Supporting Information for:

**Diboron as Reductant for Nickel-Catalyzed Reductive Coupling:**

**Rational Design and Mechanistic Studies**

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1. General experiment details and materials

Experimental: All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) were reported in Hz and referred to apparent peak multiplications. All the high-resolution mass spectrometry (HRMS) experiments were carried out using Bruker MicroTOF-QII mass instrument (ESI) or Agilent 6210 TOF mass spectrometer (APCI). IR spectra were recorded on a METTLER TOLEDO ReactIR 15 spectrometer. 1,2-Diphenylethyne were purchased from Alfa aesar. The other alkynes used here are known compounds and synthesized according to the reported methods.¹
2. Optimization of the reaction conditions

1,2-Diphenylethyne 1a (178.2 mg, 1.0 mmol), [Ni] (0.05 mmol, 5 mol %), additives and solvents (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvents was evaporated under reduced pressure, and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 2a as a yellow solid.

Table S1. Optimization of the reaction conditions

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<tr>
<th>Entry</th>
<th>[Ni] (5 mol %)</th>
<th>Additive (equiv.)</th>
<th>Solvent</th>
<th>Yield (%)</th>
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<td>Solvent</td>
<td>Yield (%)</td>
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*General conditions: 1a (178.2 mg, 1.0 mmol), [Ni] (0.05 mmol, 5 mol%), additive, solvent (1.0 mL), Ar, 120 °C for 18 h, isolated yield, unless otherwise noted. *Added PPh₃ (26.2 mg, 0.10 mmol, 10 mol%)
3. General procedure for the tetramerization

\[ \text{R}^1 \equiv \text{R}^2 \quad \xrightarrow{\text{NiCl}_2(\text{PPh}_3)_2 (5 \text{ mol } \%) \quad (\text{Bpin})_2 (30 \text{ mol } \%) \quad \text{MeOH, 120} \, ^\circ \text{C, 18 h}} \quad \text{H} \]

1,2-Diphenylethyne 1 (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (32.7 mg, 0.05 mmol, 5 mol %), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 30 mol %) and MeOH (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvents were evaporated under reduced pressure, and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1 – 5/1) to afford the desired product 2.
4. Experimental characterization data for products

(1E,3E,5E,7E)-1,2,3,4,5,6,7,8-Octaphenyl-1,3,5,7-octatetraene (2a): The title compound was prepared according to the general procedure as a yellow solid, 158.7 mg, 89% yield. $^1$H NMR (400 MHz, CDCl₃) δ 6.33 (s, 2H), 6.86-6.92 (m, 6H), 7.00-7.11 (m, 30H), 7.58 (d, $J = 7.6$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl₃) δ 126.2, 126.5, 126.6, 126.7, 127.3, 127.4, 127.7, 127.8, 129.0, 129.7, 130.0, 130.3, 133.7, 137.8, 139.1, 141.3, 142.0, 142.5, 142.7, 145.3; HRMS (APCI) calcd. for C₅₆H₄₃ [M+H]: 715.3359, found: 715.3344.

![ORTEP drawing of product 2a](image)

(1E,3E,5E,7E)-1,2,3,4,5,6,7,8-Octa(4-methylphenyl)-1,3,5,7-octatetraene (2b): The title compound was prepared according to the general procedure as a yellow solid, 169.9 mg, 82% yield. $^1$H NMR (400 MHz, CDCl₃) δ 2.13-2.25 (s, 24H), 6.22 (s, 2H), 6.80-6.93 (m, 24H), 7.04 (d, $J = 7.6$ Hz, 4H), 7.58 (d, $J = 7.6$ Hz, 4H); $^{13}$C NMR (100 MHz, CDCl₃) δ 21.1, 21.2, 21.3, 127.2, 127.7, 128.1, 128.4, 128.5, 128.8, 129.5, 129.9, 130.1, 131.3, 131.9, 135.4, 135.5, 135.6, 135.9, 136.1, 136.2, 138.4, 138.8, 141.4, 141.7, 144.1; HRMS (APCI) calcd. for C₆₄H₅₉ [M+H]: 827.4611, found: 827.4601.
(1E,3E,5E,7E)-1,2,3,4,5,6,7,8-Octa(3-methylphenyl)-1,3,5,7-octatetraene (2c): The title compound was prepared according to the general procedure as a yellow solid, 140.2 mg, 68% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.10-2.17 (s, 24H), 6.22 (s, 2H), 6.62-6.70 (m, 6H), 6.79-7.02 (m, 22H), 7.19-7.25 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.3, 21.3, 21.6, 126.0, 126.5, 126.8, 126.9, 127.0, 127.1, 127.2, 127.3, 127.5, 129.9, 130.2, 131.0, 131.2, 133.1, 135.8, 136.2, 136.6, 137.1, 138.0, 139.6, 141.8, 142.6, 143.1, 143.2, 145.2; HRMS (APCI) calcd. for C$_{64}$H$_{59}$ [M+H]: 827.4611, found: 827.4601.

(1E,3E,5E,7E)-1,2,3,4,5,6,7,8-Octa(3,5-dimethylphenyl)-1,3,5,7-octatetraene (2d): The title compound was prepared according to the general procedure as a yellow solid, 180.7 mg, 77% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.06-2.07 (m, 36H), 2.15 (s, 12H), 6.08 (s, 2H), 6.41 (s, 2H), 6.48 (s, 4H), 6.55-6.63 (m, 10H), 6.68 (s, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.0, 21.1, 21.4, 126.7, 126.9, 127.4, 127.6, 127.7, 127.8, 128.0, 128.2, 132.6, 135.1, 135.8, 136.0, 136.7, 138.1, 140.1, 143.0, 143.4, 144.2, 144.8, 146.1; HRMS (APCI) calcd. for C$_{72}$H$_{75}$ [M+H]: 939.5863, found: 939.5894.

Figure S2. ORTEP drawing of product 2d
(1E,3E,5E,7E)-1,2,3,4,5,6,7,8-Octa(4-methoxyphenyl)-1,3,5,7-octatetraene  (2e):

The title compound was prepared according to the general procedure as a yellow solid, 178.9 mg, 75% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 3.51-3.54 (m, 12H), 3.62-3.63 (m, 12H), 6.32 (s, 2H), 6.41 (s, 2H), 6.47-6.62 (m, 14H), 6.73 (d, $J = 7.6$ Hz, 2H), 6.90 (d, $J = 5.6$ Hz, 2H), 6.96-7.05 (m, 8H), 7.10 (s, 2H), 7.16 (d, $J = 7.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 54.8, 54.9, 55.0, 112.1, 112.2, 112.9, 113.1, 113.8, 115.1, 115.4, 115.8, 121.7, 122.4, 122.6, 128.0, 128.2, 128.7, 128.8, 133.6, 139.1, 140.4, 142.6, 142.6, 143.5, 145.0, 158.7, 158.8, 158.8, 159.0; HRMS (APCI) calcd. for C$_{64}$H$_{59}$O$_8$ [M+H]: 955.4204, found: 955.4203.

(1E,3E,5E,7E)-1,2,3,4,5,6,7,8-Octa(4-trifluoromethoxyphenyl)-1,3,5,7-octatetraene (2f): The title compound was prepared according to the general procedure as a yellow solid, 280.0 mg, 81% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.24 (s, 2H), 6.74-6.92 (m, 24H), 7.00-7.02 (m, 4H), 7.16-7.18 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 116.5, 116.5, 116.6, 119.0, 119.1, 119.2, 120.0, 120.4, 120.7, 121.6, 121.6, 121.7, 124.2, 124.2, 124.3, 130.2, 130.9, 131.1, 134.7, 135.0, 137.8, 141.5, 141.6, 143.1, 144.1, 147.2, 147.6, 147.6, 148.0, 148.0, 148.2, 148.2, 148.4, 148.5; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -58.2, -58.1, -58.0; HRMS (APCI) calcd. for C$_{64}$H$_{34}$F$_{24}$O$_8$ [M]: 1386.1876, found: 1386.1834.

(1E,3E,5E,7E)-1,2,3,4,5,6,7,8-Octa(4-fluorophenyl)-1,3,5,7-octatetraene (2g): The title compound was prepared according to the general procedure as a yellow solid, 117.4 mg, 83% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.20 (s, 2H), 6.72-6.83 (m, 20H), 6.86-6.89 (m, 4H), 7.02-7.06 (m, 4H), 7.25-7.29 (m, 4H); $^{13}$C NMR (100 MHz,
CDCl\textsubscript{3} δ 114.5, 114.8, 115.0, 115.2, 130.5, 130.6, 131.1, 131.1, 131.4, 131.5, 132.8, 132.8, 133.5, 134.7, 134.8, 137.5, 137.5, 138.0, 141.5, 142.2, 145.1, 160.0, 160.4, 160.5, 160.6, 162.4, 162.8, 163.0, 163.0; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ -114.8, -114.2, -114.0, -114.0; HRMS (APCI) calcd. for C\textsubscript{56}H\textsubscript{34}F\textsubscript{8} [M]: 858.2538, found: 858.2529.

(1\textit{E},3\textit{E},5\textit{E},7\textit{E})-1,2,3,4,5,6,7,8-Octa(4-chlorophenyl)-1,3,5,7-octatetraene (2h): The title compound was prepared according to the general procedure as a yellow solid, 157.8 mg, 64% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.18 (s, 2H), 6.73 (d, J = 8.4 Hz, 4H), 6.83 (d, J = 8.4 Hz, 4H), 6.95 (d, J = 8.4 Hz, 4H), 7.02-7.10 (m, 16H), 7.23-7.25 (d, J = 8.4 Hz, 4H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 128.0, 128.0, 128.4, 128.5, 130.2, 130.7, 130.8, 131.1, 132.7, 133.3, 134.0, 134.9, 136.8, 139.4, 139.9, 141.6, 142.2, 145.3; HRMS (APCI) calcd. for C\textsubscript{56}H\textsubscript{35}Cl\textsubscript{8} [M+H]: 987.0247, found: 987.0245.

(1\textit{E},3\textit{E},5\textit{E},7\textit{E})-1,2,3,4,5,6,7,8-Octa(3-chlorophenyl)-1,3,5,7-octatetraene (2i): The title compound was prepared according to the general procedure as a yellow solid, 197.1 mg, 80% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.27 (s, 2H), 6.68 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 7.2 Hz, 2H), 6.88-7.14 (m, 30H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 126.9, 127.1, 127.4, 127.5, 127.7, 128.0, 128.9, 129.1, 129.2, 129.3, 129.4, 129.8, 129.9, 133.5, 133.8, 134.0, 134.0, 134.8, 138.1, 140.3, 142.3, 143.0, 143.2, 143.5, 146.0; HRMS (APCI) calcd. for C\textsubscript{56}H\textsubscript{35}Cl\textsubscript{8} [M+H]: 987.0247, found: 987.0251.
(1E,3E,5E,7E)-1,2,3,4,5,6,7,8-Octa(4-bromophenyl)-1,3,5,7-octatetraene (2j): The title compound was prepared according to the general procedure as a yellow solid, 151.2 mg, 45% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.24 (s, 2H), 6.70 (d, $J = 8.0$ Hz, 2H), 6.78 (d, $J = 7.6$ Hz, 2H), 6.86-7.11 (m, 21H), 7.18-7.20 (m, 4H), 7.25 (s, 1H), 7.28 (d, $J = 8.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 121.7, 122.1, 122.1, 127.5, 127.7, 128.2, 128.4, 129.0, 129.4, 129.6, 129.7, 130.3, 130.4, 130.6, 132.1, 132.3, 132.6, 133.0, 134.8, 138.3, 140.7, 142.6, 143.7, 143.8, 144.0, 146.4; HRMS (APCI) calcd. for C$_{56}$H$_{35}$Br$_8$ [M+H]: 1338.62, found: 1338.6155.

1,2,3,4,5,6,7,8-Octa(4-bromophenyl)-1,3,5,7-octatetraene (2k): The title compound was prepared according to the general procedure as a yellow solid, 163.2 mg, 85% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.12-2.25 (m, 12H), 6.25-6.32 (m, 2H), 6.75-6.96 (m, 14H), 6.70-7.11 (m, 18H), 7.55-7.65 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.2, 126.3, 126.5, 127.1, 127.4, 127.6, 127.7, 127.8, 128.2, 128.5, 128.5, 128.9, 129.0, 129.6, 129.9, 130.0, 130.2, 130.3, 132.2, 132.9, 135.8, 135.9, 136.2, 136.3, 138.2, 138.3, 138.6, 138.6, 139.4, 141.9, 142.3, 144.2; HRMS (APCI) calcd. for C$_{60}$H$_{51}$ [M+H]: 771.3985, found: 771.3993.
5. Mechanistic studies
5.1 D-Labelled experiments
5.1.1 Tetrimerization in CH₃OH with D₂O as additive

1,2-Diphenylethyne 1a (178.2 mg, 1.0 mmol), NiCl₂(PPh₃)₂ (32.7 mg, 0.05 mmol, 5 mol%), B₂pin₂ (76.2 mg, 0.3 mmol, 30 mol%), CH₃OH (1.0 mL) and D₂O (20.0 mg, 1.0 mmol) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 2a as a yellow solid (142.6 mg, 80 %). The product was characterized by NMR and HRMS (APCI) (Figure S3 and S4).

Figure S3. ¹H NMR of the product 2a
5.1.2 Tetramerization in CD$_3$OD

1,2-Diphenylethyne 1a (178.2 mg, 1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (32.7 mg, 0.05 mmol, 5 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 30 mol%) and CD$_3$OD (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 2a’ as a yellow solid (155.1 mg, 86 %, > 95% D). The compound was characterized by NMR and HRMS (APCI) (Figure S5 and S6).
Figure S5. $^1$H NMR of the product 2a’

Figure S6. HRMS (APCI) of the product 2a’
5.1.3 Tetramerization in CD$_3$OH

![Chemical structure](image)

1,2-Diphenylethyne 1a (178.2 mg, 1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (32.7 mg, 0.05 mmol, 5 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 30 mol%) and CD$_3$OH (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 2a as a yellow solid (156.9 mg, 88 %). The compound was characterized by NMR and HRMS (APCI) (Figure S7 and S8).

![NMR spectrum](image)

**Figure S7.** $^1$H NMR of the product 2a
5.1.4 Tetramerization in CH$_3$OD

1,2-Diphenylethyne 1a (178.2 mg, 1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (32.7 mg, 0.05 mmol, 5 mol%), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 30 mol%) and CH$_3$OD (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 2a’ as a yellow solid (156.8 mg, 87 %, > 95% D). The compound was characterized by NMR and HRMS (APCI) (Figure S9 and S10).
Figure S9. $^1$H NMR of the product $2a'$

Figure S10. HRMS (APCI) of the product $2a'$
5.2 HRMS (ESI) studies:

\[
\begin{align*}
\text{1,2-Diphenylethyne } 1a, \text{ 1.0 mmol} & \quad \text{NiCl}_2(\text{PPh}_3)_2, \text{ 0.2 mmol} \\
& \quad \text{B}_2\text{pin}_2, \text{ 0.5 mmol} \\
& \quad \text{MeOH (2.0 mL)} \quad \text{MeOH (2.0 mL)} \\
\text{120 °C, 10 min} & \quad \text{MeOH (2.0 mL)} \\
\end{align*}
\]

1,2-Diphenylethyne 1a (178.2 mg, 1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (130.8 mg, 0.2 mmol), B$_2$pin$_2$ (114.3 mg, 0.5 mmol) and MeOH (2.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 10 minutes, some reaction mixture was taken and inject to HRMS. The HRMS (ESI) spectrum was shown in Figure S11, Figure S13 and Figure S15. Three strong peaks at \(m/z= 633.1563, 893.2363\) and 895.2460 were observed, which were correspond to the mass of dinuclear Ni-Ni complexes \([D + PPh_3 + H]^+\), \([B + 2 \text{ MeOH} + H]^+\) and \([D + 2 \text{ PPh}_3 + H]^+\).

![Figure S11. HRMS (ESI) spectrum of \([B + 2 \text{ MeOH} + H]^+\).](#)

![Figure S12. Calcd. HRMS (ESI) spectrum of \([B + 2 \text{ MeOH} + H]^+\).](#)
Figure S13. HRMS (ESI) spectrum of [D + PPh₃ + H]⁺.

Figure S14. Calcd. HRMS (ESI) spectrum of [D + PPh₃ + H]⁺.

Figure S15. HRMS (ESI) spectrum of [D + 2 PPh₃ + H]⁺.

Figure S16. Calcd. HRMS (ESI) spectrum of [D + 2 PPh₃ + H]⁺.
The result of two stage mass spectrometry indicated that the peak $m/z = 633.1544$ was recognized as $[\text{D} + \text{PPh}_3 + \text{H}]^+$. 

**Figure S17.** Two stage mass spectrum of the peak $m/z = 633.1544$.

The result of two stage mass spectrometry indicated that the peak $m/z = 895.2460$ was recognized as $[\text{D} + 2 \text{PPh}_3 + \text{H}]^+$. 

**Figure S18.** Calcd. HRMS (ESI) spectrum of $[\text{D} + \text{H}]^+$. 

**Figure S19.** Two stage mass spectrum of the peak $m/z = 895.2460$.
5.3 Stoichiometric reaction:

5.3.1 Stoichiometric reaction of 1a with Ni(COD)_2

\[
\text{Ph} \equiv \equiv \text{Ph} \quad 1a \quad \text{(1.0 mmol)} \quad 178.2 \text{ mg} \\
\rightarrow \quad \text{Ni(COD)}_2 \quad (0.2 \text{ mmol}) \\
PPh_3 \quad (0.4 \text{ mmol}) \\
\text{MeOH} \quad (3.0 \text{ mL}) \\
\text{Ar, 120 °C, 30 min} \\
\rightarrow \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{Ph} \quad \text{H} \\
\rightarrow \quad 2a, 44.5 \text{ mg}
\]

Ni(COD)$_2$ (55.2 mg, 0.2 mmol), PPh$_3$ (104.8 mg, 0.4 mmol, 2.0 equiv) and CH$_3$OH (3.0 mL) were added to a 25 mL flame-dried Young-type tube in glove box. The mixture was stirred at 120 °C for 30 minutes. After cooling to room temperature, 1,2-diphenylethyne 1a (178.2 mg, 1.0 mmol, 5.0 equiv) was added and stirred at 120 °C for 24 hours. After cooling to room temperature, the solvents was evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 2a as a yellow solid (44.5 mg).

5.3.2 Stoichiometric reaction of 3a with NiCl$_2$(PPh)$_3$_2

\[
\text{Ph} \equiv \equiv \text{Ph} \quad 3a \quad \text{(0.3 mmol)} \\
\rightarrow \quad \text{NiCl}_2(\text{PPh}_3)_2 \quad 0.3 \text{ mmol} \\
\text{CH}_3\text{OH} \quad (1.0 \text{ mL}) \\
\text{N}_2, 120 \text{ °C, 18 h} \\
\rightarrow \quad \text{No reaction}
\]

3a (145.3 mg, 0.3 mmol), NiCl$_2$(PPh)$_3$_2 (196.2 mg, 0.3 mmol), B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 30 mol%) and CH$_3$OH (1.0 mL) were added to a 25 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 18 hours. No 2a was detected.
6. Kinetic experiments

Synthesis of 2-propoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (n-PrOBpin)

\[
\text{Boric acid (4.96 g, 80 mmol), dry } n\text{-propanol (24.04 g, 400 mmol), pinacol (9.44 g, 80 mmol) and benzene (50 mL) were added to a 100 mL flame-dried reactor. After stirring at room temperature for 30 minutes, the } n\text{-propanol/water/benzene ternary azeotrope was distilled off for 12 hours, and most of the residual benzene was removed in vacuo at 30 °C. The crude product was distilled to give the title compound as a colourless liquid (11.76 g, 85%).}
\]

\[1^H\text{ NMR (400 MHz, CDCl}_3\text{) } \delta 0.80-0.85 (m, 3H), 1.16-1.17 (m, 12H), 1.47-1.52 (m, 2H), 3.69-3.73 (m, 2H).\]

\[13C\text{ NMR (100 MHz, CDCl}_3\text{) } \delta 10.0, 24.4, 24.6, 66.4, 82.4.\]

6.1 The standard IR spectra and the reactions in \( n\text{-PrOH} \)

(A) Standard IR spectra of \( n\text{-PrOBpin} \) and \( \text{B}_2\text{pin}_2 \).
(B) Standard IR spectra of 1a and 2a.

(C) Depletion of B$_2$pin$_2$ and formation of n-PrOBpin.
6.2 Different diphenylethyne (1a) loadings

In a dried self-prepared three-necked micro reactor with a magnetic stirrer, NiCl$_2$(PPh$_3$)$_2$ (19.6 mg, 0.03 mmol) and B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 30 mol%) were added. The reactor was allowed to be purged with nitrogen three times, n-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 °C and the different amount of 1,2-diphenylethyne 1a (1.0 mmol, 0.8 mmol, 0.6 mmol, 0.4 mmol) was dissolved in n-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at 120 °C for 2-6 hours. After cooling to room temperature, n-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.
In a dried self-prepared three-necked micro reactor with a magnetic stirrer, \( \text{NiCl}_2(\text{PPh}_3)_2 \text{ (19.6 mg, 0.03 mmol)} \) and the different amount of \( \text{B}_2\text{pin}_2 \text{ (0.1 mmol, 0.2 mmol, 0.3 mmol, 0.5 mmol, 0.6 mmol)} \) were added. The reactor was allowed to be
purged with nitrogen three times, \( n\)-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 °C, and the 1,2-diphenylethyne \( 1\text{a} \) (178.2 mg, 1.0 mmol) was dissolved in \( n\)-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at 120 °C for 2-6 hours. After cooling to room temperature, \( n\)-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.

<table>
<thead>
<tr>
<th>entry</th>
<th>1</th>
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<th>4</th>
<th>5</th>
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<tbody>
<tr>
<td>( \text{B}_2\text{pin}_2 ) loading (M)</td>
<td>0.05</td>
<td>0.10</td>
<td>0.15</td>
<td>0.25</td>
<td>0.30</td>
</tr>
<tr>
<td>( r_{\text{ini}} ) (10(^{-4}) M/s)</td>
<td>0.091</td>
<td>0.096</td>
<td>0.089</td>
<td>0.096</td>
<td>0.089</td>
</tr>
</tbody>
</table>

(B) \( \text{B}_2\text{pin}_2 \) Loading

\( r_{\text{ini}} \) (10\(^{-4}\) M/s) vs \( \text{B}_2\text{pin}_2 \) (M)
6.4 Different NiCl$_2$(PPh$_3$)$_2$ loadings

In a dried self-prepared three-necked micro reactor with a magnetic stirrer, the different amount of NiCl$_2$(PPh$_3$)$_2$ (0.01 mmol, 0.02 mmol, 0.03 mmol, 0.04 mmol, 0.05 mmol, 0.06 mmol, 0.08 mmol, 0.10 mmol) and B$_2$pin$_2$ (76.2 mg, 0.3 mmol, 30 mol%) were added. The reactor was allowed to be purged with nitrogen three times, $n$-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 °C, and the 1,2-diphenylethyne 1a (178.2 mg, 1.0 mmol) was dissolved in $n$-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at 120 °C for 2-6 hours. After cooling to room temperature, $n$-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.

<table>
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<tr>
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<tbody>
<tr>
<td>NiCl$_2$(PPh$_3$)$_2$ (M)</td>
<td>0.005</td>
<td>0.01</td>
<td>0.015</td>
<td>0.02</td>
<td>0.025</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
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<tr>
<td>$C_{cat}$ (M)$^2$</td>
<td>0.00002</td>
<td>0.000</td>
<td>0.00022</td>
<td>0.000</td>
<td>0.00062</td>
<td>0.000</td>
<td>0.0001</td>
<td>0.002</td>
</tr>
<tr>
<td>$r_{ini}$ (10$^{-4}$ M/s)</td>
<td>5</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>9</td>
<td>6</td>
<td>5</td>
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</table>
\[ r_{\text{ini}} = 0.0768 C_{\text{cat}}^2 \]

\[ r_{\text{ini}} = 0.0768 C_{\text{cat}}^2 - 7.43 \times 10^{-6} \quad R = 0.9968 \]
6.5 Arrhenius parameters of Nickel-catalyzed reductive coupling

\[
\begin{align*}
\text{Ph} \equiv & \equiv \text{Ph} \\
\overset{\text{NiCl}_2(\text{PPh}_3)_2 (3 \text{ mol %})}{\longrightarrow} & \overset{\text{B}_2\text{pin}_2 (30 \text{ mol %})}{\longrightarrow} \\
1a (1.0 \text{ mmol}) & \rightarrow 2a
\end{align*}
\]

In a dried self-prepared three-necked micro reactor with a magnetic stirrer, NiCl\(_2\)(PPh\(_3\))\(_2\) (19.6 mg, 0.03 mmol) and B\(_2\)pin\(_2\) (76.2 mg, 0.3 mmol) were added. The reactor was purged with nitrogen for three times, n-PrOH (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 °C, and was transferred to the different temperature (80 °C, 90 °C, 100 °C, 110 °C, 120 °C, 130 °C). And the 1,2-diphenylethyne 1a (178.2 mg, 1.0 mmol) was dissolved in n-PrOH (1.0 mL) and added in via a syringe. Then the system was stirred at the different temperature for 2-6 hours. After cooling to room temperature, n-hexadecane was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T (K(^{-1}))</th>
<th>k (mL·mol(^{-1})·s(^{-1}))</th>
<th>ln((\frac{k \cdot e^\Theta}{T}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>353</td>
<td>0.002833</td>
<td>0.0066666667</td>
<td>-10.88</td>
</tr>
<tr>
<td>363</td>
<td>0.002755</td>
<td>0.0106666667</td>
<td>-10.44</td>
</tr>
<tr>
<td>373</td>
<td>0.002681</td>
<td>0.023111111</td>
<td>-9.69</td>
</tr>
<tr>
<td>383</td>
<td>0.002611</td>
<td>0.029777778</td>
<td>-9.46</td>
</tr>
<tr>
<td>393</td>
<td>0.002545</td>
<td>0.0395555556</td>
<td>-9.20</td>
</tr>
<tr>
<td>403</td>
<td>0.002481</td>
<td>0.0986666667</td>
<td>-8.31</td>
</tr>
</tbody>
</table>
\[
\ln \left( \frac{k}{T} \right) = -\frac{6793}{T} + 8.344
\]

\[
k = \frac{k_B T}{h} \left( c^\ominus \right)^{-1} \exp\left( \frac{\Delta_r^\ominus S_m^\ominus (c^\ominus)}{R} \right) \exp\left( -\frac{\Delta_r^\ominus H_m^\ominus (c^\ominus)}{RT} \right) \tag{1}
\]

\[
\ln \left( \frac{k c^\ominus}{T} \right) = \ln \frac{k_B}{h} + \frac{\Delta_r^\ominus S_m^\ominus (c^\ominus)}{R} - \frac{\Delta_r^\ominus H_m^\ominus (c^\ominus)}{RT} \tag{2}
\]

\[
k_B: \quad 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}
\]

\[
h: \quad 6.626 \times 10^{-34} \text{ J} \cdot \text{s}
\]

\[
c^\ominus: \quad 1 \text{ mol} \cdot \text{mL}^{-1}
\]

\[
\text{[Ni]} = 0.015 \text{ mol} \cdot \text{L}^{-1}, \quad k = \frac{r}{c_{cat}^2}
\]

\[
\ln \frac{k}{T} = -\frac{6793}{T} + 8.344, \quad R = 0.9818 \tag{3}
\]

\[
\Delta_r^\ominus H_m^\ominus = 56.5 \text{ kJ} \cdot \text{mol}^{-1}
\]

\[
\Delta_r^\ominus S_m^\ominus = -128 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
\]
6.6 The role of diarylalkynes

\[ \text{R} \equiv \text{R} \xrightarrow{\text{NiCl}_2(\text{PPh}_3)_2 \ (3 \text{ mol \%})} \text{R} = \text{R} \]

In a dried self-prepared three-necked micro reactor with a magnetic stirrer, \( \text{NiCl}_2(\text{PPh}_3)_2 \) (19.6 mg, 0.03 mmol) and \( \text{B}_2\text{pin}_2 \) (76.2 mg, 0.3 mmol) were added. The reactor was purged with nitrogen for three times, \( n\text{-PrOH} \) (1.0 mL) was added in via a syringe. After the mixture was allowed to stir for 13 minutes at 120 °C, and the different of diarylethenes \( 1 \) (1.0 mmol) was dissolved in \( n\text{-PrOH} \) (1.0 mL) and added in via a syringe. Then the system was stirred at 120 °C for 2-6 hours. After cooling to room temperature, \( n\text{-hexadecane} \) was added to the reaction mixture as internal standard. The reaction mixture was analyzed by GC.

<table>
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<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k ) (x10^{-4} \text{ M/min})</td>
<td>Me</td>
<td>-2.941</td>
<td>-5.44</td>
<td>-6.4638</td>
<td>-16.508</td>
</tr>
<tr>
<td>( \sigma_p )</td>
<td>-0.17</td>
<td>0</td>
<td>0.06</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>( \log (k/k_H) )</td>
<td>-0.2671</td>
<td>0</td>
<td>0.074889</td>
<td>0.482096</td>
<td></td>
</tr>
</tbody>
</table>
7. TON experiment

1,2-Diphenylethyne 1a (3.564 g, 20.0 mmol), NiCl₂(PPh₃)₂ (1.3 mg, 0.002 mmol, 1 mol %), B₂pin₂ (1.5234 g, 6.0 mmol, 30 mol %) and MeOH (10.0 mL) were added to a 100 mL flame-dried Young-type tube. The mixture was degassed by the freeze-thaw method and supplied with 1 atm of nitrogen, and then stirred at 120 °C for 12 days. After cooling to room temperature, the solvents were evaporated under reduced pressure and the residue was directly loaded onto a silica gel column (petroleum ether/ethyl acetate = 100/1) to afford the desired product 2a (2.502 g, in 70.05 % yield, TON = 1751).

References:

8. Copies for ¹H NMR and ¹³C NMR
R = OCF₃

2f
20140715-ZCY-5-CNMR (20)

![Chemical Structure](image)

$R^1 = \text{Ph}

2k$
9. Copies for *In situ* IR spectra

![1a in DCM spectrum](image)

- Wavenumber (cm$^{-1}$)
- A. U.
$B_2pin_2$ in DCM

Wavenumber (cm$^{-1}$)

A. U.
$n$-PrOBpin in CH$_3$OH

Wavenumber (cm$^{-1}$)

A. U.
$1b$ in $n$-PrOH

Wavenumber (cm$^{-1}$)

A. U.

817
$1g$ in $n$-PrOH

\[ \text{Wavenumber (cm}^{-1}\text{)} \]

- A. U.

$1f$ 1515

\[ \text{F}_{3}\text{CO} \quad \equiv \quad \text{OCF}_3 \]

563
1h in $n$-PrOH

Wavenumber (cm$^{-1}$)

A. U.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.3 mmol), n-PrOH (2.0 mL), N$_2$, 80 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.3 mmol), $n$-PrOH (2.0 mL), N$_2$, 90 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.3 mmol), $n$-PrOH (2.0 mL), N$_2$, 100°C for 3 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.3 mmol), n-PrOH (2.0 mL), N$_2$, 110 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.3 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.3 mmol), n-PrOH (2.0 mL), N$_2$, 130 °C for 3 h.
Reaction condition: 1a (1.0 mmol), NiCl₂(PPh₃)₂ (0.01 mmol), B₂pin₂ (0.3 mmol), n-PrOH (2.0 mL), N₂, 120 °C for 3 h.
Reaction condition: \(\text{1a} (1.0 \text{ mmol}), \text{NiCl}_2(\text{PPh}_3)_2 (0.02 \text{ mmol}), \text{B}_2\text{pin}_2 (0.3 \text{ mmol}), n-\text{PrOH (2.0 mL)}, \text{N}_2, 120^\circ\text{C} \text{ for 3 h.} \)
Reaction condition: 1a (1.0 mmol), NiCl₂(PPh₃)₂ (0.03 mmol), B₂pin₂ (0.3 mmol), n-PrOH (2.0 mL), N₂, 120 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.04 mmol), B$_2$pin$_2$ (0.3 mmol), $n$-PrOH (2.0 mL), N$_2$, 120 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.05 mmol), B$_2$pin$_2$ (0.3 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 1 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.06 mmol), B$_2$pin$_2$ (0.3 mmol), $n$-PrOH (2.0 mL), N$_2$, 120 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.08 mmol), B$_2$pin$_2$ (0.3 mmol), $n$-PrOH (2.0 mL), N$_2$, 120 °C for 3 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.10 mmol), B$_2$pin$_2$ (0.3 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 4 h.
Reaction condition: 1a (0.6 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.3 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 3 h.
Reaction condition: \( \text{1b} \) (0.6 mmol), \( \text{NiCl}_2\text{(PPh}_3)_2 \) (0.03 mmol), \( \text{B}_2\text{pin}_2 \) (0.3 mmol), \( \text{n-PrOH} \) (2.0 mL), \( \text{N}_2 \), 120 °C for 7 h.
Reaction condition: 1h (0.6 mmol), NiCl₂(PPh₃)₂ (0.03 mmol), B₂pin₂ (0.3 mmol), n-PrOH (2.0 mL), N₂, 120 °C for 1 h.
Reaction condition: 1g (0.6 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.3 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.1 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 3 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.2 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 3 h.
Reaction condition: 1a (1.0 mmol), NiCl₂(PPh₃)₂ (0.03 mmol), B₂pin₂ (0.3 mmol), n-PrOH (2.0 mL), N₂, 120 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.5 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 2 h.
Reaction condition: 1a (1.0 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.6 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 2 h.
Reaction condition: 1a (0.20 mmol), NiCl₂(PPh₃)₂ (0.03 mmol), B₂pin₂ (0.6 mmol), n-PrOH (2.0 mL), N₂, 120 °C for 2 h.
Reaction condition: 1a (0.6 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.6 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 3 h.
Reaction condition: 1a (0.8 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.03 mmol), B$_2$pin$_2$ (0.6 mmol), n-PrOH (2.0 mL), N$_2$, 120 °C for 4 h.
Reaction condition: 1a (1.0 mmol), NiCl₂(PPh₃)₂ (0.03 mmol), B₂pin₂ (0.6 mmol), n-PrOH (2.0 mL), N₂, 120 °C for 2 h.