Tuning of Regioselectivity in the Coupling Reaction Involving Allenic/Propargylic Palladium Species

Shengming Ma* and Aibin Zhang

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, P. R. China

masm@pub.sioc.ac.cn

Received November 28, 2001

Two different types of coupling patterns for the Pd(0)-catalyzed coupling reaction of allenic/propargylic zinc reagents with organic halides or propargylic carbonates (acetate) with the corresponding organometallic reagents were observed. After studying the controlling factors on the regioselectivity of this reaction, we demonstrated that the steric hindrance of both reactants and the types of organic halides determine the regioselectivity of this coupling reaction. By subtle choosing of the substrates, the regioselectivity can be tuned. On the basis of these results, new methodologies for the highly regio- and stereoselective synthesis of 6-substituted hex-5-yn-2-enoates and 4,6-dialkylhexa-2,4,5-trienoates have been developed. Some of the products synthesized by the carbonate protocol cannot be prepared by the lithiation protocol because the regioselectivity of lithiation of dialkyl-substituted internal alkynes is an intrinsic problem.

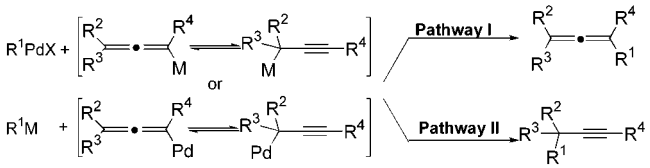
Introduction

For coupling reactions between an organic halide and an allenic/propargylic metallic reagent or allenic/propargylic palladium species and RM there are, in principle, two outcomes: (1) the formation of allenes (Pathway I) and (2) the formation of alkynes (Pathway II) (Scheme 1).

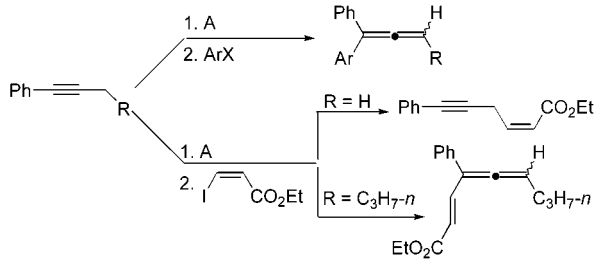
Recently, on the basis of $HgCl_2$-catalyzed monolithiation reaction of 1-arylalk-1-ynes developed in our group,[1] we observed an efficient Pd(0)-catalyzed coupling reaction of aromatic halides with allenic/propargylic zinc reagents affording 1,1-diaryl-1,2-dienes as the predominant products in a highly selective manner[2,3] (Pathway I). On the other hand, the coresponding coupling reaction with electron-deficient 1-alkenyl halides, i.e., (*Z*)-3-iodo-2-alkenoates, afforded a pathway I-type allene product (R ≠ H) or pathway II-type alkyne product (R = H) depending on the structure of alkynes[4] (Scheme 2).

From the above results, it is obvious that the structure of the organic halides and 1-arylalk-1-yne affected the regioselectivity of this type of coupling reaction greatly. In this paper, we will verify some controlling factors for the regioselectivity of this coupling reaction involving allenic/propargylic palladium species. On the basis of this study, a new methodology for the highly selective synthesis of 6-substituted hex-5-yn-2-enoates and 4,6-dialkyl-substituted hexa-2,4,5-trienoates has been developed.

Scheme 1



Scheme 2[a]



[a] A: (1) 1.5 mol % $HgCl_2$; (2) *n*-BuLi; (3) $ZnBr_2$; (4) 5 mol% $Pd(PPh_3)_4$. Without $HgCl_2$, the yields are lower.

Results and Discussion

In this coupling reaction, different regioselectivities may be derived from the competing reactivity of either allenic or propargylic palladium species. Thus, a mixture of η^1-propargylic palladium complex **A** and η^1-allenylic palladium complex **B** (**A**/**B** = 1.7/1) was synthesized according to the known procedure[5] and its corresponding coupling reaction with (2*Z*)-ethoxycarbonylethenyl zinc iodide, which was prepared from the reaction of ethyl (*Z*)-3-iodopropenoate with activated zinc powder, afforded the alkynic product ethyl 6-phenylhex-5-yn-(2*Z*)-enoate in 57% yield, exclusively. Interestingly, its coupling reaction with phenylzinc bromide afforded 1,1-diphenylpropa-1,2-diene in 60% yield, while the formation of 1,3-diphenyl-

* To whom correspondence should be addressed. Fax: (86) 21-64166128.

(1) (a) Ma, S.; Wang, L. *J. Org. Chem.* **1998**, *63*, 3497; (b) *Chin. J. Chem.* **1999**, *17*, 531.

(2) For a seminal paper of Negishi coupling reaction, see: Negishi, E.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821. For a most recent review, see: Negishi, E.; Liu, F. In *Metal-Catalyzed Cross-Coupling Reactions*; Stang, P., Diederich, F., Eds.; VCH: Weiheim, Germany, 1998; pp 1−47.

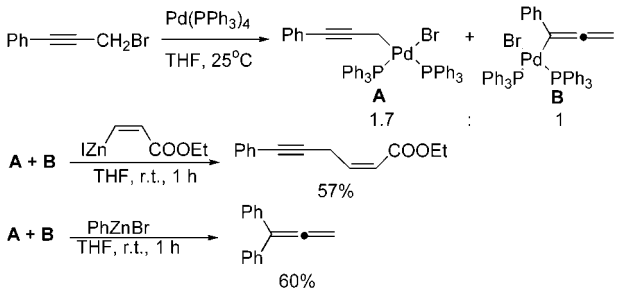
(3) Ma, S.; Zhang, A. *J. Org. Chem.* **1998**, *63*, 9601.

(4) Ma, S.; Zhang, A.; Y. Yu, Y.; Xia, W. *J. Org. Chem.* **2000**, *65*, 2287.

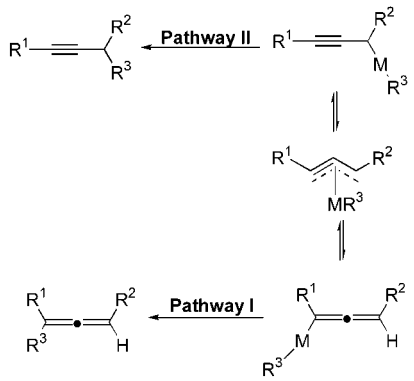
(5) Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164.

10.1021/jo0111098 CCC: $22.00
Published on Web 03/06/2002

Scheme 3



Scheme 4

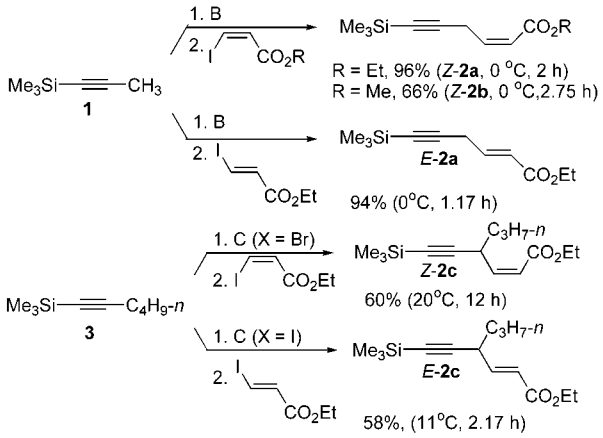


1-propyne occurred to an extent of 3∼4%, if any (Scheme 3).[6] This indicated a clear regioselectivity switch even starting from a performed 1.7:1 mixture of **A** and **B**.

On the basis of the chemistry depicted in Scheme 2, we reasoned that the steric hindrance of R^1, R^2, and R^3 may be the controlling factors for the regioselectivity of this coupling reaction (Scheme 4).[6−9]

Control of Regioselectivity in Pd-Catalyzed Coupling Reaction of Allenic/Propargylic Organometallic Reagents with Organic Halides. To increase the steric hindrance at one terminal of the alkyne, 1-(trimethylsilyl)prop-1-yne (**1**) (the bulkiness of R^1 increases, see Scheme 4) instead of 1-phenylprop-1-yne was treated with *n*-BuLi in THF at −78 °C followed by the addition of 1.5 molar equiv of $ZnBr_2$, 5 mol % $Pd(PPh_3)_4$, and ethyl (*Z*)-3-iodo-2-propenoate, and a similar reaction occurred and afforded the pathway II-type product ethyl 6-(trimethylsilyl)hex-5-yn-(2*Z*)-enoate (*Z*-**2a**) in a 96% yield.

Scheme 5[a]



[a] B: (1) *n*-BuLi, −78 °C; (2) $ZnBr_2$, −78 °C → rt.; (3) 5 mol % $Pd(PPh_3)_4$. C: (1), *n*-BuLi, −78 °C; (2) ZnX_2, rt; (3) 5 mol % $Pd(PPh_3)_4$.

A similar coupling reaction with ethyl (*E*)-3-iodo-2-propenoate afforded ethyl 6-(trimethylsilyl)hex-5-yn-(2*E*)-enoate (*E*-**2a**) in 94% yield. In both cases, the configurations of the C=C bonds remained intact. However, when 1-(trimethylsilyl)hex-1-yne (**3**) (the bulkiness of both R^1 and R^2 increases, see Scheme 4) was used instead of 1-phenylprop-1-yne, it still afforded the pathway II-type product, i.e., ethyl 6-(trimethylsilyl)-4-propylhex-5-yn-(2*Z*)-enoate (*Z*-**2c**) and ethyl 6-(trimethylsilyl)-4-propylhex-5-yn-(2*E*)-enoate (*E*-**2c**) in 60 and 58% yields, respectively (Scheme 5), a result quite contrary to that of 1-phenyl-1-hexyne.[4] This indicated that the steric hindrance of the trimethylsilyl group has a much greater impact on the regioselectivity of the current coupling reaction than an alkyl group does.

The corresponding reaction using 1-phenylprop-1-yne and aryl iodide was reported to afford a pathway I-type product.[3] To study the steric effect of the aryl group in the aryl iodide, *o*-methylphenyl iodide was used instead of phenyl iodide (increasing the steric hindrance of aryl iodide) to produce exclusively pathway I-type product **6a** in 85% yield (entry 1, Table 1). However, further study of the treatment of 1-(trimethylsilyl)prop-1-yne (**1**) with *n*-BuLi in THF at −78 °C followed by the addition of 1.5 equiv of $ZnBr_2$, 5 mol % of $Pd(PPh_3)_4$, and 0.6 equiv of phenyl iodide was carried out, and the reaction afforded a roughly 1:1 mixture of 1-(trimethylsilyl)-3-phenylprop-1-yne (**2e**) (pathway II-type) and 1-(trimethylsilyl)-1-phenylpropa-1,2-diene (**6b**) (pathway I-type) in 24 and 23% yields, respectively (entry 3, Table 1). The coupling reaction of the above organozinc reagent with 1-naphthyl iodide produced a higher ratio mixture of 1-(trimethylsilyl)-3-(1′-naphthyl)prop-1-yne (**2f**) (41%) and 1-(trimethylsilyl)-1-(1′-naphthyl)propa-1,2-diene (**6c**) (17%) (entry 4, Table 1). However, similar reaction with *o*-methylphenyl iodide afforded exclusively pathway II-type product 1-(trimethylsilyl)-3-(*o*-methylphenyl)prop-1-yne (**2d**) in 52% yield (entry 2, Table 1). The coupling reaction of the organozinc reagent formed by the treatment of 1-(*tert*-butyldimethylsilyl)prop-1-yne (**5**) (the bulkiness of R^1 was increased further, see Scheme 4) with *n*-BuLi and $ZnBr_2$ with 1-naphthyl iodide also afforded exclusively 1-(*tert*-butyldimethylsilyl)-3-(1′-naphthyl)prop-1-yne (**2g**) (pathway II-type) in 52% yield (entry 5, Table 1), indicat-

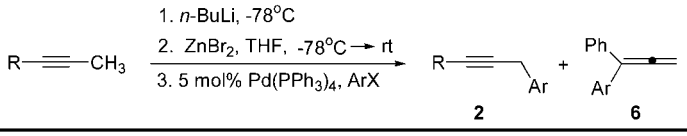
(6) (a) For the regioselective preparation of either 1,2-allenic palladium or propargylic palladium complexes from differently substituted propargylic chloride and the corresponding reaction with organozincs to afford allenes, see: Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716; Elsevier, C. J.; Kleijn, H.; Ruitenberg, K.; Vermeer, P. *Chem. Commun.* **1983**, 1529. (b) For an early example of Pd(0)-catalyzed coupling of allenyl or propargyl halides with organozincs to afford allenes, see: Ruitenberg, K.; Kleijn, H.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1981**, *22*, 1451. (c) For the Pd(0)-catalyzed cross coupling reaction of 1-alkynyl epoxides with organozincs to afford 2,3-allenols, see: Kleijn, H.; Meijer, J.; Overbeck, G. C.; Vermeer, P. *Rec. J. R. Neth. Chem. Soc.* **1982**, *101*, 97.

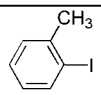
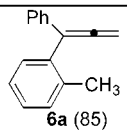
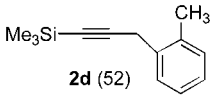
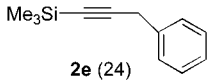
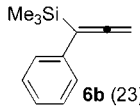
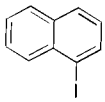
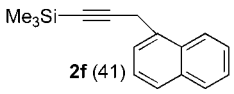
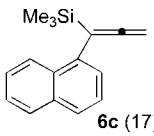
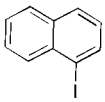
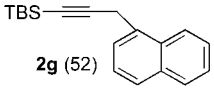
(7) For the metal-catalyzed isomerization between η^1-propargyl and η^1-allenylmetal complexes, see: Ogoshi, S.; Fukunishi, Y.; Tsutsumi, K.; Kurosawa, H. *Chem. Commun.* **1995**, 2485. Ogoshi, S.; Nishida, T.; Fukunishi, Y.; Tsutsumi, K.; Kurosawa, H. *J. Organomet. Chem.* **2001**, *620*, 190. For the cross-coupling reaction through η^1 and η^3-propargyl/allenyl-palladium (II) with organotins to afford alkynes and allenes in a highly selective manner, see: Tsutsumi, K.; Ogoshi, S.; Kakiuchi, K.; Nishiguchi, S.; Kurosawa, H. *Inorg. Chim. Acta* **1999**, *296*, 37.

(8) Keinan, E.; Bosch, E. *J. Org. Chem.* **1986**, *51*, 4006.

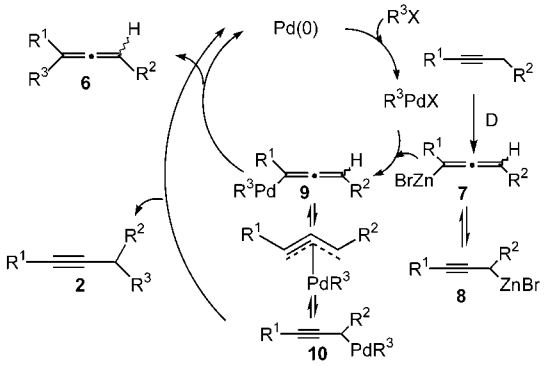
(9) For the formation of an η^1-propargyl Pt complex from the oxidative addition of propargyl halides with $Pt-PPh_3$ complexes via η^3-propargyl Pt complexes, see: Nishida, T.; Ogoshi, S.; Tsutsumi, K.; Fukunshi, Y.; Kurosawa, H. *Organomeatllics* **2000**, *19*, 4488.

Table 1. Regioselectivity of Pd(0)-Catalyzed Coupling Reaction of Allenylic/Propargylic Reagents with Organic Halides



entry	R	ArX	Temp (°C)	Time (h)	**2** (%)	**6** (%)	Ratio of **2**/**6**
1	Ph		26	5.5	-(0)	 **6a** (85)	0/100
2	Me_3Si		0 - 20	5.5	 **2d** (52)	-(0)	100/0
3	Me_3Si		28	2.25	 **2e** (24)	 **6b** (23)	51/49
4	Me_3Si		26	13.5	 **2f** (41)	 **6c** (17)	71/29
5	TBS		31	15.5	 **2g** (52)	-(0)	100/0

Scheme 6[a]



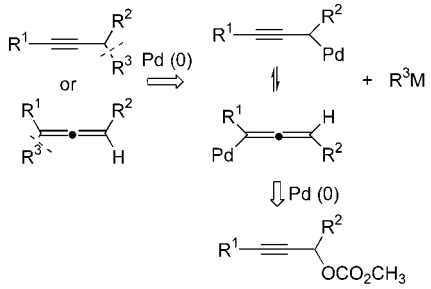
[a] D: (a) 1.5% $HgCl_2$; (b) *n*-BuLi; (c) $ZnBr_2$.

ing the increase of the hindrance of R^1 and R^3 (Scheme 4) increases the selectivity of pathway II/I.

Therefore, a plausible mechanism for this reaction is the oxidative addition reaction of an organic halide with Pd(0) to form an organopalladium intermediate R^3PdX, which would be trapped by the allenic/propargylic zinc reagents formed by the transmetalation reaction of the organolithiums with $ZnBr_2$ to afford the allenylic palladium **9** and the propargylic **10** palladium species, respectively. The formation of either allene **6** or alkyne **2** depends on the steric factors of R^1, R^2, and R^3; i.e., increasing the steric bulkiness of either R^1 or R^3 increases the tendency of forming **2**. The steric hindrance of R^1, R^2, and R^3 may determine the relative stability of η^1-propargylic Pd **10** and η^1-allenylic Pd **9** (Scheme 6).

Pd-Catalyzed Coupling Reaction of Propargylic Carbonates with Organic Zinc Reagents. On the basis of these results and the viewpoint of elementary

Scheme 7



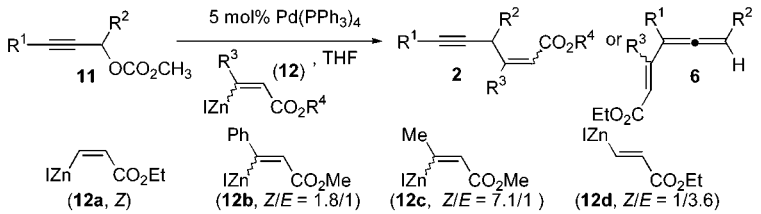
reactions in organometallic chemistry, we reasoned that ethyl 6-substituted hex-5-yn-(2Z)-enoate and 4,6-disubstituted 2,4,5-trienoates might be built up via the Pd(0)-catalyzed coupling reaction of a propargylic carbonate with an organometallic reagent by choosing suitable propargylic carbonates and organometallic reagents.[10,11] In this paradigm, since the propargylic/allenylic palladium is formed via an oxidative addition reaction, the regioselectivity of the lithiation of dialkyl-substituted internal alkynes can be circumvented (Scheme 7).

Synthesis and Structural Determination of Organozinc Reagents. The organozinc reagents were

(10) For a seminal paper on the Pd(0)-catalyzed chemistry of propargylic carbonates, see: Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196.

(11) For reviews of the Pd(0)-catalyzed reaction of propargylic carbonates with different nucleophiles, see: Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2589. Bruneau, C.; Darcel, C.; Dixneuf, P. H. *Curr. Org. Chem.* **1997**, *1*, 197. In most cases of the corresponding coupling chemistry, allenes are the only products formed, while in a few limited cases, alkynes were formed as a minor product (cf. Tsuji, J.; Sugiura, T.; Yuhara, M.; Minami, I. *J. Chem. Soc., Chem. Commun.* **1986**, 922. Tsuji, J.; Sugiura, T.; Minami, I. *Synthesis* **1987**, 603). No reasonable selective control of alkyne-formation has been reported.

Table 2. Pd(0)-Catalyzed Coupling Reaction of Methyl 3-Substituted Alk-2-ynyl Carbonates and Ethenyl Zinc Reagents

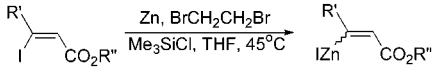


entry	11	12	Temp. (°C)	Time (h)	Product 2 (%)	Product 6 (%)
1	$Me_3Si-\equiv-CH_2OCO_2Me$ (**11a**)	**12a**	50	0.75	$Me_3Si-\equiv-CO_2Et$ *Z*-**2a** (44)	-
2	**11a**	**12b**	55	1	$Me_3Si-\equiv-CO_2Me$ (Ph) *E*-**2i** (60)	-
3	**11a**	**12c**	45	2.75	$Me_3Si-\equiv-CO_2Me$ (Me) **2j** (*Z*/*E*=4/5) (63)	-
4	$Ph-\equiv-CH_2OCO_2Me$ (**11b**)	**12a**	50	0.75	$Ph-\equiv-CO_2Et$ *Z*-**2h** (58)	-
5	**11b**	**12b**	60	2	$Ph-\equiv-CO_2Me$ (Ph) *E*-**2k** (63)	-
6	**11b**	**12d**	55	0.9	$Ph-\equiv-CO_2Et$ **2h**(*Z*/*E*=5/6) (40)	-
7	$n\text{-}C_4H_9-\equiv-CH_2OCO_2Me$ (**11c**)	**12a**	50	0.5	$n\text{-}C_4H_9-\equiv-CO_2Et$ *Z*-**2l** (55)	$n\text{-}C_4H_9$ (EtO2C) **6d** (18)
8	**11c**	**12b**	50	1.25	$n\text{-}C_4H_9-\equiv-CO_2Me$ (Ph) *E*-**2m** (44)	-
9	$Me_3Si-\equiv-$ (C_3H_7-*n*, OCO_2Me) (**11d**)	**12a**	50	2.5	$Me_3Si-\equiv-CO_2Et$ (C_3H_7-*n*) *Z*-**2c** (35)	-
10	**11d**	**12b**	55	11.5	-	-

prepared from the reaction of organic halides with activated zinc powder, and their configurations were determined by iodinolysis or hydrolysis[12] (Scheme 8).

When methyl 3-phenylprop-2-ynyl carbonate (0.5 mmol) was treated with (2*Z*)-ethoxycarbonylethenylzinc iodide[12] (0.5 mmol) in THF at rt under the catalysis of $Pd(PPh_3)_4$, the reaction did not take place. When the mixture was heated to 55 °C, besides ethyl 6-phenylhex-5-yn-(2*Z*)-enoate, the product of migration of the C=C double bond, e.g., ethyl 6-phenylhex-5-yn-3-enoate, was also obtained. Finally, the treatment of methyl 3-phenylprop-2-ynyl

Scheme 8

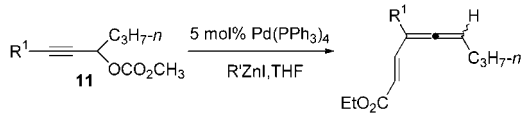


Entry	Starting halide	Time (h)	Zinc reagent formed	Ratio of *Z*/*E*
1	I, CO_2Et	21	IZn, CO_2Et	100/0 [a]
2	Ph, I, CO_2Me	21	Ph, IZn, CO_2Me	1.8/1 [b]
3	Me, I, CO_2Me	12	Me, IZn, CO_2Me	7.1/1 [a]
4	I, CO_2Et	9	IZn, CO_2Et	1/3.6 [a]

[a] Determined by iodinolysis. [b] Determined by hydrolysis.

(12) Knochel, P.; Rao, C. J. *Tetrahedron* **1993**, *49*, 29. The configuration of the C=C bond in the zinc reagent was determined to be *Z* by iodinolysis.

Scheme 9



R^1	R'ZnI	Temp. (°C)	Time (h)	Yield (%)
C_4H_9-*n*(**11e**)	**12a** (*Z*)	55	1.4	70 (*E*-**6e**)
11e	**12d** (*Z*/*E* = 1/3.6)	55	1.25	55 (*E*-**6e**)
Ph (**11f**)	**12a** (*Z*)	50	6	0

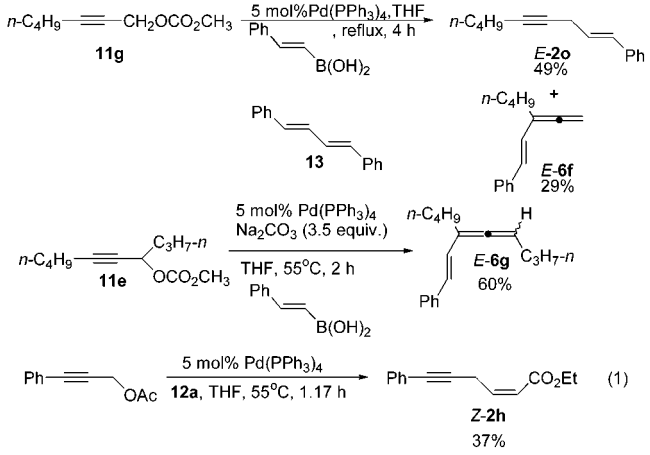
carbonate (0.65 mmol) with (2*Z*)-ethoxycarbonylethenylzinc iodide (0.5 mmol) in THF at 55 °C under the catalysis of $Pd(PPh_3)_4$ afforded ethyl 6-phenylhex-5-yn-(2*Z*)-enoate (*Z*-**2h**) as the sole product in 58% yield (entry 4, Table 2). Some representative examples are summarized in Table 2.

In Table 2, several points should be noted. (1) For the coupling reaction of **11** and **12** (entries 2, 3, 5, 6, and 8, Table 2), the stereoisomeric ratio of zinc reagents was not consistent with that of products,[12] indicating that the configuration partly changed during the reaction. The configurations of (*E*)-**2i**, (*Z*)-**2j**, and (*E*)-**2m** were determined by $^1H-^1H$ NOESY spectra. (2) For the coupling reaction of carbonate **11c** and zinc reagent **12a**, 18% of allene product (*E*)-**6d** formed due to the smaller hindrance of *n*-C_4H_9 (compared to that of Ph and $SiMe_3$). When the steric hindrance of the organozincs increased, e.g., **12b**, the reaction afforded exclusively alkyne *E*-**2m** (compare entry 7 with entry 8, Table 2), so the steric hindrance of R^1 and R^2 (Scheme 7) is responsible for the regioselectivity of the reaction. (3) R^1 in alkynes can be trimethylsilyl and alkyl groups. For alkyl groups, this protocol is extremely useful, because the regioselectivity of the lithiation of 1,2-dialkylethyne is a problem for the lithiation−coupling protocol.

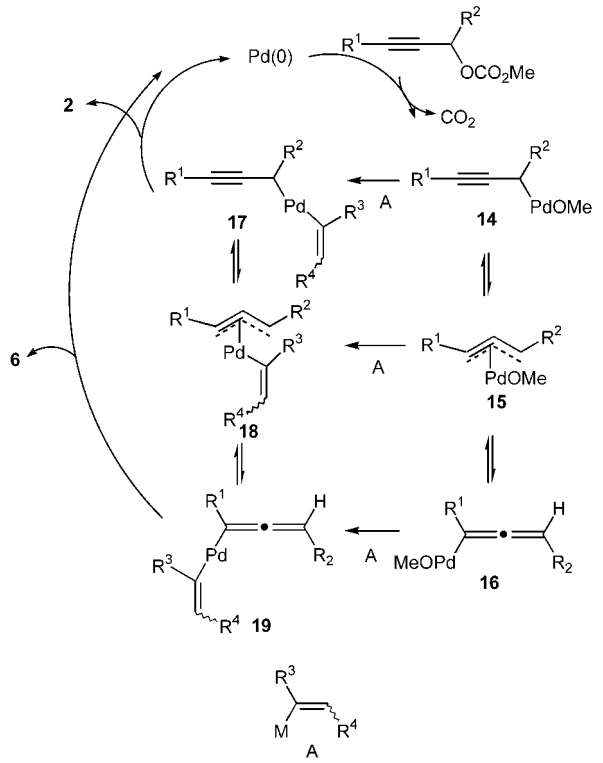
Furthermore, it is interesting to observe that the coupling reactions of methyl dec-5-ynyl carbonate **11e** (**11e** can be considered as that R^1, i.e., TMS, in **11d** was replaced with *n*-C_4H_9, and $R^2 \neq H$!) with ethoxycarbonylethenyl zinc iodide formed from the reaction of ethyl (*Z*)- and (*E*)-3-iodopropenoate with activated zinc powder both afforded the pathway I-type product ethyl 4-(*n*-butyl)nona-(2*E*),4,5-trienoate ((*E*)-**6e**) in a highly stereoselective manner (compare the results in Scheme 9 with entry 6 in Table 2). However, for methyl 1-phenylhex-1-ynyl carbonate (**11f**), a similar reaction afforded no product probably due to the instability of ethyl 4-phenylnona-(2*E*),4,5-trienoate at a higher temperature.

When (2*E*)-phenylethenylboronic acid was used instead of (2*Z*)-ethoxycarbonylethenyl zinc iodide, the reaction of methyl 2-heptynyl carbonate (**11g**) under the catalysis of $Pd(PPh_3)_4$ afforded pathway II-type product 1-phenylnona-4-yn-(1*E*)-ene (*E*-**2o**) in 49% yield as the major product and the pathway I-type product 1-phenyl-4-(*n*-butyl)-(1*E*),3,4-pentatriene (*E*-**6f**) in 29% yield. A small amount of compound **13**, which was formed by the self-coupling of (2*E*)-phenylethenylboronic acid, was also isolated. However, 3.5 equiv of sodium carbonate must be needed for the similar reaction with carbonate **11e**, which afforded *E*-**6g** as the sole product in 60% yield. This also indicates that the steric hindrance was responsible for the regioselectivity of the coupling reaction (Scheme 10). It is also obvious that the carbonate protocol provides

Scheme 10



Scheme 11



a supplementary method for the lithiation protocol involving the coupling reaction with 1-alkenyl iodide, which does not afford the coupling products in decent yields.[4] 3-Phenylprop-2-ynyl acetate can also react with zinc reagent **12a** under the catalysis of $Pd(PPh_3)_4$ to afford *Z*-**2h** in 37% yield, but the reactivity is obviously lower than that of carbonates (eq 1).

The higher reaction temperature (55 °C) indicates that the oxidative addition of propargylic carbonates with Pd(0) is the rate determining step because the Pd(0)-catalyzed coupling reaction of the propargyl/allenyl zinc reagents with organohaildes described in the first part of this paper occurred smoothly at room temperature (rt). A plausible mechanism (Scheme 11) for this reaction is the oxidative addition reaction of methyl propargylic carbonate with Pd(0) to form a mixture of η^1-allenyl/propargylic palladium species **14** and **16** and η^3-allenyl/propargylic palladium species **15**[7−9] with the loss of one molecule of CO_2,[10] which would be trapped by the organozinc reagent to afford the η^1-allenyl/propargyl

ethenyl palladium intermediates **17** and **19** and η^3-allenyl/propargyl ethenyl palladium intermediate **18**, respectively. The interconversions of η^1 Pd intermediates **14/16** and **17/19** are feasible via η^3 Pd itermediates **15** and **18**.[7,9] The relative steric hindrance of both substrates and the electronic effect of the alkenyl group determined the regioselectivity of this reaction.[7]

In conclusion, we have studied two different types of coupling patterns for the Pd(0)-catalyzed reaction of allenylic/propargylic zinc reagents with organic halides and propargylic carbonates (acetate) with organozincs. The steric hindrances of substitutents of alkynes and organic halides are responsible for the regioselectivity of the coupling reaction. By the methodology described in this paper, 6-substituted hex-5-yn-2-enoates and 4,6-dialkyl hexa-2,4,5-trienoates can be prepared with high regio- and stereoselectivity. Further study of the controlling factors for the regioselectivity is being carried out in our laboratory.

Experimental Section

Materials. 1-(Trimethylsilyl)prop-1-yne,[13] 1-(*tert*-butyldimethylsilyl)prop-1-yne,[13] 1-(trimethylsilyl)hex-1-yne,[14] methyl (*Z*)-3-iodopropenoate,[15] ethyl (*Z*)-3-iodo-2-propenoate,[15] methyl (*Z*)-3-iodo-2-butenoate,[15] methyl (*Z*)-3-phenyl-3-iodo-2-propenoate,[15] ethyl (*E*)-3-iodo-2-propenoate,[16] methyl 3-phenylprop-2-ynyl carbonate,[17] methyl 3-(trimethylsilyl)prop-2-ynyl carbonate,[17] methyl 2-heptynyl carbonate,[15] methyl 1-phenylhex-1-yn-3-yl carbonate,[17] methyl 1-(trimethylsilyl)hex-1-yn-3-yl carbonate,[17] methyl 5-decyn-4-yl carbonate,[17] 3-phenylprop-2-ynyl acetate,[18] electron-deficient alkenyl zinc reagents,[9] and (2*E*)-phenylethenylboronic acid[19] were prepared according to literature methods. Phenyl iodide, 1-naphthyl iodide, and *o*-methylphenyl iodide were commercially available and used after they were dried via azotropic evaporation with benzene. ^{1}H NMR spetra were measured using $CDCl_3$ as the solvent and Me_4Si as the internal standard.

Reaction of the Mixture of η^1-Propargylic Palladium Complex A and η^1-Allenylic Palladium Complex B with (2*Z*)-Ethoxycarbonylethenyl Zinc Iodide. To a solution of η^1-propargylic palladium complex **A** and η^1-allenic palladium complex **B**[5] (205 mg, 0.25 mmol) in THF (2 mL) was added (2*Z*)-ethoxycarbonylethenyl zinc iodide (0.5 mL, ca. 1.0 M, 0.5 mmol) at rt. After 1 h, the reaction was quenched with water, and the mixture was extracted with diethyl ether and washed with water. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane/ethyl acetate 100:1) afforded 30 mg (57%) of ethyl 6-phenylhex-5-yn-(2Z)-enoate. Its data are the same as those reported in ref 4.

Reaction of the Mixture of η^1-Propargylic Palladium Complex A and η^1-Allenylic Palladium Complex B with Phenylzinc Bromide. To a solution of phenyl iodide (102 mg, 0.5 mmol) in THF (2 mL) in a dry Schlenk tube was added 0.28 mL (0.56 mmol, 2 mol/L) of *n*-BuLi at −78 °C under N_2. After 25 min at −78 °C, dry $ZnBr_2$ (250 mg, 1.1 mmol) in THF (2 mL) was added. After 5 min at this temperature, the reaction mixture was warmed to rt and stirred for 15 min, and the mixture of η^1-propargylic palladium complex **A** and η^1-allenic palladium complex **B** (519 mg, 0.63 mmol) was added at rt. After 1 h, the reaction was quenched with water, and the mixture was extracted with diethyl ether and washed with water. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane) afforded 58 mg (60%) of 1,1-diphenylpropa-1,2-diene.[3]

$Pd(PPh_3)_4$-Catalyzed Coupling Reaction of Electron-Deficient Alkenyl Halides with Allenylic/Propargylic Zinc Reagents Formed by the Reaction of 1-(Trimethylsilyl)prop-1-yne with *n*-BuLi and $ZnBr_2$: Typical Procedure for the Synthesis of Ethyl 6-(Trimethylsilyl)hex-5-yn-(2*Z*)-enoate ((*Z*)-2a). To a solution of 1-(trimethylsilyl)prop-1-yne (95 mg, 0.85 mmol) in THF (2 mL) in a dry Schlenk tube was added *n*-BuLi (0.60 mL, 1.6 M in hexane, 0.96 mmol) at −78 °C under N_2. After 100 min at −78 °C, dry $ZnBr_2$ (390 mg, 1.73 mmol) in THF (3 mL) was added. After 10 min at this temperature, the reaction mixture was warmed to rt and stirred for 20 min, and $Pd(PPh_3)_4$ (30 mg, 0.025 mmol) and ethyl 3-iodo-(2*Z*)-propenoate (112 mg, 0.5 mmol) in THF (1 mL) were added at 0 °C. After the reaction was complete, as monitored by TLC (eluent: hexane/ethyl acetate 100:1), it was quenched with water, and the mixture was extracted with diethyl ether and washed with water. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane/ethyl acetate 200:1) afforded 101 mg (96%) of (*Z*)-**2a**: IR (film) 2177, 1715, 1645, 1181 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23 (dt, ^3J (H,H) = 11.28 Hz, ^3J (H,H) = 6.74 Hz, 1H, =CH), 5.79 (dt, ^3J (H,H) = 11.28 Hz, ^4J (H,H) = 2.11 Hz, 1H, =CH), 4.16 (q, ^3J (H,H) = 7.15 Hz, 2H, OCH_2), 3.66 (dd, ^3J (H,H) = 6.74 Hz, ^4J (H,H) = 2.11 Hz, 2H, CH_2), 1.27 (t, ^3J (H,H) = 7.15 Hz, 3H, CH_3), 0.14 (s, 9H, Me_3Si); MS (EI) *m*/*z* (%) 210 (3.54) $[M]^+$; HRMS calcd for $C_{11}H_{18}O_2Si$ 210.1071, found 210.1065. Similar reaction conditions and workup procedures were used for the synthesis of (*Z*)-**2b** and (*E*)-**2a**.

Methyl 6-(Trimethylsilyl)hex-5-yn-(2*Z*)-enoate ((*Z*)-2b). A solution of 1-(trimethylsilyl)prop-1-yne (**1**) in hexane (143 mg, molar ratio of **1** and hexane = 3:2, 0.85 mmol), $ZnBr_2$ (396 mg, 1.76 mmol), and methyl 3-iodo-(2*Z*)-propenoate (108 mg, 0.51 mmol) afforded 67 mg (66%) of (*Z*)-**2b**: IR (film) 2178, 1718, 1180 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.25 (dt, ^3J (H,H) = 11.28 Hz, ^3J (H,H) = 6.68 Hz, 1H, =CH), 5.80 (dt, ^3J (H,H) = 11.28 Hz, ^4J (H,H) = 2.03 Hz, 1H, =CH), 3.75 (s, 3H, OCH_3), 3.67 (dd, ^3J (H,H) = 6.68 Hz, ^4J (H,H) = 2.03 Hz, 2H, CH_2), 0.15 (s, 9H, Me_3Si); MS (EI) *m*/*z* (%) 196 (1.56) $[M^+]$; HRMS calcd for $C_{10}H_{16}O_2Si$ 196.0915, found 196.0919.

Ethyl 6-(Trimethylsilyl)hex-5-yn-(2*E*)-enoate ((*E*)-2a). A solution of 1-(trimethylsilyl)prop-1-yne in hexane (143 mg, molar ratio of **1** and hexane = 3:2, 0.85 mmol), $ZnBr_2$ (348 mg, 1.55 mmol), and ethyl 3-iodo-(2*E*)-propenoate (114 mg, 0.5 mmol) afforded 100 mg (94%) of (*E*)-**2a**: IR (film) 2178, 1716, 1652, 1178 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (dt, ^3J (H,H) = 15.47 Hz, ^3J (H,H) = 5.18 Hz, 1H, =CH), 6.12 (dt, ^3J (H,H) = 15.47 Hz, ^4J (H,H) = 1.98 Hz, 1H, =CH), 4.19 (q, ^3J (H,H) = 7.14 Hz, 2H, OCH_2), 3.15 (dd, ^3J (H,H) = 5.18 Hz, ^4J (H,H) = 1.98 Hz, 2H, CH_2), 1.29 (t, ^3J (H,H) = 7.14 Hz, 3H, CH_3), 0.17 (s, 9H, Me_3Si); MS (EI) *m*/*z* (%) 210 (3.78) $[M]^+$; HRMS calcd for $C_{11}H_{18}O_2Si$ 210.1071, found 210.1080.

$Pd(PPh_3)_4$-Catalyzed Coupling Reaction of Electron-Deficient Alkenyl Halides with Allenylic/Propargylic Zinc Reagent Formed by the Reaction of 1-(Trimethylsilyl)hex-1-yne with *n*-BuLi and ZnX_2: Typical Procedure for the Synthesis of Ethyl 6-(Trimethylsilyl)-4-propylhex-5-yn-(2*Z*)-enoate ((*Z*)-2c). To a solution of 1-(trimethylsilyl)hex-1-yne (131 mg, 0.85 mmol) in THF (2 mL) in a dry Schlenk tube was added *n*-BuLi (0.60 mL, 1.6 M in hexane, 0.96 mmol) at rt under N_2. After 95 min at rt, dry $ZnBr_2$ (389 mg, 1.73 mmol) in THF (3 mL) was added. After 25 min at rt, $Pd(PPh_3)_4$ (30 mg, 0.025 mmol) and ethyl 3-iodo-(2*Z*)-propenoate (113 mg, 0.5 mmol) in THF (1 mL) were added at rt. After the reaction was complete, as monitored by TLC (eluent: hexane/ethyl acetate 100:1), it was quenched with water, and the mixture was extracted with diethyl ether and washed with water. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane/ethyl acetate 200:1) afforded 75 mg (60%) of (*Z*)-**2c**: IR (film) 2169, 1716, 1641, 1128 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.10 (t, ^3J (H,H)

(13) Corey, E. J.; Katzenellenbogen, J. A.; Gilman, N. W.; Roman, S. A.; Erickson, B. *J. Am. Chem. Soc.* **1968**, *90*, 5618.
(14) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: 1988.
(15) Ma, S.; Lu, X.; Li, Z. *J. Org. Chem.* **1992**, *57*, 709. For a review, see: Ma, S.; Lu, X. *Chin. J. Chem.* **1998**, *16*, 388.
(16) Ma, S.; Lu, X. *J. Chem. Soc., Chem. Commun.* **1990**, 1643.
(17) Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225.
(18) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.
(19) Larock, R. C.; Gupta, S. K.; Brown, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 4370.

= 11.53 Hz, 1H, =CH), 5.75 (d, ^3J (H,H) = 11.53 Hz, 1H, = CH), 4.54−4.40 (m, 1H, CH), 4.16 (q, ^3J (H,H) = 7.10 Hz, 2H, OCH_2), 1.55−1.40 (m, 4H, CH_2), 1.27 (t, ^3J (H,H) = 7.10 Hz, 3H, CH_3), 0.92 (t, ^3J (H,H) = 6.94 Hz, 3H, CH_3), 0.11 (s, 9H, Me_3Si); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 165.688, 148.578, 119.092, 107.269, 85.580, 59.944, 37.226, 31.037, 19.989, 14.091, 13.629, 0.001; MS (EI) *m/z* (%) 253 (6.93) $[M + 1]^+$. Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.65; H, 9.37.

Ethyl 6-(Trimethylsilyl)-4-propylhex-5-yn-(2*E*)-enoate ((*E*)-2c). 1-(Trimethylsilyl)hex-1-yne (134 mg, 0.87 mmol), ZnI_2 (388 mg, 1.22 mmol), and ethyl 3-iodo-(2*E*)-propenoate (112 mg, 0.5 mmol) afforded 73 mg (58%) of (*E*)-**2c**: IR (film) 2169, 1720, 1651, 1178 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.82 (dd, ^3J (H,H) = 15.56 Hz, ^3J (H,H) = 5.81 Hz, 1H, =CH), 6.05 (d, ^3J (H,H) = 15.56, Hz, 1H, =CH), 4.18 (q, ^3J (H,H) = 6.98 Hz, 2H, OCH_2), 3.21 (q, ^3J (H,H) = 5.88 Hz, 1H, CH), 1.60−1.40 (m, 4H, CH_2), 1.28 (t, ^3J (H,H) = 6.98 Hz, 3H, CH_3), 0.91 (t, ^3J (H,H) = 7.01 Hz, 3H, CH_3), 0.15 (s, 9H, Me_3Si); MS (EI) *m/z* (%) 252 (1.51) $[M]^+$. Anal. Calcd for $C_{14}H_{24}O_2Si$: C, 66.61; H, 9.58. Found: C, 66.80; H, 9.59.

$Pd(PPh_3)_4$-Catalyzed Coupling Reaction of Aryl Iodide with Allenylic/Propargylic Zinc Reagents Formed by the Reaction of 1-Substituted Prop-1-yne with *n*-BuLi and $ZnBr_2$: Typical Procedure for the Synthesis of 1-Phenyl-1-(*o*-methylphenyl)propa-1,2-diene (6a). To a solution of 1-phenylprop-1-yne (97 mg, 0.85 mmol) in THF (2 mL) in a dry Schlenk tube was added *n*-BuLi (0.47 mL, 2.0 M in hexane, 0.94 mmol) at −78 °C under N_2. After 100 min at −78 °C, dry $ZnBr_2$ (378 mg, 1.68 mmol) in THF (3 mL) was added. After 5 min at this temperature, the reaction mixture was warmed to rt and stirred at rt for 20 min, and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) and *o*-methylphenyl iodide (109 mg, 0.5 mmol) in THF (1 mL) were added at rt. After the reaction was complete, as monitored by TLC (eluent: hexane), it was quenched with water, and the mixture was extracted with diethyl ether and washed with water. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane) afforded 88 mg (85%) of **6a**: IR (film) 1930, 1697, 1595, 1575, 1489, 1449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.15 (m, 9H, PhH), 5.20 (s, 2H, $=CH_2$), 2.25 (s, 3H); MS (EI) *m/z* (%) 206 (100) $[M]^+$; HRMS ($-CH_3$) calcd for $C_{15}H_{11}$ 191.0858, found 191.0852. Compounds **2d**, **6b**, **2e**, **6c**, **2f**, and **2g** were synthesized similarly.

1-(Trimethylsilyl)-3-(*o*-methylphenyl)prop-1-yne (2d). 1-(Trimethylsilyl)prop-1-yne (190 mg, 1.7 mmol), $ZnBr_2$ (635 mg, 2.82 mmol), and *o*-methylphenyl iodide (221 mg, 1 mmol) afforded 104 mg (52%) of **2d**: IR (film) 2174, 1603, 1490, 1460, 1420 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55−7.40 (m, 1H), 7.25−7.10 (m, 3H), 3.58 (s, 2H), 2.30 (s, 3H), 0.20 (s, 9H); MS (EI) *m/z* (%) 202 (7.21) $[M]^+$; HRMS ($-CH_3$) calcd for $C_{12}H_{15}Si$ 187.0939, found 187.0963.

1-(Trimethylsilyl)-1-phenylpropa-1,2-diene (6b) and 1-(Trimethylsilyl)-3-phenylprop-1-yne (2e). 1-(Trimethylsilyl)prop-1-yne (190 mg, 1.7 mmol), $ZnBr_2$ (546 mg, 2.43 mmol), and phenyl iodide (203 mg, 1 mmol) afforded 44 mg (23%) of **6b** and 46 mg (24%) of **2e**. **6b**: IR (film) 1912, 1630, 1595, 1490, 1443 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.15 (m, 5H, PhH), 4.69 (s, 2H, $=CH_2$), 0.26 (s, 9H, Me_3Si); MS (EI) *m/z* (%) 188 (35.49) $[M]^+$. **2e**: IR (film) 2176, 1697, 1601, 1492, 1451 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37−7.20 (m, 5H, PhH), 3.66 (s, 2H, CH_2), 0.20 (s, 9H, Me_3Si); MS (EI) *m/z* (%) 188 (16.06) $[M]^+$.

1-(Trimethylsilyl)-1-naphthylpropa-1,2-diene (6c) and 1-(Trimethylsilyl)-3-naphthylprop-1-yne (2f). 1-(Trimethylsilyl)prop-1-yne (93 mg, 0.85 mmol), $ZnBr_2$ (390 mg, 1.73 mmol), and naphthyl iodide (122 mg, 0.48 mmol) afforded 19 mg (17%) of **6c** and 47 mg (41%) of **2f**. **6c**: IR (film) 1919, 1625, 1459 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ 8.10−8.00 (m, 1H, ArH), 7.90−7.80 (m, 1H, ArH), 7.70 (d, ^3J (H,H) = 8.13 Hz, 1H, ArH), 7.55−7.40 (m, 3H, ArH), 7.21 (d, ^3J (H,H) = 7.02 Hz, 1H, ArH), 4.53 (s, 2H, $=CH_2$), 0.15 (s, 9H, Me_3Si); MS (EI) *m/z* (%) 238 (19.05) $[M]^+$; HRMS calcd for $C_{16}H_{18}Si$ 238.1173, found 238.1158. **2f**: IR (film) 2176, 1597, 1509, 1414 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, ^3J (H,H) = 9.00 Hz, 1H, ArH), 7.88 (d, ^3J (H,H) = 7.45 Hz, 1H, ArH), 7.77 (d, ^3J (H,H) = 8.28 Hz, 1H, ArH), 7.66 (d, ^3J (H,H) = 7.06 Hz, 1H, ArH), 7.60−7.40 (m, 3H, ArH), 4.06 (s, 2H, CH_2), 0.20 (s, 9H, Me_3Si); MS (EI) *m/z* (%) 238 (89.56) $[M]^+$; HRMS calcd for $C_{16}H_{18}Si$ 238.1173, found 238.1162.

1-(*tert*-Butyldimethylsilyl)-3-naphthylprop-1-yne (2g). 1-(*tert*-Butyldimethylsilyl)prop-1-yne (231 mg, 1.5 mmol), $ZnBr_2$ (398 mg, 1.77 mmol), and naphthyl iodide (128 mg, 0.5 mmol) afforded 73 mg (52%) of **2g**: IR (film) 2175, 1597, 1502, 1459 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05−7.25 (m, 7H, ArH), 4.08 (s, 2H, CH_2), 0.97 (s, 9H, TBS), 0.14 (s, 6H, TBS); MS (EI) *m/z* (%) 280 (11.09) $[M]^+$; HRMS calcd for $C_{19}H_{24}Si$ 280.1641, found 280.1652.

Synthesis of Organic Zinc Reagent.[9] To a dry, 25 mL three-necked flask were added activated zinc powder (1.625 g, 25 mmol), THF (3 mL), and 1,2-dibromoethane (94 mg, 0.5 mmol, 0.04 mL) under N_2 and, the mixture was heated to 65 °C for 1 min. It was then cooled to rt and treated with trimethylchloromethane (40 mg, 0.4 mmol, 0.05 mL). After 15 min at rt, a solution of organic halides (10 mmol) in THF (4 mL) was slowly added and heated to 45 °C. After the reaction was complete, as monitored by TLC, it was reserved for further use under an atmosphere of N_2. The concentrations of the organozinc reagents prepared were calculated on the basis of the assumption that the yields for these oxidative addition steps were 100%.

General Procedure for Iodinolysis of 12a, 12c, and 12d. To a solution of organozinc reagent (1 mL, ca. 1 mmol) in THF (1 mL) at −78 °C was added iodine (381 mg, 1.5 mmol) in THF (4 mL). The mixture was then warmed to rt, extracted with diethyl ether, and washed subsequently with saturated aqueous sodium thiosulfate and saturated aqueous sodium chloride. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel afforded the iodolysis product(s).

Hydrolysis of 12b. To a dilute aqueous solution of hydrochloric acid (5 mL) was added organozinc reagent **12b** (1 mL). The mixture was extracted with diethyl ether and washed with water. Drying over $MgSO_4$, rotary evaporation, and chromatography on silica gel afforded the hydroysis products.

Synthesis of Propargylic Carbonates: Typical Procedure for the Synthesis of Methyl 3-Phenylprop-2-ynyl Carbonate (11b). To a solution of 3-phenylprop-2-ynol (4.27 g, 32 mmol) and pyridine (70 mmol, 5.71 mL) in Et_2O (40 mL) at 0 °C was slowly added methyl chloroformate (64 mmol, 2.55 mL) for 5 min, and the reaction mixture was then warmed to rt. After the reaction was complete, as monitored by TLC, it was quenched with a dilute aqueous solution of hydrochloric acid, extracted with diethyl ether, and washed with saturated aqueous sodium chloride. Drying over $MgSO_4$, rotary evaporation, and recrystallization from ether afforded 5.126 g (84%) of **11b**: mp 50−51 °C (diethyl ether); IR (film) 2219, 1752, 1626, 1099 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50−7.40 (m, 2H, PhH), 7.40−7.25 (m, 3H, PhH), 4.96 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3); MS (EI) *m/z* (%) 190 (13.59) $[M]^+$. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.53; H, 5.24.

Methyl 1-(Trimethylsilyl)hex-1-yn-3-yl Carbonate (11d). 1-(Trimethylsilyl)hex-1-yn-3-ol (5.207 g, 30.6 mmol) afforded 3.538 g (51%) of **11d**, and 1.950 g (37%) of 1-(trimethylsilyl)-hex-1-yn-3-ol was recovered. **11d**: IR (film) 2177, 1747, 1180, 1119 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.23 (t, ^3J(H, H) = 6.65 Hz, 1H, CH), 3.83 (s, 3H, OCH_3), 1.90−1.70 (m, 2H, CH_2), 1.60−1.40 (m, 2H, CH_2), 0.95 (t, ^3J(H,H) = 7.40 Hz, 3H, CH_3), 0.16 (s, 9H, Me_3Si); MS (EI) *m/z* (%) 228 (0.43) $[M]^+$. Anal. Calcd for $C_{11}H_{20}O_3Si$: C, 57.86; H, 8.83. Found: C, 58.17; H, 8.66.

Methyl 1-Phenylhex-1-yn-3-yl Carbonate (11f). 1-Phenylhex-1-yn-3-ol (6.179 g, 35.5 mmol) afforded 6.08 g (74%) of **11f**, and 1.503 g (24%) of 1-phenylhex-1-yn-3-ol was recovered. **11f**: IR (film) 2236, 1747, 1597, 1489, 1441, 1181, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50−7.40 (m, 2H, PhH), 7.37−7.21 (m, 3H, PhH), 5.45 (t, ^3J(H, H) = 6.68 Hz, 1H, CH), 3.82 (s, 3H, OCH_3), 1.95−1.80 (m, 2H, CH_2), 1.65−1.50 (m, 2H, CH_2), 0.98 (t, ^3J(H, H) = 7.24 Hz, 3H, CH_3); MS (EI) *m/z* (%) 232 (6.52) $[M]^+$; HRMS calcd for $C_{14}H_{16}O_3$ 232.1095, found 232.1147.

Pd(PPh$_3$)$_4$-Catalyzed Coupling Reaction of Propargylic Carbonates with Electron-Deficient Alkenyl Zinc Iodide: General Procedures for the Syntheses of (*Z*)-2a, (*E*)-2i, 2j, (*Z*)-2h, (*E*)-2k, 2h, (*Z*)-2l, (*E*)-6d, (*E*)-2m, (*Z*)-2c, and (*E*)-6e. To a solution of propargylic carbonate (0.65 mmol) in THF (2 mL) were added Pd(PPh$_3$)$_4$ (29 mg, 0.025 mmol) and organozinc reagent[12] (0.5 mmol), and the mixture was heated according to the specific temperature in Table 2. After the reaction was complete, as monitored by TLC, it was quenched with water, and the mixture was extracted with diethyl ether and washed with water. Drying over MgSO$_4$, rotary evaporation, and chromatography on silica gel afforded the product.

Ethyl 6-(Trimethylsilyl)hex-5-yn-(2*Z*)-enoate ((*Z*)-2a). 11a (121 mg, 0.65 mmol) and **12a** (0.5 mL, ca. 1.0 M, 0.5 mmol) afforded 46 mg (44%) of (*Z*)-**2a**, and 20 mg (16.5%) of **11a** was recovered. The data of (*Z*)-**2a** are the same as above.

Methyl 6-(Trimethylsilyl)-4-phenylhex-5-yn-(2*Z*)-enoate ((*E*)-2i). 11a (102 mg, 0.55 mmol) and **12b** (0.41 mL, ca. 1.0 M, 0.41 mmol) afforded 90 mg (60%) of (*E*)-**2i**: IR (film) 2175, 1714, 1629, 1173 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.58−7.47 (m, 2H, PhH), 7.38−7.30 (m, 3H, PhH), 6.11 (s, 1H, =CH), 4.10 (s, 2H, CH$_2$), 3.74 (s, 3H, OCH$_3$), 0.01 (s, 9H, Me$_3$Si); MS (EI) *m*/*z* (%) 272 (65.04) [M]$^+$; HRMS calcd for C$_{16}$H$_{20}$O$_2$Si 272.1227, found 272.1237.

Methyl 6-(Trimethylsilyl)-4-methylhex-5-yn-(2*Z*)-enoate ((*Z*)-2j) and Methyl 6-(Trimethylsilyl)-4-methylhex-5-yn-(2*Z*)-enoate ((*E*)-2j): 11a (65 mg, 0.35 mmol) and **12c** (0.5 mL, ca. 1.0 M, 0.5 mmol) afforded 20 mg (28%) of (*Z*)-**2j** and 26 mg (35%) of (*E*)-**2j**. (*Z*)-**2j**: IR (film) 2138, 1738, 1617, 1162 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.75 (s, 1H, =CH), 3.77 (s, 2H, CH$_2$), 3.69 (s, 3H, OCH$_3$), 2.06 (s, 3H, CH$_3$), 0.18 (s, 9H, Me$_3$Si); MS (EI) *m*/*z* (%) 210 (49.89) [M]$^+$; HRMS calcd for C$_{11}$H$_{18}$O$_2$Si 210.1071, found 210.1076. (*E*)-**2j**: IR (film) 2178, 1718, 1652, 1148 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.00 (s, 1H, =CH), 3.70 (s, 2H, CH$_2$), 3.07 (s, 3H, OCH$_3$), 2.16 (s, 3H, CH$_3$), 0.18 (s, 9H, Me$_3$Si); MS (EI) *m*/*z* (%) 210 (24.57) [M]$^+$; HRMS calcd for C$_{11}$H$_{18}$O$_2$Si 210.1071, found 210.1048.

Ethyl 6-Phenylhex-5-yn-(2*Z*)-enoate ((*Z*)-2h). 11b (124 mg, 0.65 mmol) and **12a** (0.5 mL, ca. 1.0 M, 0.5 mmol) afforded 63 mg (60%) of (*Z*)-**2h**, and 27 mg of **11b** was recovered. The data of (*Z*)-**2h** are the same as those reported in ref 3.

Methyl 3,6-Diphenylhex-5-yn-(2*E*)-enoate ((*E*)-2k). **11b** (114 mg, 0.6 mmol) and **12b** (0.41 mL, ca. 1.0 M, 0.5 mmol) afforded 87 mg (63%) of (*E*)-**2k**. The data are the same as those reported in ref 4.

Ethyl 6-Phenylhex-5-yn-2-enoate (2h). 11b (124 mg, 0.65 mmol) and **12d** (0.5 mL, ca. 1.0 M, 0.5 mmol) afforded 26 mg (18.7%) of (*Z*)-**2h** and 30 mg (21.6%) of (*E*)-**2h**. Their data are the same as those reported in ref 4.

Ethyl Dec-5-yn-(2*Z*)-enoate ((*Z*)-2l) and Ethyl 4-*n*-Butylhexa-2,4,5-trienoate ((*E*)-6d). 11c (219 mg, 1.3 mmol) and **12a** (1 mL, ca. 1.0 M, 1.0 mmol) afforded 106 mg (55%) of (*Z*)-**2l** and 35 mg (18%) of (*E*)-**6d**, and 30 mg of **11c** was recovered. (*Z*)-**2l**: IR (film) 2210, 1714, 1644, 1181 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.20 (dt, ^3J(H,H) = 11.32 Hz, ^3J(H,H) = 6.80 Hz, 1H, =CH), 5.75 (dt, ^3J(H,H) = 11.32 Hz, ^4J(H,H) = 1.75 Hz, 1H, =CH), 4.13 (q, ^3J(H,H) = 7.12 Hz, 2H, OCH$_2$), 3.60−3.50 (m, 2H, CH$_2$), 2.20−2.05 (m, 2H, CH$_2$), 1.50−1.30 (m, 4H, CH$_2$), 1.25 (t, ^3J(H,H) = 7.14 Hz, 3H, CH$_3$), 0.81 (t, ^3J(H,H) = 7.05 Hz, 3H, CH$_3$); MS (EI) *m*/*z* (%) 195 (13.13) [M + 1]$^+$; HRMS calcd for C$_{12}$H$_{18}$O$_2$ 194.1302, found 194.1281. (*E*)-**6d**: IR (film) 1925, 1707, 1619 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.22 (d, ^3J(H,H) = 15.88 Hz, 1H, =CH), 5.80 (d, ^3J(H,H) = 15.88 Hz, 1H, =CH), 4.91 (s, 2H, =CH$_2$), 4.14 (q, ^3J(H,H) = 7.12 Hz, 2H, OCH$_2$), 2.15−2.00 (m, 2H, CH$_2$), 1.50−1.20 (m, 7H, CH$_2$ and CH$_3$), 0.85 (t, ^3J(H,H) = 7.12 Hz, 3H, CH$_3$); MS (EI) *m*/*z* (%) 195 (5.18) [M + 1]$^+$; HRMS calcd for C$_{12}$H$_{18}$O$_2$ 194.1302, found 194.1305.

Methyl 4-Phenyldec-5-yn-(2*E*)-enoate ((*E*)-2m). 11c (102 mg, 0.6 mmol) and **12b** (0.41 mL, ca. 1.0 M, 0.41 mmol) afforded 67 mg (44%) of (*E*)-**2m**: IR (film) 2224, 1714, 1628, 1172 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.60−7.50 (m, 2H, PhH), 7.40−7.30 (m, 3H, PhH), 6.11 (s, 1H, =CH), 4.00 (s, 2H, CH$_2$), 3.74 (s, 3H, OCH$_3$), 2.05−1.95 (m, 2H, CH$_2$), 1.35−1.15 (m, 4H, CH$_2$), 0.77 (t, ^3J(H,H) = 7.30 Hz, 3H, CH$_3$); MS (EI) *m*/*z* (%) 256 (3.52) [M]$^+$; HRMS calcd for C$_{17}$H$_{20}$O$_2$ 256.1458, found 256.1461.

Ethyl 6-(Trimethylsilyl)-4-propylhex-5-yn-(2*Z*)-enoate ((*Z*)-2c). 11d (146 mg, 0.65 mmol) and **12a** (0.5 mL, ca. 1.0 M, 0.5 mmol) afforded 44 mg (35%) of (*Z*)-**2c**, and 52 mg of **11d** was recovered. The data of (*Z*)-**2c** are the same as above.

Ethyl 4-(*n*-Butyl)non-(2*E*),4,5-trienoate ((*E*)-6e). 11e (138 mg, 0.65 mmol) and **12a** (0.6 mL, ca. 1.0 M, 0.6 mmol) afforded 108 mg (70%) of (*E*)-**6e**: IR (film) 1932, 1705, 1615, 1161, 1100 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.26 (d, ^3J(H,H) = 15.83 Hz, 1H, =CH), 5.80 (d, ^3J(H,H) = 15.83 Hz, 1H, =CH), 5.37 (bs, 1H, =CH), 4.18 (q, ^3J(H,H) = 7.07 Hz, 2H, OCH$_2$), 2.20−1.95 (m, 4H, CH$_2$), 1.60−1.20 (m, 9H, CH$_2$ and CH$_3$), 1.05−0.85 (m, 6H, CH$_3$); MS (EI) *m*/*z* (%) 236 (1.09) [M]$^+$; HRMS calcd for C$_{15}$H$_{24}$O$_2$ 236.1770, found 236.1751.

11e (106 mg, 0.5 mmol) and **12d** (1 mL, ca. 1.0 M, 1.0 mmol) afforded 65 mg (55%) of (*E*)-**6e**. The data are the same as above.

Reaction of 11f with 12a. 11f (116 mg, 0.5 mmol) and **12a** (0.5 mL, ca. 1.0 M, 0.5 mmol) afforded no product.

Pd(PPh$_3$)$_4$-Catalyzed Coupling Reaction of Propargylic Carbonates with (2*E*)-Phenylethenylboronic Acid: Typical Procedure for the Synthesis of (*E*)-2o and (*E*)-6f. To a solution of methyl 2-heptynyl carbonate (85 mg, 0.5 mmol) and Pd(PPh$_3$)$_4$ (29 mg, 0.025 mmol) in THF (2 mL) was added (2*E*)-phenylethenylboronic acid[16] (89 mg, 0.6 mmol). After the mixture was refluxed for 4 h, the reaction was quenched with water and the mixture was extracted with diethyl ether. Drying over MgSO$_4$, rotary evaporation, and chromatography on silica gel (eluent: hexane) afforded 52 mg (49%) of 1-phenylnona-4-yn-(1*E*)-ene ((*E*)-**2o**, which was contaminated with a small amount of compound **13**, see Scheme 10) and 29 mg (29%) of 1-phenyl-4-*n*-butyl-(1*E*),3,4-pentatriene ((*E*)-**6f**). (*E*)-**2o**: IR (film) 2216, 1617, 749, 698 cm^{-1}; ^{1}H NMR (300 MHz/CDCl$_3$) δ 7.45−7.20 (m, 5H, PhH), 6.65 (d, ^3J(H,H) = 15.7 Hz, 1H, =CH), 6.20 (dt, ^3J(H,H) = 15.7, ^3J(H,H) = 5.5 Hz, 1H, =CH), 3.20−3.10 (m, 2H, CH$_2$), 2.40−2.20 (m, 2H, CH$_2$), 1.60−1.40 (m, 4H, (CH$_2$)$_2$), 0.93 (t, ^3J(H,H) = 7.00 Hz, 3H, CH$_3$); MS (*m*/*z*) (%) 198 (42.37) [M]$^+$; HRMS calcd for C$_{15}$H$_{18}$ 198.1404, found 198.1394. (*E*)-**6f**: IR (film) 1932, 1600, 1493, 1450 cm^{-1}; ^{1}H NMR (300 MHz/CDCl$_3$) δ 7.45−7.15 (m, 5H, PhH), 6.70 (d, ^3J(H,H) = 16.12 Hz, 1H, =CH), 6.50 (d, ^3J(H,H) = 16.12 Hz, 1H, =CH), 4.97 (s, 2H, =CH$_2$), 2.35−2.20 (m, 2H, CH$_2$), 1.65−1.40 (m, 4H, (CH$_2$)$_2$), 0.96 (t, ^3J(H,H) = 7.26 Hz, 3H, CH$_3$); MS (*m*/*z*) (%) 198 (11.05) [M]$^+$; HRMS calcd for C$_{15}$H$_{18}$ 198.1404, found 198.1409.

3-(*n*-Butyl)-1-phenyloct-(1*E*),3,4-triene ((*E*)-6g). 11e (53 mg, 0.25 mmol), Na$_2$CO$_3$ (94 mg, 0.88 mmol), and (2*E*)-phenylethenylboronic acid (74 mg, 0.5 mmol) at 55 °C afforded 36 mg (60%) of (*E*)-**6g**: IR (film) 1931, 1618, 1597, 1490, 1458 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50−7.15 (m, 5H, PhH), 6.72 (d, ^3J(H,H) = 16.32 Hz, 1H, =CH), 6.48 (d, ^3J(H,H) = 16.32 Hz, 1H, =CH), 5.45−5.35 (m, 1H, =CH), 2.35−2.20 (m, 2H, CH$_2$), 2.20−2.05 (m, 2H, CH$_2$), 1.70−1.35 (m, 6H, CH$_2$), 1.10−0.90 (m, 6H, CH$_3$); MS (EI) *m*/*z* (%) 240 (13.23) [M]$^+$; HRMS calcd for C$_{18}$H$_{24}$ 240.1872, found 240.1875.

Synthesis of Ethyl 6-Phenylhex-5-yn-(2*Z*)-enoate ((*Z*)-2h) from the Reaction of 3-Phenylprop-2-ynyl Acetate with (2*Z*)-Ethoxycarbonylethenyl Zinc Iodide. The procedure is the same as the general procedure for the Pd(PPh$_3$)$_4$-catalyzed coupling reaction of propargylic carbonates with electron-deficient alkenyl zinc iodide. 3-Phenylprop-2-ynyl acetate (115 mg, 0.65 mmol) and **12a** (0.5 mL, ca. 1.0 M, 0.5 mmol) afforded 39 mg (37%) of (*Z*)-**2h**, and 37 mg of 3-phenylprop-2-ynyl acetate was recovered. The data are the same as those reported in ref 4.

Supporting Information Available: ^{1}H NMR spectra for all new products and ^{1}H−^{1}H NOESY spectra of *E*-**2i**, *Z*-**2j**, and *E*-**2m**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0111098