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Supporting Information

Zinc-Catalysed Hydroboration of Terminal and Internal Alkynes

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I. General considerations

Unless otherwise noted all the reactions were performed in an argon filled MBRAUN glove box or using standard Schlenk technique. All chemicals were purchased either from Sigma Aldrich or Alfa Aesar and used without further purification. Zinc triflate (98%), NaBHET₃, and pinacol borane (HBpin) were purchased from Sigma Aldrich. HBpin for bulk reactions was prepared from B₂pin₂ according to literature procedure.¹ Reagent grade solvents were purchased from SD Fine Chemicals (India), distilled and deoxygenated by freeze pump thaw cycle (three times) before using. Deuterated solvents CDCl₃, C₆D₆, Toluene-d₈, D₂O were purchased from Cambridge Isotope Laboratories and deoxygenated by freeze pump thaw cycle and stored over molecular sieves before use.

GC-MS data were acquired using GCMS-QP2010 SE SHIMADZU system. Commercially available, pre-coated TLC-sheets ALUGRAM® Xtra Sil G/UV254 were purchased from MACHEREY-NAGEL GmbH & Co. KG. The removal of solvent was performed on a rotary evaporator in vacuo at a maximum temperature of 40 °C.

All NMR spectra (¹H (400 MHz), ¹¹B (128 MHz), ¹³C{¹H} (100 MHz), ¹⁹F (376 MHz)) were recorded by a Bruker Avance 400 MHz NMR spectrometer at an ambient temperature. ¹H NMR chemical shifts were reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent (CDCl₃: δ = 7.26 ppm, C₆D₆: δ = 7.16 ppm) whereas ¹³C NMR spectra were reported relative to TMS using the carbon signals of the deuterated solvent (CDCl₃: δ = 77.16 ppm, C₆D₆: δ = 128.06 ppm). ¹¹B NMR signals were quoted relative to BF₃·Et₂O and ¹⁹F NMR signals were quoted using FCl₃ as an internal standard. ¹H NMR yields were calculated using CH₃NO₂ (nitromethane) as an internal standard. Peak values were reported downfield to TMS in ppm (parts per million) and following notation has been used to assign the peaks (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad, dd: doublet of a doublet, dt: doublet of a triplet, td: triplet of a doublet). Coupling constants values were given in Hertz's (Hz) and rounded up to the nearest whole number.

II. Synthesis of Starting Materials

Synthesis of 1-ethynyl-4-vinylbenzene (19a)

Firstly, 4-bromostyrene was synthesized according to modified literature procedure². Further Sonogashira coupling of 4-bromostyrene with trimethylsilylacetylene followed by deprotection³ furnishes the desired compound in quantitative yield.

Synthesis of 1-ethynyl-4-(phenylethynyl)benzene (20a)

1-Bromo-4-iodobenzene was synthesized by diazo coupling reaction of 4-bromoaniline in quantitative yield. Sonogashira coupling between 1-bromo-4-iodobenzene and phenyl acetylene produces 1-bromo-4-(phenylethynyl)benzene which was subjected to another Sonogashira coupling reaction without further purification with trimethylsilyl acetylene. The deprotection of silyl group resulted the desired compound³ in quantitative yield.

III. Optimisation of the Reaction Conditions

Experimental Procedure for Examples Described in Table 1

In a microwave vial equipped with magnetic stirring bar, Zinc triflate (4 mg, 0.01 mmol), NaBHET₃ (1M in THF, 10 μ l, 0.01 mmol), pinacol borane (35 μ l, 0.24 mmol), phenylacetylene (21.8 μ l, 0.2 mmol) and 1 mL of solvent were added. The reaction mixture was stirred at 80 °C for the indicated amount of time, and then eluted with Et₂O: hexane (3:7) mixture through a plug of celite ($\varnothing$ 3 mm $\times$ 8 mm). The solvent was removed in vacuo, and nitromethane was added as an internal standard. The product yield was determined from ¹H NMR using nitromethane as an internal standard.

Table S1: Screening of additives for Zn catalysed hydroboration of phenyl acetylene (1a).

Entry	Catalyst (5 mol %)	Additive (5 mol %)	Solvent	Temp (°C)	Time (h)	Product Yield (%) ^a
1	Zn(OTf) ₂	NaBHET ₃	toluene	100	20	78
2	Zn(OTf) ₂	NaBH ₄	toluene	100	20	80
3	Zn(OTf) ₂	ClSiHMe ₂	toluene	100	20	42
4	Zn(OTf) ₂	Pyridine	toluene	100	20	trace
5	Zn(OTf) ₂	NaO ^t Bu	toluene	100	20	16 ^b

Reaction conditions: Phenyl acetylene (0.2 mmol), pinacol borane (1.2 equiv, 0.24 mmol), Zn(OTf)₂ (5 mol %, 0.01 mmol), additives (5 mol%, 0.01 mmol) and toluene (1 mL) at 100 °C for 20 h under N₂ atmosphere. ^a Yields were determined by ¹H NMR using nitromethane as an internal standard. ^b 1.2 equivalent of sodium tert-butoxide was used.

Table S2: Screening of reaction time for Zn catalysed hydroboration of phenyl acetylene (1a).

Entry	Catalyst (5 mol %)	Additive (5 mol %)	Solvent	Temp (°C)	Time (h)	Product Yield (%) ^a
1	Zn(OTf) ₂	NaBHET ₃	toluene	100	6	38
2	Zn(OTf) ₂	NaBHET ₃	toluene	100	8	59
3	Zn(OTf) ₂	NaBHET ₃	toluene	100	10	85
4	Zn(OTf) ₂	NaBHET ₃	toluene	100	12	83
5	Zn(OTf) ₂	NaBHET ₃	toluene	100	20	78
5	Zn(OTf) ₂	NaBHET ₃	toluene	100	24	74

Reaction conditions: Phenyl acetylene (0.2 mmol), pinacol borane (1.2 equiv, 0.24 mmol), Zn(OTf)₂ (5 mol %, 0.01 mmol), NaBHET₃ (5 mol %, 0.01 mmol) and solvent (1 mL) at 100 °C for indicated amount of time under N₂ atmosphere. ^a Yields were determined by ¹H NMR using nitromethane as an internal standard.

Table S3: Screening of reaction temperature for Zn catalysed hydroboration of phenyl acetylene (1a).

Entry	Catalyst (5 mol %)	Additive (5 mol %)	Solvent	Temp (°C)	Time (h)	Product Yield (%) ^a
1	Zn(OTf) ₂	NaBHET ₃	toluene	RT	10	14
2	Zn(OTf) ₂	NaBHET ₃	toluene	40	10	42
3	Zn(OTf) ₂	NaBHET ₃	toluene	60	10	80
4	Zn(OTf) ₂	NaBHET ₃	toluene	80	10	92
5	Zn(OTf) ₂	NaBHET ₃	toluene	100	10	85

Reaction conditions: Phenyl acetylene (0.2 mmol), pinacol borane (1.2 equiv, 0.24 mmol), Zn(OTf)₂ (5 mol %, 0.01 mmol), NaBHET₃ (5 mol %) and solvent (1 mL) at indicated temperature for 10 h under N₂ atmosphere. ^a Yields were determined by ¹H NMR using nitromethane as an internal standard

Table S4: Screening of catalyst for Zn catalysed hydroboration of phenyl acetylene (1a).

Entry	Catalyst (5 mol %)	Additive (5 mol %)	Solvent	Temp (°C)	Time (h)	Product Yield (%) ^a
1	Zn dust	NaBHEt ₃	toluene	80	10	8
2	Zn(OTf) ₂	NaBHEt ₃	toluene	80	10	92
3	ZnCl ₂	NaBHEt ₃	toluene	80	10	90
4	ZnI ₂	NaBHEt ₃	toluene	80	10	88
5 ^b	ZnEt ₂	-	toluene	80	10	6

Reaction conditions: Phenyl acetylene (0.2 mmol), pinacol borane (1.2 equiv, 0.24 mmol), Zn source (5 mol %, 0.01 mmol), NaBHEt₃ (5 mol %) and toluene (1 mL) at 80 °C for 10 h under N₂ atmosphere. ^a Yields were determined by ¹H NMR using nitromethane as an internal standard. ^b 5 mol% of 1M diethylzinc solution in hexane was used as a catalyst.

Table S5: Screening of catalyst and additive loading for Zn catalysed hydroboration of phenyl acetylene (1a).

Entry	Catalyst (x mol %)	Additive (y mol %)	Solvent	Temp (°C)	Time (h)	Product Yield (%) ^a
1	Zn(OTf) ₂ (2.5)	NaBHET ₃ (2.5)	toluene	80	10	68
2	Zn(OTf) ₂ (2.5)	NaBHET ₃ (5)	toluene	80	10	74
3	Zn(OTf) ₂ (5)	NaBHET ₃ (2.5)	toluene	80	10	38
4	Zn(OTf) ₂ (5)	NaBHET ₃ (5)	toluene	80	10	92
5	Zn(OTf) ₂ (5)	NaBHET ₃ (10)	toluene	80	10	79
6	Zn(OTf) ₂ (10)	NaBHET ₃ (10)	toluene	80	12	91

Reaction conditions: Phenyl acetylene (0.2 mmol), pinacol borane (1.2 equiv, 0.24 mmol), Zn(OTf)₂ (indicated amount), NaBHET₃ (indicated amount) and solvent (1 mL) at 80 °C for 10 h under N₂ atmosphere. ^a Yields were determined by ¹H NMR using nitromethane as an internal standard.

Table S6: Screening of solvents for Zn catalysed hydroboration of phenyl acetylene (1a).

Entry	Catalyst (5 mol %)	Additive (5 mol %)	Solvent	Temp (°C)	Time (h)	Product Yield (%) ^a
1	Zn(OTf) ₂	NaBHET ₃	DCM	80	10	16
2	Zn(OTf) ₂	NaBHET ₃	THF	80	10	60
3	Zn(OTf) ₂	NaBHET ₃	CH ₃ CN	80	10	6
4	Zn(OTf) ₂	NaBHET ₃	benzene	80	10	72
5	Zn(OTf) ₂	NaBHET ₃	dioxane	80	10	75
6	Zn(OTf) ₂	NaBHET ₃	toluene	80	10	92
7	Zn(OTf) ₂	NaBHET ₃	1,2 DME	80	10	67

Reaction conditions: Phenyl acetylene (0.2 mmol), pinacol borane (1.2 equiv, 0.24 mmol), Zn(OTf)₂ (5 mol %, 0.01 mmol), NaBHET₃ (5 mol %) and respective solvent (1 mL) at 80 °C for 10 h under N₂ atmosphere. ^a Yields were determined by ¹H NMR using nitromethane as an internal standard.

IV. Substrate Scope

General procedure A: for catalytic reactions to calculate NMR yield

A microwave vial equipped with a magnetic stirring bar was charged with Zinc triflate (5 mol %, 4 mg, 0.01 mmol), NaBHEt₃ (1M in THF, 5 mol %, 10 µL, 0.01 mmol), pinacol borane (1.2 equiv, 35 µL, 0.24 mmol), alkynes (1 equiv, 0.2 mmol) and 1 mL of toluene. The reaction mixture was heated at 80 °C for 10 h. After completion, the reaction mixture was eluted with Et₂O: hexane (3:7) mixture through a plug of celite (Ø 3 mm × 8 mm). The solvent was removed in vacuo and the crude reaction mixture was subjected to ¹H NMR. The product yield was determined from ¹H NMR using nitromethane as an internal standard and average of two runs.

General procedure B: for small scale catalytic reactions

A microwave vial equipped with a magnetic stirring bar was charged with Zinc triflate (5 mol %, 4 mg, 0.01 mmol), NaBHEt₃ (1M in THF, 5 mol %, 10 µL, 0.01 mmol), pinacol borane (1.2 equiv, 35 µL, 0.24 mmol), alkynes (1 equiv, 0.2 mmol) and 1 mL of toluene. The reaction mixture was heated at 80 °C for 10 h. After completion, the reaction mixture was eluted with Et₂O: hexane (3:7) mixture through a plug of celite (Ø 3 mm × 8 mm). The filtrate was analyzed by GC-MS. The product was purified by silica gel column chromatography eluted with mostly EtOAc:hexane (02:98) mixture mostly.

General Procedure C: for larger scale catalytic reactions

In a screw capped long vial or in a Schlenk tube equipped with a magnetic stirring bar, Zinc triflate (5 mol %, 18.0 mg, 0.05 mmol), NaBHEt₃ (1M in THF, 5 mol %, 50 µL, 0.05 mmol), pinacol borane (1.2 equiv, 174 µL, 1.2 mmol), alkynes (1 equiv, 1 mmol) and 3 mL of toluene were added. The reaction mixture was heated at 80 °C for 10 h. After completion, the reaction mixture was eluted with Et₂O: hexane (3:7) mixture through a short plug of celite; the filtrate was analyzed by GC-MS. The product was purified by silica gel column chromatography eluted with mostly EtOAc and hexane mixture.

Spectral Data

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

Following general procedure C, colourless liquid in 85% (195 mg, 0.85 mmol) yield from phenyl acetylene (**1a**, 102 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.49 (d, *J* = 7 Hz, 2H), 7.41 (d, *J* = 18 Hz, 1H), 7.34–7.29 (m, 3H), 6.18 (d, *J* = 18 Hz, 1H), 1.32 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.2.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 149.6, 137.6, 129.0, 128.7, 127.2, 116.8 (br, *C-B*) 83.4, 24.9.

GC-MS: *m/z* 230 (*M*⁺).

(*E*)-4,4,5,5-Tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (**2b**)

Following general procedure C, yellowish liquid in 94% (229 mg, 0.94 mmol) yield from 4-methylphenylacetylene (**2a**, 116 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.33 (m, 3H), 7.14 (d, *J* = 8 Hz, 2H), 6.12 (d, *J* = 18 Hz, 1H), 2.35 (s, 3H), 1.32 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.2.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 149.6, 139.0, 134.9, 129.4, 127.1, 114.9 (br, *C-B*) 83.4, 24.9, 21.5.

GC-MS: m/z 244 (M^+).

(*E*)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

Following general procedure B, yellowish liquid in 74% (192 mg, 0.74 mmol) yield from 4-methoxyphenylacetylene (**3a**, 132 mg, 1 mmol) was obtained using 1% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.44 (d, J = 9 Hz, 2H), 7.35 (d, J = 18 Hz, 1H), 6.86 (d, J = 9 Hz, 2H), 6.01 (d, J = 18 Hz, 1H), 3.81 (s, 3H), 1.30 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.3.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 160.5, 149.2, 130.6, 128.6, 114.1, 83.3, 55.4, 25.0.

The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

GC-MS: m/z 260 (M^+).

(*E*)-2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)

Following general procedure C, colourless liquid in 92% (228 mg, 0.92 mmol) yield from 4-fluorophenylacetylene (**4a**, 120 mg, 1 mmol) was obtained using 1% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.46 (dd, J = 8, 6 Hz, 2H), 7.35 (dd, J = 18, 8 Hz, 1H), 7.01 (t, J = 8 Hz, 2H), 6.07 (dd, J = 18, 8 Hz, 1H), 1.31 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.3.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 163.2 (d, J = 249 Hz), 148.3, 133.8, 128.8 (d, J = 8 Hz), 115.8 (d, J = 22 Hz), 83.5, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

¹⁹F NMR (376 MHz, CDCl₃) δ (ppm) -112.3.

GC-MS: m/z 248 (M^+).

(*E*)-2-(4-Bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)

Following general procedure C, yellow solid in 85% (253 mg, 0.85 mmol) yield from 4-bromoethynylbenzene (**5a**, 181 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.46–7.44 (m, 2H), 7.34 – 7.32 (m, 2H), 7.28 (d, J = 13 Hz, 1H), 6.14 (d, J = 18 Hz, 1H), 1.30 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.2.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 148.2, 136.6, 131.9, 128.7, 123.0, 83.6, 25.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

GC-MS: m/z 310 (M^+).

(*E*)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (6b)

Following general procedure C, red solid in 56% (167mg, 0.56 mmol) yield from 1-ethynyl-2-(trifluoromethyl) benzene (**6a**, 170 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.77 (dd, J = 18, 2 Hz, 1H), 7.71 (d, J = 8 Hz, 1H), 7.63 (d, J = 8 Hz, 1H), 7.51 (t, J = 8 Hz, 1H), 7.36 (t, J = 8 Hz, 1H), 6.18 (d, J = 18 Hz, 1H), 1.31 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 29.6.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 144.9, 137.1, 132.0, 128.3, 127.6, 126.6, 125.8 (q, J = 6 Hz), 123.0, 83.7, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

GC-MS: m/z 283 ($M-CH_3^+$)

(E)-2-(4-ethynylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7b)

Following general procedure C, white solid in 58% (147 mg, 0.58 mmol) yield from 1,4-diethynylbenzene (**7a**, 126 mg, 1 mmol) was obtained using 4% EtOAc in hexane as eluent.

1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (d, $J = 2$ Hz, 4H), 7.36 (d, $J = 18$ Hz, 1H), 6.18 (d, $J = 18$ Hz, 1H), 3.13 (s, 1H), 1.31 (s, 12H).

^{11}B (128 MHz, $CDCl_3$) δ (ppm) 29.8.

^{13}C (100 MHz, $CDCl_3$) δ (ppm) 148.6, 138.0, 132.9, 127.0, 122.6, 83.6, 78.4, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

GC-MS: m/z 254 (M^+)

1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (8b)

Following general procedure C, white solid in 75% (287 mg, 0.75 mmol) yield from 1,4-diethynylbenzene (**8a**, 126 mg, 1 mmol) was obtained using 20% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁵

1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 (s, 4H), 7.37 (d, $J = 18$ Hz, 2H), 6.17 (d, $J = 18$ Hz, 2H), 1.30 (s, 24H).

^{11}B (128 MHz, $CDCl_3$) δ (ppm) 29.8.

^{13}C (100 MHz, $CDCl_3$) δ (ppm) 149.0, 138.1, 127.4, 117.0 (br, C-B), 83.5, 24.9.

GC-MS: m/z 382 (M^+)

(E)-3-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine(9b)

Following general procedure A, colourless oil in 37% NMR yield from 3-ethynylpyridene (**9a**, 17 mg, 0.37 mmol) was obtained. When the reaction was performed using 10 mol % of $\text{Zn}(\text{OTf})_2$ and NaBHET_3 , and 2 equiv of HBpin for 24 h 52% (by ^1H NMR spectrum) of **9b** was obtained.

The NMR is consistent with literature data.⁴

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.69 (br, s, 1H), 8.52 (br, s, 1H), 7.81 (d, $J = 8$ Hz, 1H), 7.37 (d, $J = 18$ Hz, 1H), 7.29 (dd, $J = 8, 5$ Hz, 1H), 6.25 (d, $J = 18$ Hz, 1H) 1.31 (s, 12H).

^{11}B NMR (128 MHz, CDCl_3) δ (ppm) 30.3.

(E)-4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl) vinyl)-1,3,2-dioxaborolane (10b)

Following general procedure C, colourless oil in 57% (134.52mg, 0.57 mmol) yield from 3-ethynylthiophene (**10a**, 108.16 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent. When the reaction was performed using 2 equiv of HBpin under the standard conditions 88% (by ^1H NMR spectrum) of **10b** was obtained.

The NMR is consistent with literature data.^{4,5}

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.38 (d, $J = 18$ Hz, 1H), 7.31 – 7.29 (m, 2H), 7.27-7.25 (m, 1H), 5.94 (d, $J = 18$ Hz, 1H), 1.30 (s, 12H).

^{11}B NMR (128 MHz, CDCl_3) δ (ppm) 30.5.

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 143.3, 141.4, 126.2, 125.2, 125.0, 116.2 (br, C-B), 83.5, 25.0.

GC-MS: m/z 236 (M^+)

(E)-2-(Dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b)

Following general procedure C, colourless oil in 72% (191 mg, 0.72 mmol) yield from 1-decyne (**11a**, 138 mg, 1 mmol) was obtained using 5% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.62 (dt, *J* = 18, 6 Hz, 1H), 5.41 (d, *J* = 18 Hz, 1H), 2.15-2.10 (m, 2H), 1.39 – 1.21 (m, 24H), 0.86 (t, *J* = 8 Hz, 3H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 29.9.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 155.0, 128.7, 118.7 (br, C-B), 83.1, 36.0, 32.0, 29.6, 29.4, 28.4, 25.0, 22.8, 14.3.

GC-MS: *m/z* 251 (M-CH₃)⁺

(E)-2-(3-Cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12b)

Following general procedure C, colourless oil in 65% (162 mg, 0.65 mmol) yield from 3-cyclohexyl-1-propyne (**12a**, 122 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.59(dt, *J*=18, 7 Hz 1H), 5.38 (d, *J* = 18 Hz, 1H), 2.03 (t, *J* = 7 Hz, 2H), 1.71 – 1.64 (m, 4H), 1.40-1.32 (m, 1H), 1.26 (s, 12H), 1.20-1.09 (m, 4H), 0.89 – 0.84 (m, 2H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 29.9.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 153.7, 83.2, 44.3, 37.4, 33.4, 26.7, 26.5, 25.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

GC-MS: *m/z* 235 (M-CH₃)⁺

(E)-2-(2-Cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13b)

Following general procedure A, colourless oil in 58% NMR yield from cyclopropylacetylene (**13a**, 33 mg, 0.5 mmol) was obtained.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.06 (dd, *J* = 18, 9 Hz, 1H), 5.48 (d, *J* = 18 Hz, 1H), 1.54-1.44 (m, 1H), 1.24 (s, 12H), 0.82 – 0.77 (m, 2H), 0.54 – 0.50 (m, 2H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 29.5.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 158.7, 115.0 (br, C-B), 83.1, 24.9, 17.1, 8.0.

GC-MS: *m/z* 194 (M⁺)

(E)-2-(2-Cyclopentylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14b)

Following general procedure C, colourless oil in 89% (197 mg, 0.89 mmol) yield from cyclopentylacetylene (**14a**, 94 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ(ppm) 6.62 (dd, *J* = 18, 7 Hz, 1H), 5.40 (dd, *J* = 18, 1 Hz, 1H), 2.57-2.47 (m, 1H), 1.81-1.75 (m, 2H), 1.67 – 1.61 (m, 2H), 1.58-1.53 (m, 2H), 1.40-1.33 (m, 2H), 1.27 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 29.6.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 159.1, 83.1, 46.3, 32.5, 25.4, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

GC-MS: *m/z* 222 (M⁺)

(E)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15b)

Following general procedure C, colourless oil in 83% (195 mg, 0.83 mmol) yield from cyclohexylacetylene (**15a**, 108 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ(ppm) 6.58 (dd, *J* = 18, 6 Hz, 1H), 5.37 (dd, *J* = 18, 2 Hz, 1H), 2.04 – 1.98 (m, 1H), 1.74 – 1.70 (m, 4H), 1.66 – 1.60 (m, 2H), 1.26 (s, 12H), 1.15 – 1.04 (m, 4H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.0

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 160.0, 83.1, 43.4, 32.0, 29.9, 26.1, 25.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

GC-MS: *m/z* 236 (M⁺)

(E)-4,4,5,5-tetramethyl-2-(4-vinylstyryl)-1,3,2-dioxaborolane (16b)

Following general procedure B, Colourless oil and blue fluorescent in 75% (38 mg, 0.15 mmol) yield from 1-ethynyl-4-vinylbenzene(**16a**, 25 mg, 0.2 mmol) was obtained using 10% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁵

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.46 (d, *J* = 8 Hz, 2H), 7.39-7.34 (m, 3H), 6.70 (dd, *J* = 18, 11 Hz, 1H), 6.16 (d, *J* = 18 Hz, 1H), 5.77 (d, *J* = 18 Hz, 1H), 5.26 (d, *J* = 11 Hz, 1H), 1.32(s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.4.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 149.2, 138.3, 137.2, 136.6, 127.4, 126.6, 114.4, 83.5, 25.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

GC-MS: *m/z* 256 (M⁺)

(E)-4,4,5,5-tetramethyl-2-(4-(phenylethynyl)styryl)-1,3,2-dioxaborolane (17b)

Following general procedure B, white solid in 42% (28 mg, 0.08 mmol) yield from 1-ethynyl-4-(phenylethynyl)benzene (**17a**, 40 mg, 0.2 mmol) was obtained using 15% EtOAc in hexane as eluent.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.54 - 7.45 (m, 6H), 7.40 - 7.34 (m, 4H), 6.20 (d, *J* = 18 Hz, 1H), 1.32 (s, 12H).

¹¹B (160 MHz, CDCl₃) δ (ppm) 30.1.

¹³C (125 MHz, CDCl₃) δ (ppm) 148.7, 137.4, 131.9, 131.8, 128.9, 127.1, 123.8, 123.4, 116.1 (br, *C-B*), 90.8, 89.5, 83.6, 25.0.

GC-MS: *m/z* 330 (*M*⁺)

(E)-2-(2-(Cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18b)

Following general procedure C, colourless oil in 83% (194 mg, 0.83 mmol) yield from ethynylcyclohexene (**18a**, 106 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.01 (d, *J* = 18 Hz, 1H), 5.95 (br, s, 1H), 5.41 (d, *J* = 18 Hz, 1H), 2.23-2.05 (m, 4H), 1.66-1.64 (m, 2H), 1.59-1.56 (m, 2H), 1.26 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.0.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 153.4, 137.3, 134.4, 112.5 (br, *C-B*), 83.1, 26.3, 24.9, 23.9, 22.5, 22.4.

GC-MS: *m/z* 234 (*M*⁺)

(Z)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(19b)

Following general procedure C, white solid in 67% (205 mg, 0.67 mmol) yield from diphenylacetylene (**19a**, 178 mg, 1 mmol) was obtained using 5% EtOAc in hexane as eluent. The NMR is consistent with literature data.^{4,6}

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.56 (s, 1H), 7.47 – 7.41 (m, 3H), 7.37 – 7.34 (m, 2H), 7.30 – 7.27 (m, 3H), 7.24 (dd, J = 4, 2 Hz, 2H), 1.49 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 31.0.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 143.3, 140.5, 137.1, 133.3, 130.1, 129.6, 129.0, 128.8, 128.4, 128.0, 127.7, 127.0, 126.4, 83.9, 24.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

GC-MS: m/z 291 (M-CH₃)⁺

(Z)-2-(Hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20b)

Following general procedure C, colourless oil in 70% (94.15 mg, 0.70 mmol) yield from 3-hexyne (**20a**, 82.14 mg, 1 mmol) was obtained using 5% EtOAc in hexane as eluent.

The NMR is consistent with literature data.^{4,6}

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.25 (t, J = 6 Hz, 1H), 2.15-2.10 (m, 4H), 1.26 (s, 12H), 0.97 (td, J = 8, 3 Hz, 3H), 0.93 (td, J = 8, 3 Hz, 3H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.6.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 147.2, 83.1, 24.9, 21.8, 21.6, 15.0, 14.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

GC-MS: m/z 195 (M-CH₃)⁺.

(Z)-4,4,5,5-Tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane (21b)

Following general procedure C, colourless oil in 73% (174 mg, 0.73 mmol) yield from 4-octyne (**21a**, 110 mg, 1 mmol) was obtained using 5% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁴

¹H NMR (400 MHz, CDCl₃) δ (ppm) 6.28 (t, J = 7 Hz, 1H), 2.09 (dt, J = 7, 3 Hz, 4H), 1.41-1.33 (m, 4H), 1.24 (s, 12H), 0.90 (t, J = 8 Hz, 3H), 0.87 (t, J = 8 Hz, 3H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.7.

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 146.1, 83.0, 30.8, 30.7, 24.9, 23.4, 22.5, 14.3, 14.2.

The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

GC-MS: m/z 223 ($M-CH_3$)⁺

(Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (22b) & (Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (22c)

Following general procedure C with 1.5 equiv HBpin, colourless oil in 76% (185 mg, 0.76 mmol, mixture of two isomers, **22b/22c** = 3:2) yield from 1-phenyl-1-propyne (**22a**, 116 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.^{4,7} NMR data for both the isomers are given below. (for minor isomer, the peaks have been assigned by (\$) in ¹H NMR spectrum) For the aromatic protons, the complete range is given as it is difficult to assign.

¹H NMR for 22b (400 MHz, CDCl₃) δ (ppm) 7.44-7.20 (m, 6H), 2.05 (d, J = 2 Hz, 3H), 1.35 (s, 12H).

¹H NMR for 22c (400 MHz, CDCl₃) δ (ppm) 7.44-7.20 (m, 5H), 6.78 (q, J = 7 Hz, 1H), 1.81 (d, J = 7 Hz, 3H), 1.30 (s, 12H).

¹¹B NMR (128 MHz, CDCl₃) δ (ppm) 30.6.

^{13}C NMR for 22b (100 MHz, CDCl_3) δ (ppm) 142.7, 138.0, 129.4, 128.1, 127.1, 83.5, 24.9, 16.0. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

^{13}C NMR for 22c (100 MHz, CDCl_3) δ (ppm) 142.5, 139.9, 129.1, 127.8, 125.9, 83.4, 24.8, 15.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

GC-MS: m/z 229 ($\text{M}-\text{CH}_3$)⁺

(Z)-trimethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (23b)

Following general procedure C with 1.5 equiv HBpin, colourless oil in 47% (142 mg, 0.47 mmol) yield from trimethyl(phenylethynyl)silane (**23a**, 174 mg, 1 mmol) was obtained using 2% EtOAc in hexane as eluent.

The NMR is consistent with literature data.⁸

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.02 (s, 1H), 7.33-7.27 (m, 3H), 7.24-7.22 (m, 2H), 1.30 (s, 12H), 0.01 (s, 9H).

^{11}B NMR (128 MHz, CDCl_3) δ (ppm) 31.7.

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 157.2, 141.6, 128.4, 127.8, 127.6, 83.4, 25.0, 1.1. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening

GC-MS: m/z 287 ($\text{M}-\text{CH}_3$)⁺

(Z)-trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (24b)

Following general procedure C with 1.5 equiv HBpin, colourless oil in 60% (144 mg, 0.60 mmol) yield from trimethyl(prop-1-yn-1-yl)silane (**24a**, 112 mg, 1 mmol) was obtained using hexane as eluent.

The NMR is consistent with literature data.^{4,7}

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.04 (br, s, 1H), 1.83 (s, 3H), 1.21 (s, 12H), 0.11 (s, 9H).

^{11}B NMR (128 MHz, CDCl_3) δ (ppm) 31.3.

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 156.0, 82.8, 24.8, 20.8, 0.9. The carbon directly attached to the boron atom was not detected, likely due to quadrupolar broadening.

GC-MS: m/z 225 ($\text{M}-\text{CH}_3$)⁺

Note: Unreactive alkynes including aromatic heterocycles substrates are listed below.

^a Using 2 eq HBpin, OH group gets converted to OBpin unit along with alkyne hydroboration

Figure S1: Examples of unreactive substrates

V. Mechanistic investigations

To gain insight for the proposed catalytic cycle a series of stoichiometric reactions have been performed. The reactions were monitored by ^1H and ^{11}B NMR spectroscopy.

Control Experiments

Scheme S1: Stoichiometric reaction between zinc triflate and sodium triethylborohydride

Experimental Procedure: In a NMR tube equimolar amount of Zn(OTf)_2 (7 mg, 0.02 mmol) and NaBHET_3 (1 M in THF, 20 μL , 0.02 mmol) were taken and 0.5 mL of benzene- d_6 was added. Immediately ^1H and ^{11}B NMR of resulting mixture has been recorded. As seen from Figure S2 the ^{11}B resonance of boron in NaBHET_3 shifts from -11.71 ppm to 86.73 ppm which has been assigned to BEt_3 ⁶. But we didn't observe any resonance for species **A** in the ^1H NMR spectrum of above reaction mixture.

Figure S2: ^{11}B NMR spectra of: 1) NaBHET_3 , 2) Crude reaction mixture of Zn(OTf)_2 and NaBHET_3 (1:1) at RT.

Scheme S2: Stoichiometric reaction between **A** and **1a**

Subsequent addition of phenyl acetylene (**1a**, 2.2 μL , 0.02 mmol) to the above reaction mixture showed an upfield shift for acetylenic proton of **1a** from 2.99 ppm to 2.76 ppm, which implies the side on coordination of **1a** with zinc center (Figure S3).

Figure S3: Stacked ^1H NMR spectra of: 1) Phenyl acetylene (**1a**), 2) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{phenyl acetylene}(\mathbf{1a})$ (1:1:1) (both spectra have been recorded in C_6D_6).

After that, pinacol borane (1 equiv, 0.02 mmol, 2.9 μL) was added to the above reaction mixture and heated. ^1H and ^{11}B NMR spectra has been recorded in specific time interval.

Scheme S3: Stoichiometric reaction between **B** and **HBpin**

Careful observation of the ^1H spectrum of the reaction mixture (Figure S4) reveals the formation of four doublets δ (ppm) 5.14 (d $J = 11$ Hz, 1H); 5.64 (d $J = 18$ Hz, 1H); 6.53 (d, $J = 18$ Hz, 1H); 7.84 (d, $J = 18$ Hz, 1H) among which doublets at 6.53ppm and 7.84 ppm correspond to the product.⁹ The other two set of doublets likely to form from the transient Zinc-alkenyl species.⁴

Figure S4: Stacked ^1H NMR spectra of sequential addition of reagents (expanded region from 8.8 ppm to 4.8 ppm) 1) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3$, 2) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \mathbf{1a}$, 3) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \mathbf{1a} + \text{HBpin}$, 4) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \mathbf{1a} + \text{HBpin}$ (stirred at 80 °C for 1 hr), 5) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \mathbf{1a} + \text{HBpin}$ (stirred at 80 °C for 2 hr), 6) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \mathbf{1a} + \text{HBpin}$ (stirred at 80 °C for 13 hr).

During these stoichiometric reactions, BEt_3 reacts with HBpin and generates few boron species which appeared in the ^{11}B spectra respectively at 34.1 ppm and 53.77 ppm. These boron species are assigned to EtBpin^6 and HBEt_2^6 , which leads to the unavailability of HBpin in the reaction mixture (Figure S5). As a result, $\mathbf{1a}$ remains unreacted mostly.

Figure S5: Stacked ^{11}B NMR spectra of sequential addition of reagents 1) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3$, 2) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \mathbf{1a} + \text{HBpin}$, 3) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \mathbf{1a} + \text{HBpin}$ (stirred at 80°C for 1 hr).

When a similar experiment is carried out using toluene- d_8 as solvent with 1.5 equivalent HBpin we observed the following.

Scheme S4: Stoichiometric reaction between zinc triflate and sodium triethylborohydride

Experimental Procedure: In a NMR tube equimolar amount of $\text{Zn}(\text{OTf})_2$ (7 mg, 0.02 mmol) and NaBHET_3 (1 M in THF, 20 μL , 0.02 mmol) was taken and 0.5 mL of toluene- d_8 was added. Immediately ^1H and ^{11}B NMR of resulting mixture has been recorded. As observed earlier BEt_3 has been formed.

Scheme S5: Stoichiometric reaction between **A** and BEt_3 with HBpin.

Subsequent addition of pinacol borane (1.5 equiv, 0.03 mmol, 4.4 μ L) to the above reaction mixture doesn't induce any change. However, upon heating this reaction mixture at 80 $^{\circ}$ C for 2 hours reveals the formation of EtBpin as a result of side reaction between BET_3 and HBpin (see Figure S7). After that **1a** was added, as seen from ^1H NMR (Figure S6), acetylenic proton resonance was observed at 2.75 ppm. Once the reaction was heated at 80 $^{\circ}$ C for 2 hours, characteristic doublets of the product (**1b**) appeared at 6.31 ppm and 7.6 ppm⁹ with the reducing intensity of acetylenic proton peak. Additional heating of the reaction mixture for 6 hours resulted in the consumption of all the **1a** and leads to the formation of the product. From the ^{11}B spectra (Figure S6) upon addition of **1a** to the reaction mixture of pre-heated $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$ the product started to form till the complete consumption of HBpin.

Figure S6: Stacked ^1H NMR spectra of sequential addition of reagents: 1) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3$, 2) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$, 3) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{1a} + \text{HBpin}$ (stirred at 80 $^{\circ}$ C for 2 hr), 4) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$ (stirred at 80 $^{\circ}$ C for 2 hr) + **1a**, 5) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$ (stirred at 80 $^{\circ}$ C for 2 hr) + **1a** (stirred at 80 $^{\circ}$ C for 2 hr), 6) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$ (stirred at 80 $^{\circ}$ C for 2 hr) + **1a** (stirred at 80 $^{\circ}$ C for 8 hr).

Figure S7: Stacked ^{11}B NMR spectra of sequential addition of reagents: 1) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3$, 2) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$, 3) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \mathbf{1a} + \text{HBpin}$ (stirred at 80°C for 2 hr), 4) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$ (stirred at 80°C for 2 hr) + $\mathbf{1a}$, 5) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$ (stirred at 80°C for 2 hr) + $\mathbf{1a}$ (stirred at 80°C for 2 hr), 6) $\text{Zn}(\text{OTf})_2 + \text{NaBHET}_3 + \text{HBpin}$ (stirred at 80°C for 2 hr) + $\mathbf{1a}$ (stirred at 80°C for 8 hr).

Deuterium labelling Experiments:

Experimental procedure:

Phenyl acetylene- d_1 ¹⁰ and pinacolborane- d_1 ¹¹ (DBpin) was synthesized according to the reported literature and used for the following reaction.

A microwave vial equipped with a magnetic stirring bar was charged with zinc triflate (5 mol %, 2 mg, 0.005 mmol), $NaBHET_3$ (1M in THF, 5 mol %, 5 μ L, 0.005 mmol), pinacol borane (1.2 equiv, 18 μ L, 0.12 mmol), phenyl acetylene- d_1 (1 equiv, 0.1 mmol) and 1 mL of toluene. The reaction mixture was heated at 80 °C for 10 hours. The 2H NMR of the crude reaction mixture shows peak at $\delta = 6.22$ ppm (Figure S8), which indicates a *cis* orientation of deuterium and phenyl group in **1b-D**.

Figure S8: 2H NMR (CDCl₃, 62 MHz) spectra of crude reaction mixture of $Zn(OTf)_2 + NaBHET_3 +$ **1a-D** + HBpin.

A NMR tube equipped with a magnetic stirring bar was charged with Zn(OTf)_2 (5 mol %, 1 mg, 0.0025 mmol), NaBHET_3 (1M in THF, 5 mol%, 2.5 μL , 0.0025 mmol), pinacol borane- d_1 (1.2 equiv, 0.06 mmol), **1a** (1 equiv, 0.05 mmol) and 0.4 mL of toluene. The reaction mixture was heated at 80 $^\circ\text{C}$ for 10 h. The ^2H NMR of the crude reaction mixture shows peak at $\delta = 7.32$ ppm (Figure S9), which indicates a *cis* orientation of deuterium and Bpin unit in **1b'-D**.

Figure S9: ^2H NMR (CD_2Cl_2 , 62 MHz) spectra of crude reaction mixture of $\text{Zn(OTf)}_2 + \text{NaBHET}_3 + \text{1a} + \text{DBpin}$.

Experiment with Radical Scavengers

A microwave vial equipped with a magnetic stirring bar was charged with zinc triflate (5 mol %, 4 mg, 0.01 mmol), NaBHEt₃ (1M in THF, 5 mol %, 10 μ L, 0.01 mmol), pinacol borane (1.2 equiv, 35 μ L, 0.24 mmol), phenyl acetylene (1 equiv, 0.2 mmol) and 1 mL of toluene. Then 1 equivalent of TEMPO (1 equiv, 0.2 mmol, 31 mg) or 9,10-dihydroanthracene (1 equiv, 0.2 mmol, 36 mg) was added. The reaction mixture was heated at 80 °C for 10 hours. After completion, a small portion of the reaction mixture was analysed by GCMS. The other portion of the reaction mixture was eluted with Et₂O: hexane (3:7) mixture through a plug of celite ($\varnothing$ 3 mm $\times$ 8 mm). The solvent was removed in vacuo and the crude reaction mixture was subjected to ¹H NMR. The product yield was determined from ¹H NMR using nitromethane as an internal standard.

Scheme S6: Hydroboration of 1a in presence of Radical Scavengers

When TEMPO (RS-1) is used as a radical scavenger 10% of **1b** was obtained from ¹H NMR. However, the GCMS analyses reveals that the formation of TEMPO-Bpin adduct which is in consistent with the literature reports.^{12,13} The formation of the adduct makes the HBpin unavailable for the reaction, hence the starting material is largely recovered. With 9,10-dihydroanthracene (RS-2) as a radical quencher, the product (**1b**) yield was obtained in 90%, which clearly indicated that the reaction doesn't involve any radical mechanism.

The radical clock experiment was performed using 1-(allyloxy)-2-iodobenzene (RS-3, 1 equiv, 0.2 mmol, 52 mg) as a standard substrate. **1b** was obtained in quantitative yield of 55% and 10% hydroborated product of RS-3 was obtained (see chemoselectivity experiments for details). However, we have not found any cyclized product which dismissed the possibility of radical mechanism.

VI. Competitive Chemo-selective Experiments (Described in Scheme 2)

General Procedure for Intermolecular Chemoselective Catalytic Hydroboration

In a nitrogen-filled glovebox, $\text{Zn}(\text{OTf})_2$ (5 mol%, 0.01 mmol), NaBHET_3 (5 mol%, 0.01 mmol), HBPin (1 equiv, 0.2 mmol), competitive substrates (**1a** and **19a** or **25a**) (0.2 mmol each) and toluene (1 mL) were added to a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was stirred at 80 °C temperature for 10 h. The reaction mixture was diluted with a mixture of hexane and diethyl ether (70:30, 4 mL) and filtered through a plug of celite ($\varnothing$ 3 mm $\times$ 8 mm). The solvents were removed under vacuum. The products yields were determined by ^1H NMR using nitromethane as an internal standard.

Experiment 1 (Scheme 2a)

Figure S10: ^1H NMR spectra of competitive hydroboration reaction between phenylacetylene (**1a**) and styrene (**25a**).

Experiment 2 (scheme 2b):

Figure S11: ^1H NMR spectra of competitive hydroboration reaction between phenylacetylene (**1a**) and diphenylacetylene (**19a**).

VI. Spectra of Isolated compound

The ^1H , ^{11}B , ^{13}C and ^{19}F spectra of the isolated compounds were given below. The impurities in the spectra have been marked using (# or *). In ^1H NMR spectra (for yield calculation), the internal standard nitromethane peak ($\delta = 4.32$ ppm) has been denoted with (IS).

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

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-4,4,5,5-Tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-2-(4-Methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-2-(4-Fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

^{19}F NMR, CDCl_3 , 376 MHz:

(E)-2-(4-Bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-4,4,5,5-Tetramethyl-2-(2-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (6b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-2-(4-ethynylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

1,4-bis((E)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (8b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-3-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)pyridine(9b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

(E)-4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl) vinyl)-1,3,2-dioxaborolane (10b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-2-(Dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(*E*)-2-(3-Cyclohexylprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12b)

¹H NMR, CDCl₃ 400 MHz:

¹¹B NMR, CDCl₃, 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-2-(2-Cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-2-(2-Cyclopentylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-2-(2-Cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-4,4,5,5-tetramethyl-2-(4-vinylstyryl)-1,3,2-dioxaborolane (16b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(E)-4,4,5,5-tetramethyl-2-(4-(phenylethynyl)styryl)-1,3,2-dioxaborolane (17b)

^1H NMR, CDCl_3 500 MHz:

^{11}B NMR, CDCl_3 , 160 MHz:

^{13}C NMR, CDCl_3 , 125 MHz:

(E)-2-(2-(Cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(Z)-2-(1,2-Diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(19b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(Z)-2-(Hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(Z)-4,4,5,5-Tetramethyl-2-(oct-4-en-4-yl)-1,3,2-dioxaborolane (21b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (22b) & (Z)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (22c)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(Z)-trimethyl(2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (23b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

(Z)-trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)silane (24b)

^1H NMR, CDCl_3 400 MHz:

^{11}B NMR, CDCl_3 , 128 MHz:

^{13}C NMR, CDCl_3 , 100 MHz:

VIII. References

1. H. Braunschweig, F. Guethlein, L. Mailander, T. B. Marder, *Chem. Eur. J.* **2013**, *19*, 14831-14835.
2. K. C. Nicolau, M. W. Harter, J. L. Gunzner, A. Nadin, *Leibigs Ann.l Recueil.* **1997**, 1283-1301.
3. X. Zhang, X. Xie, Y. Liu, *J. Am. Chem. Soc.* **2018**, *140*, 7385- 7389.
4. S. Mandal, P. K. Verma, K. Geetharani, *Chem. Commun.* **2018**, *54*, 13690-13693.
5. R. Mamidala, V. K. Pandey, A. Rit, *Chem. Commun.* **2019**, *55*, 989-992.
6. A. Bismuto, S. P. Thomas, M. J. Cowley, *Angew. Chem.* **2016**, *128*,15582-15585; *Angew. Chem. Int. Ed.* **2016**, *55*, 15356–15359.
7. J. R. Lawson, L. C. Wilkins, R. L. Melen, *Chem. Eur. J.* **2017**, *23*, 10997-11000.
8. L. Ferrand, Y. Lyu, A. R-Hernández, B. J. Fallon, M. Amatore, C. Aubert, M. Petit, *Synthesis* **2017**, *49*, 3895-3904.
9. M. Magre, B. Maity, A. Falconnet, L. Cavallo, M. Rueping, *Angew. Chem.* **2019**, *131*, 7099-7103; *Angew. Chem. Int. Ed.* **2019**, *58*, 7025–7029.
10. D. G. Kohler, S. N. Gockel, J. L. Kennemur, P. J. Waller, K. L. Hull, *Nat. Chem.* **2018**, *10*, 333-340.
11. M. Espinal-Viguri, S. E. Neale, N. T. Coles, S. A. Macgregor, R. L. Webster, *J. Am. Chem. Soc.* **2019**, *141*, 572–582.
12. S. K. Bose, K. Fucke, L. Liu, P. G. Steel, T. B. Marder, *Angew. Chem.* **2014**, *126*, 1829-1834; *Angew. Chem. Int. Ed.* **2014**, *53*, 1799-1803.
13. G. Vijaykumar, M. Bhunia, S. K. Mandal, *Dalton Trans.* **2019**, *48*, 5779-5784.