Supporting Information
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Rhodium-Catalysed Hydroboration of Terminal Alkynes Using Pinacolborane Promoted by Tri(2-furyl)phosphine

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Supplementary Information

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Experimental procedures and spectroscopic data

$^1$H and $^13$C spectra

methyl $(E)$-2,6-dimethylnon-2-en-8-ynoate (2)

$(\pm)$-Methyl $(2E,7E)$-2,6-dimethyl-8-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-2,7-dienoate (3)

$(E)$-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (4)

$(E)$-2-(Hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

$(E)$-t$^c$t-Butyldimethyl((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)silane (6)

$(E)$-2-(4-(Methoxymethoxy)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)

$(E)$-2-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (8)

X-Ray structure

Rh[P(2-Fu)$_3$]$_2$(CO)Cl
**Experimental**

All reactions were run under nitrogen gas atmosphere with oven-dried glassware. Anhydrous toluene was distilled from sodium metal. The other solvents and reagents were used as received. Column chromatography was carried out on silica gel 230-400 mesh, and analytical TLC on glass plates (silica gel 60, F254). All 1H NMR spectra were recorded on a JEOL ECA 400 MHz or Bruker Advance DPX at 400 MHz in CDCl3 solutions. 13C NMR spectra were recorded in CDCl3 on the same instruments at the corresponding frequency. Chemical shifts are recorded in ppm and coupling constants are recorded in Hz.

**General Procedure**

**Hydroboration:**

**Method A:** Tri(2-furyl)phosphine (0.02 mmol, 4.7 mg) and [Rh(CO)2Cl]2 (0.01 mmol, 3.9 mg) were mixed in toluene (10 mL) at room temperature. After stirring for 10 minutes, the alkyne (1 mmol) in toluene (1 mL) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.2 mmol, 174 µL) were added into the mixture. The reaction was stirred under N2 at room temperature and monitored by TLC. After quenching with H2O, the reaction mixture was extracted with Et2O. The organic phase was dried over MgSO4 and then was concentrated under reduced vacuum. The residue was purified with column chromatography on silica gel.

**Method B:** Following the procedure of method A but with a ratio of Fu3P and Rh was 2:1.

**Method C:** Following the procedure of method A but with preformed Rh(Fu3P)2(CO)Cl (0.02 mmol) as the catalyst.

**Preparation of Rh(Fu3P)2(CO)Cl (9)**

Tri(2-furyl)phosphine (474 mg, 2.04 mmol) was added to the solution of [Rh(CO)2Cl]2 (200 mg, 0.51 mmol) in toluene (20 mL) at room temperature. A pale yellow precipitate appeared immediately. After stirring for 10 min, the mixture was cooled to 0 °C. The mixture was filtered and washed with cold ethanol (10 mL × 2) and Et2O (10 mL × 2), and the pale yellow solid was dried in air.

m.p.:168-169 °C

IR(neat) cm⁻¹: 2021, 1380, 1210, 1120, 1000, 720.

**Preparation of methyl (E)-2,6-dimethylnon-2-en-8-ynoate (2)**

![Chemical structure](image)
Ozone in oxygen was bubbled through the solution of the alkene (1g, 6.65 mmol) in CH₂Cl₂ (20 mL) at -78 °C. The reaction was monitored by TLC. When the starting material was consumed, the mixture was flushed with O₂ for 10 min. After warming to room temperature, the ylide (2.32g, 6.65 mmol) was added and the mixture was heated at reflux for 4 hr. The reaction was cooled down to room temperature, and the solvent was removed under reduced pressure. The residue was taken up in the minimum amount of CH₂Cl₂, and excess hexane was added. The precipitate was removed by filtration through celite, the filtrate was concentrated in vacuo and purified via column chromatography.

Data

**methyl (E)-2,6-dimethylnon-2-en-8-ynoate (2)**  
Overall yield: 77%. Colorless oil.  
¹H NMR (400 MHz, CDCl₃) δ 6.75 (t, J= 7.3 Hz, 1H), 2.20-2.14 (m, 4H), 1.96 (s, 1H), 1.84 (s, 3H), 1.72-1.60 (m, 3H), 1.00 (d, J= 6.4 Hz, 3H)  
¹³C NMR (100 MHz, CDCl₃) δ 168.8, 142.4, 127.9, 83.0, 69.7, 51.9, 34.7, 32.2, 26.4, 25.8, 19.5, 12.6.  
IR(neat) cm⁻¹: 3302, 2114, 1713, 1651, 1381, 1265, 1096, 934, 818, 741, 633.  
HRMS: (EI) Calcd. C₁₂H₁₉O₂ (M+H)⁺ For 195.1385, Found: 195.1383; MS: (ESI) 217.99 (M+Na)⁺

**(±)-methyl (2E,7E)-2,6-dimethyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-2,7-dienoate (3)**  
¹H NMR (400 MHz, CDCl₃) δ 6.74 (t, J=7.5 Hz, 1H), 6.58 (ddd, J=18.0, 7.7, 3.6, 1H), 5.43 (d, J=18.0 Hz, 1H), 3.73 (s, 3H), 2.23-2.11 (m, 2H), 2.06-2.00 (m, 2H), 1.83 (s,3H), 1.65-1.56 (m, 1H), 1.51-1.39 (m, 1H), 1.27 (s, 12H), 0.91 (d, J=4.0 Hz, 3H).  
¹³C NMR (100 MHz, CDCl₃) δ 168.9, 153.0, 142.9, 127.6, 83.2, 51.9, 43.6, 35.5, 32.3, 26.4, 25.0, 19.7, 12.5.  
IR(neat) cm⁻¹:3390, 2978, 2953, 2926, 2872, 1713, 1634, 1435, 1362, 1321, 1269, 1250, 1165, 1146,1092.
HRMS: (EI) Calcd. C_{18}H_{31}BO_{4}Na (M+Na)^+ For 345.2213, Found: 345.2221; MS: (ESI) 323.02 (M+H)^+.

\[
\text{Ph} \xrightarrow{\text{B-O}} \\
(\text{E})-4,4,5,5\text{-tetramethyl-2-styryl-1,3,2-dioxaborolane}^1 (4)
\]
\^1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.48-7.26 (m, 6H), 6.17 (d, \(J=16.0\) Hz, 1H), 1.32 (s, 12H).
\^13C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 149.7, 137.7, 129.1, 128.7, 127.2, 116.5 (br), 83.6, 24.7.

\[
\text{C}_4\text{H}_9 \xrightarrow{\text{B-O}} \\
(\text{E})-2\text{-(hex-1-en-1-yl)-4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolane}^2 (5)}
\]
Method A, t=80 min. Yield: 80%. Colorless oil.
\^1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 6.3 (dt, \(J=16.0, 6.8\) Hz, 1H), 5.42 (d, \(J=16.0\) Hz, 1H), 2.15 (dt, \(J=6.8, 6.4\) Hz, 2H), 1.42-1.26 (m, 18H), 0.88 (t, \(J=7.3\) Hz, 3H).
\^13C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 154.9, 118.8 (br), 83.2, 35.7, 30.6, 25.0, 22.5, 14.1.

\[
\text{TBSO} \xrightarrow{\text{B-O}} \\
(\text{E})\text{-tert-butylidimethyl(\text{3-(4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolan-2-yl}allyl)oxy})silane}^3 (6)
\]
\^1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 6.67 (dt, \(J=18.0, 3.6\) Hz, 1H), 5.75 (dd, \(J= 18.0, 1.8\) Hz, 1H), 4.24 (dd, \(J= 3.6, 1.4\) Hz, 2H), 1.27 (s, 12H), 0.91 (s, 12H), 0.06 (s, 6H).
\^13C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 152.4, 83.4, 64.8, 26.2, 25.0, 18.7, -5.1.

\[
\text{OMOM} \xrightarrow{\text{B-O}} \\
(\text{E})-2\text{-(4-(methoxymethoxy)pent-1-en-1-yl)-4,4,5,5\text{-tetramethyl-1,3,2-dioxaborolane}} (7)
\]
Method A, t=2.5 hr. Yield: 75%. Colorless oil.
\^1H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 6.62-6.54 (m, 1H), 5.47 (d, \(J=16.0\) Hz, 1H), 4.65-4.58 (m, 2H), 3.80-3.75 (m, 1H), 3.20 (s, 3H), 2.43-2.24 (m, 2H), 1.23 (s, 12H), 1.14 (d, \(J=5.9\) Hz, 3H).
\^13C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 150.4, 121.5 (br), 95.0, 83.2, 72.4, 55.4, 43.6, 25.0, 20.4.
IR(neat) cm\(^{-1}\): 2976, 2929, 2887, 1635, 1466, 1400, 1363, 1321, 1146, 1130, 1101, 1038, 970, 918, 849.
HRMS: (EI) Calcd. $\text{C}_{13}\text{H}_{26}\text{BO}_4$ (M+H)$^+$ For 257.1924, Found: 257.1937; MS: (ESI) 256.99.

(\textit{E})-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol$^4$ (8)

Method A, t=90 min. Yield: 61%. Colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.69 (d, $J=20.0$ Hz, 1H), 5.59 (d, $J=20.0$ Hz, 1H), 1.72 (br, 1H), 1.29-1.17 (m, 18H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.0, 113.7 (br), 83.5, 72.0, 29.3, 24.8.

References:


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