Nickel-Catalyzed Intermolecular Coupling of 1,3-Dienes and Aldehydes via Transmetalation of Nickelacycles with Diisobutylaluminum Acetylacetonate

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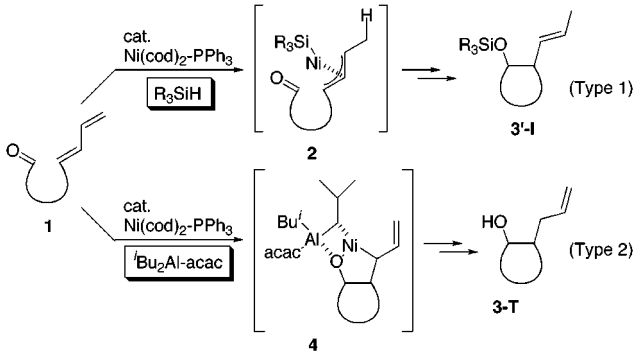
Intermolecular coupling reactions of 1,3-dienes and aldehydes via transmetalation of nickelacycle intermediate with $^{i}Bu_2Al$−acac were investigated. In the reactions, a linear adduct or a branched adduct was produced, depending upon the nature of 1,3-dienes and aldehydes, via two nickelacycles that were relatively stable among the four possible nickelacycles because of the equilibrium with π-allynickel forms.

Introduction

Since the first nickel-promoted co-oligomerization of 1,3-dienes was reported by Reed in 1954,[1] many efforts have been made to achieve the nickel-promoted or -catalyzed oligomerization of 1,3-dienes with other multiple bonds.[2] The intramolecular version of this type of reaction is especially useful for producing various cyclic compounds in a stereoselective manner.[3] In this context, we have already succeeded in the stereoselective cyclization of 1,3-diene and a tethered aldehyde, as shown in Scheme 1.[4] The cyclization of 1,3-diene **1** having a tethered aldehyde with a catalytic amount of Ni(0) complex and PPh_3 in the presence of R_3SiH proceeded via π-allylnickel intermediate **2** to give **3′-I**, having an internal olefin in the side chain, in a stereoselective manner (Type 1 reaction, Scheme 1).[4a] On the other hand, we also found that the cyclization of **1** using the same catalyst system in the presence of diisobutylaluminum acetylacetonate ($^{i}Bu_2Al$−acac) instead of R_3SiH stereoselectively produced **3-T** having a terminal olefin in the side chain (Type 2 reaction, Scheme 1).[4h]

Scheme 1



It was thought that the reaction in the presence of $^{i}Bu_2Al$−acac proceeded via a transmetalation of the nickelacycle **4**, formed by oxidative cycloaddition of **1** to Ni(0) complex and $^{i}Bu_2Al$−acac.

The Type 1 reaction has been further extended to an intermolecular coupling reaction of 1,3-dienes and aldehydes as shown in Scheme 2, in which homoallyl alcohol derivative **7** was obtained in a stereoselective manner from 1,3-diene **5** and aldehyde **6** via π-allylnickel intermediate **8**.[5]

On the other hand, an intermolecular coupling reaction of 1,3-dienes and aldehyde in the presence of $^{i}Bu_2Al$−acac (Type 2 reaction) has not been investigated. In this Type 2 intermolecular coupling reaction, it was possible to produce nickelacycle intermediates **I**−**IV** (Scheme 3). It was expected that the reaction course could be con-

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(3) For [4 + 4] cycloadditions, see: (a) Wender, P. A.; Tebbe, M. J. *Synthesis* **1991**, 1089. (b) Wender, P. A.; Ihle, N. C.; Correia, C. R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5904. (c) Wender, P. A.; Ihle, N. C. *Tetrahedron Lett.* **1987**, *28*, 2451. (d) Wender, P. A.; Snapper, M. L. *Tetrahedron Lett.* **1987**, *28*, 2221. (e) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678. For [4 + 2] cycloadditions, see: (f) Wender, P. A.; Smith, T. E. *Tetrahedron* **1998**, *54*, 1255. (g) Wender, P. A.; Smith, T. E. *J. Org. Chem.* **1996**, *61*, 824. (h) Wender, P. A.; Smith, T. E. *J. Org. Chem.* **1995**, *60*, 2962. (i) Wender, P. A.; Jenkins, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 6432. For a cyclization of 1,3-diene and allene, see: (j) Wender, P. A.; Jenkins, T. E.; Suzuki, S. *J. Am. Chem. Soc.* **1995**, *117*, 1843. For other cyclizations related to 1,3-dienes, see: (k) Tamao, K.; Kobayashi, K.; Ito, Y. *Synlett.* **1992**, 539. (l) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Synth. Org. Chem. Jpn.* **1990**, *48*, 381. (m) Montgomery, J.; Oblinger, E.; Savchenko, A. V. *J. Am. Chem. Soc.* **1997**, *119*, 4911.

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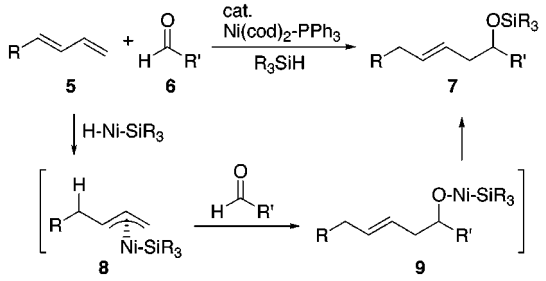
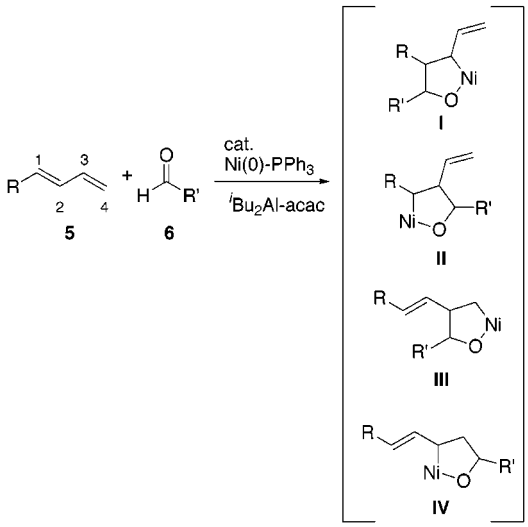
Scheme 2



Scheme 3



trolled kinetically or thermodynamically, depending upon the stability of nickelacycle intermediates **I**−**IV**. Herein, we report the results of investigation of intermolecular coupling reactions of 1,3-dienes and aldehydes via nickelacycle intermediates (Type 2 reaction).

Results and Discussion

First, the reaction of 1,3-diene **5a** and benzaldehyde **6a** was investigated (Scheme 4). Treatment of **5a** and **6a** (1:1 mixture) with 20 mol % of Ni(0)−PPh_3 complex, generated from $NiCl_2(PPh_3)_2$ (20 mol %) and BuLi (40 mol %),[7] in the presence of $^iBu_2Al$−acac (1.5 equiv) in toluene gave linear adduct **10a** (62%), branched adduct **11a** (7%), and 1:2 adduct **12a** (8%). The geometry of the olefin in **10a** was exclusively controlled to be an *E*-configuration. Products **11a** and **12a** were obtained as the sole products, although the stereochemistry of those products could not be determined at this stage.

The outline of the mechanism of this intermolecular coupling reaction is depicted in Scheme 5. It was thought that the linear adduct **10** was produced via nickelacycle intermediate **IV**, which was formed by a C−C bond-forming reaction between C4 in 1,3-diene **5** and the carbonyl carbon of aldehyde **6**. The transmetalation of nickelacycle **IV** with $^iBu_2Al$−acac gave **13**. β-Elimination of the isobutyl group on the nickel metal in **13** occurred

Scheme 4

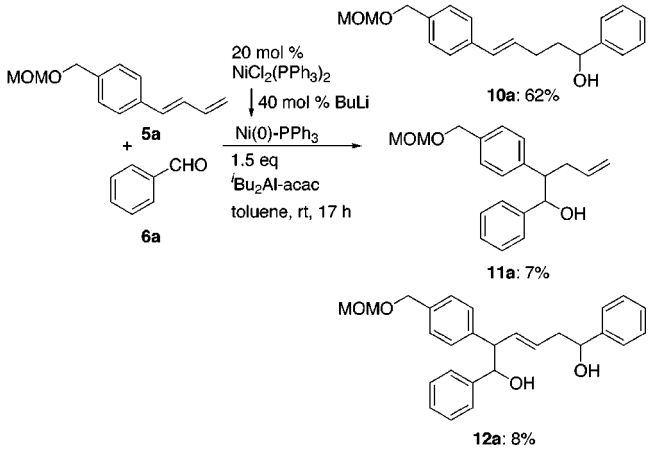
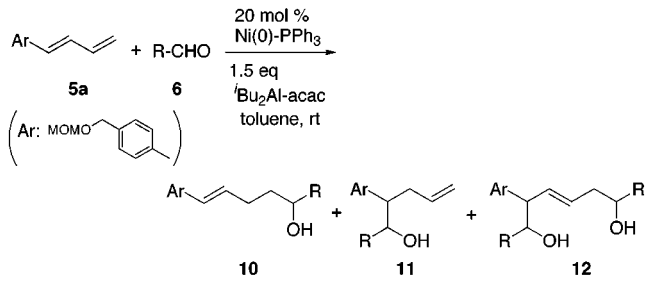


Table 1. Reaction of 5a with Various Aldehydes



run	aldehyde (R-)	time (h)	yield (%) 10	11	12	ratio 10 : 11
1[a]	(6a)	17	62	7	8	8.9 : 1
2[b]		19	61	22	1	2.8 : 1
3[c]		22	61	19	—	3.2 : 1
4[a]	MeO (6b)	13	78	8	5	9.8 : 1
5[a]	MeO_2C (6c)	22	34	15	—	2.3 : 1
6[a]	(6d)	24	62	22	—	2.8 : 1
7[a]	^{i}Pr- (6e)	16	57	22	—	2.6 : 1
8[a]	^{n}Pr- (6f)	15	26	61	—	1 : 2.3

[a] Reaction was carried out using a Ni complex generated from 20 mol % $NiCl_2(PPh_3)_2$ and 40 mol % BuLi. [b] Reaction was carried out using a Ni complex genrated from 20 mol % $Ni(acac)_2$ and 40 mol % DIBAL-H in the presence of 40 mol % PPh_3. [c] Reaction was carried out using a Ni complex generated from 20 mol % $Ni(cod)_2$ and 40 mol % PPh_3.

to give **14** along with the evolution of isobutene, from which **10** was obtained via reductive elimination and acidic workup. The branched adduct **11** was thought to be formed via nickelacycle intermediate **I** in a manner similar to that described above.

These results indicate that nickelacycle intermediates **I** and **IV** are relatively stable among the four possible nickelacycles in Scheme 3. It is thought that nickelacycle **I** or **IV** was in equilibrium with π-ally-**I** or **IV**, which would result in an increase in the stability of **I** and **IV**. The 1:2 adduct **12** would be produced from the reaction of π-allylnickel intermediates **13′** and/or **15′** with aldehyde **6** to give **12** via **17** and/or **18** (Scheme 6).

The intermolecular coupling reaction of 1,3-diene **5a** and various aldehydes was investigated, and the results are summarized in Table 1.

(6) For other examples of nickel-promoted or -catalyzed intermolecular coupling of 1,3-diene and a carbonyl compound, see: (a) Baker, R.; Cook, A. H.; Crimmin, M. J. *J. Chem. Soc., Chem. Commun.* **1975**, 727. (b) Baker, R.; Crimmin, M. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1264. (c) Kimura, M.; Ezoe, A.; Shibata, K.; Tamaru, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4033.

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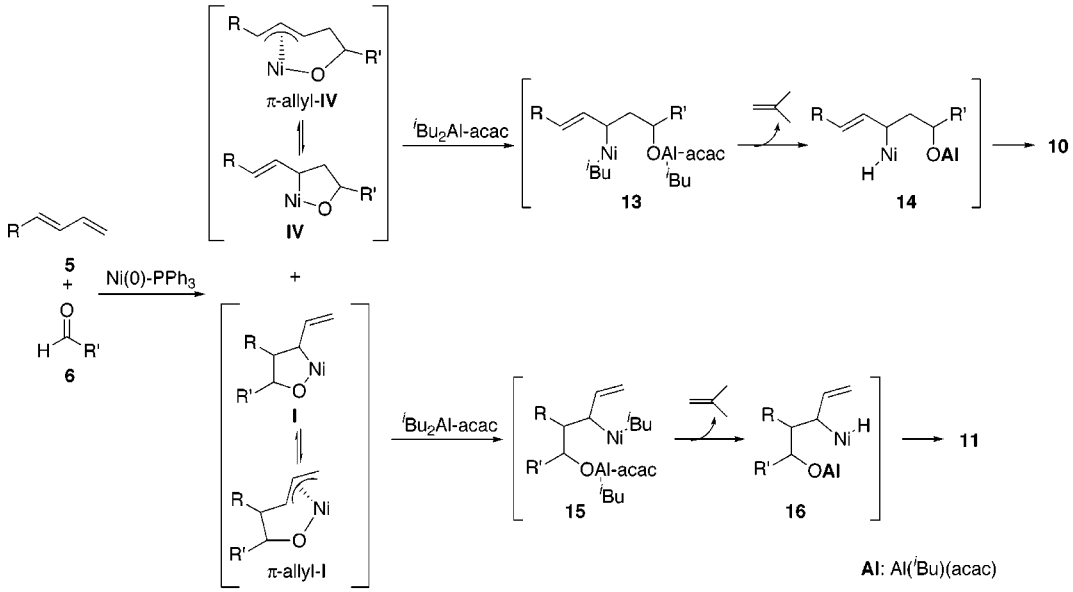
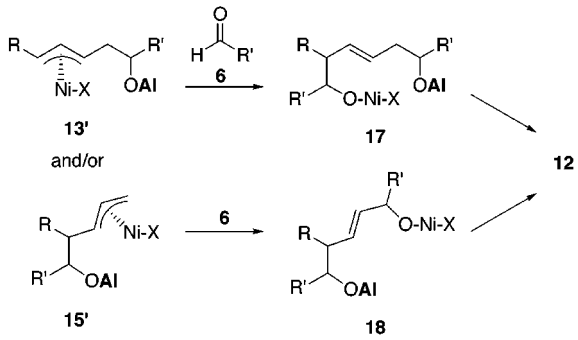
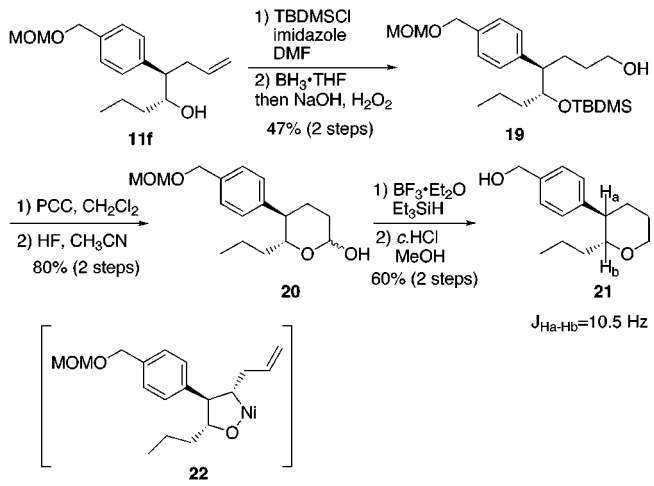
Scheme 5



Scheme 6



Scheme 7

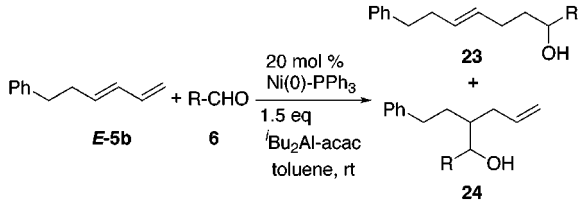


The reaction of **5a** and benzaldehyde **6a** using an Ni(0)−PPh_3 catalyst generated by reduction of $Ni(acac)_2$ with DIBAL-H in the presence of PPh_3[8] afforded linear adduct **10a** in 61% yield, branched adduct **11a** in 22% yield, and 1:2 adduct **12a** in 1% yield (run 2). The use of Ni(0)−PPh_3 generated from $Ni(cod)_2$ and PPh_3 also increased the formation of branched adduct **11a** (run 3). The ratio of linear adduct **10** to branched adduct **11** was varied in the reaction of **5a** and **6** depending upon the nature of aldehydes, and **10** and **11** were obtained as single isomers in all of the reactions shown in Table 1. It was interesting that the formation of branched adduct **11** was increased in the case of the aldehyde having an electron-withdrawing group on the aromatic ring and in the case of aliphatic aldehydes (runs 5 and 6−8, respectively). Notably, the reaction of **5a** and 1-butanal **6f** gave branched adduct **11f** in 61% yield as a major product (run 8). The branched adduct was also increased in the absence of chloride anion (runs 2 and 3), which was derived from the starting catalyst, $NiCl_2(PPh_3)_2$.

To determine the stereochemistry of **11f**, the compound **11f** was converted into **21** as shown in Scheme 7. From the coupling constant between Ha and Hb in the ^1H NMR spectrum of **21**, the stereochemistry of **11f** was unambiguously determined. Thus, it was thought that **11f** was produced via the nickelacycle **22**.

(8) Krysan, D. J.; Mackenzie, P. B. *J. Org. Chem.* **1990**, *55*, 4229. Also see, ref 3j,k.

Table 2. Reaction of *E*-5b with Various Aldehydes[a]

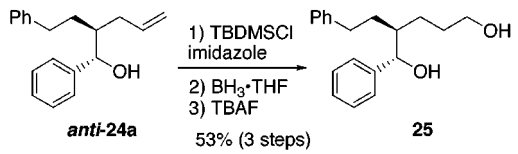


run	aldehyde (R-)	time (h)	yield (%) 23	yield (%) 24	ratio 23 : 24
1	(6a)	21	30	42	1 : 1.4
2	(6d)	17	48	19	2.5 : 1
3	^{n}Pr- (6f)	17	34	38	1 : 1.1

[a] Reaction was carried out using a Ni complex genrated from 20 mol % $Ni(acac)_2$ and 40 mol % DIBAL-H in the presence of 40 mol % PPh_3.

Next, intermolecular coupling reactions of 1,3-diene ***E*-5b** and various aldehydes were carried out (Table 2). The reaction of ***E*-5b** and benzaldehyde **6a** gave the linear adduct **23a** in 30% yield and the branched adduct ***anti*-24a** in 42% yield as a single isomer (run 1). The

Scheme 8



***anti*-24a** **25**

stereochemistry of ***anti*-24a** was determined by X-ray analysis of **25** derived from ***anti*-24a** (Scheme 8). In the case of aldehyde **6d**, the linear adduct **23d** was produced in preference to the branched adduct **24d** (Table 2, run 2). The reaction of ***E*-5b** and 1-butanal **6f** gave the coupling products **23f** and **24f** in 72% total yield, although the ratio of **23f** to **24f** was almost 1:1 (run 3). The branched adducts **24d** and **24f** were also obtained as single isomers in each case.

Compared with the reaction of ***E*-5b** and **6a** (Table 2, run 1), the reaction of ***Z*-5b** (*Z*:*E* = 6.8:1) and **6a** produced preferentially branched adducts ***syn*-24a** and ***anti*-24a** in 61% total yield in a ratio of 1.4:1[9] along with linear adduct **23a** in 13% yield (Scheme 9).

It is apparent that the branched adducts ***syn*-24a** and ***anti*-24a** were produced from nickelacycle ***syn*-26** and ***anti*-26** in Scheme 10, respectively.

Thus, this result indicates that ***syn*-26**, which seemed to be more unstable than ***anti*-26a** because all of the substituents on the nickelacycle are in the syn-configuration, was preferentially produced in this reaction, although the reason for this is not clear.

In conclusion, we developed an intermolecular coupling reaction of 1,3-dienes and aldehydes via transmetalation of a nickelacycle intermediate with $^{i}Bu_2Al-acac$ (Type 2 reaction). In this reaction, a linear adduct or branched adduct was produced depending upon the nature of 1,3-dienes and aldehydes via nickelacycle **I** or **IV** (Scheme 3), which are relatively stable among the four possible nickelacycles because of the equilibrium with π-ally-**I** or **IV**.

Experimental Section

General. All manipulations were performed under an argon atmosphere unless otherwise mentioned. All solvents and reagents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70−230 mesh), and flash chromatography was performed on silica gel 60 (Merck, 230−400 mesh) using the indicated solvent. NMR spectra were measured on a JEOL EX 270 (^{1}H at 270 MHz, ^{13}C at 67.5 MHz), JEOL AL 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz), or Bruker ARX-500 (^{1}H at 500 MHz) magnetic resonance spectrometer. Infrared spectra were recorded on a Perkin-Elmer FTIR 1605 spectrometer. Mass spectra were measured on Perkin-Elmer Q-Mass 910, JEOL DX-303, JEOL JMS−HX110, and JEOL JMS−FAB mate mass spectrometers. Fast-atom bombardment (FAB) mass spectra were obtained using glycerol or NBA as a matrix. Melting point was measured on a Yanaco MP-J3 melting point apparatus.

General Procedure for the Coupling Reaction Using a Ni Complex Generated from $NiCl_2(PPh)_3$ and BuLi: Method A. To a suspension of $NiCl_2(PPh_3)_2$ (20 mol % to substrate) in degassed toluene (0.02 M) was added BuLi (40 mol % to substrate) at 0 °C, and the mixture was stirred at the same temperature for 20 min. To the mixture was added $^{i}Bu_2Al-acac$ (1.5 equiv to substrate) at 0 °C, and the mixture was stirred at the same temperature for 15 min. Then, a solution of diene **5** and aldehyde **6** (1.0 equiv to diene) in degassed toluene (0.1 M) was added to the mixture at 0 °C, and the mixture was stirred at room temperature for several hours. To the mixture was added 10% HCl aqueous solution at 0 °C, and the organic layer was extracted with Et_2O. The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution and brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel to give the corresponding coupling products.

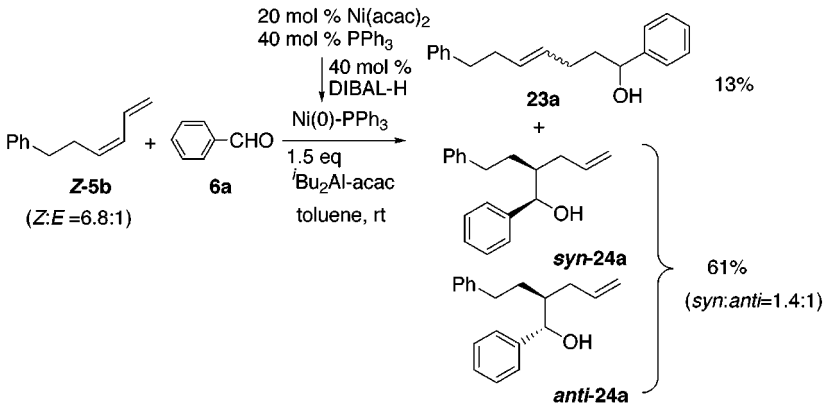
General Procedure for the Coupling Reaction Using a Ni Complex Generated from $Ni(acac)_2$, PPh_3, and DIBAL-H: Method B. To a suspension of $Ni(acac)_2$ (20 mol % to substrate) and PPh_3 (40 mol % to substrate) in degassed toluene (0.02 M) was added DIBAL-H (40 mol % to substrate) at 0 °C, and the mixture was stirred at room temperature for 25 min. To the mixture was added $^{i}Bu_2Al-acac$ (1.1 equiv to substrate) at 0 °C, and the mixture was stirred at the same temperature for 20 min. Then, a solution of diene and aldehyde **6** (1.0 equiv. to substrate) in degassed toluene (0.1 M) was added to the mixture at 0 °C, and the mixture was stirred at room temperature for several hours. To the mixture was added 10% HCl aqueous solution at 0 °C, and the organic layer was extracted with Et_2O. The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution and brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel to give the corresponding coupling products.

General Procedure for the Coupling Reaction Using a Ni Complex Generated from $Ni(cod)_2$ and PPh_3: Method C. To a solution of $Ni(cod)_2$ (20 mol % to substrate) and PPh_3 (40 mol % to substrate) in degassed toluene (0.02 M) was added $^{i}Bu_2Al-acac$ (1.0 M in toluene, 0.75 mL, 0.75 mmol) at 0 °C, and the mixture was stirred at the same temperature for 15 min. Then, a solution of diene **5** and aldehyde **6** (1.0 equiv to diene) in degassed toluene (0.1 M) was added to the mixture at 0 °C, and the mixture was stirred at room temperature. To the mixture was added 10% HCl aqueous solution at 0 °C, and the organic layer was extracted with Et_2O. The combined organic layer was washed with saturated $NaHCO_3$ aqueous solution and brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel to give the corresponding coupling products.

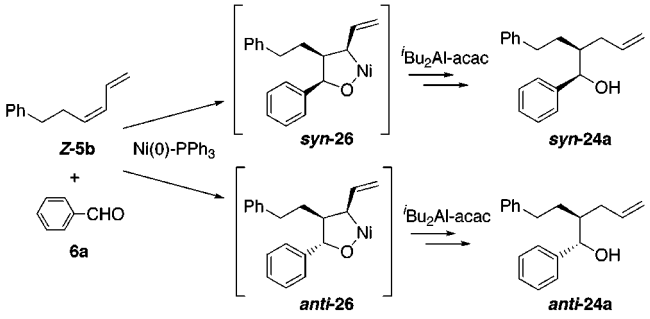
(4*E*)-5-(4-Methoxymethoxymethylphenyl)-1-phenylpent-4-en-1-ol (10a), 2-(4-Methoxymethoxymethylphenyl)-1-phenylpent-4-en-1-ol (11a), and (3*E*)-2-(4-Methoxymethoxymethylphenyl)-1,6-diphenylhex-3-ene-1,6-diol (12a): (Table 1, Run 1). Following the general procedure (Method A), a crude product, which was obtained from the coupling reaction of **5a** (102.8 mg, 0.50 mmol) and **6a** (0.052 mL, 0.51 mmol) using a Ni complex generated from $NiCl_2(PPh_3)_2$ (65.4 mg, 0.10 mmol) and BuLi (1.52 M in hexane, 0.13 mL, 0.20 mmol) in the presence of $^{i}Bu_2Al-acac$ (1.0 M in toluene, 0.75 mL, 0.75 mmol) at room temperature for 17 h, was purified by column chromatography on silica gel (hexane−AcOEt, 10/1, 7/1, 5/1, and 2/1) to give **10a** (96.4 mg, 62%), **11a** (11.1 mg, 7%), and **12a** (16.2 mg, 8%). **10a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.87 (brs, 1H), 1.87−2.04 (m, 2H), 2.26−2.36 (m, 2H), 3.41 (s, 3H), 4.56 (s, 2H), 4.69 (s, 2H), 4.74 (dt, J = 6.3, 12.7 Hz, 1H), 6.22 (dt, J = 15.8, 6.7 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 7.26−7.55 (m, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 29.0, 38.2, 54.8, 68.5, 73.3, 95.1, 125.7, 127.1, 127.8, 128.0, 129.6, 130.0, 136.1, 137.0, 144.6; IR (neat) 3448, 1606, 1046 cm^{-1}; LRMS (EI) *m*/*z* 313 (M^+ + H), 294, 250, 232, 141, 130, 116, 105, 91, 77, 45; HRMS (EI) calcd for $C_{20}H_{24}O_3$ 312.1726, found 312.1697. **11a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.88 (d, J = 3.4 Hz, 1H), 2.53 (m, 2H), 3.00 (ddd, J = 4.6, 6.3 10.4 Hz, 1H), 3.32 (s, 3H), 4.46 (s, 2H), 4.61 (s, 1H), 4.75−4.76 (m, 1H), 4.87 (d, J = 10.1 Hz, 1H), 4.88 (d, J = 17.0 Hz, 1H), 5.53 (ddd, J = 6.9, 10.1, 17.0 Hz, 1H), 7.24−7.63 (m, 9H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 34.3, 53.0, 55.3, 69.0, 78.0, 95.7, 116.1, 126.5, 127.3, 127.9, 128.9, 135.9, 136.8, 140.5, 142.6; IR (neat) 3446, 1640, 1212, 916 cm^{-1}; LRMS (EI) *m*/*z* 294 ($M^+ - H_2O$), 219, 144, 128, 104, 91; HRMS (EI) calcd for $C_{20}H_{24}O_3$ 312.1726, found 312.1727.

(9) Products ***syn*-24a** and ***anti*-24a** were obtained as an inseparable mixture. Treatment of the mixture with PCC gave the corresponding ketone as a single isomer, by which the stereochemistry of ***syn*-24a** was determined to be the syn-configuration.

Scheme 9



Scheme 10



12a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (ddd, J = 9.0, 9.1, 15.1 Hz, 1H), 2.46−2.50 (m, 1H), 2.73 (brs, 1H), 2.92 (brs, 1H), 3.62 (s, 3H), 3.51 (dd, J = 8.1, 9.0 Hz, 1H), 4.49 (s, 2H), 4.61−4.64 (m, 1H), 4.64 (s, 2H), 4.75 (d, J = 8.1 Hz, 1H), 5.60 (ddd, J = 5.7, 9.1, 15.2 Hz, 1H), 5.93 (dd, J = 9.0, 15.2 Hz, 1H), 7.01 (d, J = 8.2 Hz, 2H), 7.10−7.35 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.2, 55.4, 58.2, 68.8, 72.9, 77.2, 95.4, 125.5, 126.4, 127.2, 127.2, 127.8 (2C), 127.9, 128.2, 129.9, 133.4, 135.7, 140.2, 141.7, 143.6; IR (neat) 3418, 1044 cm^{-1}; LRMS (FAB) m/z 441 (M^+ + Na), 401, 339, 277, 249, 233; HRMS (FAB) calcd for $C_{27}H_{30}O_4Na$ (M^+ + Na) 441.2042, found 441.2047.

Table 1, Run 2. Following the general procedure (Method B), a crude product, which was obtained from the coupling reaction of **5a** (102.1 mg, 0.50 mmol) and **6a** (0.052 mL, 0.51 mmol) using a Ni complex generated from $Ni(acac)_2$ (25.9 mg, 0.10 mmol), PPh_3 (52.5 mg, 0.20 mmol), and DIBAL-H (1.01 M in toluene, 0.2 mL, 0.20 mmol) in the presence of ^{i}Bu$_2$Al−acac (1.0 M in toluene, 0.55 mL, 0.55 mmol) at room temperature for 19 h, was purified by column chromatography on silica gel (hexane−AcOEt, 10/1, 7/1, 5/1, and 2/1) to give **10a** (95.3 mg, 61%), **11a** (35.5 mg, 22%), and **12a** (3.0 mg, 1%).

Table 1, Run 3. Following the general procedure (Method C), a crude product, which was obtained from the coupling reaction of **5a** (102.8 mg, 0.50 mmol) and **6a** (0.052 mL, 0.51 mmol) using a Ni complex generated from $Ni(cod)_2$ (27.4 mg, 0.10 mmol) and PPh_3 (52.6 mg, 0.20 mmol) in the presence of ^{i}Bu$_2$Al−acac (1.0 M in toluene, 0.75 mL, 0.75 mmol) at room temperature for 22 h, was purified by column chromatography on silica gel (hexane−AcOEt, 10/1, 5/1, and 2/1) to give **10a** (95.3 mg, 61%) and **11a** (30.4 mg, 19%).

(4*E*)-5-(4-Methoxymethoxymethylphenyl)-1-(4-methoxyphenyl)pent-4-en-1-ol (10b), 2-(4-Methoxymethoxymethylphenyl)-1-(4-methoxyphenyl)pent-4-en-1-ol (11b) and (3*E*)-2-(4-Methoxymethoxymethylphenyl)-1,6-bis-(4-methoxyphenyl)pent-3-ene-1,6-diol (12b): (Table 1, Run 4). Following the general procedure (Method A), a crude product, which was obtained from the coupling reaction of **5a** (102.2 mg, 0.50 mmol) and **6b** (0.062 mL, 0.51 mmol) using a Ni complex generated from $NiCl_2(PPh_3)_2$ (65.4 mg, 0.10 mmol) and BuLi (1.52 M in hexane, 0.13 mL, 0.20 mmol) in the presence of ^{i}Bu$_2$Al−acac (1.0 M in toluene, 0.75 mL, 0.75 mmol) at room temperature for 13 h, was purified by column chromatography on silica gel (hexane−AcOEt, 10/1, 7/1, 5/1, and 2/1) to give **10b** (132.9 mg, 78%), **11b** (12.2 mg, 7%), and **12b** (11.3 mg, 5%). **10b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.78 (d, J = 3.2 Hz, 1H), 1.82−2.03 (m, 2H), 2.27 (dt, J = 13.1, 6.5 Hz, 2H), 3.41 (s, 3H), 3.81 (s, 3H), 4.56 (s, 2H), 4.69 (s, 2H), 6.21 (dt, J = 16.0, 6.7 Hz, 1H), 6.39 (d, J = 16.0 Hz, 1H), 6.88−7.33 (m, 8H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 29.1, 38.2, 54.9, 68.6, 73.1, 95.2, 113.6, 125.8, 127.0, 127.9, 129.7, 130.1, 136.2, 136.7, 137.0, 158.7; IR (neat) 3440, 1246, 1044 cm^{-1}; LRMS (EI) m/z 342 (M^+), 324, 130, 121, 91; HRMS (EI) calcd for $C_{21}H_{26}O_4$ 342.1832, found 342.1826. **11b**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.83 (d, J = 3.5 Hz, 1H), 2.39−2.65 (m, 2H), 2.97 (ddd, J = 4.5, 6.5, 10.9 Hz, 1H), 3.32 (s, 3H), 3.69 (s, 3H), 4.45 (s, 2H), 4.61 (s, 2H), 4.72 (dd, J = 3.5, 6.5 Hz, 1H), 4.80 (dd, J = 1.7, 10.2 Hz, 1H), 4.90 (dd, J = 1.7, 17.1 Hz, 1H), 5.54 (ddt, J = 10.2, 17.1, 6.9 Hz, 1H), 6.68 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 34.7, 53.0, 55.2, 69.1, 77.6, 95.7, 113.4, 116.1, 127.7, 127.7, 129.0, 134.7, 135.9, 136.9, 140.6, 158.0; IR (neat) 3450, 1612, 1512, 1248, 1044 cm^{-1}; LRMS (EI) m/z 324 ($M^+ - H_2O$), 263, 249, 144, 129, 109, 91; HRMS (EI) calcd for $C_{21}H_{24}O_3$ ($M^+ - H_2O$) 324.1725, found 324.1733. **12b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (brs, 1H), 2.33−2.52 (m, 2H), 2.64 (brs, 1H), 3.38 (s, 3H), 3.49 (dd, J = 8.3, 9.0 Hz, 1H), 3.74 (s, 3H), 3.80 (s, 3H), 4.50 (s, 2H), 4.56−4.66 (m, 1H), 4.66 (s, 2H), 4.72 (d, J = 8.3 Hz, 1H), 5.62 (ddd, J = 6.2, 8.6, 15.2 Hz, 1H), 5.92 (dd, J = 9.0, 15.2 Hz, 1H), 6.72 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 7.11 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 43.2, 55.2, 55.3, 55.4, 58.3, 68.9, 72.6, 76.8, 95.5, 113.2, 113.6, 126.7, 127.6, 127.8, 128.0, 129.9, 133.6, 133.9, 135.7, 135.8, 140.3, 158.5, 158.6; IR (neat) 3420, 1612, 1514, 1248, 1038 cm^{-1}; LRMS (EI) m/z 460 ($M^+ - H_2O$), 442 ($M^+ - 2H_2O$), 412, 380, 324, 262, 137, 121; HRMS (EI) calcd for $C_{29}H_{30}O_4$ ($M^+ - 2H_2O$) 442.2144, found 442.2142.

(4*E*)-1-(4-Methoxycarbonylphenyl)-5-(4-methoxymethoxymethylphenyl)-pent-4-en-1-ol (10c) and 1-(4-Methoxycarbonylphenyl)-2-(4-methoxymethoxymethylphenyl)-pent-4-en-1-ol (11c): (Table 1, Run 5). Following the general procedure (Method A), a crude product, which was obtained from the coupling reaction of **5a** (102.6 mg, 0.50 mmol) and **6c** (82.5 mg, 0.51 mmol) using a Ni complex generated from $NiCl_2(PPh_3)_2$ (65.4 mg, 0.10 mmol) and BuLi (1.52 M in hexane, 0.13 mL, 0.20 mmol) in the presence of ^{i}Bu$_2$Al−acac (1.0 M in toluene, 0.75 mL, 0.75 mmol) at room temperature for 22 h, was purified by column chromatography on silica gel (hexane−AcOEt, 10/1, 7/1, 5/1, and 2/1) to give **10c** (62.8 mg, 34%) and **11c** (27.9 mg, 15%). **10c**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.85−2.09 (m, 2H), 1.97 (d, J = 3.6 Hz, 1H), 2.31 (dt, J = 7.1, 7.4 Hz, 2H), 3.41 (s, 3H), 3.92 (s, 3H), 4.57 (s, 2H), 4.69 (s, 2H), 4.82 (m, 1H), 6.21 (dt, J = 15.8, 7.1 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 7.26−7.34 (m, 4H), 7.44 (d, J = 8.3 Hz, 2H), 8.03 (d, J = 8.3 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 29.1, 38.5,

52.0, 55.3, 68.9, 73.4, 95.5, 125.8, 126.0, 128.1, 129.3, 129.7, 129.8, 130.3, 136.6, 137.0, 149.8, 166.9; IR (neat) 3462, 1722, 1610, 1280, 1046 cm^{-1}; LRMS (EI) *m/z* 370 (M^+), 322, 308, 293, 275, 231, 163, 144, 130, 92; HRMS (EI) calcd for $C_{22}H_{26}O_5$ 370.1780, found 370.1787. **11c**: ^1H NMR (270 MHz, $CDCl_3$) δ 2.05 (d, $J = 4.0$ Hz, 1H), 2.54−2.65 (m, 2H), 3.06 (dt, $J = 9.7$, 6.1 Hz, 1H), 3.39 (s, 3H), 3.89 (s, 3H), 4.53 (s, 2H), 4.69 (s, 2H), 4.87−4.90 (m, 2H), 4.96 (dd, $J = 2.0$, 17.0 Hz, 1H), 5.59 (ddt, $J = 10.3$, 17.0, 6.3 Hz, 1H), 7.04 (d, $J = 8.3$ Hz, 2H), 7.21 (d, $J = 3.4$ Hz, 2H), 7.24 (d, $J = 3.4$ Hz, 2H), 7.90 (d, $J = 8.3$ Hz, 2H); IR (neat) 3462, 1722, 1610, 1280, 1046 cm^{-1}; LRMS (EI) *m/z* 352 ($M^+ - H_2O$), 322, 291, 252, 231, 219,144, 129, 105; HRMS (EI) calcd for $C_{22}H_{26}O_5$ 370.1780, found 370.1787.

(4*E*)-1-Cyclohexyl-5-(4-methoxymethoxymethylphenyl)-pent-4-en-1-ol (10d) and 1-Cyclohexyl-2-(4-methoxymethoxymethylphenyl)pent-4-en-1-ol (11d): (Table 1, Run 6). Following the general procedure (Method A), a crude product, which was obtained from the coupling reaction of **5a** (102.6 mg, 0.50 mmol) and **6d** (0.062 mL, 0.51 mmol) using a Ni complex generated from $NiCl_2(PPh_3)_2$ (65.6 mg, 0.10 mmol) and BuLi (1.52 M in hexane, 0.13 mL, 0.20 mmol) in the presence of $^iBu_2Al$−acac (1.0 M in toluene, 0.75 mL, 0.75 mmol) at room temperature for 24 h, was purified by column chromatography on silica gel (hexane−AcOEt, 10/1, 7/1, 5/1, and 2/1) to give **10d** (99.1 mg, 62%) and **11d** (35.0 mg, 22%). **10d**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.99−1.38 (m, 6H), 1.37 (d, $J = 4.7$ Hz, 1H), 1.51−1.84 (m, 7H), 2.34 (dt, $J = 6.8$, 6.8 Hz, 2H), 3.41 (s, 3H), 3.41−3.46 (m, 1H), 4.56 (s, 2H), 4.69 (s, 2H), 6.24 (dt, $J = 15.8$, 6.8 Hz, 1H), 6.42 (d, $J = 15.8$ Hz, 1H), 7.27 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 26.0, 26.1, 26.3, 27.7, 29.0, 29.4, 33.5, 43.6, 55.0, 68.6, 75.2, 95.2, 125.7, 127.9, 129.4, 130.6, 136.1, 137.1; IR (Nujol) 3316, 1060 cm^{-1}; LRMS (EI) *m/z* 318 (M^+), 300, 256, 238, 217, 204, 173, 142, 130; HRMS (EI) calcd for $C_{20}H_{30}O_3$ 318.2195, found 318.2202. **11d**: ^1H NMR (270 MHz, $CDCl_3$) δ 1.05−1.26 (m, 6H), 1.47 (d, $J = 5.1$ Hz, 1H), 1.54−1.82 (m, 5H), 2.47 (m, 1H), 2.65 (m, 1H), 2.85 (ddd, $J = 3.8$, 7.1, 10.3 Hz, 1H), 3.42 (s, 3H), 3.48 (m, 1H), 4.57 (s, 2H), 4.72 (s, 2H), 4.86 (dd, $J = 2.2$, 10.3 Hz, 1H), 4.95 (dd, $J = 2.2$, 17.4 Hz, 1H), 5.61 (ddt, $J = 10.3$, 17.4, 7.0 Hz, 1H), 7.15 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 25.9, 26.3, 26.4, 26.5, 30.3, 35.1, 39.8, 48.4, 55.3, 69.2, 79.9, 95.8, 115.8, 128.1, 128.5, 135.8, 137.2, 142.2; IR (neat) 3484, 1640, 1514, 1046 cm^{-1}; LRMS (EI) *m/z* 300 ($M^+ - H_2O$), 259, 238, 215, 144, 129; HRMS (EI) calcd for $C_{20}H_{30}O_3$ 318.2195, found 318.2193.

(6*E*)-2-Methyl-7-(4-methoxymethoxymethylphenyl)hept-6-en-3-ol (10e) and 2-Methyl-4-(4-methoxymethoxymethylphenyl)oct-7-en-4-ol (11e): (Table 1, Run 7). Following the general procedure (Method A), a crude product, which was obtained from the coupling reaction of **5a** (102.7 mg, 0.50 mmol) and **6e** (0.046 mL, 0.51 mmol) using a Ni complex generated from $NiCl_2(PPh_3)_2$ (65.4 mg, 0.10 mmol) and BuLi (1.52 M in hexane, 0.13 mL, 0.20 mmol) in the presence of $^iBu_2Al$−acac (1.0 M in toluene, 0.75 mL, 0.75 mmol) at room temperature for 16 h, was purified by column chromatography on silica gel (hexane−AcOEt, 10/1, 7/1, 5/1, and 2/1) to give **10e** (79.0 mg, 57%) and **11e** (30.8 mg, 22%). **10e**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.92 (d, $J = 1.7$ Hz, 3H), 0.94 (d, $J = 1.7$ Hz, 3H), 1.34 (d, $J = 5.3$ Hz, 1H), 1.51−1.74 (m, 3H), 2.17−2.46 (m, 2H), 3.39−3.47 (m, 1H), 3.41 (s, 3H), 4.57 (s, 2H), 4.67 (s, 2H), 6.24 (dt, $J = 15.8$, 6.8 Hz, 1H), 6.43 (d, $J = 15.8$ Hz, 1H), 7.26−7.35 (m, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 17.1, 18.7, 29.6, 33.6, 33.6, 55.2, 68.8, 76.0, 95.5, 125.9, 128.1, 129.7, 130.7, 136.4, 137.2; IR (neat) 3448 cm^{-1}; LRMS (EI) *m/z* 278 (M^+), 260, 205, 173, 159, 155, 142, 130; HRMS (EI) calcd for $C_{17}H_{26}O_3$ 278.1882, found 278.1904. **11e**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.84 (d, $J = 6.7$ Hz, 3H), 0.91 (d, $J = 6.7$ Hz, 3H), 1.43−1.56 (m, 1H), 1.48 (d, $J = 5.3$ Hz, 1H), 2.36−2.48 (m, 1H), 2.75 (m, 1H), 2.68−2.81 (m, 2H), 3.42 (s, 3H), 3.54 (ddd, $J = 4.0$, 5.3, 6.3 Hz, 1H), 4.56 (s, 2H), 4.72 (s, 2H), 4.87 (dd, $J = 1.4$, 10.1 Hz, 1H), 4.95 (dd, $J = 1.4$, 17.1 Hz, 1H), 5.62 (ddt, $J = 10.1$, 17.1, 6.9 Hz, 1H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 15.2, 20.2, 29.8, 36.1, 49.4, 55.3, 69.1, 80.1, 95.8, 115.9, 128.1, 128.4, 135.9, 137.1, 142.1; IR (neat) 3488, 1640, 1514, 998 cm^{-1}; LRMS (EI) *m/z* 217 ($M^+ - CH_2OCH_3$), 206, 175, 144, 129, 105; HRMS (EI) calcd for $C_{17}H_{26}O_3$ 278.1882, found 278.1856.

(7*E*)-8-(4-Methoxymethoxymethylphenyl)oct-7-en-4-ol (10f) and 5-(4-Methoxymethoxymethylphenyl)oct-7-en-4-ol (11f): (Table 1, Run 8). Following the general procedure (Method A), a crude product, which was obtained from the coupling reaction of **5a** (102.5 mg, 0.50 mmol) and **6f** (0.046 mL, 0.51 mmol) using a Ni complex generated from $NiCl_2(PPh_3)_2$ (65.6 mg, 0.10 mmol) and BuLi (1.52 M in hexane, 0.13 mL, 0.20 mmol) in the presence of $^iBu_2Al$−acac (1.0 M in toluene, 0.75 mL, 0.75 mmol) at room temperature for 15 h, was purified by column chromatography on silica gel (hexane−AcOEt, 10/1, 7/1, 5/1, and 2/1) to give **10f** (36.1 mg, 26%) and **11f** (85.0 mg, 61%). **10f**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.94 (t, $J = 6.7$ Hz, 3H), 1.31−1.53 (m, 5H), 1.54−1.69 (m, 2H), 1.62 (dt, $J = 7.0$, 7.2 Hz, 2H), 3.41 (s, 3H), 3.62−3.72 (brs, 1H), 4.56 (s, 2H), 4.69 (s, 2H), 6.23 (dt, $J = 15.8$, 7.0 Hz, 1H), 6.41 (d, $J = 15.8$ Hz, 1H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 14.0, 18.7, 29.2, 36.9, 39.7, 55.2, 68.8, 71.0, 95.5, 125.9, 128.1, 129.7, 130.6, 136.4, 137.2; IR (neat) 3438, 1046 cm^{-1}; LRMS (EI) *m/z* 278 (M^+), 260, 216, 205, 199, 173, 130; HRMS (EI) calcd for $C_{17}H_{26}O_3$ 278.1882, found 278.1886. **11f**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.86 (t, $J = 7.0$ Hz, 3H), 1.17−1.51 (m, 4H), 1.44 (d, $J = 5.9$ Hz, 1H), 2.42−2.52 (m, 1H), 2.64−2.74 (m, 2H), 2.75 (m, 1H), 3.42 (s, 3H), 3.71−3.77 (brs, 1H), 4.57 (s, 2H), 4.72 (s, 2H), 4.89 (dd, $J = 1.7$, 10.2 Hz, 1H), 4.98 (dd, $J = 1.7$, 17.0 Hz, 1H), 5.65 (ddt, $J = 10.2$, 17.0, 6.9 Hz, 1H), 7.14−7.32 (m, 4H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 13.9, 19.0, 35.5, 36.8, 55.0, 55.3, 69.1, 75.2, 95.8, 116.0, 128.1, 128.6, 136.0, 137.0, 141.6; IR (neat) 3450, 1640, 1514, 1048 cm^{-1}; LRMS (EI) *m/z* 260 ($M^+ - H_2O$), 217, 199, 175, 144, 129, 105; HRMS (EI) calcd for $C_{17}H_{24}O_2$ ($M^+ - H_2O$) 260.1795, found 260.1776.

(4E)-1,7-Diphenylhept-4-en-1-ol (23a) and 2-(2-Phenylethyl)-1-phenylpent-4-en-1-ol (24a): (Table 2, Run 1). Following the general procedure (Method B), a crude product, which was obtained from the coupling reaction of ***E*-5b** (78.2 mg, 0.50 mmol) and **6a** (0.052 mL, 0.51 mmol) using a Ni complex generated from $Ni(acac)_2$ (25.8 mg, 0.10 mmol), PPh_3 (52.9 mg, 0.20 mmol), and DIBAL-H (1.01 M in toluene, 0.2 mL, 0.2 mmol) in the presence of $^iBu_2Al$−acac (1.0 M in toluene, 0.55 mL, 0.55 mmol) at room temperature for 21 h, was purified by column chromatography on silica gel (hexane, hexane−AcOEt, 20/1, 10/1, and 5/1) to give **23a** (40.5 mg, 30%) and **24a** (55.9 mg, 42%). **23a**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.73−1.85 (m, 3H), 2.03−2.07 (m, 2H), 2.31 (dt, $J = 6.1$, 7.4 Hz, 2H), 2.66 (t, $J = 7.4$ Hz, 2H), 4.60−4.63 (m, 1H), 5.44 (dt, $J = 15.4$, 6.1 Hz, 1H), 5.48 (dt, $J = 15.4$, 6.1 Hz, 1H), 7.15−7.35 (m, 10H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 28.8, 34.3, 36.0, 38.7, 73.9, 125.9, 126.0, 128.1, 127.5, 128.2, 128.4, 130.2, 142.0, 144.7; IR (neat) 3374, 3026, 2926, 2852, 1602, 1494, 1452 cm^{-1}; LRMS (EI) *m/z* 248 ($M^+ - H_2O$), 170, 157, 144, 129, 120, 107, 104, 91; HRMS (EI) calcd for $C_{19}H_{20}$ ($M^+ - H_2O$) 248.1565, found 248.1568. **24a**: ^1H NMR (270 MHz, $CDCl_3$) δ 1.43−1.69 (m, 2H), 1.76−1.92 (m, 1H), 1.83 (d, $J = 3.5$ Hz, 1H), 2.27 (t, $J = 6.3$ Hz, 2H), 2.46−2.69 (m, 2H), 4.68 (dd, $J = 3.5$, 6.4 Hz, 1H), 5.03−5.13 (m, 2H), 5.84 (ddt, $J = 10.0$, 17.1, 7.1 Hz, 1H), 7.05−7.37 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.3, 33.2, 33.5, 44.2, 76.1, 116.5 (CH_2), 125.6, 126.4, 127.2, 128.2, 128.2, 136.8, 142.2, 143.2; IR (neat) 3420, 1602, 1494 cm^{-1}; LRMS (EI) *m/z* 248 ($M^+ - H_2O$), 219, 206, 157, 144, 129, 107, 91; HRMS (EI) calcd for $C_{19}H_{20}$ ($M^+ - H_2O$) 248.1565, found 248.1561.

(4*E*)-1-Cyclohexyl-7-phenylhept-4-en-1-ol (23d) and 1-Cyclohexyl-2-(2-phenylethyl)-pent-4-en-1-ol(24d): (Table 2, Run 2). Following the general procedure (Method B), a crude product, which was obtained from the coupling reaction of ***E*-5b** (78.1 mg, 0.49 mmol) and **6d** (0.062 mL, 0.51 mmol) using a Ni complex generated from $Ni(acac)_2$ (25.9 mg, 0.10 mmol), PPh_3 (52.8 mg, 0.20 mmol), and DIBAL-H (1.01 M in toluene, 0.2 mL, 0.20 mmol) in the presence of $^iBu_2Al$−acac (1.0 M in toluene, 0.55 mL, 0.55 mmol) at room temperature for 21 h, was purified by column chromatography on silica gel (hexane, hexane−AcOEt, 20/1, 10/1, and 5/1) to give **23d** (65.5 mg, 48%) and **24d** (25.9 mg, 19%). **23d**: ^1H NMR (500 MHz,

$CDCl_3$) δ 1.00−1.77 (m, 14H), 2.05 (m, 1H), 2.15 (m, 14H), 2.31 (dt, J = 6.3, 7.3 Hz, 2H), 2.67 (t, J = 7.3 Hz, 2H), 3.32−3.33 (m, 1H), 5.46 (dt, J = 15.4, 6.3 Hz, 1H), 5.50 (dt, J = 15.4, 6.3 Hz, 1H), 7.16−7.19 (m, 3H), 7.26−7.29 (m, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 26.2, 26.3, 26.5, 27.7, 29.1, 29.2, 33.8, 34.3, 36.0, 43.7, 75.6, 125.7, 128.2, 128.4, 129.9, 130.7, 142.0; IR (neat) 3374, 3026, 2924, 2850, 1602, 1496, 1450 cm^{-1}; LRMS (EI) m/z 272 (M^+), 254 ($M^+ - H_2O$), 171, 143, 129, 104, 95, 91; HRMS (EI) calcd for $C_{19}H_{26}$ ($M^+ - H_2O$) 254.2035, found 254.2017. **24d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94−1.75 (m, 14H), 1.78−1.88 (m, 2H), 2.05−2.13 (m, 1H), 2.27−2.30 (m, 1H), 2.54−2.69 (m, 2H), 3.34 (m, 1H), 5.02 (d, J = 10.3 Hz, 1H), 5.07 (d, J = 17.3 Hz, 1H), 5.79−5.89 (m, 1H), 7.15−7.29 (m, 5H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 26.1, 26.3, 26.5, 28.5, 29.7, 32.1, 32.9, 33.3, 38.9, 40.6, 77.6, 116.0, 125.7, 128.3, 137.7, 142.6; IR (neat) 3404, 2924, 2852, 1602, 1496, 1450 cm^{-1}; LRMS (EI) m/z 254 ($M^+ - H_2O$), 213, 160, 149, 143, 117, 104, 95, 91; HRMS (EI) calcd for $C_{19}H_{26}$ ($M^+ - H_2O$) 254.2035, found 254.2012.

(7*E*)-10-Phenyldec-7-en-4-ol (23f) and 5-(2-Phenylethyl)oct-7-en-4-ol (24f): (Table 2, Run 3). Following the general procedure (Method B), a crude product, which was obtained from the coupling reaction of ***E*-5b** (78.5 mg, 0.50 mmol) and **6f** (0.046 mL, 0.51 mmol) using a Ni complex generated from $Ni(acac)_2$ (25.6 mg, 0.10 mmol), PPh_3 (52.4 mg, 0.20 mmol), and DIBAL-H (1.01 M in toluene, 0.2 mL, 0.20 mmol) in the presence of ^{i}Bu$_2$Al−acac (1.0 M in toluene, 0.55 mL, 0.55 mmol) at room temperature for 21 h, was purified by column chromatography on silica gel (hexane, hexane−AcOEt, 20/1, 10/1, and 5/1) to give **23f** (39.5 mg, 34%) and **24f** (44.0 mg, 38%). **23f**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, J = 7.0 Hz, 3H), 1.35−1.48 (m, 7H), 2.07−2.12 (m, 2H), 2.31 (dt, J = 6.3, 7.2 Hz, 2H), 2.66 (t, J = 7.2 Hz, 2H), 3.57−3.60 (m, 1H), 5.44 (dt, J = 15.4, 6.3 Hz, 1H), 5.49 (dt, J = 15.4, 6.3 Hz, 1H), 7.17 (m, 3H), 7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 18.9, 34.4, 36.1, 37.1, 39.7, 71.2, 125.6, 128.1, 128.3, 129.8, 130.5, 141.9; IR (neat) 3382, 1638, 1496 cm^{-1}; LRMS (EI) m/z 214 ($M^+ - H_2O$), 189, 171, 160, 158, 130, 104, 91; HRMS (EI) calcd for $C_{16}H_{22}$ ($M^+ - H_2O$) 214.1721, found 214.1742. **24f**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93 (t, J = 6.9 Hz, 3H), 1.26−1.81 (m, 7H), 1.29 (d, J = 5.2 Hz, 1H), 2.11−2.33 (m, 2H), 2.65 (t, J = 8.0 Hz, 2H), 3.67 (dt, J = 5.2, 5.2 Hz, 1H), 5.00−5.13 (m, 2H), 5.84 (ddt, J = 10.0, 17.1, 7.2 Hz, 1H), 7.13−7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 18.9, 28.9, 34.4, 36.1, 37.1, 39.7, 71.2, 125.6, 128.1, 128.3, 129.8, 130.5, 141.9; IR (neat) 3356, 1604, 1496 cm^{-1}; LRMS (EI) m/z 214 ($M^+ - H_2O$), 189, 171, 160, 158, 130, 104, 91; HRMS (EI) calcd for $C_{16}H_{22}$ ($M^+ - H_2O$) 214.1721, found 214.1742.

Registry Number. (3*E*)-6-Phenyl-1,3-hexadiene (***E*-5b**), 77605-16-4; (3*Z*)-6-phenyl-1,3-hexadiene (***Z*-5b**), 77605-17-5.

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Supporting Information Available: Experimental Procedures and spectral data for the synthesis of substrate **5a** and for preparations of **21** (from **11f**) and **25** (from ***anti*-24a**) and an ORTEP diagram of **25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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