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

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Supporting Information

I. General experimental procedures	S1
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General comments: All reactions were carried out under a nitrogen atmosphere vacuum line and glove box techniques. Solvents were purified by distillation from appropriate drying agents under a nitrogen atmosphere. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded in CDCl_3 , ^{11}B NMR (96.24 MHz) was recorded in CDCl_3 in the presence of $\text{BF}_3\text{etherate}$ reference and ^{31}P NMR (121.4 MHz) was recorded in CDCl_3 . GCMS analysis were performed on HP GCMS instrument (Model GCD PLUS), with EI detector and 30 m methyl silicone column.

Procedure for the synthesis of (Z)-2-(5-chloro-2-ethylpent-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b). Identical to **3a** except that 2-(5-chloropent-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was used. ^1H NMR (300 MHz): δ 1.00 (t, 3H, $J_{\text{HH}} = 7.5$ Hz), 1.23 (s, 12H), 1.86 (m, 2H), 2.10 (q, 2H, $J_{\text{HH}} = 7.2$ Hz), 2.49 (t,

2H, $J_{\text{HH}} = 8.1$ Hz), 3.49 (t, 2H, $J_{\text{HH}} = 6.9$ Hz); ^{11}B NMR (96.24 MHz): δ 28.06; ^{13}C NMR (75.5 MHz): δ 12.1, 24.7, 29.6, 31.6, 32.6, 44.8, 82.6, 166.6; MS (m/z) 259 (0.1), 258 (0.2), 246 (0.1), 229 (0.3), 201 (2.1), 157 (1.7), 139 (7.1), 101 (11.9), 81 (15.6), 67 (19.3), 59 (25.9), 55 (37.1), 41 (100), 29 (32.6).

Procedure for the synthesis of (Z)-diethyl 2-ethylhex-1-enylphosphonate (3c).

Identical to **3a** except that diethyl hex-1-enylphosphonate was used. ^1H NMR (300 MHz): δ 0.89 (t, 3H, $J_{\text{HH}} = 6.9$ Hz), 1.02 (t, 3H, $J_{\text{HH}} = 7.5$ Hz), 1.29 (dt, 6H, $J_{\text{HH}} = 6.9$ Hz, $^4J_{\text{PH}} = 0.3$ Hz), 1.40-1.50 (overlap, 4H), 2.21 (q, 2H, $J_{\text{HH}} = 6.2$ Hz), 2.47 (dt, 2H, $J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{PH}} = 1.5$ Hz), 4.00-4.15 (m, 4H), 5.31 (d, 1H, $^2J_{\text{PH}} = 18.3$ Hz); ^{31}P NMR (121.4 MHz): δ 20.15; ^{13}C NMR (75.5 MHz): δ 11.7, 13.8, 16.1 (d, $^3J_{\text{PC}} = 6.5$ Hz), 22.7, 24.9 (d, $^3J_{\text{PC}} = 4.1$ Hz), 31.1, 31.9 (d, $^3J_{\text{PC}} = 14.07$ Hz), 62.5 (d, $^2J_{\text{PC}} = 5.4$ Hz), 108.7 (d, $^1J_{\text{PC}} = 189.6$ Hz), 163.9 (d, $^2J_{\text{PC}} = 13.5$ Hz); MS (m/z) 248 (9.8), 219 (39.2), 163 (68.6), 81 (68.9), 41 (89.2), 29 (100).

Procedure for the synthesis of (Z)-diethyl 2-phenylbut-1-enylphosphonate (3d).

Identical to **3a** except that diethyl 2-phenylethynylphosphonate was used. ^1H NMR (300 MHz): δ 1.05 (t, 3H, $J_{\text{HH}} = 7.8$ Hz), 1.17 (dt, 6H, $J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{PH}} = 0.3$ Hz), 2.48 (q, 2H, $J_{\text{HH}} = 6.3$ Hz), 3.90-4.10 (m, 4H), 5.81 (d, 1H, $^2J_{\text{PH}} = 14.1$ Hz), 7.13-7.45 (overlap, 5H); ^{31}P NMR (121.4 MHz): δ 18.24; ^{13}C NMR (75.5 MHz): δ 12.0, 16.1 (d, $^3J_{\text{PC}} = 6.2$ Hz), 34.4 (d, $^3J_{\text{PC}} = 21.5$ Hz), 61.7 (d, $^2J_{\text{PC}} = 6.04$ Hz), 116.6 (d, $^1J_{\text{PC}} = 185.1$ Hz), 127.5, 127.8, 128.1, 129.5, 148.4, 165.1 (d, $^2J_{\text{PC}} = 12.6$ Hz); MS (m/z) 268 (7.8), 266 (15.7), 209 (12.7), 137 (30.4), 128 (100), 102 (33.3), 77 (19.6), 55 (60.8), 29 (45.1).

Procedure for the synthesis of (Z)-2-(1- $^2\text{H}_1$ -2-[(2- $^2\text{H}_1$)ethyl]hex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e). Identical to **3c** except that the reaction was worked up with D_2O .

^1H NMR (300 MHz): δ 0.91 (t, 3H, $J_{\text{HH}} = 7.2$ Hz), 1.06 (t, 2H, $J_{\text{HH}} = 7.2$ Hz), 1.27 (s, 12H), 1.50-1.83 (overlap, 4H), 2.12 (t, 2H, $J_{\text{HH}} = 7.2$), 2.42 (t, 2H, $J_{\text{HH}} = 7.5$ Hz); ^{11}B NMR (96.24 MHz): δ 28.55; ^{13}C NMR (75.5 MHz): δ 13.0, 13.9, 22.6, 24.8, 31.6, 31.9, 34.6, 82.4, 167.2; MS (m/z) 240 (0.3), 244 (0.3), 198 (2.8), 182 (5.7), 140 (27.9), 101 (22.1), 83 (34.6), 55 (42.3), 43 (82.9), 41 (100), 29 (40.4).

Procedure for the synthesis of (*E*)-2-(1-bromo-2-[(2- $^2\text{H}_1$)ethyl]hex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **4b.** Identical to **4a** except that the reaction was worked up with D_2O . ^1H NMR (300 MHz): δ 0.90 (t, 3H, $J_{\text{HH}} = 7.2$ Hz), 1.03 (t, 2H, $J_{\text{HH}} = 7.2$ Hz), 1.28 (s, 12H), 1.50-1.83 (overlap, 4H), 2.35 (t, 2H, $J_{\text{HH}} = 7.2$), 2.40 (t, 2H, $J_{\text{HH}} = 7.5$ Hz); ^{11}B NMR (96.24 MHz): δ 27.55; ^{13}C NMR (75.5 MHz): δ 13.1, 13.9, 22.7, 24.8, 31.7, 31.9, 34.5, 82.2, 165.1; MS (m/z) 319 (6.7), 317 (7.3), 262 (26.1), 260 (27.3), 238 (4.8), 195 (14.6), 139 (11.7), 101 (37.8), 84 (32.5), 59 (30.0), 43 (69.7), 41 (100).

Procedure for the synthesis of (*E*)-2-(1-bromo-5-chloro-2-ethylpent-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c**).** Identical to **4a** except that 2-(5-chloropent-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was used. ^1H NMR (300 MHz): δ 1.02 (t, 3H, $J_{\text{HH}} = 7.6$ Hz), 1.28 (s, 12H), 1.75 (m, 2H), 2.12 (q, 2H, $J_{\text{HH}} = 7.5$ Hz), 2.54 (t, 2H, $J_{\text{HH}} = 7.5$ Hz), 3.55 (t, 2H, $J_{\text{HH}} = 6.9$ Hz); ^{11}B NMR (96.24 MHz): δ 27.35; ^{13}C NMR (75.5 MHz): δ 13.0, 22.6, 24.6, 28.8, 31.1, 44.2, 84.1, 158.0; MS (m/z) 338 (1.5), 337 (0.7), 279 (2.7), 278 (6.8), 277 (2.0), 238 (0.6), 193 (7.9), 101 (78.9), 84 (11.0), 55 (41.0), 41 (100); Anal. Calcd. for $\text{C}_{13}\text{H}_{23}\text{BBrClO}_2$: C, 46.27; H, 6.87; B, 3.20; Br, 23.68; Cl, 10.50. Found: C, 46.08; H, 6.99; B, 3.30; Br, 23.50; Cl, 10.66.

Procedure for the synthesis of (*E*)-diethyl 1-bromo-2-propylhex-1-enylphosphonate (4d). Identical to **4a** except that diethyl hex-1-ynylphosphonate was used and the product was separated on silica gel (80% petroleum ether: 20% ethyl acetate). ^1H NMR (300 MHz): δ 0.92 (t, 3H, $J_{\text{HH}} = 6.9$ Hz), 1.08 (t, 3H, $J_{\text{HH}} = 7.8$ Hz), 1.35 (dt, 6H, $J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{PH}} = 0.3$ Hz), 1.40-1.51 (overlap, 4H), 2.43 (q, 2H, $J_{\text{HH}} = 7.8$ Hz), 2.74 (dt, 2H, $J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{PH}} = 1.5$ Hz), 4.13-4.20 (m, 4H); ^{31}P NMR (121.4 MHz): δ 10.79; ^{13}C NMR (75.5 MHz): δ 11.3, 13.9, 16.2 (d, $^3J_{\text{PC}} = 6.6$ Hz), 22.8, 31.2, 32.0 (d, $^3J_{\text{PC}} = 13.7$ Hz), 34.0 (d, $^3J_{\text{PC}} = 3.7$ Hz), 62.5 (d, $^2J_{\text{PC}} = 5.4$ Hz), 106.8 (d, $^1J_{\text{PC}} = 208.1$ Hz), 165.4 (d, $^2J_{\text{PC}} = 16.0$ Hz); MS (m/z) 328 (3.4), 326 (3.4), 299 (1.9), 297 (1.9), 247 (100), 219 (14.7), 191 (26.5), 149 (12.5), 135 (5.9), 109 (19.6), 79 (18.6), 67 (16.2), 29 (14.7); Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{BrO}_3\text{P}$: C, 44.05; H, 7.39; Br, 24.42; P, 9.47. Found: C, 43.89; H, 7.30; Br, 24.55; P, 9.59.

Procedure for the synthesis of (*E*)-diethyl 1-bromo-2-[(2- $^2\text{H}_1$)ethyl]hex-1-enylphosphonate (4e). Identical to **4d** except that the reaction was worked up with D_2O . ^1H NMR (300 MHz): δ 0.92 (t, 3H, $J_{\text{HH}} = 6.9$ Hz), 1.20 (t, 2H, $J_{\text{HH}} = 6.9$ Hz), 1.32 (t, 6H, $J_{\text{HH}} = 7.2$ Hz), 1.37-1.50 (overlap, 4H), 2.74 (dt, 2H, $J_{\text{HH}} = 6.6$ Hz, $^4J_{\text{PH}} = 2.7$ Hz), 2.72 (t, 2H, $J_{\text{HH}} = 7.2$ Hz), 4.03-4.12 (m, 4H); ^{31}P NMR (121.4 MHz): δ 18.33; ^{13}C NMR (75.5 MHz): δ 12.3, 13.7, 16.2 (d, $^3J_{\text{PC}} = 6.6$ Hz), 22.8, 31.4, 32.4 (d, $^3J_{\text{PC}} = 15.6$ Hz), 34.2 (d, $^3J_{\text{PC}} = 3.6$ Hz), 62.8 (d, $^2J_{\text{PC}} = 6.5$ Hz), 107.3 (d, $^1J_{\text{PC}} = 203.3$ Hz), 162.2 (d, $^2J_{\text{PC}} = 11.9$ Hz); MS (m/z) 329 (5.9), 327 (6.0), 300 (21.6), 298 (21.6), 248 (56.9), 192 (25.5), 150 (14.7), 80 (43.1), 43 (46.08), 29 (100).

Procedure for the synthesis of (*E*)-diethyl 1-bromo-2-phenylbut-1-enylphosphonate (4f). Identical to **4d** except that diethyl 2-phenylethynylphosphonate was used. **4f**: ^1H NMR (300 MHz): δ 0.98 (t, 3H, $J_{\text{HH}} = 7.8$ Hz), 1.12 (dt, 6H, $J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{PH}} = 0.3$ Hz), 2.71 (q, 2H, $J_{\text{HH}} = 7.2$ Hz), 3.76-

4.00 (m, 4H), 7.18-7.40 (overlap, 5H); ^{31}P NMR (121.4 MHz): δ 9.51; ^{13}C NMR (75.5 MHz): δ 13.3, 16.1 (d, $^3J_{\text{PC}} = 6.5$ Hz), 34.4 (d, $^3J_{\text{PC}} = 17.7$ Hz), 62.8 (d, $^2J_{\text{PC}} = 5.6$ Hz), 112.8 (d, $^1J_{\text{PC}} = 202.0$ Hz), 127.1, 128.3, 128.0, 141.2 (d, $^3J_{\text{PC}} = 16.9$ Hz), 164.4 (d, $^2J_{\text{PC}} = 12.4$ Hz); MS (m/z) 346 (35.3), 344 (35.3), 289 (20.6), 237 (25.5), 209 (99.8), 191 (43.1), 135 (21.6), 128 (100), 115 (25.0), 77 (19.6), 29 (50.0); Anal. Calcd. for $\text{C}_{14}\text{H}_{20}\text{BrO}_3\text{P}$: C, 48.43; H, 5.81; Br, 23.01; P, 8.92. Found: C, 48.30; H, 5.81; Br, 22.88; P, 9.05.

Procedure for the synthesis of (Z)-2-(1-bromo-2-(2-bromoethyl)-5-chloropent-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b). Identical to **4a** except that diethyl 5-chloropent-1-ynylphosphonate was used. ^1H NMR (300 MHz): δ 1.28 (s, 12H), 1.77 (m, 2H), 2.17 (t, 2H, $J_{\text{HH}} = 7.5$ Hz), 2.54 (t, 2H, $J_{\text{HH}} = 7.5$ Hz), 3.50 (t, 2H, $J_{\text{HH}} = 6.6$ Hz), 3.55 (t, 2H, $J_{\text{HH}} = 7.0$ Hz); ^{11}B NMR (96.24 MHz): δ 27.43; ^{13}C NMR (75.5 MHz): δ 22.5, 24.6, 28.7, 31.1, 43.8, 44.2, 84.0, 157.3; MS (m/z) 417 (1.8), 415 (6.5), 414 (5.6), 339 (1.9), 337 (6.7), 335 (4.5), 334 (4.5), 318 (1.4), 336 (3.8), 191 (9.8), 169 (8.5), 93 (83.7), 84 (28.3), 59 (47.1), 43 (75.0), 41 (100), 29 (29.8); Anal. Calcd. for $\text{C}_{13}\text{H}_{22}\text{BBr}_2\text{ClO}_2$: C, 37.50; H, 5.33; B, 2.60; Br, 38.38; Cl, 8.51. Found: C, 37.63; H, 5.42; B, 2.51; Br, 38.20; Cl, 8.44.

Procedure for the synthesis of (Z)-diethyl 1-bromo-2-(2-bromoethyl)hex-1-enylphosphonate (5c). Identical to **4d** except that two equiv. of bromine were used. **5c:** ^1H NMR (300 MHz): δ 0.92 (t, 3H, $J_{\text{HH}} = 6.9$ Hz), 1.35 (dt, 6H, $J_{\text{HH}} = 6.6$ Hz, $^4J_{\text{PH}} = 0.3$ Hz), 1.40-1.51 (overlap, 4H), 2.78 (dt, 2H, $J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{PH}} = 1.5$ Hz), 2.98 (t, $J_{\text{HH}} = 7.2$ Hz), 3.48 (t, $J_{\text{HH}} = 8.1$ Hz), 4.13-4.20 (m, 4H); ^{31}P NMR (121.4 MHz): δ 9.33; ^{13}C NMR (75.5 MHz): δ 13.7, 16.1 (d, $^3J_{\text{PC}} = 6.5$ Hz), 22.6, 27.6, 31.0, 34.6 (d, $^3J_{\text{PC}} = 3.8$ Hz), 41.3 (d, $^3J_{\text{PC}} = 13.7$ Hz), 62.7 (d, $^2J_{\text{PC}} = 5.4$ Hz), 110.4 (d, $^1J_{\text{PC}} =$

205.7 Hz), 159.5 (d, $^2J_{\text{PC}} = 16.9$ Hz); MS (m/z) 408 (0.3), 406 (0.4), 404 (0.4), 377 (1.0), 327 (56.7), 325 (56.0), 271 (21.2), 269 (22.0), 189 (8.6), 133 (15.4), 107 (100), 65 (55.8), 43 (43.8), 28 (97.1); Anal. Calcd. for $\text{C}_{12}\text{H}_{23}\text{Br}_2\text{O}_3\text{P}$: C, 35.49; H, 5.71; Br, 39.35; P, 7.63. Found: C, 35.38; H, 5.89; Br, 39.41; P, 7.72.

Procedure for the synthesis of (*E*)-diethyl 1,4-dibromo-2-phenylbut-1-enylphosphonate (5d). Identical to **5c** except that diethyl 2-phenylethynylphosphonate was used. ^1H NMR (300 MHz): δ 1.41 (dt, 6H, $J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{PH}} = 0.6$ Hz), 3.27 (t, $J_{\text{HH}} = 6.9$ Hz), 3.68 (dt, 2H, $J_{\text{HH}} = 6.9$ Hz, $^5J_{\text{PH}} = 2.1$ Hz), 4.17-4.35 (m, 4H), 7.17-7.42 (overlap, 5H); ^{31}P NMR (121.4 MHz): δ 9.73; ^{13}C NMR (75.5 MHz): δ 16.3 (d, $^3J_{\text{PC}} = 6.6$ Hz), 29.6, 44.0 (d, $^3J_{\text{PC}} = 26.5$ Hz), 63.2 (d, $^2J_{\text{PC}} = 5.4$ Hz), 112.2 (d, $^1J_{\text{PC}} = 203.3$ Hz), 127.0, 128.3, 128.5, 141.2 (d, $^3J_{\text{PC}} = 16.4$ Hz), 158.3 (d, $^2J_{\text{PC}} = 16.9$ Hz); MS (m/z) 429 (0.1), 428 (0.1), 427 (0.3), 426 (0.1), 425 (0.2), 349 (100), 347 (100), 319 (12.3), 317 (12.3), 291 (62.7), 289 (63.0), 209 (38.2), 128 (94.1), 77 (19.8), 29 (40.2); Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{Br}_2\text{O}_3\text{P}$: C, 39.46; H, 4.49; Br, 37.51; P, 7.27. Found: C, 39.55; H, 4.62; Br, 37.38; P, 7.14.