Notes

Synthesis and Selective Transformations of 1-Alkenyl-4-alkyl Diboronates

Guillaume Desurmont,† Stacey Dalton,†
Dean M. Giolando,† and Morris Srebnik*,‡

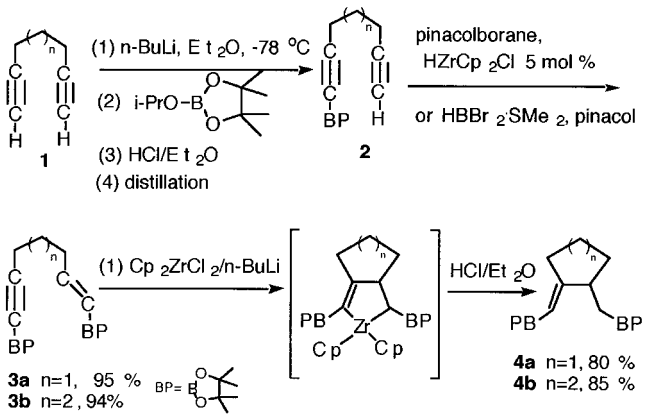
Department of Chemistry, University of Toledo, Toledo, Ohio 43606, and Department of Natural Products, Hebrew University in Jerusalem, P.O. Box 1172, Ein Kerem Jerusalem 91010, Israel

Received April 8, 1997

Organoboranes offer a wealth of transformations of the C−B bond.[1] Highly selective reactions are possible at C_{sp^3}−B and C_{sp^2}−B bonds. In general, the C_{sp^2}−B bond undergoes reactions under more mild conditions. This is especially true of transition metal catalyzed reactions such as the Suzuki−Miyaura cross-coupling reaction of alkenyl/aryl halides with alkenyl/arylboranes[2] or transmetalations of organoboranes to zinc or copper.[3] Thus the likelihood of selective and sequential reactions of C_{sp^3}−B bonds in the presence of C_{sp^2}−B bonds in the same molecule is high. Compounds containing C_{sp^3}−B and C_{sp^2}−B bonds in the same carbon skeleton have not been described before.[4] This paper describes the synthesis of 1-alkenyl-4-alkyl diboronates, **4**, and several selective and sequential transformations.

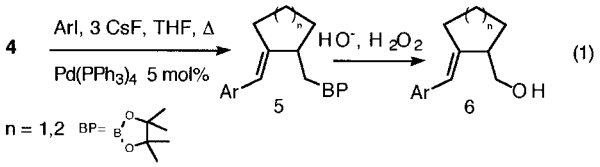
Synthesis of **4** started with lithiation of diyne **1** (excess) with *n*-BuLi followed by treatment with pinacol isopropyl borate to give **2**. Excess diyne **1** was removed under high vacuum. Distillation then provided **2**. Hydroboration of **2** with either pinacolborane catalyzed by $HZrCp_2Cl$[5] or with $HBBr{\cdot}SMe_2$ followed by treatment with pinacol furnished **3**, from which **4** was obtained by reductive cyclization with Negishi's reagent followed by treatment with anhydrous HCl in ether (Scheme 1).[6,7] No attempt was made to isolate and characterize the borazirconocycles at this point.[8] A notable feature in the ^1H NMR spectra of **4a** and **4b** is the upfield multiplets of the

Scheme 1. Synthesis of 4



diastereotopic H4 hydrogens which establishes that cyclization had indeed taken place. On the other hand, the methyl hydrogens of the dioxaborolane rings in both **4a** and **4b** absorb as singlets at δ 1.20 and 1.21, respectively. Compounds **4** are moisture- and air-stable liquids and could be purified by silica gel chromatography.

A possible reaction exploiting the different reactivity of the two boron groups in **4** would be Suzuki−Miyaura coupling.[2] In this regard, CsF has recently been used by Wright et al. in boronic acid coupling reactions.[9] We have also found CsF very useful.[10] To our gratification, Suzuki−Miyaura coupling of **4** with 1 equiv of aryl iodide occurred exclusively at the C_{sp^2}−B bond to give **5** (eq 1).[11] The results with various aryl iodides are summarized in Table 1. While many transformations of C_{sp^3}−B bonds are possible[1] the most facile is without a doubt oxidation. Thus, oxidation of **5** (HO^-, H_2O_2) quantitatively provided **6** (eq 1), demonstrating that sequential transformation of the two boron moieties in **4** is indeed feasible. Results are reported in Table 1. The sequence of **4** to **6** is the first example, to our knowledge, of selective and sequential transformations of two different C−B bonds in the same carbon skeleton.



In conclusion, we have developed a synthesis of novel molecules, **4**, which contain alkenyl and alkyl boronates on the same carbon skeleton. They are useful compounds

† University of Toledo.
‡ Hebrew University.

(1) Matteson, Donald, S. *Stereodirected Synthesis with Organoboranes*; Springer; Berlin: 1995. (b) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988. (c) Mukhailov, B. M.; Bubnov, Yu. N. *Organoboron Compounds in Synthesis*; Harwood: Chur, 1984.

(2) Miyaura, N.; Suzuki, A. *Chem. Rev. (Washington, D.C.)* **1995**, *95*, 2457.

(3) From alkenylboranes to zinc: (a) Srebnik, M. *Tetrahedron Lett.* **1991**, *32*, 2449. (b) Oppolzer, W. O.; Radinov, R. N. *Helv. Chim. Acta* **1992**, *75*, 170. (c) Oppolzer, W. O.; Radinov, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1593. (d) Alkylboranes to zinc: Langer, F.; Waas, J.; Knochel, P. *Tetrahedron Lett.* **1993**, *34*, 5261. (Alkenyl)(dialkyl)boranes to copper: (e) Chu, K.-H.; Wang, K. K. *J. Org. Chem.* **1986**, *51*, 767. (f) Brown, H. C.; Molander, G. A. *J. Org. Chem.* **1981**, *46*, 647. (g) Ichikawa, J.; Hamada, S.; Sonoda, T.; Kobayashi, H. *Tetrahedron Lett.* **1992**, *33*, 337. (Dialkenyl)(chloro)boranes to copper: (h) Yatagai, H. *J. Org. Chem.* **1980**, *45*, 1640.

(4) (Alkenyl)(alkyl)boranes on the other hand are very common. Mikhailov, B. M.; Bubnov, Yu. N., ref 1c, Chapter 2.

(5) Pereira, S.; Srebnik, M. *Tetrahedron Lett.* **1996**, *37*, 3283.

(6) (a) Negishi, E.; Takahashi, T. *Acc. Chem. Res* **1994**, *27*, 124. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev. (Washington, D.C.)* **1988**, *88*, 1047.

(7) Reagents based on "Cp_2Ti" (Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422) or $Ti(O\text{-}i\text{-}Pr)_4/i$-PrMgCl (Urabe, H.; Hata, T.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 4261) did not give satisfactory yields of **4**.

(8) (a) We have recently synthesized and characterized acyclic borazirconocenes. For a review, see: Zheng, B.; Deloux, L.; Pereira, S.; Skrzypczak-Jankun, E.; Cheesman, B. V.; Sabat, M.; Srebnik, M. *J. Appl. Organomet. Chem.* **1996**, *10*, 267. (b) Nöth and Metzler have isolated and characterized by single-crystal X-ray analysis several bisdiboracyclopentadienyl zirconocycles. (a) Metzler, N.; Nöth, H.; Thomann, M. *Organometallics* **1993**, *12*, 2423. (b) Metzler, N. *Zur Synthesis, elktronischen Struktur und Reaktivität von Alkinylboranen*; Ludwig-Maximilians University; Munich, March 1994.

(9) Wright, S. F.; Hageman, D. L.; McClure, L. D. *J. Org. Chem.* **1994**, *59*, 6095.

(10) (a) Deloux, L.; Srebnik, M. *Tetrahedron Lett.* **1996**, *37*, 2735. (b) Deloux, L.; Srebnik, M. *J. Org. Chem.* **1995**, *60*, 3276.

(11) Aryl bromides were much less effective. Triflates were not tried.

S0022-3263(97)00629-4 CCC: $14.00

Table 1. Transformations of 1-Alkenyl-4-alkyl Diboronates 4

Entry	4	ArX	5,[a] Yield, % Isolated	6[b]
1	**4a**	phenyl iodide	**5a** 93	**6a**
2	**4a**	2-iodo-anisole	**5b** 85	**6b**
3	**4a**	2-thienyl iodide	**5c** 94	**6c**
4	**4b**	phenyl iodide	**5d** 91	**6d**
5	**4b**	4-iodo-anisole	**5e** 90	**6e**
6	**4b**	2-thienyl iodide	**5f** 94	**6f**
7	**4b**	4-iodotoluene	**5g** 93	**6g**

[a] Reaction conditions: **4**:ArX:CsF:$Pd(PPh_3)_4$ = 1:1:3:0.05, in refluxing THF for 12 h. [b] In each case the alcohols were obtained quantitatively as determined and GCMS and in >95% isolated yields, by oxidation of **5** with H_2O_2/NaOH.

that react selectively at the alkenylboronate moiety in a number of reactions such as Suzuki−Miyaura coupling to give **5**. The alkylboronate group can then be transformed as desired. In the present case, oxidation of **5** to the alcohols **6** was demonstrated. Other selective transformations of the alkenylboron group in the presence of the alkylboron group should be possible.[1] Since reductive cyclization of terminal alkynes with "$ZrCp_2$" is not feasible,[6,12] the current method provides access to a group of compounds not available by this method.

Experimental Section

Glassware, syringes, and needles were oven dried at 120 °C, assembled while hot, and dried under a flow of Ar. All reactions were done under a positive pressure of argon. Solvents were distilled from sodium benzophenone ketyl and used immediately. All ^{11}B, ^{13}C, and ^1H NMR spectra were recorded on a Varian VXR-400 spectrometer at 128.3, 100.6, and 400 MHz, respectively. Mass spectra were obtained on a GC/MS fitted with a 25 m methylsilicone column. GC analysis were obtained on a GC Hewlett-Packard Model 5790 A. Yields are summarized in Table 1.

Synthesis of 1-Alkenyl-4-alkyl Diboronates. The synthesis of **4a** is typical. To a stirred solution of 1,6-heptadiene (4.6 g, 50 mmol) in ether (150 mL) cooled to −78 °C was added dropwise *n*-BuLi (6.2 mL, 1.6 M, 10 mmol). After 30 min of additional stirring, this solution was added dropwise to a solution of isopropyl pinacol borate (1.86 g, 10 mmol) in ether (50 mL) likewise cooled to −78 °C and the mixture stirred for an additional 2 h. The mixture was quenched with anhydrous HCl/Et_2O (5 mL, 2 M). The solution was filtered, and volatiles were removed in vacuo. Distillation gave pure **2a**. Yield: 2.07 g, 9.5 mmol, 95%; $bp_{0.4}$ = 96 °C; ^1H NMR ($CDCl_3$) δ = 2.37 (t, J = 7.02 Hz, 2 H), 2.31−2.27 (m, 2 H), 1.93 (t, J = 2.63, 1 H), 1.73 (quintet, J = 7.04, 2 H), 1.24 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ = 103.52, 84.08, 83.22, 69.02, 26.99, 24.66, 18.63, 18.51, 17.57; ^{11}B NMR ($CDCl_3$) δ = 23.92; MS (EI) m/z (relative intensity) 218 (M^+, 0.06). **2a** (2.00 g, 9.17 mmol) in CH_2Cl_2 (10 mL) was hydroborated with $HBBr_2{\cdot}SMe_2$ (10 mL, 1 M in CH_2Cl_2 for 12 h at 25 °C). Pinacol (1.12 g, 9.5 mmol) was added and the reaction mixture stirred for 1 h. Volatiles were removed in vacuo, and the residue was extracted with hexanes to furnish **3a** after removal of the hexanes: yield 3.01 g, 8.7 mmol, 80%; ^1H NMR ($CDCl_3$) δ = 6.59−6.49 (m, 1 H), 5.40 (d, J = 17.83, 1 H), 2.26−2.15 (m, 2 H), 2.14−2.09 (m, 2 H), 1.59 (quintet, J = 7.32, 2 H), 1.21 (s, 24 H); ^{13}C NMR ($CDCl_3$) δ = 153.03, 106.12, 83.09, 68.49, 34.57, 27.01, 24.79, 24.75, 17.91; ^{11}B NMR ($CDCl_3$) δ = 30.23, 23.51; MS (EI) m/z (relative intensity) 346 (M^+, 0.23). Without further purification **3a** in THF (10 mL) was added quickly and in one portion to the zirconocene butenyl complex prepared from Cp_2ZrCl_2 (2.54 g, 8.7 mmol) and *n*-BuLi (10.9 mL, 17.4 mmol, 1.6 M in hexanes) in THF (20 mL) at −78 °C, containing 1,4-dioxane (34.8 mmol). The cold bath was removed, and after reaching room temperature the reaction was stirred for 12 h. It was then cooled to 0 °C, and anhydrous HCl in ether (10 mL, 20 mmol) was added followed by water. Ether was added and the organic layer separated and worked up in the usual manner to yield **4a**: yield 2.42 g, 6.95 mmol, 80%; ^1H NMR ($CDCl_3$) δ = 5.14 (s, 1 H), 2.66−2.60 (m, 1 H) 2.46−2.42 (m, 1 H), 1.90−1.88 (m, 1 H), 1.71−1.69 (m, 1 H), 1.51−1.46 (m, 1 H), 1.35−1.08 (m, 2 H), 1.20 (s, 24 H), 0.85−0.82 (t, J = 7.00 Hz, 1 H), 0.73−0.67 (q, J = 8.45, 1 H); ^{13}C NMR ($CDCl_3$) δ = 176.25, 106.39, 82.93, 82.43, 43.12, 34.25, 33.16, 24.90, 24.70, 23.97, 15.72; ^{11}B NMR ($CDCl_3$) δ = 33.33, 29.80; MS (EI) m/z (relative intensity): 348 (M^+, 0.01).

Preparation of **4b** was similar except that 1,7-octadiyne was used. **2b**: ^1H NMR ($CDCl_3$) δ = 2.34−2.29 (m, 2 H), 2.29−2.16 (m, 2 H), 1.95−1.94 (m, 1H), 1.67−1.64 (m, 4 H), 1.28 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ = 102.53, 83.93, 83.24, 68.49, 27.26, 26.87, 24.56, 19.01, 18.93, 17.80; ^{11}B NMR ($CDCl_3$) δ = 23.82; MS (EI) m/z (relative intensity): 217 (M^+ − 15, 0.33). **3b**: ^1H NMR ($CDCl_3$) δ = 6.67−6.58 (m, 1 H), 5.48 (d, J = 18.02, 1 H), 2.32−2.21 (m, 2 H), 2.18−2.23 (m, 2 H), 1.75−1.58 (m, 4 H), 1.26 (s, 24 H); ^{13}C NMR ($CDCl_3$) δ = 153.79, 119.07, 104.70, 83.96, 82.96, 35.11, 27.50, 27.29, 24.73, 24.68, 19.32; ^{11}B NMR ($CDCl_3$) δ = 30.08, 23.21; MS (EI) m/z (relative intensity) 360 (M^+, 0.18). **4b**: ^1H NMR ($CDCl_3$) δ = 5.00 (s, 1 H), 2.95−2.92 (m, 1 H), 2.33−2.30 (m, 1 H), 2.14−2.07 (m, 1 H), 1.80−1.76 (m, 1 H), 1.67−1.35 (m, 4 H), 1.22 (s, 12 H), 1.19 (s, 12 H), 1.19−1.00 (m, 1 H), 0.89−0.84 (m, 1 H), 0.81−0.76 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ = 170.67, 107.31, 82.90, 82.45, 42.71, 37.19, 33.02, 29.13, 25.34, 24.91, 24.87, 24.73, 24.71, 15.69; ^{11}B NMR ($CDCl_3$) δ = 32.92, 29.73; MS (EI) m/z (relative intensity): 347 (M^+ − 15, 0.01).

Procedure for Suzuki−Miyaura Coupling of 4. The reactions were run on a 0.5 mmol scale. Preparation of **5a** is typical. A solution of **4a** (0.5 mmol), 0.176 g in THF (5 mL), was treated with $Pd(PPh_3)_4$ (0.025 mmol, 0.029 g), CsF (1 mmol, 0.152 g), and phenyl iodide (0.5 mmol, 0.102 g). The reaction mixture was refluxed for 48 h, then diluted in hexanes, washed with brine, dried over Na_2SO_4, concentrated in vacuo, and chromatographed on silica gel to yield **5a** as an oil (0.139 g, 93%): ^1H NMR ($CDCl_3$) δ = 7.32−7.27 (m, 5 H), 6.28−6.26 (m, 1 H), 2.77−2.72 (m, 1 H), 2.68−2.53 (m, 2 H), 1.99−1.93 (m, 1 H), 1.89−1.84 (m, 1 H), 1.68−1.60 (m, 1 H), 1.27 (s, 6 H), 1.26 (s, 6 H), 1.33−1.20 (m, 2 H), 0.98−0.92 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ = 152.06, 139.05, 128.12, 125.54, 120.04, 120.03, 83.04, 42.35, 34.33, 31.27, 24.97, 24.80, 24.63, 16.12; ^{11}B NMR ($CDCl_3$) δ = 33.33; MS (EI) m/z (relative intensity): 298 (M^+, 0.78).

5b: ^1H NMR ($CDCl_3$) δ = 7.28−7.25 (m, 1 H), 7.12−7.07 (m, 1 H), 6.86−6.76 (m, 1 H), 6.47−6.43 (m, 1 H), 3.74 (s, 3 H), 2.73−2.65 (m, 1 H), 2.52−2.47 (m, 2 H), 1.95−1.86 (m, 1 H), 1.78−1.71 (m, 1 H), 1.19 (s, 6 H), 1.18 (s, 6 H), 1.29−1.14 (m, 2 H), 1.93−0.85 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ = 156.60, 151.88, 128.81, 128.11, 126.85, 120.05, 114.26, 110.34, 82.97, 55.42, 41.97, 34.45, 31.16, 24.97, 24.71, 16.95; ^{11}B NMR ($CDCl_3$) δ = 33.52; MS (EI) m/z (relative intensity): 326 (M^+, 0.72).

5c: ^1H NMR ($CDCl_3$) δ = 7.13−7.11 (m, 1 H), 6.94−6.92 (m, 1 H), 6.83−6.82 (m, 1 H), 6.46−6.42 (m, 1 H), 2.68−2.63 (m, 1 H), 2.57−2.37 (m, 2 H), 1.91−1.83 (m, 2 H), 1.64−1.51 (m, 1 H), 1.19 (s, 6 H), 1.18 (s, 6 H), 1.27−1.17 (m, 1 H), 1.13−1.08 (m, 1 H), 0.88−0.82 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ = 150.64, 143.18, 126.79, 124.66, 123.65, 113.68, 83.07, 42.10, 34.96, 31.80, 24.96, 24.79, 24.49, 16.35; ^{11}B NMR ($CDCl_3$) δ = 33.15; MS (EI) m/z (relative intensity): 304 (M^+, 0.78).

5d: ^1H NMR ($CDCl_3$) δ = 6.17 (s, 1 H), 2.58−2.55 (m, 1 H), 2.43−2.40 (m, 1 H), 2.02−1.99 (m, 1 H), 1.80−1.77 (m, 1 H),

(12) Negishi, E. In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon Press: New York, 1991; Vol. 5, p 1163.

1.73−1.66 (m, 1 H), 1.54−1.24 (m, 4 H), 1.17 (s, 12 H),1.11 (q, J = 7.32, 1 H), 0.86 (q, J = 7.54, 1 H); ^{13}C NMR ($CDCl_3$) δ = 147.62, 138.91, 129.02, 127.92, 125.64, 119.86, 82.98, 40.92, 37.11, 28.63, 28.37, 24.90, 24.85, 15.75; ^{11}B NMR ($CDCl_3$) δ = 34.45; MS (EI) m/z (relative intensity): 312 (M^+, 0.87).

5e: ^{1}H NMR ($CDCl_3$) δ = 7.06−7.02 (m, 2 H), 6.86−6.83 (m, 2 H), 6.18 (s, 1 H), 3.79 (s, 1 H), 2.58−2.52 (m, 1 H), 2.41−2.38 (m, 1 H), 2.04−1.96 (m, 1 H), 1.79−1.77 (m, 1 H), 1.68−1.61 (m, 1 H), 1.59−1.26 (m, 4 H) 1.24 (s, 12 H), 0.90−0.86 (m, 1 H), 0.86−0.82 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ = 146.50, 146.49, 131.40, 130.05, 119.29, 113.40, 82.95, 55.24, 40.88, 37.06, 28.52, 28.32, 24.89, 24.85, 15.83; ^{11}B NMR ($CDCl_3$) δ = 35.01; MS (EI) m/z (relative intensity): 342 (M^+, 0.61).

5f: ^{1}H NMR ($CDCl_3$) δ = 7.17−7.15 (m, 1 H), 6.97−6.95 (m, 1 H), 6.87−6.86 (m, 1 H), 6.30 (s, 1 H), 2.88−2.83 (m, 1 H), 2.52−2.47 (m, 1 H), 2.28−2.25 (m, 1 H), 1.87−1.82 (m, 1 H), 1.74−1.66 (m, 1 H), 1.58−1.51 (m, 2 H), 1.49−1.43 (m, 2 H), 1.23 (s, 12 H), 1.26−1.12 (m, 1 H), 0.97−0.91 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ = 147.81, 141.35, 126.60, 126.18, 123.56, 112.89, 83.04, 41.16, 37.07, 29.33, 28.02, 24.89, 24.72, 16.02; ^{11}B NMR ($CDCl_3$) δ = 34.27; MS (EI) m/z (relative intensity): 318 (M^+, 0.59).

5g: ^{1}H NMR ($CDCl_3$) δ = 7.22−6.98 (m, 4 H), 6.13 (s, 1 H), 2.59−2.54 (m, 1 H), 2.45−2.39 (m, 1 H), 2.25 (s, 3 H), 2.02−1.97 (m, 1 H), 1.81−1.73 (m, 1 H), 1.68−1.64 (m, 1 H), 1.50−1.25 (m, 4 H), 1.16 (s, 12 H), 1.16−1.08 (m, 1 H), 0.88−0.86 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ = 147.04, 135.93, 128.91, 128.64, 127.92, 119.71, 82.96, 40.91, 37.09, 28.60, 28.35, 24.90, 24.85, 21.12, 16.21; ^{11}B NMR ($CDCl_3$) δ = 33.71; MS (EI) m/z (relative intensity): 326 (M^+, 1.0).

Preparation of 6. Preparation of **6a** is typical. A solution of **5a** (30 mg, 0.082 mmol) in 1 mL of THF was treated with 1.1 equiv of H_2O_2 (30% w/w) at 0 °C. The ice bath was removed, and the reaction mixture was stirred overnight at 25 °C, extracted with ether, washed with brine, and dried over Na_2SO_4 to give **6a** (GC yield: 92%) as a colorless oil which was purified on two analytical silica gel plates: isolated yield 15 mg, 0.078 mmol, 95%; ^{1}H NMR ($CDCl_3$) δ = 7.34 (m, 5 H), 6.39 (m, 1 H), 3.69 (m, 2H), 2.89−2.79 (m, 1 H), 2.73−2.54 (m, 2 H), 1.97−1.80 (m, 2 H), 1.78−1.69 (m, 1H), 1.69−1.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 150.29, 146.75, 138.27, 128.25, 126.16, 122.44, 65.47, 48.75, 31.70, 28.68, 25.10; IR (NaCl) cm^{-1} = 3413.

6b: ^{1}H NMR ($CDCl_3$) δ = 7.35−7.33 (m, 1 H), 7.23−7.19 (m, 1 H), 6.96−6.93 (m, 1 H), 6.89−6.87 (m, 1 H), 6.61 (s, 1 H), 3.85 (s, 3 H), 3.75−3.65 (m, 2 H), 2.87−2.83 (m, 1 H), 2.57−2.53 (m, 2 H), 1.95−1.92 (m, 1 H), 1.84−1.81 (m, 1 H), 1.72−1.58 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ = 152.73, 143.08, 126.11, 124.80, 124.52, 117.65, 114.45, 108.22, 65.10, 55.43, 48.47, 32.33, 29.74, 26.17; IR (NaCl) cm^{-1} = 3413.

6c: ^{1}H NMR ($CDCl_3$) δ = 2.27−2.24 (m, 1 H), 7.04−7.02 (m, 1 H), 6.96−6.95 (m, 1 H), 6.64−6.63 (m, 1 H), 3.70−3.68 (m, 2 H), 2.82−2.78 (m, 1 H), 2.68−2.53 (m, 2 H), 1.94−1.90 (m, 2 H), 1.88−1.79 (m, 1 H), 1.66−1.62 (m, 1 H), 1.58−1.52 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ = 145.05, 142.28, 126.91, 125.58, 124.41, 115.75, 65.09, 48.52, 32.11, 29.33, 24.83; IR (NaCl) cm^{-1} = 3383.

6d: ^{1}H NMR ($CDCl_3$) δ = 7.45−7.21 (m, 5 H), 6.34−6.31 (m, 1 H), 3.94−3.90 (m, 1 H), 3.72−3.66 (m, 1 H), 2.47−2.45 (m, 2 H), 2.43−2.29 (m, 1 H), 1.90−1.83 (m, 1 H), 1.64−1.40 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ = 142.56, 137.79, 129.04, 128.09, 126.22, 123.72, 63.97, 47.33, 30.13, 27.81, 27.27, 23.45; MS (EI) m/z (relative intensity): 202 (M^+, 0.28); IR (NaCl) cm^{-1} = 3383.

6e: ^{1}H NMR ($CDCl_3$) δ = 7.16−7.14 (m, 2 H), 6.88−6.85 (m, 2 H), 6.27 (s, 1 H), 3.91−3.89 (m, 1 H), 3.88 (s, 3 H), 3.67−3.64 (m, 2 H), 2.48−2.42 (m, 1 H), 2.33−2.31 (m, 2 H), 1.82−1.80 (m, 1 H), 1.67−1.52 (m, 3 H), 1.51−1.46 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ = 158.03, 141.78, 130.27, 130.15, 123.30, 113.55, 63.93, 55.28, 47.30, 30.07, 27.75, 27.14, 23.41; MS (EI) m/z (relative intensity): 232 (M^+, 0.14); IR (NaCl) cm^{-1} = 3413.

6f: ^{1}H NMR ($CDCl_3$) δ = 7.22−7.20 (m, 1 H), 7.00−6.98 (m, 1 H), 6.94−6.93 (m, 1 H), 6.40 (s, 1 H), 3.89−3.84 (m, 1 H), 3.68−3.67 (m, 1 H), 2.74−2.69 (m, 1 H), 2.50−2.45 (m, 2 H), 1.80−1.44 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ = 142.03, 140.26, 127.05, 126.70, 124.23, 116.63, 64.00, 47.55, 30.07, 27.93, 27.44, 23.20; MS (EI) m/z (relative intensity): 208 (M^+, 0.28); IR (NaCl) cm^{-1} = 3413.

6g: ^{1}H NMR ($CDCl_3$) δ = 7.17−7.09 (m, 4 H), 6.30 (s, 1 H), 3.94−3.86 (m,1 H), 3.72−3.63 (m, 1 H), 2.52−2.43 (m, 2 H), 2.35 (s, 3 H), 2.37−2.29 (m, 1 H), 1.88−1.77 (m, 1 H), 1.68−1.36 (m, 6 H); ^{13} C NMR ($CDCl_3$) δ = 141.90, 135.91, 129.04, 128.94, 128.09, 123.67, 63.95, 47.32, 30.09, 27.77, 27.22, 23.43, 21.15; MS (EI) m/z (relative intensity): 216 (M^+, 0.33); IR (NaCl) cm^{-1} = 3415.

Acknowledgment. The authors acknowledge the University of Toledo for a teaching fellowship (G.D.) and the State of Ohio Academic Challenges Program for providing funds for a high-field NMR spectrometer. Special thanks go to Dr. Craig Blankenship of Boulder Scientific for generous quantities of $ZrCp_2Cl_2$, to Dr. N. G. Bhat for very helpful discussions regarding the chemistry of alkenyl boronates, and to Mr. Alex Spivak for his unselfish devotion to maintaining the lab.

JO970629T