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Studies on the zirconium-mediated alkyne–aldehyde coupling reactions: a facile synthesis of stereodefined allylic alcohols and (*Z*)-2-en-4-yn-1-ols

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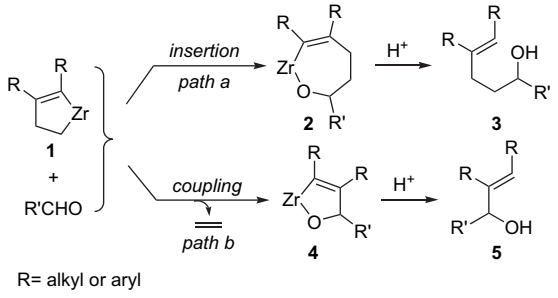
Abstract—An improved zirconium-mediated alkyne–aldehyde cross-coupling reaction has been achieved to afford the stereodefined (*Z*)-allylic alcohols or 3-iodinated allylic alcohols selectively via protonolysis or iodinolysis of the corresponding five-membered oxazirconacycles. This method has also been successfully applied to the synthesis of (*Z*)-enynols through cross-coupling reactions of three different components involving alkyne, aldehyde, and alkynyl bromide in a one-pot procedure.

1. Introduction

The selective coupling of alkynes with unsaturated molecules such as alkynes, alkenes, ketones, aldehydes, nitriles, etc. by use of a low-valent zirconocene equivalent has been shown to lead to a variety of carbo- and heterometallacycles.[1] The in situ generated zirconacycles are important intermediates in a wide range of selective (including chemo-, regio-, and stereoselective) reactions.[1] Although much progress has been achieved in this area, there are only a limited number of reports on the alkyne coupling reactions with aldehydes to give five-membered oxazirconacycles.[2] The known procedures involve: (i) addition of aldehyde to zirconocene–alkyne complexes.[2e–g] The alkyne complexes used for this type of reaction are usually prepared by hydrozirconation of an alkyne followed by methylation with MeLi and elimination of methane from the alkenyl(methyl)zirconocene. The resulting alkyne complexes are trapped with trimethylphosphine.[2e,f] This method requires costly phosphine ligands and $Cp_2Zr(H)Cl$. (ii) Reaction of zirconacyclopentenes with aldehydes as reported by Takahashi et al. (only one alkyne was tested to afford moderate NMR yields of oxazirconacycles).[2a,b] However, there is no systematic studies on this chemistry. In principle, two types of reactions of zirconacyclopentenes with aldehydes have been reported, one involves insertion of aldehydes at alkyl–zirconium bond (Scheme 1, path a)[2b] and the other involves the coupling of alkynes with aldehydes with concomitant extrusion of ethylene (path b).[2a] Negishi et al. found that when the reaction was run at low temperature (≤25 °C), the insertion product **3** became the major product, while the formation of **5** was less than 2%. Recently, we have developed an efficient synthetic approach to stereodefined dihydrofurans or furans via gold-catalyzed cyclization of (*Z*)-2-en-4-yn-1-ols.[3] Within this program, (*Z*)-enynols derived from zirconium-mediated alkyne–aldehyde coupling reactions were substrates.



Scheme 1. Reaction patterns of aldehyde addition with metallacyclopentenes.

Initially, we applied the literature reaction conditions[2a] (addition of aldehyde to zirconacycle at 0 °C, then warmed up to 50 °C) for the alkyne–aldehyde coupling via zirconacyclopentenes. However, it was found that the byproducts of direct insertion reactions were always formed in comparable yields along with desired allylic alcohols. For example, the reaction between 1,2-dipropylzirconacyclopentene **1a** and benzaldehyde (1.5 equiv) afforded insertion product 1-phenyl-4-propyloct-4-en-1-ol **3a** and coupling product 1-phenyl-2-propylhex-2-en-1-ol **5a** in 98% combined NMR yield with

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a ratio of 1:1 (determined by NMR). These unsatisfactory results prompted us to optimize the reaction conditions to enhance the selectivity of the desired cross-coupling reactions. In this paper, we describe the detailed studies on Zr-mediated alkyne–aldehyde coupling reactions under improved conditions, in which the above-mentioned insertion reactions are mostly suppressed. This reaction has also been applied to an efficient and one-pot synthesis of highly substituted, stereodefined allylic alcohols and (*Z*)-2-en-4-yn-1-ols.

2. Results and discussion

2.1. Zirconium-mediated alkyne–aldehyde coupling reactions

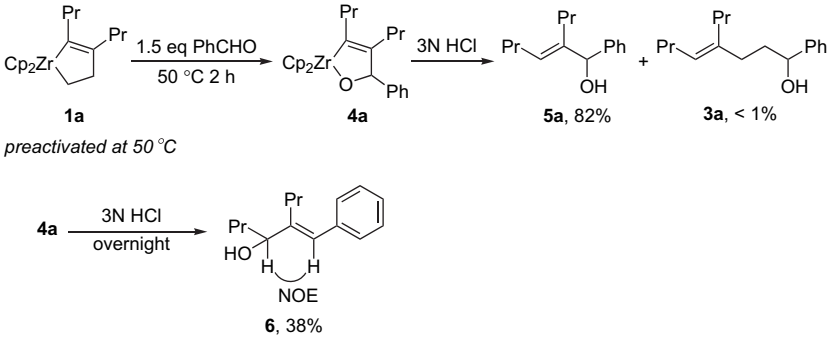
Zirconacyclopentenes are known to undergo cross-coupling reaction with unsaturated compounds through facile β,β′-carbon–carbon bond cleavage reaction along with elimination of one ethylene molecule.[4] It seems that once the system is 'preactivated', the behavior of ethylene ligand should be more labile and easy to be eliminated from the metal center. Thus this system is expected to be feasible to perform the desired alkyne–aldehyde cross-coupling reactions, and minimize the possibility of direct insertion reactions. Consequently, we found that simply heating the reaction mixture of zirconacycle **1a** up to 50 °C for a few minutes followed by slow addition of benzaldehyde, the desired coupling product **5a** was formed in 82% NMR yield with high isomerical purity (>99%) as shown in Scheme 2. The amount of **3a**, which is the major product at 0 °C, was <1%. Interestingly, when the reaction mixture of **4a** was quenched with 3 N HCl for overnight, the stereodefined product **6** could be generated in 38% isolated yield through acid-induced allylic isomerization.[5] The (*E*)-configuration of C=C bond in **6** was determined by the ^{1}H–^{1}H NOESY spectrum.

The results of the preparation of allylic alcohols from alkynes and aldehydes are summarized in Table 1. As shown in Table 1, alkyl, aryl, and heteroaryl aldehydes are all compatible with coupling conditions. The corresponding allylic alcohols were formed in good to high yields. For alkyl-substituted alkyne, addition of aldehyde at 0 °C (then warmed up to 50 °C) always resulted in the formation of byproducts of type **3**. The ratio of **3/5** is varied from 0.6:1 to 2.5:1.[6] However, under the 'preactivated' conditions, the selectivity was significantly improved to more than 89%, implying the undesired formation of **3** was mostly suppressed (Table 1, entry 1–4). We checked two cases of the reaction with aryl-substituted alkyne, the results indicated that there was no significant difference in product yields and selectivity under the above two reaction conditions.[6,7] The coupling product **5** was formed predominantly with >98% selectivity (entry 5–10). When bis(thienyl)alkyne was employed, the corresponding alcohol **5h** was formed in a good yield of 72% (entry 8). Substitution at C-1 with a thienyl group resulted in a quick allylic isomerization during the acidic quenching, and the two products of **5i** were obtained in a ratio of 3:1 with a combined yield of 88% (entry 9). When the aldehyde tethered with an alkyne moiety such as 4-(phenylethynyl)benzaldehyde was used, the coupling reaction selectively occurred at the carbonyl moiety, furnishing the product **5j** in 90% yield, while the triple bond in the substrate remained intact (entry 10). Interestingly, with 1-trimethylsilyl-1-hexyne, two regioisomers of **5k** and **5l** were formed in 22% and 33% yields, respectively (entry 11). The regioselectivity is lower than that observed in the coupling reaction of silylated alkynes with nitriles,[4a] in which only one regioisomer (silyl group substituted at the α-position in azazirconacycles) was observed.

2.2. Iodination of oxazirconacycles 4

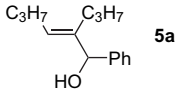
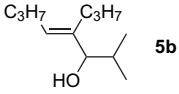
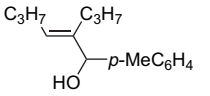
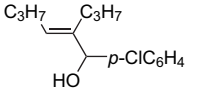
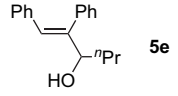
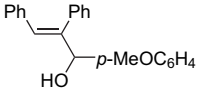
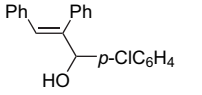
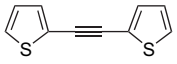
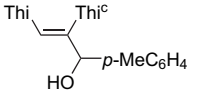
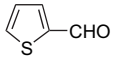
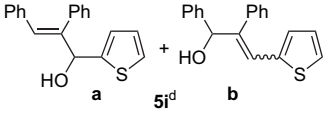
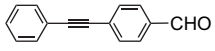
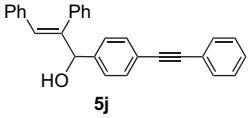
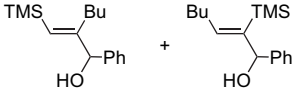
The oxazirconacycles **4** produced by this method are versatile synthetic intermediates, which can be trapped with electrophiles to afford tetrasubstituted olefins with high stereoselectivity. We found that iodination of zirconacycle **4a** with 3 equiv of iodine at room temperature proceeded at the alkenyl-zirconium moiety to afford stereodefined (*Z*)-3-iodo-1-phenyl-2-propylhex-2-en-1-ol **7a**[8] in 59% yield (Scheme 3). The use of 1.5 equiv of I_2 resulted in a prolonged reaction time (55% for 5 h).

Takahashi et al. had reported that addition of copper salt is effective for the iodination of C(sp^2)–Zr bond in zirconacyclopentadienes and zirconacyclopentenes.[9] With the use of 20% CuI, the amount of iodination reagent (I_2) could be reduced to 1.2 equiv, and the product **7a** was formed in 56% yield but prolonged reaction time (8 h) was required. The results of iodination are summarized in Table 2. ICl could also be used as an effective iodination reagent (Table 2, entries 2, 4–7). It should be noted that in most cases, ICl was more effective than I_2. Interestingly, when diphenyl-substituted zirconacycle **4b** was subjected to CuI-mediated iodination condition, the product was formed as a mixture of *Z* and *E* isomers in 76% yield with the ratio

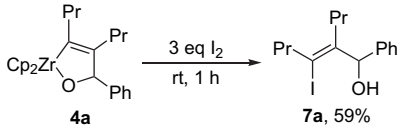


Scheme 2. Alkyne–aldehyde coupling reaction through a preactivated zirconacyclopentene.

Table 1. Formation of stereodefined allylic alcohols via alkyne–aldehyde coupling reactions

Entry	Alkyne	Aldehyde	Product	Yield[a] %	Selectivity %	
					5	**3**
1	C_3H_7—≡—C_3H_7	PhCHO	 **5a**	82 (63)	>99	<1
2	C_3H_7—≡—C_3H_7	^{i}PrCHO	 **5b**	61 (56)	90	10
3	C_3H_7—≡—C_3H_7	*p*-MeC_6H_4CHO	 **5c**	69 (59)	97	3
4	C_3H_7—≡—C_3H_7	*p*-ClC_6H_4CHO	 **5d**	80 (63)[b]	89	11
5	Ph—≡—Ph	^{n}PrCHO	 **5e**	86 (66)	99	<1
6	Ph—≡—Ph	*p*-$MeOC_6H_4CHO$	 **5f**	98 (60)	98	<2
7	Ph—≡—Ph	*p*-ClC_6H_4CHO	 **5g**	93 (69)	>99	<1
8		*p*-MeC_6H_4CHO	 **5h**	72 (57)	>99	<1
9	Ph—≡—Ph		 **a** **5i**[d] **b**	88 (70)	>99	<1
10	Ph—≡—Ph		 **5j**	90 (64)	>99	<1
11	TMS—≡—Bu	PhCHO	 **5k** **5l**	77 (55)[e]	—	—

[a] NMR yields and isolated yields are given in parentheses. All the reactions were carried out at 50 °C for 1–3 h by the addition of 1.5 equiv of aldehyde to a reaction mixture of zirconacyclopentenes preactivated at 50 °C.
[b] The product was concomitant with small amount of byproduct.
[c] Thi is 2-thienyl group.
[d] The ratio of **a/b** (or **b/a**)=3:1. Only one alkene isomer of **b** was obtained, the geometry of C=C bond in isomer **b** was not defined.
[e] Combined yield. Compounds **5k** and **5l** were isolated in 22% and 33% yields, respectively.



4a **7a**, 59%

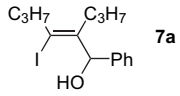
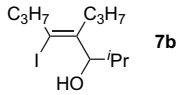
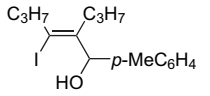
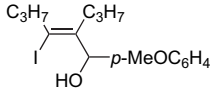
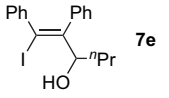
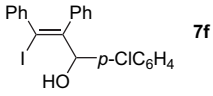
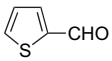
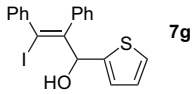
Scheme 3. Iodination of oxazirconacycles **4**.

of 4:1 (Scheme 4). This result indicated that stereoisomerization occurred during the reaction. A similar isomerization was observed in the iodination of phenyl-substituted vinyl zirconocene complexes.[10] However, without the use of copper salt, no isomerization occurred as shown in Table 2, entry 5.

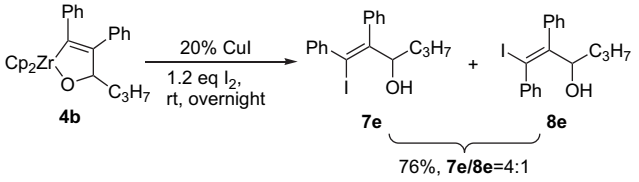
2.3. One-pot procedure for the formation of (*Z*)-enynols

(*Z*)-2-En-4-yn-1-ols have been utilized in recent years as highly versatile precursors for diversity-oriented organic synthesis. They undergo a variety of transformations to generate heterocycles such as furans or dihydrofurans, which are useful intermediates in the synthesis of natural products and pharmaceuticals.[11] Therefore, a stereoselective and efficient synthesis of these intermediates is of great interest. The

Table 2. Synthesis of iodinated allylic alcohols via iodinolysis of oxazirconacyclopentenes

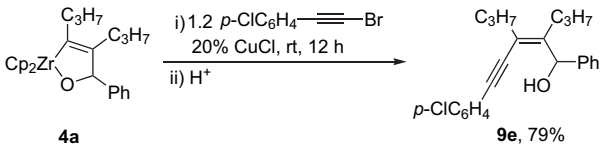
Entry	Alkyne	Aldehyde	Product	Yield[a] (%)
1	C_3H_7—≡—C_3H_7	PhCHO	 **7a**	59[b]
2	C_3H_7—≡—C_3H_7	^{i}PrCHO	 **7b**	42
3	C_3H_7—≡—C_3H_7	*p*-MeC_6H_4CHO	 **7c**	58[b]
4	C_3H_7—≡—C_3H_7	*p*-$MeOC_6H_4CHO$	 **7d**	53
5	Ph—≡—Ph	^{n}PrCHO	 **7e**	55
6	Ph—≡—Ph	*p*-ClC_6H_4CHO	 **7f**	50
7	Ph—≡—Ph		 **7g**	40

[a] Isolated yields. Unless noted, all the reactions were carried out at 0 °C for 1 h using 3 equiv of ICl.
[b] The reaction was carried out at room temperature using 3 equiv of I_2.

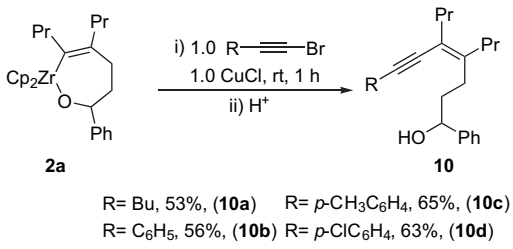


Scheme 4. Stereoisomerization during the iodination process.

preparation of (*Z*)-enynols is usually achieved through multi-step transformations involving Pd/Cu-catalyzed coupling of the terminal alkynes with vinylic halides, addition of alk-1-ynes to vinyl ketones followed by acid-catalyzed allylic isomerization, reduction of methyl (*Z*)-2-en-4-ynoates, KO^{t}Bu-promoted coupling reactions of aldehydes and alkynes, etc.[11a,c,i] Nevertheless, enhancing the efficiency of the synthesis of these compounds is still highly demanded. We recently reported an efficient synthetic approach to stereodefined (*Z*)-enynols **1** via zirconium-mediated cross-coupling reactions of three different components involving alkyne, ketone, and alkynyl bromide in a one-pot procedure.[12] This method is useful for the construction of (*Z*)-enynols with a tertiary alcoholic group at C-1. We envisioned that the same methodology could be used here to provide (*Z*)-enynols with a secondary alcoholic group at C-1. Our first target was to find suitable reaction conditions under which alkynylation of oxazirconacycles **4** would efficiently proceed. Thus the coupling reaction of zirconacycle **4a** with alkynyl bromide was chosen to be tested under our standard reaction conditions used in alkyne–ketone coupling system.[12] Treatment of **4a** with 2 equiv of CuCl, 2 equiv of LiCl, and *p*-chlorophenyl ethynyl bromide at room temperature and stirring the mixture for 12 h afforded (*Z*)-enynol **9e** in 56% yield after hydrolysis. However, further optimization of the reaction condition revealed that the reaction proceeded with 20% of CuCl and 1.2 equiv of alkynyl bromide in the absence of LiCl to afford the higher yield of 79% (Scheme 5). The reaction mechanism for this alkynylation was assumed through transmetalation of Zr–C(sp^2) bond to a Cu–C bond,[13] which would be more reactive toward electrophiles, followed by subsequent sp–sp^2 coupling reaction along with the elimination of CuBr. CuBr can also effect the transmetalation reactions. Therefore, the alkynylation can be carried out with a catalytic amount of CuCl. This reaction also indicated that aldehyde-derived zirconacycles **4** are very reactive toward electrophiles and may have valuable synthetic potential for other transformations. The representative reactions of various alkynyl bromides with zirconacycles **4** are listed in Table 3. Alkynyl bromide bearing alkyl or aryl substituent reacted very well with oxazirconacycles to afford enynols **9** in 46–83% yields. The cyclohexenyl substituted alkynyl bromide has also been examined, and the corresponding product **9h** was formed smoothly in 80% yield (Table 3, entry 8). A wide range of aromatic aldehydes could be used, furnishing the corresponding enynols in good to high yields. When an aliphatic aldehyde such as butyraldehyde was subjected to the reaction, the product **9i** was formed in a satisfied yield of 59% (Table 3, entry 9). On the other hand, this alkynylation could be efficiently applied to the seven-membered oxazirconacycles **2** that was formed in high yield through direct insertion reactions.[2a] As shown in Scheme 6, the reaction of **2a** with a variety of alkynyl bromide in the presence of a stoichiometric amount of CuCl afforded **10a–d** in good yields.



Scheme 5. Alkynylation of oxazirconacycle **4**.



Scheme 6. Alkynylation of seven-membered oxazirconacycles.

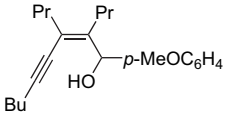
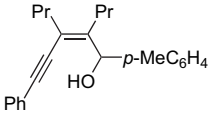
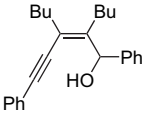
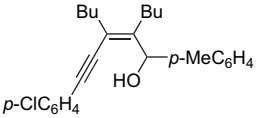
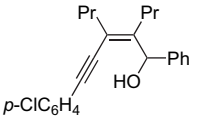
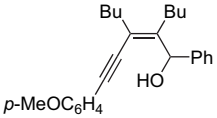
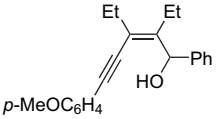
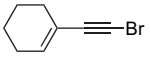
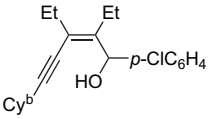
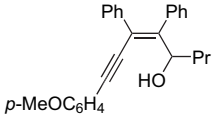
In summary, we have developed an improved procedure for zirconium-mediated alkyne–aldehyde coupling reactions. The stereodefined allylic alcohols or 3-iodinated allylic alcohols were selectively formed via protonolysis or iodinolysis of the corresponding five-membered oxazirconacycles. The method has also been successfully applied to the synthesis of (*Z*)-enynols through three-component coupling reactions of alkyne, aldehyde, and alkynyl bromide in a one-pot procedure. We are currently exploring the new synthetic potential of oxazirconacycles.

3. Experimental section

3.1. General methods

All reactions were carried out using standard Schlenk techniques under nitrogen. THF was distilled from sodium/

Table 3. Formation of (*Z*)-2-en-4-yn-1-ol through three-component coupling reactions

Entry	Alkyne	Aldehyde	Alkynyl bromide	Product	Yield[a] (%)
1	Pr—≡—Pr	*p*-$MeOC_6H_4CHO$	Bu—≡—Br	 **9a**	46
2	Pr—≡—Pr	*p*-MeC_6H_4CHO	Ph—≡—Br	 **9b**	83
3	Bu—≡—Bu	PhCHO	Ph—≡—Br	 **9c**	77
4	Bu—≡—Bu	*p*-MeC_6H_4CHO	*p*-ClC_6H_4—≡—Br	 **9d**	68
5	Pr—≡—Pr	PhCHO	*p*-ClC_6H_4—≡—Br	 **9e**	79
6	Bu—≡—Bu	PhCHO	*p*-$MeOC_6H_4$—≡—Br	 **9f**	73
7	Et—≡—Et	PhCHO	*p*-$MeOC_6H_4$—≡—Br	 **9g**	78
8	Et—≡—Et	*p*-ClC_6H_4CHO		 **9h**	80
9	Ph—≡—Ph	PrCHO	*p*-$MeOC_6H_4$—≡—Br	 **9i**	59

[a] Isolated yields. All the reactions were carried out at room temperature for overnight using 20% CuCl and 1.2 equiv of alkynyl bromide.
[b] Cy is cyclohexenyl group.

benzophenone. All commercial reagents were used without further purification. Zirconocene dichloride, aldehydes, and alkynes were used as purchased. Ethylmagnesium bromide (1.0 M solution in THF) was used as purchased and/or prepared in this lab (titrated[14] as 0.94–1.07 M THF solution). Zirconacyclopentenes **1**[2a] were prepared according to the previously published procedures. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ (containing 1% TMS) solutions. ^{1}H NMR spectra were recorded with tetramethylsilane (0.00 ppm) as an internal standard; ^{13}C NMR spectra were recorded with $CDCl_3$ (77.00 ppm) as an internal standard. NMR yields were determined using dibromomethane as an internal standard.

3.2. A typical procedure for zirconium-mediated alkyne–aldehyde coupling reactions under 'preactivated' conditions

To a solution of Cp_2ZrCl_2 (0.365 g, 1.25 mmol) in THF (5 mL) was added EtMgBr (1.0 M THF solution, 2.5 mmol) at −50 °C. After stirring for 1 h at the same temperature, 4-octyne (0.11 g, 1 mmol) was added and the reaction mixture was warmed up to 0 °C and stirred for 3 h. The thus formed zirconacyclopentene was heated up to 50 °C for a few minutes (ca. 5 min), followed by slow addition of benzaldehyde (0.15 mL, 1.5 mmol) at the same temperature. After stirring for 2 h, the mixture was quenched with 3 N HCl solution (usually, within 2 min) and extracted with ether. The extract was washed with $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=15:1). An orange-yellow liquid of allylic alcohol **5a** (137 mg, 63%) was obtained. NMR yield: 82%.

3.2.1. (*E*)-1-Phenyl-2-propylhex-2-en-1-ol (5a). ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.80 (t, J=7.2 Hz, 3H), 0.92 (t, J=7.2 Hz, 3H), 1.14–1.47 (m, 4H), 1.75–1.99 (m, 2H), 2.04 (q, J=7.2 Hz, 2H), 2.32 (br s, 1H), 5.08 (s, 1H), 5.58 (t, J=7.8 Hz, 1H), 7.19–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.8, 14.3, 22.6, 22.9, 29.6, 29.8, 77.9, 126.5, 127.0, 127.1, 128.0, 141.2, 142.8; IR (neat) 3421, 2958, 2930, 2871, 1491, 1454, 1034 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{22}O$ 218.1671, found 218.1679.

3.2.2. (*E*)-2-Methyl-4-propyloct-4-en-3-ol (5b). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=30:1) afforded the title product in 56% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.83 (d, J=6.6 Hz, 3H), 0.86–0.93 (m, 9H), 1.29–1.48 (m, 5H), 1.69–1.80 (m, 1H), 1.86–2.03 (m, 4H), 3.61 (d, J=7.2 Hz, 1H), 5.32 (t, J=7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9, 14.6, 18.1, 19.8, 22.9, 23.2, 29.6, 30.0, 31.6, 82.7, 127.7, 141.1; IR (neat) 3442, 2958, 2871, 1466, 1379, 1006 cm^{-1}; HRMS (EI) calcd for $C_9H_{17}O$ $[M-C_3H_7]^+$ 141.1279, found 141.1282.

3.2.3. (*E*)-2-Propyl-1-*p*-tolylhex-2-en-1-ol (5c). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=15:1) afforded the title product in 59% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.82 (t, J=6.9 Hz, 3H), 0.92 (t, J=7.5 Hz, 3H), 1.20–1.30 (m, 2H), 1.42 (q, J=7.3 Hz, 2H), 1.74–1.84 (m, 1H), 1.92–2.13 (m, 4H), 2.32 (s, 3H), 5.07 (s, 1H), 5.60 (t, J=7.2 Hz, 1H), 7.11 (d, J=8.1 Hz, 2H), 7.21 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9, 14.4, 21.0, 22.6, 22.9, 29.6, 29.9, 77.7, 126.5, 126.6, 128.8, 136.8, 139.9, 141.2; IR (neat) 3380, 2958, 2930, 2870, 1512, 1464, 1036 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{24}O$ 232.1827, found 232.1837.

3.2.4. (2*E*)-1-(4-Chlorophenyl)-2-propylhex-2-en-1-ol (5d). Purification of the crude product by column chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=8:1) afforded the title product in 63% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.81 (t, J=7.2 Hz, 3H), 0.92 (t, J=7.2 Hz, 3H), 1.16–1.45 (m, 4H), 1.76–2.08 (m, 5H), 5.10 (s, 1H), 5.58 (t, J=7.2 Hz, 1H), 7.26–7.28 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.90, 14.40, 22.75, 22.86, 29.65, 29.74, 77.58, 127.85, 127.93, 128.23, 132.86, 141.02, 141.22; IR (neat) 3382, 2958, 2871, 1596, 1489, 1464, 1091, 828 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{21}OCl$ 252.1281, found 252.1281.

3.2.5. (*E*)-1,2-Diphenylhex-1-en-3-ol (5e). Purification of the crude product by column chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=5:1) afforded the title product in 66% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89 (t, J=6.6 Hz, 3H), 1.37–1.56 (m, 4H), 1.87 (br s, 1H), 4.45 (t, J=6.0 Hz, 1H), 6.65 (s, 1H), 6.90–6.93 (m, 2H), 7.05–7.10 (m, 3H), 7.16–7.20 (m, 2H), 7.29–7.36 (m, 3H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9, 18.9, 37.54, 77.1, 126.6, 126.7, 127.3, 127.8, 128.6, 129.2, 129.2, 136.5, 138.4, 144.9; IR (neat) 3488, 2870, 1598, 1494 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{20}O$ 252.1514, found 252.1510.

3.2.6. (*E*)-1-(4-Methoxyphenyl)-2,3-diphenylprop-2-en-1-ol (5f). The mixture was quenched with 1 N HCl. Purification of the crude product by column chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=5:1 to 2:1) afforded the title product in 60% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.41 (br s, 1H), 3.74 (s, 3H), 5.45 (s, 1H), 6.77–7.24 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 55.1, 78.5, 113.6, 126.5, 126.7, 127.2, 127.8, 128.1, 128.4, 129.2, 129.3, 133.7, 136.4, 138.2, 144.1, 158.9; IR (neat) 3419, 2930, 1609, 1510, 1249, 1173, 1033 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{20}O_2$ 316.1463, found 316.1466.

3.2.7. (*E*)-1-(4-Chlorophenyl)-2,3-diphenylprop-2-en-1-ol (5g). Purification of the crude product by column chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=10:1 to 5:1) afforded the title product in 69% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.49 (br s, 1H), 5.48 (s, 1H), 6.82 (s, 1H), 6.88–6.94 (m, 4H), 7.05–7.09 (m, 3H), 7.18–7.28 (m, 7H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 78.5, 127.0, 127.4, 127.4, 127.9, 128.1, 128.3, 128.5, 129.2, 129.3, 133.2, 136.0, 137.6, 140.1, 143.5; IR (neat) 3385, 3055, 1598, 1491, 1446, 1090 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{17}ClO$ 320.0968, found 320.0952.

3.2.8. (*Z*)-2,3-Di(2-thienyl)-1-*p*-tolylprop-2-en-1-ol (5h). Purification of the crude product by column chromatography on silica gel (300–400 mesh) (petroleum ether/ethyl acetate=25:1 to 20:1) afforded the title product in 57% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.24 (br s, 1H), 2.33 (s, 3H), 5.43 (s, 1H), 6.70 (dd, J=3.3, 1.2 Hz, 1H), 6.87–7.24 (m, 9H), 7.36 (dd, J=5.1, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$,

Me_4Si) δ 21.2, 78.5, 104.8, 124.1, 126.1, 126.7, 126.9, 127.3, 128.6, 129.0, 129.4, 134.3, 136.8, 137.6, 138.3, 139.5; IR (neat) 3415, 2920, 2859, 1511, 1439, 1423, 1376, 1035, 700 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}OS_2$ 312.0643, found 312.0641.

3.2.9. (*E*)-2,3-Diphenyl-1-(2-thienyl)prop-2-en-1-ol and 1,2-diphenyl-3-(2-thienyl)prop-2-en-1-ol (5i). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afforded the title products as a mixture of two isomers in the ratio of 3:1 with a combined yield of 70%. ^1H NMR ($CDCl_3$, Me_4Si) two isomers δ 2.79 (br s, 1H), 2.95 (br s, 1H), 5.36 (s, 1H), 5.66 (s, 1H), 6.75–7.23 (m); ^{13}C NMR ($CDCl_3$, Me_4Si) two isomers δ 74.7, 78.7, 120.2, 125.0, 125.1, 125.9, 125.9, 126.6, 126.7, 126.8, 126.9, 127.3, 127.5, 127.8, 127.8, 128.0, 128.4, 128.4, 128.6, 129.2, 129.3, 129.7, 136.1, 137.1, 137.6, 139.9, 141.2, 141.9, 143.2, 146.2; HRMS (EI) calcd for $C_{19}H_{16}OS$ 292.0922, found 292.0930.

3.2.10. (*E*)-2,3-Diphenyl-1-(4-phenylethynyl-phenyl)-prop-2-en-1-ol (5j). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afforded the title product in 64% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 2.35 (br s, 1H), 5.53 (s, 1H), 6.85 (s, 1H), 6.90–6.96 (m, 3H), 7.06–7.09 (m, 3H), 7.19–7.23 (m, 3H), 7.28–7.34 (m, 6H), 7.45–7.53 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 78.9, 89.3, 89.5, 122.4, 123.1, 126.7, 126.9, 127.4, 127.5, 127.9, 128.2, 128.3, 128.5, 129.3, 129.4, 131.5, 131.5, 136.1, 137.6, 141.8, 143.5; IR (neat) 3564, 3401, 2974, 2855, 1598, 1508, 1494, 1443, 1069 cm^{-1}; HRMS (EI) calcd for $C_{29}H_{22}O$ 386.1671, found 386.1672.

3.2.11. (*E*)-1-Phenyl-2-((trimethylsilyl)methylene)hexan-1-ol (5k). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=30:1) afforded the title product in 22% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.03 (s, 9H), 0.73 (t, J=6.9 Hz, 3H), 1.10–1.28 (m, 4H), 1.68–1.77 (m, 1H), 1.90 (br s, 1H), 1.98–2.08 (m, 1H), 5.01 (s, 1H), 5.68 (d, J=1.2 Hz, 1H), 7.13–7.27 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.3, 13.9, 23.1, 32.3, 33.1, 77.6, 122.2, 127.0, 127.7, 128.4, 142.4, 159.5; IR (neat) 3416, 2957, 2872, 1614, 1494, 1454, 1248, 836, 699 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{26}OSi$ 262.1753, found 262.1757.

3.2.12. (*Z*)-1-Phenyl-2-(trimethylsilyl)hept-2-en-1-ol (5l). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=30:1) afforded the title product in 33% isolated yield. The structure was also confirmed by 2D NMR experiments of ^1H–^1H COSY, HMQC, and HMBC. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.20 (s, 9H), 1.12 (t, J=6.6 Hz, 3H), 1.52–1.64 (m, 4H), 2.08 (br s, 1H), 2.44 (q, J=7.2 Hz, 2H), 5.46 (s, 1H), 6.50 (dt, J=7.8, 0.9 Hz, 1H), 7.41–7.54 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 0.5, 14.1, 22.6, 31.5, 32.1, 78.8, 126.9, 127.1, 128.1, 140.9, 143.2, 144.2; IR (neat) 3403, 2957, 2927, 2873, 1609, 1493, 1453, 1248, 840, 700 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{26}OSi$ 262.1753, found 262.1758.

3.2.13. (*E*)-1-Phenyl-2-propylhex-1-en-3-ol (6). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.89–0.98 (m, 6H), 1.36–1.67 (m, 6H), 1.75 (br s, 1H), 2.10–2.20 (m, 1H), 2.26–2.36 (m, 1H), 4.21 (t, J=6.6 Hz, 1H), 6.51 (s, 1H), 7.18–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 14.5, 19.1, 22.5, 30.5, 38.1, 76.2, 125.3, 126.3, 128.1, 128.6, 137.7, 145.5; IR (neat) 3374, 2958, 2931, 2871, 1493, 1455, 1022, 748, 698 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{20}$ $[M-H_2O]^+$ 200.1565, found 200.1567.

3.3. A typical procedure for iodination reactions

To a mixture of oxazirconacycle **4a** prepared as above was added iodine (0.76 g, 3 mmol) at room temperature. After stirring for 1 h, the mixture was quenched with 3 N HCl solution and extracted with ether. The extract was washed with $NaHCO_3$, $Na_2S_2O_3$, brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate=30:1 to 20:1). A light-yellow liquid of allylic alcohol **7a** (204 mg, 59%) was obtained. The spectral data are the same as previous published one.[8]

3.3.1. (*Z*)-5-Iodo-2-methyl-4-propyloct-4-en-3-ol (7b). Purification of the crude product by column chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=30:1 to 20:1) afforded the title product in 42% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.86 (d, J=6.9 Hz, 3H), 0.91–0.96 (m, 6H), 1.06 (d, J=6.6 Hz, 3H), 1.25–1.63 (m, 4H), 1.67 (s, 1H), 1.77–1.88 (m, 1H), 2.00–2.10 (m, 1H), 2.19–2.29 (m, 1H), 2.41–2.64 (m, 2H), 4.29 (d, J=8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.0, 14.6, 18.9, 19.2, 23.1, 24.3, 31.1, 32.5, 43.1, 87.1, 108.5, 144.3; IR (neat) 3417, 2960, 2871, 1615, 1464, 1379, 1095, 1022 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{23}IO$ 310.0794, found 310.0800.

3.3.2. (*Z*)-3-Iodo-2-propyl-1-*p*-tolylhex-2-en-1-ol (7c). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=30:1) afforded the title product in 58% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.77 (t, J=7.2 Hz, 3H), 0.94 (t, J=7.5 Hz, 3H), 0.99–1.06 (m, 1H), 1.29–1.39 (m, 1H), 1.57–1.69 (m, 2H), 1.92–2.02 (m, 1H), 2.09–2.19 (m, 2H), 2.30 (s, 3H), 2.48–2.59 (m, 2H), 5.89 (s, 1H), 7.13 (d, J=8.1 Hz, 2H), 7.33 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.0, 14.5, 21.1, 23.1, 23.9, 30.8, 43.1, 82.4, 108.3, 125.2, 128.8, 136.7, 138.6, 145.1; IR (neat) 3423, 2959, 2929, 2870, 1511, 1459, 1171, 1098, 1034 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{23}IO$ 358.0794, found 358.0804.

3.3.3. (*Z*)-3-Iodo-1-(4-methoxyphenyl)-2-propylhex-2-en-1-ol (7d). The solvent was evaporated in vacuo (a small amount of Et_3N was added in order to avoid the decomposition of the product during the evaporation) and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate=15:1). The title compound was formed in 53% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.78 (t, J=7.5 Hz, 3H), 0.94 (t, J=7.2 Hz, 3H), 0.99–1.07 (m, 1H), 1.25–1.41 (m, 1H), 1.57–1.69 (m, 2H), 1.93–2.19 (m, 3H), 2.51–2.57 (m, 2H), 3.79 (s, 3H), 5.87 (d, J=3.6 Hz, 1H), 6.86 (d, J=6.6 Hz, 2H), 7.36 (d, J=6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.0, 14.5, 23.1, 23.9, 30.8, 43.1, 55.2, 82.2, 108.2, 113.5, 126.5, 133.7, 145.2, 158.7; IR (neat) 3471, 2931, 2870, 1611, 1510, 1463, 1248, 1170,

1036 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{23}IO_2$ 374.0743, found 374.0728.

3.3.4. (*Z*)-1-Iodo-1,2-diphenylhex-1-en-3-ol (7e). Purification of the crude product by column chromatography on silica gel (300–400 mesh) (petroleum ether/ethyl acetate=25:1) afforded the title product in 55% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.98 (t, J=5.7 Hz, 3H), 1.43–1.67 (m, 5H), 4.92–4.97 (m, 1H), 6.95–7.16 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 19.0, 37.7, 80.3, 101.5, 127.0, 127.2, 127.5, 127.7, 129.2, 130.0, 136.1, 143.9, 149.6; IR (neat) 3406, 2957, 2931, 2871, 1488, 1441, 1117, 1072, 697 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{19}IO$ 378.0481, found 378.0491.

3.3.5. (*Z*)-1-(4-Chlorophenyl)-3-iodo-2,3-diphenylprop-2-en-1-ol (7f). Purification of the crude product by column chromatography on silica gel (300–400 mesh) (petroleum ether/ethyl acetate=25:1) afforded the title product in 50% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 2.29 (s, 1H), 6.26 (s, 1H), 6.66–6.69 (m, 2H), 6.94–7.09 (m, 8H), 7.28–7.41 (m, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 81.1, 103.1, 127.1, 127.3, 127.4, 127.6, 127.6, 128.4, 129.2, 130.2, 133.2, 135.0, 139.6, 143.6, 148.8; IR (neat) 3416, 1705, 1597, 1488, 1441, 1090, 1013 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{16}ClO$ $[M-I]^+$ 319.0890, found 319.0881.

3.3.6. (*Z*)-3-Iodo-2,3-diphenyl-1-thiophen-2-ylprop-2-en-1-ol (7g). The solvent was evaporated in vacuo (a small amount of Et_3N was added in order to avoid the decomposition of the product during the evaporation) and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate=20:1). The title compound was formed in 40% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 2.34 (s, 1H), 6.39 (s, 1H), 6.85–6.88 (m, 2H), 6.99–7.16 (m, 10H), 7.27–7.29 (d, J=5.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 79.5, 102.0, 124.2, 125.1, 126.9, 127.5, 127.5, 127.7, 127.8, 129.2, 130.2, 135.0, 143.7, 145.4, 148.7; IR (neat) 3409, 3054, 1488, 1441, 1068, 1030, 697 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{15}IOS$ 417.9888, found 417.9900.

3.3.7. (*E*)-1-Iodo-1,2-diphenylpent-1-en-3-ol (8e). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.76 (t, J=6.9 Hz, 3H), 1.23–1.47 (m, 5H), 4.43 (t, J=6.6 Hz, 1H), 7.24–7.47 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.73, 18.79, 38.31, 70.05, 103.17, 127.77, 128.09, 128.25, 128.31, 128.34, 129.25, 141.97, 142.95, 151.17; IR (neat) 3431, 3055, 2930, 2871, 1598, 1492, 1443, 1012, 700 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{19}IO$ 378.0481, found 378.0497.

3.4. A typical procedure for alkynylation reactions

To a mixture of oxazirconacycle **4a** prepared as above were added CuCl (0.02 g, 0.2 mmol) and 1-bromoethynyl-4-chloro-benzene (0.26 g, 1.2 mmol). After stirring at room temperature for overnight, the mixture was quenched with 3 N HCl solution and extracted with ether. The extract was washed with $NaHCO_3$, brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was purified by chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=15:1). A yellow liquid of (*Z*)-enynol **9e** (0.28 g, 79%) was obtained.

3.4.1. (*Z*)-5-(4-Chlorophenyl)-1-phenyl-2,3-dipropylpent-2-en-4-yn-1-ol (9e). ^1H NMR ($CDCl_3$, Me_4Si) δ 0.80 (t, J=7.2 Hz, 3H), 0.97 (t, J=7.5 Hz, 3H), 1.26–1.36 (m, 2H), 1.61–1.71 (m, 2H), 1.94–2.09 (m, 2H), 2.23 (t, J=7.2 Hz, 2H), 2.44 (s, 1H), 6.27 (s, 1H), 7.19–7.32 (m, 7H), 7.47–7.49 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.8, 14.7, 21.8, 23.7, 29.7, 33.8, 75.1, 90.2, 92.2, 120.7, 121.9, 125.3, 126.9, 128.0, 128.5, 132.4, 133.8, 142.4, 149.8; IR (neat) 3446, 3061, 2960, 2930, 2871, 1489, 1465, 1091, 827, 701 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{25}ClO$ 352.1594, found 352.1581.

The spectral data of **9a**,**b**,**f**,**h**,**i** have been reported.[3]

3.4.2. (*Z*)-2,3-Dibutyl-1,5-diphenylpent-2-en-4-yn-1-ol (9c). Purification of the crude product by column chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=15:1) afforded the title product in 77% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.80 (t, J=7.2 Hz, 3H), 0.95 (t, J=6.9 Hz, 3H), 1.21–1.43 (m, 6H), 1.59–1.69 (m, 2H), 1.99–2.12 (m, 2H), 2.19 (s, 1H), 2.27 (t, J=8.1 Hz, 2H), 6.30 (s, 1H), 7.22–7.51 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.7, 14.1, 22.5, 23.3, 27.2, 30.8, 31.7, 32.5, 75.2, 89.3, 93.4, 121.1, 123.6, 125.4, 126.9, 127.9, 128.1, 128.3, 131.3, 142.5, 149.1; IR (neat) 3443, 2956, 2870, 1596, 1490, 1450, 1023, 754, 690 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{30}O$ 346.2297, found 346.2310.

3.4.3. (*Z*)-2,3-Dibutyl-5-(4-chlorophenyl)-1-*p*-tolylpent-2-en-4-yn-1-ol (9d). Purification of the crude product by column chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=10:1) afforded the title product in 68% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.81 (t, J=6.9 Hz, 3H), 0.94 (t, J=7.5 Hz, 3H), 1.19–1.26 (m, 3H), 1.3–1.42 (m, 3H), 1.57–1.67 (m, 2H), 1.94–2.14 (m, 2H), 2.25 (t, J=8.1 Hz, 2H), 2.30 (s, 3H), 2.47 (s, 1H), 6.23 (s, 1H), 7.10 (d, J=7.5 Hz, 2H), 7.22 (d, J=8.7 Hz, 2H), 7.30 (d, J=8.7 Hz, 2H), 7.36 (d, J=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.6, 14.0, 20.9, 22.4, 23.2, 27.2, 30.8, 31.6, 32.5, 75.1, 90.4, 92.1, 120.4, 122.1, 125.2, 128.5, 128.7, 132.4, 133.7, 136.3, 139.4, 149.9; IR (neat) 3442, 2957, 2928, 2871, 1512, 1489, 1465, 1091, 1033, 1014, 827 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{31}ClO$ 394.2063, found 394.2071.

3.4.4. (*Z*)-2,3-Diethyl-5-(4-methoxyphenyl)-1-phenylpent-2-en-4-yn-1-ol (9g). Purification of the crude product by column chromatography on neutral Al_2O_3 (petroleum ether/ethyl acetate=10:1) afforded the title product in 78% isolated yield. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.80 (t, J=7.5 Hz, 3H), 1.20 (t, J=7.5 Hz, 3H), 2.00–2.18 (m, 2H), 2.28 (q, J=7.5 Hz, 2H), 2.52 (s, 1H), 3.74 (s, 3H), 6.30 (s, 1H), 6.80 (d, J=8.1 Hz, 2H), 7.18–7.35 (m, 5H), 7.50 (d, J=7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.3, 14.9, 20.0, 25.1, 55.1, 75.1, 87.7, 93.3, 113.8, 115.7, 122.3, 125.3, 126.7, 127.9, 132.7, 142.6, 148.9, 159.2; IR (neat) 3460, 2965, 2932, 2873, 1603, 1463, 1450, 1248, 831 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{24}O_2$ 320.1776, found 320.1780.

3.4.5. (*Z*)-1-Phenyl-4,5-dipropylundec-4-en-6-yn-1-ol (10a). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=20:1)

afforded the title product in 53% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.82–0.94 (m, 9H), 1.26–1.68 (m, 9H), 1.78–1.91 (m, 2H), 1.95–2.18 (m, 4H), 2.28–2.37 (m, 2H), 2.48–2.58 (m, 1H), 2.65–2.72 (m, 1H), 4.62 (t, J=6.9 Hz, 1H), 7.23–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.55, 13.69, 14.21, 19.05, 21.74, 21.96, 31.08, 33.01, 33.94, 37.47, 73.60, 81.05, 92.59, 119.11, 125.74, 127.13, 128.18, 144.49, 145.14; HRMS (EI) calcd for $C_{23}H_{34}O$ 326.2610, found 326.2618.

3.4.6. (*Z*)-1,7-Diphenyl-4,5-dipropylhept-4-en-6-yn-1-ol (10b). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afforded the title product in 56% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.89–0.97 (m, 6H), 1.34–1.48 (m, 2H), 1.54–1.67 (m, 2H), 1.86–1.98 (m, 2H), 2.03–2.23 (m, 4H), 2.39–2.61 (m, 3H), 4.63–4.67 (m, 1H), 7.2–7.4 (m, 10H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.74, 14.23, 21.75, 22.08, 31.44, 33.41, 33.63, 37.60, 73.96, 90.26, 92.00, 118.68, 123.85, 125.78, 127.22, 127.50, 128.12, 128.26, 131.19, 144.44, 147.83; HRMS (EI) calcd for $C_{25}H_{30}O$ 346.2297, found 346.2293.

3.4.7. (*Z*)-1-Phenyl-4,5-dipropyl-7-(*p*-tolyl)hept-4-en-6-yn-1-ol (10c). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afforded the title product in 65% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.91 (t, J=7.2 Hz, 3H), 0.94 (t, J=7.2 Hz, 3H), 1.32–1.45 (m, 2H), 1.60 (sex, J=7.5 Hz, 2H), 1.85–1.97 (m, 2H), 2.03–2.20 (m, 4H), 2.31 (s, 3H), 2.38–2.61 (m, 3H), 4.62–4.67 (m, 1H), 7.05–7.33 (m, 9H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.72, 14.20, 21.32, 21.74, 22.05, 31.40, 33.37, 33.64, 37.58, 73.92, 89.54, 92.11, 118.77, 120.76, 125.77, 127.16, 128.22, 128.87, 131.06, 137.47, 144.43, 147.30; IR (neat) 3408, 3027, 2958, 2929, 2870, 1509, 1453, 816, 700 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{32}O$ 360.2453, found 360.2463.

3.4.8. (*Z*)-7-(4-Chlorophenyl)-1-phenyl-4,5-dipropylhept-4-en-6-yn-1-ol (10d). Purification of the crude product by column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afforded the title product in 63% isolated yield. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.95 (t, J=7.2 Hz, 3H), 0.97 (t, J=7.2 Hz, 3H), 1.41–1.48 (m, 2H), 1.57–1.65 (m, 2H), 1.92–1.99 (m, 2H), 2.12–2.25 (m, 4H), 2.30 (br s, 1H), 2.46–2.57 (m, 2H), 4.67–4.71 (m, 1H), 7.27–7.37 (m, 9H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.75, 14.25, 21.77, 22.11, 31.45, 33.46, 33.57, 37.56, 74.08, 90.87, 91.28, 118.51, 122.40, 125.83, 127.36, 128.36, 128.45, 132.42, 133.41, 144.42, 148.49; IR (neat) 3394, 2958, 2930, 2870, 1489, 1454, 1089, 827, 700 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{27}Cl$ $[M-H_2O]^+$ 362.1801, found 362.1809.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.12.051.

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