

# Zirconocene-Mediated Preparation of 1,3-, 1,4-, and 2,3-Dibora-1,3-butadienes: Their Isolation and Characterization and Use in Suzuki–Miyaura Coupling

Guillaume Desurmont, Rita Klein, Stefan Uhlenbrock, Eric Laloë, Laurent Deloux,<sup>1</sup> Dean M. Giolando, Yong Wah Kim, Schubert Pereira,<sup>2</sup> and Morris Srebnik<sup>\*,3</sup>

Department of Chemistry, University of Toledo, Toledo, Ohio 43606

Received March 7, 1996<sup>®</sup>

Hydrozirconation of 1-alkynyl pinacolboronates, **1**, with HZrCp<sub>2</sub>Cl provides *gem*-borazirconocenes **2**. The latter when treated with CuBr gives the homocoupled (1*E*,3*E*)-2,3-dibora-1,3-butadienes, **3**, in good yield (62–67%). The reaction works even for hindered **2** (R = *t*-Bu). Structure **3** was assigned on the basis of NMR. Suzuki–Miyaura coupling of **3a** (R = *n*-Bu) with PhI in the presence of CsF leads to the replacement of both boron groups by phenyl and hydrogen to give **6** in 76% yield. Zirconocene-mediated coupling of **1** leads to diastereomeric products: (1*E*,3*E*)-1,3-dibora-1,3-butadienes, **4**, in 7–26% isolated yields and (1*E*,3*E*)-1,4-dibora-1,3-butadienes, **5**, in 17–34% isolated yields. The two isomers can be separated by selective precipitation of **5** from the reaction mixture in pentane (–20 °C) followed by silica gel chromatography to give pure **4**. The reaction does not work when R in **1** is the *t*-Bu group. Assignments of structures for **4** and **5** were done on the basis of 1D and 2D NMR experiments. In addition, a single-crystal X-ray analysis of **5a** showed it to be a highly planar and linearly oriented molecule. Suzuki–Miyaura coupling of **4a** proceeded to replace the terminal boron group exclusively, while the internal boron group of **4a** remained intact.

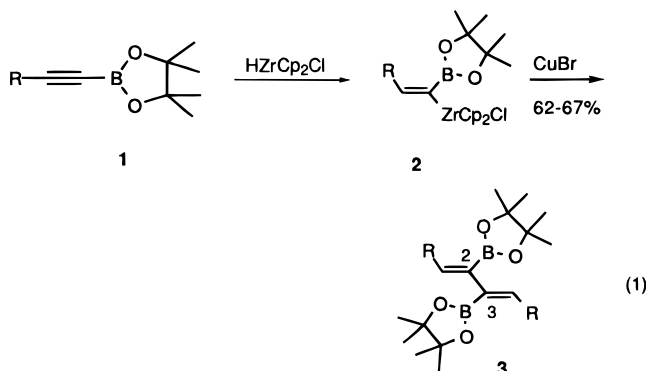
Various dibora compounds bridged by one, two, or three carbons have been prepared and characterized.<sup>4</sup> Dibora compounds have found use in specifically binding guest molecules.<sup>5</sup> They have also been explored as chiral Lewis acids containing two Lewis acid binding sites.<sup>6</sup> Intriguing diboraheterocycles have been synthesized from the acyclic precursors.<sup>7</sup> Boronic esters and acids are very useful in the Suzuki–Miyaura cross-coupling reaction.<sup>8</sup> The use of a dibora species in that reaction has not been reported.

As part of our program utilizing zirconocene-mediated synthesis of new boronic esters,<sup>9</sup> we were interested in preparing a series of 1,3-, 1,4- and 2,3-dibora compounds from 1-alkynyl pinacolboronates, **1**. We envisioned that 2,3-dibora compounds could be obtained from *gem*-borazirconocenes<sup>10</sup> by copper-mediated coupling.<sup>11</sup> Since the coupling is known to proceed with retention of

stereochemistry, only a single diastereomeric 2,3-dibora-1,3-butadiene would be expected. The 1,3- and 1,4-dibora compounds would be accessible by zirconocene-mediated carbon–carbon bond formation<sup>12</sup> of suitable 1-alkynyl boronates.

## Results and Discussion

**Synthesis and Isolation.** When a solution of a *gem*-borazirconocene, **2**, prepared from **1** by hydrozirconation, was treated with CuBr in THF, the yellow color was discharged and coupling occurred to provide 2,3-dibora-1,3-butadienes, **3** (eq 1). They were isolated by



silica gel chromatography in good yields (Table 1). Compounds **3** are stable to water and air and did not

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, July 1, 1996.

(1) Present address: BASF Aktiengesellschaft, ZKP/Forschung Polyolefine und PVC, 67056 Ludwigshafen, Germany.

(2) Present address: Fresh Products Inc., 4010 South Av, Toledo, OH 43615.

(3) Address from September 1996: Department of Natural Products, Hebrew University in Jerusalem, POB 12272, Jerusalem 91120, Israel.

(4) Some leading references are as follows: (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834. (b) Matteson, D. S. *Synthesis* **1975**, 147. (c) Krämer, A.; Pritzkow, H.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 927. (d) Katz, H. E. *Organometallics* **1987**, *6*, 1134.

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**Table 1. (1*E*,3*E*)-2,3-Dibora-1,3-butadienes, 3**

entry	R	H(1)/H(4), mult, <i>J</i> (Hz)	B(2)/ B(3) <sup>a</sup>	C(1)/ C(4)	C(2)/ C(3) <sup>b</sup>	yield, % <sup>c</sup>
a	<i>n</i> -Bu	6.01, t, 7.90	30.6	143.6,	135.7	65
b	<i>t</i> -Bu	5.91, s	30.7	149.9	131.1	59
c	Ph(CH <sub>2</sub> ) <sub>2</sub>	6.08, t, 8.64	30.3	143.1	136.2	67
d	Ph(CH <sub>2</sub> ) <sub>3</sub>	6.05, t, 7.96	29.7	143.3	136.2	65
e	Cl(CH <sub>2</sub> ) <sub>3</sub>	5.91, t, 7.60	30.1	142.1	136.9	64
f	cyclopentyl	5.87, d, 9.52	30.6	148	133.9	62

<sup>a</sup> Relative to BF<sub>3</sub>·etherate. <sup>b</sup> Due to the boron quadrupole, C(2) resonances are all broad and of low intensity. <sup>c</sup> Isolated.

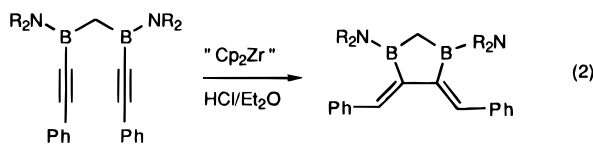
**Table 2. (1*E*,3*E*)-1,4-Dibora-1,3-butadienes, 5**

entry	R	H(1)/H(4), mult	B(1)/ B(4) <sup>a</sup>	C(1)/ C(4) <sup>b</sup>	C(2)/ C(3)	yield, % <sup>c</sup> (GC)
a	<i>n</i> -Bu	5.49, s	30.3	115.6	164.6	34 (52)
c	Ph(CH <sub>2</sub> ) <sub>2</sub>	6.08, s	30.3	117.0	162.9	17 (43)
e	Cl(CH <sub>2</sub> ) <sub>3</sub>	5.55, s	30.9	117.5	161.6	24 (31)
f	cyclopentyl	4.94, s	30.6	114.0	171.3	28 (31)
g	phenyl	5.40, s	30.5	123.6	160.6	33 (52)

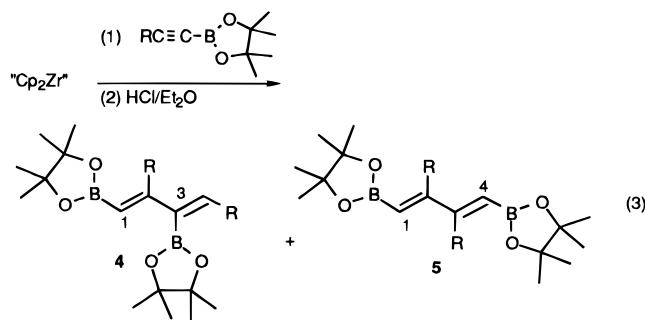
<sup>a</sup> Relative to BF<sub>3</sub>·etherate. <sup>b</sup> Due to the boron quadrupole, C(2) resonances are all broad and of low intensity. <sup>c</sup> Isolated.

isomerize or decompose on prolonged heating to 150 °C under an inert atmosphere.

Recently, Nöth and co-workers prepared two 1,3-bis-(dialkylamino)-*cis*-bis(4,5-phenylmethylidene)-1,3-diborolane derivatives using zirconocene-mediated coupling of methylene-bridged bis(alkynyl)boranes.<sup>13</sup> Since the alkynes were tethered, only one product was obtained (eq 2).

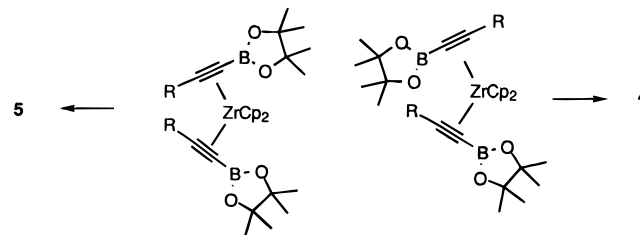


We tried zirconocene-induced coupling on a series of 1-alkynyl pinacolboronates. In our case, two regioisomers were obtained: **4** and **5** (eq 3). No 2,3-dibora-1,3-

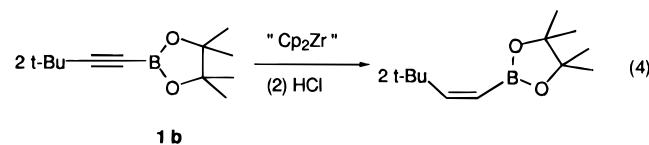


butadienes, **3**, were detected. This is in contrast to the reported coupling of (1-(trimethylsilyl)phenyl)acetylene in the presence of zirconocene which gave only the 1,4-disilyl product.<sup>14</sup> Hafnium- and titanium-induced coupling of other silylacetylenes also yielded exclusively 1,4-disilyl products.<sup>15</sup> Thus the regioselectivity observed in our case is in agreement with placing the more bulky substituents away from the newly formed carbon-

carbon bond,<sup>16</sup> since it is generally thought that sterics dominate in the ring-closure step.<sup>14</sup> The pinacolboronate moiety is apparently too large to provide 2,3-diborabutadienes when other less hindered insertion pathways are available.



In agreement with this hypothesis was our inability to ring close **1b** (R = *t*-Bu). One equivalent of **1b** did indeed complex with zirconocene as evidenced by obtaining the *cis-tert*-butylalkenyl pinacolboronate<sup>17</sup> after HCl workup. However when 2 equiv of **1b** was used, only the *cis-tert*-butylalkenyl pinacolboronate again could be detected by GCMS and no ring-closure product was detected (eq 4). Generally, essentially 1:1 mixtures



of **4** and **5** were obtained (Experimental Section). This would present a formidable problem in isolation since the *R<sub>f</sub>* values of **4** and **5** are rather similar. Fortunately, we discovered considerable difference in their solubility in hydrocarbon solvents. Thus treatment of the crude reaction mixture containing **4** and **5** with either hexanes or pentane resulted in precipitation of pure **5**, leaving **4** in solution. The latter could then be easily purified by silica gel chromatography. Yields of combined **4** and **5** were high (Tables 2 and 3). After some experimentation we found that the addition of 4 equiv of 1,4-dioxane improved yields considerably.<sup>18</sup> As was the case with butadienes **3**, butadienes **4** and **5** are very stable to air, water, and heat. Prolonged heating at 150 °C or more under an inert atmosphere did not cause any noticeable deterioration or isomerization. Furthermore, no equilibration of **4** and **5** occurred under the conditions of the reaction. Either pure **4** or **5** (R = *n*-Bu) was recovered unchanged after stirring with 1 equiv of Cp<sub>2</sub>Zr in THF at 25 °C for 48 h.

**Structure Determination.** Hydrozirconation is known to occur in a syn manner.<sup>19</sup> Since coupling of 1-alkenylzirconocenes proceeds with retention of stereochemistry,<sup>11</sup> (2*E*,3*E*)-butadienes, **3**, would be the expected products of homocoupling of **2**. NMR data are consistent with this assignment. Thus only two <sup>13</sup>C resonances in the alkene region of **2** were observed, with the broadening of C(1) due to the boron quadrupole. C-(1)/C(4) resonances (~143–148 ppm) in **3** are at a much

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(18) THF was the solvent of choice. Additives such as TMEDA or HMPTA in various proportions were not as effective as 1,4-dioxane. The ratio of **4**:**5** was independent of solvent or additive.

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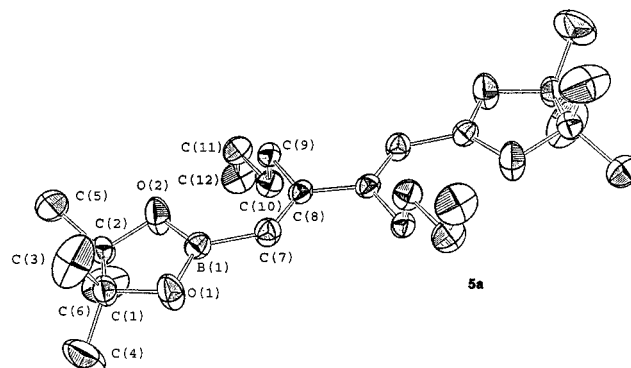
**Table 3. (1E,3E)-1,3-Dibora-1,3-butadienes, 4**

entry	R	H(1)	H(4), mult <i>J</i> (Hz)	B(1)/B(3) <sup>a</sup>	C(1) <sup>b</sup>	C(2)	C(3) <sup>b</sup>	C(4)	yield, % <sup>c</sup> (GC)
a	<i>n</i> -Bu	5.16, s	6.21, t, 7.7	30.6	114.8	166.8	137.8	144.51	26 (39)
c	Ph(CH <sub>2</sub> ) <sub>2</sub>	5.26, s	6.34, t, 7.7	30.8	116.0	165.3	137.5	143.5	7 (36)
e	Cl(CH <sub>2</sub> ) <sub>3</sub>	5.28, s	6.19, t, 7.7	30.9	116.8	164.1	138.4	142.6	15 (60)
f	cyclopentyl	5.06, s	5.88, d, 9.9	30.3	114.8	171.8	134.8	151.6	34 (45)
g	phenyl	5.76, s	6.91, s	30.7	118.9	162.3	140.0	142.9	16 (43)

<sup>a</sup> Relative to BF<sub>3</sub>·etherate. <sup>b</sup> Due to the boron quadrupole, C(2) resonances are all broad and of low intensity. <sup>c</sup> Isolated.

lower field than that observed for C(1)/C(4) in butadiene (117.5 ppm), while C(2)/C(3) resonances are in the same range (135–136 ppm) as the C(2)/C(3) resonance in butadiene (137.2 ppm). The downfield shift of C(1)/C(4) can be accounted for by  $\pi$ -back-bonding of the CC double bond with the formally empty  $p_z$  orbital on boron. The deshielding of C(2)/C(3) is governed primarily by mesomeric ( $\pi$ ) effects, while C(1)/C(4) resonances remain relatively unchanged due to competitive  $\pi$ -back-bonding between the oxygen atoms and boron.<sup>20</sup> Peak count is also consistent with the symmetrical nature of **3**. The <sup>11</sup>B values (~30 ppm) indicate considerable B–C(pp) $\pi$  interaction leading to coplanarity of the dioxaborolane ring with the butadiene system (*vide infra*).<sup>21</sup> With **3** in hand, assignment of symmetrical **5**<sup>22</sup> was straightforward (Table 2). The H1/H4 resonances in **5** were all singlets as expected. The C(2)/C(3) peaks are at a much lower field than the resonances observed in **3** while the C(1)/C(4) is shifted upfield and absorbs in the same range as butadiene. This can be accounted for by the same reasoning used to explain the shifts in **3**.<sup>19</sup> Since the <sup>11</sup>B values of **5** are consistent with considerable B–C(pp) $\pi$  interaction and since **5** were all crystalline solids, we decided to determine the structure of **5a** in the solid state.

A search of the Cambridge Crystallographic data base indicated that **5a**<sup>23</sup> is the first reported structure for a 1,4-dibora-1,3-butadiene system. The asymmetric unit in **5a** consists of a five membered heterocyclic ring that is bonded to the terminal atom of the butadiene moiety (C(7)). Attached to the second carbon atom of this unit (C(8)) is an *n*-butyl group. The second half of the molecule is generated by a crystallographic inversion center resulting in a trans position of the ring systems (Figure 1). All bond distances and angles are in good



**Figure 1.** ORTEP drawing of **5a** with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg.): O(1)–C(1), 1.457(4); O(1)–B(1), 1.358(4); O(2)–C(2), 1.470(4); O(2)–B(1), 1.369(4); C(1)–C(2), 1.553(4); C(1)–C(3), 1.513(5); C(1)–C(4), 1.530(5); C(2)–C(5), 1.516(5); C(2)–C(6), 1.522(5); C(7)–C(8), 1.360(4); C(7)–B(1), 1.547(5); C(1)–O(1)–B(1), 108.9(2); C(2)–O(2)–B(1), 107.1(2); O(1)–C(1)–C(2), 102.5(2); O(1)–C(1)–C(3), 105.8(3); O(1)–C(1)–C(4), 107.3(3); C(2)–C(1)–C(3), 113.2(3); C(2)–C(1)–C(4), 115.6(3); C(3)–C(1)–C(4), 111.3(3); O(2)–C(2)–C(1), 103.2(2); O(2)–C(2)–C(5), 105.7(2); O(2)–C(2)–C(6), 107.0(3); C(1)–C(2)–C(5), 116.5(3); C(1)–C(2)–C(6), 113.8(3); C(5)–C(2)–C(6), 109.7(3); C(8)–C(7)–B(1), 128.5(3); O(1)–B(1)–O(2), 112.9(3); O(1)–B(1)–C(7), 120.9(3); O(2)–B(1)–C(7), 126.2(3).

agreement with the values quoted for similar structures.<sup>21</sup> The heterocyclic ring system exhibits a slight envelope conformation with O(1)–B(1)–O(2)–C(1) in the plane and the remaining carbon atom out of the plane (0.36 Å for C(2)). The most prominent feature of this molecule is its high planarity and linearity (see Supporting Information). Least-squares calculations for the plane consisting of B(1), O(1), C(1), C(2), O(2), C(7), and C(8) showed a maximum deviation of 0.15 Å for C(2). The average distance for these atoms from this plane is just 0.06 Å. An additional calculation of the dihedral angle between the planar part of the heterocyclic ring and the BC=CC olefin part revealed a value of 4.48°. In a zirconocene dioxaborolane 1,1-bimetallic compound<sup>21</sup> this angle was found to be close to 90°. The high planarity in **5a** is most likely caused by conjugation effects. Furthermore, it is noteworthy that the distance between B(1) and C(7), the first carbon atom of the butadiene moiety, exhibits with 1.547(5) Å the same bond length as an sp<sup>3</sup>-hybridized boron atom to an alkyne unit in an amino-alkynylborane.<sup>24</sup> The thermal stability of **5a**, its flatness, and linearity would appear to make it an excellent candidate for evaluation as a liquid crystal.<sup>25</sup> The UV of **5a**,  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>) = 266 ( $\epsilon$  = 17 247), is consistent with an *s-transoid* conformation in solution.

(20) Cheesman, B. V.; Deloux, L.; Srebnik, M. *Magn. Reson. Chem.* **1995**, *33*, 724.

(21) The degree of coplanarity is determined by sterics. We have shown that, in **2b** (R = *t*-Bu), the plane of the dioxaborolane ring is tilted almost 90° to the plane of the alkene: Zheng, B.; Deloux, L.; Skrzypczak-Jankun, E.; Cheesman, B. V.; Pereira, S.; Sabat, M.; Srebnik, M. *J. Mol. Struct.* **1996**, *374*, 291.

(22) Compounds **5** represent a new diborabutadiene system. However, Metzler and Nöth have reported a zirconocycle incorporating a 1,4-dibora-1,3-butadiene: Metzler, N. *Zur Synthese, elektronischen Struktur und Reaktivität von Alkynylboranen*; Ph.D. dissertation, Ludwig-Maximilians-Universität; München, Germany, 1994.

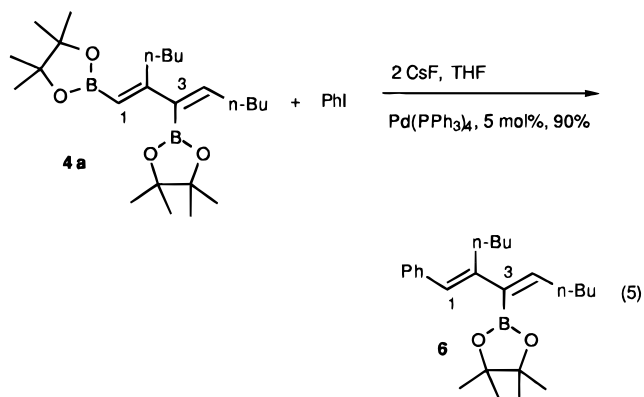
(23) Crystal data for **5a** (C<sub>24</sub>H<sub>14</sub>B<sub>2</sub>O<sub>2</sub>):  $M_r$  = 418.24; monoclinic, space group  $P2_1/n$  with  $a$  = 6.377(1) Å,  $b$  = 17.103(2) Å,  $c$  = 12.266(4) Å,  $\beta$  = 94.26(2)°,  $V$  = 1334.0 Å<sup>3</sup>,  $\rho$  = 1.07 g cm<sup>−3</sup>,  $Z$  = 2,  $F(000)$  = 460, Enraf Nonius CAD 4 diffractometer. The structure was solved by direct methods. Data were collected at 190 K with Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å). Data were corrected for Lorentz and polarization effects as well as for decay (0.1%) and absorption [empirical,  $T_{\text{min}}$  = 0.96,  $T_{\text{max}}$  = 0.99,  $\mu$  = 0.6 cm<sup>−1</sup>]. From 2896 measured and 2654 unique reflections, 1389 reflections were considered "observed" [ $F_o > 3\sigma(F_o)$ ] and used for refinement. All non-H atoms were refined with anisotropic displacement parameters. All H atoms were calculated and allowed to ride on their corresponding carbon atom with fixed isotropic contributions ( $U_{\text{iso}}(\text{fix}) = 1.3 U_{\text{eq}}$  bonding atom). The structure converted for 136 refined parameters to an  $R$  ( $R_w$ ) value of 0.063 (0.076). The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , with  $w = 4F_o^2/\sigma^2(F_o^2)$ .

(24) Metzler, N.; Nöth, H. *Chem. Ber.* **1995**, *128*, 711.

(25) Giroud-Godquin, A.-M.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375.

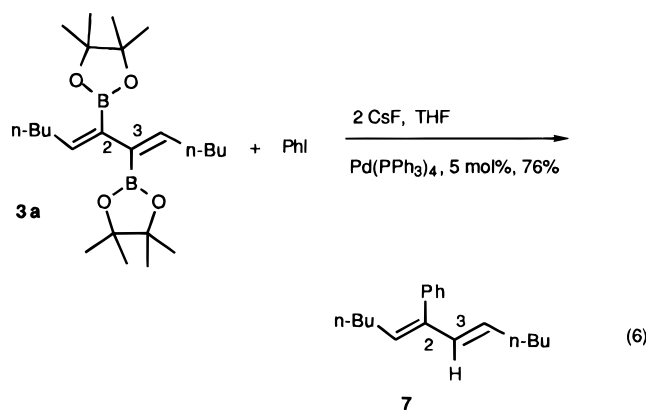
Unlike the highly crystalline **5**, butadienes **4**, which constitute a new dibora-1,3-butadiene system, were oils whose structures were determined by NMR analysis (Table 3). The unsymmetrical nature of **4** was evident from the multiple peaks in their  $^{13}\text{C}$  spectra.  $^1\text{H}$  NMR spectra of **4** indicated two vinylic protons: one a singlet and the other a multiplet (except **4g**,  $\text{R} = \text{Ph}$ , which was also a singlet).  $^{13}\text{C}$  NMR of **4** showed four peaks attributable to the butadiene unit, two of which were broad resonances of low intensity due to boron quadrupolar relaxation. These were assigned to C(1)/C(3). Correlation and specific assignments were then determined by  $^{13}\text{C}$ – $^1\text{H}$  HETCOR experiments (Table 3). Thus C(1) in **4** absorbs in the same range ( $\sim 115$  ppm) as it does in **5** (Table 2), and C(3) in **4** ( $\sim 137$  ppm) is similar to **3** (Table 1), due to analogous arguments outlined above.  $^{11}\text{B}$  NMR spectra of **4** ( $\sim 30$  ppm) again indicated a high degree of orbital interaction.

**Suzuki–Miyaura coupling** has proven to be a highly successful method for CC bond formation.<sup>8</sup> Since our dibora-1,3-butadiene systems are novel, it was of interest to see if the boron groups could be differentiated in the Suzuki–Miyaura coupling reaction. Suzuki–Miyaura coupling of a dibora species has not been reported before. Compounds **3a** and **4a** were investigated since the boron groups on **5** would not be expected to show chemoselectivity. Reaction of **4a** with 1 equiv of  $\text{PhI}$ , 2 equiv of  $\text{CsF}$ ,<sup>26</sup> and 5 mol %  $\text{Pd}(\text{PPh}_3)_4$  in THF (reflux 2 days), yielded only one product **6** (eq 5), in



which differentiation of the two boron atoms indeed had occurred, with coupling only at the less hindered boron on C(1). The assignment of **6** follows from its NMR spectra. H(1) in **4a** (5.19, s) is shifted downfield in **6** (6.38 ppm) whereas H(4) in **4a** (6.21 ppm) remains almost unchanged in **6** (6.20 ppm). In  $^{13}\text{C}$ , the broad resonance of C(1) in **4a** (114.8 ppm) disappeared while the C(3) peak in **4a** (137.8 ppm) shifted slightly in **6** (135.1 ppm).  $^{13}\text{C}$ – $^1\text{H}$  HETCOR experiments on **6** also confirmed the connectivity of the new CC bond.

Suzuki–Miyaura coupling of **3a** under the same conditions as for **4a** did not lead to the desired replacement of one boron group by phenyl and retention of the other boron. Rather, concomitant hydrogenation of the 3-boryl group led to **7** (eq 6). The salient features of the  $^1\text{H}$  NMR spectra of **7** are the loss of the pinacol methyl groups and the loss of symmetry in going from **3a** to **7** as can be discerned from the three vinylic



protons, H(3) 6.23 (d,  $J = 16.5$  Hz), H(1) 5.58 (t,  $J = 8.23$  Hz), H(4) 5.11 (dt,  $J = 16.5$  and  $8.23$  Hz) in **7**.

The three systems described in this paper offer intriguing possibilities. The planarity of **5a** and its very oriented shape suggest potential for liquid crystal properties. Selective Suzuki–Miyaura coupling is possible for **4**. Sequential coupling is being investigated in this respect. Additional studies are being conducted with **3** to achieve replacement of one boron group and retention of the other.

## Experimental Section

Glassware, syringes, and needles were oven dried at  $120^\circ\text{C}$ , assembled while hot, and dried under a flow of Ar. All reactions were done under a positive pressure of Ar. Solvents were distilled from sodium benzophenone ketyl and used immediately. All  $^{11}\text{B}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$  NMR spectra were recorded on a Varian VXR-400 spectrometer at 128.3, 100.6, and 400 MHz. 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. Compounds **1** were synthesized according to the literature.<sup>27</sup> X-ray structure analysis of **5a** was done on a Enraf Nonius CAD 4 diffractometer. UV/vis spectra were obtained on a Hewlett Packard 8452 A diode array spectrophotometer. Microanalysis was performed in-house on a Perkin-Elmer 2400 CHN elemental analyzer.

**General Procedure for the Preparation of 3.** The preparation of **3a** is typical. To a stirred suspension of  $\text{Cp}_2\text{ZrCl}(\text{H})$ <sup>28</sup> (1.05 mmol, 0.271 g) in dry THF at  $25^\circ\text{C}$  under an atmosphere of Argon was added **1a** (0.208 g, 1 mmol) in THF (5 mL). The reaction was stirred for an additional 30 min until it turned clear and became orange in color. After the addition of  $\text{CuBr}$  (1 mmol, 0.143 g) the reaction mixture was stirred for 10 h to give the desired product, with the deposition of metallic copper. The reaction mixture was then quenched with an aqueous solution of saturated ammonium chloride, filtered, and extracted twice with hexanes. The organic solutions were combined, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated. Chromatography of the residue on silica (5% ether/hexane) afforded **3a** (0.135 g, 65%) as an oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 5.97$  (t,  $J = 7.90$  Hz, 2 H), 2.25 (q,  $J = 7.25$  Hz, 4 H), 1.35–1.26 (m, 8 H), 1.25 (s, 24 H), 0.89 (t,  $J = 7.03$  Hz, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 143.6$ , 135.7, 83.0, 32.2, 31.5, 24.9, 22.3, 14.0.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 30.6$ . MS (EI)  $m/z$  (relative intensity): 418 ( $\text{M}^+$ , 0.66).

**3b. Preparation** as described for the general procedure using **1b** (0.208 g, 1 mmol) provided **3b** as crystals obtained from hexanes by slow evaporation, as a solid (0.113 g, 59%).

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Mp: 208 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.91 (s, 2 H), 1.28 (s, 24 H), 1.04 (s, 18 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 149.9, 83.4, 34.3, 30.3, 25.2.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.7. MS (EI)  $m/z$  (relative intensity): 403 ( $\text{M}^+ - 15$ , 0.09). Anal. Calcd for  $\text{C}_{24}\text{H}_{44}\text{B}_2\text{O}_4$ : C, 68.92; H, 10.62. Found: C, 68.95; H, 10.69.

**3c.** Preparation as described for the general procedure using **1c** (0.256 g, 1 mmol) afforded **3c** (0.171 g, 59%). Mp: 215 °C with decomposition.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.31–7.13 (m, 10 H), 6.08 (t,  $J$  = 8.64 Hz, 2 H), 2.76–2.54 (m, 8 H), 1.25 (s, 24 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 143.1, 142.3, 136.2, 128.5, 128.1, 125.5, 83.0, 36.4, 33.6, 24.9.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.3. MS (EI)  $m/z$  (relative intensity): 457 ( $\text{M}^+ - 53$ , 2.5). Anal. Calcd for  $\text{C}_{32}\text{H}_{44}\text{B}_2\text{O}_4$ : C, 74.73; H, 8.62. Found: C, 74.63; H, 8.60.

**3d.** Preparation as described for the general procedure using **1d** (0.270 g, 1 mmol) afforded **3d** (0.175 g, 65%). Mp: >215 °C with decomposition.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.28–7.12 (m, 10 H), 6.05 (t,  $J$  = 7.96 Hz, 2 H), 2.62 (t,  $J$  = 7.69 Hz, 4 H), 2.31 (q,  $J$  = 7.32 Hz, 4 H), 1.71 (m, 4 H), 1.23 (s, 24 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 143.3, 142.8, 136.2, 128.4, 128.1, 125.4, 83.0, 35.5, 31.7, 31.4, 24.8.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 29.7. MS (EI)  $m/z$  (relative intensity): 357 ( $\text{M}^+ - 181$ , 0.42).

**3e.** Preparation as described for the general procedure using **1e** (0.228 g, 1 mmol) afforded **3e** (0.146 g, 64%) as an oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.91 (t,  $J$  = 7.60 Hz, 2 H), 3.47 (t,  $J$  = 6.88 Hz, 4 H), 2.35 (q,  $J$  = 7.32 Hz, 4 H), 1.70 (m, 4 H), 1.21 (s, 24 H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = 142.1, 136.9, 83.2, 44.6, 32.8, 29.0, 24.9.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.1. MS (EI)  $m/z$  (relative intensity): 458/460 ( $\text{M}^+$ , 0.33/0.11). Anal. Calcd for  $\text{C}_{22}\text{H}_{38}\text{B}_2\text{Cl}_2\text{O}_4$ : C, 57.65; H, 8.36. Found: C, 57.66; H, 8.38.

**3f.** Preparation as described for the general procedure using **1f** (0.222 g, 1 mmol) to provide **3f** as a solid (0.137 g, 62%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.87 (d,  $J$  = 9.52 Hz, 2 H), 2.76 (m, 2 H), 1.82–1.75 (m, 4 H), 1.62–1.48 (m, 8 H), 1.25 (s, 24 H), 1.28–1.20 (m, 4 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 148.0, 83.0, 42.6, 34.1, 25.5, 24.8.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.6. MS (EI)  $m/z$  (relative intensity): 442 ( $\text{M}^+$ , 0.11). Anal. Calcd for  $\text{C}_{26}\text{H}_{44}\text{B}_2\text{O}_4$ : C, 70.61; H, 10.03. Found: C, 70.96; H, 10.00.

**General Procedure for the Preparation of 4 and 5.** The preparation of **4a** and **5a** is typical. To a stirred suspension of  $\text{Cp}_2\text{ZrCl}_2$  (5.0 mmol, 1.42 g) in dry THF (6 mL) at –78 °C under an atmosphere of argon was added dropwise 10 mmol of *n*-BuLi, and the solution was allowed to stir for 2 h. Then 1,4-dioxane (20 mmol, 4 equiv, 1.65 mL) was added, followed by **1a** (10.0 mmol, 2.082 g). The cooled bath was immediately removed to allow the reaction mixture to reach room temperature. The reaction was stirred overnight and quenched with ethereal HCl (3.17 M, 3 mL) at 0 °C, followed by treatment with  $\text{H}_2\text{O}$ . The resulting solution was extracted twice with dry ether. The organic solution was dried, concentrated *in vacuo* and analyzed by GC (**4a:5a** = 43:57 in 91% yield). Then **5a** was precipitated at –20 °C in pentane and collected by filtration. Chromatography of the filtrate on silica (5% ether/hexane) afforded **4a**. Data for **4a** are as follows. Yield: 0.551 g, 26%. Suitable crystals for X-ray analysis were grown from a slowly evaporating hexane solution. Mp: 91 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 6.21 (t,  $J$  = 7.6 Hz, 1 H), 5.16 (s, 1 H), 2.56 (t,  $J$  = 7.6 Hz, 2 H), 2.22 (q,  $J$  = 7.0 Hz, 2 H), 1.40–1.23 (m, 8 H), 1.27 (s, 12 H), 0.85 (t,  $J$  = 6.6 Hz, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 166.8, 144.5, 137.8, 114.81, 83.30, 82.37, 32.54, 32.18, 31.89, 31.51, 24.85, 22.53, 22.25, 13.92.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.56. MS (EI)  $m/z$  (relative intensity): 418 ( $\text{M}^+$ , 0.02). Data for **5a** are as follows. Yield: 0.704 g, 34%. Mp: 91 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.49 (s, 2 H), 2.59 (t,  $J$  = 7.7 Hz, 4 H), 1.28 (m, 8 H), 1.25 (s, 24 H), 0.87 (t,  $J$  = 7.0 Hz, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 164.6, 115.6, 82.8, 32.7, 31.8, 24.8, 22.7, 13.9.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.33. MS (EI)  $m/z$  (relative intensity): 418 ( $\text{M}^+$ , 0.01). UV:  $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) = 266 ( $\epsilon$  = 17 247). Anal. Calcd for  $\text{C}_{24}\text{H}_{44}\text{B}_2\text{O}_4$ : C, 68.92; H, 10.62. Found: C, 68.92; H, 10.60.

**Preparation of 4c and 5c** followed the procedure described above using **1c** (10 mmol, 2.561 g) and afforded **4c** and **5c** in

a 46:54 ratio in 79% GC yield. Data for **4c** are as follows. Yield: 0.184 g, 0.36 mmol, 7%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.30–7.12 (m, 10 H), 6.34 (t,  $J$  = 7.7 Hz, 1 H), 5.25 (s, 1 H), 2.86 (t,  $J$  = 8.4 Hz, 2 H), 2.74 (t,  $J$  = 8.4 Hz, 2 H), 2.62 (m, 4 H), 1.31 (s, 12 H), 1.26 (s, 12 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 165.3, 143.5, 143.5, 141.76, 137.5, 128.5, 128.3, 128.0, 125.8, 125.6, 125.5, 116.0, 83.5, 82.6, 36.7, 36.1, 35.3, 33.7, 24.9, 24.9.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.75. Data for **5c** are as follows. Yield: 0.439 g, 0.86 mmol, 17%. Mp: 138 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.26–7.15 (m, 10H), 5.68 (s, 2H), 2.92 (m, 4H), 2.68 (m, 4H), 1.28 (s, 24H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  = 162.9, 142.6, 128.6, 128.12, 125.6, 117.5, 83.0, 37.2, 34.4, 24.9.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 31.65. MS (EI)  $m/z$  (relative intensity): 386 ( $\text{M}^+ - 128$ , 0.20). Anal. Calcd for  $\text{C}_{32}\text{H}_{44}\text{B}_2\text{O}_4$ : C, 74.73; H, 8.62. Found: C, 74.52; H, 8.58.

**Preparation of 4e and 5e** followed the procedure described above using **1e** (10 mmol, 2.282 g) to afford **4e** and **5e** in a 66:34 ratio in 91% yield (GC). Data for **4e** are as follows. Yield: 0.336 g, 0.74 mmol, 15%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 6.19 (t,  $J$  = 7.7 Hz, 1 H), 5.23 (s, 1 H), 3.51 (t,  $J$  = 6.6 Hz, 2 H), 3.48 (t,  $J$  = 7.0 Hz, 2 H), 2.72 (t,  $J$  = 7.3 Hz, 2 H), 2.40 (q,  $J$  = 7.3 Hz, 2 H), 1.84 (m, 4 H), 1.29 (s, 12 H), 1.23 (s, 12 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 164.1, 142.6, 138.4, 116.8, 83.3, 82.4, 44.7, 44.2, 32.5, 32.3, 30.1, 28.9, 24.6, 24.5.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.90. MS (EI)  $m/z$  (relative intensity): 443 ( $\text{M}^+ - 15$ , 0.03). Data for **5e** are as follows. Yield: 0.537 g, 1.21 mmol, 24%. Mp: 143 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.55 (s, 2 H), 3.48 (t,  $J$  = 7.0 Hz, 4 H), 2.73 (t,  $J$  = 7.7 Hz, 4 H), 1.82 (q,  $J$  = 7.7 Hz, 4 H), 1.26 (s, 24 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 161.6, 117.5, 83.1, 44.9, 33.2, 29.5, 24.9, 24.8.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.86. MS (EI)  $m/z$  (relative intensity): 443 ( $\text{M}^+ - 15$ , 0.06). Anal. Calcd for  $\text{C}_{22}\text{H}_{38}\text{B}_2\text{Cl}_2\text{O}_4$ : C, 57.65; H, 8.36. Found: C, 57.56; H, 8.34.

**Preparation of 4f and 5f** followed the procedure as described above using **1f** (10 mmol, 2.20 g) to give **4f** and **5f** in a ratio of 59:41 and a GC yield of 76%. Data for **4f** are as follows. Yield: 0.744 g, 1.69 mmol, 34%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 5.88 (d,  $J$  = 9.9, 1 H), 5.06 (s, 1 H), 3.25 (m, 1 H), 2.93 (q,  $J$  = 8.8 Hz, 1 H), 1.80–1.37 (m, 16 H), 1.24 (s, 12 H), 1.22 (s, 12 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 83.41, 82.97, 82.73, 45.64, 41.92, 34.40, 32.67, 32.39, 31.56, 27.61, 26.75, 25.99, 25.64, 25.25, 25.15, 24.90.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.30. MS (EI)  $m/z$  (relative intensity): 427 ( $\text{M}^+ - 15$ , 0.06). Data for **5f** are as follows. Yield: 0.610 g, 1.37 mmol, 28%. Mp: 129 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 4.94 (s, 2 H), 3.09 (m, 2 H), 1.76 (m, 4 H), 1.60 (m, 4 H), 1.47 (m, 8 H), 1.24 (s, 24 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 171.8, 151.6, 134.8, 114.8, 114.0, 82.7, 45.7, 33.01, 25.2, 24.8.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.62. MS (EI)  $m/z$  (relative intensity): 442 ( $\text{M}^+$ , 0.03). Anal. Calcd for  $\text{C}_{26}\text{H}_{44}\text{B}_2\text{O}_4$ : C, 70.61; H, 10.03. Found: C, 69.96; H, 9.96.

**Preparation of 4g and 5g** followed the procedure described above using **1g** (10 mmol, 2.27 g) give **4g** and **5g** in a ratio of 45:55 and in GC yield of 95%. Data for **4g** are as follows. Yield: 0.363 g, 0.79 mmol, 16%. Mp: 98 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.39–7.17 (m, 10 H), 6.91 (s, 1 H), 5.76 (s, 1 H), 1.38 (s, 12 H), 1.08 (s, 12 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 162.3, 142.9, 141.42, 140.15, 140.0, 138.5, 129.8, 128.4, 128.1, 127.9, 127.6, 127.2, 127.1, 118.9, 83.8, 82.8, 25.1, 24.8, 24.5.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.71. MS (EI)  $m/z$  (relative intensity): 458 ( $\text{M}^+$ , 0.05). Data for **5g** are as follows. Yield: 0.741 g, 1.62 mmol, 33%. Mp: 218 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.28–7.24 (m, 10 H), 5.39 (s, 2 H), 0.99 (s, 24 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 160.57, 141.13, 129.71, 127.41, 126.93, 123.60, 83.03, 24.47.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 30.47. MS (EI)  $m/z$  (relative intensity): 458 ( $\text{M}^+$ , 0.04). Anal. Calcd for  $\text{C}_{28}\text{H}_{36}\text{B}_2\text{O}_4$ : C, 73.40; H, 7.92. Found: C, 73.38; H, 7.93.

**Procedure for Suzuki–Miyaura Coupling of Dibora-butadienes with Phenyl Bromide.** Preparation of **7** is typical. A solution of **3a** (0.5 mmol) in 0.209 g in THF (5 mL) was treated with  $\text{Pd}(\text{PPh}_3)_4$  (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, diluted in hexanes, washed with brine, and dried over  $\text{Na}_2\text{SO}_4$ , and concentrated

*in vacuo* and chromatographed on silica gel to yield **7** as an oil (0.092 g, 76%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.34–7.11 (m, 5 H), 6.23 (d,  $J$  = 16.5 Hz, 1 H), 5.58 (t,  $J$  = 8.23 Hz, 1H), 5.11 (dt,  $J$  = 16.5 and 8.23 Hz, 1 H), 2.03 (m, 2 H), 1.88 (m, 2 H), 1.32–1.18 (m, 8H), 0.86–0.81 (m, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 141.4, 139.1, 134.1, 131.7, 131.4, 129.5, 127.9, 126.4, 32.4, 32.0, 31.7, 28.4, 22.3, 13.9. MS (EI)  $m/z$  (relative intensity): 242 ( $\text{M}^+$ , 0.83).

**Preparation of 6** was as described above using **4a** (0.5 mmol, 0.209 g). Yield = 90% (0.166 g).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.31–7.14 (m, 5 H), 6.38 (s, 1 H), 6.20 (t,  $J$  = 8.4 Hz, 1 H), 2.40 (t,  $J$  = 9.2 Hz, 2 H), 2.29 (q,  $J$  = 8.0 Hz, 2 H), 1.51–1.25 (m, 8 H), 1.33 (s, 12 H), 0.92 (t,  $J$  = 10 Hz, 3 H), 0.87 (t,  $J$  = 8.8 Hz, 3 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 145.6, 142.0, 138.8, 129.7, 127.95, 126.8, 125.9, 83.4, 32.1, 31.8, 31.3, 28.9, 24.9, 24.8, 22.9,

22.4, 14.0.  $^{11}\text{B}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 32.17. MS (EI)  $m/z$  (relative intensity): 368 ( $\text{M}^+$ , 0.17).

**Acknowledgment.** We thank the University of Toledo for fellowships that made this research possible and the State of Ohio Academic Challenges Program for providing funds for a high-field 400 MHz NMR spectrometer.

**Supporting Information Available:** X-ray crystallographic tables (data collection parameters, positional and thermal parameters, and bond distances and angles) and an ORTEP diagram (side view) for **5a**, NMR spectra for **3a**, and HETCOR plots of **4a,c** and **6** (17 pages). Ordering information is given on any current masthead page.

OM960178N