Articles

Nickel-Catalyzed Cross-Coupling Reaction of Allyl Halides with Alkynyltins

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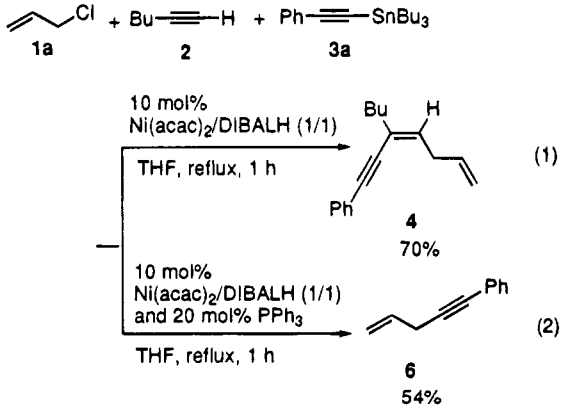
A cross-coupling reaction of allyl halides **1** with alkynyltins **3** in the presence of "$Ni(PR_3)_n$" (R = Ph, OEt, or OPh) catalyst was carried out in THF at reflux to give 1,4-enynes. The regioselectivity of the coupling of **1f-i** with **3a** was investigated in the presence of various phosphorus ligands. Interestingly, prenyl (**1j**) and geranyl chlorides (**1k**) selectively reacted with **3** at the more-hindered positions of substituted η^3-allylnickel intermediates **21** (M = Ni) to yield **23** and **25**, respectively. Regioselectivity in these reactions may result from greater steric crowding between the phosphorus ligand and the disubstituted position in **26b** than in **26a**. In contrast, the palladium-catalyzed reactions of **1j** and **1k** with **3** selectively gave **22** and **24**, respectively. Thus, the steric crowding in a Pd analogue of **26b** is less than that in a Ni analogue of **26b**, since Pd has a larger covalent radius than Ni.

The palladium-catalyzed coupling of organic electrophiles with organotins, known as the Stille coupling, is a highly versatile method for carbon–carbon bond formation and has been widely used as a synthetic tool.[1] In our search for other transition-metal-catalyzed reactions with organotins, we found that a nickel complex catalyzed the three-component coupling reaction of allyl chloride **1a** with 1-alkyne **2** and alkynyltin **3a** to regio- and stereoselectively provide 1,3,6-dienyne **4** in good yield (eq 1).[2] This reaction may proceed via the insertion of **2** into



η^3-allylnickel intermediate **5**,[3] which is generated from the reaction of nickel complex with **1a**,[4] followed by transmetalation of **3a** and then reductive elimination of **7** (Scheme 1). In the course of investigating this reaction, we observed that 1,4-enyne **6** was the sole product when PPh_3 was added to the reaction depicted in eq 1 (i.e., eq 2). This suggests that the coordination of PPh_3 to **5** inhibits the insertion of **2** into **5**; thus, the direct coupling of **1a** with **3a** gave **6**. We have conducted an investigation of this cross-coupling reaction of allyl halides **1** with alkynyltins **3** in the presence of nickel catalyst.[5]

Results and Discussion

The reaction of 3-chloro-1-propene (**1a**) (1 equiv) with (phenylethynyl)tributyltin (**3a**) (1.02 equiv) in THF was carried out in the presence of various nickel complexes (Table 1). In the presence of 10 mol % $Ni(acac)_2$ and DIBALH, which was the catalytic system in eq 1,[2] the coupling of **1a** with **3a** gave 1-phenyl-4-penten-1-yne (**6**) in a yield of 26% after reflux for 20 h in THF (run 1). When 20 mol % PPh_3 was added to the reaction, the coupling reaction occurred more smoothly to afford **6** (runs 2 and 3). Other nickel complexes such as $NiCl_2(PPh_3)_2$ or $NiCl_2/PPh_3$ could be used as the catalyst under reflux conditions (runs 5 and 6), but in the presence of $Ni(OAc)_2$ the reaction did not proceed at all (run 7). While neither PBu_3 nor 1,2-bis(diphenylphosphino)-ethane (dppe) was suitable (runs 8 and 9), $P(OEt)_3$ and $P(OPh)_3$ were each effective in the coupling reaction (runs 11 and 12). Each catalytic reaction proceeded more smoothly at reflux than at room temperature (runs 3 vs 2, 5 vs 4, and 11 vs 10). Although the same coupling

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(1) Recent reviews: (a) Stille, J. K. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Mitchell, T. N. *Synthesis* **1992**, 803. (c) Ritter, K. *Synthesis* **1993**, 735.

(2) Ikeda, S.; Cui, D.-M.; Sato, Y. *J. Org. Chem.* **1994**, *59*, 6877. Also see: Ikeda, S.; Sato, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5975.

(3) For the insertion of alkynes into η^3-allylnickel intermediates, see: (a) Chiusoli, G. P. *Acc. Chem. Res.* **1973**, *6*, 422. (b) Casser, L.; Chiusoli, G. P.; Guerrieri, F. *Synthesis* **1973**, 509. (c) Llebaria, A.; Moretó, J. M. *J. Organomet. Chem.* **1993**, *451*, 1.

(4) For the preparation and reaction of η^3-allylnickel complexes, see: (a) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8. (b) Billington, D. C. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, p 423.

(5) The nickel-catalyzed reaction of allyl acetate with **2** to give **6** has been reported. See: Catellani, M.; Chiusoli, G. P.; Salerno, G.; Dallatomasina, F. *J. Organomet. Chem.* **1978**, *146*, C19.

0022-3263/95/1960-5752$09.00/0

Scheme 1

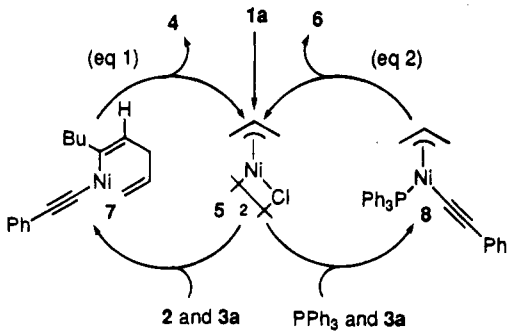


Table 1. Nickel-Catalyzed Coupling of 1a with 3a[a]

run	catalyst	temp	time, h	yield of 6,[b] %
1	$Ni(acac)_2$/DIBALH	reflux	20	(26)
2	$Ni(acac)_2$/DIBALH/PPh_3	rt	1	65
3	$Ni(acac)_2$/DIBALH/PPh_3	reflux	1	71
4	$NiCl_2(PPh_3)_2$	rt	20	0
5	$NiCl_2(PPh_3)_2$	reflux	1	66
6	$NiCl_2/PPh_3$	reflux	4	53
7	$Ni(OAc)_2/PPh_3$	reflux	20	0
8	$Ni(acac)_2$/DIBALH/PBu_3	reflux	20	(5)
9	$Ni(acac)_2$/DIBALH/dppe[c]	reflux	6	21
10	$Ni(acac)_2$/DIBALH/$P(OEt)_3$	rt	20	0
11	$Ni(acac)_2$/DIBALH/$P(OEt)_3$	reflux	1	77
12	$Ni(acac)_2$/DIBALH/$P(OPh)_3$	reflux	2	72
13	$Pd_2(dba)_3$[d]/PPh_3	reflux	1	(18)
			20	65

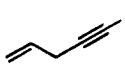
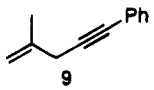
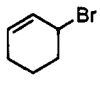
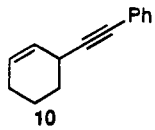
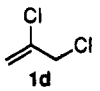
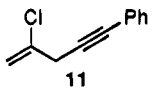
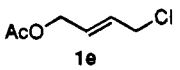
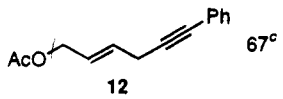
[a] Reaction conditions: nickel complex (0.1 mmol), DIBALH (1 M in hexane, 0.11 mL), phosphine or phosphite (0.2 mmol), **1a** (1.0 mmol), and **3a** (1.02 mmol) in THF (5 mL). [b] Isolated yield. GC yield is in parentheses. [c] 1,2-Bis(diphenylphosphino)ethane (0.1 mmol). [d] 0.05 mmol.

reaction occurred in the presence of palladium complex, a longer reaction time was required than in the presence of nickel catalyst (run 13).[6]

On the basis of these results, the nickel-catalyzed cross-coupling in the presence of $P(OEt)_3$ of a variety of substrates, **1a–e**, with **3a** was carried out, leading to **6** and **9–12** in good yields. These results are summarized in Table 2. 3-Bromo-1-propene (**1a**, X = Br) and 3-bromocyclohexene (**1c**) could also be used in the coupling reaction. A chlorine atom at the vinylic position of 2,3-dichloropropene (**1d**) and an acetoxy group at the allylic position of 1-acetoxy-4-chloro-2-butene (**1f**) remained in the coupling products **11** and **12**, respectively, under these reaction conditions. Product **12** was determined to be an *E*-isomer based on its ^1H NMR spectrum.

This coupling may proceed via the transmetalation of **3** to **5** followed by reductive elimination of **8** (*vide supra*, Scheme 1). Since carbon–carbon bond formation by reductive elimination may result from the *cis* orientation of the allyl unit and alkynyl unit on the metal center,[7] regioselective coupling via the equilibrium of intermediates **14a** and **14b** can be observed in the reaction of η^3-allylnickel intermediates **13** with **3** (eq 3). Therefore, we examined the nickel-catalyzed coupling of some allyl halides **1f–i** with **3a** in the presence of various phosphorus additives (Table 3). Reactions of both 3-chloro-1-

Table 2. Reaction of Variety of 1 with 3[a]

1	time, h	product 6	yield,[b] %
 1a: X = Cl	1	 6	77
X = Br	1		75
 1b	6	 9	71
 1c	4	 10	58
 1d	20	 11	78
 1e	20	 12	67[c]

[a] Reaction conditions: $Ni(acac)_2$ (0.1 mmol), DIBALH (1 M in hexane, 0,11 mL), $P(OEt)_3$ (0.2 mmol), **1** (1.0 mmol), and **3a** (1.02 mmol) in THF (5 mL) at reflux. [b] Isolated yield. [c] 3-(Acetoxymethyl)-1-phenyl-4-penten-1-yne as a minor product was detected by ^1H NMR after isolation (<4%).

butene (**1f**) and 1-chloro-2-butene (**1g**) resulted in coupling at the less-substituted terminus of the η^3-crotylnickel intermediate **13** (R^3 = Me) (i.e., reductive elimination from **14a**) to furnish (*E*)-**15** as the major coupling product (**15/16** ratio = 60/40) (runs 1 and 4). A similar result was observed in the presence of $P(OPh)_3$ instead of $P(OEt)_3$ (runs 2 and 5). In contrast, when PPh_3 was used in the reaction rather than a phosphite, the coupling of **1f** and **1g** with **3a** occurred at the more-hindered position (methyl-substituted allylic carbon) of **13** (R^3 = Me) (i.e., reductive elimination from **14b**) to give **16** as the main product (**15/16** ratio = 35/65) (runs 3 and 6).[8] The reactions in the presence of bulkier P(*o*-tolyl)$_3$ and $AsPh_3$, which is an excellent ligands for Stille coupling,[10] did not proceed well (runs 7 and 8). On the other hand, moderately selective coupling of trimethylsilyl-substituted **1h** occurred at the less-hindered terminus of **13** (R^3 = Me_3Si) to furnish **17** (runs 9 and 10). The reaction of **1i** gave (*E*)-**19** almost exclusively (**19/20** = 100/0) (runs 11 and 12).[8a]

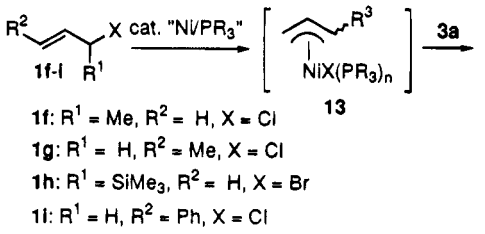
Interestingly, prenyl chloride (**1j**) and geranyl chloride (**1k**, isomeric purity: >95%) reacted regioselectively with **3** (eqs 4 and 5) at the more-hindered position of intermediate **21** (M = Ni, R = OEt or Ph) to yield **23** and **25**, respectively (runs 1, 2, 4, and 5 in Table 4).[8a] In contrast, the palladium-catalyzed reactions of **1j** and **1k** occurred at the less-hindered position of **21** (M = Pd, R = Ph) to selectively give **22** and **24**, respectively (runs 3, 6, and 7). It should be noted that a loss of stereochemistry in **24** (isomeric purity: ~85%) was observed in each reaction of **1k**.

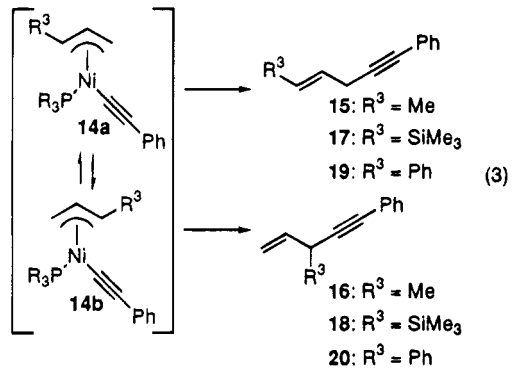
The electronic nature of the ancillary ligand[7ab,11] and steric interaction between the ligand and the substituted

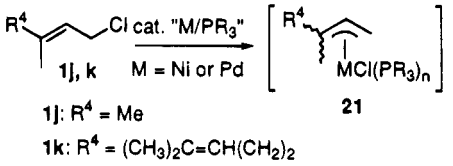
(6) Kosugi and Migita reported the palladium-catalyzed reaction of **1a** with **3a** to give **6a** in 32% yield. See: Kosugi, M.; Migita, T. *J. Synth. Org. Chem. Jpn.* **1980**, *38*, 1142.

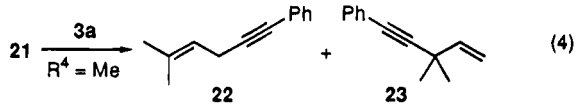
(7) (a) Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310. (b) Kurosawa, H.; Shiba, K.; Hirako, K.; Kakiuchi, K.; Ikeda, I. *J. Chem. Soc., Chem. Commun.* **1994**, 1099. Also see: (c) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

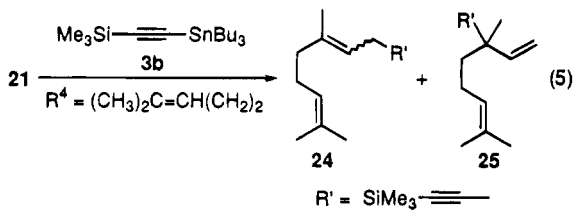
(8) A similar tendency to substitute at the more-hindered position has already been reported in the "$Ni(PPh_3)_n$"-catalyzed reaction of substituted allylic electrophiles, with the exception of the reaction of allyl sulfides,[9] with Grignard reagents. See: (a) Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735. (b) Hayashi, T.; Konishi, M.; Yokota, K.-I.; Kumada, M. *J. Organomet. Chem.* **1985**, *285*, 359.











allyl unit on the metal center[12] may control the regiochemistry in this coupling via the substituted η^3-allylnickel intermediates. Regiochemistry in the present nickel-catalyzed coupling of **1e–i** with **3a** may also be influenced by the net result of these two competing factors, although the details are unclear. In the couplings of **1j** and **1k** with **3**, we propose that the regioselectivity results from greater steric crowding between the phosphorus ligand and the disubstituted position in intermediate **26b** than that in **26a** (Scheme 2). Thus, the equilibrium between **26a** and **26b** lies so far toward **26a** that **23** or **25** is obtained selectively. In contrast, the steric crowding may be less in a Pd analogue of **26b** than in a Ni analogue of **26b**, due to the larger covalent radius of Pd than Ni.[13] Consistent with this, substitution at the less-hindered position of **21** (M = Pd) (i.e., reductive elimination from the Pd analogue of **26b**) was observed in the palladium-catalyzed reaction of **1j** and **1k** with **3**. A similar tendency for selective coupling at the less-hindered position of **21** (M = Pd) has also been observed in other palladium-catalyzed reactions with various organometallics.[14,15]

Table 3. Nickel-Catalyzed Coupling of 1f–i with 3a[a]

run	1	additive	time, h	yield,[b] %	ratio[c]
1	**1f**	$P(OEt)_3$	4	70	**15/16** = 59/41
2		$P(OPh)_3$	4	78	60/40
3		PPh_3	4	59	32/68
4	**1g**	$P(OEt)_3$	4	65 (76)	60/40
5		$P(OPh)_3$	4	75 (88)	59/41
6		PPh_3	4	47 (63)	35/65
7		P(*o*-tolyl)$_3$	20	trace	*d*
8		$AsPh_3$	20	trace	*d*
9	**1h**	$P(OEt)_3$	4	67	**17/18** = 63/37
10		PPh_3	4	36	55/45
11	**1i**	$P(OEt)_3$	6	79	**19/20** = 100/0
12		PPh_3	6	60	100/0

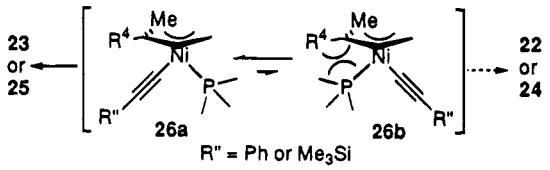
[a] Reaction conditions: $Ni(acac)_2$ (0.1 mmol), DIBALH (1 M in hexane, 0.11 mL), additive (0.2 mmol), **1** (1.0 mmol), and **3a** (1.02 mmol) in THF (5 mL) at reflux. [b] Isolated yield. GC yield is in parentheses. [c] Determined by ^1H NMR after isolation. [d] Could not be determined.

Table 4. Nickel or Palladium-Catalyzed Coupling of 1j–k with 3[a]

run	1	3	M/PR_3	time, h	yield,[b] %	ratio[c]
1	**1j**	**3a**	$Ni/P(OEt)_3$	20	64	**22/23** = <5/>95[d]
2			Ni/PPh_3	20	72	<3/>97[d]
3			Pd^e/PPh_3	48	49	75/25
4	**1k**[f]	**3b**	$Ni/P(OEt)_3$	20	79	**24/25** = 23/77[g]
5			Ni/PPh_3	20	59	10/90[g]
6			Pd^e/PPh_3	20	31	85/15[g]
7			Pd^e/PPh_3	48	49	86/14[g]

[a] Reaction conditions: $Ni(acac)_2$ (0.1 mmol), DIBALH (1 M in hexane, 0.11 mL), PR_3 (0.2 mmol), **1** (1.0 mmol), and **3** (1.02 mmol) in THF (5 mL) at reflux. [b] Isolated yield. [c] Determined by ^1H NMR after isolation. [d] Determined by GC analysis of the reaction mixture. Minor product **22** was not detected by ^1H NMR after isolation. [e] $Pd_2(dba)_3$ (0.05 mmol) instead of $Ni(acac)_2$/DIBALH was used. [f] Isomeric purity: >95% by ^1H NMR. [g] Isomeric purity of **24**: ~85% by GC.

Scheme 2



Experimental Section

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. THF was distilled from Na benzophenone ketyl.

(9) (a) Okamura, H.; Takei, H. *Tetrahedron Lett.* **1979**, 3425.
(10) (a) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (b) Farina, V.; Krishnan, B.; Marshall, D. R.; Roth, G. P. *J. Org. Chem.* **1993**, *58*, 5434.
(11) (a) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416. (b) Temple, J. S.; Schwartz, J. *J. Am. Chem. Soc.* **1980**, *102*, 7381. (c) Hayasi, Y.; Riediker, M.; Temple, J. S.; Schwartz, J. *Tetrahedron Lett.* **1981**, *28*, 2629.
(12) Keinan, E.; Sahai, M. *J. Chem. Soc., Chem. Commun.* **1984**, 648.
(13) Kurosawa, H.; Ohnishi, H.; Emoto, M.; Chatani, N.; Kawasaki, Y.; Murai, S.; Ikeda, I. *Organometallics* **1990**, *9*, 3038.
(14) (a) Matsushita, H.; Negishi, E. *J. Am. Chem. Soc.* **1981**, *103*, 2882. (b) Negishi, E.; Chatterjee, S.; Matsushita, H. *Tetrahedron Lett.* **1981**, *22*, 3737. (c) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833. (d) Katsumura, S.; Fujiwara, S.; Isoe, S. *Tetrahedron Lett.* **1987**, *28*, 1191. (e) Echavarren, A. M.; Tueting, D. R.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 4039.
(15) For an example of a moderately selective reaction at the more-hindered site of **10** (M = Pd) with anions of dialkyl malonates, see: Åkermark, B.; Hannson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679.

Tris(dibenzylideneacetone)dipalladium(0),[16] 1-acetoxy-4-chloro-2-butene,[17] 3-bromo-3-(trimethylsilyl)-1-propene,[18] (phenylethynyl)tributyltin,[19] and [(trimethylsilyl)ethynyl]tributyltin[19] were prepared as described elsewhere.

Typical Procedure. To a solution of $Ni(acac)_2$ (26 mg, 0.1 mmol) and $P(OEt)_3$ (33 mg, 0.2 mmol) in THF (5 mL) was added DIBALH (1.0 M toluene solution, 0.11 mL) at 0 °C under N_2, and the mixture was stirred for 5 min. To this solution was then added (phenylethynyl)tributyltin (**3a**) (400 mg, 1.02 mmol) and 3-chloro-1-butene (**1a**) (76 mg, 1.0 mmol) at 0 °C, and the mixture was stirred at reflux for 1 h. To this mixture was added aqueous NH_4F (30 mL), and the resulting mixture was stirred for 30 min at room temperature to remove Bu_3SnCl. The organic layer was separated by Celite, and the aqueous layer was extracted with Et_2O (3 × 30 mL) . The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane, R_f = 0.34) to yield 1-phenyl-4-penten-1-yne (**6**) (109 mg, 77%) as a colorless oil. An analytical sample of the product was obtained by bulb-to-bulb distillation (bp 110 °C (25 mmHg)). For GC yield, an appropriate hydrocarbon (n-$C_{11}H_{24}$) calibrated against the purified product was added before the catalytic reaction.

1-Phenyl-4-penten-1-yne (6): a colorless oil; bp 110 °C (25 mmHg); R_f = 0.34 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.21 (dt, J = 5.3, 1.7 Hz, 2 H), 5.18 (dq, J = 9.9, 1.6 Hz, 1 H), 5.42 (dq, J = 16.8, 1.7 Hz, 1 H), 5.86 (ddt, J = 16.8, 10.0, 5.3 Hz, 1 H), 7.27−7.48 (m, 5 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 23.69, 82.86, 86.52, 116.21, 123.68, 127.73, 128.19, 131.57, 132.44; IR (neat) 756, 691 cm^{-1}; MS (DIEI, 70 eV) m/z (rel int) 142 (M^+, 100), 141 (98), 115 (68). Anal. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 92.81; H, 7.34.

1-Phenyl-4-methyl-4-penten-1-yne (9): a colorless oil; bp 140 °C (20 mmHg); R_f = 0.31 (hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.84 (s, 3 H), 3.11 (s, 2 H), 4.87 (m, 1 H), 5.07 (m, 1 H), 7.24−7.42 (m, 5 H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 22.12, 28.15, 82.80, 87.06, 111.76, 123.79, 127.68, 128.18, 131.56, 140.53. IR (neat) 895, 756, 691 cm^{-1}; GCMS (EI, 70 eV) m/z (rel int) 156 (M^+, 100), 155 (51), 141 (80), 128 (24), 115 (91). Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.98.

3-(Phenylethynyl)cyclohexene (10): a colorless oil; bp 100 °C (2.0 mmHg); R_f = 0.31 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.57−2.09 (m, 6 H), 3.27−3.33 (m, 1 H), 5.70−5.82 (m, 2 H), 7.24−7.52 (m, 5 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.63, 24.66, 27.98, 29.36, 80.27, 92.83, 123.88, 127.03, 127.51, 128.01, 128.10, 131.59; IR (neat) 3028, 2932, 2861, 2838, 1489, 1443, 754, 691 cm^{-1}; GCMS (EI, 70 eV) m/z (rel int) 182 (M^+, 100), 181 (40), 167 (59), 166 (25), 165 (34), 154 (57), 153 (48), 152 (33), 141 (27), 128 (24), 115 (29). Anal. Calcd for $C_{14}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.28; H, 7.94.

4-Chloro-1-phenyl-4-penten-1-yne (11): a colorless oil; bp 140 °C (3 mmHg); R_f = 0.34 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.45 (s, 3 H), 5.35 (d, J = 1.7 Hz, 1 H), 5.63 (d, J = 1.7 Hz, 1 H), 7.26−7.45 (m, 5 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.99, 83.93, 84.08, 113.46, 123.02, 128.21, 128.28, 131.66, 136.96; IR (neat) 1638, 1491, 1128, 889, 756, 691 cm^{-1}; GCMS (EI, 70 eV) m/z (rel int) 178 (M^+ + 2, 26), 176 (M^+, 81), 142 (20), 141 (100), 139 (42), 115 (96); HRMS for $C_{11}H_9Cl$ (M^+, ^{35}Cl), calcd, 176.0393, found, 176.0398.

(*E*)-1-Phenyl-6-acetoxy-4-hexen-1-yne (12): a colorless oil; bp 140 °C (3 mmHg); R_f = 0.20 (hexane/AcOEt = 9/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 3 H), 3.20 (dq, J = 5.1, 1.6 Hz, 2 H), 4.58 (dq, J = 6.1, 1.1 Hz, 2 H), 5.85 (dtt, J = 15.2, 5.1, 1.1 Hz, 1 H), 5.93 (dtt, J = 15.2, 6.0, 1.6 Hz, 1 H), 7.27−7.44 (m, 5 H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 20.93, 22.42, 64.44, 83.02, 86.09, 123.50, 125.80, 127.87, 128.19, 129.36, 131.61, 170.74; IR (neat) 1740, 1231, 1026, 970, 758, 693 cm^{-1}; GCMS (EI, 70 eV) m/z (rel int) 214 (M^+, 0), 155 (M^+−AcO, 39), 154 (100), 153 (93), 152 (25), 128 (32), 115 (44). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.42; H, 6.59.

A mixture of (*E*)-1-phenyl-4-hexen-1-yne (15) and 1-phenyl-3-methyl-4-penten-1-yne (16): a colorless oil; bp 120 °C (30 mmHg); R_f = 0.29 (hexane); ^{1}H NMR of **15** (270 MHz, $CDCl_3$) δ 1.70 (dq, J = 6.4, 1.7 Hz, 3 H), 3.11 (ddq, J = 5.5, 1.7, 1.7 Hz, 2 H), 5.49 (dtq, J = 15.2, 5.5, 1.5 Hz, 1 H), 5.76 (dqt, J = 15.2, 6.4, 1.6 Hz, 1 H), 7.24−7.42 (m, 5 H); ^{1}H NMR of **16** (270 MHz, $CDCl_3$) δ 1.35 (d, J = 6.9 Hz, 3 H), 3.37 (dqt, J = 7.3, 6.9, 1.6 Hz, 1 H), 5.08 (dt, J = 9.9, 1.5 Hz, 1 H), 5.34 (dt, J = 16.5, 1.5 Hz, 1 H), 5.88 (ddd, J = 16.5, 9.9, 1.5 Hz, 1 H), 7.24−7.42 (m, 5 H); ^{13}C NMR of mixture of **15** and **16** (67.8 MHz, $CDCl_3$) δ 17.68, 21.26, 22.61, 30.19, 82.10, 82.61, 87.67, 91.50, 114.11, 123.76, 123.85, 125.03, 126.97, 127.64, 127.67, 128.18, 131.59, 139.26; IR of mixture of **15** and **16** (neat) 756, 691 cm^{-1}; GCMS of **15** (EI, 70 eV) m/z (rel int) 156 (M^+, 100), 155 (M^+−1, 43), 141 (62), 128 (30), 115 (72); GCMS of **16** (EI, 70 eV) m/z (rel int) 156 (M^+, 100), 141 (93), 128 (36), 115 (49). Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 91.96; H, 7.88.

A mixture of 1-phenyl-5-(trimethylsilyl)-4-penten-1-yne (17) and 1-phenyl-3-(trimethylsilyl)-4-penten-1-yne (18): a colorless oil; bp 120 °C (30 mmHg); R_f = 0.29 (hexane); ^{1}H NMR of **17** (400 MHz, $CDCl_3$) δ 0.09 (s, 9 H), 3.23−3.31 (m, 2 H), 6.05−6.06 (c, 2 H), 7.23−7.47 (m, 5 H); ^{1}H NMR of **18** (400 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 2.79 (dt, J = 6.5, 1.4 Hz, 1 H), 5.06 (dt, J = 10.1, 1.5 Hz, 1 H), 5.28 (dt, J = 17.1, 1.5 Hz, 1 H), 5.85 (ddd, J = 17.1, 10.1, 6.6 Hz, 1 H), 7.24−7.47 (m, 5 H); ^{13}C NMR of mixture of **17** and **18** (100.5 MHz, $CDCl_3$) δ −3.36, −1.27, 26.32, 27.71, 83.36, 84.25, 86.73, 88.76, 113.04, 123.79, 124.52, 127.25, 127.71, 128.14, 128.20, 131.46, 131.62, 131.66, 134.07, 139.53; IR of mixture of **17** and **18** (neat) 841, 756 cm^{-1}; GCMS of **17** (EI, 70 eV) m/z (rel int) 214 (M^+, 31), 199 (100), 183 (29), 159 (28), 115 (24), 73 (99); GCMS of **18** (EI, 70 eV) m/z (rel int) 214 (M^+, 9), 199 (22), 73 (100). Anal. Calcd for $C_{14}H_{18}Si$: C, 78.44; H, 8.46. Found: C, 78.32; H, 8.31.

(*E*)-1,5-Diphenyl-1-penten-4-yne (19): a colorless oil; bp 170 °C (2.8 mmHg); R_f = 0.23 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (dd, J = 5.6, 1.8 Hz, 2 H), 6.29 (dt, J = 15.8, 5.7 Hz, 1 H), 6.75 (dt, J = 15.8, 1.8 Hz, 1 H), 7.24−7.50 (m, 10 H); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 23.00, 82.85, 86.73, 123.65, 124.25, 126.27, 127.33, 127.81, 128.23, 128.52, 131.43, 131.62, 137.10; IR (neat) 756, 691, 401 cm^{-1}; GCMS (EI, 70 eV) m/z (rel int) 219 (M^+ + 1, 20), 218 (M^+, 100), 217 (85), 215 (43), 203 (31), 202 (53). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.59; H, 6.61.

3,3-Dimethyl-1-phenyl-4-penten-1-yne (23): a colorless oil; bp 100 °C (10 mmHg); R_f = 0.34 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.39 (s, 6 H), 5,02 (dd, J = 10.2, 1.3 Hz, 1 H), 5.37 (dd, J = 17.0, 1.3 Hz, 1 H), 5.88 (dd, J = 17.0, 10.1 Hz, 1 H), 7.40−7.44 (m, 5H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.47, 34.77, 82.12, 94.86, 111.66, 123.83, 127.60, 128.12, 131.59, 144.51; IR (neat) 2874, 756, 691 cm^{-1}; GCMS (EI, 70 eV) m/z (rel int) 170 (M^+, 91), 156 (33), 155 (100), 154 (33), 153 (34), 129 (34), 128 (55), 127 (31), 115 (97), 91 (20), 77 (31); HRMS of for $C_{13}H_{14}$ (M^+) calcd 170.1095, found, 170.1092.

A mixture of 5-methyl-1-phenyl-4-hexen-1-yne (22) and 23. These compounds were prepared from palladium-catalyzed reaction of **1j** with **3a**: a colorless oil; bp 95 °C (3.5 mmHg); R_f = 0.34 (hexane); ^{1}H NMR of **22** (500 MHz, $CDCl_3$) δ 1.74 (s, 3 H), 1.75 (s, 3 H), 3.10 (d, J = 7.0 Hz, 2 H), 5.25−5.29 (m, 1 H), 7.23−7.29 (m, 5H); IR of mixture of **22** and **23** (neat) 2967, 2924, 1491, 1443, 756, 691 cm^{-1}; GCMS of **22** (EI, 70 eV) m/z (rel int) 170 (M^+, 95), 155 (100), 154 (26), 153 (23), 129 (21), 128 (25), 115 (37), 91 (29); HRMS of **22** for $C_{13}H_{14}$ (M^+) calcd 170.1095, found 170.1075.

(*E*)- and (*Z*)-5,9-Dimethyl-1-(trimethylsilyl)-4,8-decadien-1-yne (24): a colorless oil; bp 110 °C (15 mmHg); R_f = 0.25 (hexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ [0.13 (s, minor), 0.15 (s, major), 9 H], 1.61 (br s, 6 H), 1.68 (s, 3 H), 1.95−2.12 (c, 4 H), 2.94 (dd, J = 6.7 Hz, 2 H), 5.05−5.11 (m, 1 H), 5.15−5.20 (m, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 0.15, 16.10, 17.68,

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18.91 (minor), 19.03, 25.68, 26.26 (minor), 26.44, 31.92 (minor), 39.41, 83.69, 106.04, 118.63, 119.32 (minor), 124.03, 131.55, 137.32; IR (neat) 2961, 2919, 2176, 1250, 843 cm^{-1}; GCMS (EI, 70 eV) *m/z* (rel int) 234 (M^+, 7), 219 (20), 149 (19), 145 (15), 123 (60), 73 (99), 69 (100), 59 (25). Anal. Calcd for $C_{15}H_{26}Si$: C, 76.84; H, 11.18. Found: C, 76.47; H, 11.34.

3,7-Dimethyl-3-[2-(trimethylsilyl)ethynyl]-1,6-octadiene (25): a colorless oil; bp 90 °C (35 mmHg); R_f = 0.34 (hexane); ^1H NMR (270 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 1.26 (s, 3 H), 1.61 (s, 3 H), 1.68 (s, 3 H), 1.34–1.55 (m, 2 H), 1.98–2.11 (m, 2 H), 5.09–5.15 (m, 1 H), 5.04 (dd, J = 10.2, 1.7 Hz, 1 H), 5.36 (dd, J = 17.2, 1.7 Hz, 1 H), 5.65 (dd, J = 17.4, 10.1 Hz, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 0.27, 17.54, 24.10, 25.68, 28.05, 39.64, 42.00, 87.44, 110.39, 113.05, 124.21, 131.59, 143.04; IR (neat) 2967, 2928, 843 cm^{-1}; GCMS (EI, 70 eV) *m/z* (rel int) 234 (M^+, 1), 219 (7), 145 (16), 83 (23), 74 (29), 55 (26). Anal. Calcd for $C_{15}H_{26}Si$: C, 76.84; H, 11.18. Found: C, 76.82; H, 11.34.

Supporting Information Available: ^1H NMR spectra for **11**, **23**, and a mixture of **22** and **23** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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