Nickel-Catalyzed Coupling Reaction of 1,3-Disubstituted Secondary Allylic Carbonates and Lithium Aryl- and Alkenylborates

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This account describes coupling reaction of 1,3-disubstituted secondary allylic carbonates with lithium aryl- and alkenylborates in the presence of a nickel catalyst. Borates examined are **4**, **5**, and **6**, and reactivity and selectivity were investigated using the allylic carbonates **1a** and **1b**. Coupling of **1a**,**b** with borates **4** was effected with the nickel catalyst, $NiCl_2(PPh_3)_2$ or $NiCl_2$(dppf), in THF at 45−65 °C to provide products **3** in good yields with almost 100% regio- and stereoselectivities. Trivalent organoboranes prepared from acetylenes by hydroboration with catecholborane also underwent coupling reaction with **1a**,**b** after transformation to borates **5** with MeLi. Though coupling using **4** and **5** required elevated temperature (45−65 °C), cyclic borates **6** prepared *in situ* from boronates **8** and MeLi were found to couple with **1a**,**b** at room temperature or below. Regio- and stereoselectivities were almost 100% as were observed in the cases of **4** and **5**. In these reactions, palladium complexes such as $Pd(PPh_3)_4$, $Pd_2(dba)_3{\cdot}CHCl_3 + 2\ PPh_3$ showed no catalytic activity. Stereochemical aspect of the present reaction was studied using cyclohexenyl carbonate **24** with 2-furylborate **4e** and phenylborate **6a**, and was found to proceed with overall *anti* fashion. With additional experiments, the mechanism of the present reaction was discussed in terms of transient π-allylnickel intermediates.

Introduction

Transition metal-catalyzed coupling reactions of allylic substrates with aryl- and alkenyl-metallic reagents are an important carbon−carbon bond-forming reactions in organic synthesis.[1] Numerous organometallic reagents based on aluminum,[2] boron,[3] magnesium,[4] tin,[3i,5] zinc,[2c,e,6] zirconium,[2a,d,f,7] and mercury[8] have been reported to enter into the coupling reaction with allylic alcohol derivatives and halides mostly in the presence of palladium and/or nickel catalysts.[9] In general, allylic halides show higher reactivity than alcohol derivatives, and the reaction is influenced by steric hindrance from π-allylmetal intermediates. We propose that the reaction of 1,3-disubstituted secondary allylic alcohol derivatives is a most important coupling process in organic synthesis. However, reactions with such sterically hindered substrates have been examined to some extent with highly reactive Grignard reagents. Thus, we initiated a study to find a

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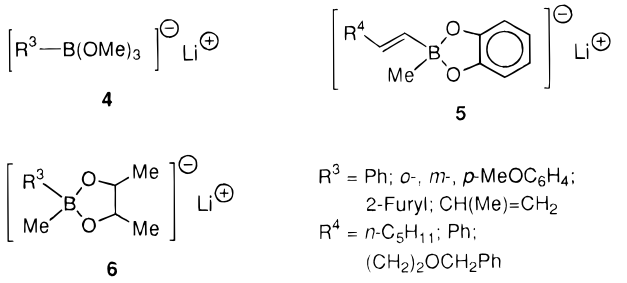
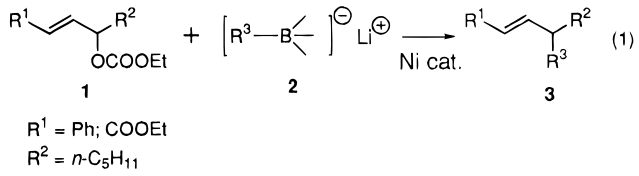
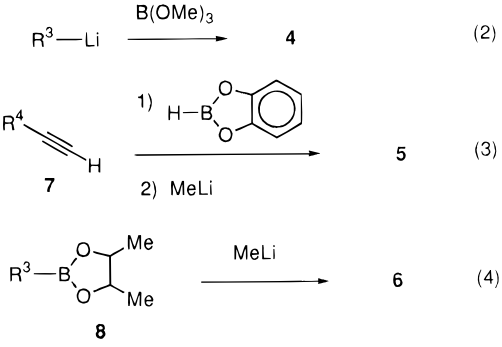
Chart 1. Borates 4−6 used as 2 in the Coupling Reaction with 1 (eq 1)



new reagent/catalyst system, so that secondary allylic substrates could react under mild conditions and still tolerate reactive functional groups.

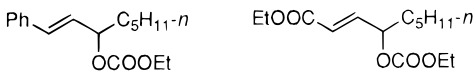


We selected lithium aryl- and alkenyl-borates **2** (eq 1) for the following reasons: (1) $NaBPh_4$,[3a] one of the organoborates, as well as trivalent organoboranes[3b] couple mostly with 1- or 3-monosubstituted primary allylic acetates in the presence of palladium catalysts; (2) in general, borates are almost neutral species; (3) several methods are known for the preparation of organoborates and/or their precursors.[10,11] In practice the borates **4** and **5** shown in Chart 1 were chosen as reagents for **2** and prepared *in situ* from the corresponding organolithiums and $B(OMe)_3$ (eq 2) or from the corresponding acetylenes



7 via hydroboration with catecholborane followed by reaction with MeLi (eq 3).

Reaction conditions were explored with the 1,3-disubstituted allylic carbonate **1a**. In considering synthetic application, the ester **1b** was also selected as the substrate: installation of sp^2 species at the γ position of α,β-unsaturated esters.[12] Although our attempts to apply the



literature reaction conditions involving palladium catalysts to the coupling of **1a** with **4**,**5** were in vain, nickel complexes were found to catalyze the coupling to provide **3** regioselectively (eq 1). Since higher temperatures (45−65 °C) are needed, we have continued this investigation and discovered that *borates **6** derived from cyclic boronates **8** and MeLi (eq 4) are more reactive reagents*, and the reaction proceeds at room temperature or below. In this paper we describe a full account of these new reagent/catalyst systems.[13]

Results and Discussion

Coupling Reaction of 1 with Methoxyborates 4. The borates **4a**−**f** (R^3 = Ph, $MeOC_6H_4$, 2-furyl, C(Me)=CH_2) were prepared by mixing the corresponding organolithium and $B(OMe)_3$ at 0 °C for 15 min in THF (eq 2) and used immediately for the coupling reaction without isolation. Preliminary examination was carried out by using the allylic carbonate **1a** and 2−3 equiv of phenylborate (**4a**, R^3 = Ph) or 2-furylborate (**4e**, R^3 = 2-furyl) in the presence of 5−10 mol % of a palladium or a nickel complex in THF. The products were analyzed by 300 MHz ^1H NMR spectroscopy, and the results are summarized in Table 1. When reaction was attempted with **4a** at 60 °C in the presence of 10 mol % $Pd(PPh_3)_2$ (prepared *in situ* from $Pd_2(dba)_3{\cdot}CHCl_3$[14] and 2 equiv of PPh_3) according to Fiaud,[3a] methyl ether **9** was obtained as the major product (66% yield), and the yield of the desired product **3a** (R^1 = R^3 = Ph, R^2 = n-C_5H_{11}) was <10% (entry 1). Formation of **9** was also catalyzed by

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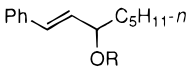
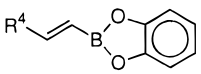


9: R = Me
10: R = Et

Pd(dppf)[15] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) (entry 2). In contrast to the palladium catalysts, nickel complexes, $NiCl_2(PPh_3)_2$[16] and $NiCl_2$(dppf),[17] showed efficient catalytic activity to provide the desired product **3a** in 97% and 98% yield, respectively, after 12−16 h at 60−65 °C (entries 3 and 4). Regio- and *trans* olefin-selectivities for **3a** were both >99% by ^{1}H NMR spectroscopy. These results suggest the presence of transient π-allylnickel intermediate and are in agreement with that reported for the nickel-catalyzed coupling of 3-aryl substituted allylic alcohols and their ethers with Grignard reagents.[4a,c,h,n] In these experiments, methyl ether **9** was not detected. The nickel complexes also catalyzed coupling of **1a** with the furylborate **4e** to provide **3e** selectively in 84−88% yield (entries 8 and 9). Reactivity of **4e** was higher than that of phenylborate **4a**: the reaction was completed within 4−8 h at 45−60 °C, while more drastic conditions (>12 h, 60−65 °C) were required for **4a**. Both nickel catalysts, $NiCl_2(PPh_3)_2$ and $NiCl_2$(dppf), showed an excellent catalytic activity for **4e** as well as **4a**.

To survey the present reaction, organoborates **4b**−**f** and the carbonates **1a**,**b** were subjected to the reaction in the presence of $NiCl_2$(dppf) in THF. The results are also shown in Table 1. Reaction of **1a** with *o*-, *m*-, and *p*-methoxyphenylborates **4b**−**d** afforded the coupling products **3b**−**d** in good yields (entries 5−7). Coupling with alkenylborate **4f** afforded **3f** in 46% yield (entry 10). α,β-Unsaturated ester **1b** also reacted with **4e** to provide γ-substituted product **3g** in 67% yield (entry 11). The last example demonstrates that the ester group can withstand the reaction conditions. Further examples using borate **4e** (reaction with the carbonate **24**) and similar borates of the types **5** and **6** are presented later. In all the cases examined, regio- and/or *cis* isomer(s) or the methyl ether was not detected in the NMR spectra.

Coupling Reaction of 1 with Borates 5 Derived from Acetylenes via Hydroboration. Since hydroboration of acetylenes affords stereodefined trivalent alkenylboranes,[18] combination of the hydroboration and subsequent transformation to borates adds another advantage to the present reaction. We prepared three



11a: $R^4 = n\text{-}C_5H_{11}$
11b: R^4 = Ph
11c: $R^4 = (CH_2)_2OCH_2Ph$

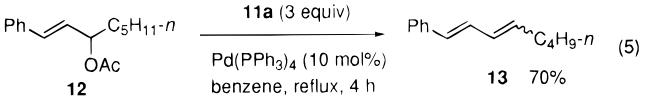
alkenylboronates **11a**−**c** according to the literature procedures[11a,c] and explored such a possibility. First, an organometallic which serves as the fourth ligand to afford the borate was explored using **11a**. Among *n*-BuLi, MeLi, *n*-BuMgBr, and MeMgI examined, MeLi provided the best result.[19] Thus, borate **5a** ($R^4 = n\text{-}C_5H_{11}$) had been prepared *in situ* by mixing **11a** and 1 equiv of MeLi in THF at 0 °C for 15 min (eq 3) and was submitted to the reaction with the carbonate **1a** in the presence of the nickel catalyst (10 mol %, prepared from $NiCl_2$(dppf) and 2 MeLi) in THF−MeCN[20] (1:1) at 60 °C overnight to afford the desired product **3h**, regio- and stereoselectively, in 70% yield (Table 2, entry 1). A similar reaction using 10 mol % $Pd(PPh_3)_4$ in place of the nickel catalyst gave a mixture of unidentified products.

Table 1. Palladium- and Nickel-Catalyzed Coupling Reaction of 1 and 4[a]

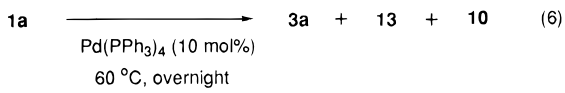
entry	catalyst	carbonate 1	borate 4	R^3	yield, % 3[b]	9
1	$Pd(PPh_3)_2$[c]	**1a**	**4a**	Ph	**3a**, <10	66
2	Pd(dppf)[c]	**1a**	**4a**	Ph	**3a**, 0	54
3	$NiCl_2(PPh_3)_2$	**1a**	**4a**	Ph	**3a**, 97	0
4	$NiCl_2$(dppf)	**1a**	**4a**	Ph	**3a**, 98	0
5	$NiCl_2$(dppf)	**1a**	**4b**	*o*-$MeOC_6H_4$	**3b**, 86	0
6	$NiCl_2$(dppf)	**1a**	**4c**	*m*-$MeOC_6H_4$	**3c**, 81	0
7	$NiCl_2$(dppf)	**1a**	**4d**	*p*-$MeOC_6H_4$	**3d**, 89	0
8	$NiCl_2(PPh_3)_2$	**1a**	**4e**	2-furyl	**3e**, 84	0
9	$NiCl_2$(dppf)	**1a**	**4e**	2-furyl	**3e**, 88	0
10	$NiCl_2$(dppf)	**1a**	**4f**	$C(Me)=CH_2$	**3f**, 46	0
11	$NiCl_2$(dppf)	**1b**	**4e**	2-furyl	**3g**, 67	*d*

[a] Reactions were carried out with 2−3 equiv of **4** in the presence of 5−10 mol % of the catalyst in THF at 45−65 °C for 4−16 h. [b] R^1 = Ph for **3a**−**f**; R^1 = COOEt for **3g**. $R^2 = n\text{-}C_5H_{11}$. [c] Prepared *in situ* from $Pd_2(dba)_3{\cdot}CHCl_3$ and the corresponding phosphine ligand. [d] No corresponding methyl ether was produced.

In relation to the present reaction, Suzuki and his coworkers have shown the coupling reactions of trivalent alkenylboronates of type **11** and primary substrates, 3-phenylallyl phenoxide[3b,k] and acetate,[3b] in the presence of the palladium catalysts. Since no example is given for secondary 1,3-disubstituted allylic esters, the possibility of providing a coupling product from alkenyl-



(5)



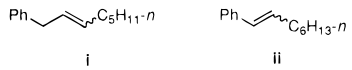
(6)

solvent	yield, %	3a : 13 : 10
THF	95	18 : 9 : 73
THF-MeCN (1 : 1)	87	27 : 56 : 17

boronate **11a** with acetate **12** or carbonate **1a** (eqs 5, 6) was explored. Under Suzuki's conditions diene **13** was obtained in 70% yield when acetate **12** was reacted with **11a** (eq 5), while a 18:82 mixture of **3a** (desired product)

(15) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.
(16) Venanzi, L. M. *J. Chem. Soc.* **1958**, 719.
(17) Hayashi, T.; Konishi, M.; Yokota, K.; Kumada, M. *Chem. Lett.* **1980**, 767.
(18) (a) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley: New York, 1975. (b) Brown, H. C.; Campbell, J. B., Jr. *Aldrichim. Acta* **1981**, *14*, 3. (c) Negishi, E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1983; Vol. 7, Chapter 45.8, p 303.

(19) Borate derived from **11a** and MeMgI afforded the diene **13**, while borates from *n*-BuLi or *n*-BuMgBr gave the reduction products **i** and **ii**.



(20) Addition of MeCN resulted in somewhat better yields of the products **3**.

Table 2. Nickel-Catalyzed Coupling Reactions of 1 and 5[a]

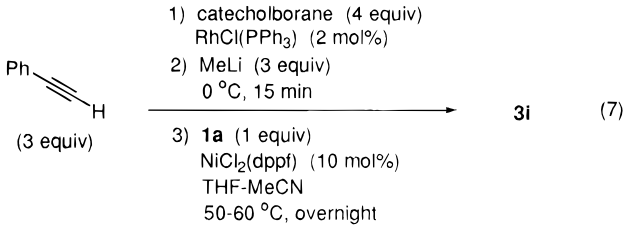
entry	carbonate 1	borate 5	borate R^4	product[b] 3	product[b] yield, %
1[c]	**1a**	**5a**	n-C_5H_{11}	**3h**	70
2	**1a**	**5b**	Ph	**3i**	87
3	**1a**	**5c**	$(CH_2)_2OCH_2Ph$	**3j**	50
4	**1b**	**5b**	Ph	**3k**	86

[a] The catalyst (5−10 mol %) was prepared *in situ* from $NiCl_2$(dppf) and 2 equiv of MeLi before use (0 °C, 15−60 min), and the reactions were carried out at 50−60 °C overnight. [b] R^1 = Ph for **3h**−**j**; R^1 = COOEt for **3k**. R^2 = n-C_5H_{11}. [c] When 10 mol % of $Pd(PPh_3)_4$ was used instead of $NiCl_2$(dppf), a mixture of unidentified products was obtained.

and **13** was produced in THF−MeCN (1:1) at 60 °C overnight (the optimized conditions for the nickel-catalyzed coupling). Use of carbonate **1a** resulted in production of mixtures of **3a**, **13**, and **10** (eq 6). In contrast to these results, neither **10** nor **13** was detected in the nickel-catalyzed reaction of **1a** and borate **5a**.

To examine the reactivity and selectivity of the borate **5** and nickel system, reaction of the allylic carbonates **1a**,**b** and the MeLi-derived alkenyl borates **5b**,**c** in the presence of $NiCl_2$(dppf) was investigated. The results are also summarized in Table 2. In all the cases the reactions proceeded regio- and stereoselectively to afford **3i**−**k** in good to moderate yields. In no case was the corresponding ethyl ether detected.

Although isolated boronates **11a**−**c** were used to prepare the borates **5a**−**c** for the present reaction (Table 2), borates prepared *in situ* from the acetylenes can be used directly. To give an example of a one-pot reaction, MeLi (3 equiv) and, after 15 min at 0 °C, MeCN, the carbonate **1a**, and $NiCl_2$(dppf) (10 mol %) were added to a THF solution of **11b**, which had been prepared in the usual way,[11c] and the solution was stirred at 50−60 °C overnight to furnish **3i** in 50% isolated yield (eq 7).



Three-Step One Pot Reaction

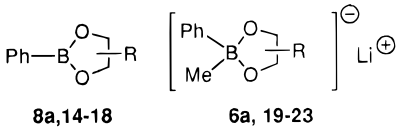
Coupling Reaction of 1 with Borates 6 Derived from Cyclic Boronate Esters 8. In the above sections we described the nickel-catalyzed coupling of 1,3-disubstituted allylic carbonates **1** and aryl- or alkenylborates **4** and **5** under almost neutral conditions. However, the reaction required a higher temperature and longer reaction time and this situation could be unacceptable in certain cases if it were utilized for the preparation of complicated compounds. To raise the reactivity, we decided to investigate the possibility of changing the structure of borates. We believe that the lower reactivity is due to the electron-withdrawing nature of the methoxide ligand on **4** and, perhaps, to lower concentration of **4** in the equilibrium[10e] with the corresponding trivalent boronate. This is expected to be marginally reactive from the study using boronates **11a** (*vide supra*) and also **8a** (R^3 = Ph) (data not shown). This hypothesis led us to examine a series of MeLi-derived cyclic borates such as **6** (Chart 1). In the following paragraphs, we describe the successful results of this study.

Table 3. Nickel-Catalyzed Coupling Reaction of 1a and the Cyclic Borates 6a, 19−23[a]

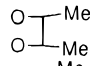
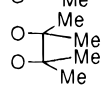
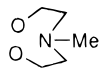
entry	borate	catalyst[b]	temp, °C	time, h	yield of **3a**,[c] %
1	**19**	A	40	12	95
2	**20**	A	35	12	84
3	**6a**	A	rt[d]	4	88
4	**6a**	A	5	12	97
5	**6a**	B	rt[d]	4	87
6	**21**	A	40	17	60[e]
7	**22**	A	65	15	<10 [f,g]
8	**23**	A	40	17	0

[a] The borates were prepared by addition of MeLi (3 equiv) to a mixture of the corresponding boronates (4 equiv) and the nickel catalyst (5−10 mol %) in THF and used for the coupling reaction. [b] Catalyst: A = $NiCl_2$(dppf); B = $NiCl_2(PPh_3)_2$. [c] R^1 = R^3 = Ph, R^2 = n-C_5H_{11}. [d] 15−25 °C. [e] (*E*)-3-Methyl-1-phenyl-1-octene was coproduced in a 29% yield. [f] Recovered **1a**. [g] Use of MeCN as cosolvent resulted in somewhat better yield of ca. 30%.

Because of the lowest reactivity of phenylborate **4a** (R^3 = Ph) (>12 h, 60−65 °C) (*vide supra*), reactions of **1a** and 3 equiv each of phenylborates **6a**, **19**−**23** which possess various types of diol ligands were examined first in the presence of 5−10 mol % of $NiCl_2$(dppf) or $NiCl_2(PPh_3)_2$ in THF. Phenylboronates **8a**,[21] **14**−**18** were prepared from $PhB(OH)_2$[10a,h] and the diols according to the literature procedures[10b,d] and transformed into the borates **6a**, **19**−**23** by addition of MeLi before use (0 °C, 15 min).

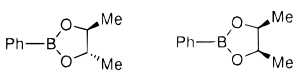


8a,14-18 **6a, 19-23**

Boronate	Borate	
14	**19**	
15	**20**	
8a	**6a**	
16	**21**	
17	**22**	
18	**23**	

Reaction conditions and results are summarized in Table 3. With **19** and **20** reactions with $NiCl_2$(dppf)

(21) Phenylboronate ester **8a** prepared from a stereoisomeric mixture of 2,3-butanediols (Tokyo Kasei, Japan) was a 1:4 mixture of *dl*- and *meso*-isomers by ^{1}H NMR spectroscopy (signals for *dl*-isomer were determined by using phenylboronate ester derived from (*R*,*R*)-2,3-butanediol) and was used without separation. Other boronates were mixtures of *dl*- and *meso*-isomers.

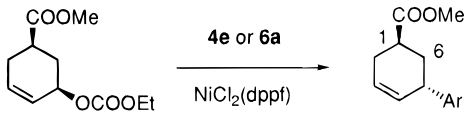


dl-**8a** *meso*-**8a**

proceeded at 35−40 °C and after 12 h **3a** was obtained in high yields (entries 1, 2). Introduction of an electron-donating methyl substituent increased the reactivity further (entry 3): reaction at room temperature for 4 h furnished **3a** in 88% yield. Even at lower temperature (ca. 5 °C) **3a** was obtained in good yield (entry 4). However, the presence of four methyl groups lowered the reactivity (entry 6), inferring severe steric hindrance in the transmetalation with the π-allylnickel intermediate. In the case of catechol boronate ester **17**, borate formation with MeLi was found to be different from the other cases: an unidentified precipitation was observed and most of **1a** was recovered in the subsequent coupling reaction (entry 7). Addition of MeCN as cosolvent improved the yield a little. Treatment of **1a** with borate **23** bearing a nitrogen-containing ligand resulted in recovery of **1a** (entry 8). In the reaction with **6a**, $NiCl_2(PPh_3)_2$ showed an almost equal reactivity with $NiCl_2$(dppf) (entry 5). Palladium catalyst was totally ineffective for coupling **1a** and **6a**.

To define the scope of this new system, reactions using other combinations of allylic carbonates **1a**,**b** and borates **6a**−**f** were examined next. Borate precursors **8b**−**f** were prepared from 2,3-butanediol and corresponding boronic acids in a similar manner to **8a** and converted to borates **6b**−**f** with MeLi.[21] The results are listed in Table 4. In all cases reactions proceeded at room temperature and were completed within several hours to furnish the products **3b**−**g**,**l** in high yields. As in the case of borates **4** and **5**, the ester group also proved compatible with this reagent/catalyst system (entries 6, 7). In no case, was regio- and/or stereoisomer(s) detected in the ^{1}H NMR spectra of the crude products.

Stereochemical Aspect of the Coupling Reaction. The stereochemistry of the present reaction was studied by using the cyclic substrate **24** (*cis*/*trans*, >99%), which was prepared from methyl *cis*-5-hydroxy-3-cyclohexene-1-carboxylate.[5c,22] The reaction was carried out by using borates of types **4** and **6** in the presence of $NiCl_2$(dppf) (eq 8).



(8)

24

25: Ar = 2-furyl
26: Ar = Ph

reagent	conditions	product	yield, %
4e	55 - 60 °C, 4 h	**25**	92
6a	room temp., 12 h	**26**	95

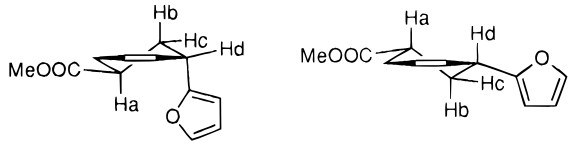
First, reaction with 2-furylborate **4e** was performed at 55−60 °C to furnish **25** with >95% stereoisomeric purity in 92% yield. Its stereochemistry was established to be *trans* by the 300 MHz ^{1}H NMR spectrum and by comparison with that of *cis* isomer **27** which was prepared by isomerization of **25** with NaOMe in MeOH. Coupling constants of the C-6 axial hydrogen (Hb) of the *trans* isomer **25** at δ 1.99 are J_{ab} = 11.3 Hz, J_{bc} = 12.8 Hz, J_{bd} = 5.7 Hz, and those of *cis* isomer **27** at δ 1.77 are

(22) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

Table 4. Nickel-Catalyzed Reaction of 1a,b and Cyclic Borates 6a−f at Room Temperature[a]

	borate		borate	carbonate	time,	product[b]	
entry	**6**	R^3	precursor	**1**	h	**3**	yield, %
1	**6b**	*o*-$MeOC_6H_4$	**8b**	**1a**	12	**3b**	98
2	**6c**	*m*-$MeOC_6H_4$	**8c**	**1a**	7	**3c**	99
3	**6d**	*p*-$MeOC_6H_4$	**8d**	**1a**	4	**3d**	90
4	**6e**	2-furyl	**8e**	**1a**	7	**3e**	85
5	**6f**	C(Me)=CH_2	**8f**	**1a**	5	**3f**	73
6	**6a**	Ph	**8a**	**1b**	5	**3l**	96
7	**6e**	2-furyl	**8e**	**1b**	5	**3g**	93

[a] Reactions were carried out at room temperature (15−25 °C) in the presence of $NiCl_2$(dppf) (5−10 mol %) in THF. [b] R^1 = Ph for **3b**−**f**; R^1 = COOEt for **3g**,**l**. R^2 = *n*-C_5H_{11}.



trans isomer **25** *cis* isomer **27**

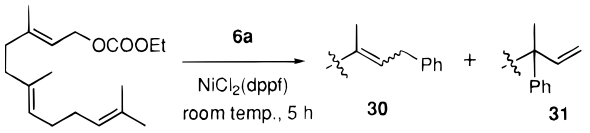
Figure 1. Structures and plausible conformers of *trans* and *cis* isomers **25** and **27**.

$J_{ab} = J_{bc} = 12.6$ Hz, $J_{bd} = 11.2$ Hz, indicating the assigned stereochemistry and the conformation shown in Figure 1.

The same stereochemical outcome was obtained with phenylborate **6a** (eq 8). The *trans* stereochemistry of the product **26** was assigned by comparison of the ^{1}H NMR spectrum with reported data.[5c]

In conclusion, we have clarified the stereochemical aspect of the present reaction as proceeding with overall inversion. This result indicates the "hard" nucleophilicity of the borates.[23]

Mechanism. To understand the mechanistic aspect of the present reaction, additional experiments were performed. (1) When the regioisomer of **1a** (i.e., **28**) was subjected to the reaction with the catecholborane-derived borate **5b** (R^4 = Ph) under the same reaction conditions as used for **1a** and **5b**, the same product **3i** was produced regio- and stereoselectively in 80% yield (Scheme 1). (2) The same sense was observed in the reaction of **28** and the cyclic borate **6a** (R^3 = Ph) (Scheme 1). (3) In all the cases, the double bond in the product was placed regioselectively to conjugate with the existing π-system. Without such a π-system, a mixture of regioisomers was produced (eq 9) though in high yield. (4) Although Ni(II)



(9)

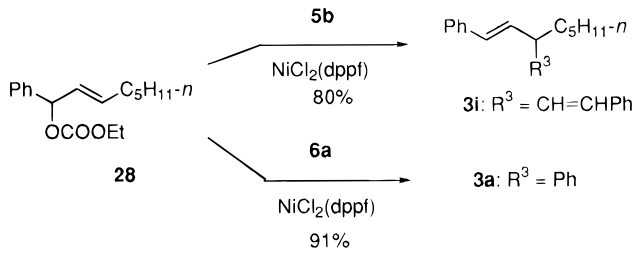
29 **30** **31**

30 : **31** = 3 : 1

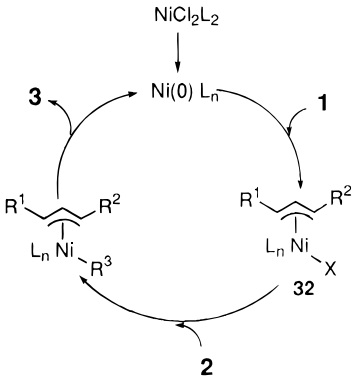
complexes were used without any pretreatment in the series of reactions using the borates **4**, the nickel(0) complexes prepared *in situ* from $NiCl_2$(dppf) and 2 equiv of *n*-BuLi or MeLi also catalyzed the reaction of **1a** with **4a**,**e**, and *vice versa* with **5b** and **6a**. In the light of the above results, the stereochemical outcome obtained with the cyclic substrate **24**, and the facts that (π-allyl)(aryl)-Ni complexes undergo reductive elimination to afford

(23) Keinan, E.; Roth, Z. *J. Org. Chem.* **1983**, *48*, 1769.

Scheme 1



Scheme 2. Plausible Mechanism of the Nickel-Catalyzed Coupling Reaction



allyl−aryl products,[24] it is conceivable that the reaction did proceed as depicted in Scheme 2, a typical cycle for the nickel catalyzed reaction:[25] (1) formation of Ni(0) complexes under the reaction conditions,[26] (ii) *anti* oxidative addition of the Ni(0) complexes to the allylic carbonate **1** to produce the allyl−Ni intermediate **32**, (iii) transmetalation with the borate **2** (= **4**, **5**, **6**) and (iv) *syn* reductive elimination with retention of configuration to afford **3**.

Conclusions

We presented new reagent/catalyst systems for coupling of 1,3-disubstituted secondary allyic carbonates. Remarkable points of the present reaction are the following: (1) substrate-controlled regioselection is observed in all cases; (2) the reaction proceeds under mild and almost neutral conditions; (3) borates can be prepared by several methods[10,11] from corresponding organolithiums and $B(OR)_3$, acetylenes, bromoacetylenes, aldehydes, etc.; (4) to the best of our knowledge γ-substitution of α,β-unsaturated carbonyl compounds with the "hard" organometallics is realized for the first time, which are *inter alia* important process in organic synthesis.[12] In addition, overall inversion is secured in the cyclic substrate. Prediction of the stereochemical outcome when applied to other cyclic substrates is now possible. Reaction with chiral allylic carbonates and application to natural product synthesis will be presented in due course.

Experimental Section

General Methods. Infrared (IR) spectra are reported in wave numbers (cm^{-1}). ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured in $CDCl_3$ using $SiMe_4$ (δ = 0 ppm) and the center line of $CDCl_3$ triplet (δ = 77.1 ppm) as internal standards, respectively. The following solvents were distilled before use: THF (from Na/benzophenone), Et_2O (from Na/benzophenone), and CH_2Cl_2 (from CaH_2). Methyllithium (MeLi) in Et_2O and *n*-butyllithium (*n*-BuLi) in hexane were prepared as a 0.75−1.25 M solution by the usual procedures and stocked under a nitrogen atmosphere. Phenyllithium (PhLi) (1.01 M in cyclohexane−Et_2O) was purchased from Kanto Chemical Co., Inc. The following nickel catalysts were prepared according to the literature methods: $NiCl_2(PPh_3)_2$,[16] $NiCl_2$(dppf).[17]

Preparations of Allylic Carbonates. (*E*)-3-(Ethoxycarbonyloxy)-1-phenyl-1-octene (1a). To an ice cold stirred solution of *trans*-cinnamaldehyde (25.2 mL, 200 mmol) in Et_2O (100 mL) was added an ethereal solution of *n*-$C_5H_{11}MgBr$ (260 mL, 1.0 M in Et_2O, 260 mmol) dropwise over 1 h. After 10 min, saturated NH_4Cl was added, and the mixture was extracted with hexane twice. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford quantitatively (*E*)-1-phenyl-1-octen-3-ol as a yellow oil, which was used for the next reaction without purification: ^1H NMR δ 0.80 (t, J = 7.1 Hz, 3 H), 1.25−1.50 (m, 6 H), 1.52−1.73 (m, 2 H), 4.28 (q, J = 6.8 Hz, 1 H), 6.23 (dd, J = 6.8, 16 Hz, 1 H), 6.57 (d, J = 16 Hz, 1 H), 7.20−7.50 (m, 5 H).

To an ice cold stirred solution of (*E*)-1-phenyl-1-octen-3-ol (1.25 g, 6.15 mmol) in CH_2Cl_2 (25 mL) were added pyridine (1.99 mL, 24.6 mmol) and ethyl chloroformate (1.18 mL, 12.3 mmol). The ice bath was removed, and the solution was stirred overnight at room temperature. Then saturated $NaHCO_3$ was added, and the mixture was extracted with hexane twice. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the crude product as a brown oil. Purification by chromatography (AcOEt/hexane) afforded **1a** (1.44 g, 85%) as a colorless oil: bp 150 °C/<0.1 Torr; ^1H NMR δ 0.88 (t, J = 6.8 Hz, 3 H), 1.25−1.45 (m, 9 H), 1.62−1.87 (m, 2 H), 4.19 (q, J = 7.0 Hz, 2 H), 5.21 (q, J = 7.0 Hz, 1 H), 6.14 (dd, J = 7.0, 16 Hz, 1 H), 6.65 (d, J = 16 Hz, 1 H), 7.20−7.42 (m, 5 H); ^{13}C NMR δ 154.7, 136.4, 133.1, 128.6, 128.0, 127.3, 126.7, 79.0, 63.8, 34.7, 31.6, 24.8, 22.5, 14.3, 14.0; IR (neat) 1738 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 74.24; H, 8.82.

Ethyl (*E*)-4-(Ethoxycarbonyloxy)-2-nonenoate (1b). A mixture of (*E*)-1-iodo-1-octen-3-ol[27] (1.0 g, 3.9 mmol), Et_3N (1.1 mL, 7.8 mmol), EtOH (1.2 mL, 20 mmol), and $PdCl_2(PPh_3)_2$ (69 mg, 0.01 mmol) was stirred overnight at 62 °C under a carbon monoxide atmosphere. Then Et_2O and saturated NH_4Cl were added. The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford quantitatively ethyl (*E*)-4-hydroxy-2-nonenoate, which was used for the next reaction without purification: ^1H NMR δ 0.89 (t, J = 6.8 Hz, 3 H), 1.25−1.48 (m, 9 H), 1.54−1.66 (m, 2 H), 4.20 (q, J = 7.0 Hz, 2 H), 4.30 (q, J = 5.4 Hz, 1 H), 6.03 (d, J = 15 Hz, 1 H), 6.94 (dd, J = 5.4, 15 Hz, 1 H).

Ethyl (*E*)-4-hydroxy-2-nonenoate was converted to **1b** in a similar manner to **1a** in 85% yield: bp 130 °C/<0.1 Torr; ^1H NMR δ 0.89 (t, J = 6.0 Hz, 3 H), 1.23−1.48 (m, 12 H), 1.60−1.82 (m, 2 H), 4.20 (q, J = 7.6 Hz, 4 H), 5.21 (q, J = 5.6 Hz, 1 H), 6.00 (d, J = 16 Hz, 1 H), 6.83 (dd, J = 5.6, 16 Hz, 1 H); ^{13}C NMR δ 166.0, 154.5, 144.8, 122.0, 76.4, 64.2, 60.6, 33.9, 31.5, 24.5, 22.5, 14.3, 14.0; IR (neat) 1745, 1725 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.71; H, 9.09.

Methyl *cis*-5-(Ethoxycarbonyloxy)-3-cyclohexene-1-carboxylate (24). Methyl *cis*-5-hydroxy-3-cyclohexene-1-carboxylate was prepared according to the procedure of Trost[22] and converted to **24** in a similar manner to **1a** in 57% overall yield: bp 150 °C/<0.1 Torr; ^1H NMR δ 1.32 (t, J = 7.5 Hz, 3 H), 1.83 (dt, J = 9.2, 12 Hz, 1 H), 2.28−2.35 (m, 2 H), 2.40−2.49 (m, 1 H), 2.73 (ddt, J = 2.9, 12, 7.7 Hz, 1 H), 3.70 (s, 3 H), 4.21 (q, J = 7.5 Hz, 1 H), 5.21−5.30 (m, 1 H), 5.71 (d, J = 10 Hz, 1 H), 5.89 (ddt, J = 1.7, 10, 3.4 Hz, 1 H); ^{13}C NMR δ 174.4, 154.7, 129.6, 126.3, 72.7, 63.9, 51.9, 37.7, 30.5, 27.2, 14.3; IR (neat) 1736, 1253 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_5$: C, 57.89; H, 7.07. Found: C, 58.04; H, 7.21.

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(*E*)-1-(Ethoxycarbonyloxy)-1-phenyl-2-octene (28). To an ice cold stirred solution of (*E*)-2-octenal (1.5 mL, 10 mmol) in Et_2O (10 mL) was added PhLi (12 mL, 12 mmol) dropwise over 10 min. After 10 min, saturated NH_4Cl was added, and the mixture was extracted with hexane twice. The combined organic layers were concentrated in vacuo to afford quantitatively (*E*)-1-phenyl-2-octen-1-ol as a yellow oil, which was used for the next reaction without purification: ^{1}H NMR δ 0.88 (t, J = 6.7 Hz, 3 H), 1.28−1.50 (m, 6 H), 1.50−1.72 (m, 2 H), 4.27 (q, J = 6.3 Hz, 1 H), 6.23 (dd, J = 6.3, 16 Hz, 1 H), 6.56 (d, J = 16 Hz, 1 H), 7.17−7.42 (m, 5 H).

(*E*)-1-Phenyl-2-octen-1-ol was converted to **28** in a similar manner to **1a** in 88% yield: bp 150 °C/<0.1 Torr; ^{1}H NMR δ 0.88 (t, J = 6.8 Hz, 3 H), 1.22−1.47 (m, 9 H), 1.62−1.90 (m, 2 H), 4.20 (q, J = 7.1 Hz, 2 H), 5.22 (q, J = 7.4 Hz, 1 H), 6.15 (dd, J = 7.4, 16 Hz, 1 H), 6.65 (d, J = 16 Hz, 1 H), 7.22−7.45 (m, 5 H); ^{13}C NMR δ 154.7, 136.3, 133.1, 128.6, 128.0, 127.3, 126.7, 79.0, 63.8, 34.7, 31.6, 24.8, 22.5, 14.3, 14.0; IR (neat) 1741 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.59; H, 8.74.

(2*E*,6*E*)-1-(Ethoxycarbonyloxy)-3,7,11-trimethyl-2,6,10-dodecatriene (29). The title compound was prepared from farnesol in a similar manner to **1a** in 85% yield: bp 130 °C/<0.1 Torr; ^{1}H NMR δ 1.29 (t, J = 7.5 Hz, 3 H), 1.53−1.73 (m, 12 H), 1.82−2.17 (m, 8 H), 4.18 (q, J = 7.5 Hz, 2 H), 4.63 (d, J = 7.5 Hz, 2 H), 5.03−5.15 (m, 2 H), 5.38 (t, J = 7.5 Hz, 1 H); ^{13}C NMR δ 155.3, 143.1, 135.5, 131.3, 124.4, 123.6, 117.9, 64.5, 63.8, 39.7, 39.6, 26.8, 26.2, 25.7, 17.7, 16.5, 16.0, 14.3; IR (neat) 1743 cm^{-1}. Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 73.38; H, 10.49.

Preparations of Boronate Esters. Method A. To a stirred solution of catecholborane (4.8 mL, 45 mmol) in benzene (7.5 mL) were added acetylene (45 mmol) and $RhCl(PPh_3)_3$ (21 mg, 0.022 mmol). After stirring for 1.5 h at room temperature, the solution was concentrated in vacuo, and the residue was distilled at reduced pressure to afford **11**.

Method B. To an ice cold stirred suspension of NaH (4.32 g, 50% content in mineral oil, 90 mmol) in THF (100 mL) was added 3-butyn-1-ol (2.27 mL, 30 mmol) dropwise over 10 min. After 10 min, benzyl bromide (10.7 mL, 90 mmol) and dimethylformamide (6.87 mL, 90 mmol) were added. The ice bath was removed and the mixture was stirred for 3 h at room temperature. Then saturated NH_4Cl was added, and the mixture was extracted with hexane twice. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the crude product as an oil. Purification by chromatography (hexane) and distillation under reduced pressure (70 °C/1 Torr) afforded 1-(benzyloxy)-3-butyne (4.42 g, 92%) as a colorless oil: ^{1}H NMR δ 2.01 (t, J = 2.6 Hz, 1 H), 2.52 (dt, J = 5.3, 7.5 Hz, 2 H), 3.62 (t, J = 7.5 Hz, 2 H), 4.58 (s, 2 H), 7.25−7.42 (m, 5 H).

1-(Benzyloxy)-3-butyne was converted to the boronate ester **11c** in a similar manner to method A.

Method C. To a stirred suspension of phenylboronic acid[10a,h] (2.0 g, 16 mmol) in benzene (50 mL) were added the diol (16 mmol) and $MgSO_4$ (10 g). The mixture was stirred overnight at room temperature and filtered. The filtrate was concentrated in vacuo to afford the crude product as an oil. Purification by chromatography (AcOEt/hexane) and distillation under reduced pressure afforded the phenylboronate ester as a colorless oil.

Method D. To an ice cold stirred solution of furan (2.17 mL, 30 mmol) in THF (50 mL) was added *n*-BuLi (30 mmol) over 30 min. After 2 h, the solution was added to B(O-*i*-Pr)$_3$ (6.9 mL, 30 mmol) dissolved in Et_2O (100 mL) over 30 min at −78 °C. Stirring was continued for 1 h at −78 °C, and the solution was warmed up to room temperature over 2 h. Then 3 N HCl was added, and the mixture was extracted with AcOEt twice. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the crude boronic acid as a solid, which was transformed to the boronate ester **8e** directly in a similar manner to method C.

Method E. To a stirred solution of the aryl or alkenyl bromide (30 mmol) in THF (50 mL) was added *n*-BuLi (30 mmol) over 30 min at −78 °C. After 2 h, the solution was added to B(O-*i*-Pr)$_3$ (6.9 mL, 30 mmol) dissolved in Et_2O (100 mL) over 30 min at −78 °C. Stirring was continued for 1 h at −78 °C, and the solution was warmed up to room temperature over 2 h. Then 3 N HCl was added, and the mixture was extracted with AcOEt twice. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the crude boronic acid as a solid, which was transformed to the boronate ester directly in a similar manner to method C.

4,5-Dimethyl-2-phenyl-1,3,2-dioxaborolane (8a):[10b,28a] yield 100% by method C; bp 90 °C/1 Torr; ^{1}H NMR δ 1.28 and 1.40 (2d (4:1), J = 7.5 and 7.5 Hz, 6 H), 4.12−4.22 and 4.65−4.77 (2m (1:4), 2 H), 7.33−7.50 (m, 3 H), 7.82 (d, J = 7.5 Hz, 2 H).

4,5-Dimethyl-2-(2-methoxyphenyl)-1,3,2-dioxaborolane (8b): yield 41% by method E; bp 130 °C/1 Torr; ^{1}H NMR δ 1.31 and 1.41 (2d (2:1), J = 4.7 and 4.7 Hz, 6 H), 3.77 (s, 3 H), 4.14−4.25 and 4.64−4.76 (2m (1:2), 2 H), 6.89 (d, J = 5.2 Hz, 1 H), 6.97 (t, J = 4.7 Hz, 1 H), 7.42 (t, J = 5.2 Hz, 1 H), 7.74 (d, J = 4.7 Hz, 1 H); IR (neat) 1601, 1578 cm^{-1}. Anal. Calcd for $C_{11}H_{15}BO_3$: C, 64.12; H, 7.34. Found: C, 63.54; H, 7.60.

4,5-Dimethyl-2-(3-methoxyphenyl)-1,3,2-dioxaborolane (8c): yield 52% by method E; bp 130 °C/1 Torr; ^{1}H NMR δ 1.29 and 1.40 (2d (4:1), J = 8.0 and 8.0 Hz, 6 H), 3.83 (s, 3 H), 4.13−4.24 and 4.65−4.77 (2m (1:4), 2 H), 7.01 (ddd, J = 1.7, 3.3, 10 Hz, 1 H), 7.24−7.34 (m, 2 H), 7.41 (d, J = 10 Hz, 1 H); IR (neat) 1573 cm^{-1}. Anal. Calcd for $C_{11}H_{15}BO_3$: C, 64.12; H, 7.34. Found: C, 64.12; H, 7.64.

4,5-Dimethyl-2-(4-methoxyphenyl)-1,3,2-dioxaborolane (8d): yield 61% by method E; bp 130 °C/1 Torr; ^{1}H NMR δ 1.29 and 1.39 (2d (5:1), J = 8.3 and 8.3 Hz, 6 H), 3.82 (s, 3 H), 4.10−4.20 and 4.61−4.73 (2m (1:5), 2 H), 6.90 (d, J = 11 Hz, 2 H), 7.75 (d, J = 11 Hz, 2 H); IR (neat) 1741, 1606 cm^{-1}. Anal. Calcd for $C_{11}H_{15}BO_3$: C, 64.12; H, 7.34. Found: C, 65.33; H, 7.35.

4,5-Dimethyl-2-(2-furyl)-1,3,2-dioxaborolane (8e): yield 62% by method D; bp 80 °C/1 Torr; ^{1}H NMR δ 1.30 and 1.40 (2d (3:1), J = 8.3 and 8.3 Hz, 6 H), 4.15−4.24 and 4.65−4.76 (2m (1:3), 2 H), 6.46 (dd, J = 2.7, 4.3 Hz, 1 H), 7.09 (d, J = 4.3 Hz, 1 H), 7.68 (d, J = 2.7 Hz, 1 H); IR (neat) 1574, 1097 cm^{-1}. Anal. Calcd for $C_8H_{11}BO_3$: C, 57.89; H, 6.68. Found: C, 57.45; H, 6.75.

4,5-Dimethyl-2-(1-methylethenyl)-1,3,2-dioxaborolane (8f): yield 61% by method E; bp 80 °C/15 Torr; ^{1}H NMR δ 1.23 and 1.32 (2d (7:3), J = 6.0 and 6.0 Hz, 6 H), 1.83 (s, 3 H), 4.00−4.10 and 4.52−4.64 (2m (3:7), 2 H), 5.66 (s, 1 H), 5.77 (s, 1 H); IR (neat) 1619 cm^{-1}. Anal. Calcd for $C_7H_{13}BO_2$: C, 60.06; H, 9.36. Found: C, 59.80; H, 9.47.

2-[(*E*)-1-Heptenyl]-1,3,2-benzodioxaborole (11a):[29] yield 61% by method A; bp 90 °C/<0.1 Torr; ^{1}H NMR δ 0.90 (t, J = 6.8 Hz, 3 H), 1.25−1.38 (m, 4 H), 1.42−1.58 (m, 2 H), 2.22−2.30 (m, 2 H), 5.78 (d, J = 18 Hz, 1 H), 6.98−7.12 (m, 3 H), 7.17−7.26 (m, 2 H).

2-[(*E*)-2-Phenylethenyl]-1,3,2-benzodioxaborole (11b):[18a] yield 58% by method A; bp 130 °C/<0.1 Torr; ^{1}H NMR δ 6.48 (d, J = 19 Hz, 1 H), 7.10 (dd, J = 3.8, 7.5 Hz, 2 H), 7.26 (dd, J = 3.8, 7.5 Hz, 2 H), 7.32−7.45 (m, 3 H), 7.49 (d, J = 7.5 Hz, 2 H), 7.78 (d, J = 19 Hz, 1 H).

2-[(*E*)-4-(Benzyloxy)-1-butenyl]-1,3,2-benzodioxaborole (11c): yield 57% by method B; bp 155 °C/<0.1 Torr; ^{1}H NMR δ 2.61 (q, J = 5.5 Hz, 2 H), 3.62 (t, J = 5.5 Hz, 2 H), 4.55 (s, 2 H), 5.89 (d, J = 11 Hz, 1 H), 6.99−7.11 (m, 3 H), 7.17−7.39 (m, 7 H); IR (neat) 3051, 1646 cm^{-1}. Anal. Calcd for $C_{17}H_{17}BO_3$: C, 72.89; H, 6.12. Found: C, 72.92; H, 6.20.

2-Phenyl-1,3,2-dioxaborinane (14):[28a,b] yield 100% by method C; bp 90 °C/1 Torr; ^{1}H NMR δ 2.00−2.10 (m, 2 H), 4.15 (t, J = 5.6 Hz, 4 H), 7.30−7.43 (m, 3 H), 7.77 (d, J = 7.5 Hz, 2 H).

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2-Phenyl-1,3,2-dioxaborolane (15):[28a−c] yield 100% by method C; bp 80 °C/1 Torr; ^{1}H NMR δ 4.38 (s, 4 H), 7.30−7.50 (m, 3 H), 7.82 (d, J = 7.5 Hz, 2 H).

2-Phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16):[28d] yield 100% by method C; bp 100 °C/1 Torr; ^{1}H NMR δ 1.34 (s, 12 H), 7.32−7.50 (m, 3 H), 7.81 (d, J = 7.5 Hz, 2 H).

2-Phenyl-1,3,2-benzodioxaborole (17):[28c] yield 100% by method C; bp 100 °C/<0.1 Torr; ^{1}H NMR δ 7.14 (dd, J = 4.3, 7.7 Hz, 2 H), 7.32 (dd, J = 4.3, 7.7 Hz, 2 H), 7.46−7.62 (m, 3 H), 8.09 (d, J = 8.3 Hz, 2 H).

General Procedures for Coupling Reactions. Method A. To an ice cold stirred solution of $B(OMe)_3$ (112 mg, 1.08 mmol) in THF (3 mL) was added PhLi (0.80 mL, 0.81 mmol) dropwise over 5 min under a nitrogen atmosphere. After 15 min, the ice bath was removed, and the solution was warmed up to room temperature. The carbonate (0.27 mmol) and the nickel catalyst (0.027 mmol) were added, and the solution was stirred overnight at 60−65 °C. Then saturated $NaHCO_3$ was added, and the mixture was extracted with hexane twice. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the crude product as a brown oil. Purification by chromatography (AcOEt/hexane) afforded the coupling product as a colorless oil.

Method B. To an ice cold stirred solution of furan (73.5 mg, 1.08 mmol) in THF (3 mL) was added *n*-BuLi (0.81 mmol) dropwise over 5 min under a nitrogen atmosphere. The solution was stirred at 0 °C for 2 h, and then $B(OMe)_3$ (112 mg, 1.08 mmol) was added. After 15 min, the ice bath was removed and the solution was warmed up to room temperature. The carbonate (0.27 mmol) and the nickel catalyst (0.027 mmol) were added, and the solution was stirred at 45−60 °C for 4−13 h. Workup and purification in a similar manner to method A afforded the coupling product.

Method C. To a stirred solution of the aryl or alkenyl bromide (0.81 mmol) in THF (3 mL) was added *n*-BuLi (1.08 mmol) dropwise over 10 min under a nitrogen atmosphere at −78 °C. The solution was stirred at −78 °C for 2 h, and then $B(OMe)_3$ (112 mg, 1.08 mmol) was added. After 15 min, the cooling bath was removed, and the solution was warmed up to room temperature. The carbonate (0.27 mmol) and the nickel catalyst (0.027 mmol) were added, and the solution was stirred overnight at 60−65 °C. Workup and purification in a similar manner to method A afforded the coupling product.

Method D. To an ice cold stirred suspension of the nickel catalyst (0.036 mmol) in THF (2 mL) was added MeLi (0.072 mmol) under a nitrogen atmosphere. The solution was stirred at 0 °C for 15−60 min, and then the alkenyl boronate ester (1.44 mmol) and MeLi (1.08 mmol) were added. After 15 min, the ice bath was removed and the solution was warmed up to room temperature. The carbonate (0.36 mmol) and MeCN (2 mL) were added, and the solution was stirred overnight at 50−60 °C. Workup and purification in a similar manner to method A afforded the coupling product.

Method E. To an ice cold stirred suspension of the boronate ester (1.08 mmol) and the nickel catalyst (0.027 mmol) in THF (3 mL) was added MeLi (0.81 mmol) dropwise over 5 min under a nitrogen atmosphere. After 15 min, (the ice bath was removed and the solution was warmed up to room temperature for the reaction at >room temperature) the carbonate (0.27 mmol) was added, and the solution was stirred at 5−65 °C for 4−15 h. Workup and purification in a similar manner to method A afforded the coupling product.

(*E*)-1,3-Diphenyl-1-octene (3a): yield 98% by method A and 88−97% by method E; bp 170 °C/<0.1 Torr; ^{1}H NMR δ 0.88 (t, J = 5.6 Hz, 3 H), 1.19−1.42 (m, 6 H), 1.72−1.88 (m, 2 H), 3.39 (q, J = 7.5 Hz, 1 H), 6.32 (dd, J = 7.5, 15 Hz, 1 H), 6.39 (d, J = 15 Hz, 1 H), 7.12−7.39 (m, 10 H); ^{13}C NMR δ 144.8, 137.7, 134.6, 129.3, 128.5, 127.7, 127.1, 126.2, 49.3, 36.0, 31.9, 27.4, 22.6, 14.2; IR (neat) 3040, 1598 cm^{-1}. Anal. Calcd for $C_{20}H_{24}$: C, 90.85; H, 9.15. Found: C, 91.34; H, 8.97.

(*E*)-3-(2-Methoxyphenyl)-1-phenyl-1-octene (3b): yield 86% by method C and 98% by method E; bp 180 °C/<0.1 Torr; ^{1}H NMR δ 0.85 (t, J = 7.6 Hz, 3 H), 1.19−1.42 (m, 6 H), 1.68−1.81 (m, 2 H), 3.83 (s, 3 H), 3.88 (q, J = 7.5 Hz, 1 H), 6.31−6.44 (m, 2 H), 6.84−6.96 (m, 2 H), 7.12−7.37 (m, 7 H); ^{13}C NMR δ 157.1, 138.1, 134.3, 133.3, 129.2, 128.4, 127.9, 127.0, 126.8, 126.2, 120.7, 110.9, 55.6, 41.7, 35.1, 31.9, 27.4, 22.6, 14.1; IR (neat) 1600 cm^{-1}. Anal. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 86.10; H, 8.30.

(*E*)-3-(3-Methoxyphenyl)-1-phenyl-1-octene (3c): yield 81% by method C and 99% by method E; bp 180 °C/<0.1 Torr; ^{1}H NMR δ 0.85 (t, J = 5.7 Hz, 3 H), 1.17−1.43 (m, 6 H), 1.71−1.83 (m, 2 H), 3.38 (q, J = 7.2 Hz, 1 H), 3.81 (s, 3 H), 6.30 (dd, J = 7.2, 16 Hz, 1 H), 6.40 (d, J = 16 Hz, 1 H), 6.70−6.87 (m, 3 H), 7.10−7.38 (m, 6 H); ^{13}C NMR δ 159.8, 146.6, 137.7, 134.4, 129.5, 129.4, 128.5, 127.0, 126.2, 120.1, 113.7, 111.2, 55.2, 49.3, 35.9, 31.9, 27.4, 22.6, 14.1; IR (neat) 1595, 1255 cm^{-1}. Anal. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 84.97, H, 9.19.

(*E*)-3-(4-Methoxyphenyl)-1-phenyl-1-octene (3d): yield 89% by method C and 90% by method E; bp 180 °C/<0.1 Torr; ^{1}H NMR δ 0.86 (t, J = 6.6 Hz, 3 H), 1.18−1.40 (m, 6 H), 1.68−1.82 (m, 2 H), 3.35 (q, J = 7.3 Hz, 1 H), 3.79 (s, 3 H), 6.29 (dd, J = 7.3, 16 Hz, 1 H), 6.37 (d, J = 16 Hz, 1 H), 6.82−6.89 (m, 2 H), 7.12−7.36 (m, 7 H); ^{13}C NMR δ 158.0, 137.8, 136.9, 134.9, 129.0, 128.6, 128.5, 127.0, 126.2, 113.9, 55.3, 48.3, 36.0, 31.9, 27.4, 22.7, 14.2; IR (neat) 1613, 1248 cm^{-1}. Anal. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.20; H, 8.99.

(*E*)-3-(2-Furyl)-1-phenyl-1-octene (3e): yield 88% by method B and 85% by method E; bp 150 °C/<0.1 Torr; ^{1}H NMR δ 0.87 (t, J = 6.4 Hz, 3 H), 1.24−1.44 (m, 6 H), 1.58−1.94 (m, 2 H), 3.51 (q, J = 7.6 Hz, 1 H), 6.04 (d, J = 2.5 Hz, 1 H), 6.22 (dd, J = 7.6, 16 Hz, 1 H), 6.29−6.32 (dd, J = 1.3, 2.5 Hz, 1 H), 6.42 (d, J = 16 Hz, 1 H), 7.15−7.39 (m, 6 H); ^{13}C NMR δ 157.7, 141.1, 137.4, 131.2, 130.6, 128.5, 127.2, 126.3, 110.1, 104.7, 42.8, 33.8, 31.8, 27.0, 22.6, 14.1; IR (neat) 1715 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.06; H, 8.81.

(*E*)-3-(1-Methylethenyl)-1-phenyl-1-octene (3f): yield 46% by method C and 73% by method E; bp 80 °C/<0.1 Torr; ^{1}H NMR δ 0.88 (t, J = 6.6 Hz, 3 H), 1.22−1.41 (m, 6 H), 1.43−1.65 (m, 2 H), 1.72 (s, 3 H), 2.79 (q, J = 7.5 Hz, 1 H), 4.79 (d, J = 4.5 Hz, 2 H), 6.12 (dd, J = 7.5, 15 Hz, 1 H), 6.37 (d, J = 15 Hz, 1 H), 7.15−7.40 (m, 5 H); ^{13}C NMR δ 147.9, 137.9, 133.5, 129.7, 128.5, 127.0, 126.1, 110.5, 50.7, 32.9, 32.0, 27.2, 22.7, 20.2, 14.2; IR (neat) 1642 cm^{-1}. Anal. Calcd for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 88.72; H, 10.77.

Ethyl (*E*)-4-(2-Furyl)-2-nonenoate (3g): yield 67% by method B and 93% by method E; bp 150 °C/<0.1 Torr; ^{1}H NMR δ 0.87 (t, J = 6.7 Hz, 1 H), 1.20−1.38 (m, 9 H), 1.62−1.90 (m, 2 H), 3.51 (q, J = 7.5 Hz, 1 H), 4.18 (q, J = 7.5 Hz, 2 H), 5.81 (d, J = 15.7 Hz, 1 H), 6.06 (d, J = 3.2 Hz, 1 H), 6.31 (dd, J = 2.0, 3.2 Hz, 1 H), 6.95 (dd, J = 7.5, 15.7 Hz, 1 H), 7.14 (d, J = 2.0 Hz, 1 H); ^{13}C NMR δ 166.5, 155.4, 148.8, 141.6, 121.9, 110.2, 105.6, 60.4, 41.9, 33.0, 31.6, 26.9, 22.5, 14.3, 14.0; IR (neat) 1720, 1650 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.79; H, 9.27.

(1*E*,4*E*)-3-Pentyl-1-phenyl-1,4-decadiene (3h): yield 70% by method D; bp 150 °C/<0.1 Torr; ^{1}H NMR δ 0.87 (t, J = 6.0 Hz, 6 H), 1.20−1.40 (m, 12 H), 1.96−2.08 (m, 4 H), 2.73−2.85 (m, 1 H), 5.36 (dd, J = 6.0, 16 Hz, 1 H), 5.43 (dt, J = 6.0, 16 Hz, 1 H), 6.12 (dd, J = 7.0, 16 Hz, 1 H), 6.32 (d, J = 16 Hz, 1 H), 7.15−7.40 (m, 5 H); ^{13}C NMR δ 138.0, 134.5, 132.9, 130.6, 128.9, 128.5, 126.9, 126.1, 46.1, 35.4, 32.7, 32.0, 31.5, 29.3, 27.1, 22.7, 22.6, 14.2; IR (neat) 1600 cm^{-1}; MS *m*/*e* (rel intensity, %) 284 (M$^+$, 86), 227 (54), 214 (33), 157 (97), 144 (84), 141 (50), 128 (80), 117 (98), 115 (100), 109 (49), 43 (50), 41 (56). Anal. Calcd for $C_{21}H_{32}$: C, 88.66; H, 11.34. Found: C, 88.56; H, 11.91.

(*E*)-1-Phenyl-3-[(*E*)-2-phenylethenyl]-1-octene (3i): yield 87% by method D; bp 190 °C/<0.1 Torr; ^{1}H NMR δ 0.86 (t, J = 6.0 Hz, 3 H), 1.20−1.40 (m, 6 H), 1.56−1.62 (m, 2 H), 2.96−3.07 (m, 1 H), 6.19 (dd, J = 7.5, 16 Hz, 2 H), 6.41 (d, J = 16 Hz, 2 H), 7.15−7.39 (m, 10 H); ^{13}C NMR δ 137.8, 133.4, 129.7, 128.6, 127.1, 126.2, 46.5, 35.3, 32.0, 27.1, 22.7, 14.2; IR (neat) 1598 cm^{-1}; MS *m*/*e* (rel intensity, %) 290 (M$^+$, 79), 220 (94), 206 (100), 205 (78), 204 (51), 191 (51), 141 (52), 129 (72), 128 (60), 117 (55), 115 (71), 91 (67). Anal. Calcd for $C_{22}H_{26}$: C, 90.98; H, 9.02. Found: C, 91.14; H, 8.83.

(*E*)-1-(Benzyloxy)-5-[(*E*)-2-phenylethenyl]-3-decene (3j): yield 50% by method D; bp 280 °C/<0.1 Torr; ^{1}H NMR δ 0.86 (t, J = 6.0 Hz, 3 H), 1.20−1.50 (m, 8 H), 2.32−2.43 (m, 2 H),

2.76−2.87 (m, 1 H), 3.51 (t, J = 6.0 Hz, 2 H), 4.51 (s, 2 H), 5.40−5.55 (m, 2 H), 6.11 (dd, J = 7.5, 16 Hz, 1 H), 6.34 (d, J = 16 Hz, 1 H), 7.15−7.40 (m, 10 H); ^{13}C NMR δ 138.7, 137.9, 135.1, 134.1, 129.1, 128.5, 128.4, 127.7, 127.5, 126.9, 126.4, 126.1, 72.9, 70.3, 46.2, 35.2, 33.2, 31.9, 27.0, 22.7, 14.2; IR (neat) 1681 cm^{-1}; MS m/e (rel intensity, %) 348 (M^+, 6), 277 (42), 257 (99.5), 240 (99.9), 213 (55), 171 (55), 169 (100), 155 (56), 143 (95), 129 (91), 117 (98), 115 (51), 105 (55), 92 (71), 91 (72). Anal. Calcd for $C_{25}H_{32}O$: C, 86.15; H, 9.25. Found: C, 85.39; H, 9.70.

Ethyl (*E*)-4-[(*E*)-2-Phenylethenyl]-2-nonenoate (3k): yield 86% by method D; bp 180 °C/<0.1 Torr; ^{1}H NMR δ 0.88 (t, J = 5.6 Hz, 3 H), 1.18−1.40 (m, 9 H), 1.46−1.62 (m, 2 H), 2.94−3.06 (m, 1 H), 4.17 (q, J = 7.5 Hz, 2 H), 5.85 (d, J = 16 Hz, 1 H), 6.06 (dd, J = 7.5, 16 Hz, 1 H), 6.39 (d, J = 16 Hz, 1 H), 6.94 (dd, J = 7.5, 16 Hz, 1 H), 7.17−7.40 (m, 5 H); ^{13}C NMR δ 166.7, 151.1, 137.2, 131.1, 130.9, 128.6, 127.4, 126.2, 120.9, 60.3, 45.8, 34.4, 31.8, 26.9, 22.6, 14.3, 14.1; IR (neat) 1723 cm^{-1}; MS m/e (rel intensity, %) 286 (M^+, 97), 257 (99.5), 241 (87), 216 (48), 215 (61), 214 (61), 213 (42), 212 (70), 195 (90), 187 (58), 182 (72), 170 (65), 169 (58), 167 (100), 157 (75), 156 (70), 155 (97), 144 (47), 142 (56), 129 (87), 128 (83), 117 (62), 115 (85), 112 (74), 91 (61). Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.21; H, 9.41.

Ethyl (*E*)-4-Phenyl-2-nonenoate (3l): yield 96% by method E; bp 160 °C/<0.1 Torr; ^{1}H NMR δ 0.85 (t, J = 6.3 Hz, 3 H), 1.17−1.35 (m, 9 H), 1.66−1.83 (m, 2 H), 3.38 (q, J = 7.5 Hz, 1 H), 4.17 (q, J = 7.3 Hz, 2 H), 5.77 (d, J = 16 Hz, 1 H), 7.06 (dd, J = 7.5, 16 Hz, 1 H), 7.14−7.35 (m, 5 H); ^{13}C NMR δ 166.7, 152.0, 142.5, 128.7, 127.8, 126.7, 120.7, 60.3, 48.6, 35.0, 31.7, 27.2, 22.5, 14.3, 14.1; IR (neat) 1721 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.11; H, 9.39.

Methyl *trans*-5-(2-Furyl)-3-cyclohexene-1-carboxylate (25): yield 92% by method B; ^{1}H NMR δ 1.99 (ddd, J = 5.7, 11.3, 12.8 Hz, 1 H), 2.20 (dt, J = 12.8, 3.2 Hz, 1 H), 2.24−2.38 (m, 2 H), 2.64 (dddd, J = 3.2, 5.7, 9.5, 11.3 Hz, 1 H), 3.56−3.63 (m, 1 H), 3.67 (s, 3 H), 5.75−5.83 (m, 1 H), 5.84−5.92 (m, 2 H), 5.99 (dt, J = 3.2, 1.0 Hz, 1 H), 6.28 (dt, J = 3.2, 2.1 Hz, 1 H), 7.34 (dd, J = 1.0, 2.1 Hz, 1 H); ^{13}C NMR δ 175.9, 157.3, 141.5, 127.2, 126.1, 110.0, 105.9, 51.7, 35.7, 33.7, 29.8, 27.5; IR (neat) 1732, 1173 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.60; H, 6.92.

For comparison, product **25** was treated with a catalytic amount of NaH in MeOH to give a mixture of **25** and *cis* isomer **27**. ***Cis* Isomer 27:** ^{1}H NMR δ (diagnostic peaks) 1.77 (dt, J = 11.2, 12.6 Hz, 1 H), 2.36−2.45 (m, 1 H), 6.02 (dt, J = 3.4, 0.8 Hz, 1 H), 7.32 (dd, J = 0.8, 1.9 Hz, 1 H).

Methyl *trans*-5-Phenyl-3-cyclohexene-1-carboxylate (26): yield 95% by method E and the following ^{1}H NMR spectra were in good agreement with those reported for *trans* isomer:[5c] ^{1}H NMR δ 1.98 (dt, J = 13, 3.8 Hz, 1 H), 2.17 (ddd, J = 6.2, 11, 13 Hz, 1 H), 2.31−2.40 (m, 2 H), 2.61 (ddt, J = 3.8, 6.2, 9.4 Hz, 1 H), 3.52−3.61 (m, 1 H), 3.65 (s, 3 H), 5.78 (d, J = 13 Hz, 1 H), 5.95 (d, J = 13 Hz, 1 H), 7.17−7.35 (m, 5 H).

(6*E*)-1-Phenyl-3,7,11-trimethyl-2,6,10-dodecatriene (30) and (6*E*)-3-Phenyl-3,7,11-trimethyl-1,6,10-dodecatriene (31): yield 96% by method E; bp 150 °C/<0.1 Torr; 3:1 mixture of **30**:**31**; ^{1}H NMR δ 1.37−1.72 (m, 9 H), 1.92−2.16 (m, 8 H), 3.35 (d, J = 7.5 Hz, 2 H for **30**), 5.01−5.16 (m, 2 H for **30** and 4 H for **31**), 5.34 (t, J = 7.5 Hz, 1 H for **30**), 6.04 (dd, J = 11, 18 Hz, 1 H for **31**), 7.12−7.62 (m, 5 H); IR (neat) 1491 cm^{-1}. Anal. Calcd for $C_{21}H_{30}$: C, 89.30; H, 10.70. Found: C, 88.94; H, 10.57.

Three-Step One Pot Reaction. To a stirred solution of catecholborane (1.44 mL, 1.0 M in THF, 1.44 mmol) were added phenylacetylene (110 mg, 1.08 mmol) and $RhCl(PPh_3)_3$ (6.7 mg, 0.0072 mmol) under a nitrogen atmosphere. The solution was stirred at room temperature for 1 h and cooled at 0 °C, and MeLi was added (1.08 mmol) over 5 min. After 15 min, the ice bath was removed, and the solution was warmed up to room temperature. The carbonate **1a** (99.5 mg, 0.36 mmol), MeCN (2 mL), and $NiCl_2$(dppf) (24.6 mg, 0.036 mmol) were added, and the solution was stirred at 50−60 °C overnight. Then saturated $NaHCO_3$ was added, and the mixture was extracted with hexane twice. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the crude product as a brown oil. Purification by chromatography (AcOEt/hexane) afforded **3i** (52 mg, 50%) as a colorless oil.

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