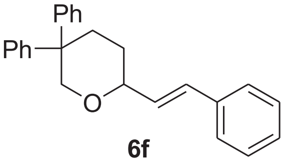
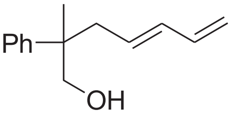
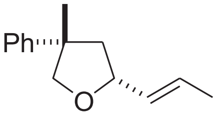
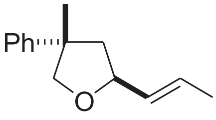
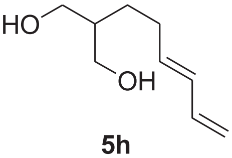
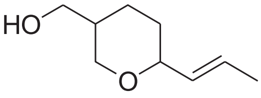
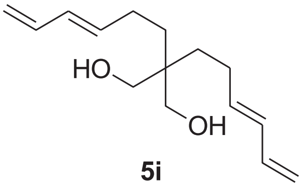
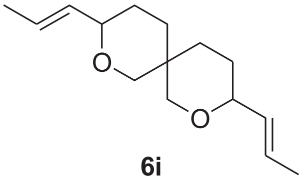
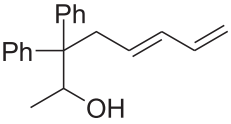
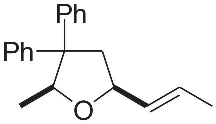
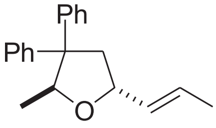
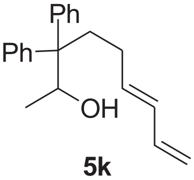
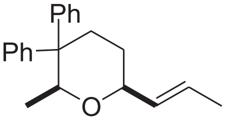
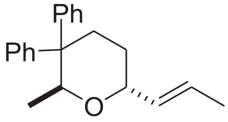
After establishing the optimal conditions, we examined the scope of the gold-catalyzed intramolecular hydroalkoxylation (Table 2). We applied the (PPh$_3$)AuCl/AgOTf catalytic system to the intramolecular cycloisomerization of various conjugated dienyl alcohols in toluene at 60 °C. All reactions using (PPh$_3$)AuCl/AgOTf in Table 2 provided *E* isomer and trace amount of byproducts. Because of the negligible amount, the structures of byproducts including *Z* isomer could not be isolated and identified. Under the optimized reaction conditions, conjugated dienyl alcohol **5a** underwent cycloisomerization smoothly to furnish the 5-*exo* 1,4-addition cyclic ether **6a** (entry 1), and **5b** and **5c** afforded 6-*exo* 1,4-addition cyclic ethers (entries 2 and 3). Five- and six-membered ring formations were rapid and smooth; however, seven-membered ring formation was not effective. Instead of giving the corresponding seven-membered cyclic ether, (*E*)-2,2-diphenylnona-6,8-dien-1-ol (**5d**) produced the tetrahydropyran **6d** in 66% yield after 12 h (entry 4). The reaction was carried out several times and the product was clearly confirmed by 2D NMR. This was an unexpected result. Although there was no literature precedent for this kind of intramolecular hydroalkoxylation cyclization, gold(I)-catalyzed alkene hydroamination to give seven-membered ring was reported to be sluggish and the alkene isomerization was observed as an alternative.[17] In addition, similar alkene migration was also reported for (PPh$_3$)AuOTf-catalyzed intermolecular hydroalkoxylation.[18] Thus, we envisioned the possible mechanism of this unusual cyclization based on the alkene isomerization. Presumably, gold-catalyzed isomerization of a terminal diene to an internal diene is much faster than seven-membered ring cyclization. The subsequently generated internal diene would be cyclized rapidly to tetrahydropyran.

Table 2
Intramolecular hydroalkoxylation of conjugated dienyl alcohols catalyzed by (PPh$_3$)AuCl/AgOTf in toluene at 60 °C[a]

Entry	Substrate	Product	Time (h)	Yield[b] (%)
1	 **5a**	 **6a**	12	60
2	 **5b**	 **6b**	1	81
3	 **5c**	 **6c**	12	62
4	 **5d**	 **6d**	12	66
5	 **5e**	 **6e**  **6e'**	2	60 (**6e**/**6e'**=1:2)

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	Product	Time (h)	Yield[b] (%)
6	 **5f**	 **6f**	3	47
7	 **5g**	 **6g** (±)  **6g'** (±)	4	70 (**6g**/**6g**′=2:1)
8	 **5h**	 **6h**	3.5	74[c]
9	 **5i**	 **6i**	9	63[d]
10	 **5j**	 **6j** (±)  **6j'** (±)	2	69[e] (**6j**/**6j**′=3:1)
11	 **5k**	 **6k** (±)  **6k'** (±)	12	80 (**6k**/**6k**′=1:3)

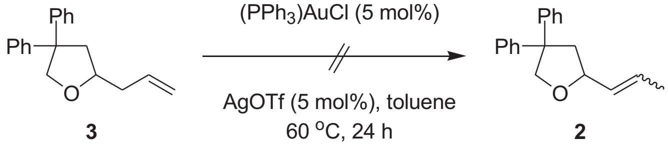
[a] Reaction conditions: conjugated dienyl alcohol (0.2 mmol), Au-catalyst (5 mol %), Ag salt (5 mol %), toluene (1 mL).
[b] Isolated yields.
[c] two isomers are not separable (dr=2:1).
[d] Three stereoisomers were isolated (dr=2:1:1).
[e] 2,5-*cis* isomer and 2,5-*trans* isomer are not separable.

Meanwhile, the reactions were general for both terminal dienes and internal dienes. The internal-diene cycloisomerizations were faster than the corresponding terminal-diene cyclization reactions (Table 1, entry 6 vs Table 2, entries 5 and 6). Alkyl-substituted internal diene **5e** afforded a 1:2 mixture of 5-*exo* 1,4-addition product **6e** and 6-*endo* product **6e**′ (entry 5). However, aryl-substituted internal diene **5f** allowed only 6-*endo* cyclic ether **6f** in 3 h (entry 6). The 5-*exo-trig* cyclization was predominant for terminal dienes, whereas 6-*endo-trig* cyclization was a major route for internal diene cyclizations. The structures of **6e**, **6e**′, and **6f** were unambiguously confirmed by 2D NMR (H–H COSY), which can be found in Supplementary data. The mechanistic reason for this regioselectivity is quite puzzling and is still under investigation. However, 6-*endo-trig* cyclization for the internal diene hydroalkoxylation has been already reported in the previous literatures.[14] Another feature of note is that substituting C-2 with different groups gave rise to the 2,4,4-trisubstituted products **6g** and **6g**′, which were obtained in 70% yield and 2:1 dr, favoring the 2,4-*cis* diastereomer (entry 7). The two isomers were separable by column chromatography and unambiguously identified by 1D-NOE experiments (see Supplementary data). Interestingly, the conjugated dienyl diol **5h** gave the monocyclized product in 74% yield (entry 8), whereas the conjugated dienyl diol **5i** containing two 1,3-dienes gave the double cyclization product **6i** with a mixture of isomers in 63% yield (entry 9).

Many naturally occurring tetrahydrofurans and tetrahydropyrans contain 2,5-disubstituents and 2,6-disubstituents, respectively. Therefore, we were interested in the diastereoselectivity in the cyclization of conjugated dienyl secondary alcohols. The cyclization of substrates containing secondary –OH groups proceeded smoothly and provided 2,5-disubstituted tetrahydrofuran and 2,6-disubstituted tetrahydropyran (entries 10 and 11). Interestingly, **5k** favored the formation of *trans*-2,6-disubstituted tetrahydropyran **6k′** with 3:1 diastereoselectivity, which was confirmed by 1D-NOE (see Supplementary data). Notably, gold(I)-catalyzed diene hydroalkoxylation exhibits the opposite diastereoselectivity to allene hydroalkoxylation favoring *cis*-2,6-disubstituted tetrahydropyran.[4e] Likewise, **5j** preferred the formation of *cis*-2,6-disubstituted tetrahydrofuran **6j** with 3:1 diastereoselectivity.

Mechanistically, we envisage a plausible pathway for hydroalkoxylation of conjugated dienyl alcohols based on the previously reported gold(I)-catalyzed hydroamination mechanism of 1,3-dienes (Scheme 1).[19] $(PPh_3)AuOTf$, produced from the reaction of $(PPh_3)AuCl$ and AgOTf, binds to the conjugated diene. Coordination of the gold(I) species to the conjugated diene of **1** gives a gold(I)–diene complex **A**.[20] Then, intramolecular addition of –OH generates the η^1-allylgold intermediate **B** with the newly formed C–O bond. Allylic isomerization of **B** leads to **C**. Protonolysis of the C–Au bond of **C** affords the η^2-alkene gold intermediate **D**. Replacement of the double bond of **D** with triflate produces the tetrahydrofuran **2** and regenerates the reactive species $(PPh_3)AuOTf$ in the catalytic cycle.

In the proposed mechanism there was a concern that the terminal olefin product **3** might be initially formed and isomerized to the internal olefin product **2** during the Au-catalyzed intramolecular hydroalkoxylation. In order to clarify the isomerization concern, we isolated the terminal olefin product **3** and treated compound **3** with optimum reaction conditions $(PPh_3)AuCl/AgOTf$). However, no isomerization was observed at 60 °C after 24 h and **3** was recovered.[21] It means that the terminal olefin product **3** is not formed under the optimum reaction conditions and mechanistically protonolysis of the C–Au bond of η^1-allylgold intermediate **B** does not occur under the optimum reaction conditions. Instead, the intermediate **B** is converted to intermediate **C** exclusively.



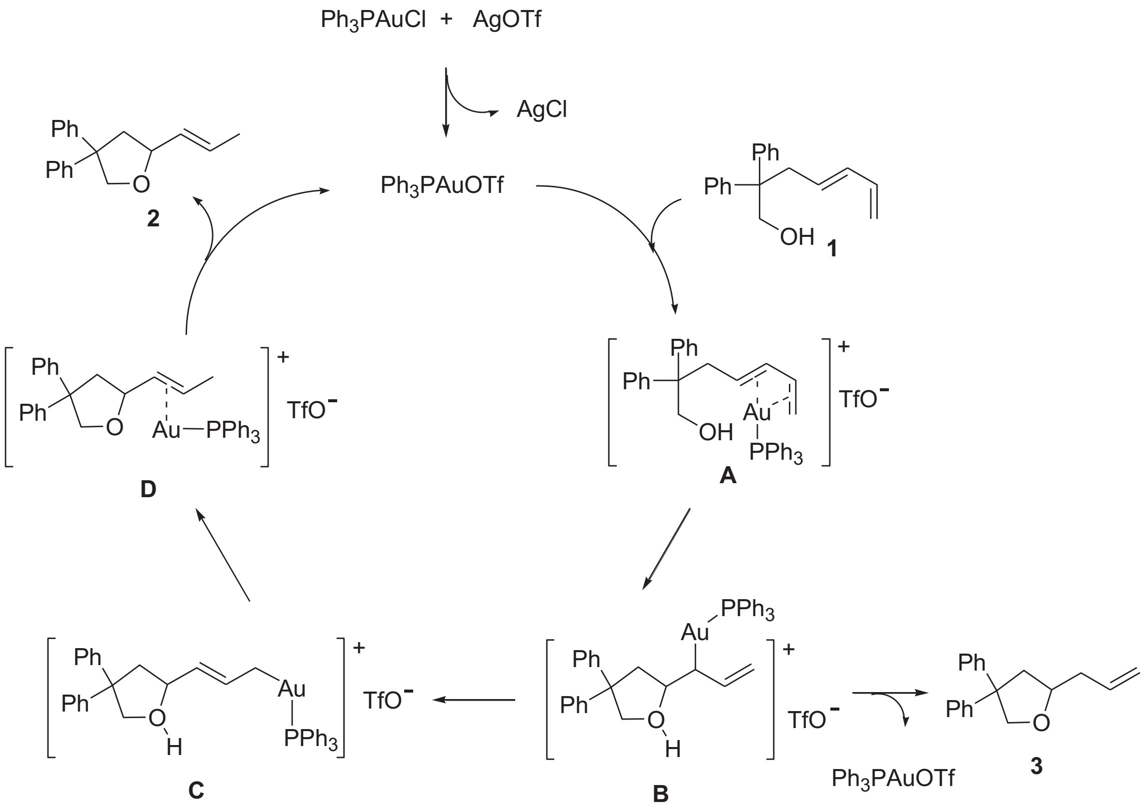
3. Conclusion

In conclusion, $(PPh_3)AuOTf$, generated in situ from the combination of $(PPh_3)AuCl$ and AgOTf, catalyzes intramolecular hydroalkoxylation of conjugated dienyl alcohols, which offers a facile synthetic route for formation of five- and six-membered rings such as tetrahydrofuran and tetrahydropyran. The cycloisomerizations proceed with a variety of substrates, including terminal dienes, internal dienes, primary alcohols, and secondary alcohols, through *exo-trig* and *endo-trig* modes of cyclization. We believe that this method will be a good entry for the synthesis of tetrahydrofuran and tetrahydropyran-containing natural products. Thus, our ongoing research is focused on the application of this new method toward the synthesis of complex cyclic ether natural products.

4. Experimental

4.1. General method

Reagents were purchased from commercial suppliers, and used without further purification. Reactions were performed in flame-



Scheme 1. Plausible reaction mechanism for intramolecular hydroalkoxylation of conjugated dienyl alcohol **1**.

dried glassware under positive Ar pressure with magnetic stirring. TLC was performed on 0.25 mm E. Merck silica gel 60 F_{254} plates and visualized under UV light (254 nm) or by staining with cerium ammonium molybdate (CAM). Flash chromatography was performed on E. Merck 230–400 mesh silica gel 60. NMR spectra were recorded on Varian Unity 400 instruments at 24 °C. Chemical shifts are expressed in parts per million relative to TMS (^{1}H, 0 ppm), $CDCl_3$ (^{1}H, 7.26 ppm; ^{13}C, 77.2 ppm); coupling constants are expressed in hertz. High-resolution mass spectra electrospray ionization (HRMS-ESI) was obtained on an Agilent technologies 6220 TOF LC/MS spectrometer. Infrared spectra were recorded on FTIR (FTS-135) made by Bio-Rad.

4.2. Representative procedure for intramolecular hydroalkoxylation of conjugated dienyl alcohols (Table 1, entry 6)

A mixture of $(PPh_3)AuCl$ (5.0 mg, 0.01 mmol) and AgOTf (2.5 mg, 0.01 mmol) in anhydrous toluene (0.2 mL) was stirred at room temperature for 10 min, treated with a solution of **1** (57 mg, 0.21 mmol) in toluene (0.8 mL), and the resulting suspension was stirred at 60 °C for 12 h. Progress of the reaction was monitored by TLC. Upon the completion of the reaction, solvent was evaporated. The residue was purified by column chromatography (49:1 hexane/EtOAc) to afford **2** (48 mg, 85%) as a colorless oil.

*4.2.1. (E)-4,4-Diphenyl-2-(prop-1-enyl)tetrahydrofuran (**2**).*[4e] TLC: R_f 0.56 (9:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.25 (m, 6H), 7.23–7.18 (m, 4H), 5.68 (dq, *J*=15.2, 6.4 Hz, 1H), 5.53 (ddd, *J*=15.2, 8.0, 1.6 Hz, 1H), 4.64 (dd, *J*=8.8, 1.2 Hz, 1H), 4.38 (m, 1H), 4.13 (d, *J*=8.8 Hz, 1H), 2.61 (ddd, *J*=12.4, 6.0, 1.2 Hz, 1H), 2.42 (dd, *J*=12.4, 9.6 Hz, 1H), 1.68 (dd, *J*=6.4, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 146.0, 132.0, 128.7, 128.6, 128.5, 127.4 (2C), 126.7, 126.5, 79.8, 77.5, 56.4, 45.5, 17.9. HRMS *m*/*z* calcd for $C_{19}H_{20}ONa$ $[M+Na]^+$ 287.1406, found 287.1402. IR (KBr film): 1493, 1446, 1047, 699 cm^{-1}.

*4.2.2. 2-Allyl-4,4-diphenyltetrahydrofuran (**3**).* Colorless oil. TLC: R_f 0.60 (9:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.18 (m, 10H), 5.81 (m, 1H), 5.12–5.04 (m, 2H), 4.62 (d, *J*=8.4 Hz, 1H), 4.13 (d, *J*=8.4 Hz, 1H), 4.09 (m, 1H), 2.59 (dd, *J*=12.4, 6.0 Hz, 1H), 2.45–2.28 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 146.1, 134.9, 128.6, 128.5, 127.4, 127.3, 126.6, 126.4, 117.4, 78.2, 77.1, 56.2, 44.5, 40.5, 17.9. HRMS *m*/*z* calcd for $C_{19}H_{20}ONa$ $[M+Na]^+$ 287.1406, found 287.1404. IR (KBr film): 2923, 1493, 1261, 1073, 699 cm^{-1}.

*4.2.3. (1E,5E)-1,6-Bis(4,4-diphenyltetrahydrofuran-2-yl)hexa-1,5-diene (**4**).* Light yellow oil. TLC: R_f 0.48 (9:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.18 (m, 20H), 5.84 (AB quartet, *J*=5.6 Hz, 2H), 5.83 (AB quartet, *J*=5.6 Hz, 2H), 4.69 (dd, *J*=8.8, 1.2 Hz, 2H), 4.48–4.43 (m, 2H), 4.15 (d, *J*=8.8 Hz, 2H), 4.04–4.02 (m, 4H), 2.67 (ddd, *J*=12.0, 6.0, 1.2 Hz, 2H), 2.45 (dd, *J*=12.0, 9.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 145.5, 135.3, 128.7, 128.6, 127.5, 127.3, 127.2, 126.8, 126.6, 78.4, 56.4, 45.3, 44.4, 29.9. IR (KBr film): 2924, 1490, 1260, 699 cm^{-1}. HRMS *m*/*z* calcd for $C_{38}H_{38}O_2Na$ $[M+Na]^+$ 549.2764, found 549.2805.

*4.2.4. (E)-3-(Prop-1-enyl)-2-oxaspiro[4.5]decane (**6a**).* Colorless oil. TLC: R_f 0.73 (4:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 (dq, *J*=15.2, 6.8 Hz, 1H), 5.49 (ddq, *J*=15.2, 7.2, 1.6 Hz, 1H), 4.30 (q, *J*=7.2 Hz, 1H), 3.62 (d, *J*=8.4 Hz, 1H), 3.53 (d, *J*=8.4 Hz, 1H), 1.88 (dd, *J*=12.4, 6.8 Hz, 1H), 1.69 (dd, *J*=6.8, 1.6 Hz, 3H), 1.50–1.36 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6, 127.7, 79.7, 78.6, 45.2, 44.3, 37.1, 35.7, 26.2, 24.2, 23.8, 17.8. HRMS *m*/*z* calcd for $C_{12}H_{24}ON$ $[M+NH_4]^+$ 198.1852, found 198.1852. IR (KBr film): 2924, 2853, 1449, 1050, 962 cm^{-1}.

*4.2.5. (E)-5,5-Diphenyl-2-(prop-1-enyl)tetrahydro-2H-pyran (**6b**).* Colorless oil. TLC: R_f 0.70 (4:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.40 (m, 2H), 7.30–7.23 (m, 4H), 7.19–7.14 (m, 4H), 5.72 (dqd, *J*=15.6, 6.4, 1.2 Hz, 1H), 5.48 (ddq, *J*=15.2, 6.8, 1.6 Hz, 1H), 4.65 (dd, *J*=12.0, 2.4 Hz, 1H), 3.88 (m, 1H), 3.59 (d, *J*=12.0 Hz, 1H), 2.51–2.40 (m, 2H), 1.68 (dd, *J*=6.8, 1.6 Hz, 3H), 1.61–1.56 (m, 1H), 1.40–1.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 145.9, 132.2, 129.1, 128.4, 128.2, 127.8, 127.2, 126.5, 125.8, 78.6, 75.0, 45.9, 34.7, 28.4, 18.0. HRMS *m*/*z* calcd for $C_{20}H_{22}ONa$ $[M+Na]^+$ 301.1563, found 301.1559. IR (KBr film): 2934, 1494, 1004, 699 cm^{-1}.

*4.2.6. (E)-3-(Prop-1-enyl)-2-oxaspiro[5.5]undecane (**6c**).* Colorless oil. TLC: R_f 0.73 (4:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.69 (dqd, *J*=15.2, 6.4, 1.2 Hz, 1H), 5.52 (ddq, *J*=15.2, 6.4, 1.6 Hz, 1H), 3.78 (dd, *J*=11.2, 2.8 Hz, 1H), 3.66 (m, 1H), 3.12 (d, *J*=11.2 Hz, 1H), 1.75 (ddd, *J*=13.2, 6.0, 3.2 Hz, 1H), 1.69 (ddd, *J*=6.4, 1.6, 0.8 Hz, 3H), 1.61–1.54 (m, 2H), 1.52–1.40 (m, 8H), 1.22 (td, *J*=13.2, 4.4 Hz, 1H), 1.14–1.18 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6, 127.2, 79.1, 76.7, 36.8, 34.3, 32.1, 31.4, 27.8, 27.0, 21.8, 21.7, 18.0. HRMS *m*/*z* calcd for $C_{13}H_{26}ON$ $[M+NH_4]^+$ 212.2009, found 212.2010. IR (KBr film): 2925, 2848, 1451, 1077, 772 cm^{-1}.

*4.2.7. (E)-2-(But-1-enyl)-5,5-diphenyltetrahydro-2H-pyran (**6d**).* Viscous colorless oil. TLC: R_f 0.53 (19:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.41 (m, 2H), 7.3–7.14 (m, 8H), 5.75 (dtd, *J*=15.2, 6.0, 0.8 Hz, 1H), 5.45 (ddt, *J*=15.2, 7.2, 1.6 Hz, 1H), 4.66 (dd, *J*=12.0, 2.4 Hz, 1H), 3.90 (m, 1H), 3.60 (d, *J*=12.0 Hz, 1H), 2.53–2.41 (m, 2H), 2.03 (quin, *J*=7.2 Hz, 2H), 1.59 (ddd, *J*=13.6, 6.0, 3.6 Hz, 1H), 1.41–1.31 (m, 1H), 0.97 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 145.9, 134.6, 129.8, 129.1, 128.4, 128.2, 127.2, 126.5, 125.8, 78.8, 75.0, 45.9, 34.8, 28.6, 25.5, 13.4. HRMS *m*/*z* calcd for $C_{21}H_{24}ONa$ $[M+Na]^+$ 315.1719, found 315.1723. IR (KBr film): 2959, 2845, 1494, 1078, 698 cm^{-1}.

*4.2.8. (E)-2-(Hex-1-enyl)-4,4-diphenyltetrahydrofuran (**6e**).* Colorless oil. TLC: R_f 0.72 (9:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.17 (m, 10H), 5.65 (dt, *J*=15.2, 6.8 Hz, 1H), 5.50 (dd, *J*=15.2, 7.6 Hz, 1H), 4.65 (d, *J*=8.8 Hz, 1H), 4.38 (m, 1H), 4.13 (d, *J*=8.8 Hz, 1H), 2.60 (ddd, *J*=12.4, 6.0, 0.8 Hz, 1H), 2.42 (dd, *J*=12.4, 9.6 Hz, 1H), 2.04–1.99 (m, 2H), 1.35–1.25 (m, 4H), 0.87 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 146.0, 134.0, 130.5, 128.6, 128.5, 127.3, 127.2, 126.6, 126.5, 79.8, 77.1, 56.4, 45.6, 32.0, 31.4, 22.4, 14.1. HRMS *m*/*z* calcd for $C_{22}H_{27}O$ $[M+H]^+$ 307.2056, found 307.2065. IR (KBr film): 2955, 1494, 1054, 699 cm^{-1}.

*4.2.9. (E)-2-(Pent-1-enyl)-5,5-diphenyltetrahydro-2H-pyran (**6e′**).* Colorless oil. TLC: R_f 0.74 (9:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.41 (m, 2H), 7.30–7.24 (m, 4H), 7.18–7.15 (m, 4H), 5.69 (dtd, *J*=15.2, 6.8, 0.8 Hz, 1H), 5.46 (ddt, *J*=15.2, 6.8, 1.2 Hz, 1H), 4.65 (dd, *J*=12.0, 2.4 Hz, 1H), 3.89 (m, 1H), 3.59 (d, *J*=12.0 Hz, 1H), 2.49–2.43 (m, 2H), 2.01–1.95 (m, 2H), 1.60–1.56 (m, 1H), 1.41–1.33 (m, 3H), 0.88 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 146.0, 132.8, 131.0, 129.1, 128.5, 128.2, 127.2, 126.5, 125.8, 78.8, 75.0, 45.9, 34.8, 34.6, 28.6, 22.4, 13.9. HRMS *m*/*z* calcd for $C_{22}H_{27}O$ $[M+H]^+$ 307.2056, found 307.2053. IR (KBr film): 2956, 1494, 1105, 698 cm^{-1}.

*4.2.10. (E)-5,5-Diphenyl-2-(2-phenylethenyl)-tetrahydro-2H-pyran (**6f**).* White solid. Mp: 118–120 °C. TLC: R_f 0.77 (4:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.43 (m, 2H), 7.37–7.16 (m, 13H), 6.62 (d, *J*=16.0 Hz, 1H), 6.22 (dd, *J*=16.0, 6.0 Hz, 1H), 4.73 (dd, *J*=12.0, 2.4 Hz, 1H), 4.14–4.09 (m, 1H), 3.68 (d, *J*=12.0 Hz, 1H), 2.55–2.47 (m, 2H), 1.72 (qd, *J*=6.0, 3.6 Hz, 1H), 1.51–1.41 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 145.9, 137.0, 130.8, 130.4, 129.1, 128.7, 128.5, 128.3, 127.8, 127.2, 126.7, 126.6, 125.9, 78.5, 75.0, 46.0, 34.8, 28.6. HRMS m/z calcd for $C_{25}H_{24}ONa$ $[M+Na]^+$ 363,1719, found 363.1722. IR (KBr film): 2940, 1493, 1446, 1089, 764 cm^{-1}.

*4.2.11. (E)-4-Methyl-4-phenyl-2-(prop-1-enyl)tetrahydrofuran (**6g**, **6g′**). Compound **6g***: Colorless oil. TLC: R_f 0.42 (19:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.30 (m, 2H), 7.25–7.19 (m, 3H), 5.73 (dqd, J=14.8, 6.4, 0.8 Hz, 1H), 5.51 (ddq, J=14.8, 8.0, 1.6 Hz, 1H), 4.59 (m, 1H), 4.0 (d, J=8.0 Hz, 1H), 3.95 (dd, J=8.0, 0.8 Hz, 1H), 2.23 (ddd, J=12.0, 6.0, 0.8 Hz, 1H), 2.00 (dd, J=12.0, 9.6 Hz, 1H), 1.70 (dd, J=6.4, 1.6 Hz, 3H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 132.3, 128.6, 128.1, 126.3, 126.1, 80.1, 78.9, 48.1, 46.2, 28.2, 17.9. HRMS m/z calcd for $C_{14}H_{19}O$ $[M+H]^+$ 203.1430, found 203.1431. IR (KBr film): 2963, 1496, 1048 cm^{-1}. *Compound **6g′***: Colorless oil. TLC: R_f 0.45 (19:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.29 (m, 4H), 7.23–7.19 (m, 1H), 5.72–5.65 (m, 1H), 5.62–5.56 (m, 1H), 4.37 (q, J=7.6 Hz, 1H), 4.04 (d, J=8.4 Hz, 1H), 3.91 (d, J=8.4 Hz, 1H), 2.43 (dd, J=12.4, 7.6 Hz, 1H), 1.83 (dd, J=12.4, 7.6 Hz, 1H), 1.70 (dd, J=6.4, 0.8 Hz, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 132.6, 128.6, 128.2, 126.3, 126.2, 80.4, 79.0, 48.0, 46.9, 28.6, 17.9. HRMS m/z calcd for $C_{14}H_{18}ONa$ $[M+Na]^+$ 225.1250, found 225.1255. IR (KBr film): 2962, 1496, 1047, 771 cm^{-1}.

*4.2.12. (E)-(6-(Prop-1-enyl)tetrahydro-2H-pyran-3-yl)methanol (**6h**).* Colorless oil. TLC: R_f 0.33 (1:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76–5.67 (m, 1H, *major/minor*), 5.53–5.47 (m, 1H, *major/minor*), 4.12 (qd, J=4.4, 2.0 Hz, 1H, *major*), 3.99 (dt, J=2.0, 11.6 Hz, 1H, *minor*), 3.86 (dd, J=8.0, 10.4 Hz, 1H, *minor*), 3.80–3.75 (m, 1H, *minor*), 3.74–3.67 (m, 2H, *minor*), 3.64 (dd, J=2.8, 11.6 Hz, 1H, *major*), 3.51 (dd, J=10.8, 5.6 Hz, 1H, *major*), 3.45 (dd, J=10.8, 6.8 Hz, 1H, *major*), 3.22 (t, J=11.2 Hz, 1H, *major*), 1.90–1.73 (m, 2H, *major/minor*), 1.70–1.68 (m, 3H, *major/minor*), 1.55–1.48 (m, 1H, *major/minor*), 1.45–1.38 (m, 1H, *major/minor*), 1.29–1.19 (m, 1H, *major/minor*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.2 (*major*), 132.1 (*minor*), 127.4 (*minor*), 127.3 (*major*), 78.5 (*major/minor*), 71.0 (*major*), 68.4 (*minor*), 65.1 (*major*), 63.4 (*minor*), 38.7 (*major*), 36.0 (*minor*), 31.6 (*major/minor*), 27.9 (*minor*), 26.7 (*major*), 24.4 (*minor*), 18.0 (*major*). HRMS m/z calcd for $C_9H_{17}O_2$ $[M+H]^+$ 157.1223, found 157.1227. IR (KBr film): 3386, 2931, 2853, 1449, 1085 cm^{-1}.

*4.2.13. 3,9-Di((E)-prop-1-enyl)-2,8-dioxaspiro[5.5]undecane (**6i**). Isomer A*: Colorless oil. TLC: R_f 0.57 (15:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73–5.64 (m, 2H), 5.53–5.46 (m, 2H), 4.29 (d, J=10.4 Hz, 2H), 3.66 (m, 2H), 3.09 (d, J=10.4 Hz, 2H), 1.68 (dd, J=6.4, 1.0 Hz, 3H), 1.46–1.25 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3, 126.9, 78.7, 71.8, 34.2, 31.5, 28.3, 18.0. HRMS m/z calcd for $C_{15}H_{25}O_2$ $[M+H]^+$ 237.1849, found 237.1848. IR (KBr film): 2924, 1716, 1652, 1455, 1073 cm^{-1}. *Isomer B*: Colorless oil. TLC: R_f 0.55 (15:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74–5.65 (m, 2H), 5.55–5.46 (m, 2H), 4.23 (dd, J=12.0, 2.4 Hz, 1H), 3.70–3.63 (m, 2H), 3.49 (dd, J=11.0, 2.4 Hz, 1H), 3.22 (d, J=11.6 Hz, 1H), 3.20 (dd, J=12.0, 1.6 Hz, 1H), 2.35 (ddd, J=13.2, 6.8, 2.8 Hz, 1H), 1.69 (m, 6H), 1.62–1.10 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.24, 132.23, 127.6, 127.5, 79.3, 79.0, 76.2, 72.3, 33.1, 31.8, 28.6, 27.8, 27.2, 18.0. HRMS m/z calcd for $C_{15}H_{24}O_2Na$ $[M+Na]^+$ 259.1669, found 259.1665. IR (KBr film): 2933, 1723, 1447, 1075, 966 cm^{-1}. *Isomer C*: Colorless oil. TLC: R_f 0.53 (15:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73–5.66 (m, 2H), 5.55–5.49 (m, 2H), 3.71 (m, 2H), 3.46 (dd, J=11.2, 2.4 Hz, 2H), 3.18 (d, J=11.2 Hz, 2H), 2.16 (ddd, J=13.6, 6.4, 3.6 Hz, 2H), 1.70 (ddd, J=6.8, 7.6, 0.8 Hz, 6H), 1.53–1.25 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.1, 127.6, 78.9, 75.2, 32.2, 29.0, 27.4, 18.0. HRMS m/z calcd for $C_{15}H_{24}O_2Na$ $[M+Na]^+$ 259.1669, found 259.1661. IR (KBr film): 2935, 1734, 1451, 1068 cm^{-1}.

*4.2.14. (E)-2-Methyl-3,3-diphenyl-5-(prop-1-enyl)tetrahydrofuran (**6j**, **6j′**).* Colorless oil. *TLC*: R_f 0.66 (9:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.17 (m, 8H, **6j**/**6j′**), 7.09–7.05 (m, 2H, **6j**/**6j′**), 5.72–5.44 (m, 2H, **6j**/**6j′**), 4.90 (q, J=6.4 Hz, 1H, **6j**), 4.79–4.72 (m, 2H, **6j′**), 4.22 (m, 1H, **6j**), 3.09 (dd, J=13.6, 8.0 Hz, 1H, **6j′**), 2.67 (dd, J=12.0, 10.4 Hz, 1H, **6j**), 2.34–2.28 (m, 1H, **6j**/**6j′**), 1.71 (dd, J=6.0, 0.8 Hz, 3H, **6j**), 1.65 (dd, J=6.4, 1.2 Hz, 3H, **6j′**), 1.06 (d, J=6.0 Hz, 3H, **6j′**), 0.90 (d, J=6.4 Hz, 3H, **6j**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1 (**6j**), 147.4 (**6j′**), 145.5 (**6j**), 145.0 (**6j′**), 133.2 (**6j′**), 132.6 (**6j**), 129.1 (**6j′**), 128.7 (**6j**), 128.6 (**6j′**), 128.4 (**6j′**), 128.3 (**6j**), 128.2 (**6j**), 128.1 (**6j′**), 128.0 (**6j**), 127.9 (**6j**), 127.5 (**6j′**), 126.5 (**6j**), 126.4 (**6j′**), 126.3 (**6j**/**6j′**), 80.5 (**6j**), 79.3 (**6j′**), 78.4 (**6j**), 77.6 (**6j′**), 59.3 (**6j**), 58.9 (**6j′**), 47.8 (**6j′**), 43.9 (**6j**), 21.0 (**6j**), 20.8 (**6j′**), 17.9 (**6j**), 17.5 (**6j′**). IR (KBr film): 2970, 1494, 1075, 699 cm^{-1}. HRMS m/z calcd for $C_{20}H_{22}ONa$ $[M+Na]^+$ 301.1563, found 301.1555.

*4.2.15. (E)-2-Methyl-3,3-diphenyl-6-(prop-1-enyl)tetrahydro-2H-pyran (**6k**, **6k′**). 2,6-cis-Isomer **6k***: Colorless oil. TLC: R_f 0.46 (19:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.56 (m, 2H), 7.29–7.17 (m, 8H), 5.74 (dqd, J=15.6, 6.4, 0.8 Hz, 1H), 5.58 (ddq, J=15.6, 7.2, 1.6 Hz, 1H), 4.03 (m, 1H), 3.74 (q, J=6.8 Hz, 1H), 2.64 (td, J=13.2, 3.6 Hz, 1H), 2.10 (dt, J=13.2, 3.6 Hz, 1H), 1.70 (ddd, J=6.4, 1.6, 0.8 Hz, 3H), 1.50 (dq, J=13.2, 2.8 Hz, 1H), 1.38–1.34 (m, 1H), 1.27 (d, J=6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 144.7, 132.6, 131.6, 129.4, 127.8, 127.5, 127.4, 126.4, 125.6, 82.3, 79.9, 51.2, 38.5, 28.6, 18.1, 18.0. HRMS m/z calcd for $C_{21}H_{25}O$ $[M+H]^+$ 293.1900, found 293.1901. IR (KBr film): 2923, 1652, 1115, 701 cm^{-1}. *2,6-trans-Isomer **6k′***: White solid. Mp: 97–99 °C. TLC: R_f 0.43 (19:1 hexane/EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45–7.43 (m, 2H), 7.28–7.21 (m, 5H), 7.15–7.09 (m, 3H), 5.69 (dqd, J=15.2, 6.4, 0.8 Hz, 1H), 5.44 (ddq, J=15.2, 6.4, 1.6 Hz, 1H), 4.91 (q, J=6.4 Hz, 1H), 4.13 (m, 1H), 2.66 (td, J=13.2, 3.6 Hz, 1H), 2.20 (m, 1H), 1.66 (dd, J=6.4, 1.6 Hz, 3H), 1.48 (dq, J=13.2, 3.2 Hz, 1H), 1.23–1.19 (m, 1H), 0.99 (d, J=6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 147.9, 132.8, 129.3, 128.4, 127.9, 127.5, 127.4, 126.0, 125.5, 74.5, 70.1, 48.3, 29.2, 28.4, 17.9, 15.4. HRMS m/z calcd for $C_{21}H_{24}NaO$ $[M+H]^+$ 293.1900, found 293.1892. IR (KBr film): 2937, 1494, 1111, 750 cm^{-1}.

Acknowledgements

This work was supported by the grant from the National Core Research Center Program (No. 2012-0000952) of the Ministry of Science & Technology and by the Ewha Global Top5 Grant 2011 of Ewha Womans University.

Supplementary data

^{1}H and ^{13}C NMR spectra of **2**–**4**, **6a**–**k′**, 1D-NOE spectra of **6g**, **6g′**, **6k**, and **6k′**, and experimental procedure for the synthesis of substrates **5a**–**k** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.03.120. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Elliot, M. C.; Williams, E. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2303–2340; (b) Elliot, M. C. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1291–1318; (c) Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309–3362; (d) Kotsubi, H. *Synlett* **1992**, 97–106.
2. (a) Weiss, C. J.; Marks, T. J. *Dalton Trans.* **2010**, *39*, 6576–6588; (b) Widenhoefer, R. A. *Chem.—Eur. J.* **2008**, *14*, 5382–5391.
3. Yu, X.; Seo, S.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 7244–7245.
4. (a) Kim, S.; Kang, D.; Shin, S.; Lee, P. H. *Tetrahedron Lett.* **2010**, *51*, 1899–1901; (b) Eom, D.; Kang, D.; Lee, P. H. *J. Org. Chem.* **2010**, *75*, 7447–7450; (c) Zhang, Z.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 283–285; (d) Belting, V.; Krause, N. *Org. Lett.* **2006**, *8*, 4489–4492; (e) Zhang, Z.; Liu, C.; Kinder, R. E.; Han, X.; Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2006**, *128*, 9066–9073.
5. (a) Arbour, J. L.; Rzepa, H. S.; White, A. J. P.; Hii, K. K. *Chem. Commun.* **2009**, 7125–7127; (b) Kim, S.; Lee, P. H. *Adv. Synth. Catal.* **2008**, *350*, 547–551; (c) Yang, C.-G.; Reich, N. W.; Shi, Z.; He, C. *Org. Lett.* **2005**, *7*, 4553–4556.
6. (a) Kim, S.; Lee, P. H. *J. Org. Chem.* **2012**, *77*, 215–220; (b) Adrio, L. A.; Quek, L. S.; Taylor, J. G.; Hii, K. K. *Tetrahedron* **2009**, *65*, 10334–10338; (c) Ito, Y.; Kato, R.;

Hamashima, K.; Kataoka, Y.; Oe, Y.; Ohta, T.; Furukawa, I. *J. Organomet. Chem.* **2007**, *692*, 691–697.

7. (a) Bhuvaneswari, S.; Jeganmohan, M.; Cheng, C.-H. *Chem.—Eur. J.* **2007**, *13*, 8285–8293; (b) Qian, H.; Han, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 9536–9537.
8. (a) Zanardi, A.; Mata, J. A.; Peris, E. *Organometallics* **2009**, *28*, 4335–4339; (b) Qiu, S.; Wei, Y.; Liu, G. *Chem.—Eur. J.* **2009**, *15*, 2751–2754; (c) Zawisza, A.; Fenet, B.; Sinou, D. *Eur. J. Org. Chem.* **2007**, 2296–2309; (d) Patil, N. T.; Lutete, L. M.; Wu, H.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 4270–4279; (e) Kadota, I.; Lutete, L. M.; Shibuya, A.; Yamamoto, Y. *Tetrahedron Lett.* **2001**, *42*, 6207–6210; (f) Jonasson, C.; Horvath, A.; Baeckvall, J.-E. *J. Am. Chem. Soc.* **2000**, *122*, 9600–9609.
9. Coulombel, L.; Rajzmann, M.; Pons, J.-M.; Olivero, S.; Duñach, E. *Chem.—Eur. J.* **2006**, *12*, 6356–6365.
10. (a) Seo, S.; Marks, T. J. *Chem.—Eur. J.* **2010**, *16*, 5148–5162; (b) Motta, A.; Fragala, I. L.; Marks, T. J. *Organometallics* **2010**, *29*, 2004–2012; (c) Dzudza, A.; Marks, T. J. *Chem.—Eur. J.* **2010**, *16*, 3403–3422; (d) Dzudza, A.; Marks, T. J. *Org. Lett.* **2009**, *11*, 1523–1526; (e) Seo, S.; Yu, X.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 263–276.
11. Hong, S.; Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 15878–15892.
12. Yeh, M.-C. P.; Yeh, W.-J.; Tu, L.-H.; Wu, J.-R. *Tetrahedron* **2006**, *62*, 7466–7470.
13. Yeh, M.-C. P.; Tsao, W.-C.; Tu, L.-H. *Organometallics* **2005**, *24*, 5909–5915.
14. Coulombel, L.; Weïwer, M.; Duñach, E. *Eur. J. Org. Chem.* **2009**, 5788–5795.
15. (a) Alcaide, B.; Almendros, P.; Alonso, J. M. *Molecules* **2011**, *16*, 7815–7843; (b) Wegner, H. A.; Auzias, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8236–8247; (c) Huang, H.; Zhou, Y.; Liu, H. *Beilstein J. Org. Chem.* **2011**, *7*, 897–936; (d) Hopkinson, M. N.; Gee, A. D.; Gouverneur, V. *Chem.—Eur. J.* **2011**, *17*, 8248–8262.
16. Jeong, Y.; Kim, D.-Y.; Choi, Y.; Ryu, J.-S. *Org. Biomol. Chem.* **2011**, *9*, 374–378.
17. Liu, X.-Y.; Li, C.-H.; Che, C.-M. *Org. Lett.* **2006**, *8*, 2707–2710.
18. Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2005**, *127*, 6966–6967.
19. (a) Sanguramath, R. A.; Hooper, T. N.; Butts, C. P.; Green, M.; McGrady, J. E.; Russell, C. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 7592–7595; (b) Yeh, M.-C. P.; Pai, H.-F.; Lin, Z.-J.; Lee, B.-R. *Tetrahedron* **2009**, *65*, 4789–4794; (c) Kovács, G.; Ujaque, G.; Lledós, A. *J. Am. Chem. Soc.* **2008**, *130*, 853–864; (d) Nguyen, R.-V.; Yao, X.; Li, C.-J. *Org. Lett.* **2006**, *8*, 2397–2399.
20. Brouwer, C.; He, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1744–1747.
21. No isomerization of **3** to **2** in the presence of TfOH was observed either at 60 °C after 24 h.