Ni-Catalyzed Cross Coupling of Alkoxide-Containing Vinyl Halides with Grignard Reagents. A "One-Pot" Synthesis of 2-[(Trimethylsilyl)methyl]-2-propen-1-yl Acetate

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Received October 8, 1996

Transition-metal-promoted reactions are extremely useful transformations for many reasons. Perhaps the most useful property of transition-metal complexes is the high degree of selectivity they exhibit in the many different reactions in which they are employed. Late transition metals display a high degree of coordinating affinity for alkene and alkyne moieties.[1] Thus, reactions that involve these groups, such as catalytic hydrogenation[2] and metal-catalyzed allylic substitution reactions,[3] can tolerate a wide range of functionality. For example, esters, amides, alcohols, and amines are generally compatible with the conditions in which these reactions are performed.[2,3] There is great flexibility without the need for protecting group chemistry, then, for synthetic routes that are based on transition-metal-catalyzed reactions.

In the present study, we needed to prepare the azadiene/silane **1** for use in tandem reaction studies involving a Diels−Alder/electrophilic substitution sequence.[4] This strategy is being employed for the rapid construction of polysubstituted pyridine and piperidine-based compounds. Therefore, we devised the route shown retrosynthetically in Scheme 1.

Intermediate **4** is pivotal in this approach, and there is abundant literature on the subject of cross coupling vinyl halide or pseudohalide substrates with [(trimethylsilyl)methyl]magnesium chloride,[5] or the corresponding organoaluminum reagent,[6] to provide compounds possessing the allylsilane motif in **4**. Compound **6a** (R = H) is a convenient starting material for this sequence, and it is available from Aldrich for less than $2 per gram.

It occurred to us initially that whether we attempted to cross couple the alcohol first or oxidize to the aldehyde and then couple that protection would be required. Additional steps required to protect and deprotect are particularly undesirable when dealing with small molecules because recovery from each step can prove difficult owing to product volatility.

It is known from Grignard chemistry that additions to substrates containing an alcohol group can be effected if greater than 2 equiv of anion is used, which eliminates the need for protection.[7] This is not a desirable option if the Grignard reagent is expensive or requires a number of steps to prepare. We envisioned that we could use this fundamental concept in the cross-coupling step. However, instead of using excess Grignard reagent, deprotonation could be carried out *in situ* with *n*-butyllithium prior to coupling (Scheme 2 and Table 1). Treatment of the lithium salt derived from **6a** with **5a** in the presence of 5% $NiDPPPCl_2$ (DPPP = 1,3-bis(diphenylphosphino)-propane) provided **7a** in 70% yield.

Interestingly, attempted cross coupling of the protected alcohol (R = tetrahydropyran (THP)) failed completely. This may be due to a steric effect imposed by the protecting group. Cross couplings were carried out with a number of other Grignard reagents to see if the procedure was general, and it seems to be for the partners chosen (see Table 1, entries 2−4). Other vinyl halo/alcohols were also tried to see if the nature of the halogen itself or the relationship between the position of the halogen and the alcohol was important. Treatment of either substrates **8a**, **8b**,[8] or **10b**[9] with a number of Grignard reagents provided the corresponding coupled product in suitable yield (see Table 1, entries 5−8 and 10).

The iodo compound **10a** proved to be more challenging to work with. Attempted cross coupling of **10a** with ethylmagnesium bromide led to a very low yield of **11d**, which was accompanied by a sizable amount of cyclohex-2-en-1-ol. Deprotonation of **10a** with *n*-butyllithium followed by quenching with NH_4Cl revealed that lithium−halogen exchange had consumed about half of the starting material prior to the coupling step. Deprotonation instead with NaH provided a homogeneous solution of anion with no loss of iodide. However, the presence of cyclohex-2-en-1-ol in this product mixture indicates that Ni-catalyzed reduction of the iodide was also contributing to low product yield. No further iodides were investigated on the basis of these results.

The procedure even appears to be tolerant of higher alcohols. Diol **12**[10] was treated with 2 equiv of *n*-butyllithium and then cross coupled with 3 equiv of **5d**, providing **13** in 78% yield (Scheme 3).

(1) For general discussions regarding transition metal coordinating affinity, see: (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1994; pp 44−139. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 57−278.

(2) For selective catalytic hydrogenation of multiple bonds, see: (a) Evans, D. A.; Morrissey, M. M. *J. Am. Chem. Soc.* **1984**, *106*, 3866−3868. (b) Thompson, H. W.; Naipawer, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 6379−6386.

(3) For a review of Pd-catalyzed allylic substitutions containing examples illustrating selectivity with such functional groups, see: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173−1192.

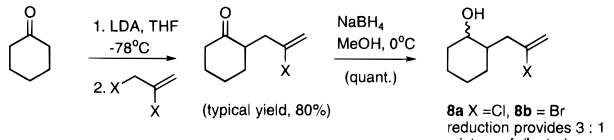
(4) Organ, M. G.; Winkle, D. D. *J. Org. Chem.* **1997**, in press.

(5) (a) Hayashi, T.; Fujiwa, T.; Okamoto, Y.; Katsuro, Y.; Kumada, M. *Synthesis* **1981**, 1001−1003. (b) Hayashi, T.; Katsuro, Y.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 3915−3918. (c) Armstrong, R. J.; Harris, F. L.; Weiler, L. *Can. J. Chem.* **1982**, *60*, 673−675.

(6) Saulnier, M. G.; Kadow, J. F.; Tun, M. M.; Langley, D. R.; Vyas, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 8320−8321.

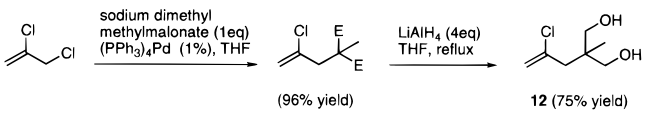
(7) Johnson, M. R.; Nakata, T.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4343−4346.

(8) Compounds **8a** and **8b** were prepared as indicated in the following equation using well established chemistry:



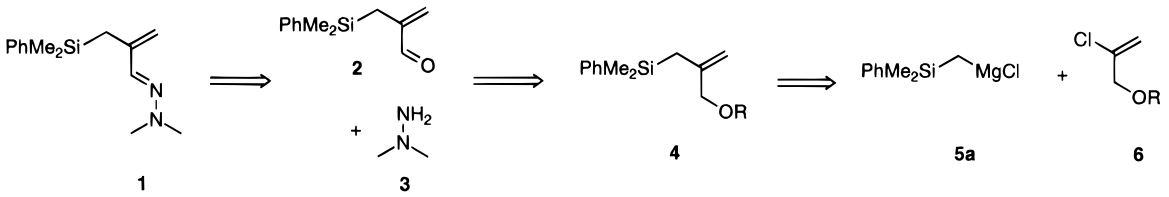
(9) Compounds **10a**,**b** were produced by reaction of $NaBH_4/CeCl_3$ (Luche reduction, see: Germal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454) with the corresponding 2-halocyclohex-2-en-1-one, which generally proceeds with quantitative recovery. These precursors were prepared following the method of Johnson; see: Johnson, C. R.; Adams, J. P.; Braun, M. P.; Senanayake, C. B. W.; Wovkulich, P. M.; Uskokovic, M. R. *Tetrahedron Lett.* **1992**, *33*, 917−918.

(10) Compound **12** was prepared as indicated in the following equation:



S0022-3263(96)01900-7 CCC: $14.00

Scheme 1



Scheme 2

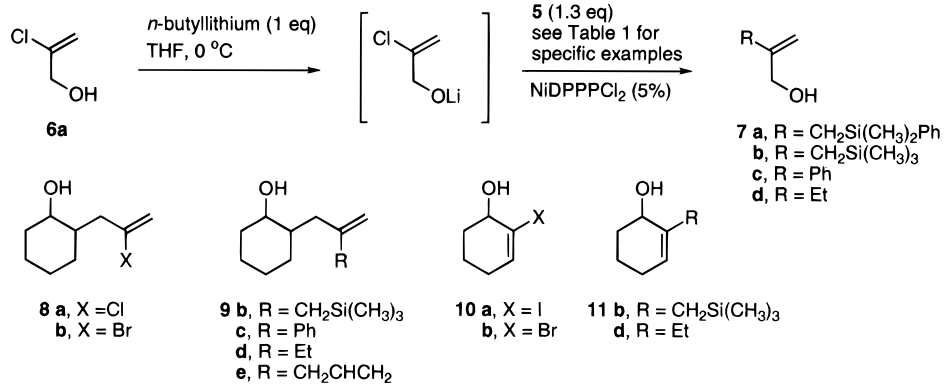
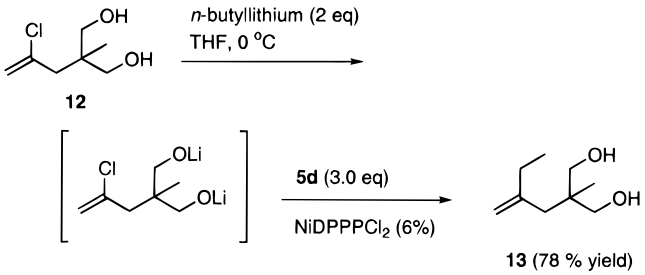


Table 1. Ni-Catalyzed Cross Coupling of Lithium Alkoxide-Containing Vinyl Halides with Grignard Reagents

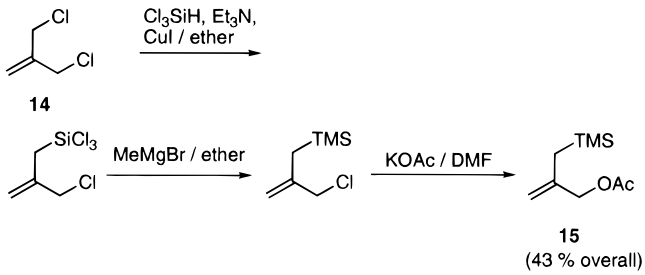
entry	starting alcohol	Grignard reagent (RMgX)	ratio of alcohol:RMgX	product	% yield[a]
1	**6a**	$Ph(Me)_2SiCH_2MgCl$ (**5a**)	1.3:1	**7a**	70[b]
2	**6a**	Me_3SiCH_2MgCl (**5b**)	1:1.5	**7b**	69
3	**6a**	PhMgBr (**5c**)	1:1.2	**7c**	86
4	**6a**	EtMgBr (**5d**)	1:1.3	**7d**	83
5	**8a** (X = Cl)	Me_3SiCH_2MgCl (**5b**)	1:1.4	**9b**	66
6	**8a** (X = Cl)	PhMgBr (**5c**)	1:1.4	**9c**	76
7	**8b** (X = Br)	EtMgBr (**5d**)	1:1.4	**9d**	83
8	**8a** (X = Cl)	H_2CCHCH_2MgBr (**5e**)	1:2.8	**9e**	76
9	**10a** (X = I)	EtMgBr (**5d**)	1:1.4	**11d**	10[c]
10	**10b** (X = Br)	Me_3SiCH_2MgCl (**5b**)	1:1.4	**11b**	67

[a] All reported yields are based on purified material following silica gel chromatography. [b] Grignard is first formed in diethyl ether and the solvent replaced with THF prior to cross-coupling. See the Experimental Section for details. [c] Deprotonation with *n*-butyllithium leads to approximately 50% lithium/halogen exchange as a competing process. Further reduction to cyclohex-2-en-1-ol is observed during the course of the Ni coupling. See discussion in text.

Scheme 3



Compound **15**, first prepared in 1983,[11a] is a useful trimethylenemethane (TMM) precursor for ring annulations leading to the formation of 5-membered rings via Pd catalysis.[12,13] It has also found use in allylic substitution chemistry using Lewis acid catalysis.[14] In light of this general interest, a number of approaches have been devised for the efficient synthesis of **15**.[11] At almost $37 per gram, a good in-house synthesis of **15** is necessary to make working with it practical. The most straightforward of these routes reported to date is the three-step sequence shown here, which provides **15** in 43% yield.[11c]



We report here that the methodology developed in this report allows for the one-pot synthesis of **15** in 50% yield from **6a** (see Scheme 4). Of note, **6a** is not a severe lachrymator as many haloalkenes are, including **14**, and it is therefore easy to handle. Cross coupling was carried

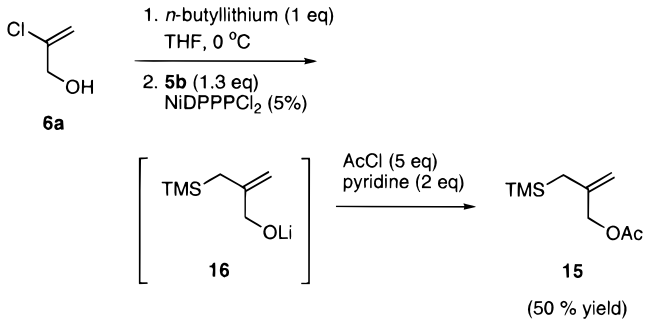
(11) (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2315−2325. (b) Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.* **1984**, *62*, 58−66. (c) Trost, B. M.; Buch, M.; Miller, M. L. *J. Org. Chem.* **1988**, *53*, 4887−4888. (d) Hosomi, A.; Hashimoto, H.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 951−954. (e) Sarkar, T. K. *Synthesis* **1990**, 1101−1111.

(12) (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 3733−3735. (b) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2326−2335. (b) Trost, B. M.; Parquette, J. R. *J. Org. Chem.* **1994**, *59*, 7568−7569. (c) Naz, N.; Al-Tel, T. H.; Al-Abed, Y.; Voelter, W. *J. Org. Chem.* **1996**, *61*, 3250−3255. (d) Jones, M. D.; Kemmitt, R. D. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1201−1203.

(13) For related work, see: (a) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183−5186. (b) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1985**, *26*, 3825−3828.

(14) (a) Trost, B. M.; Seoane, P.; Mignani, S.; Acemoglu, M. *J. Am. Chem. Soc.* **1989**, *111*, 7487−7500. (b) Knapp, S.; O'Connor, U.; Mobilio, D. *Tetrahedron Lett.* **1980**, *21*, 4557−4560.

Scheme 4



out as it had been previously in the production of **7b**. When this reaction was judged complete by TLC analysis, pyridine (2 equiv) and acetyl chloride (5 equiv) were added and the reaction worked up. This sequence allows for reaction to take place at both the halide and alcohol site in one operation in a selective fashion.

It is of interest to note that **15** is a substrate for Ni-catalyzed allylic ionization of the acetate. Further, excess Grignard reagent could potentially react at the newly formed ester site. Despite these potential side reactions, analysis of the reaction mixture by both TLC and proton NMR spectroscopy indicates that only coupled alcohol derived from intermediate **16** and acetate **15** are present at the end of the first and second step in the sequence, respectively. In fact, most of the reactions reported in this study are clean "spot-to-spot" transformations, and we believe that product volitility is the chief contributor to yield reduction in most cases.

In summary, we have developed a convenient and general one-pot strategy for the cross coupling of vinyl halide compounds containing one or more alcohol moieties with Grignard reagents using Ni catalysis. This procedure involves *in situ* deprotonation of the alcohol(s) with *n*-butyllithium followed by cross-coupling with $NiDPPPCl_2$. This preserves the reactivity of the alkoxide such that it can then be reacted selectively following coupling as demonstrated by the production of **15**.

Experimental Section

All reactions were carried out under a positive atmosphere of dry argon. Diethyl ether (Et_2O) and tetrahydrofuran (THF) solvents were distilled from sodium benzophenone prior to use. Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ at 300 MHz for proton spectra and at 75 MHz for carbon spectra. Chemical shifts are listed relative to $CHCl_3$ (δ 7.24) for ^{1}H NMR and (δ 77.00) for ^{13}C NMR. ^{13}C NMR spectra obtained using the APT pulse sequence (indicated by APT in parentheses prior to the δ symbol) display positive signals (i.e., (+)) for quaternary carbons and carbons that are attached to an even number of protons. Signals for carbons that are attached to an odd number of protons are negative (i.e., (−)).

General Cross-Coupling Procedure. The following procedure is general for the cross couplings performed in this study, and any deviations are noted in the directions for specific compounds.

2-[(Trimethylsilyl)methyl]-2-propen-1-ol (7b). Into a flame-dried 25 mL round-bottom flask containing a stir bar was added 122 mg of magnesium turnings (5.02 mmol) followed by 15 mL of dry THF. The Mg surface was activated with three drops of dibromoethane followed by the addition of 569 μL of (chloromethyl)trimethylsilane (500 mg, 4.08 mmol). This mixture was refluxed for 1 h and then cooled back to room temperature following formation of **5b**. In a separate dried flask, 291 mg of **6a** (3.14 mmol) was dissolved in 20 mL of dry THF and 2.06 mL of *n*-butyllithium (3.14 mmol, 1.52 M solution in hexanes, Aldrich) added at 0 °C. After being stirred for 10 min, this mixture was transferred by cannula into the flask containing the Grignard reagent followed by 85 mg of $NiDPPPCl_2$ (0.16 mmol). The reaction was then set to reflux and the progress monitored by TLC. After being refluxed for 3 h, the mixture was cooled to room temperature and quenched with 10 mL of saturated NH_4Cl. Forty milliliters of ether was added, the layers were separated, and the organic layer was dried over anhydrous $MgSO_4$. Following solvent removal *in vacuo*, the crude mixture was loaded on top of a prepacked silica gel column and flashed (solvent: 15% ethyl acetate/hexanes), providing 310 mg of **7a** (69% yield) as a clear oil: ^{1}H NMR δ 4.88 (d, J = 2.2 Hz, 1H), 4.65 (s, 1H), 3.96 (s, 2H), 1.51 (s, 3H), −0.05 (s, 9H); ^{13}C NMR δ 146.85, 106.57, 66.99, 23.20, −1.35; IR (neat) 3330, 3077 cm^{-1}; HRMS calcd for $C_7H_{16}OSi$ 144.0971, found 144.0973.

2-[(Dimethylphenylsilyl)methyl]-2-propen-1-ol (7a). The general coupling procedure was followed with two exceptions. In this case, **5a** was the limiting reagent instead of **6a**. Second, Grignard formation of **5a** did not proceed in THF, but it did form in diethyl ether. Thus, **5a** was formed in ether, an equal volume of THF added, and the ether removed by pushing the vapor out through the reflux condenser where it was collected into a short path distillation unit that was affixed to the top of the reflux condenser. With this change to the general procedure, 400 mg of **6a** (4.32 mmol), 2.8 mL of *n*-butyllithium (4.32 mmol, 1.52 M solution in hexanes, Aldrich), 532 mg of (chloromethyl)dimethylphenylsilane (2.88 mmol), 95 mg of magnesium turnings (3.90 mmol), and 65 mg of $NiDPPPCl_2$ (0.12 mmol) provided 416 mg of **7b** (70% yield) as a clear oil. The product was purified by flash chromatography using 20% ethyl acetate in hexanes: ^{1}H NMR δ 7.52−7.49 (m, 2H), 7.39−7.33 (m, 3H), 4.90 (d, J = 1.5 Hz, 1H), 4.66 (s, 1H), 3.81 (s, 2H), 1.76 (s, 3H), 0.31 (s, 6H); ^{13}C NMR (APT) δ 146.17 (+), 138.54 (+), 133.52 (−), 129.12 (−), 127.80 (−), 107.49 (+), 66.86 (+), 22.44 (+), −3.07 (−); IR (neat) 3335, 3070, 3050, 3022 cm^{-1}; HRMS calcd for $C_{12}H_{18}OSi$ 206.1127, found 206.1126.

2-Phenyl-2-propen-1-ol (7c). Following the general coupling procedure, 169 mg of **6a** (2.12 mmol), 1.39 mL of *n*-butyllithium (2.12 mmol, 1.52 M solution in hexanes, Aldrich), 400 mg of bromobenzene (2.55 mmol), 77 mg of magnesium turnings (3.18 mmol), and 75 mg of $NiDPPPCl_2$ (0.14 mmol) provided 245 mg of **7c** (86% yield) as a pale yellow oil. The product was purified by flash chromatography using 20% ethyl acetate in hexanes: ^{1}H NMR δ 7.47−7.26 (m, 5H), 5.48 (s, 1H), 5.26 (s, 1H), 4.55 (br s, 2H), 1.71 (br s, 1H); ^{13}C NMR (APT) δ 147.05 (+), 138.49 (+), 128.24 (−), 127.62 (−), 125.83 (−), 112.09 (+), 64.29 (+); IR (neat) 3350, 3084, 3057, 3032, cm^{-1}; HRMS calcd for $C_9H_{10}O$ 134.0732, found 134.0732.

2-Ethyl-2-propen-1-ol (7d). Following the general coupling procedure, 261 mg of **6a** (2.82 mmol), 1.86 mL of *n*-butyllithium (2.82 mmol, 1.52 M solution in hexanes, Aldrich), 400 mg of bromoethane (3.67 mmol), 110 mg of magnesium turnings (4.52 mmol), and 92 mg of $NiDPPPCl_2$ (0.17 mmol) provided 203 mg of **7d** (83% yield) as a clear oil: the product was purified by flash chromatography using 20% ethyl acetate in hexanes: ^{1}H NMR δ 5.00 (s, 1H), 4.86 (s, 1H), 4.08 (br s, 2H), 2.07 (q, J = 7.4 Hz, 2H), 1.63 (br s, 1H), 1.08 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 150.63, 107.89, 65.86, 25.61, 12.06; IR (neat) 3334, 3086 cm^{-1}; HRMS calcd for $C_5H_{10}O$ 86.0732, found 86.0730.

2-[2-[(Trimethylsilyl)methyl]-2-propenyl]cyclohexanol (9b). Following the general coupling procedure, 115 mg of **8a** (0.66 mmol, 3:1 mixture of diastereomers), 435 μL of *n*-butyllithium (0.66 mmol, 1.52 M solution in hexanes, Aldrich), 114 mg of (chloromethyl)trimethylsilane (0.93 mmol), 24 mg of magnesium turnings (0.99 mmol), and 22 mg of $NiDPPPCl_2$ (0.04 mmol) provided 98 mg of **9b** (66% yield, 3:1 mixture of diastereomers) as a clear oil that solidified on sitting in the freezer. The product was purified by flash chromatography using 25% ethyl acetate in hexanes. Spectral data for the major isomer are included here: ^{1}H NMR δ 4.67 (br s, 1H), 4.56 (br s, 1H), 3.27 (m, 1H), 2.40 (dd, J = 14.4, 7.2 Hz, 1H), 2.05−0.84 (m, 13H), 0.04 (s, 9H); ^{13}C NMR (APT) δ 147.71 (+), 108.83 (+), 75.79 (−), 43.12 (+), 43.04 (−), 35.24 (+), 30.93 (+), 26.36 (+), 25.51 (+), 24.75 (+), −1.31 (−); IR (neat) 3366, 3072 cm^{-1}; HRMS calcd for $C_{13}H_{26}OSi$ 226.1754, found 226.1744.

2-(2-Phenyl-2-propenyl)cyclohexanol (9c). Following the general coupling procedure, 110 mg of **8a** (0.63 mmol, 3:1 mixture of diastereomers), 416 μL of *n*-butyllithium (0.63 mmol, 1.52 M solution in hexanes, Aldrich), 139 mg of bromobenzene (0.89 mmol), 23 mg of magnesium turnings (0.95 mmol), and 21

mg of $NiDPPPCl_2$ (0.04 mmol) provided 104 mg of **9c** (76% yield, 3:1 mixture of diastereomers) as a clear oil. The product was purified by flash chromatography using 15% ethyl acetate in hexanes. Spectral data for the major isomer are included here: ^{1}H NMR δ 7.46−7.60 (m, 5H), 5.31 (d, J = 2.2 Hz, 1H), 5.08 (s, 1H), 3.27−3.18 (m, 3H), 2.20−0.88 (m, 10H); ^{13}C NMR δ 147.47, 140.94, 128.32, 127.38, 126.28, 113.93, 75.29, 43.32, 39.22, 35.60, 30.32, 25.30, 24.85; IR (neat) 3383, 3081, 3057, 3024 cm^{-1}; HRMS calcd for $C_{15}H_{20}O$ 216.1515, found 216.1522.

2-(2-Ethyl-2-propenyl)cyclohexanol (9d). Following the general coupling procedure, 56 mg of **8b** (0.28 mmol, 3:1 mixture of diastereomers), 184 μL of *n*-butyllithium (0.28 mmol, 1.52 M solution in hexanes, Aldrich), 61 mg of bromoethane (0.39 mmol), 12 mg of magnesium turnings (0.48 mmol), and 9 mg of $NiDPPPCl_2$ (0.02 mmol) provided 39 mg of **9d** (83% yield, 3:1 mixture of diastereomers) as a clear oil. The product was purified by flash chromatography using 15% ethyl acetate in hexanes. Spectral data for the major isomer are included here: ^{1}H NMR δ 4.78 (s, 2H), 3.26 (m, 1H), 2.50 (dd, J = 14.0, 5.9 Hz, 1H), 2.05 (t, J = 7.4 Hz, 2H), 2.02−1.18 (m, 10H), 1.04 (t, J = 7.4 Hz, 3H), 0.89 (m, 1H); ^{13}C NMR (APT) δ 151.20 (+), 109.44 (+), 75.81 (−), 43.03 (−), 41.15 (+), 35.32 (+), 30.77 (+), 28.35 (+), 25.49 (+), 24.80 (+), 12.23 (−); IR (neat) 3350, 3079 cm^{-1}; HRMS calcd for $C_{11}H_{20}O$ 168.1515, found 168.1516.

2-[2-(2-Propenyl)-2-propenyl]cyclohexanol (9e). Following the general coupling procedure, 104 mg of **8a** (0.60 mmol, 3:1 mixture of diastereomers), 394 μL of *n*-butyllithium (0.60 mmol, 1.52 M solution in hexanes, Aldrich), 1.68 mL of allylmagnesium bromide (1.68 mmol, 1 M solution in diethyl ether, Aldrich), and 19 mg of $NiDPPPCl_2$ (0.04 mmol) provided 82 mg of **9e** (76% yield, 3:1 mixture of diastereomers) as a clear oil. The product was purified by flash chromatography using 15% ethyl acetate in hexanes. Spectral data for the major isomer are included here: ^{1}H NMR δ 5.90−5.68 (m, 1H), 5.20−4.91 (m, 2H), 4.79 (s, 2H), 3.29−3.17 (m, 1H), 2.78−2.65 (m, 2H), 2.54−2.36 (m, 1H), 2.30−0.75 (m, 11H); ^{13}C NMR δ 147.66, 136.21, 116.27, 111.78, 75.55, 42.91, 40.52, 40.35, 35.37, 30.61, 25.44, 24.78; IR (neat) 3360, 3077 cm^{-1}; HRMS calcd for $C_{12}H_{20}O$ 180.1515, found 180.1510.

2-[(Trimethylsilyl)methyl]-2-cyclohexen-1-ol (11b). Following the general coupling procedure, 205 mg of **10b** (1.16 mmol), 762 μL of *n*-butyllithium (1.16 mmol, 1.52 M solution in hexanes, Aldrich), 199 mg of (chloromethyl)trimethylsilane (1.62 mmol), 45 mg of magnesium turnings (1.86 mmol), and 38 mg of $NiDPPPCl_2$ (0.07 mmol) provided 143 mg of **11b** (67% yield) as a clear oil. The product was purified by flash chromatography using 15% ethyl acetate in hexanes: ^{1}H NMR δ 5.29 (br s, 1H), 3.84 (br s, 1H), 2.20−1.20 (m, 9H), −0.05 (s, 9H); ^{13}C NMR δ 136.81, 122.86, 68.09, 32.03, 25.38, 23.60, 17.77, −1.35; IR (neat) 3354, 3024, 3051 cm^{-1}; HRMS calcd for $C_{10}H_{20}OSi$ 184.1284, found 184.1284.

4-Ethyl-2-(hydroxymethyl)-4-penten-1-ol (13). Following the general coupling procedure, 200 mg of **12** (1.21 mmol), 1.60 mL of *n*-butyllithium (2.42 mmol, 1.52 M solution in hexanes, Aldrich), 396 mg of bromoethane (3.63 mmol), 88 mg of magnesium turnings (3.63 mmol), and 39 mg of $NiDPPPCl_2$ (0.07 mmol) provided 149 mg of **13** (78% yield) as a clear oil. The product was purified by flash chromatography using 35% ether acetate in pentane: ^{1}H NMR δ 4.85 (d, J = 1.5 Hz, 1H), 4.71 (s, 1H), 3.51−3.41 (m, 6H), 2.05−1.98 (m, 4H), 1.01 (t, J = 8.1 Hz, 3H), 0.79 (s, 3H); ^{13}C NMR δ 148.06, 112.23, 69.59, 40.00, 39.72, 30.84, 18.94, 12.61; IR (neat) 3370, 3085 cm^{-1}; HRMS calcd for $C_9H_{18}O_2$ + H 159.1386, found 159.1391.

2-[(Trimethylsilyl)methyl]-2-propen-1-yl Acetate (15). Following the general coupling procedure, 269 mg of **6a** (2.91 mmol), 1.91 mL of *n*-butyllithium (2.91 mmol, 1.52 M solution in hexanes, Aldrich), 500 mg of (chloromethyl)trimethylsilane (4.08 mmol), 113 mg of magnesium turnings (4.66 mmol), and 95 mg of $NiDPPPCl_2$ (0.07 mmol) were combined and the reaction monitored. When the coupling was judged complete by TLC analysis, the solution was cooled to 0 °C and 691 mg of pyridine (8.73 mmol) added followed by 681 mg of acetyl chloride (8.73 mmol). The acetylation was monitored carefully by TLC, and after 10 min, the reaction was diluted with ether and washed successively with 10% HCl and saturated $NaHCO_3$ solutions. Following drying over anhydrous $MgSO_4$, the solvent was removed *in vacuo*. The product was purified by flash chromatography (pentane) to provide 271 mg (50% yield) of **15**. Spectral data compared well with that of the literature.[11c]

Acknowledgment. This work was supported in part by a research grant from Eli Lilly and Company.

Supporting Information Available: ^{1}H or ^{13}C NMR spectra for compounds **7a**−**d**, **9b**−**e**, **11b**,**d**, and **15** (11 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.

JO961900U