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Palladium-Catalyzed Cross-Coupling Reaction of Organoboron Compounds with Organic Triflates[1]

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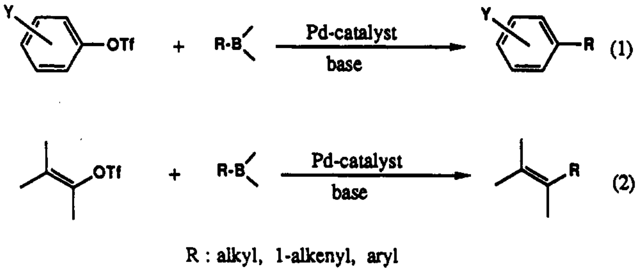
The cross-coupling reaction of 9-alkyl-9-borabicyclo[3.3.1]nonane (9-R-9-BBN), 1-alkenyl-1,3,2-benzodioxaborole, or aryl boronic acid with 1-alkenyl or aryl triflates in the presence of K$_3$PO$_4$ (1.5 equiv) and a catalytic amount of Pd(PPh$_3$)$_4$ or Cl$_2$Pd(dppf) resulted in high yields. The reaction conditions are sufficiently mild so that a variety of functionalized alkenes, alkadienes, and arenes are readily obtained. The utility of the present reaction was demonstrated by the cyclization of ω-alkenyl triflates leading to a benzo-fused cycloalkene and bicyclic alkene via a hydroboration-intramolecular coupling sequence.

In our previous papers, we reported the palladium-catalyzed cross-coupling reaction of alkyl;[2] 1-alkenyl;[3] and arylboron[4] derivatives with organic halides such as alkyl,[2c,e] 1-alkenyl, aryl, 1-alkynyl, allylic, and benzylic halides. The reaction has many attractive features of a general carbon-carbon bond formation method: a variety of organoboron compounds are readily accessible by hydroboration of alkenes and alkynes, the stereochemistry of 1-alkenyl groups both on boron and halides are completely retained in the products, many functional groups including ester, ketone, and aldehyde are tolerated, and high turnovers of the palladium catalysts are observed. The versatility of the boron cross-coupling reaction has been amply demonstrated by several groups for the stereospecific syntheses of natural products and related compounds.[5]

Although we have studied most thoroughly the cross-coupling reaction with organic halides, the recent discovery that trifluoromethanesulfonates (triflates) undergo clean couplings with organostannane,[6] aluminum,[7] and zinc[8] reagents prompted us to study the related reaction of organoboron compounds (eqs 1 and 2). Triflates are especially valuable as partners for the cross-coupling reaction, in part due to the easy access from phenols or carbonyl enolates which allows the regioselective formation of aryl and 1-alkenyl electrophiles.[9] Particularly, ready availability of cycloalkenyl triflates from cyclic ketones is of greater advantage than the synthesis of corresponding halides.



Herein, we report on the scope and limitation of the palladium-catalyzed boron coupling reaction with triflates and their synthetic application, as well as the effects of varying the reaction conditions.

Results and Discussion

Reaction Conditions. Both the palladium complex and a base are essential for the reaction to proceed (Table I). The common mechanism[10] of a transition-metal-catalyzed cross-coupling reaction between organometallic reagents and electrophiles involves sequential oxidative addition, transmetalation, and reductive elimination. The difficulty in using organoboron compounds for such a cross-coupling reaction is attributable to the very slow rate of

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(1) Preliminary results of this work were reported: Oh-e, T.; Miyaura, N.; Suzuki, A. *Synlett.* **1990**, 221–223. During the course of our study, the cross-coupling reaction of aryl triflates with arylboronic acids were reported: Huth, A.; Beez, I.; Schumann, I. *Tetrahedron* **1989**, *45*, 6679–6682. Shieh, W.-C.; Carlson, J. A. *J. Org. Chem.* **1992**, *57*, 379–381, and ref 15.

(2) (a) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Sato, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314–321. (b) Hoshino, Y.; Ishiyama, T.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1988**, *29*, 3983–3986. (c) Ishiyama, T.; Miyaura, N.; Suzuki, A. *Ibid.* **1991**, *32*, 6923–6926. (d) Miyaura, N.; Ishikawa, M.; Suzuki, A. *Ibid.* **1992**, *33*, 2571–2574. (e) Ishiyama, T.; Abe, S.; Miyaura, N.; Suzuki, A. *Chem. Lett.* **1992**, 691–694.

(3) (a) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972–980. (b) Miyaura, N.; Sato, M.; Suzuki, A. *Tetrahedron Lett.* **1986**, *27*, 3745–3748. (c) Sato, M.; Miyaura, N.; Suzuki, *Chem. Lett.* **1986**, 1329–1332. (d) Miyaura, N.; Suzuki, A. *Org. Synth.* **1990**, *68*, 130–136. (e) Suzuki, A. *Pure Appl. Chem.* **1985**, *57*, 1749–1758. (f) Suzuki, A. *Ibid.* **1991**, *63*, 419–422.

(4) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513–519. (b) Watanabe, T.; Miyaura, N.; Suzuki, A. *Synlett.* **1992**, 207–210.

(5) Palytoxin: Uenishi, J.; Beau, J.-M.; Armstrong, R. W.; Kishi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 4756–4758. Chlorothricolide: Roush, W.; Riva, R. *J. Org. Chem.* **1988**, *53*, 710–712. 5,6-DiHETE: Nicolaou, K. C.; Ramphal, J. Y.; Palazon, J. M.; Spanevello, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 587–588. Tamoxifen: Potter, G. A.; McCague, R. *J. Org. Chem.* **1990**, *55*, 6184–6187. Leukotriene B$_4$: Kobayashi, Y.; Shimazaki, T.; Taguchi, H.; Sato, F. *J. Org. Chem.* **1990**, *55*, 5324–5355. Dihydroxyserrulatic acid: Uemura, M; Nishimura, H.; Minami, T.; Hayashi, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5402–5410. Polyphenylenes: Rehahn, M.; Schluter, A.-D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060–1063. Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592–4593. Wallow, T. I.; Novak, B. M. *Ibid.* **1991**, *113*, 7411–7412. Miller, T. M.; Neena, T. X.; Zayas, R.; Bair, H. E. *Ibid.* **1992**, *114*, 1018–1025.

(6) (a) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033–3040. (b) Echavarren, A. M.; Stille, J. K. *Ibid.* **1987**, *109*, 5478–5489. (c) Rano, T. A.; Greenlee, M. L.; DeNino, F. P. *Tetrahedron Lett.* **1990**, *31*, 2853–2856. (d) Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500–7506. (e) Echavarren, A. M.; Stille, J. K. *Ibid.* **1988**, *110*, 1557–1565.

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

(8) Burini, A. A.; Cacchi, S.; Delmastro, M.; Marinelli, F.; Pietroni, B. *Synlett.* **1990**, 47–48.

(9) (a) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85–126. (b) Comins, D. L.; Dehghani, A. *Tetrahedron Lett.* **1992**, *33*, 6299–6302.

(10) (a) Kochi, J. K. *Organometallic Mechanism, and Catalysis*; Academic: New York, 1987. (b) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic: New York, 1985. (c) Hartley, F. R. *The Chemistry of the Metal-Carbon Bond*; Patai, S., Ed.; Wiley: New York, 1985. (d) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

0022-3263/93/1958-2201$04.00/0

Table I. Reaction Conditions for the Cross-Coupling of Phenyl Triflate with 9-Octyl-9-BBN[a]

entry	catalyst	solvent	temp (°C)	yield (%)[b] 5 h	24 h	36 h
1	$PdCl_2(dppf)$	THF	65	99		
2	$Pd(PPh_3)_4$	THF	65	61	97	
3	$Pd(PPh_3)_4$	DMF	65	94		
4	$Pd(PPh_3)_4$	dioxane	85	99		
5	$Pd(PPh_3)_4$	dioxane	65	64	92	
6	$Pd(PPh_3)_4$	dioxane	20		4	9
7	$Pd(DBA)_2$/ $4(MeO)_3C_6H_2PPh_2$[c]	dioxane	20		75	91
8	$Pd(DBA)_2$/ $4[(MeO)_3C_6H_2]_2PPh$[d]	dioxane	20		62	87

[a] Reactions of phenyl triflates (1 mmol) with 9-octyl-9-BBN derivatives (1.1 mmol) were carried out in 4 mL of solvent by using 2.5 mol % of palladium catalyst and K_3PO_4 (1.5 mmol). [b] GLC yields are based on phenyl triflate employed. [c] Diphenyl(2,4,6-trimethoxyphenyl)phosphine. [d] Bis(2,4,6-trimethoxyphenyl)phenylphosphine.

transmetalation due to the low nucleophilicity of organic groups on boron. We have shown previously[2-4] that the addition of a base greatly facilitates the cross-coupling of organoboron reagents with electrophiles by acceleration of the rate of the transmetalation step. Although we used relatively strong bases such as aqueous NaOH and NaOEt in ethanol for the reaction of vinylic boronates with organic halides, powdered K_3PO_4 suspended in dioxane is sufficient to accelerate the coupling with triflates.

The reaction of 9-octyl-9-BBN (9-borabicyclo[3.3.1]-nonane) readily proceeds in THF at 65 °C in the presence of 2.5 mol % of $PdCl_2(dppf)$ and 1.5 equiv of K_3PO_4 (entry 1). Although $Pd(PPh_3)_4$ catalyst is less effective at 65 °C in THF, it gives a comparable yield of octylbenzene by carrying the reaction in dioxane at 85 °C (entry 4). Very recently, it was reported[11a] that the use of tris(2,4,6-trimethoxyphenyl)phosphine as a ligand of palladium extremely enhances the rate of coupling of organotin reagents with halides and triflates. This ligand does not give good results for the present coupling, but phenylphosphines having one or two 2,4,6-trimethoxyphenyl groups are significantly more effective, allowing the couplings to proceed at room temperature (entries 7 and 8). The superiority of bulky phosphines over triphenylphosphine is most likely due to acceleration of the rate of oxidative addition of triflate to the palladium(0) complex by ready formation of a coordinatively unsaturated palladium species.[11] It is also known that such an electron-rich palladium(0) complex has a higher tendency to undergo oxidative addition.[11b] These mild conditions can be anticipated to be useful for coupling with thermally labile or base-sensitive triflates.[6c]

While the conditions optimized above are found to work effectively for most of the 1-alkenyl and aryl triflates and alkyl-, 1-alkenyl-, and arylboron compounds, the coupling often fails to proceed due to the decomposition of catalyst, precipitating palladium black at the early stage of the reaction. Presumably, triphenylphosphine used as a ligand of palladium reacts with triflate to give phosphonium salt 3, as shown in eqs 3 and 4.[12] Addition of potassium bromide (1.1 equiv) is effective in preventing such a decomposition of the catalyst (Table II), which is known[6a] to convert the

Table II. Effects of Metal Halides on the Cross-Coupling of 4-*tert*-Butylcyclohexenyl Triflate with *p*-Tolylboronic Acid[a]

entry	MX	equiv	yield (%)[b]
1	none		37
2	KI	1.1	52
3	KBr	1.1	88
4	LiCl	1.1	42
5	LiCl	3.0	11

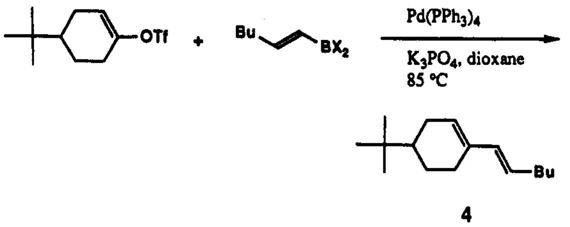
[a] Reactions of 4-*tert*-butylcyclohexenyl triflate (1 mmol), and *p*-tolylboronic acid (1.1 mmol) were carried out in 5 mL of dioxane at 85 °C for 24 h with 2.5 mol % of $Pd(PPh_3)_4$, K_3PO_4 (1.5 mmol), and metal halides. [b] GLC yields are based on the triflate employed.

$$\mathrm{ROTf} \xrightarrow{\mathrm{Pd(0)}} \underset{\mathbf{1}}{[\mathrm{R{-}Pd}]^-[\mathrm{OTf}]^+} \xrightarrow{\mathrm{MX}} \underset{\mathbf{2}}{\mathrm{R{-}Pd{-}X}} \quad (3)$$

$$\mathbf{1} + \mathrm{Ph_3P} \longrightarrow \underset{\mathbf{3}}{[\mathrm{Ph_3PR}]^-[\mathrm{OTf}]^+} + \mathrm{Pd(0)} \quad (4)$$

extremely labile cationic palladium species 1 to organopalladium bromide 2 (eq 3). Lithium chloride or potassium iodide is less effective. The results suggest that the rate of metathetical displacement of the halide ion with organoboron reagent is very susceptible to the halide ligand on the palladium(II) complex 2.

Boron Reagents. A comparison of 1-hexenyl derivatives of 1,3,2-benzodioxaborole, 9-BBN, bis(3-methyl-2-butyl)borane (disiamylborane), dicyclohexylborane, and boronic acid in a reaction with 4-*tert*-butylcyclohexenyl triflate in dioxane at 85 °C for 5 h in the presence of K_3PO_4 (1.5 equiv) and $Pd(PPh_3)_4$ (2.5 mol %) indicates that higher yields of diene 4 can be obtained by the use of 1,3,2-benzodioxaborole and 9-BBN derivatives, 79% and 83% (eq 5). Other boron reagents give modest to poor yields of 4. A similar tendency of the effects of hydroboration reagents on the yields is observed in the aryl-vinyl coupling between *p*-methoxyphenyl triflate and 1-hexenylboron derivatives.



(5)

4

BX_2 = $BO_2C_6H_4$ (79 %), 9-BBN (83 %), $B(Sia)_2$ (3 %), $B(Chx)_2$ (2 %), $B(OH)_2$ (33 %).

For arylation of triflates, boronic acid produces better results than the corresponding boronic esters, and 9-alkyl-9-BBN derivatives are the best reagent of choice for alkylation.

Reactivity of Triflates over Halides. In the palladium-catalyzed cross-coupling reactions of boron,[2-4] tin,[13] and zinc[14] compounds with organic halides, the order of reactivity I > Br ≫ Cl is commonly observed. To establish the relative reactivity of the trifluoromethanesulfyl group over halides, an equimolar mixture of bromobenzene and phenyl triflate is allowed to react with an equivalent of 9-octyl-9-BBN in dioxane at 85 °C in the presence of K_3-

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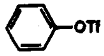
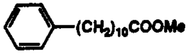
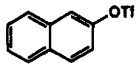
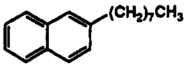
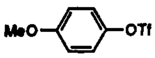
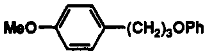
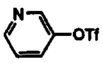
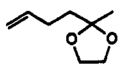
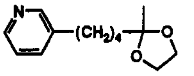
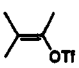
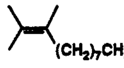
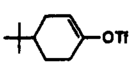
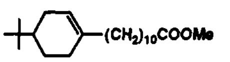
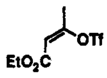
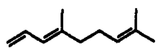
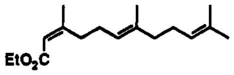
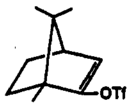
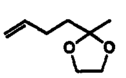
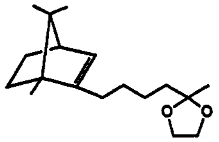
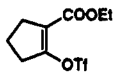
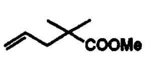
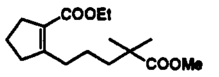
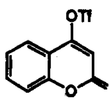
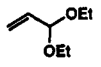
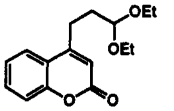
[11] (a) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585–9595. (b) Ben-David, Y.; Portony, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1816–1817.

[12] Kowalski, M. H.; Hinkle, R. J.; Stang, P. J. *J. Org. Chem.* **1989**, *54*, 2783–2784.

[13] Stille, J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524.

[14] Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340–348.

Table III. Cross-Coupling Reaction of Triflates with 9-Alkyl-9-BBN Derivatives

entry	triflate	alkene	reaction time (h)		product	yield (%)[a]	
			A[b]	B[b]		A[b]	B[b]
1		$CH_2{=}CH(CH_2)_8COOMe$	5	5		87	99 (82)
2		1-octene	5	5		82[c]	97 (96)
3		$CH_2{=}CHCH_2OPh$	5	5		92	76 (70)
4			5			65	
5		1-octene		5			91 (67)
6		$CH_2{=}CH(CH_2)_8COOMe$	5	5		89	99 (86)
7			18			65	
8			18	18		57	74 (73)
9			18			(71)	
10			5			(64)	

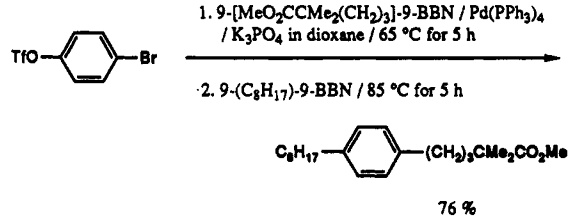
[a] GLC yields are based on the triflates employed, and the isolated yields are in parentheses. [b] Coupling reactions were conducted for 5–18 h by using triflates (1 mmol), 9-alkyl-9-BBN (1.1 mmol), Pd catalyst (0.025 mmol), K_3PO_4(1.5 mmol), and solvent (4–6 mL). The catalyst, solvent, and reaction temperature are as follows. Procedure A: $Pd(PPh_3)_4$ in dioxane at 85 °C. Procedure B: $PdCl_2(dppf)$ in THF at the reflux temperature.

PO_4 (1.5 equiv) and $Pd(PPh_3)_4$ (2.5 mol %). Analysis of the reaction mixture indicates that 24% and 66% of unreacted bromobenzene and phenyl triflate are recovered. Under similar conditions, iodobenzene is consumed exclusively in the presence of phenyl triflate. Thus, the order of reactivity is I > Br > OTf.

A highly selective coupling of boron reagent through the carbon–bromine bond is accomplished in the reaction of 9-octyl-9-BBN with *p*-bromophenyl triflate resulting in *p*-octylphenyl triflate (66%) and 1,4-dioctylbenzene (<1%).[15] Although the relative reactivity of bromobenzene over phenyl triflate is only 2.2, the great change in selectivity on going to *p*-bromophenyl triflate can be explained by the very strong electron-withdrawing effect of the trifluoromethanesulfoxy group which activates the carbon–bromine bond to oxidative addition. The sequential cross-coupling reaction of 4-bromophenyl triflate with two 9-alkyl-9-BBN derivatives, obtained from two different alkenes, furnished the unsymmetrically substituted benzene derivative in a yield of 76% (eq 6).

The change in selectivity dependent on the coordination number of the phosphine ligands which is reported in the related tin coupling reaction[6b] is not observed.

Reaction Scope. 9-Alkyl-9-BBN derivatives obtained by hydroboration of alkenes with 9-BBN are directly subjected to cross-coupling with aryl or 1-alkenyl triflates at 85 °C in dioxane in the presence of K_3PO_4 (1.5 equiv) and $Pd(PPh_3)_4$ (2.5 mol %) (procedure A) or at the refluxing temperature of THF by using K_3PO_4 (1.5 equiv) and $PdCl_2(dppf)$ (2.5 mol %) (procedure B) to provide good yields of geometrically pure alkylated alkenes and arenes (Table III).



(6)

There are no large differences in the yields and selectivities of coupling products between procedures A and B. However, the reaction can be carried out at lower temperature, and slightly higher yields can be commonly achieved by using the $PdCl_2(dppf)$ catalyst. Under these conditions, the reaction proceeds with complete retention of the double bond geometry of vinylic triflates over 99% (entry 7).

It is convenient to use 9-BBN as a hydroboration reagent[16] since a variety of functionalized alkylboron derivatives are readily prepared by the corresponding terminal alkenes shown in Table III. Although the 9-alkyl-9-BBN derivatives thus obtained are quite inert to many

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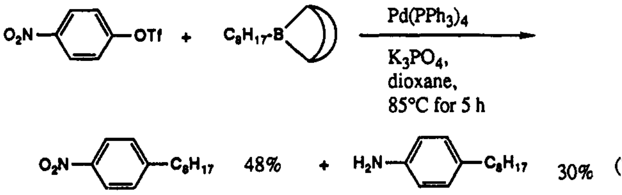
[15] A similar chemoselectivity was reported: Snieckus, V. PACIFICHEM, Honolulu, Hawaii, December, 1989, Abstract ORGN 499, and ref 6b.

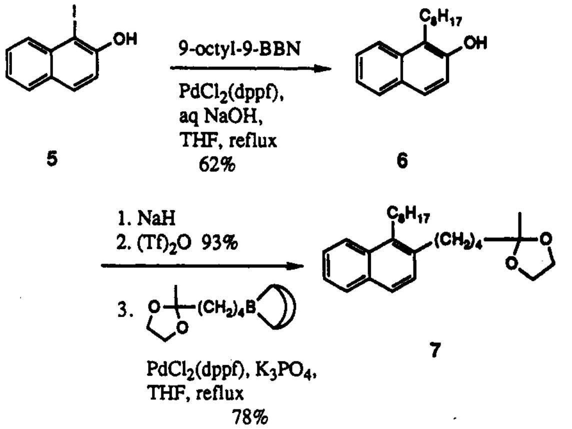
functional groups under the conditions for cross-coupling,[2] the reduction of the nitro group is unexpectedly observed to occur during the coupling of 9-octyl-9-BBN with 4-nitrophenyl triflate (eq 7). Our preliminary experiment



(7)

indicates that nitroarenes such as *p*-nitrotoluene are reduced to amine by 2 equiv of 9-octyl-9-BBN and K_3PO_4 (3 equiv) in dioxane at 80 °C for 10 h with a yield of 40%. Although the yield is improved to 52% in a similar reaction in the presence of $Pd(PPh_3)_4$ (2 mol %), the reduction without catalyst suggests that reaction proceeds through the analogous reduction mechanism[17] of carbonyl compounds or acetyl chloride, where one of the bridgehead hydrogens acts as a hydride.

The usefulness of a combination of coupling reactions with haloarenes and triflates are demonstrated by sequential cross-coupling of two different 9-alkyl-9-BBN derivatives with 1-iodo-2-naphthol (**5**) (eq 8). The reaction of 9-octyl-9-BBN with iodonaphthol gives 1-octyl-2-naphthol (**6**) in a yield of 62% which is subsequently converted to the corresponding triflate in 93% yield. The coupling of the triflate with an another alkylborane affords the unsymmetrically disubstituted naphthalene **7** in 78% yield.



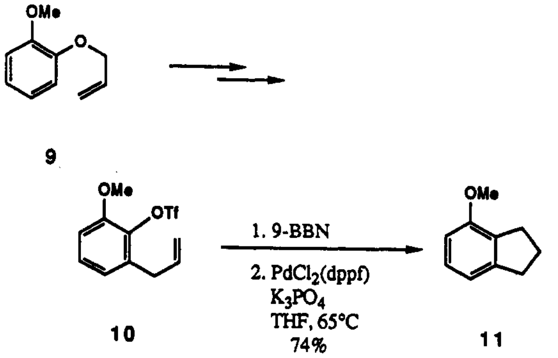
(8)

In Table IV, the results of cross-coupling of 1-alkenyl- and arylboronic acids or their esters with triflates in the presence of 1.5 equiv of K_3PO_4 and 2.5 mol % of $Pd(PPh_3)_4$ are summarized. (*E*)-1-Alkenylboronates can be most conveniently prepared by hydroboration of alkynes with catecholborane (1,3,2-benzodioxaborole)[16,18] (entries 1–3). Substitution of (*Z*)-(1-bromo-1-alkenyl)boronates, obtained by hydroboration of 1-bromo-1-alkynes with dibromoborane–dimethyl sulfide, with potassium hydrotriisopropoxyborate[19] or alkyllithium[20] provides (*Z*)-1-alkenylboronates stereoselectively (entries 4 and 5). The cross-coupling of these boron reagents with triflates proceeds while retaining the original configuration of the double bonds to provide conjugated dienes stereoselectively (entries 1–5).

Triflates of α,β-unsaturated ketone and ester derivatives are rather sensitive to the base (entries 2–4). Fortunately, these triflates react with vinylic boronates at very fast coupling rates, since these are activated to oxidative addition by an electron-withdrawing group[21] and presumably also the transmetalation step.[13,22] The reaction is applied for syntheses of prostaglandin B_1 analog (entry 3) and a valuable precursor[23] for stereodefined exocyclic alkene (entry 4).

Intramolecular Cross-Coupling. We reported[2a] previously the intramolecular cross-coupling reaction for cyclization of haloalkenes via the hydroboration–coupling sequence. Good yields of five- and six-membered rings were readily achieved by treating haloalkenes with 9-BBN, followed by the palladium catalyst and a base. The usefulness of the procedure was demonstrated by the synthesis of stereodefined exocyclic alkenes.[2d] However, the scope of the reaction is still limited by the availability of haloalkenes, particularly due to the lack of a simple method for preparing cyclic haloalkenes from ketone precursors.

The ready availability of triflate from phenol and carbonyl precursors[9] now offers a valuable tool for the five- or six-membered annulation of benzenes or ketones (eqs 9 and 10). Claisen rearrangement[24] of allyl phenyl ether is a convenient way to introduce an allylic group at the ortho position of phenol, which is converted to triflate **10** by sequential treatments with NaH and trifluoromethanesulfonic acid anhydride. The hydroboration of **10** with 9-BBN and subsequent intramolecular cross-coupling gives indan **11** in a yield of 74% (eq 9).



(9)

Analogously, allylation of 2-carbomethoxycycloheptanone (**12**), followed by treatment with lithium diisopropylamide and *N*-phenyltrifluoromethanesulfonimide[25]

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(16) For general reviews: (a) Brown, H. C. *Organic Synthesis via Boranes*; Wiley: New York, 1975. (b) Lane, C. F. *Synthetic Reagents*; Pizey, J. S., Ed.; Ellis Harwood: New York, 1977. (c) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic: New York, 1988.

(17) (a) Yamamoto, Y.; Toi, H.; Sonoda, A.; Murahashi, S. *J. Am. Chem. Soc.* **1976**, *98*, 1965–1967. (b) Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2832–2836; (c) *J. Am. Chem. Soc.* **1976**, *98*, 1964–1965; (d) *J. Organomet. Chem.* **1975**, *90*, C1–C5.

(18) (a) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370–4373. (b) Lane, C. F. *Tetrahedron* **1976**, *32*, 981–990.

(19) (a) Brown, H. C.; Imai, T. *Organometallics* **1984**, *3*, 1392–1395. (b) Brown, H. C.; Somayaji, V. *Synthesis* **1984**, 919–920.

(20) (a) Brown, H. C.; Imai, T.; Bhat, N. G. *J. Org. Chem.* **1986**, *51*, 5277–5282. (b) Brown, H. C.; Bhat, N. G. *Tetrahedron Lett.* **1988**, *29*, 21–24.

(21) Stille, J. K.; Lau, K. S. *Acc. Chem. Res.* **1977**, *10*, 434–442, and ref 10.

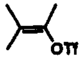
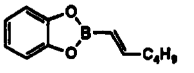
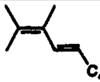
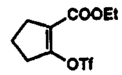
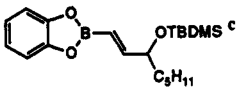
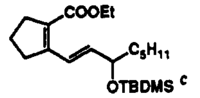
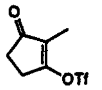
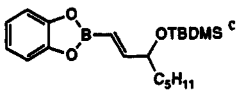
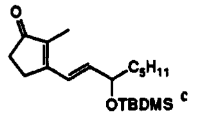
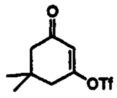
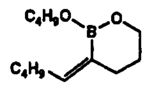
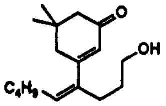
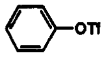
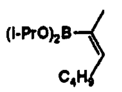
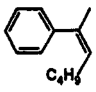
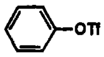
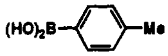
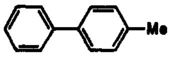
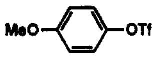
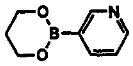
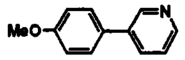
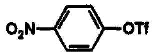
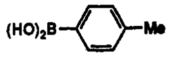
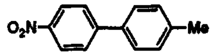
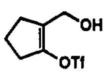
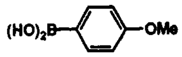
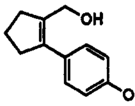
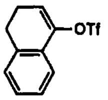
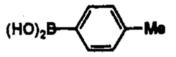
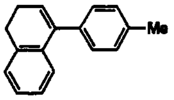
(22) (a) Sato, N.; Ishiyama, T.; Miyaura, N.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3471–3473. (b) Yanagi, T.; Oh-e, T.; Miyaura, N.; Suzuki, A. *Ibid.* **1989**, *62*, 3892–3895.

(23) Piers, E.; Yeung, B. W. A. *J. Org. Chem.* **1984**, *49*, 4567–4569.

(24) Allen, C. F. H.; Gates, J. M. *Org. Synth.* **1955**, *3*, 418–420.

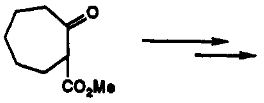
(25) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979–982.

Table IV. Cross-Coupling Reaction of Triflates with 1-Alkenyl- and Arylboron Compounds[a]

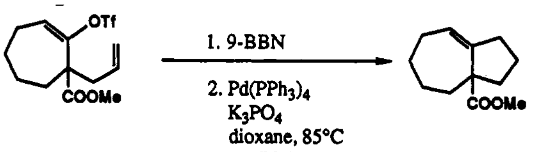
entry	triflate	borane	reaction time (h)	product	yield (%)[b]
1			5		99 (82)
2			10		(96)
3			5		(93)
4			5		78
5			5		(68)
6			5		83[d]
7			5		(46)
8			2		(82)
9			5		(77)
10			5 20		58 99[d]

[a] Reactions were carried out in 5 mL of dioxane at 85 °C for 2–20 h by using 2.5 mol % of $Pd(PPh_3)_4$, K_3PO_4 (1.5 mmol), triflates (1 mmol), and boron compounds (1.1 mmol), unless otherwise noted. [b] GLC yields are based on the triflates employed, and the isolated yields are in parentheses. [c] TBDMS is *tert*-butyldimethylsilyl. [d] Reactions were conducted in the presence of KBr (1.1 mmol).

($PhN(Tf)_2$), provides the triflate **13**, which is subjected to hydroboration–coupling to give **14** in 76% yield (eq 10).



12



13 **14** (10)

Since the synthesis of the compounds having a metal and a leaving group in the same molecule is rather difficult by other methods, the hydroboration–coupling approach provides an efficient way for cyclization of haloalkenes and alkenyl triflates via intramolecular cross-coupling.

Experimental Section

All experiments were carried out under a nitrogen atmosphere. Dioxane and THF were distilled from benzophenone ketyl before use. A commercial anhydrous K_3PO_4 was used directly. The IR spectra were recorded on a Hitachi Perkin-Elmer Model 125 spectrometer. The ^1H NMR were measured with a Hitachi R-90H (90 MHz) or a JEOL EX-400 (400 MHz) spectrometer by using $CDCl_3$ and TMS as a solvent and an internal reference. Mass spectra were recorded on a JEOL JMS-D 300 for high resolution analysis and a Finnigan ITD 800 for GC-mass analysis. GC analysis were performed by a fused silica capillary column (OV-1, 25 m).

Palladium Catalyst. Tetrakis(triphenylphosphine)palladium(0),[26] bis(dibenzylideneacetone)palladium ($Pd(DBA)_2$),[27] and dichlorobis[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) ($Cl_2Pd(dppf)$)[28] were prepared by using the literature procedures.

Boron Reagents. Catecholborane (1,3,2-benzodioxaborole) and 9-borabicyclo[3.3.1]nonane (9-BBN) in THF from Aldrich Chemical Co. were used directly. The preparations of 2-[(*E*)-1-hexenyl]-1,3,2-benzodioxaborole,[3d] diisopropyl [(*Z*)-(2-hepten-2-yl)]boronate,[22b] 2-[(*E*)-3-(*tert*-butyldimethylsiloxy)-1-octenyl]-1,3,2-benzodioxaborole,[29] (4-methylphenyl)boronic acid,[30] and (4-methoxyphenyl)boronic acid[30] were reported previously.

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[26] Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121–123.

[27] Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253–266.

[28] Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158–163.

[29] Nicolaou, K. C.; Ramphal, J. Y.; Abe, Y. *Synthesis* **1989**, 898–901.

[30] Bean, F. R.; Johnson, J. R. *J. Am. Chem. Soc.* **1932**, *54*, 4415–4425. Nesmeyanov, A. N.; Sokolik, R. A. *Methods of Element-Organic Chemistry*, Vol. 1; North-Holland: Amsterdam, 1967.

The synthesis of 3-[(*E*)-pentylidene]-2-butoxy-1,2-oxaborinane and 2-(3-pyridyl)-1,3,2-dioxaborinane are as follows.

3-[(*E*)-Pentylidene]-2-butoxy-1,2-oxaborinane. To a solution of diisopropyl [(*Z*)-1-bromo-1-hexenyl]boronate[19,20] (13 mmol) in THF (26 mL) was added slowly a solution of [3-(1-ethoxyethoxy)propyl]lithium[31] in ether (13 mmol) at −78 °C. After being stirred for 30 min, the mixture was allowed to warm up to room temperature. A solution of sodium methoxide in methanol (2 M, 13 mL) was added, and then the solution was heated to reflux for 2 h. The reaction mixture was poured into aqueous HCl (0.5 M, 100 mL) and stirred vigorously for 15 min. The resulting boronic acid was extracted three times with a 40-mL portion of ether, washed with brine (40 mL), and dried over $MgSO_4$. After evaporation of solvent, butanol (40 mL) was added to the residue. Distillation gave the boronate in a yield of 94% (2.73 g): bp 64–68 °C (0.06 mmHg); ^1H NMR δ 0.893 (t, 3 H, J = 6.5 Hz), 0.92 (t, 3 H, J = 6.5 Hz), 1.1–1.6 (m, 8 H), 1.6–1.8 (m, 2 H), 2.2–2.3 (m, 4 H), 3.87 (t, 2 H, J = 6.1 Hz), 4.00 (t, 2 H, J = 5.3 Hz), 6.01 (t, 1 H, J = 5.3 Hz).

2-(3-Pyridyl)-1,3,2-dioxaboronane. A 100-mL flask was charged with 3-bromopyridine (42 mmol) and 80 mL of ether. A solution of butyllithium in hexane (28 mL of 1.5 M, 42 mmol) was added at −78 °C over 30 min. After being stirred for 30 min, the mixture was slowly warmed up to −35 °C. The precipitation of yellow solid, presumably lithiopyridine, was observed. The mixture was cooled again to −78 °C, and then trimethoxyborane (42 mmol) was added over a period of 0.5 h. After the cold bath was repacked, the mixture was stirred and allowed to warm up to room temperature overnight. 1,3-Propanediol (42 mmol) was added at 0 °C, and the solution was stirred for 1 h. Then, the mixture was treated with methanesulfonic acid (42 mmol) at 0 °C for 30 min. To the mixture was added Celite (ca 10 g), and the solution was stirred thoroughly at room temperature. The solid was filtered off, and the filtrate was evaporated to dryness to give the crude boronate. The product was dissolved in benzene (200 mL) and filtered of some insoluble solid, and the filtrate was evaporated to give the desired pyridylboronate. This was finally recrystallized from 40 mL of ethyl acetate at −15 °C with a yield of 60% (4.08 g); mp 96 °C (in air); ^1H NMR δ 1.80–2.20 (m, 2 H), 4.17 (t, 4 H, J = 5.7 Hz), 7.05–7.25 (m, 1 H), 7.85–8.05 (m, 1 H), 8.45–8.60 (m, 1 H), 8.90 (s, 1 H).

Alkenyl and Aryl Triflates. Phenyl, 4-bromophenyl, 4-nitrophenyl, 2-naphthyl, 3-pyridyl, and 4-methoxyphenyl trifluoromethanesulfonates (triflate) and 4-((trifluoromethanesulfonyl)oxy)coumarin were prepared from the corresponding phenols by the reported procedures.[6b,9] The following triflates were also prepared according to the literature methods: 4-*tert*-butylcyclohexenyl triflate,[6a,9b] 3-methyl-2-buten-2-yl triflate,[32] ethyl (*Z*)-3-((trifluoromethanesulfonyl)oxy)-2-butenoate,[7] ethyl 2-((trifluoromethanesulfonyl)oxy)cyclopentenecarboxylate,[7] 2-methyl-3-((trifluoromethanesulfonyl)oxy)-2-cyclopentenone,[33] (2-hydroxymethyl)cyclopentenyl triflate,[7] 4-((trifluoromethanesulfonyl)oxy)-1,2-dihydronaphthalene,[9b,25] and 2-((trifluoromethanesulfonyl)oxy)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene.[9b,34]

Reaction Conditions (Tables I and II). The best conditions for the preparation of octylbenzene were determined by the following general procedures.

Palladium catalyst (0.025 mmol) and powdered K_3PO_4 (1.5 mmol) were added to a flask equipped with a reflux condenser and a septum inlet. The flask was flushed with nitrogen and charged with 4 mL of solvent. One millimole of phenyl triflate and a solution of 9-octyl-9-BBN in THF (1 M, 1.1 mmol) were added by means of a hypodermic syringe through the septum inlet. Then, the mixture was stirred at the temperature indicated in Table I. The yields based on phenyl triflate were monitored by GC analysis using heptadecane as an internal standard.

In the same way, the reaction of 9-octyl-9-BBN (1 M solution in THF, 1.1 mmol) with phenyl triflate (1 mmol) in dioxane (5 mL) was carried out at 85 °C for 24 h in the presence of $Pd(PPh_3)_4$ (0.025 mmol), lithium or potassium halide (1.1 or 3 mmol), and K_3PO_4 (1.5 mmol). GC yields are summarized in Table II.

Effect of Boron Reagent. To a flask were added $Pd(PPh_3)_4$ (0.025 mmol) and K_3PO_4 (1.5 mmol), and the flask was flushed with nitrogen. Dioxane (5 mL), 1-hexenylboron compound in THF (1 M, 1.1 mmol), and 4-*tert*-butylcyclohexenyl triflate (1 mmol) were added, and the mixture was stirred at 85 °C for 5 h. The residual borane was oxidized with 3 M NaOH (0.5 mL) and 30% H_2O_2 (0.5 mL) at room temperature for 1 h. The 1-hexenylboron reagents and GC yields of 4-*tert*-butyl-1-[(*E*)-1-hexenyl]cyclohexene were as follows: (*E*)-1-hexenyl-1,3,2-benzodioxaborole (79%), 9-BBN (83%), disiamylborane (3%), dicyclohexylborane (2%), and boronic acid (33%).

Relative Reactivity of Triflates. To a mixture of bromobenzene (0.5 mmol), phenyl triflate (0.5 mmol), $Pd(PPh_3)_4$ (0.025 mmol), and K_3PO_4 (1.5 mmol) in dioxane (5 mL) was added a solution of 9-octyl-9-BBN in THF (1 M, 0.5 mmol), and then the solution was stirred at 85 °C for 5 h. The mixture was diluted with benzene (10 mL) and treated with 3 M NaOAc (1 mL) and 30% H_2O_2 (0.5 mL) at room temperature for 1 h. GC analysis of the reaction mixture indicated the formation of octylbenzene (0.49 mmol) and the recoveries of bromobenzene (0.12 mmol) and phenyl triflate (0.33 mmol).

The same reaction of 9-octyl-9-BBN with a mixture of iodobenzene (0.5 mmol) and phenyl triflate (0.5 mmol) under the above conditions gave iodobenzene (trace), phenyl triflate (0.3 mmol), and octylbenzene (0.45 mmol). The material balance indicates that some of phenyl triflate is consumed for reasons that are not well understood.

A similar cross-coupling reaction between 9-octyl-9-BBN in THF (1 M, 1 mmol) and 4-bromophenyl triflate (1.0 mmol) in dioxane (5 mL) at 85 °C for 5 h in the presence of $Pd(PPh_3)_4$ (0.025 mmol) and K_3PO_4 (1.5 mmol) gave 4-octylphenyl triflate (77%) and 1,4-dioctylbenzene (3%). However, we did not observe the formation of any detectable amount of 4-octylbromobenzene.

Methyl 5-(4-Octylphenyl)-2,2-dimethylpentanoate. To a solution of 9-BBN in THF (0.5 M, 1.1 mmol) was added methyl 2,2-dimethyl-4-pentenoate (1 mmol) at 0 °C, and the mixture was stirred for 16 h at room temperature. Dioxane (4 mL), K_3PO_4 (3 mmol), $Pd(PPh_3)_4$ (0.025 mmol), and finally 4-bromophenyl triflate (1 mmol) were added to the above borane solution. After 5 h of stirring at 65 °C, 9-octyl-9-BBN in THF (1 M, 1.1 mmol) was added at room temperature. The mixture was stirred at 85 °C for an additional 5 h. The residual borane was oxidized with 3 M NaOAc (1 mL) and 30% H_2O_2 (0.8 mL) for 1 h at room temperature. The product was isolated in 74% yield (0.246 g) by chromatography over silica gel with hexane/ether = 40/1: IR 1735 cm^{-1}; ^1H NMR δ 0.87 (t, 3 H, J = 5.6 Hz), 1.15 (s, 6 H), 1.20–1.40 (m, 12 H), 1.40–1.70 (m, 4 H), 2.48 (t, 4 H, J = 5.6 Hz), 3.63 (s, 3 H), 7.07 (s, 4 H); MS, *m/e* 159 (5), 216 (88), 273 (10), 300 (100), 332 (3); exact mass calcd for $C_{22}H_{36}O_2$ 332.2715, found 332.2714.

General Procedure for the Cross-Coupling of 9-Alkyl-9-BBN with Triflates (Table III). An oven-dried flask equipped with a reflux condenser and a septum inlet was flushed with nitrogen and charged with a solution of 9-BBN (0.5 M, 1.1 mmol) and then alkene (1.1 mmol) at 0 °C. The mixture was warmed up slowly to room temperature and stirred for 4–6 h to give a solution of 9-alkyl-9-BBN.

Procedure A. To the above solution were added dioxane (4 mL), powdered K_3PO_4 (1.5 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), and aryl or 1-alkenyl triflate (1 mmol). The mixture was heated at 85 °C for 5–16 h. The mixture was diluted with hexane or benzene (ca. 10 mL) at room temperature, and the residual borane was oxidized with 3 M NaOH (0.5 mL) and 30% H_2O_2 (0.5 mL) for 1 h. The product was extracted, washed with brine, dried over $MgSO_4$, and finally isolated by chromatography over silica gel.

Procedure B. To the borane solution obtained above were added additional THF (3 mL), powdered K_3PO_4 (1.5 mmol), $PdCl_2(dppf)$ (0.025 mmol), and aryl or 1-alkenyl halide (1 mmol). The mixture was stirred under reflux for 5–16 h. The workup procedure is same as the procedure A.

The compounds prepared by the above procedures are as follows.

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(31) Gardette, M.; Alekxakis, A.; Normant, J. F. *Tetrahedron* **1984**, *40*, 2741–2750.

(32) Stang, P. J.; Dueber, T. E. *Org. Synth.* **1974**, *54*, 79–84.

(33) Stang, P. J.; Treptow, W. *J. Med. Chem.* **1981**, *24*, 468.

(34) Bentz, H.; Subramanian, L. R.; Hanack, M. *Tetrahedron Lett.* **1977**, 9–12.

Octylbenzene and 2-Octylnaphthalene. The products were directly compared with authenic samples.[2a]

(10-Carbomethoxydecanyl)benzene: IR (film) 1740 cm^{-1}; ^{1}H NMR δ 1.28 (br s, 12 H), 1.4–1.7 (m, 4 H), 2.30 (t, 2 H, *J* = 7.6 Hz), 2.60 (t, 2 H, *J* = 7.4 Hz), 3.66 (s, 3 H), 7.1–7.3 (m, 5 H); MS, *m/e* 91 (100), 104 (46), 135 (19), 226 (23), 244 (80), 245 (83), and 276 (15); exact mass calcd for $C_{18}H_{28}O_2$ 276.2089, found 276.2073.

4-(3-Phenoxypropyl)anisole: mp 60.4 °C; ^{1}H NMR δ 1.86–2.23 (m, 2 H), 2.76 (t, 2 H, *J* = 7.5 Hz), 3.78 (s, 3 H), 3.94 (t, 2 H, *J* = 6.3 Hz), 6.7–7.3 (m, 9 H); MS, *m/e* 121 (89), 148 (41), 242 (100); exact mass calcd for $C_{16}H_{13}O_2$ 242.1307, found 242.1314.

3-[5,5-(Ethylenedioxy)hexyl]pyridine: ^{1}H NMR δ 1.30 (s, 3 H), 1.4–1.8 (m, 6 H), 2.62 (t, 2 H, *J* = 7.1 Hz), 3.92 (s, 4 H), 7.0–7.2 (m, 1 H), 7.35–7.50 (m, 1 H), 8.44 (br s, 2 H); MS, *m/e* 87 (100), 92 (11), 106 (7), 135 (8), 206 (10); exact mass calcd for $C_{13}H_{19}O_2N$ 221.1416, found 221.1392.

1,2-Dimethyl-2-undecene: ^{1}H NMR δ 0.88 (t, 3 H, *J* = 5.5 Hz), 1.26 (br s, 12 H), 1.63 (s, 9 H), 2.00 (t, 2 H, *J* = 7.0 Hz); MS *m/e* 83 (100), 97 (25), 125 (6), 182 (81); exact mass calcd for $C_{13}H_{26}$ 182.2034, found 182.2016.

Methyl 11-(4-*tert*-butylcyclohexenyl)undecanoate: IR (film) 1746 cm^{-1}; ^{1}H NMR δ 0.86 (s, 9 H), 1.27 (br s, 16 H), 1.5–2.1 (m, 9 H), 2.31 (t, 2 H, *J* = 7.3 Hz), 3.66 (s, 3 H), 5.38 (br s, 1 H); MS, *m/e* 41 (100), 185 (30), 230 (11), 248 (29), 280 (42), 305 (16), 336 (6); exact mass calcd for $C_{22}H_{40}O_2$ 336.3028, found 336.3024.

Ethyl (2*Z*,6*E*)-3,7,11-trimethyl-2,6,10-dodecatrienoate: Ir (film) 1722 and 1655 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.26 (t, 3 H, *J* = 7.3 Hz), 1.60 (s, 3 H), 1.62 (s, 3 H), 1.68 (s, 3 H), 1.89 (d, 3 H, *J* = 0.98 Hz), 1.95–2.01 (m, 2 H), 2.03–2.09 (m 2 H), 2.14–2.21 (m, 2 H), 2.65 (t, 2 H, *J* = 7.3 Hz), 4.14 (q, 2 H, *J* = 7.3 Hz), 5.09 (t, 1 H, *J* = 7.3 Hz), 5.17 (t, 1 H, *J* = 7.3 Hz), 5.65 (d, 1 H, *J* = 0.97 Hz); MS, *m/e* 42 (100), 69 (61), 81 (31), 121 (33), 149 (19), 191 (16), 221 (20), 264 (16); exact mass calcd for $C_{17}H_{28}O_2$ 264.2089, found 264.2065. The product was directly compared with an authentic (2*E*,6*E*)-isomer.[2a]

2-[5,5-(Ethylenedioxy)hexyl]-1,7,7-trimethylbicyclo[2.2.1]-hept-2-ene: ^{1}H NMR (400 MHz) δ 0.74 (s, 3 H), 0.76 (s, 3 H), 0.93 (s, 3 H), 1.31 (s, 3 H), 1.39–1.49 (m, 5 H), 1.61–1.67 (m, 2 H), 1.75–1.83 (m, 1 H), 1.90–1.97 (m, 2 H), 2.19 (t, 1 H, *J* = 3.4 Hz), 3.93 (m, 4 H), 5.50 (m, 1 H); MS, *m/e* 87 (100), 128 (35), 173 (33), 188 (12), 201 (34), 217 (82), 263 (13), 278 (7); exact mass calcd for $C_{18}H_{30}O_2$ 278.2246, found 278.2255.

Methyl 5-(2-carbomethoxycyclopentyl)-2,2-dimethylpentanoate: IR (film) 1735, 1712, 1641 cm^{-1}; ^{1}H NMR δ 1.16 (s, 6 H), 1.29 (t, 3 H, *J* = 7.1 Hz), 1.4–2.0 (m, 6 H), 2.3–2.5 (m, 6 H), 3.65 (s, 3 H), 4.18 (q, 2 H, *J* = 7.1 Hz); MS, *m/e* 41 (100), 121 (58), 135 (56), 149 (58), 176 (25), 189 (34), 204 (48), 223 (13), 236 (50), 282 (5); exact mass calcd for $C_{16}H_{26}O_4$ 282.1831, found 282.1837.

4-(3,3-Diethoxypropyl)coumarin: IR (film) 1725, 1613, 1608, 1590 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.24 (t, 6 H, *J* = 7.3 Hz), 2.01 (m, 2 H), 2.88 (t, 2 H, *J* = 7.3 Hz), 3.55 (q, 2 H, *J* = 7.3 Hz), 3.69 (q, 2 H, *J* = 7.3 Hz), 4.60 (t, 1 H, *J* = 5.1 Hz), 6.30 (s, 1 H), 7.27–7.36 (m, 2 H), 7.48–7.56 (m, 1 H), 7.69 (dd, 1 H, *J* = 7.8 and 1.5 Hz); MS, *m/e* 116 (91), 160 (65), 185 (100), 232 (34), 276 (1); exact mass calcd for $C_{16}H_{20}O_4$ 276.1361, found 276.1383.

2-[5,5-(Ethylenedioxy)hexyl]-1-octylnaphthalene (7). A mixture of $Cl_2Pd(dppf)$ (0.075 mmol), 1-iodo-2-naphthol (3 mmol), 9-octyl-9-BBN in THF (1 M, 3.3 mmol), and aqueous 3 M NaOH (3 mL) in THF (12 mL) was refluxed for 24 h. The product was extracted with benzene, washed with water, dried over $MgSO_4$, and finally isolated by chromatography over silica gel with benzene in 62% yield (0.476 g). **6**: IR (film) 3350, 1625, 1603, 1590, 825, 740 cm^{-1}; ^{1}H NMR δ 0.871 (t, 3 H, *J* = 6.5 Hz), 1.1–1.8 (m, 12 H), 3.02 (t, 2 H, *J* = 6.8 Hz), 4.80 (s, 1 H), 6.9–7.9 (m, 6 H); MS, *m/e* 157 (100), 181 (21), 207 (27), 256 (76). Alternatively, the cross-coupling of 9-octyl-9-BBN with 1-iodo-2-(methoxymethoxy)naphthalene under the similar conditions gave a 72% yield of 2-(methoxymethoxy)-1-octylnaphthalene which was quantitatively deprotected to **6** by treatment with a catalytic amount of HCl in methanol at room temperature.

To a suspension of NaH (1.9 mmol) in ether (4.5 mL) was added a solution of 1-octylnaphthol (**6**) (1.5 mmol) in ether at 0 °C. After 3 h of stirring at room temperature, trifluoromethanesulfonic acid anhydride (1.5 mmol) was added, and the mixture was refluxed overnight. The mixture was treated with water (15 mL), and then the product was extracted with ether, washed with 5% NaOH, and dried over $MgSO_4$. Isolation by chromatography over silica gel with hexane gave the corresponding triflate in 93% yield.

To a solution of 9-BBN in THF (0.5 M, 1.1 mmol) was added 5,5-(ethylenedioxy)-1-hexene[2a] (1.1 mmol) at 0 °C, and the mixture was stirred for 5 h at room temperature. Dioxane (5 mL), $Pd(PPh_3)_4$ (0.025 mmol), K_3PO_4 (1.5 mmol), and 1-octyl-2-naphthyl triflate (1 mmol) were then added. After being heated at 85 °C for 24 h, the mixture was treated with aqueous 3 M NaOH (0.5 mL) and 30% H_2O_2 (0.5 mL) for 1 h. The product was extracted with benzene, washed with water, and dried over $MgSO_4$. Chromatography over silica gel with benzene gave **7** in 82% yield (0.313 g): ^{1}H NMR (400 MHz) δ 0.89 (t, 3 H, *J* = 6.9 Hz), 1.25–1.41 (m, 8 H), 1.33 (s, 3 H), 1.47–1.58 (m, 4 H), 1.59–1.74 (m, 6 H), 3.94 (m, 4 H), 7.28 (d, 1 H, *J* = 8.3 Hz), 7.92 (t, 1 H, *J* = 7.8 Hz), 7.47 (t, 1 H, *J* = 7.8 Hz), 7.62 (d, 1 H, *J* = 8.3 Hz), 7.78 (d, 1 H, *J* = 7.8 Hz), 8.01 (d, 1 H, *J* = 8.3 Hz); MS, *m/e* 87 (100), 320 (13), 338 (5), 367 (4), 382 (11); exact mass calcd for $C_{26}H_{38}O_2$ 382.2872, found 382.2845.

General Procedure for the Cross-Couplings of Aryl- and 1-Alkenylboron Compounds with Triflates (Table IV). A mixture of aryl- or 1-alkenylboron compound (1.1 mmol), aryl or 1-alkenyl triflate (1 mmol), $Pd(PPh_3)_4$ (0.025 mmol), and K_3PO_4 (1.5 mmol) in dioxane (5 mL) was heated to 85 °C for 5–16 h. The mixture was diluted with benzene (10 mL) and treated with aqueous 3 M NaOH (0.5 mL) and 30% H_2O_2 (0.5 mL) for 1 h at room temperature to oxidize the residual borane. The product was extracted with hexane or benzene, washed with brine, and dried over $MgSO_4$. Isolation by column chromatography over silica gel gave following compounds.

(*Z*)-2-Phenyl-2-heptene,[3c] **4-methylbiphenyl,**[4a] **3-(4-methoxyphenyl)pyridine,**[4a] **and 4-nitro-4′-methylbiphenyl**:[1] we reported previously the syntheses of these compounds.

(4*E*)-2,3-Dimethyl-2,4-nonadiene: ^{1}H NMR δ 0.90 (t, 3 H, *J* = 6.5 Hz), 1.2–1.5 (m, 4 H), 1.76 (s, 9 H), 2.0–2.2 (m, 2 H), 5.57 (dt, 1 H, *J* = 6.5 and 15.4 Hz), 6.49 (d, 1 H, *J* = 15.4 Hz); MS, *m/e* 67 (100), 109 (69), 123 (8), 137 (10), 152 (86); exact mass calcd for $C_{11}H_{20}$ 152.1565, found 152.1536.

2-[(*E*)-3-(*tert*-Butyldimethylsiloxy)-1-octenyl]-2-carbethoxycyclopentene: IR (film) 1712, 1642, 1600 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.03 (s, 3 H), 0.06 (s, 3 H), 0.876 (t, 3 H, *J* = 7.3 Hz), 0.892 (s, 9 H), 1.30 (t, 3 H, *J* = 7.3 Hz), 1.21–1.59 (m, 8 H), 1.85 (m, 2 H), 2.63 (t, 2 H, *J* = 7.3 Hz), 2.70 (t, 2 H, *J* = 7.3 Hz), 4.21 (q, 2 H, *J* = 7.3 Hz), 4.18–4.25 (m, 1 H), 5.86 (dd, 1 H, *J* = 6.8 and 15.6 Hz), 7.30 (d, 1 H, *J* = 15.6 Hz); ^{13}C NMR δ −4.75, −4.15, 14.05, 14.41, 18.27, 21,25, 22.62, 24.93, 25.93, 31.82, 34.33, 34.44, 38.31, 59.84, 73.76, 124.36, 129.11, 140.98, 151.39, 165.97; MS, *m/e* 323 (100), 351 (19), 380 (3); exact mass calcd for $C_{22}H_{40}O_3Si$ 380.2747, found 380.2758. Anal. Calcd for $C_{22}H_{40}O_3Si$: C, 69.49; H, 10.60. Found: C, 69.34; H, 10.62.

3-[(*E*)-3-(*tert*-Butyldimethylsiloxy)-1-octenyl]-2-methyl-2-cyclopentenone: IR (film) 1700, 1650, 1613 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.04 (s, 3 H), 0.07 (s, 3 H), 0.89 (t, 3 H, *J* = 6.8 Hz), 0.92 (s, 9 H), 1.24–1.41 (m, 6 H), 1.50–1.58 (m, 2 H), 1.79 (s, 3 H), 2.42 (m, 2 H), 2.63 (m, 2 H), 4.31 (m, 1 H), 6.23 (dd, 1 H, *J* = 5.4 and 15.6 Hz), 6.76 (d, 1 H, *J* = 15.6 Hz); ^{13}C NMR δ −4.75, −4.41, 8.05, 14.01, 18.25, 22.57, 24.80, 25.66, 25.75, 25.86, 31.82, 33.67, 38.04, 72.81, 123.12, 136.41, 141.31, 163.48, 209.82; MS, *m/e* 75 (100), 223 (18), 265 (39), 279 (67), 321 (4), 336 (21); exact mass calcd for $C_{20}H_{36}O_2Si$ 336.2485, found 336.2504. Anal. Calcd for $C_{20}H_{36}O_2Si$: C, 71.44; 10.79. Found C, 70.98; H, 11.02.

5,5-Dimethyl-3-[(*E*)-1-hydroxy-4-nonen-4-yl]-2-cyclohexenone: IR (film) 3425, 1705, 1670, 1618 cm^{-1}; ^{1}H NMR δ 0.87 (t, 3 H, *J* = 7.3 Hz), 1.08 (s, 6 H), 1.22–1.35 (m, 4 H), 1.56–1.64 (m, 3 H), 2.00 (q, 2 H, *J* = 7.3 Hz), 2.23 (s, 2 H), 2.23 (t, 2 H, *J* = 7.3 Hz), 2.27 (s, 2 H), 3.63 (t, 2 H, *J* = 6.3 Hz), 5.34 (t, 1 H, *J* = 7.3 Hz), 5.81 (s, 1 H); ^{13}C NMR δ 13.95, 22.35, 28.35, 28.64, 31.14, 32.06, 32.17, 33.89, 43.31, 51.06, 62.05, 128.35, 128.64, 139.43, 160.93, 199.91; MS, 42 (100), 207 (43), 221 (22), 246 (7), 264 (27); exact mass calcd for $C_{17}H_{28}O_2$ 264.2089, found 264.2076.

1-(Hydroxymethyl)-2-(4-methoxyphenyl)cyclopentene: ^{1}H NMR δ 1.49 (br s, 1 H), 2.01 (q, 2 H, *J* = 7.0 Hz), 2.5–2.9 (m, 4 H), 3.81 (s, 3 H), 4.30 (s, 2 H), 6.87 (d, 2 H, *J* = 9.0 Hz), 7.19 (d, 2 H, *J* = 9.0 Hz); MS, *m/e* 108 (69), 121 (52), 147 (74), 158 (26), 173 (62), 186 (20), 204 (100); exact mass calcd for $C_{13}H_{16}O_2$ 204.1151, found 204.1178.

1,2-Dihydro-4-(4-methylphenyl)naphthalene: ^{1}H NMR δ 2.30 (s, 3 H), 2.2–2.5 (m, 2 H), 2.76 (t, 2 H, $J = 7.1$ Hz), 5.97 (t, 1 H, $J = 4.6$ Hz), 6.9–7.3 (m, 8 H); MS, *m/e* 205 (62), 220 (100); exact mass calcd for $C_{17}H_{16}$ 220.1252, found 220.1280.

Intramolecular Cross-Coupling (Eqs 9 and 10). 4-Methoxyindan (11). To a solution of 9-BBN in THF (0.5 M, 1.1 mmol) was added triflate **10** (0.97 mmol) at 0 °C, and the solution was stirred for 6 h at room temperature. Additional THF (4 mL), $Cl_2Pd(dppf)$ (0.025 mmol), and K_3PO_4 (1.5 mmol) were added, and the mixture was refluxed for 10 h. The mixture was treated with 3 M NaOH (0.5 mL) and 30% H_2O_2 (0.5 mL) for 0.5 h at room temperature. The organic phase was washed with brine and dried over $MgSO_4$. The product **11** was isolated by chromatography over silica gel with hexane/ether = 20/1 in 74% yield (0.106 g): ^{1}H NMR δ 1.9–2.2 (m, 2 H), 2.7–3.0 (m, 4 H), 3.82 (s, 3 H), 6.6–7.3 (m, 3 H); MS, *m/e* 117 (100), 133 (17), 147 (31), 148 (79); exact mass calcd for $C_{10}H_{12}O$ 148.0888, found 148.0878.

2,3-Trimethylene-3-carbomethoxycycloheptene (14). To a solution of lithium diisopropylamide (4.4 mmol) in dimethoxyethane (DME) (12 mL) was added a solution of 2-allyl-2-carbomethoxycycloheptanone (4 mmol) in DME (8 mL) at −78 °C. Then, a solution of $PhN(Tf)_2$ (4.28 mmol) in DME (8 mL) was added. After 30 min at −78 °C, the mixture was allowed to stand at 0 °C for overnight. The reaction mixture was diluted with benzene, washed with aqueous 10% $NaHCO_3$ and brine, and finally dried over $MgSO_4$. Chromatography over silica gel with hexane/ether = 30/1 gave **13** in 60% yield (0.854 g); IR (film) 1742, 1678, 1645 cm^{-1}; ^{1}H NMR δ 1.60–1.81 (m, 2 H), 1.88–2.30 (m, 4 H), 2.50–2.69 (m, 2 H), 3.75 (s, 3 H), 5.0–5.8 (m, 3 H), 6.01 (t, 1 H, $J = 6.4$ Hz); MS, *m/e* 193 (11), 209 (100), 268 (5), 342 (9).

A solution of 9-BBN in THF (0.5 M, 1.1 mmol) and triflate **13** (1.0 mmol) was mixed at 0 °C, and the mixture was stirred for 6 h at room temperature. Dioxane (5 mL), K_3PO_4 (1.5 mmol), and $Pd(PPh_3)_4$ (0.025 mmol) were added. This was stirred at 85 °C for overnight (ca. 15 h), cooled to room temperature, and diluted with benzene (30 mL). The resulting solution was washed with brine, dried, and chromatographed over silica gel with hexane/ether = 20/1 to give a oil in 76% yield (0.148 g). **14**: IR (film) 1732 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.21–1.32 (m, 1 H), 1.42 (m, 1 H), 1.51–1.74 (m, 5 H), 1.79–1.87 (m, 1 H), 1.95–2.16 (m, 3 H), 2.17–2.23 (m, 1 H), 2.31–2.41 (m, 1 H), 2.45–2.53 (m, 1 H), 3.71 (s, 3 H), 5.79 (m, 1 H); MS, *m/e* 135 (100), 178 (2), 194 (13); exact mass calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1307.

Supplementary Material Available: Proton NMR spectra (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.