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Synthesis of 2-boryl-1,3-butadienes from tributylphosphine stabilized zirconacyclopropenes and alkynes

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ABSTRACT

Boryl zirconacyclopropenes stabilized with tributylphosphine react with alkynes (terminal and internal) to give predominately 2-boryl-1,3-butadienes, **5**, in 40–81% isolated yields. Products **5** are accompanied by 1-boryl-1,3-butadienes in 8–30% when terminal alkynes are inserted. However, the use of an internal alkyne (3-hexyne) gave predominantly **6c**.

1. Introduction

While 1-boryl-1,3-butadienes are available by numerous means and are extremely useful intermediates especially in the Diels–Alder reaction [1–3], the chemistry of the isomeric 2-boryl-1,3-dienes lags in development because of a paucity of general methods available for their synthesis. Among these methods are Carboni's free-radical addition of bromomethane sulfonyl bromide to 2-propenylboronate and subsequent vinylogous Ramberg–Bäcklund reaction in 81% yield [4]. Miyaura and Suzuki hydroborated 1,4-dichloro-2-butyne with pinacolborane and then used zinc to reduce the 2-boryl-1,4-dichloro-2-butene to the parent 2-boryl-1,3-butadiene which they subsequently used in Diels–Alder reactions [5]. Knochel coupled his 1,1-borylzinc reagents with iodooctene under Negishi conditions (one example) [6]. Renaud has reported on ring-closing metathesis (RCM) of enynylboronates to cyclic 1,3-dienylboronates (Fig. 1) [7].

We have over the years demonstrated the usefulness of 1-alkynylboronates in conjunction with zirconium chemistry to prepare highly substituted vinylboronates [8]. In the past we unsuccessfully tried to prepare 2-boryl-1,3-dienes by zirconation of 1-alkynylboronates and alkyne insertion. Only a mixture of dimeric 1,3- and 1,4-dienylboronates were obtained [9]. However, the former could be easily isolated by silica gel chromatography and when subjected to Suzuki–Miyaura coupled on C1 to provide 2-boryl-1,3-dienes which we converted into α,β-unsaturated ketones by oxidation with H_2O_2, pH 8 or TMANO/H_2O. A subsequent Suzuki–Miyaura coupling gave highly substituted stereoisomers (Scheme 1) [10].

In principle, the vinylboronate moiety in the 2-boryl-1,3-dienes could undergo many additional transformations typical of the group [11]. However, the method is limited to identical R groups. It is well established that phosphines stabilize zirconacycles by coordination to the empty zirconium *d* orbital [12]. We reasoned that phosphine coordination should also be effective in stabilizing borylzirconacyclopropenes obtained by zirconation of 1-alkynylboronates with Negishi reagent (Cp_2ZrCl_2/2*n*-BuLi) [13]. Indeed, we have recently demonstrated this to be the case in the synthesis of 3-hydroxyvinylboronates which we could not prepare previously [14]. In this communication we report our results in the preparation of Bu_3P stabilized borylzirconacyclopropenes and their reaction with terminal and internal alkynes to give primarily 2-boryl-1,3-dienes (Scheme 2).

2. Results and discussion

Phosphine stabilized borylzirconacyclopropenes **2**, obtained by the reaction of alkynylboronates with Negishi reagent (Cp_2ZrCl_2/2*n*-BuLi) in the presence of tributylphosphine, reacted successfully with various alkynes. Other phosphines were less effective [12]. Generally, alkyne insertion in α-boronatozirconacyclopropenes **2** presumably produced α-boronatozirconacyclopentenes **3** and **4**

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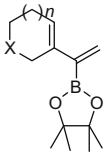


Fig. 1. Renaud's 2-boryl-1,3-dienes.

intermediates since upon hydrolysis with HCl/ether, two main boryl-1,3-butadienyl boronate regioisomers **5** and **6** were usually obtained.

The reaction with terminal alkynes always produced 2-boryl-1,3-butadienes **5** (68–92% yield, 40–81% isolated yield), in which the insertion of the alkyne in boronatozirconacyclopropenes **2** was on C2 as a major regioisomer. In addition, a minor regioisomer **6** in which the insertion on C1 (of **2**) was also present (Fig. 2). In some cases (entries a, b, d, e, and i), additional isomers in 3–21% overall yield were detected in the reaction mixture together with products **5** and **6** (Table 1).

These products are apparently regio- or stereoisomers since they showed identical molecular weight by GC/MS, and ^{11}B NMR in the alkenylboronate region at ~30 ppm (Table 1). As a result of the presence of these isomers and their relatively low yield, attempts to isolate them were unsuccessful. Additionally, compounds **6** were always obtained as mixture together with compound **5** (65/35% mixture ratio, respectively) except **6f** which was isolated as a pure product.

On the other hand, unlike terminal alkynes, 3-hexyne (entry c, Table 1) gave compound **6c** in which the insertion was on C1 of the intermediate **2** as a major regioisomer in 78% isolated yield. The other regioisomer **5c** was obtained in ~8% and was not isolated. We believe that this variation in selectivity is apparently due to steric factors. The oily compounds (**5**, **6f**, and **6c**) were isolated as pure products by silica gel chromatography, and characterized by GC/MS, ^{1}H, ^{11}B, ^{13}C NMR, and elemental analysis.

Zirconation of ω-chloropentynylboronate, for instance 5-chloropentynylboronate and 6-chlorohexynylboronate, did not proceed possibly because of Wittig reaction with tributylphosphine. Also, apparently due to steric effects, attempts to insert phenylacetylene, diphenylacetylene and *t*-butylacetylene in butyl boronatozirconacyclopropene **2** were unsuccessful.

The regioselectivity of the products was determined from ^{1}H NMR, since the singlet (5.33–5.34 ppm) for isomer **6** (which except for **6c** and **6f** was generally obtained as a mixture with **5**) corresponds to a vinyl H on C1, which is evidence of insertion of the alkyne on C1 of boronatozirconacyclopropene **2**. On the other hand, the triplet (5.99–6.17 ppm) for isomer **5** which corresponds to vinyl hydrogen on C1 split by the two allyl hydrogens is indicative of insertion of the alkyne on C2 of boronatozirconacyclopropene **2** (Fig. 2). Also, ^{11}B NMR (29.55–31.30 ppm) and ^{13}C NMR data are consistent with 2-boryl-1,3-butadienes structure. The double bond carbons were detected in the region (126.58–161.51 ppm) except the quadrapole carbon. Regarding trimethylsilyl and phenyl

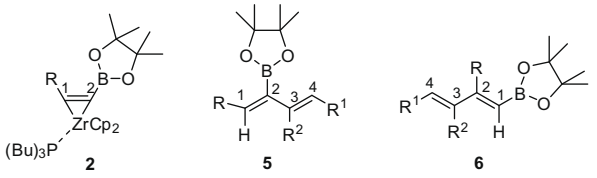
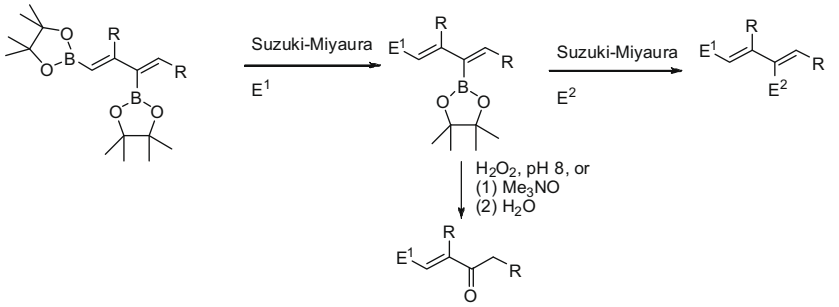
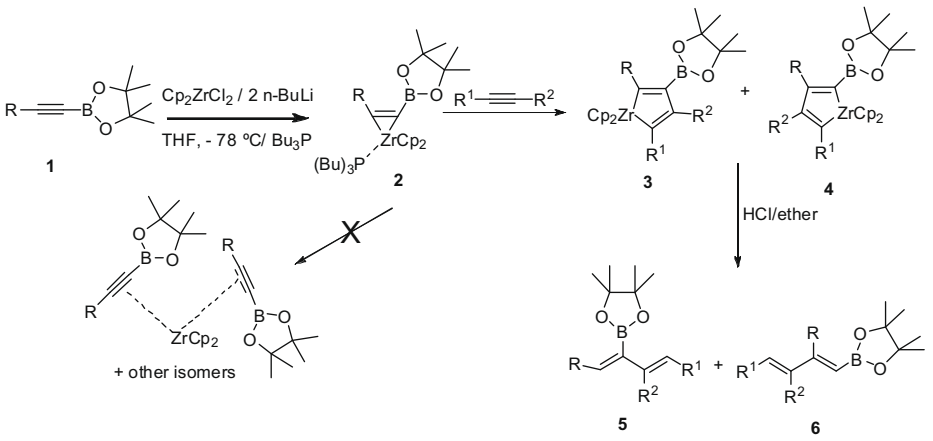


Fig. 2. Compounds **5** and **6** obtained by addition of an alkyne to borylzirconacycle propene **2**.

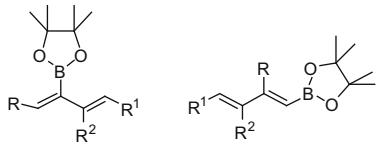


Scheme 1.



Scheme 2.

Table 1
Products of alkynes insertion in α-boronatozirconacyclopropenes **2**



5 **6**

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Entry	R	R^1	R^2	Yield (%) of **5**[a,b] (isolated yield, %[c])	Yield (%) of **6**[a,b] (isolated yield, %[c])	Yield (%) of other isomers[a,b,d] (number of isomers)
a	*n*-Bu	3-Cl-Pr	H	86 (72)	10[d]	4 (1)
b	*n*-Bu	4-Cl–Bu	H	87 (70)	10[d]	3 (1)
c	*n*-Bu	Ethyl	Ethyl	8[d]	92 (78)	–
d	*n*-Bu	*n*-Bu	H	69 (45)	11[d]	20 (2)
e	*n*-Pent	Octyl	H	72 (50)	9[d]	19 (2)
f	*n*-Pent	Trimethylsilyl	H	70 (48)	30 (23)	–
g	Trimethylsilyl	3-Cl-Pr	H	92 (81)	8[d]	–
h	Trimethylsilyl	Octyl	H	89 (75)	11[d]	–
i	Ph	Pentyl	H	68 (40)	11[d]	21 (2)

[a] Conversion was >98% as determined by GC/MS and ^{11}B NMR of the reaction mixture.
[b] Yields were determined by GC/MS and ^{11}B NMR of the reaction mixture.
[c] After silica gel isolation.
[d] Not isolated.

acetylboronates (entries g, h and i), we believe that regioisomer **5** was obtained since the singlet in ^1H NMR at 6.37 ppm, 6.31 ppm and 6.88 ppm, respectively, corresponds to a vinyl hydrogen on C1 compared to vinyl hydrogens on C1 of compounds **6** that have a chemical shift in the region (5.33–5.34 ppm).

3. Conclusion

We have demonstrated that it is possible to prepare 2-boryl-1,3-butadienes by insertion of an alkyne into tributylphosphine stabilized borylzirconacyclopropenes to give primarily **5**. Compounds **5** are invariably accompanied by small amounts of **6**. In one example using 3-hexyne mainly **6c** was obtained. The present methodology enable the construction of 2-boryl-1,3-butadienes using two different alkynes.

4. Experimental

4.1. General Information

All reactions were carried out under a nitrogen atmosphere vacuum line and glovebox techniques. Solvents were purified by distillation from appropriate drying agents under a nitrogen atmosphere. ^1H NMR (300 MHz and 500 MHz) and ^{13}C NMR (75.5 MHz and 125.7 MHz) were recorded in $CDCl_3$, ^{11}B NMR (160.3 MHz) was recorded in $CDCl_3$ (relative to standard: $BF_3{\cdot}OEt_2$). GC/MS analysis was performed on HP GC/MS instrument (Model GCD PLUS), with EI detector and 30 m methyl silicone column.

4.2. Synthesis of ***5a***

To 0.306 g (1.05 mmol) of zirconocene dichloride dissolved in 7 mL of dry THF at −78 °C was added 1.05 mL of 2 M *n*-BuLi (2.1 mmol) dropwise in a 25 mL round-bottom flask. After stirring at −78 °C for 2 h, 0.212 g (1.05 mmol) of tributylphosphine was added to the reaction and it was allowed to warm to room temperature. After stirring at room temperature for 2 h, it was again cooled to −78 °C and 0.187 g (0.9 mmol) of 2-(hex-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added and the reaction was warmed gradually to room temperature and stirred overnight. Again, the reaction was cooled to −78 °C and 2.5 mmol of 5-chloropentyne was added after which the mixture was stirred for 12 h at room temperature. The reaction was worked up with HCl/ether and the product was separated on silica gel column (90% petroleum ether/10% dichloromethane). The yellow oil was obtained in 72% yield and was analyzed by GC/MS, elemental analysis, and NMR spectroscopy. ^1H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, 3H, J_{HH} = 7.2 Hz), 1.24–1.68 (overlap, 4H), 1.30 (s, 12H), 1.83 (m, 2H), 2.18–2.31 (overlap, 4H), 3.52 (t, 2H, J_{HH} = 6.6 Hz), 5.66 (dt, 1H, J_{HH} = 15.6 Hz, J_{HH} = 6.9 Hz), 6.02–6.15 (overlap, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.81, 24.84, 27.29, 28.15, 30.40, 32.20, 32.51, 44.72, 83.55, 128.54, 136.25, 146.45; ^{11}B NMR (160.3 MHz, $CDCl_3$): 30.48; MS(EI): *m*/*z* (%) 314 (1.9), 313 (1.5), 312 (5.6), 311 (1.4), 297 (1.7), 269 (0.7), 255 (15.6), 211 (7.4), 199 (8.3), 183 (4.7), 155 (9.0), 141 (3.3), 105 (13.7), 101 (100), 85 (26.6), 84 (13.2), 83 (29.1), 79 (30.0), 55 (19.8); Anal. Calcd. for $C_{17}H_{30}BClO_2$: C, 65.30; H, 9.67; Cl, 11.34. Found: C, 65.12; H, 9.55; Cl, 11.48%.

4.3. Synthesis of ***5b***

Identical with that of **5a** except addition of 6-chlorohexyne, and the oily product was obtained in 70% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, 3H, J_{HH} = 7.2 Hz), 1.29 (s, 12H), 1.30–1.80 (overlap, 8H), 2.06 (dt, 2H, J_{HH} = 7.2 Hz, J_{HH} = 6.9 Hz), 2.22 (dt, 2H, J_{HH} = 7.5 Hz, J_{HH} = 6.9 Hz), 3.50 (t, 2H, J_{HH} = 6.6 Hz), 5.67 (dt, 1H, J_{HH} = 15.9 Hz, J_{HH} = 6.9 Hz), 5.99–6.10 (overlap, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.55, 24.80, 27.10, 27.97, 31.23, 31.94, 32.02, 32.22, 44.96, 83.26, 129.71, 135.20, 145.63; ^{11}B NMR (160.3 MHz, $CDCl_3$): 30.54; MS(EI): *m*/*z* (%) 328 (0.9), 327 (0.8), 326 (2.9), 325 (0.6), 311 (0.9), 269 (8.8), 225 (5.2), 198 (2.9), 161 (0.6), 149 (7.0), 135 (4.9), 107 (12.6), 101 (100), 85 (34.0), 84 (16.9), 83 (35.6), 55 (31.2); Anal. Calcd. for $C_{18}H_{32}BClO_2$: C, 66.17; H, 9.87; Cl, 10.85. Found: C, 65.97; H, 9.73; Cl, 11.02%.

4.4. Synthesis of ***6c***

Identical with that of **5a** except addition of 2 mmol of 3-hexyne, and the oily product was obtained in 78% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, 3H, J_{HH} = 7.2 Hz), 0.92 (t, 3H, J_{HH} = 7.5 Hz), 0.99 (t, 3H, J_{HH} = 7.5 Hz), 1.24–1.41 (overlap, 4H), 1.27 (s, 12H), 2.12 (dq, 2H, J_{HH} = 7.5 Hz, J_{HH} = 7.3 Hz), 2.24 (q, 2H, J_{HH} = 7.5 Hz), 2.60 (t, 2H, J_{HH} = 7.5 Hz), 5.33 (s, 1H), 5.61 (t, 1H, J_{HH} = 7.5 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.70, 13.97, 14.38, 21.19, 22.33, 24.51, 24.89, 31.78, 32.22, 83.36, 129.89, 138.47, 142.75; ^{11}B NMR (160.3 MHz, $CDCl_3$): 31.30; MS(EI): *m*/*z* (%) 292 (20.9), 277 (2.5), 263 (9.0), 235 (20.4), 192 (23.3), 163 (40.7), 135 (64.6), 121 (51.3), 101 (100), 84 (55.9), 83 (34.5), 55 (66.4); Anal. Calcd. for $C_{18}H_{33}BO_2$: C, 73.97; H, 11.38. Found: C, 74.09; H, 11.52%.

4.5. Synthesis of ***5d***

Identical with that of **5a** except addition of 2 mmol of 1-hexyne, and the oily product was obtained in 45% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 3H, J_{HH} = 7.2 Hz), 0.88 (t, 3H, J_{HH} = 6.3 Hz), 1.18–1.59 (overlap, 8H), 1.32 (s, 12H), 2.05 (dt, 2H, J_{HH} = 6.9 Hz, J_{HH} = 6.3 Hz), 2.23 (dt, 2H, J_{HH} = 7.5 Hz, J_{HH} = 7.2 Hz), 5.71 (dt, 1H, J_{HH} = 15.6 Hz, J_{HH} = 6.9 Hz), 6.01 (t, 1H, J_{HH} = 7.8 Hz), 6.05 (d, 1H, J_{HH} = 15.9 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.90, 14.03, 24.55, 24.70, 29.68, 32.24, 32.90, 35.82, 37.49, 83.02, 126.58, 142.92, 144.51; ^{11}B NMR (160.3 MHz, $CDCl_3$): 29.77; MS(EI): *m*/*z* (%) 292 (0.3), 265 (0.2), 264 (1.2), 235 (0.4), 224 (0.4), 191 (0.4), 179 (0.4), 154 (1.3), 139 (3.2), 125 (10.5), 97 (63.8), 83 (79.9), 69

(73.4), 57 (92.7), 55 (100); Anal. Calcd. for $C_{81}H_{33}BO_2$: C, 73.97; H, 11.38. Found: C, 74.15; H, 11.51%.

4.6. Synthesis of **5e**

Identical with that of **5a** except addition of 2 mmol 1-decyne to the phosphine stabilized three membered ring zirconacycle of 2-(hept-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, and the oily product was obtained in 50% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.872 (t, 3H, J_{HH} = 7.2 Hz), 0.874 (t, 3H, J_{HH} = 7.2 Hz), 1.25–1.42 (overlap, 18H), 1.32 (s, 12H), 2.04 (dt, 2H, J_{HH} = 7.2 Hz, J_{HH} = 6.9 Hz), 2.22 (dt, 2H, J_{HH} = 7.2 Hz, J_{HH} = 6.6 Hz), 5.71 (dt, 1H, J_{HH} = 15.9 Hz, J_{HH} = 6.9 Hz), 6.02 (t, 1H, J_{HH} = 7.8 Hz), 6.06 (d, 1H, J_{HH} = 16.2 Hz); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.03, 14.11, 22.50, 22.68, 29.27, 29.29, 29.36, 29.49, 29.51, 29.70, 31.49, 31.63, 31.92, 33.16, 83.30, 131.07, 134.50, 144.99; ^{11}B NMR (160.3 MHz, $CDCl_3$): 30.54; MS(EI): *m*/*z* (%) 362 (4.1), 347 (1.1), 305 (9.0), 261 (5.6), 249 (3.2), 235 (6.1), 191 (7.1), 163 (12.6), 149 (12.2), 121 (16.0), 101 (100), 85 (55.8), 84 (33.9), 83 (53.0), 55 (43.7); Anal. Calcd. for $C_{23}H_{43}BO_2$: C, 76.23; H, 11.96. Found: C, 76.38; H, 12.08%.

4.7. Synthesis of **5f**

Identical with that of **5e** except addition of 2 mmol of trimethylsilylacetylene, and the oily product was obtained in 48% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.06 (s, 9H), 0.88 (t, 3H, J_{HH} = 6.9 Hz), 1.23–1.42 (overlap, 6H), 1.33 (s, 12H), 2.24 (dt, 2H, J_{HH} = 7.5 Hz, J_{HH} = 7.5 Hz), 5.85 (d, 1H, J_{HH} = 18.9 Hz), 6.17 (t, 1H, J_{HH} = 7.8 Hz), 6.55 (d, 1H, J_{HH} = 18.9 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ −1.15, 13.99, 24.89, 29.37, 29.69, 31.48, 31.76, 83.43, 129.52, 148.13, 148.77; ^{11}B NMR (160.3 MHz, $CDCl_3$): 30.80; MS(EI): *m*/*z* (%) 322 (10.8), 307 (18.7), 279 (0.3), 265 (12.7), 237 (3.7), 222 (23.3), 195 (33.4), 180 (31.6), 149 (30.0), 137 (27.2), 123 (40.1), 101 (86.4), 73 (100), 59 (37.8); Anal. Calcd. for $C_{18}H_{35}BO_2Si$: C, 67.06; H, 10.94. Found: C, 67.22; H, 11.09%.

4.8. Synthesis of **6f**

Identical with that of **5f**, and the oily product was obtained in 23% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.07 (s, 9H), 0.89 (t, 3H, J_{HH} = 6.9 Hz), 1.26 (s, 12H), 1.28–1.39 (overlap, 6H), 2.57 (t, 2H, J_{HH} = 7.2 Hz), 5.34 (s, 1H), 6.05 (d, 1H, J_{HH} = 19.2 Hz), 6.48 (d, 1H, J_{HH} = 18.9 Hz); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ −1.31, 14.07, 22.41, 24.79, 29.69, 30.23, 32.03, 82.74, 131.38, 148.35, 161.51; ^{11}B NMR (160.3 MHz, $CDCl_3$): 29.55; MS(EI): *m*/*z* (%) 322 (1.0), 307 (4.3), 279 (0.1), 266 (4.0), 248 (6.1), 209 (7.1), 207 (5.0), 183 (8.2), 165 (11.4), 137 (4.7), 109 (13.0), 84 (100), 73 (50.0), 59 (16.4); Anal. Calcd. for $C_{18}H_{35}BO_2Si$: C, 67.06; H, 10.94. Found: C, 67.43; H, 11.28%.

4.9. Synthesis of **5g**

Identical with that of **5a** except addition of 5-chloropentyne to the phosphine stabilized three membered ring zirconacycle of trimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)-silane, and the oily product was obtained in 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.15 (s, 9H), 1.33 (s, 12H), 1.89 (m, 2H), 2.25 (dt, 2H, J_{HH} = 7 Hz, J_{HH} = 7 Hz), 3.56 (t, 2H, J_{HH} = 7 Hz), 5.97 (dt, 1H, J_{HH} = 15.5 Hz, J_{HH} = 7 Hz), 6.18 (d, 1H, J_{HH} = 15.5 Hz), 6.37 (s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 0.44, 25.43, 30.46, 32.37, 44.73, 83.85, 130.92, 139.90, 148.34; ^{11}B NMR (160.3 MHz, $CDCl_3$): 29.80; MS(EI): *m*/*z* (%) 330 (0.2), 328 (0.8), 313 (1.9), 271 (0.8), 251 (0.4), 231 (3.2), 193 (0.6), 171 (3.1), 151 (2.5), 137 (12.7), 109 (13.1), 84 (100), 83 (33.8), 55 (18.3); Anal. Calcd. for $C_{16}H_{30}BClO_2Si$: C, 58.45; H, 9.20; Cl, 10.78. Found: C, 58.29; H, 9.08; Cl, 10.90%.

4.10. Synthesis of **5h**

Identical with that of **5g** except addition of 2 mmol of 1-decyne, and the oily product was obtained in 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.15 (s, 9H), 0.89 (t, 3H, J_{HH} = 6.5 Hz), 1.21–1.42 (overlap, 6H), 1.34 (s, 12H), 2.08 (dt, 2H, J_{HH} = 7 Hz, J_{HH} = 7 Hz), 6.00 (dt, 1H, J_{HH} = 15.5 Hz, J_{HH} = 7 Hz), 6.14 (d, 1H, J_{HH} = 15.5 Hz), 6.31 (s, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 0.48, 14.38, 22.91, 25.39, 29.54, 32.12, 33.43, 83.81, 133.82, 138.47, 146.70; ^{11}B NMR (160.3 MHz, $CDCl_3$): 29.65; MS(EI):m/z (%) 364 (1.1), 349 (1.7), 307 (4.0), 293 (1.9), 267 (2.0), 251 (1.7), 221 (1.8), 191 (4.8), 181 (4.4), 137 (5.5), 123 (11.0), 103 (11.3), 84 (100), 55 (19.5); Anal. Calcd. for $C_{21}H_{41}BO_2Si$: C, 69.21; H, 11.34. Found: C, 68.98; H, 11.18%.

4.11. Synthesis of **5i**

Identical with that of **5a** except addition of 2 mmol of 1-heptyne to the phosphine stabilized three membered ring zirconacycle of 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane, and the oily product was obtained in 40% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, 3H, J_{HH} = 7.2 Hz), 1.26–1.74 (overlap, 6H), 1.31 (s, 12H), 2.12 (dt, 2H, J_{HH} = 7.5 Hz, J_{HH} = 6.9 Hz), 5.82 (dt, 1H, J_{HH} = 15.6 Hz, J_{HH} = 7.2 Hz), 6.29 (d, 1H, J_{HH} = 15.6 Hz), 6.88 (s, 1H), 7.16–7.42 (overlap, 5H); ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 13.47, 23.60, 24.88, 28.93, 31.28, 33.07, 83.77, 126.95, 127.10, 127.84, 133.52, 135.39, 137.30, 139.59; ^{11}B NMR (160.3 MHz, $CDCl_3$): 30.99; MS(EI): *m*/*z* (%) 326 (10.5), 311 (1.2), 282 (0.3), 269 (7.5), 239 (0.6), 226 (7.4), 198 (37.7), 169 (23.0), 155 (28.1), 128 (37.0), 115 (18.9), 101 (95.8), 84 (100), 83 (42.1), 55 (31.3); Anal. Calcd. for $C_{21}H_{31}BO_2$: C, 77.30; H, 9.58. Found: C, 77.51; H, 9.70%.

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