New Three-Component Synthesis of 1,3-Dienes Employing Nickel Catalysis

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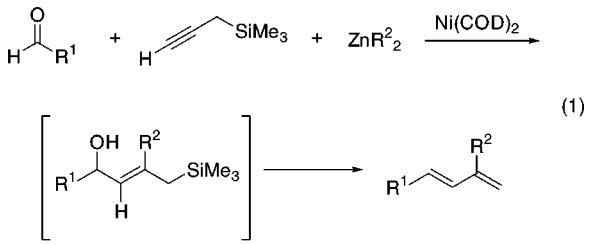
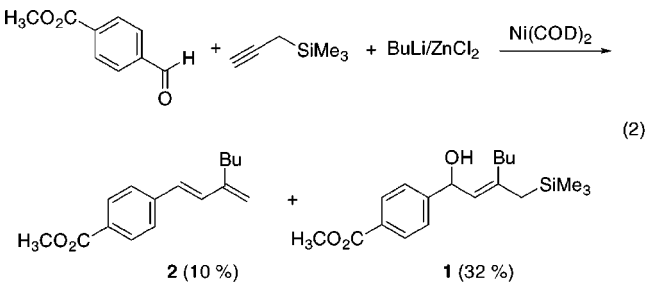
1,3-Dienes are broadly useful compounds in a wide variety of applications.[1,2] As part of our program directed toward the development of new nickel-catalyzed coupling reactions,[3] we were attracted to 1,3-dienes as potential synthetic targets. Previous studies demonstrated that the three-component nickel-catalyzed coupling of organozincs, alkynes, and aldehydes efficiently provides functionalized allylic alcohols.[3b] Herein, we describe this process, in which propargyltrimethylsilane participates to afford δ-hydroxy allylsilanes that directly eliminate trimethylsilanol to afford 1,3-disubstituted 1,3-dienes (eq 1).[4]



(1)

In a typical procedure, the organozinc was generated by transmetalation of an organolithium with zinc chloride in THF. A 3:2 ratio of organolithium to zinc chloride was typically employed, and optimization of the reactions at lower organozinc concentrations was not attempted. A THF solution of $Ni(COD)_2$ was added, followed by a THF solution of an aldehyde and propargyltrimethylsilane. Couplings were generally completed in 30 min at 0 °C to afford a mixture of 1,3-diene and δ-hydroxy allylsilane.[4,5] After extractive workup, the resulting mixture was stirred overnight with silica gel in CH_2Cl_2 to facilitate elimination of any remaining δ-hydroxy allylsilane. In general, the diene formation was nearly complete prior to treatment with silica gel unless a structural or electronic feature of the δ-hydroxy allylsilane impedes elimination of Me_3SiOH (vide infra). Couplings with electron-rich aromatic aldehydes and sp^3-hybridized organozincs were most efficient, with yields ranging from 48% to 75% (Table 1, entries 1−4). Yields with an electron-deficient aldehyde were somewhat suppressed (Table 1, entries 5−6), and an example with an aliphatic aldehyde proceeded in modest yield (Table 1, entry 7). Attempts to generate 1,3-dienes derived from sp^2-hybridized organozincs and attempts to couple substituted propargyl silanes were not efficient. In all cases, the (*E*)-isomer of the C-1/C-2 alkene was exclusively generated. The product of direct addition of the organozinc to the aldehyde was also observed in most instances.

The coupling described in entry 5 (Table 1) was the only instance of intermolecular couplings in which an appreciable quantity of a δ-hydroxy allylsilane was isolated prior to treatment with silica gel (eq 2). Presumably this stability is derived from destabilization of the developing positive charge at the benzylic position during the elimination of Me_3SiOH. Allylsilane **1** was readily converted to diene **2** upon treatment with silica gel in CH_2Cl_2. Synthetically useful preparative quantities of the δ-hydroxy allylsilanes could not be obtained because of the facility of the silanol elimination under the reaction conditions.



(2)

The reductive cyclization of ynals employing triethylsilane was recently reported in connection with our synthetic studies of the allopumiliotoxin alkaloids.[6] According to this protocol, the nickel-catalyzed triethylsilane-mediated reductive cyclization of functionalized propargylsilane **3** was attempted. In contrast to the facile elimination of trimethylsilanol in intermolecular couplings (Table 1), the stable δ-silyloxy allylsilane **4** was isolated as a single isomer in 75% yield upon treatment of **3** with triethylsilane and $Ni(COD)_2/PBu_3$ in THF (Scheme 1). The 1,3-diene **5** was then readily generated upon treatment of **4** with TsOH in CH_2Cl_2. Alternatively, this class of functionally rich allylsilanes may be useful in a variety of other synthetic applications.[7]

We speculate that the mechanism of this process involves the formation of oxametallacycle **6** followed by nickel/oxygen bond cleavage by transmetalation of the

(1) For recent reviews, see: (a) Oppolzer, W. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, Chapter 4.1, pp 315−400. (b) Roush, W. R. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, Chapter 4.4, pp 513−550.

(2) For representative recent preparative methods, see: (a) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **1999**, *121*, 4068. (b) Kinoshita, A.; Sakakibara, N.; Mori, M. *J. Am. Chem. Soc.* **1997**, *119*, 12388. (c) Murakami, M.; Ubukata, M.; Ito, Y. *Tetrahedron Lett.* **1998**, *39*, 7361.

(3) (a) Montgomery, J.; Oblinger, E.; Savchenko, A. V. *J. Am. Chem. Soc.* **1997**, *119*, 4911. (b) Oblinger, E.; Montgomery, J. *J. Am. Chem. Soc.* **1997**, *119*, 9065. (c) Seo, J.; Chui, H. M. P.; Heeg, M. J.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 476.

(4) For preparation of dienes via elimination of δ-hydroxy allylsilanes, see: (a) Angoh, A. G.; Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 534. (b) Maeta, H.; Suzuki, K. *Tetrahedron Lett.* **1992**, *33*, 5969. (c) Yamashita, K.; Sato, F. *Tetrahedron Lett.* **1996**, *37*, 7275. (d) Nativi, C.; Taddei, M.; Mann, A. *Tetrahedron* **1989**, *45*, 1131.

(5) For alternative methods for preparing δ-hydroxy allylsilanes, see: (a) Matsumoto, T.; Kitano, Y.; Sato, F. *Tetrahedron Lett.* **1988**, *29*, 5685. (b) Kitano, Y.; Matsumoto, T.; Wakasa, T.; Okamoto, S.; Shimazaki, T.; Kobayashi, Y.; Sato, F.; Miyaji, K.; Arai, K. *Tetrahedron Lett.* **1987**, *28*, 6351.

(6) Tang, X. Q.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 6098.

(7) For reviews of the utility of allylsilanes in other applications, see: (a) Roush, W. R. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 1.1, pp 1−53. (b) Fleming, I. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 2.2, pp 563−593. (c) Kleinman, E. F.; Volkman, R. A. In *Comprehensive Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 4.3, pp 975−1006.

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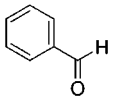
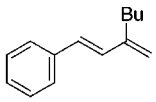
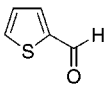
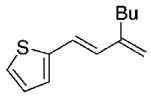
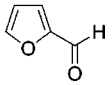
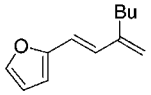
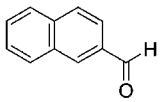
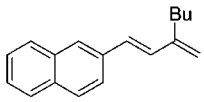
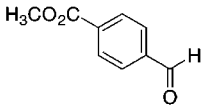
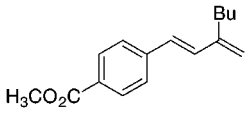
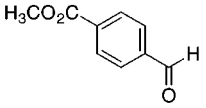
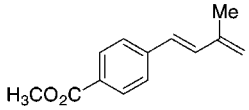
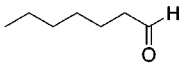
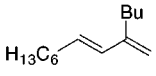
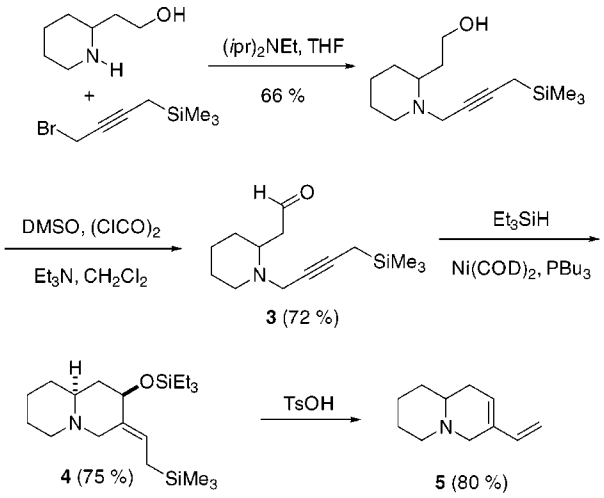
Table 1

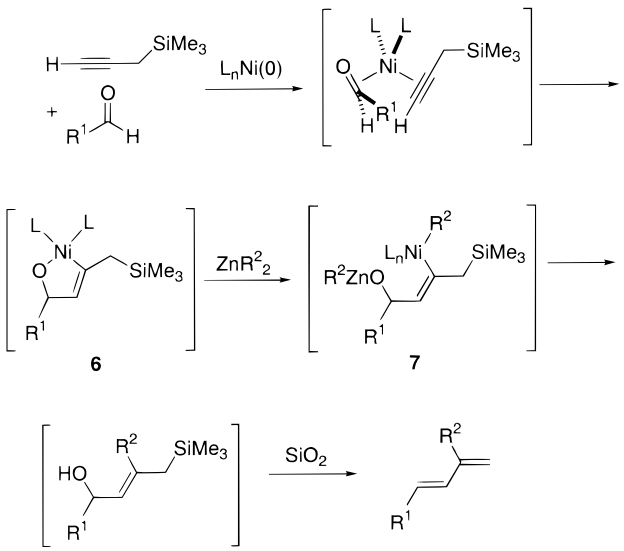
entry	aldehyde	organozinc	diene	isolated yield (%)
1		$BuLi / ZnCl_2$		58
2		$BuLi / ZnCl_2$		48
3		$BuLi / ZnCl_2$		52
4		$BuLi / ZnCl_2$		75
5		$BuLi / ZnCl_2$		37
6		$MeLi / ZnCl_2$		41
7		$BuLi / ZnCl_2$		50[a]

[a] This product was obtained in ~90% purity, contaminated with ~10% of an uncharacterized silyl-containing byproduct.

Scheme 1



Scheme 2



organozinc (Scheme 2).[8] Reductive elimination of the resulting alkenyl nickel intermediate **7** would afford the zinc alkoxide of the δ-hydroxy allylsilane. Quenching the reaction mixture and treating with silica gel lead to elimination of the silanol and formation of the 1,3-diene. An analogous mechanism could be operative in the intramolecular triethylsilane-mediated procedure.

In summary, a novel approach to the synthesis of 1,3-dienes has been developed by the three-component nickel-catalyzed coupling of aldehydes, organozincs, and propargylsilanes. The fully intermolecular reaction allowed

(8) For related mechanistic proposals, see: (a) Tsuda, T.; Kiyoi, T.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2554. (b) Kimura, M.; Fujimatsu, H.; Ezoe, A.; Shibata, K.; Shimizu, M.; Matsumoto, S.; Tamaru, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 397. (c) Sato, Y.; Takanashi, T.; Hoshiba, M.; Mori, M. *Tetrahedron Lett.* **1998**, *39*, 5579. (d) Crowe, W. E.; Rachita, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6787. (e) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1995**, *117*, 6785. (f) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 3182.

construction of simple acyclic dienes, whereas an intramolecular variant with triethylsilane allowed preparation of a more complex diene within a bicyclic template.

Experimental Section

Unless otherwise noted, reagents were commercially available and were used without purification. Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from calcium hydride. All organolithium reagents were freshly titrated with 2,5-dimethoxybenzyl alcohol. Zinc chloride was dried at 150 °C at 0.1 mmHg overnight, thoroughly ground by mortar and pestle in an inert atmosphere glovebox, and then dried again overnight at 150 °C at 0.1 mmHg. $Ni(COD)_2$ and anhydrous $ZnCl_2$ were stored and weighed in an inert atmosphere glovebox. All reactions were conducted in flame-dried glassware under a nitrogen or argon atmosphere.

General Procedure for Three-Component Couplings to Make 1,3-Dienes. A solution of the organozinc was prepared by addition of organolithium (3.0 equiv) to a 0 °C solution of $ZnCl_2$ (0.5 M, 2.0 equiv) in THF with stirring at 0 °C for 15 min. To this solution, a 0.05 M THF solution of $Ni(COD)_2$ (0.2 equiv) and a solution (0.25 M in THF relative to the aldehyde) containing the aldehyde (1.0 equiv) and propargyltrimethylsilane (1.2 equiv) were added sequentially to the organozinc reagent. After consumption of starting material by TLC analysis (typically 0.5 h at 0 °C), the reaction mixture was quenched with NH_4Cl/NH_4OH pH = 8 buffer, extracted with ether, washed with brine, dried with $MgSO_4$, filtered, and concentrated under vacuum. The residue then was dissolved in 10 mL of CH_2Cl_2, and SiO_2 (5 g) was added. The mixture was stirred at 25 °C overnight, and the mixture was directly concentrated by rotary evaporation. The residue adsorbed onto silica gel was transferred to a silica gel column and was chromatographed to afford dienes of >95% purity as estimated by ^1H NMR.

(*E*)-1-Phenyl-3-butyl-1,3-butadiene. (Table 1, entry 1)[9] By means of the general procedure, benzaldehyde (102 μL, 1.0 mmol), propargyltrimethylsilane (179 μL, 1.2 mmol), *n*-BuLi (3.0 mmol, 1.2 mL of a 2.5 M hexane solution), $ZnCl_2$ (273 mg, 2.0 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (92:8 hexanes/EtOAc), 108 mg (58%) of product as a yellow oil that was homogeneous by TLC analysis: ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.37 (m, 2H), 7.27 (m, 1H), 6.86 (d, *J* = 16.4 Hz, 1H), 6.63 (d, *J* = 16.4 Hz, 1H), 5.18 (s, 1H), 5.11 (s, 1H), 2.38 (t, *J* = 7.6 Hz, 2H), 1.59 (m, 2H), 1.45 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 138.6, 132.3, 129.7, 128.9, 128.5, 127.5, 117.3, 32.9, 31.7, 23.8, 15.2; IR (film) 2956, 1602 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{14}H_{18}$ 186.1409, found 186.1410 (M^+).

(*E*)-1-(2-Thienyl)-3-butyl-1,3-butadiene. (Table 1, entry 2) By means of the general procedure, 2-thiophenecarboxaldehyde (93 μL, 1.0 mmol), propargyltrimethylsilane (179 μL, 1.2 mmol), *n*-BuLi (3.0 mmol, 1.2 mL of a 2.5 M hexane solution), $ZnCl_2$ (273 mg, 2.0 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (92:8 hexanes/EtOAc), 93 mg (48%) of product as a yellow oil that was homogeneous by TLC analysis: ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (m, 1H), 7.01 (m, 2H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.67 (d, *J* = 16.0 Hz, 1H), 5.14 (d, *J* = 1.6 Hz, 1H), 5.07 (d, *J* = 1.6 Hz, 1H), 2.33 (t, *J* = 7.6 Hz, 2H), 1.56 (m, 2H), 1.43 (m, 2H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 144.2, 132.1, 128.6, 126.8, 125.2, 122.2, 117.1, 32.8, 31.6, 23.8, 15.2; IR (film) 2955, 1598 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{12}H_{16}S$ 192.0973, found 192.0976 (M^+).

(*E*)-1-(2-Furanyl)-3-butyl-1,3-butadiene. (Table 1, entry 3) By means of the general procedure, 2-furaldehyde (83 μL, 1.0 mmol), propargyltrimethylsilane (179 μL, 1.2 mmol), *n*-BuLi (3.0 mmol, 1.2 mL of a 2.5 M hexane solution), $ZnCl_2$ (273 mg, 2.0 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (92:8 hexanes/EtOAc), 92 mg (52%) of product as a yellow oil that was homogeneous by TLC analysis: ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 1.5 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.38−6.41 (m, 2H), 6.29 (d, *J* = 3.5 Hz, 1H), 5.13 (s, 1H), 5.05 (d, *J* = 1.0 Hz, 1H), 2.28 (t, *J* = 7.7 Hz, 2H), 1.52 (m, 2H), 1.40 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 146.6, 142.6, 130.5, 116.9, 116.7, 112.2, 108.7, 32.3, 31.2, 23.4, 14.7; IR (film) 2956, 1608 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{12}H_{16}O$ 176.1201, found 176.1197 (M^+).

(*E*)-1-(2-Naphthyl)-3-butyl-1,3-butadiene. (Table 1, entry 4) By means of the general procedure, 2-naphthaldehyde (156 mg, 1.0 mmol), propargyltrimethylsilane (179 μL, 1.2 mmol), *n*-BuLi (3.0 mmol, 1.2 mL of a 2.5 M hexane solution), $ZnCl_2$ (273 mg, 2.0 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (pure hexanes), 177 mg (75%) of product as a white solid that was homogeneous by TLC analysis. The product could be recrystallized from CH_3OH/H_2O: mp 41−42 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (m, 4H), 7.68 (dd, *J* = 9.0, 1.0 Hz, 1H), 7.47 (m, 2H), 6.98 (d, *J* = 16 Hz, 1H), 6.79 (d, *J* = 16 Hz, 1H), 5.23 (s, 1H), 5.14 (s, 1H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.62 (m, 2H), 1.48 (m, 2H), 1.02 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 135.7, 134.5, 133.7, 132.3, 128.9, 128.7, 128.6, 128.4, 127.2, 126.9, 126.5, 124.3, 117.0, 32.6, 31.3, 23.5, 14.8; IR (film) 2956, 2929, 2860, 1603 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{18}H_{20}$ 236.1565, found 236.1569. (M^+).

(*E*)-1-(4-Carbomethoxyphenyl)-3-butyl-1,3-butadiene (2). (Table 1, entry 5) By means of the general procedure, methyl 4-formylbenzoate (164 mg, 1.0 mmol), propargyltrimethylsilane (179 μL, 1.2 mmol), *n*-BuLi (3.0 mmol, 1.2 mL of a 2.5 M hexane solution), $ZnCl_2$ (273 mg, 2.0 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (90:10 hexanes/EtOAc), 90 mg (37%) of product as pale yellow solid that was homogeneous by TLC analysis. The solid could be recrystallized from pure hexane to afford product as white needles: mp 36−38 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 16.4 Hz, 1H), 6.70 (d, *J* = 16.4 Hz, 1H), 5.31 (s, 1H), 5.25 (s, 1H), 4.02 (s, 3H), 2.45 (t, *J* = 7.6 Hz, 2H), 1.61−1.69 (m, 2H), 1.47−1.56 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 147.2, 143.2, 134.9, 131.1, 129.8, 128.0, 127.4, 118.9, 53.2, 32.8, 31.7, 23.9, 15.2; IR (film) 2952, 1722, 1605 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{16}H_{20}O_2$ 244.1463, found 244.1462. (M^+).

(*E*)-1-(4-Carbomethoxylphenyl)-3-(trimethylsilylmethyl-)hept-2-en-1-ol (1). By means of the general procedure but without silica gel treatment, methyl 4-formylbenzoate (164 mg, 1.0 mmol), propargyltrimethylsilane (179 μL, 1.2 mmol), *n*-BuLi (3.0 mmol, 1.2 mL of a 2.5 M hexane solution), $ZnCl_2$ (273 mg, 2.0 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (90:10 hexanes/EtOAc), 107 mg (32%) of product as a yellow oil that was homogeneous by TLC analysis (10% of **2** was also obtained, data given above): ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 5.54 (d, *J* = 9.2 Hz, 1H), 5.18 (d, *J* = 9.2 Hz, 1H), 3.93 (s, 3H), 2.09−2.27(m, 2H), 1.82 (s, 1H), 1.57 (s, 2H), 1.34−1.51 (m, 4H), 0.96 (t, *J* = 7.0 Hz, 3H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 150.8, 144.1, 130.8, 129.8, 126.7, 126.1, 71.2, 53.1, 33.4, 32.1, 28.3, 24.0, 15.1, 0.02; HRMS (EI) *m/e* calcd for $C_{19}H_{30}O_3Si$ 334.1964, [M − H_2O] 316.1859, found 316.1860 ([M − H_2O]$^+$).

(*E*)-1-(4-Carbomethoxyphenyl)-3-methyl-1,3-butadiene. (Table 1, entry 6) By means of the general procedure, methyl 4-formylbenzoate (164 mg, 1.0 mmol), propargyltrimethylsilane (179 μL, 1.2 mmol), MeLi (3.0 mmol, 2.1 mL of a 1.4 M diethyl ether solution), $ZnCl_2$ (273 mg, 2.0 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (90:10 hexanes/EtOAc), 82 mg (41%) of product as a white solid that was homogeneous by TLC analysis. The solid could be recrystallized from hexane to form white crystals: mp 100−101 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 16 Hz, 1H), 6.56 (d, *J* = 16 Hz, 1H), 5.19 (s, 1H), 5.16 (s, 1H), 3.92 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 142.6, 142.5, 134.8, 130.7, 129.4, 128.3, 126.9, 119.7, 52.8, 19.2; IR (film) 2948, 1719, 1606 cm^{-1}; HRMS (EI) *m/e* calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0990. (M^+).

(*E*)-2-Butyl-1,3-decadiene. (Table 1, entry 7)[10] By means of the general procedure, heptaldehyde (114 mg, 1.0 mmol), pro-

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pargyltrimethylsilane (179 μL, 1.2 mmol), *n*-BuLi (3.0 mmol, 1.2 mL of a 2.5 M hexane solution), $ZnCl_2$ (273 mg, 2.0 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) were employed to produce, after flash chromatography (pure hexanes), 97 mg (50%) of product in ~90% purity as a yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (d, *J* = 15.5 Hz, 1H), 5.70 (dt, *J* = 16.0, 6.5 Hz, 1H), 4.87 (d, *J* = 2.0 Hz, 1H), 4.84 (s, 1H), 2.19 (t, *J* = 7.6 Hz, 2H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.27−1.49 (m, 12H), 0.86−0.97 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 132.0, 130.3, 112.8, 32.9, 32.0, 31.8, 30.6, 29.4, 28.9, 22.8, 22.7, 14.2, 14.1; IR (film) 2927, 1605 cm^{-1}; HRMS (EI) *m*/*e* calcd for $C_{14}H_{26}$ 194.2035, found 194.2035. (M^+).

2-[1-(4-Trimethylsilyl-2-butynyl)piperidin-2-yl]ethanol. To a solution of 2-piperidineethanol (129 mg, 1.0 mmol) in 5 mL of THF was added $(i\text{-Pr})_2$EtN (194 mg, 1.5 mmol) and 1-trimethylsilyl-4-bromobutyne (205 mg, 1.0 mmol) at room temperature, and the reaction mixture was stirred overnight. The mixture was quenched with saturated aqueous $NaHCO_3$, extracted with ether, washed with brine, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (10% MeOH in CH_2Cl_2) on silica gel to afford the product (168 mg, 66%) as yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.13 (br s, 1H), 3.85−3.95 (m, 2H). 3.65−3.69 (m, 1H), 3.29 (m, 1H), 2.76−2.79 (m, 1H), 2.67−2.70 (m, 1H), 2.48 (td, *J* = 11.5 Hz, 2.5 Hz, 1H), 1.99−2.06 (m, 1H), 1.71−1.74 (m, 1H), 1.46−1.64 (m, 7H), 1.22−1.29 (m, 1H), 0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.9, 72.4, 60.4, 57.6, 53.3, 44.2, 32.6, 29.6, 25.7, 24.4, 7.27, −1.74.

1-(4-Trimethylsilyl-2-butynyl)piperidin-2-yl]acetaldehyde (3). To a solution of oxalyl chloride (131 μL, 1.5 mmol) in 10 mL of CH_2Cl_2 was added DMSO (213 μL, 3.0 mmol) dropwise at −78 °C. After the mixture stirred for 0.5 h, the alcohol described above (254 mg, 1.0 mmol) was added neat, and stirring at −78 °C was continued for 0.5 h. Et_3N (767 μL, 5.5 mmol) was added, and the mixture was allowed to warm to room temperature. The mixture was quenched with saturated aqueous $NaHCO_3$, extracted with ether, washed with brine, dried with $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography (2:1 Et_2O/hexane) on silica gel to afford compound **3** (181 mg, 72%) as yellow oil that was homogeneous by TLC analysis.: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (t, 1H), 3.56 (dt, *J* = 17.7 Hz, 2.4 Hz, 1H), 3.25 (dt, *J* = 17.7 Hz, 2.4 Hz, 1H), 2.82−2.89 (m, 1H), 2.66−2.73 (m, 1H), 2.40−2.57(m, 3H), 1.23−1.74 (m, 8H), 0.08 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.7, 83.9, 72.3, 54.8, 53.4, 47.3, 44.2, 32.4, 26.1, 24.4, 7.25, −1.73.

(2*R,9*aS**)-3-[(*E*)-2-Trimethylsilylethylidene]-2-(triethylsilyloxy)octahydroquinolizine (4).** To a solution of $Ni(COD)_2$ (55 mg, 0.2 mmol) in THF was added dropwise PBu_3 (100 μL, 0.4 mmol) at room temperature. After 5 min at room temperature, the solution was cooled to 0 °C, and Et_3SiH (0.80 mL, 5.0 mmol) was added dropwise. Then a 0.3 M solution of compound **3** (252 mg, 1.0 mmol) in THF was added dropwise. The reaction mixture was stirred at room temperature for 20−24 h until TLC analysis indicated disappearance of the ynal. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, extracted with ether, washed with brine, dried with $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography (1:1 hexane/ether) on silica gel to afford compound **4** (276 mg, 75%) as yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.61 (dd, *J* = 11 Hz, 6.0 Hz, 1H), 4.05 (dd, *J* = 10.5 Hz, 4.0 Hz, 1H), 3.52 (d, *J* = 12.5 Hz, 1H), 2.88 (d, *J* = 11.5 Hz, 1H), 2.26 (d, *J* = 11.5 Hz, 1H), 1.96 (d, *J* = 10 Hz, 1H), 1.89 (s, broad, 1H), 1.76 (ddd, *J* = 12 Hz, 5.0 Hz, 2.5 Hz, 1H), 1.54−1.70 (m, 5H), 1.21−1.40 (m, 4H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.61 (q, *J* = 8.0 Hz, 6H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.6, 117.3, 72.4, 61.7, 56.6, 55.7, 44.9, 33.4, 26.2, 24.7, 18.8, 7.66, 5.60, −1.08; IR (film) 2952, 1459 cm^{-1}; HRMS (EI) *m*/*e* calcd for $C_{20}H_{41}NOSi_2$ 367.2726, found 367.2720 (M^+). On irradiation of the C-2 proton at δ 4.05, NOEs were observed on the C-4 axial proton at δ 2.26 (2%), the C-9a axial proton at δ 1.89 (1%), and the C-1 equatorial proton at δ 1.76 (3%), confirming that the C-2 proton is axial. This was in accord with ^{1}H NMR analysis; coupling constants of vicinal 2-H/1-H_{ax} and 2-H/1-H_{eq} were observed at 10.5 and 4.0 Hz, respectively, the former of which confirms a trans diaxial relationship between the two corresponding protons 2-H and 1-H_{ax}. The alkene configuration was determined to be *E* given a 6% NOE of the signal at δ 1.66 (one of the allylic H next to Si) upon irradiation of the signal at δ 3.52 (one of the allylic H next to N).

7-Vinyl-1,3,4,6,9,9a-hexahydro-2*H*-quinolizine (5). To a solution of compound **4** (368 mg, 1.0 mmol) in CH_2Cl_2 was added $TsOH\cdot H_2O$ (190 mg, 1.0 mmol). The mixture was stirred at 25 °C overnight, quenched with saturated aqueous $NaHCO_3$, extracted with ether, washed with brine, dried with $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by flash chromatography (5% MeOH in CH_2Cl_2) on silica gel to afford compound **5** (130 mg) in 80% yield as yellow oil that was obtained in ~95% purity: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.28 (dd, *J* = 18.0 Hz, 11.0 Hz, 1H), 5.72 (s, 1H), 4.98 (d, *J* = 18.0 Hz, 1H), 4.90 (d, *J* = 11.0 Hz, 1H), 3.46 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 11.0 Hz, 1H), 2.75 (d, *J* = 15.5 Hz, 1H), 2.06−2.20 (m, 4H), 1.60−1.77 (m, 4H), 1.20−1.36 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 133.9, 126.5, 110.3, 57.6, 56.4, 54.0, 34.2, 33.7, 26.1, 24.6; IR (film) 2929, 2858, 2767, 1611 cm^{-1}; HRMS (EI) *m*/*e* calcd for $C_{11}H_{17}N$ 163.1361, found 163.1360 (M^+).

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Supporting Information Available: Copies of ^{1}H NMR spectra for compounds reported in Scheme 1 and Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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