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Novel Vinyl Phosphonates and Vinyl Boronates by Halogenation, Allylation, and Propargylation of α-Boryl- and α-Phosphonozirconacyclopentenes

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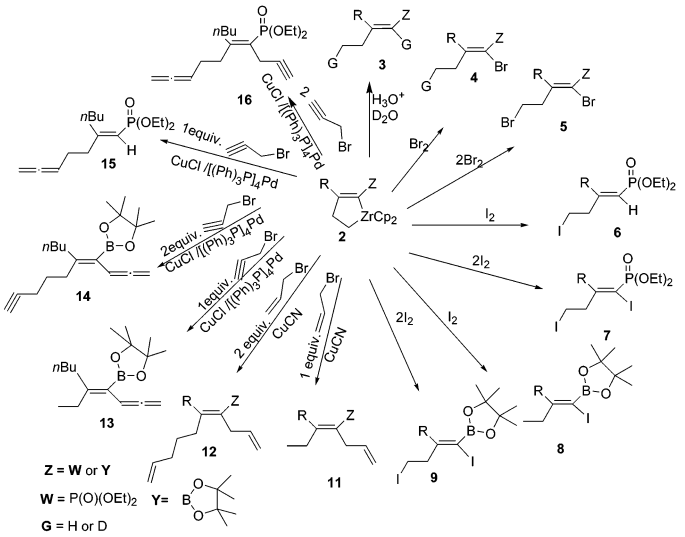

α-Phosphonozirconacyclopentenes or α-borylzirconacyclopentenes react by bromination, iodination, allylation, and propargylation to generate unique vinyl boronates and vinyl phosphonates not obtainable by other methods. The reaction proceeds in two steps, with both high regio- and stereoselectivity. With the vinyl boronates, the Zr−Csp2 bond is initially cleaved by 1 equiv of electrophile. With the phosphonates, either the Zr−Csp2 bond (allyl bromide, Br_2) or the Zr−Csp3 bond (I_2, propargyl bromide) may be initially cleaved. The addition of a second equivalent of an electrophile results in disubstitution.

Introduction

Vinyl boronates and vinyl phosphonates are two important classes of compounds. Vinyl boronates are useful partners in various cross-coupling schemes, in particular Suzuki−Miyaura coupling.[1] Since they are used in the preparation of pharmaceuticals and fine chemicals, a high degree of stereoselectivity is required in their preparation. Various methods have been developed for the preparation of vinyl boronates. Stoichiometric hydroboration of alkynes with hindered hydroborating reagents provides vinyl boronates with very high regio- and stereoselectivity.[2] Hydrozirconation/borylation is another similar method.[3] (*Z*)-Vinyl boronates can be obtained by hydrogenation of 1-alkynylboronates[4] and more recently by metal-catalyzed *trans*-hydroboration of terminal alkynes with catechol or pinacolborane.[5] A very effective method for obtaining disubstituted vinyl boronates with very high regio- and steroselectivity relies on hydrozirconation of 1-alkynylboronates followed by C−Zr bond cleavage with

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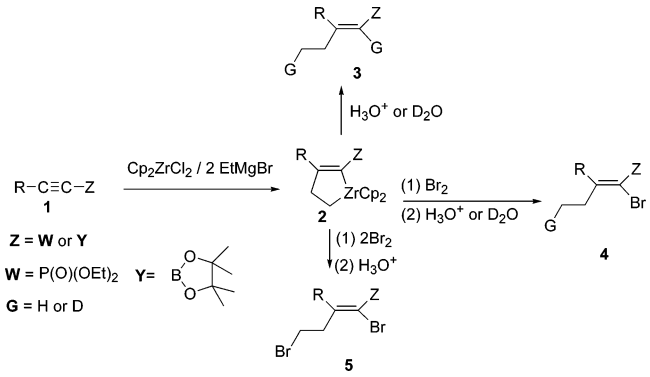
electrophiles.[6] A complementary method for obtaining disubstituted vinyl boronates relies on palladium-catalyzed borlyation of vinyl bromides and triflates with bis-(pinacolata)diborane.[7] Also, we have recently shown that vinyl boronates are pharmacologically active as MMP-2 inhibitors.[8] Vinyl phosphonates are useful intermediates in organic transformations.[9] They are accessible by a variety of methods, including metalations[10] of readily available 1-alkynylphosphonates,[11] by lithium salts,[12] the Arbusov reaction,[13] the Heck reaction,[14] olefination reactions,[15] radical trapping,[16] and various other catalytic preparations.[17] Vinyl phosphonates are compounds that have a wide range of applications in many areas, such as copolymers,[18] polymer additives,[19] flame retardants,[20] intermediates for drugs,[21]agrochemicals,[22] in further transformations,[23] and other applications.[24] Functionalzed vinyl phosphonates are thus important and can be transformed into many products.[25]

Results and Discusion

In this paper, we provide useful transformations involving α-borylzirconacyclopentenes and α-phosphonozirconacyclopentenes **2** which are smoothly prepared by the reaction between the reagent Cp_2ZrCl_2/2EtMgBr with alkynylboranates and alkynylphoshonates **1** respectively.

SCHEME 1



Bromination of 2. It has been shown that bromination of zirconacyclopentenes with Br_2 or NBS initially cleaves the Zr−Csp2 bond.[26] Direct hydrolysis of **2** by H_3O^+ or D_2O provides products **3**, but when the α-phosphonozirconacyclopentenes or the α-borylzirconacyclopentenes were treated with 1 equiv of bromine, insertion occurred preferentially into the Zr−Csp2 bond to produce compounds **4** (Scheme 1). Halogenation of **2** using 2 equiv of Br_2 provided products **5** (Table 1). Regio- and stereochemistry of the brominated products were determined by NMR data and are consistent with a zirconacyclopentene intermediate.

Iodination of 2. Iodination of zirconacyclopentenes has been shown to be dependent on substitution of the double bond.[26] In general, the more hindered the substituent on C1 of the double bond in the zirconacyclopentenes, the more likely that iodination will cleave the Csp3−Zr bond. Takahashi has developed a procedure to selectively cleave the Csp2−Zr bond that involves initial methanolysis followed by iodination with I_2. He has recently reported results for the iodination of α-phosphonozirconacyclopentenes, but the selectivity was low and was always accompanied by oxidation of the phosphines to the phosphines oxide.[27] We have been investigating reactions involving complexes of 1-alkynylphosphonates

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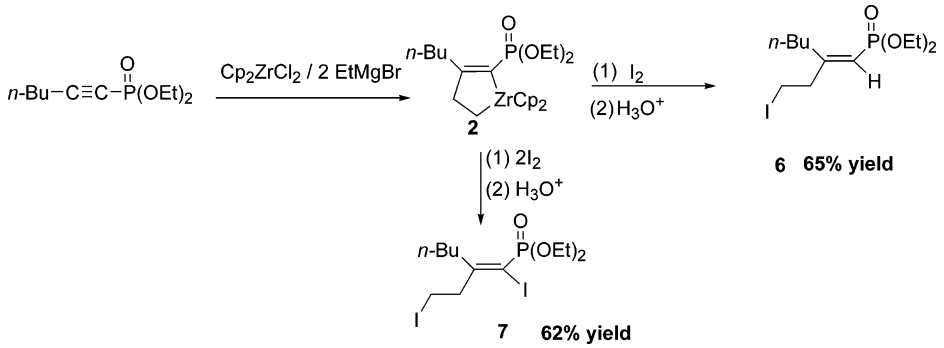
SCHEME 2



SCHEME 3

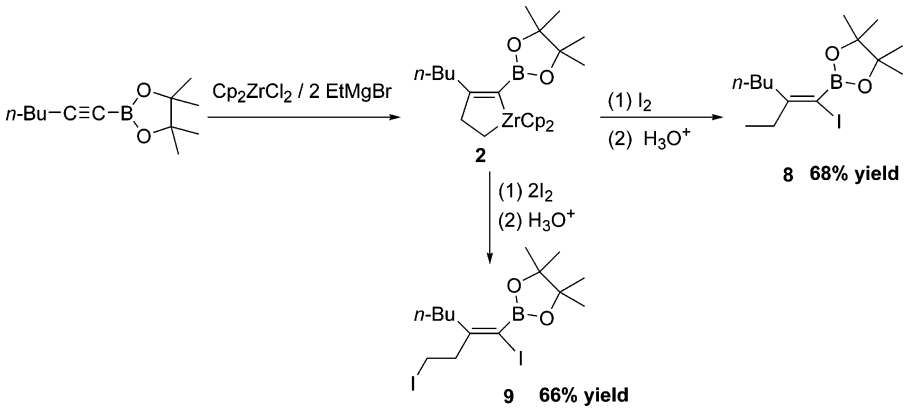


TABLE 1. Hydrolysis and Bromination of 2

product	R	Z	G	% isolated yield[a]
3a	*n*Bu	Y	H	85
3b	ClC_3H_6	Y	H	83
3c	*n*Bu	W	H	85
3d	Ph	W	H	84
3e	*n*Bu	Y	D	75
4a	*n*Bu	Y	H	73
4b	*n*Bu	Y	D	67
4c	ClC_3H_6	Y	H	72
4d	*n*Bu	W	H	70
4e	*n*Bu	W	D	65
4f	Ph	W	H	71
5a	*n*Bu	Y	-	69
5b	ClC_3H_6	Y	-	65
5c	*n*Bu	W	-	67
5d	Ph	W	-	63

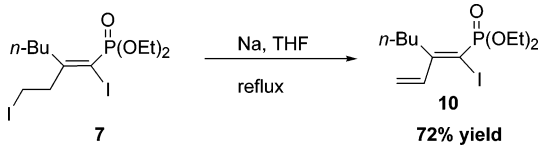
[a] GC and NMR yields of the reaction mixture were >95%.

and 1-alkynylboronates with group IV reagents. Highly regio- and stereoselective transformations are possible.[10,28] In the present case, iodinolyis of α-phosphonozirconacyclopentenes with 1 equiv of I_2 cleaves the Zr−Csp3 bond (Scheme 2).

On the other hand, α-borylzirconacyclopentenes react preferentially at the Zr−Csp2 bond (Scheme 3).

The reason for this is probably due to sterics. When 2 equiv of I_2 was used, both Zr−Csp3 and Zr−Csp2 bonds were cleaved to give the diiodo species. Analogous diiodo compounds have been converted into cyclobutenes.[29]

SCHEME 4



When **7** was treated with sodium metal, HI was eliminated to give the 1,3-butadiene which is equivalent of ligand replacement of ethylene with acetylene.[30] The assigned stereochemistry is consistent with NMR data (Scheme 4[8]).

Allylation of 2. The reaction of 1 equiv of allyl bromide with either α-phosphonozirconacyclopentenes or α-borylzirconacyclopentenes in the presence of CuCN resulted in selective insertion of the Zr−Csp2 bond.[31] With 2 equiv of allyl bromide the diallylated products were obtained (Scheme 5).

Propargylation of 2. Addition of 1 equiv of propargyl bromide to α-borylzirconacyclopentene **2a** in the presence of an equivalent amount of CuCl and 3 mol % of $[(Ph)_3P]_4Pd$ afforded regioselectivly the allene product **13** in which the insertion was on the Zr−Csp2 bond. When 2 equiv of propargyl bromide was used, double insertion occurred to produce the products **14** (Scheme 6). But unfortunately, all efforts to isolate **14** as a pure compound by silica gel chromatography techniques failed, and it could only be analyzed by GCMS.

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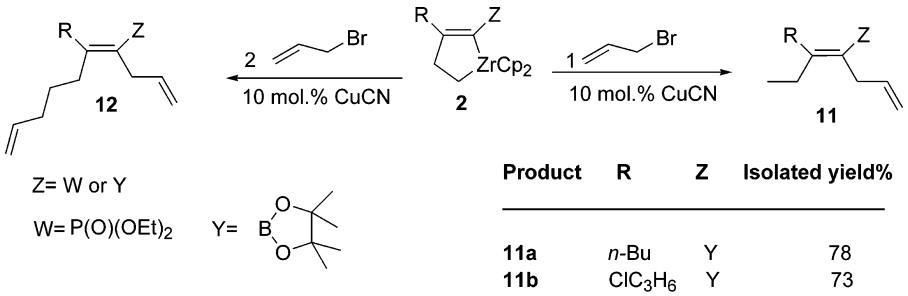
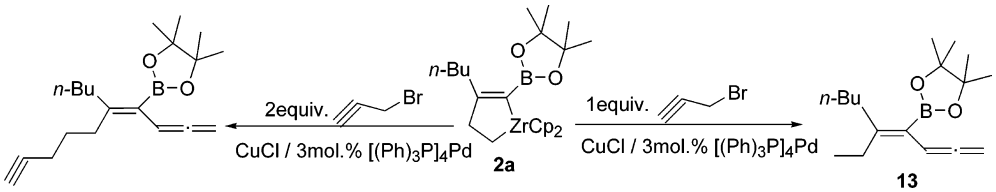
SCHEME 5

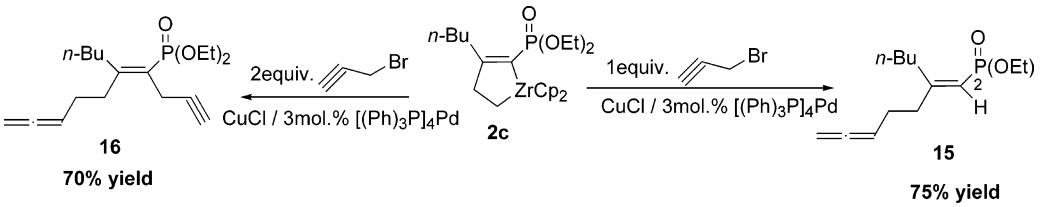


Product	R	Z	Isolated yield%
11a	*n*-Bu	Y	78
11b	ClC_3H_6	Y	73
11c	*n*-Bu	W	69
12a	*n*-Bu	Y	65
12b	*n*-Bu	W	60

SCHEME 6



SCHEME 7



On the other hand, under the same reaction conditions, when α-phosphonozirconacyclopentene **2c** was reacted with 1 equiv of propargyl bromide, regioselective insertion on the Zr−Csp3 bond took place to provide compound **15**. This variation in the regioselectivity is also apparently due to steric reasons. In the case of addition of 2 equiv of propargyl bromide, compound **16** was obtained (Scheme 7).

Conclusion

We have presented an approach for the preparation of novel vinyl boronates and vinyl phosphonates by bromination, iodination, allylation, and propargylation of α-borylzirconacyclopentenes and α-phosphonozirconacyclopentenes. The reaction proceeds in two steps, both with high regio- and stereoselectivity. In the case of the vinyl boronates, the Zr−Csp2 bond is initially cleaved by 1 equiv of electrophile. With the phosphonates, either the Zr−Csp2 bond (allyl bromide, Br_2) or the Zr−Csp3 bond (I_2, propargyl bromide) may be initially cleaved.

Experimental Section

Procedure for the Synthesis of (*Z*)-2-(2-Ethylhex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a). To 0.306 g (1.05 mmol) of zirconecene dichloride dissolved in 7 mL of dry THF at −78 °C was added 1.05 mL of 2 M EtMgBr (2.1 mmol) dropwise in a 25 mL round-bottom flask. After being stirred for 1 h at −78 °C, 1 mmol of 2-(hex-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The reaction was gradually warmed to 0 °C, stirred for 3 h, and quenched with diluted HCl solution. Then the oily product was extracted by Et_2O. ^{1}H NMR (300 MHz): δ 0.90 (t, 3H, J_{HH} = 7.2 Hz), 1.02 (t, 3H, J_{HH} = 7.2 Hz), 1.26 (s, 12H), 1.50−1.83 (overlap, 4H), 2.12 (q, 2H, J_{HH} = 7.2), 2.40 (t, 2H, J_{HH} = 7.5 Hz), 5.11 (s, 1H). ^{11}B NMR (96.24 MHZ): δ 28.54. ^{13}C NMR (75.5 MHz): δ 12.2, 13.9, 22.6, 24.8, 31.5, 31.8, 34.7, 82.4, 169.0. MS *m/z*: 238 (1.9), 219 (2.9), 196 (3.8), 153 (12.5), 139 (63.5), 84 (29.8), 55 (43.3), 43 (91.4), 41 (100), 29 (51.0).

Procedure for the Synthesis of (*E*)-2-(1-Bromo-2-ethylhex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a). To 0.306 g (1.05 mmol) of zirconecene dichloride dissolved in 7 mL of dry THF at −78 °C was added 1.05 mL of 2 M EtMgBr (2.1 mmol) dropwise in a 25 mL round-bottom flask. After the mixture was stirred for 1 h at −78 °C, 1 mmol of 2-(hex-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The reaction was gradually warmed to 0 °C and stirred for 3 h. Then 1 equiv of bromine was added, and the reaction was warmed to room temperature and allowed to stir overnight. The reaction was worked up with diluted HCl, and the product was extracted with diethyl ether (2 × 15 mL), separated on silica gel column (90% petroleum ether/10% diethyl ether), and analyzed by GCMS, elemental analysis, and NMR spectroscopy. ^{1}H NMR (300 MHz): δ 0.90 (t, 3H, J_{HH} = 6.3 Hz), 1.06 (t, 3H, J_{HH} = 7.8 Hz), 1.30 (s, 12H), 1.20−1.48 (overlap, 4H), 2.38 (q, 2H, J_{HH} = 7.2 Hz), 2.41 (t, 2H, J_{HH} = 7.2 Hz). ^{11}B NMR (96.24 MHZ): δ 30.54. ^{13}C NMR (75.5 MHz): δ 11.5, 13.9, 22.6,

24.6, 30.0, 31.38, 34.7, 84.1, 158.0. MS *m/z*: 318 (9.6), 316 (11.5), 261 (30.8), 259 (31.0), 237 (4.8), 195 (13.5), 139 (12.5), 101 (34.6), 83 (32.7), 59 (30.8), 43 (69.2), 41 (100), 29 (39.4). Anal. Calcd for $C_{14}H_{26}BBrO_2$: C, 53.03; H, 8.27; B, 3.41; Br, 25.20. Found: C, 52.92; H, 8.13; B, 3.52; Br, 25.33.

Procedure for the Synthesis of (*Z*)-2-(1-Bromo-2-(2-bromoethyl)hex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a). Identical to **4a** except that 2 equiv of bromine was used. ^{1}H NMR (300 MHz): δ 0.99 (t, 3H, J_{HH} = 7.5 Hz), 1.28 (s, 12H), 1.21−1.55 (overlap, 4H), 2.42 (t, 2H, J_{HH} = 7.5 Hz), 2.88 (t, 2H, J_{HH} = 7.5 Hz), 3.43 (t, 2H, J_{HH} = 8.1 Hz). ^{11}B NMR (96.24 MHZ): δ 27.12. ^{13}C NMR (75.5 MHz): δ 13.8, 22.4, 24.6, 28.3, 31.2, 35.5, 43.3, 84.4, 155.5. MS *m/z*: 398 (1.9), 396 (3.8), 394 (2.1), 317 (14.4), 315 (14.7), 275 (10.4), 273 (12.5), 238 (10.6), 217 (21.6), 215 (21.5), 187 (17.3), 109 (44.2), 101 (100), 83 (52.9), 67 (52.2), 41 (58.7), 29 (12.4). Anal. Calcd for $C_{14}H_{25}BBr_2O_2$: C, 42.47; H, 6.36; B, 2.73; Br, 40.36. Found: C, 42.55; H, 6.42; B, 2.62; Br, 40.22.

Procedure for the Synthesis of (*E*)-Diethyl 2-(2-Iodoethyl)hex-1-enylphosphonate (6). Identical to **4d** except that 1 equiv of iodine was used. ^{1}H NMR (300 MHz): δ 0.91 (t, 3H, J_{HH} = 6.9 Hz), 1.32 (t, 6H, J_{HH} = 7.2 Hz), 1.35−1.48 (overlap, 4H), 2.50 (dt, 2H, J_{HH} = 7.2 Hz, $^4J_{PH}$ = 2.1 Hz), 2.72 (t, 2H, J_{HH} = 7.5 Hz), 3.23 (t, 2H, J_{HH} = 7.5 Hz), 4.03−4.20 (m, 4H), 5.38 (d, 1H, J_{HH} = 16.8 Hz). ^{31}P NMR (121.4 MHZ): δ 18.29. ^{13}C NMR (75.5 MHz): δ 13.9, 16.4 (d, $^3J_{PC}$ = 6.5 Hz), 22.8, 30.56, 32.9 (d, $^3J_{PC}$ = 6.8 Hz), 41.7 (d, $^3J_{PC}$ = 22.8 Hz), 48.5 (d, $^3J_{PC}$ = 15.8 Hz), 61.4 (d, $^2J_{PC}$ = 5.4 Hz), 113.5 (d, $^1J_{PC}$ = 188.8 Hz), 164.1 (d, $^2J_{PC}$ = 7.5 Hz). MS *m/z*: 374 (41.2), 345 (62.7), 317 (16.7), 289 (41.2), 247 (77.5), 219 (34.3), 191 (85.3), 109 (95.1), 79 (86.3), 43 (66.7), 29 (100). Anal. Calcd for $C_{12}H_{24}IO_3P$: C, 38.52; H, 6.46; I, 33.91; P, 8.28. Found: C, 38.41; H, 6.40; I, 34.03; P, 8.18.

Procedure for the Synthesis of (*Z*)-Diethyl 1-Iodo-2-(2-iodoethyl)hex-1-enylphosphonate (7). Identical to **6** except that 2 equiv of iodine was used. **7**. ^{1}H NMR (300 MHz): δ 0.88 (t, 3H, J_{HH} = 6.9 Hz), 1.31 (t, 6H, J_{HH} = 7.2 Hz), 1.40−1.51 (overlap, 4H), 2.78 (dt, 2H, J_{HH} = 6.6 Hz, $^4J_{PH}$ = 1.5 Hz), 2.97 (dt, 2H, J_{HH} = 7.8 Hz, $^4J_{PH}$ = 2.2 Hz), 3.17 (t, J_{HH} = 6.6 Hz), 4.00−4.20 (m, 4H). ^{31}P NMR (121.4 MHZ): δ 10.56. ^{13}C NMR (75.5 MHz): δ 13.8, 16.1 (d, $^3J_{PC}$ = 6.6 Hz), 22.6, 31.1, 34.7 (d, $^3J_{PC}$ = 4.9 Hz), 48.5 (d, $^3J_{PC}$ = 15.8 Hz), 62.7 (d, $^2J_{PC}$ = 5.4 Hz), 110.4 (d, $^1J_{PC}$ = 205.7 Hz), 159.5 (d, $^2J_{PC}$ = 16.9 Hz). MS *m/z*: 500 (4.6), 415 (4.6), 373 (100), 345 (17.4), 317 (34.7), 246 (45.8), 107 (20.8), 65 (55.8), 43 (33.8), 28 (57.7). Anal. Calcd for $C_{12}H_{23}I_2O_3P$: C, 28.82; H, 4.64; I, 50.75; P, 6.19. Found: C, 28.97; H, 4.50; I, 50.66; P, 6.28.

Procedure for the Synthesis of (*E*)-2-(2-Ethyl-1-iodohex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8). Identical to **4a** except that 1 equiv of iodine was used. ^{1}H NMR (300 MHz): δ 0.90 (t, 3H, J_{HH} = 6.0 Hz), 1.03 (t, 3H, J_{HH} = 7.8 Hz), 1.29 (s, 12H), 1.25−1.47 (overlap, 4H), 2.38 (q, 2H, J_{HH} = 7.5 Hz), 2.40 (t, 2H, J_{HH} = 7.2 Hz). ^{11}B NMR (96.24 MHZ): δ 27.60. ^{13}C NMR (75.5 MHz): δ 11.5, 13.9, 22.6, 24.6, 30.1, 31.3, 34.6, 84.0, 157.2. MS *m/z*: 364 (17.6), 307 (20.6), 195 (22.1), 137 (21.6), 109 (78.4), 101 (100), 83 (60.0), 55 (39.2), 41 (52.0). Anal. Calcd for $C_{14}H_{26}BIO_2$: C, 46.19; H, 7.20; B, 2.97; I, 34.86. Found: C, 46.02; H, 7.07; B, 3.11; I, 35.03.

Procedure for the Synthesis of (*Z*)-2-(1-Iodo-2-(2-iodoethyl)hex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9). Identical to **8** except that 2 equiv of iodine was used. ^{1}H NMR (300 MHz): δ 0.95 (t, 3H, J_{HH} = 7.3 Hz), 1.28 (s, 12H), 1.20−1.50 (overlap, 4H), 2.40 (t, 2H, J_{HH} = 7.3 Hz), 2.80 (t, 2H, J_{HH} = 7.5 Hz), 3.40 (t, 2H, J_{HH} = 7.5 Hz). ^{11}B NMR (96.24 MHZ): δ 27.59. ^{13}C NMR (75.5 MHz): δ 13.8, 22.4, 24.6, 28.3, 31.1, 35.3, 42.1, 84.3, 155.6. MS *m/z*: 490 (15.7), 363 (14.5), 307 (19.9), 195 (22.7), 137 (25.6), 109 (66.7), 101 (77.3), 83 (54.8), 55 (52.2), 41 (100). Anal. Calcd for $C_{14}H_{25}BI_2O_2$: C, 34.32; H, 5.14; B, 2.21; I, 51.80. Found: C, 34.21; H, 5.02; B, 2.33, I, 51.90.

Procedure for the Synthesis of (*Z*)-Diethyl 1-Iodo-2-vinylhex-1-enylphosphonate (10). Into a 25 mL round-bottom flask was injected 8 mL of dry THF by syringe followed by the addition of 0.50 g (1 mmol) of **9** and 4 mmol of sodium metal successively. The flask was equipped with a condenser under nitrogen, and the reaction was left under reflux overnight. After workup, the reaction mixture was concentrated by vacuum and separated on a silica gel column (80% petroleum ether/20% ethyl acetate). **10**. ^{1}H NMR (300 MHz): δ 0.91 (t, 3H, J_{HH} = 6.9 Hz), 1.28 (dt, 6H, J_{HH} = 7.2 Hz, $^4J_{PH}$ = 0.3 Hz), 1.30−1.50 (overlap, 4H), 3.00 (dt, 2H, J_{HH} = 7.8 Hz, $^4J_{PH}$ = 1.5 Hz), 4.05−4.20 (m, 4H), 5.45 (dd,, 1H, $^3J_{HH}$ = 10.8 Hz, $^2J_{HH}$ = 3.3 Hz), 5.63 (d, 1H, $^3J_{HH}$ = 17.1 Hz), 6.75−6.85 (m, 1H). ^{31}P NMR (121.4 MHz): δ 11.52. ^{13}C NMR (75.5 MHz): δ 16.2 (d, $^3J_{PC}$ = 6.6 Hz), 21.0, 22.9, 31.4 (d, $^3J_{PC}$ = 4.6 Hz), 32.5, 62.7 (d, $^2J_{PC}$ = 5.6 Hz), 113.0 (d, $^1J_{PC}$ = 190.0 Hz), 122.1, 143.1 (d, $^3J_{PC}$ = 22.0 Hz), 162.7 (d, $^2J_{PC}$ = 9.2 Hz). MS *m/z*: 372 (21.1), 330 (33.1), 287 (42.6), 274 (23.4), 245 (69.2), 189 (60.6), 135 (26.6), 128 (39.4), 107 (100), 91 (55.3), 81 (48.9), 65 (44.7). Anal. Calcd for $C_{12}H_{22}IO_3P$: C, 38.73; H, 5.96; I, 34.10; P, 8.32. Found: C, 38.88; H, 6.11; I, 34.31; P, 8.20.

Procedure for the Synthesis of (*E*)-2-(5-Ethylnona-1,4-dien-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11a). To 0.306 g (1.05 mmol) of zirconecene dichloride dissolved in 7 mL of dry THF at −78 °C was added 1.05 mL of 2 M EtMgBr (2.1 mmol) dropwise in a 25 mL round-bottom flask. After the mixture was stirred for 1 h at −78 °C, 1 mmol of 2-(hex-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The reaction was gradually warmed to 0 °C and stirred for 3 h. Then 10 mol % of CuCN was added followed by 1 equiv of allyl bromide, and the reaction was warmed to rt and allowed to stir overnight. The reaction was worked up with diluted HCl, and the product was extracted with diethyl ether (2 × 15 mL), separated on silica gel column (90% petroleum ether/10% diethyl ether), and analyzed by GCMS, elemental analysis, and NMR spectroscopy. ^{1}H NMR (300 MHz): δ 0.90 (t, 3H, J_{HH} = 6.9 Hz), 0.96 (t, 3H, J_{HH} = 7.5 Hz), 1.29 (s, 12H), 1.30−1.45 (overlap, 4H), 2.13 (q, 2H, J_{HH} = 6.5 Hz), 2.20 (t, 2H, J_{HH} = 7.0 Hz), 2.80 (d, 2H, J_{HH} = 3.4 Hz), 4.845.11 (m, 2H), 5.43−5.77 (m, 1H, J_{HH} = 6.9 Hz). ^{11}B NMR (96.24 MHz): δ 31.48. ^{13}C NMR (75.5 MHz): δ 13.2, 14.1, 23.0, 24.8, 25.1, 32.5, 34.8, 35.3, 82.7, 113.8, 138.4, 157.6. MS *m/z*: 278 (48.0), 263 (5.9), 249 (5.9), 221 (19.6), 177 (24.5), 149 (48.0), 135 (42.2), 108 (63.7), 101 (100), 84 (80.4), 55 (79.4), 43 (73.5), 41 (91.2), 29 (28.4). Anal. Calcd for $C_{17}H_{31}BO_2$: C, 73.38; H, 11.23; B, 3.89. Found: C, 73.22; H, 11.32; B, 3.93.

Procedure for the Synthesis of (*Z*)-2-(5-Butyldeca-1,4,9-trien-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12a). Identical to **11a** except for the addition of 2 equiv of allyl bromide. ^{1}H NMR (300 MHz): δ 0.90 (t, 3H, J_{HH} = 6.9 Hz), 1.25 (s, 12H), 1.20−1.48 (overlap, 6H), 2.06−2.19 (overlap, 4H, J_{HH} = 6.5 Hz), 2.29 (m, 2H), 2.87 (d, 2H, J_{HH} = 3.9 Hz), 4.84 (m, overlap, 4H), 5.40−5.80 (m, overlap, 2H). ^{11}B NMR (96.24 MHZ): δ 31.97. ^{13}C NMR (75.5 MHz): δ 13.2, 14.1, 23.0, 24.8, 25.1, 32.5, 34.8, 35.3, 82.7, 113.8, 138.4, 157.6. MS *m/z*: 318 (3.9), 276 (5.9), 261 (11.8), 207 (16.7), 136 (82.4), 101 (74.5), 84 (100), 55 (55.9), 41 (49.0), 29 (11.4). Anal. Calcd for $C_{20}H_{35}BO_2$: C, 75.47; H, 11.08; B, 3.40. Found: C, 75.56; H, 10.88; B, 3.31.

Procedure for the Synthesis of (*E*)-2-(5-Ethylnona-1,2,4-trien-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13). To 0.306 g (1.05 mmol) of zirconecene dichloride dissolved in 7 mL of dry THF at −78 °C was added 1.05 mL of 2 M EtMgBr (2.1 mmol) dropwise in a 25 mL round-bottom flask. After the mixture was stirred for 1 h at −78 °C, 1 mmol of 2-(hex-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The reaction was gradually warmed to 0 °C and stirred for 3 h. Then the catalytic system of 1 mmol of CuCl/5mol % of $(Ph_3P)_4Pd$ was added followed by 1 equiv of propargyl bromide, and the reaction was warmed to room temperature and allowed to stir overnight. The reaction was worked up with

diluted HCl, and the product was extracted with diethyl ether (2 × 15 mL), separated on silica gel column (90% petroleum ether/10% diethyl ether), and analyzed by GCMS, elemental analysis, and NMR spectroscopy. ^{1}H NMR (300 MHz): δ 0.90 (t, 3H, J_{HH} = 7.2 Hz), 1.00 (t, 3H, J_{HH} = 7.5 Hz), 1.30 (s, 12H), 1.35−1.45 (overlap, 4H), 2.20 (q, 2H, J_{HH} = 7.2 Hz), 2.31 (t, 2H, J_{HH} = 7.0 Hz), 4.84 (d, 2H, 6.9 Hz), 6.15 (t, 1H). ^{11}B NMR (96.24 MHZ): δ 31.06. ^{13}C NMR (75.5 MHz): δ 13.5, 14.0, 22.7, 24.7, 24.8, 30.0, 30.2, 81.2, 83.3, 95.7, 156.7, 208.6. MS *m/z*: 276 (15.4), 261 (3.8), 219 (34.6), 175 (6.7), 119 (33.7), 101 (100), 84 (44.2), 55 (34.6), 43 (54.9), 41 (73.1), 29 (35.6). Anal. Calcd for $C_{17}H_{29}BO_2$: C, 73.92; H, 10.58; B, 3.91. Found: C, 73.82; H, 10.44; B, 4.07.

Procedure for the Synthesis of (*Z*)-2-(5-Butyldeca-1,2,4-trien-9-yn-4-yl)-4,4,5-trimethyl-1,3,2-dioxaborolane (14). Identical to **13** except for the addition of 2 equiv of propargyl bromide. MS *m/z*: 314 (4.9), 285 (2.9), 185 (10.1), 157 (20.6), 143 (47.1), 128 (41.2), 83 (47.1), 55 (70.59), 43 (73.5), 41 (100).

Procedure for the Synthesis of (*E*)-Diethyl 2-Butylhepta-1,5,6-trienylphosphonate (15). Identical to **13** except that diethyl hex-1-ynylphosphonate was used. ^{1}H NMR (300 MHz): δ 0.91 (t, 3H, J_{HH} = 7.2 Hz), 1.28 (dt, 6H, J_{HH} = 6.9 Hz, $^4J_{PH}$ = 0.3 Hz), 1.23−1.50 (overlap, 4H), 2.18 (m, 2H), 2.27 (t, 2H, J_{HH} = 8.1 Hz), 2.49 (dt, 2H, J_{HH} = 6.9 Hz, $^4J_{PH}$ = 2.1 Hz), 3.90−4.15 (m, 4H), 4.65−4.70 (m, 2H), 5.08 (t, 1H, J_{HH} = 6.6 Hz), 5.35 (d, 1H, $^3J_{PH}$ = 18.3 Hz). ^{31}P NMR (121.4 MHZ): δ 19.47. ^{13}C NMR (75.5 MHz): δ 13.9, 16.3 (d, $^3J_{PC}$ = 6.6 Hz), 22.9, 26.0, 30.7, 33.6, 37.2, 61.3 (d, $^2J_{PC}$ = 5.4 Hz), 75.5, 88.9, 112.3 (d, $^1J_{PC}$ = 190.0 Hz), 162.7 (d, $^2J_{PC}$ = 9.2 Hz), 208.2.; MS (*m/z*) 286 (12.7), 285 (23.5), 249 (48.0), 244 (100), 229 (50.0), 192 (57.8), 148 (64.1), 138 (38.2), 91 (22.5), 53 (40.2), 29 (45.1). Anal. Calcd for $C_{15}H_{27}O_3P$: C, 62.92; H, 9.50; P, 10.82. Found: C, 63.06; H, 9.35; P, 10.6.

Procedure for the Synthesis of (*E*)-Diethyl 5-Butyldeca-4,8,9-trien-1-yn-4-ylphosphonate (16). Identical to **14** except that diethyl hex-1-ynylphosphonate was used. ^{1}H NMR (300 MHz): δ 0.92 (t, 3H, J_{HH} = 7.2 Hz), 1.32 (dt, 6H, J_{HH} = 6.9 Hz, $^4J_{PH}$ = 0.3 Hz), 1.20−1.50 (overlap, 4H), 2.30 (t, 1H), 2.31 (m, 2H), 2.54 (t, 2H, J_{HH} = 7.6 Hz), 2.75 (dt, 2H, J_{HH} = 6.9 Hz, $^4J_{PH}$ = 2.1 Hz), 4.00−4.15 (m, 4H), 4.65−4.70 (m, 4H), 4.68 (m, 2H, J_{HH} = 3.3 Hz), 5.35 (t, 1H, J_{HH} = 6.6 Hz). ^{31}P NMR (121.4 MHZ): δ 17.86. ^{13}C NMR (75.5 MHz): δ 13.8, 16.2 (d, $^3J_{PC}$ = 6.6 Hz), 22.7, 26.1, 30.0, 33.8, 36.9, 37.3, 62.55 (d, $^2J_{PC}$ = 5.5 Hz), 65.2, 74.6, 75.7, 89.0, 111.5 (d, $^1J_{PC}$ = 196.7 Hz), 163.5 (d, $^2J_{PC}$ = 10.1 Hz), 207.5. MS *m/z*: 324 (7.9), 295 (17.8), 267 (10.9), 239 (13.7), 211 (15.8), 185 (58.4), 143 (96.0), 129 (99.9), 128 (99.9), 105 (49.5), 91 (89.1), 65 (35.6), 41 (36.6), 29 (100). Anal. Calcd for $C_{18}H_{29}O_3P$: C, 66.64; H, 9.01; P, 9.55. Found: C, 66.45; H, 9.32; P, 9.33.

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Supporting Information Available: General experimental procedures, ^{1}H, ^{11}B, ^{11}C, and ^{31}P spectra, GC/MS spectra, and elemental analysis for compounds **3b**−**e**, **4b**−**f**, and **5b**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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