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Supporting Information

Catalyst-free and Solvent-free Hydroboration of Alkynes

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I. Copies of NMR spectra



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Figure S2: ¹³C NMR of (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (2a)¹



Figure S4: ¹H NMR of (*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2b)²



Figure S6: ¹¹B NMR of (*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2b)¹²



Figure S7: ¹H NMR of (*E*)-4,4,5,5-tetramethyl-2-(2-methylstyryl)-1,3,2-dioxaborolane $(2c)^7$



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Figure S10: ¹H NMR of (*E*)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)¹



Figure S11: ¹³C NMR of (*E*)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)¹



Figure S12: ¹¹B NMR of (E)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)¹²



Figure S13: ¹H NMR of (*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)¹



Figure S14: ¹³C NMR of (*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)¹



Figure S15: ¹¹B NMR of (*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)¹²



Figure S16: ¹⁹F NMR of (*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)¹²



Figure S17: ¹H NMR of (*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)¹⁴



Figure S18: ¹³C NMR of (*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f)¹⁴



Figure S19: ¹¹B NMR of (*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**)¹³



Figure S20: ¹H NMR of (*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)⁹



Figure S22: ¹¹B NMR of (*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)¹²



Figure S23: ¹H NMR of (*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (2h)²



Figure S24: ¹³C NMR of (*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (2h)²



Figure S25: ¹¹B NMR of (*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (**2h**)



Figure S26: ¹H NMR of (Z)-4,4,5,5-Tetramethyl-2-(1,2-diphenyl-1-enyl)-1,3,2-dioxaborolane (2j)¹



Figure S27: ¹³C NMR of (*Z*)-4,4,5,5-Tetramethyl-2-(1,2-diphenyl-1-enyl)-1,3,2-dioxaborolane (2j)¹



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Figure S29: ¹H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (2k)⁶



Figure S30: ¹³C NMR of (E)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (2k)⁶



Figure S31: ¹¹B NMR of (*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl)-1,3,2-dioxaborolane (2k)⁶





Figure S32: ¹H NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (21)¹⁴

Figure S33: ¹³C NMR of (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (2l)¹⁴



Figure S34: (E)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (2l)



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Figure S37: ¹¹B NMR of (*E*)-2-(4-ethynylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m)¹²



Figure S38: ¹H NMR of 1,4-bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (2n)¹²



 $Figure \ S40: \ ^{11}B \ NMR \ of \ 1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl) benzene \ (2n)^{12} \$



Figure S41: ¹H NMR of (*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (20)¹⁴



Figure S42: ¹³C NMR of (*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (20)¹⁴



Figure S43: ¹¹B NMR of (*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (**20**)¹⁴



Figure S44: ¹H NMR of methyl (*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)vinyl)benzoate (**2p**)⁶



Figure S45: ¹³C NMR of (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (2p)⁶



Figure S46: ¹¹B NMR of (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (2p)⁶



Figure S47: ¹H NMR of (*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane $(2q)^7$



Figure S48: ¹³C NMR of (*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q)⁷



Figure S49: ¹¹B NMR of (*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2q**)⁷



Figure S50: ¹H NMR of (*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r)⁴



Figure S51: ¹³C NMR of (*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r)⁴



Figure S52: ¹¹B NMR of (*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r)⁴



Figure S53: ¹H NMR of (E)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexan-1-ol (2s)⁷



 $Figure \ S54: \ ^{13}C \ NMR \ of \ (E) - 1 - (2 - (4,4,5,5 - tetramethyl - 1,3,2 - dioxaborolan - 2 - yl) vinyl) cyclohexan - 1 - ol \ (2s)^7 \$



Figure S55: ¹¹B NMR of (E)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexan-1-ol (2s)⁷



Figure S56: Mass Spectrum of (E)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexan-1-ol (2s)⁷





Figure S57: Mass Spectrum of (E)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)cyclohexan-1-ol (2s)⁷



Figure S58: ¹H NMR of (*E*)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2t**)⁵



Figure S59: ¹³C NMR of (*E*)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2t**)⁵



Figure S60: ¹¹B NMR of (*E*)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2t**)⁵



Figure S61: ¹H NMR of (*E*)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2u**)⁶



Figure S62: ¹³C NMR of (*E*)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)⁶



Figure S63: ¹¹B NMR of (*E*)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2u**)



Figure S64: ¹H NMR of (*E*)-(2-(Allyloxy)vinyl)benzene (3a)⁸



Figure S65: ¹³C NMR of (*E*)-(2-(Allyloxy)vinyl)benzene (3a)⁸



Figure S66: ¹H NMR of Potassium trans-styryltrifluoroborate (3b)⁹



Figure S67: ¹³C NMR of Potassium trans-styryltrifluoroborate (3b)⁹



Figure S68: ¹H NMR of (*E*)-(2-Iodovinyl)benzene (3c)¹⁰



Figure S70: ¹H NMR of (*E*)-4-Styryl-1,1'-biphenyl (**3d**)¹¹



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

Figure S71: ¹³C NMR of (*E*)-4-Styryl-1,1'-biphenyl (**3d**)¹¹



Figure S72: ¹H NMR of (*E*)-(2-Azidovinyl)benzene (3e)¹⁰



Figure S73: ¹³C NMR of (*E*)-(2-Azidovinyl)benzene (3e)¹⁰

Determination of the by-product formation from crude reaction mixture.



Figure S74: ¹H NMR of crude reaction mixture of phenyl acetylene and HBpin in CDCl₃



Figure S75: ¹¹B NMR of crude reaction mixture of phenyl acetylene and HBpin in CDCl₃¹⁵

II. Chemoselective hydroboration of phenyl acetylene over ester





^aYields were calculated based on ¹H NMR, Using 1,3,5-trimethoxybenzene as an internal standard.



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