Supporting information

Zirconium-catalyzed synthesis of alkenylaminoboranes: from a reliable preparation of alkenylboronates to a direct stereodivergent access to alkenylbromides.

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Supporting information

1. ADDITIONAL DATA: .................................................................................................................. 3
2. GENERAL CONSIDERATIONS .................................................................................................. 4
3. GENERAL PROCEDURE AND CORRESPONDING DATA ......................................................... 4
4. NMR SPECTRA ...................................................................................................................... 35
1. Additional Data:

Table 1: Zr-catalyzed hydroboration using DIPOB

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*a* isolated yield

Table 2: Zr-catalyzed hydroboration using DIPAB

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*a* no PhMgBr was added
2. General Considerations

All chemicals were used without further purification. Methyl-tert-butyl ether and diethyl ether were dried over sodium/benzophenone and freshly distilled prior to use. Methanol was dried from calcium hydride and freshly distilled prior to use. Pinacol, néopentylglycol and 1,8-diaminonaphthalene were recrystallized from benzene before use and stored under an argon atmosphere for a maximum of 7 days. Silica gel chromatography was performed using 230–400 mesh silica gel purchased from Merck. Eluted plates were visualized using ultraviolet light or stained in aqueous KMnO₄ (KMnO₄ 3g, K₂CO₃ 20g, aqueous 5% NaOH 5 mL, H₂O 300 mL). ¹H, ¹³C and ¹¹B NMR spectra were recorded at room temperature (25°C) in chloroform-d₃ or C₆D₆ using Bruker Avance 300 (300 MHz). ¹H and ¹³C NMR chemical shifts (δ) are given in ppm relative to tetramethylsilane (internal standard). J values are quoted in Hertz. The following abbreviations were used to describe the multiplicities: s = singlet, bs = broad singlet, d = doublet, m = multiplet, t = triplet, dd = doublet of doublet, td = triplet of doublet, q = quadruplet, quint = quintuplet, etc. The carbon signal bound to the boron was not observed in most cases due to quadrupolar relaxation. ¹¹B NMR spectra were recorded at 25°C and chemical shifts (δ) are given in ppm relative to BF₃·OEt₂ (internal standard). GC-MS analyses were performed on HP 6890 series GC-system equipped with a J&W Scientific DB-1701 capillary column, a HP 5973 mass selective detector (EI) using the following method: 70°C for 1 min then 20°C/min until 230°C then 6 min at 230°C. Infrared spectra (IR) were recorded on a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer as neat films on NaCl windows or as solids with KBr pellets. The melting points (Mp) were recorded on a Mettler Toledo DSC1-star system using the following method: 30°C to 300°C at 10°C/min.

3. General Procedure and corresponding data

Procedure A for the synthesis of N,N-dilisopropylamine-borane complex [105416-38-4]

To a stirred solution of dilisopropylamine (70.6 mL, 0.5 mol) and NaBH₄ (30 g, 0.79 mol) in THF (500 mL) was added at 0°C over a period of 45 minutes sulfuric acid (16 mL, 0.3 mol). The mixture was allowed to warm to room temperature and stirred for 3 hours. The crude product was concentrated under vacuum and the residue was taken with CH₂Cl₂, and then filtrated to eliminate all solid residues. The filtrate was washed with water (4x100 mL). The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to give the product obtained as a colorless oil which solidified upon cooling (50.8 g, 90%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 0.96 (d, ³JHH = 6.6Hz, 6H), 1.05 (d, ³JHH = 6.6Hz, 6H), 1.91 (q, ³JHB = 91Hz, 3H), 2.72 – 2.90 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 19.0, 21.1, 52.1. ¹¹B NMR (128 MHz, CDCl₃) δ (ppm) -21.3 (q, ³JHB = 91.4 Hz). Mp 20–25 ºC (hexane).
Procedure B for the synthesis of \(N,N\)-diisopropylaminoborane [22092-92-8]

\[
\text{NH} \cdot \text{BH}_3 \xrightarrow{\text{neat, 200°C}} \text{N} - \text{BH}_2
\]

\(N,N\)-diisopropylamine-borane complex was heated carefully at 200°C under an argon atmosphere during 10 hours and then cooled to room temperature. The resulting crude \(N,N\)-diisopropylaminoborane was distilled at atmospheric pressure between 70 - 80°C to afford 38g (85% over 2 steps) of \(N,N\)-diisopropylaminoborane as a colorless liquid with yields being generally above 95%.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ (ppm) 1.04 (d, \(^3\)J\(_{\text{HH}}\) = 6.6 Hz, 12H), 3.01 – 3.29 (m, 2H), 4.76 (s, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) δ (ppm) 21.7, 51.4. \(^{11}\)B NMR (128 MHz, CDCl\(_3\)) δ (ppm) 34.8 (t, \(J = 127.2\) Hz).

Procedure C for the hydroboration of terminal alkynes using \(N,N\)-diisopropylaminoborane

\[
\begin{align*}
\text{R} = & \equiv \text{H} \\
1. \text{DIPOB (1.1 equiv.)} & \rightarrow \text{H} \xrightarrow{\text{2. HClZrCp}_2 (12 mol\%)} \text{BHN(Pr)}_2
\end{align*}
\]

To a suspension of the desired alkyne (1.0 mmol; 1.0 equiv.) in dry MTBE (1 mL) were added diisopropylaminoborane (125 mg; 1.1 mmol; 1 equiv.) and Schwartz reagent (30.9 mg; 12 mol%) at room temperature. The reaction mixture was then heated to 70°C using an oil bath for 4 hours. After cooling to room temperature, the resulting mixture was filtered on celite eluting with dry pentane. The pentane solution was finally concentrated under vacuum leading to pure (E)-alkenylaminoborane. None of these compounds showed sufficient stability to provide reliable MS or HRMS. They also hydrolyse and degrade rapidly on SiO\(_2\) or Al\(_2\)O\(_3\).

\(N,N\)-diisopropyl-1-[B-(E)-hexen-1-yl]-boranamine (2a)

\(2a\) was synthesized according to General Procedure C from 1-hexyne [693-02-7] on a 1 mmol scale (conversion 100%).

Formula: C\(_{12}\)H\(_{26}\)BN

Mol. Wt.: 195.16 g.mol\(^{-1}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) δ (ppm) 0.83 – 0.92 (m, 3H), 1.09 – 1.21 (m, 12H), 1.26 – 1.48 (m, 4H), 2.09 – 2.26 (m, 2H), 3.33 (hept, \(^3\)J\(_{\text{HH}}\) = 6.8 Hz, 1H), 3.98 (hept, \(^3\)J\(_{\text{HH}}\) = 6.8 Hz, 1H), 5.91 – 6.09 (dd, \(J = 16.9, 6.7\) Hz, 1H), 6.35 (dt, \(J = 16.8, 6.5\) Hz, 1H). \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) δ (ppm) 37.1 (br s). RF unstable on silica. MS (ESI+) m/z: unstable.
**N,N-diisopropyl-1-[B-(1E)-octen-1-yl]-boranamine (2b)**

52 was synthesized according to **General Procedure C** from 1-octyne [629-05-0] on a 1 mmol scale and obtained as an orange oil (196.8 mg, 89%).

Formula: C\textsubscript{14}H\textsubscript{30}BN

Mol. Wt.: 221.20 g.mol\textsuperscript{-1}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 1.12 – 1.19 (m, 12H), 1.24 – 1.34 (m, 11H), 2.18 (dt, \(J = 7.6, 3.8\) Hz, 2H), 3.33 (hept, \(J = 6.8\) Hz, 1H), 4.00 (hept, \(J = 6.8\) Hz, 1H), 6.02 (dd, \(J = 16.9, 6.6\) Hz, 1H), 6.37 (dt, \(J = 16.9, 6.4\) Hz, 1H). \textsuperscript{13}C NMR (76 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 14.3, 23.1, 23.8, 26.4, 31.1, 37.3, 44.3, 46.2, 155.1. Carbon adjacent to boron not observed.

\textsuperscript{11}B NMR (96 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 37.3 (br s).

**Rf unstable on silica** MS (ESI+) m/z: unstable.

\[\text{N,N-bis(1-isopropyl)-1-[(1E)-2-methyl-1-buten-1-yl-1-ol]-boranamine (2c)}\]

54 was synthesized according to **General Procedure C** from 2-methyl-3-butyne-2-ol [115-19-5] on a 1 mmol scale and obtained as a yellow oil (179.5 mg, 72%).

Formula: C\textsubscript{11}H\textsubscript{24}BNO

Mol. Wt.: 197.13 g.mol\textsuperscript{-1}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 1.19 (s, 3H), 1.34 (s, 3H), 1.53 (s, 12H), 3.32 (hept, \(J = 13.3, 6.7\) Hz,1H), 4.04 (hept, \(J = 13.5, 6.7\) Hz, 1H), 6.18 (dt, \(J = 17.3, 8.5\) Hz, 1H), 6.42 (t, \(J = 15.1\) Hz, 1H). \textsuperscript{13}C NMR (76 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 24.5, 24.8, 29.1, 71.8, 159.7. Carbon adjacent to boron not observed.

\textsuperscript{11}B NMR (96 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 36.4 (br s). **Rf unstable on silica.** MS (ESI+) m/z: unstable.

\[\text{N,N-diisopropyl-1-[B-(1E)-ethyn-1-yl-toluene]-boranamine (2d)}\]

(2e) was synthesized according to **General Procedure C** from 4-ethynyltoluene [766-97-2] on a 1 mmol scale (conversion 100%).

Formula: C\textsubscript{15}H\textsubscript{34}BN

Mol. Wt.: 229.17 g.mol\textsuperscript{-1}
Supporting information

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 1.19 – 1.23 (m, 12H), 2.35 (s, 3H), 3.32 (hept, \(^{3}J_{HH} = 6.8\) Hz, 1H), 4.12 (hept, \(^{3}J_{HH} = 6.8\) Hz, 1H), 6.31 (m, 1H), 6.75 (m, 1H), 7.13 (m, 3H), 7.40 (m, 1H). \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 36.3 (br s). \(R_f\) unstable on silica. MS (ESI\(^+\)) m/z: unstable.

\(N,N\)-diisopropyl-1-[B-(1E)-1-phenylethen-1-yl]boranamine [858347-30-5] (2e)

55 was synthesized according to General Procedure C from 1-ethynyl-benzene [536-74-3] on a 1 mmol scale and obtained as a yellow oil (197.9 mg, 92%).

Formula: \(C_{14}H_{22}BN\)

Mol. Wt.: 215.15 g.mol\(^{-1}\)

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 1.27 (d, \(J = 6.7\) Hz, 6H), 1.30 (d, \(J = 6.7\) Hz, 6H), 3.45 (hept., \(J = 6.7\) Hz, 1H), 4.21 (hept., \(J = 6.7\) Hz, 1H), 6.89 (d, \(J = 6.5\) Hz, \(J = 17.4\) Hz, 1H), 7.24 (d, \(J = 17.4\) Hz, 1H), 7.30-7.60 (m, 5H). \(^{13}\)C NMR (76 MHz, CDCl\(_3\)) \(\delta\) (ppm) 23.2, 26.7, 46.7, 49.6, 127.3, 128.4, 128.8, 139.2, 150.9. Carbon adjacent to boron not observed. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 35.8 (br s). \(R_f\) unstable on silica. MS (ESI\(^+\)) m/z: unstable.

\(N,N\)-diisopropyl-1-[B-(1E)-4-fluoro-1-phenylethen-1-yl]boranamine (2f)

53 was synthesized according to General Procedure C from 1-ethynyl-4-fluorobenzene [766-98-3] on a 1 mmol scale and obtained as a yellow solid (200.5 mg, 86%).

Formula: \(C_{14}H_{21}BFN\)

Mol. Wt.: 233.14 g.mol\(^{-1}\)

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 1.18 – 1.24 (m, 12H), 3.36 (hept, \(J = 6.7\) Hz, 1H), 4.10 (hept, \(J = 6.7\) Hz, 1H), 6.71 (dd, \(J = 17.5\), 6.6 Hz, 1H), 6.97 – 7.15 (m, 3H), 7.31 – 7.47 (m, 2H). \(^{13}\)C NMR (76 MHz, CDCl\(_3\)) \(\delta\) (ppm) 21.3, 24.3, 44.2, 48.6, 125.3, 126.6, 128.8, 138.1, 151.0. Carbon adjacent to boron not observed. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 36.3 (br s). \(R_f\) unstable on silica. MS (ESI\(^+\)) m/z: unstable.
Procedure D for the synthesis of alkenyldiazaborolanes

1. DIPOB (1.1 equiv.), HClZrCp₂ (12 mol%), MTBE, 70°C, 4h
2. MeOH (3.0 equiv.), -40°C, 1h
3. FeCl₃ (5 mol%), imidazole (3.0 equiv.), 1,8-diaminonaphthalene (1.0 equiv.), MeCN:H₂O (1:1), r.t., 4h

To a suspension of the desired alkyne (1.0 mmol; 1.0 equiv.) in dry MTBE (1 mL) were added DIPOB (123 mg; 1.1 mmol; 1.1 equiv.) and Schwartz reagent (30.9 mg; 12 mol%). The reaction mixture was then heated to 70°C using an oil bath for 4 hours. After cooling to -40°C, dry methanol (121 μL; 3.0 mmol; 3.0 equiv.) was added and the mixture was left to stir for 1 hour. The mixture was then concentrated under vacuum. To a solution of the methyl alkenylborate (1.0 mmol; 1.0 equiv.) in MeCN (4 mL) was added sequentially a solution of FeCl₃ (5 mol%) in H₂O (4 mL), imidazole (204 mg; 3.0 mmol; 3.0 equiv.) and 1,8-diaminonaphthalene (158.2 mg; 1.0 mmol; 1.0 equiv.). The resulting cloudy, dark purple mixture was stirred at room temperature for 4 hours. The reaction was then diluted with H₂O (5 mL) and extracted with EtOAc (3 x 8 mL). The combined organic extracts were dried over anhydride Na₂SO₄, filtered and concentrated under vacuum. The resulting viscous orange oil was then purified by column chromatography (on a silica gel being deactivated prior to use with 5 mol% Et₃N) affording the title compound.

2,3-dihydro-[B-2-(E)-1-hexen-1-yl]-1H-naphtho[1,8-de]-[1,3,2]-diazaborine [1437786-77-0] (3a)¹

(3a) was synthesized according to General Procedure D from 1-hexyne [693-02-7] on a 1 mmol scale and obtained as an orange oil (165.0 mg, 66%). [eluent: 100% hexane]

Formula: C₁₆H₁₉BN₂
Mol. Wt.: 250.15 g.mol⁻¹

¹H NMR (300 MHz, CDCl₃) δ (ppm) 0.93 (t, J = 7.1 Hz, 3H), 1.31 – 1.48 (m, 4H), 2.15 – 2.27 (m, 2H), 5.56 (d, J = 18.0 Hz, 1H), 5.70 (s, 1H), 6.31 – 6.35 (m, 1H), 6.37 (d, J = 18.1 Hz, 2H), 6.93 – 7.03 (m, 2H), 7.03 – 7.13 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 13.9, 22.2, 30.8, 35.5, 105.5, 117.3, 119.7, 127.5, 136.3, 141.3, 148.1. Carbon adjacent to boron not observed. ¹¹B NMR (96 MHz, CDCl₃) δ (ppm) 27.3 (br s). MS (ESI⁺) m/z: 251.3 [M+H]⁺ RF (EtOAc 10% /Hexane) 0.38.

2,3-dihydro-[B-2-(E)-1-octen-1-yl]-1H-naphtho[1,8-de]-[1,3,2]-diazaborine [1147459-15-1] (3b)

(3b) was synthesized according to General Procedure D from 1-octyne [629-05-0] on a 1 mmol scale and obtained as an orange oil (189.1 mg, 68%). [eluent: 100% hexane]

Formula: C_{18}H_{23}BN

Mol. Wt.: 278.21 g.mol^{-1}

$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.91 (t, $J = 6.6$ Hz, 3H), 1.26 – 1.37 (m, 6H), 1.44 – 1.53 (m, 2H), 2.20 (td, $J = 7.8, 1.3$ Hz, 2H), 5.56 (dt, $J = 18.0, 1.3$ Hz, 1H), 5.70 (s, 1H), 6.26 – 6.43 (m, 2H), 7.00 (d, $J = 8.1$ Hz, 2H), 7.04 – 7.16 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 14.1, 22.6, 28.6, 28.9, 31.7, 35.9, 105.5, 117.3, 119.7, 127.5, 136.3, 141.3, 148.2. Carbon adjacent to boron not observed.

$^{11}$B NMR (96 MHz, CDCl$_3$) δ (ppm) 27.5 (br s).

MS (ESI+) m/z: 279.6 [M+H]+. Rf (EtOAc 10% /Hexane) 0.37

2,3-dihydro-[B-2-(E)-1-phenylethen-1-yl]-1H-naphtho[1,8-de]-[1,3,2]-diazaborine [1147458-75-0] (3d)

(3d) was synthesized according to General Procedure D from 1-ethynylbezene [536-74-3] on a 1 mmol scale and obtained as a yellow oil (108.0 mg, 40%). [eluent: 100% hexane]

Formula: C_{18}H_{15}BN

Mol. Wt.: 270.14 g.mol^{-1}

$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 5.86 (s, 2NH), 6.30 (s, 1H), 6.31 – 6.41 (m, 1H), 6.99 – 7.07 (m, 2H), 7.11 (d, $J = 7.3$ Hz, 2H), 7.17 (d, $J = 10.5$ Hz, 2H), 7.28 – 7.42 (m, 3H), 7.48 – 7.55 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 105.8, 117.6, 126.8, 127.6, 128.7, 136.4, 137.5, 141.1, 143.7. Carbon adjacent to boron not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ (ppm) 27.2 (br s). IR (NaCl, cm$^{-1}$) 3411, 3048, 1601, 1502, 1408, 1372, 1336, 1166, 818. Rf (Hexane) 0.40.

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2,3-dihydro-[B-2-(E)-4-methyl-1-phenylethen-1-yl]-1H-naphtho[1,8-de]-[1,3,2]-diazaborine [1147458-93-2] (3e)

(3e) was synthesized according to General Procedure D from 4-ethynyltoluene [766-97-2] on a 1 mmol scale and obtained as an orange oil (164.8 mg, 58%). [eluent: 100% hexane]

Formula: C_{19}H_{17}BN_{2}
Mol. Wt.: 284.17 g.mol^{-1}

^{1}H NMR (300 MHz, CDCl_{3}) δ (ppm): 2.37 (s, 3H), 5.85 (s, 2NH), 6.23 – 6.31 (m, 1H), 6.36 (dd, J = 7.2, 1.0 Hz, 1H), 7.02 (dd, J = 8.3, 0.9 Hz, 2H) 7.11 (dd, J = 6.9, 1.2 Hz, 2H), 7.13 – 7.21 (m, 3H), 7.41 (d, J = 8.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_{3}) δ (ppm): 21.3, 105.7, 117.5, 123.9, 126.7, 127.6, 129.4, 138.7, 141.2, 143.6. Carbon adjacent to boron not observed. ^{11}B NMR (96 MHz, CDCl_{3}) δ (ppm): 29.5 (br s).

IR (NaCl, cm^{-1}): 3052, 1625, 1599, 1504, 1409, 1372, 1144, 983, 746. RF (Hexane) 0.37

2-[(E)-2-(4-Fluorophenylethenyl)-2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborine (3f)

^{1}H NMR (400 MHz, CDCl_{3}) δ (ppm): 5.82 (br s, 2H), 6.24 (d, J = 18.7 Hz, 1H), 6.37 (d, J = 7.3 Hz, 2H), 7.00 – 7.18 (m, 7H), 7.44-7.51 (m, 2H). ^{13}C NMR (100 MHz, CDCl_{3}) δ (ppm): 105.8, 115.6 (d, J_{C-F} = 21.7 Hz), 117.6, 119.8, 121.6, 121.6, 128.4 (d, J_{C-F} = 21.7 Hz), 133.8 (d, J_{C-F} = 2.5 Hz), 136.4, 141.0, 142.3, 162.9 (d, J_{C-F} = 248.5 Hz). ^{11}B NMR (128 MHz, CDCl_{3}) δ (ppm): 27.6 (br s). ^{19}F NMR (376 MHz, CDCl_{3}) δ (ppm): -112.7 (s).

HRMS m/z (ESI, TOF) [M]+ calcd for C_{18}H_{14}BFN_{2} 288.12268; found 288.12269.
2-[(1E,9E)-10-(2,3-Dihydro-1H-1,3-diaza-2-boraphenalene-2-yl)-1,9-decadienyl]-2,3-dihydro-1H-1,3-diaza-2-boraphenalene (3g)

![Chemical structure](image)

$^{1}\text{H NMR (400 MHz, CDCl}_3\text{) }\delta$ (ppm) 1.31-1.42 (m, 4H), 1.43-1.53 (m, 4H), 2.17-2.25 (m, 4H), 5.57 (d, $J$ = 17.9 Hz, 2H), 5.70 (br s, 2H), 6.31 (d, $J$ = 7.3 Hz, 2H), 6.37 (dt, $J$ = 17.9, 6.6 Hz, 2H), 7.01 (d, $J$ = 8.2 Hz, 4H), 7.10 (d, $J$ = 8.4 Hz, 4H). $^{13}\text{C NMR (100 MHz, CDCl}_3\text{) }\delta$ (ppm) 28.5, 29.0, 35.8, 105.5, 117.4, 119.7, 123.8, 127.5, 136.3, 141.2, 147.9. $^{11}\text{B NMR (128 MHz, CDCl}_3\text{) }\delta$ (ppm) 27.3 (br s). HRMS m/z (ESI, TOF) [M]+ calcd for C$_{30}$H$_{32}$B$_2$N$_4$ 470.28076; found 470.28070.

2,3-dihydro-[B-2-(E)-5-chloro-1-hexen-1-yl]-1H-naphtho[1,8-de]-[1,3,2]-diazaborine (3h)

![Chemical structure](image)

(3h) was synthesized according to General Procedure D from 5-chloropentyne [14267-92-6] on a 1 mmol scale and obtained as a yellow oil (189.4 mg, 68%). [eluent: 100% hexane]

Formula: C$_{15}$H$_{16}$BCIN$_2$

Mol. Wt.: 270.57 g.mol$^{-1}$

$^{1}\text{H NMR (300 MHz, CDCl}_3\text{) }\delta$ (ppm) 1.84 – 2.00 (m, 2H), 2.37 (td, $J$ = 7.9, 1.3 Hz, 2H), 3.58 (t, $J$ = 6.6 Hz, 2H), 5.55 – 5.75 (m, 2H), 6.21 – 6.38 (m, 2H), 6.95 – 7.04 (m, 2H), 7.07 – 7.15 (m, 2H). $^{13}\text{C NMR (75 MHz, CDCl}_3\text{) }\delta$ (ppm) 31.3, 32.8, 44.3, 105.6, 117.5, 127.5, 136.3, 141.1, 145.5. Carbon adjacent to boron not observed. $^{11}\text{B NMR (96 MHz, CDCl}_3\text{) }\delta$ (ppm) 27.3 (br s). MS (ESI+) m/z: 271.7 [M+H]$^+$ HRMS m/z (ESI, TOF) [M+H]$^+$ calcd for C$_{15}$H$_{17}$N$_2$BCl 271.11678; found 271.11647. IR (NaCl, cm$^{-1}$) 2042, 1706, 1622, 1390, 1145, 832, 736, 711, 700. $\text{Rf (EtOAc 5% /Hexane) 0.35.}$
2,3-dihydro-[B-2-(E)-2-(cyclohex-1-en-1-yl)vinyl]-1H-naphtho[1,8-de]-[1,3,2]diazaborine (3i)

(3i) was synthesized according to General Procedure D from 1-ethynyl-cyclohexene [931-49-7] on a 1 mmol scale and obtained as a brown oil (145.3 mg, 53%). [eluent: 100% hexane]

Formula: C_{18}H_{19}BN_2
Mol. Wt.: 274.17 g.mol⁻¹

\(^1\)H NMR (300 MHz, CDCl₃) δ (ppm) 1.68 (ddt, J = 10.6, 5.6, 4.5 Hz, 4H), 2.20 (s, 4H), 5.57 (d, J = 18.4 Hz, 1H), 5.76 (s, 1H), 5.96 (s, 1H), 6.33 (dd, J = 7.3, 0.8 Hz, 2H), 6.79 (d, J = 18.4 Hz, 2H), 6.94 – 7.04 (m, 2H), 6.94 – 7.04 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 22.4, 22.5, 24.0, 26.1, 105.6, 117.3, 127.5, 133.3, 136.8, 137.0, 141.3, 147.4. Carbon adjacent to boron not observed.

\(^{11}\)B NMR (96 MHz, CDCl₃) δ (ppm) 28.3 (br s). MS (ESI⁺) m/z: 275.3 [M+H⁺]. HRMS m/z (ESI, TOF) [M⁺] calcd for C_{18}H_{19}BN_2 274.1636; found 274.1634.

IR (NaCl, cm⁻¹) 1978, 2934, 1714, 1634, 1608, 1474, 1372, 1346, 1146, 982, 852, 674.

Rf (EtOAc 2% /Hexane) 0.35.

2,3-dihydro-[B-2-(E)-2-(1-tert-butyl)-1-dimethyl(4-penten-1-yloxy)-silane-1H-naphtho[1,8-de]-[1,3,2]diazaborine (3j)

(3j) was synthesized according to General Procedure D on a 1 mmol scale from (1-tert-butyl)-1-dimethyl(4-pentyn-1-yloxy)-silane [61362-77-4] and obtained as a yellow oil (194.2 mg, 53%). [eluent: 100% hexane]

Formula: C_{21}H_{31}BN_2OSi
Mol. Wt.: 366.39 g.mol⁻¹

\(^1\)H NMR (300 MHz, CDCl₃) δ (ppm) 0.09 (s, 6H), 0.94 (s, 9H), 1.63-1.75 (m, 2H), 2.23 – 2.32 (m, 2H), 3.64 (t, J = 6.3 Hz, 2H), 5.59 (dt, J = 18.1, 1.6 Hz, 1H), 5.70 (s, 2H), 6.32 (d, J = 7.3 Hz, 2H), 6.38 (dt, J = 18.2, 6.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 2H), 7.11 (t, J = 7.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) -5.22, 25.9, 31.7, 32.2, 62.5, 105.6, 117.4, 127.5, 141.2, 147.5. Carbon adjacent to boron not observed.

\(^{11}\)B NMR (96 MHz, CDCl₃) δ (ppm) 28.0 (br s). MS (ESI⁺) m/z: 367.5 [M+H⁺]. HRMS m/z (ESI, Orbitrap) [M⁺] calcd for C_{21}H_{31}BN_2OSi 366.2293, found 366.2293. RF (EtOAc 10% /Hexane) 0.46
(3k) was synthesized according to General Procedure D from 3-butyne-1-yl-benzene [766-98-3] on a 1 mmol scale and obtained as a whiteish oil (277.3 mg, 93%). [eluent: 100% hexane]

Formula: C\textsubscript{20}H\textsubscript{19}BN\textsubscript{2}

Mol. Wt.: 298.20 g.mol\textsuperscript{-1}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ (ppm) 2.57 (ddd, J = 12.8, 7.1, 5.7 Hz, 2H), 2.76 – 2.87 (m, 2H), 5.57 – 5.77 (m, 3H), 6.34 (dt, J = 12.1, 6.0 Hz, 2H), 6.43 (ddd, J = 16.9, 11.6, 5.3 Hz, 1H), 7.04 (dd, J = 8.3, 0.9 Hz, 1H), 7.08 – 7.18 (m, 2H), 7.22 – 7.27 (m, 2H), 7.34 (ddd, J = 12.6, 8.8, 4.0 Hz, 2H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) δ (ppm) 35.0, 37.5, 105.6, 117.4, 125.9, 127.5, 128.4, 128.4, 136.3, 141.2, 141.6, 146.7. Carbon adjacent to boron not observed.

\textsuperscript{11}B NMR (96 MHz, CDCl\textsubscript{3}) δ (ppm) 27.9 (br s). MS (ESI\textsuperscript{+}) m/z: 299.6 [M+H] \textsuperscript{+}. IR (NaCl, cm\textsuperscript{-1}) 3412, 1625, 1504, 1372, 1144, 818, 763, 691. Rf (Hexane) 0.38

2-[(E)-5-(2,3-Dihydro-1H-1,3-diaza-2-boraphenalen-2-yl)-4-pentenyl]-1,3-isoindolinedione (3l)

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ (ppm) 1.82-1.92 (m, 2H), 2.21-2.30 (m, 2H), 3.73 (t, J = 7.1 Hz, 1H), 5.57 (d, J = 18.2 Hz, 1H), 5.66 (br s, 2H), 6.28 (d, J = 7.3 Hz, 2H), 6.30 (m, 1H), 6.99 (d, J = 8.2 Hz, 2H), 7.08 (t, J = 8.3 Hz, 2H), 7.62 (dd, J = 5.5, 2.9 Hz, 2H), 7.82 (dd, J = 5.4, 2.9 Hz, 2H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ (ppm) 27.0, 33.0, 37.5, 105.5, 117.3, 119.6, 123.1, 124.7, 132.0, 133.8, 136.2, 141.1, 145.9, 168.4. \textsuperscript{11}B NMR (128 MHz, CDCl\textsubscript{3}) δ (ppm) 27.5 (br s). MS (ESI\textsuperscript{+}) m/z: 381.2 [M]+. HRMS m/z (ESI, TOF) [M]+ calcd for C\textsubscript{23}H\textsubscript{20}BN\textsubscript{3}O\textsubscript{2} 381.1643, found 381.1640.

\footnote{K. Sasaki, T. Hayashi, Angew. Chem. Int. Ed. 2010, 49, 8145-8147.}
Procedure E for the synthesis of pinacol alkenylboronates

1. DIPOB (1.1 equiv.), HCl\textsubscript{2}ZrC\textsubscript{2} (12 mol%), MTBE, 70°C, 4h
2. MeOH (3.0 equiv.), -40°C, 1h
3. Pinacol (1.0 equiv.), Et\textsubscript{2}O, -40°C to r.t., 4h

To a suspension of the desired alkyne (1.0 mmol; 1.0 equiv.) in dry MTBE (1 mL) were added DIPOB (123.2 mg; 1.1 mmol; 1.1 equiv.) and Schwartz reagent (30.9 mg; 12 mol%). The reaction mixture was then heated to 70°C using an oil bath for 4 hours. After cooling to -40°C, dry methanol (121 μL; 3.0 mmol; 3.0 equiv.) was added and the mixture was left to stir for 1 hour. The mixture was then concentrated under vacuum. To a solution of the methyl alkenylborate (1.0 mmol; 1.0 equiv.) in Et\textsubscript{2}O (1 mL) at -40°C was added sublimated pinacol (118 mg; 1.0 mmol; 1.0 equiv.). The reaction was stirred for 4 hours and then diluted with Et\textsubscript{2}O (10 mL). The organic layer was washed with a 50 g/L CuCl\textsubscript{2} aqueous solution (3 x 10 mL), dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated under vacuum to afford the pure pinacol alkenylboronate.

**B-2-(E)-(Hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** [126688-97-9] (4a)

(4a) was synthesized according to General Procedure E from 1-hexyne [693-02-7] on a 1 mmol scale and obtained as a colorless oil (195.4 mg, 93%).

Formula: C\textsubscript{12}H\textsubscript{23}BO\textsubscript{2}
Mol. Wt.: 210.12 g.mol\textsuperscript{-1}

\(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) δ (ppm) 0.89 (t, J = 7.2 Hz, 3H), 1.27 (s, 12H), 1.30 – 1.35 (m, 2H), 1.37 – 1.42 (m, 2H), 2.13 – 2.17 (m, 2H), 5.43 (d, J = 18.0 Hz, 1H), 6.61 – 6.66 (m, 1H). \(^{13}\)C NMR (75 MHz, CDCl\textsubscript{3}) δ (ppm) 13.9, 22.2, 24.8, 30.3, 35.5, 83.0, 154.8. Carbon adjacent to boron not observed. \(^{11}\)B NMR (96 MHz, CDCl\textsubscript{3}) δ (ppm) 29.9 (br s). MS (ESI+) m/z: 211.3 [M+H]\textsuperscript{+} IR (NaCl, cm\textsuperscript{-1}) 3401, 2978, 1639, 1360, 1144, 971, 849.

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B-2-(E)-(oct-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [83947-55-1] (4b)\(^4\)

(4b) was synthesized according to **General Procedure E** from 1-octyne [629-05-0] on a 1 mmol scale and obtained as a whiteish oil (228.7 mg, 96%).

**Formula:** C\(_{14}\)H\(_{27}\)BO\(_2\)

**Mol. Wt.:** 238.18 g.mol\(^{-1}\)

**\(^1\)H NMR (300 MHz, CDCl\(_3\))** δ (ppm) 0.87 (t, \(J = 6.7\) Hz, 3H), 1.26 (s, 12H), 1.38 – 1.74 (m, 8H), 2.12 (dd, \(J = 10.4, 4.0\) Hz, 2H), 5.42 (dt, \(J = 18.0, 1.5\) Hz, 1H), 6.63 (dt, \(J = 17.9, 6.4\) Hz, 1H). **\(^{13}\)C NMR (75 MHz, CDCl\(_3\))** δ (ppm) 14.1, 22.6, 24.7, 28.2, 28.9, 31.7, 35.6, 82.9, 154.8. Carbon adjacent to boron not observed. **\(^{11}\)B NMR (96 MHz, CDCl\(_3\))** δ (ppm) 29.8 (br s). **MS (ESI+)** m/z: 239.3 [M+H]\(^+\) IR (NaCl, cm\(^{-1}\)) 3402, 2923, 1638, 1327, 1144, 970, 891.

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B-(E)-(2-methyl-but-3-en-2-ol)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [581802-26-8] (4c)\(^5\)

(4c) was synthesized according to **General Procedure E** from 2-methyl-3-butyn-2-ol [115-19-5] on a 1 mmol scale and obtained as a whiteish oil (133.6 mg, 63%).

**Formula:** C\(_{11}\)H\(_{21}\)BO\(_3\)

**Mol. Wt.:** 212.10 g.mol\(^{-1}\)

**\(^1\)H NMR (300 MHz, CDCl\(_3\))** δ (ppm) 1.27 (s, 12H), 1.31 (s, 6H), 5.61 (d, \(J = 18.2\) Hz, 1H), 6.75 (t, \(J = 19.5\) Hz, 1H). **\(^{13}\)C NMR (75 MHz, CDCl\(_3\))** δ (ppm) 24.5, 24.8, 29.1, 71.8, 83.3, 159.7. Carbon adjacent to boron not observed. **\(^{11}\)B NMR (96 MHz, CDCl\(_3\))** δ (ppm) 30.3 (br s). **MS (ESI+)** m/z: 213.3 [M+H]\(^+\) IR (NaCl, cm\(^{-1}\)) 3416, 2978, 2932, 1639, 1474, 1458, 1146, 971, 851, 675.

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(B-2-(E)-(styr-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [83947-56-2] (4d)\(^4\)

(4d) was synthesized according to General Procedure E from 1-ethynyl-benzene [536-74-3] on a 1 mmol scale and obtained as a colorless oil (223.2 mg, 97%).

Formula: C\(_{14}\)H\(_{19}\)BO\(_2\)
Mol. Wt.: 230.11 g.mol\(^{-1}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 1.32 (s, 12H), 6.17 (d, \(J = 18.4\) Hz, 1H), 7.28 – 7.45 (m, 4H), 7.47 – 7.52 (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 24.6, 24.8, 83.3, 127.0, 128.5, 128.9, 137.4, 149.5. Carbon adjacent to boron not observed. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 29.9 (br s). MS (ESI+) m/z: 231.2 [M+H]\(^+\) IR (NaCl, cm\(^{-1}\)) 3026, 2978, 2930, 2858, 1945, 1638, 1362, 1145, 1004, 971, 849, 746, 699.

(4h) was synthesized according to General Procedure E from 5-chloro-1-pentyne [14267-92-6] on a 1 mmol scale and obtained as a yellow oil (216.7 mg, 94%).

Formula: C\(_{11}\)H\(_{20}\)BClO\(_2\)
Mol. Wt.: 230.54 g.mol\(^{-1}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 1.26 (s, 12H), 1.83 – 1.96 (m, 2H), 2.24 – 2.36 (m, 2H), 3.48 – 3.57 (m, 2H), 5.48 (dt, \(J = 18.0, 1.5\) Hz, 1H), 6.58 (dt, \(J = 17.9, 6.4\) Hz, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 24.7, 24.8, 31.0, 32.7, 44.3, 83.1, 152.1. Carbon adjacent to boron not observed. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 28.5 (br s). MS (ESI+) m/z: 231.6 [M+H]\(^+\) IR (NaCl, cm\(^{-1}\)) 2978, 2958, 2857, 1639, 1463, 1363, 1145, 999, 971, 650.

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Supporting information

**B-2-(E)-(2-(Cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [245432-97-7] (4i)**

(4i) was synthesized according to **General Procedure E** from 1-ethynyl-cyclohexene [931-49-7] on a 1 mmol scale and obtained as a colorless oil (206.0 mg, 88%).

Formula: C_{14}H_{23}BO_{2}
Mol. Wt.: 234.15 g.mol^{-1}

\(^1H\) NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 1.27 (s, 12H), 1.62 – 1.88 (m, 4H), 2.13 – 2.55 (m 4H), 5.42 (d, \(J=18.3\) Hz, 1H), 5.96 (s, 1H), 7.02 (d, \(J=18.2\) Hz, 1H). \(^{13}C\) NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 22.3, 22.4, 23.7, 24.7, 26.1, 83.0, 134.2, 137.1, 153.2. Carbon adjacent to boron not observed. \(^{11}B\) NMR (96 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 28.4 (br s).

**B-2-(E)-(5-[[1,1-dimethylethyl]dimethylsilyloxy]-1-penteny-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [277331-67-6] (4j)**

(4j) was synthesized according to **General Procedure E** on a 1 mmol scale from (1-tert-butyl)dimethyl(4-pentyn-1-yloxy)-silane [61362-77-4] and obtained as a yellow oil (300.2 mg, 92%).

Formula: C_{17}H_{35}BO_{3}Si
Mol. Wt.: 326.36 g.mol^{-1}

\(^1H\) NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 0.01 – 0.05 (m, 9H) 0.88 (s, 14H), 1.23 (s, 6H), 1.56 – 1.71 (m, 3H), 2.13 – 2.25 (m, 3H), 3.54 – 3.66 (m, 4H), 5.44 (dt, \(J=17.9\), 1.5 Hz, 1H), 6.64 (dt, \(J=17.9\), 6.4 Hz, 1H). \(^{13}C\) NMR (75 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) -5.27, 18.3, 23.8, 24.7, 25.9, 26.0, 28.6, 31.3, 32.1, 32.7, 62.5, 63.3, 83.0, 154.1. Carbon adjacent to boron not observed. \(^{11}B\) NMR (96 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 27.9 (br s). MS (ESI+) m/z: 327.5 [M+H]. IR (NaCl, cm\(^{-1}\)) 2978, 2955, 2931, 2858, 1639, 1471, 1365, 1146, 1103, 837, 775.

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**Supporting information**

*B-2-(E)-(4-phenyl-but-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [172512-84-4] (4k)*

(4k) was synthesized according to **General Procedure E** from 4-phenyl-1-butynyl [766-98-3] on a 1 mmol scale and obtained as a colorless oil (253.0 mg, 98%).

Formula: C₁₆H₂₃BO₂  
Mol. Wt.: 258.17 g.mol⁻¹

**¹H NMR (300 MHz, CDCl₃) δ (ppm) 1.28 (s, 12H), 2.43 – 2.56 (m, 2H), 2.68 – 2.82 (m, 2H), 5.51 (dt, J = 18.0, 1.5 Hz, 1H), 6.72 (dt, J = 18.0, 6.2 Hz, 1H), 7.20 (d, J = 6.9 Hz, 3H), 7.26 (s, 2H).**

**¹³C NMR (75 MHz, CDCl₃) δ (ppm) 24.8, 34.6, 37.5, 83.1, 125.8, 128.3, 128.4, 141.8, 153.4. Carbon adjacent to boron not observed.**

**¹¹B NMR (96 MHz, CDCl₃) δ (ppm) 27.9 (br s).**

**MS (ESI+) m/z: 259.3 [M+H]⁺**

**IR (NaCl, cm⁻¹) 3062, 2978, 2932, 2858, 1725, 1604, 1321, 1165, 971, 892, 746, 676.**

*B-2-(E)-(5-phthalimido-pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [2215133-07-4] (4l)*

(4l) was synthesized according to **General Procedure E** from 2-(4-pentyn-1-yl)-1H-isoindole-1,3(2H)-dione [6097-07-0] on a 1 mmol scale and obtained as a whiteish oil (300.2 mg, 88%).

Formula: C₁₉H₂₄BNO₄  
Mol. Wt.: 341.21 g.mol⁻¹

**¹H NMR (300 MHz, CDCl₃) δ (ppm) 1.25 (s, 12H), 1.89 – 1.73 (m, 2H), 2.18 – 2.23 (m, 2H), 3.57 – 3.73 (m, 2H), 5.40 – 5.51 (m, 1H), 6.52 – 6.66 (m, 1H), 7.42 – 7.63 (m, 1H), 7.65 – 7.75 (m, 2H), 7.79 – 7.85 (m, 1H).**

**¹³C NMR (75 MHz, CDCl₃) δ (ppm) 24.7, 26.9, 27.0, 33.0, 33.2, 37.7, 39.2, 81.9, 83.0, 123.2, 129.9, 132.1, 133.8, 152.5, 153.0, 168.3. Carbon adjacent to boron not observed.**

**¹¹B NMR (96 MHz, CDCl₃) δ (ppm) 27.8 (br s).**

**MS (ESI+) m/z: unstable on heating**

**IR (NaCl, cm⁻¹) 3463, 2978, 1852, 1741, 1725, 1690, 1361, 908, 771, 736.**

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Supporting information

\[ \text{B-2-\{E\}-[\{5-\text{(1,1-dimethylethyl)dimethylsilyl\}-1-ethen-1-yl\}-4,4,5,5-tetramethyl-1,3,2-di} \text{o} \text{xaborolane (4m)} \]

(4m) was synthesized according to General Procedure E from tert-butyl(dimethylsilyl)acetylene [86318-63-8] on a 1 mmol scale and obtained as a yellow oil (254.8 mg, 95%).

Formula: C\(_{14}\)H\(_{29}\)BO\(_2\)Si
Mol. Wt.: 268.28 g.mol\(^{-1}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 0.03 (s, 6H), 0.88 (s, 9H), 1.28 (s, 12H), 6.26 (d, \(J = 21.9\) Hz, 1H), 7.11 (d, \(J = 21.9\) Hz, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) -6.51, 16.4, 24.6, 24.8, 26.5, 26.7, 83.3, 155.3. Carbon adjacent to boron not observed. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 28.9 (br s). MS (ESI+) \(m/z\): 269.2 [M+H]\(^+\). HRMS \(m/z\) (ESI, Orbitrap) [M+H]\(^+\) calcd for C\(_{14}\)H\(_{30}\)BO\(_2\)Si 269.2103; found 269.2104. IR (NaCl, cm\(^{-1}\)) 3416, 2978, 2932, 1639, 1474, 1458, 1350, 1146, 971, 851, 675.

\[ \text{B-2-\{E\}-\{4-bromo-\text{but-1-en-1-yl\}-4,4,5,5-tetramethyl-1,3,2-di} \text{xaborolane [1613271-48-9]} \text{\ (4n)} \]

(4n) was synthesized according to General Procedure E from 4-bromo-1-butyn [38771-21-0] on a 1 mmol scale and obtained as a yellow oil (255.3 mg, 98%).

Formula: C\(_{10}\)H\(_{18}\)BBrO
Mol. Wt.: 260.597 g.mol\(^{-1}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 1.26 (s, 12H), 2.72 (qd, \(J = 7.3, 1.4\) Hz, 2H), 3.43 (dd, \(J = 14.0, 6.8\) Hz, 2H), 5.53 (dt, \(J = 18.0, 1.4\) Hz, 1H), 6.54 (dt, \(J = 18.0, 6.3\) Hz, 1H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 24.8, 30.7, 38.8, 83.3, 149.5. Carbon adjacent to boron not observed. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 29.9 (br s). MS (ESI+) \(m/z\): 261.7 [M+H]\(^+\). IR (NaCl, cm\(^{-1}\)) 2978, 2927, 2857, 1639, 1463, 1320, 1145, 999, 971, 850.

(4o) was synthesized according to General Procedure E from 9-ethynyl-9H-Fluoren-9-ol [13461-74-0] on a 1 mmol scale and obtained as a yellow oil (294.6 mg, 92%).

Formula: C_{21}H_{23}BO_3
Mol. Wt.: 320.20 g.mol⁻¹

$^1$H NMR (300 MHz, CDCl₃) δ (ppm) 1.23 (s, 12H), 5.91 – 6.04 (m, 1H), 6.57 – 6.68 (m, 1H), 7.28 – 7.32 (m, 2H), 7.34 – 7.40 (m, 2H), 7.45 (dd, J = 6.7, 0.7 Hz, 2H), 7.63 (d, J = 7.3 Hz, 2H). $^{13}$C NMR (75 MHz, CDCl₃) δ (ppm) 15.3, 24.8, 27.0, 49.7, 65.8, 83.3, 120.1, 124.7, 128.1, 129.2, 139.6, 147.6, 152.7. Carbon adjacent to boron not observed.

$^{11}$B NMR (96 MHz, CDCl₃) δ (ppm) 27.5 (br s). MS (ESI⁺) m/z: 321.5 [M+H]+.
Procedure F for the synthesis of neopentyl glycol alkenylboronates

To a suspension of the desired alkyne (1.0 mmol; 1.0 equiv.) in dry MTBE (1 mL) were added DIPOB (123.2 mg; 1.1 mmol; 1.1 equiv.) and Schwartz reagent (30.9 mg; 12 mol%). The reaction mixture was then heated to 70°C using an oil bath for 4 hours. After cooling to -40°C, dry methanol (121.0 μL; 3.0 mmol; 3.0 equiv.) was added and the mixture was left to stir for 1 hour. The mixture was then concentrated under vacuum. To the solution containing methyl alkenylborate (1.0 equiv., 1 mmol) in Et₂O (1 mL) was added sublimated neopentyl glycol (104.1 mg; 1.0 mmol; 1.0 equiv.) at -40°C. The reaction was stirred for 4 hours, warmed to room temperature and then diluted with Et₂O (10 mL). The organic layer was washed with a 50 g/L CuCl₂ aqueous solution (3 x 10 mL), dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum to afford the pure neopentyl glycol alkenylboronate.

\[ \text{B-2-(E)-(hex-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane [1218988-11-4] (5a)} \]

(5a) was synthesized according to General Procedure F from 1-hexyne [693-02-7] on a 1 mmol scale and obtained as a colorless oil (160.8 mg, 93%).

Formula: C₁₁H₂₁BO₂
Mol. Wt.: 196.10 g.mol⁻¹

\(^1\)H NMR (300 MHz, CDCl₃) δ (ppm) 0.82 – 0.91 (m, 3H), 0.96 (d, J = 2.4 Hz, 6H), 1.23 – 1.46 (m, 4H), 2.13 (td, J = 7.9, 1.4 Hz, 2H), 3.62 (s, 4H), 5.33 (dt, J = 17.8, 1.5 Hz, 1H), 6.53 (dt, J = 17.8, 6.5 Hz, 1H).

\(^{13}\)C NMR (75 MHz, CDCl₃) δ (ppm) 13.9, 21.8, 22.2, 30.6, 31.7, 35.2, 72.0, 151.9. Carbon adjacent to boron not observed.

\(^{11}\)B NMR (96 MHz, CDCl₃) δ (ppm) 27.0 (br s). MS (ESI⁺) m/z: 197.3 [M+H]⁺

IR (NaCl, cm⁻¹) 3420, 2959, 2929, 2868, 1638, 1479, 1416, 1341, 1255, 1144, 1122, 998, 929, 812, 667.

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**B-2-(E)-(styr-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (5d)**

![Structure Image]

(5d) was synthesized according to **General Procedure F** from 1-ethynyl-benzene [536-74-3] on a 1 mmol scale and obtained as a white oil (185.8 mg, 97%).

**Formula:** C_{13}H_{17}BO_{2}

**Mol. Wt.:** 216.09 g.mol^{-1}

**1H NMR (300 MHz, CDCl_{3}) δ (ppm)**

1.01 (s, 6H), 3.71 (s, 4H), 6.13 (dd, J = 18.3, 7.5 Hz, 2H), 7.26 (s, 3H), 7.46 (dd, J = 20.9, 6.4 Hz, 2H).  

**13C NMR (75 MHz, CDCl_{3}) δ (ppm)**

21.9, 31.8, 72.2, 127.0, 128.5, 137.8, 147.1. Carbon adjacent to boron not observed.

**11B NMR (96 MHz, CDCl_{3}) δ (ppm)** 26.4 (br s).

**MS (ESI+) m/z:** 217 [M+H]^+.

**HRMS m/z (ESI, Orbitrap) [M+H]^+** calcd for C_{13}H_{18}^{11}BO_{2} 217.1394; found 217.1394.  

**IR (NaCl, cm^{-1})** 3085, 3027, 2930, 1805, 1724, 1638, 1496, 1378, 1201, 1089, 997, 746, 698.

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**B-2-(E)-(5-chloropent-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (5h)**

![Structure Image]

(5h) was synthesized according to **General Procedure F** from 5-chloro-1-pentyne [14267-92-6] on a 1 mmol scale and obtained as a colorless oil (181.8 mg, 94%).

**Formula:** C_{10}H_{18}^{11}BClO_{2}

**Mol. Wt.:** 216.51 g.mol^{-1}

**1H NMR (300 MHz, CDCl_{3}) δ (ppm)**

0.96 (d, J = 4.6 Hz, 6H), 1.82 – 1.95 (m, 2H), 2.21 – 2.38 (m, 2H), 3.49 – 3.58 (m, 2H), 3.63 (s, 4H), 5.40 (dt, J = 17.8, 1.5 Hz, 1H), 6.49 (dt, J = 17.8, 6.5 Hz, 1H).  

**13C NMR (75 MHz, CDCl_{3}) δ (ppm)**

21.8, 31.2, 31.8, 32.5, 44.4, 72.0, 149.3. Carbon adjacent to boron not observed.

**11B NMR (96 MHz, CDCl_{3}) δ (ppm)** 25.6 (br s).  

**MS (ESI+) m/z:** 217.8 [M+H]^+.  

**HRMS m/z (ESI, TOF) [M+H]^+** calcd for C_{10}H_{19}^{11}BClO_{2} 217.1161; found 217.1161.  

**IR (NaCl, cm^{-1})** 2923, 283, 1460, 1376, 1064, 654.
**B-2-(E)-((cyclohex-1-en-1-yl)vinyl)-5,5-dimethyl-1,3,2-dioxaborinane (5i)**

(5i) was synthesized according to General Procedure F from 1-ethynyl-cyclohexene [931-49-7] on a 1 mmol scale and obtained as a colorless oil (180.5 mg, 88%).

Formula: C₁₃H₂₁BO₂
Mol. Wt.: 220.12 g.mol⁻¹

**¹H NMR (300 MHz, CDCl₃)** δ (ppm) 0.98 (s, 6H), 1.62 (dtt, J = 11.6, 8.6, 5.9 Hz, 4H), 2.14 (s, 4H), 3.65 (s, 4H), 5.35 (d, J = 18.1 Hz, 1H), 5.92 (s, 1H), 6.95 (d, J = 18.1 Hz, 1H).

**¹³C NMR (75 MHz, CDCl₃)** δ (ppm) 21.8, 22.4, 22.5, 23.9, 26.1, 31.8, 72.1, 133.2, 137.1, 150.9. Carbon adjacent to boron not observed.

**¹¹B NMR (96 MHz, CDCl₃)** δ (ppm) 26.5 (br s).

**MS (ESI⁺)** m/z: 221.4 [M+H]⁺. HRMS m/z (ESI, Orbitrap) [M+H]⁺ calcd for C₁₃H₂₂¹¹BO₂ 221.1707; found 221.1707.

**IR (NaCl, cm⁻¹)** 3409, 2978, 2864, 1714, 1634, 1455, 1347, 1146, 983, 851, 674, 578.

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**B-2-(1E)-(1-tert-butyl)dimethylsilyloxy-1-penteny-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (5j)**

(5j) was synthesized according to General Procedure F from (1,1-dimethylethyl)dimethyl(4-pentyn-1-olxy)-silane [61362-77-4] on a 1 mmol scale and obtained as a yellowish oil (300.9 mg, 96%).

Formula: C₁₆H₃₃BO₃Si
Mol. Wt.: 313.5 g.mol⁻¹

**¹H NMR (300 MHz, CDCl₃)** δ (ppm) 0.00 – 0.05 (m, 6H), 0.86 – 0.89 (m, 9H), 0.96 (s, 6H), 1.57 – 1.70 (m, 4H), 2.12 – 2.24 (m, 2H), 3.63 (s, 4H), 5.36 (dt, J = 17.8, 1.5 Hz, 1H), 6.55 (dt, J = 17.8, 6.4 Hz, 1H).

**¹³C NMR (76 MHz, CDCl₃)** δ (ppm) -5.25, 21.8, 25.9, 31.6, 31.7, 31.8, 62.7, 72.0, 151.3. Carbon adjacent to boron not observed.

**¹¹B NMR (96 MHz, CDCl₃)** δ (ppm) 26.0 (br s). **MS (ESI⁺)** m/z: 314.7 [M+H]⁺. HRMS m/z (ESI, Orbitrap) [M+H]⁺ calcd for C₁₆H₃₄¹¹BO₃Si 313.2364; found 313.2367. **IR (NaCl, cm⁻¹)** 2978, 2955, 2932, 2892, 1640, 1471, 1365, 1104, 837, 776.
Supporting information

**B-2-(1E)-(4-phenylbut-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (5k)**

![Structure of 5k](image)

(5k) was synthesized according to General Procedure F from 4-phenyl-1-butene [766-98-3] on a 10 mmol scale and obtained as a colorless oil (2.29 g, 98%).

Formula: C_{15}H_{21}BO_2
Mol. Wt.: 244.14 g.mol\(^{-1}\)

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 0.97 (s, 6H), 2.40 – 2.52 (m, 2H), 2.72 (dt, \(J = 9.7, 6.7\) Hz, 2H), 3.64 (s, 4H), 5.42 (dd, \(J = 17.8, 0.7\) Hz, 1H), 6.62 (dt, \(J = 17.8, 6.3\) Hz, 1H), 7.13 – 7.23 (m, 3H), 7.26 (s, 2H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 21.8, 31.8, 34.8, 37.2, 71.9, 72.0, 125.8, 128.2, 128.3, 128.4, 128.5, 141.9, 150.6. Carbon adjacent to boron not observed.

\(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 26.1 (br s).

MS (ESI+) m/z: 245.3 [M+H]+.
HRMS m/z (ESI, Orbitrap) [M+H]+ calcd for C_{15}H_{22}BO_2 245.1707; found 245.1708.

**B-2-(E)-(5-phthalimido-pent-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (5l)**

![Structure of 5l](image)

(5l) was synthesized according to General Procedure F from 2-(4-pentyn-1-yl)-1H-isindole-1,3(2H)-dione [6097-07-0] on a 1 mmol scale and obtained as a whiteish oil (287.9 mg, 88%).

Formula: C_{18}H_{23}BO_4
Mol. Wt.: 327.19 g.mol\(^{-1}\)

\(^{1}\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 0.92 – 0.97 (m, 6H), 1.72 – 1.89 (m, 2H), 2.20 (dd, \(J = 13.9, 6.9\) Hz, 2H), 3.60 (s, 4H), 3.68 (dd, \(J = 14.0, 6.8\) Hz, 2H), 5.37 (d, \(J = 17.8\) Hz, 1H), 6.51 (dt, \(J = 17.8, 6.3\) Hz, 1H), 7.64 – 7.75 (m, 2H), 7.83 (dd, \(J = 5.4, 3.0\) Hz, 2H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 21.8 24.7, 26.9, 27.0, 33.0, 33.2, 37.7, 39.2, 81.9, 83.0, 123.2, 129.9, 132.1, 133.8, 152.5, 153.0, 168.3. Carbon adjacent to boron not observed.

\(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) (ppm) 25.9 (br s). MS (ESI+) m/z: 328.2 [M+H]+. HRMS m/z (ESI, Orbitrap) [M+H]+ calcd for C_{18}H_{23}BO_4 328.1715; found 328.1716.
Supporting information

*B-2-(E)-(4-bromobut-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (5n)*

(5n) was synthesized according to General Procedure F from 4-bromo-1-butyn-1-yl) on a 1 mmol scale and obtained as a colorless oil (212.3 mg, 98%).

Formula: C₉H₁₆BBrO₂
Mol. Wt.: 246.94 g·mol⁻¹

¹H NMR (300 MHz, CDCl₃) δ (ppm) 0.93 – 0.98 (m, 6H), 2.70 (m, 2H), 3.37 – 3.46 (m, 2H), 3.63 (s, 4H), 5.39 – 5.51 (m, 1H), 6.46 (dt, J = 17.8, 6.4 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 21.8, 31.2, 31.8, 38.6, 72.1, 146.8. Carbon adjacent to boron not observed. ¹¹B NMR (96 MHz, CDCl₃) δ (ppm) 25.6 (br s). MS (ESI⁺) m/z: 248.0 [M+H⁺]. HRMS m/z (ESI, TOF) [M+H⁺] calcld for C₉H₁₇¹¹B⁺BrO₂ 247.0499; found 247.0500. IR (NaCl, cm⁻¹) 2958, 2928, 2857, 1640, 1464, 1362, 1146, 999, 972, 850, 677.

Procedure G for the synthesis of *E* bromoalkenes

To a suspension of the desired alkyne (1.0 equiv.) in dry MTBE (1 mL/mmol) were added DIPOB (1.1 equiv.) [from DIPAB thermolysis] and Schwartz reagent (12 mol%). The reaction mixture was then heated to 70°C using an oil bath for 4h. After cooling to -78°C dry methanol (3.0 equiv.) was added and the mixture was left to stir for 1h. The mixture was then concentrated under vacuum. To a solution of the methyl alkenylborate (1.0 equiv., 1 mmol) in a mixture of THF:H₂O (1:1) (1 mL/mmol) was added CuBr₂ (2.0 equiv.). The reaction was stirred for 16 hours at 70°C. After cooling back to room temperature, the mixture was concentrated under vacuum and purified by column chromatography on silica gel to afford pure *E* bromoalkene. The *E:Z* ratio was then determined based on ¹H NMR.
(E)-1-bromo-1-octene [51751-87-2] (E)-6b

\[ \text{Br} \]

(E)-7b was synthesized according to General Procedure G from 1-octyne [629-05-0] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (74.5 mg, 39%).

Ratio (Z:E) > 1:99
Formula: C\(_8\)H\(_{15}\)Br
Mol. Wt.: 191.11 g.mol\(^{-1}\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm): 0.88 (t, \(J = 6.7\) Hz, 3H), 1.19 – 1.45 (m, 8H), 2.03 (dt, \(J = 7.4, 3.9\) Hz, 2H), 6.01 (dd, \(J = 13.5, 1.1\) Hz, 1H), 6.16 (dd, \(J = 13.8, 6.8\) Hz, 1H).\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 14.0, 22.5, 28.5, 28.6, 31.6, 32.9, 104.0, 138.3. MS (ESI+) m/z: 192.3[M+H]+ IR (NaCl, cm\(^{-1}\)) 2924, 2854, 1460, 1376, 722. Rf (Hexane) 0.35

(E)-2-bromoethenyl-benzene [103-64-0] (E)-6d

\[ \text{Br} \]

(E)-7d was synthesized according to General Procedure G from 1-ethynyl-4-methyl-benzene [536-74-3] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (131.8 mg, 72%).

Ratio (Z:E) > 1:99
Formula: C\(_8\)H\(_7\)Br
Mol. Wt.: 183.05 g.mol\(^{-1}\)

\(^1\)H NMR (300 MHz, C\(_6\)D\(_6\)) \(\delta\) (ppm): 6.34 (d, \(J = 14.0\) Hz, 1H), 6.84 – 6.79 (m, 2H), 6.85 (d, \(J = 14.0\) Hz, 1H), 6.97 (m, 3H). \(^{13}\)C NMR (75 MHz, C\(_6\)D\(_6\)) \(\delta\) (ppm): 106.6, 126.1, 128.0, 128.5, 135.9, 137.1. MS (ESI+) m/z: 184.2[M+H]+ IR (NaCl, cm\(^{-1}\)) 3084, 3027, 2927, 1945, 1620, 1497, 1454, 1217, 935, 758, 699. Rf (Hexane) 0.44

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1-(E)-2-bromoethenyl-4-methyl-benzene [60655-80-3] (E)-6e\textsuperscript{16}

\[
\begin{array}{c}
\text{Br} \\
\text{H} \\
\end{array}
\]

(E)-7e was synthesized according to General Procedure G from 4-ethynyltoluene [766-97-2] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (88.7 mg, 45%).

Ratio (Z:E) > 1:99
Formula: C\textsubscript{9}H\textsubscript{9}Br
Mol. Wt.: 197.08 g.mol\textsuperscript{-1}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm) 2.34 (d, \( J = 8.5 \) Hz, 3H), 6.71 (d, \( J = 14.0 \) Hz, 1H), 7.26 (s, 5H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm) 21.2, 105.4, 126.0, 128.9, 129.5, 133.2, 137.0, 138.2. MS (ESI+) m/z: 198.3[M+H]\textsuperscript{+} · IR (NaCl, cm\textsuperscript{-1}) 2921, 1603, 1509, 1410, 949, 937, 826, 770, 726. Rf (Hexane) 0.33

(1E,9E)-1,10-dibromo-1,9-decadiene [863596-11-6] (E)-6g\textsuperscript{16}

\[
\begin{array}{c}
\text{Br} \\
\text{H} \\
\end{array}
\]

(E)-7g was synthesized according to General Procedure G from 1,9-decadiyne [1720-38-3] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (165.7 mg, 56%).

Ratio (Z:E) = 2:98
Formula: C\textsubscript{10}H\textsubscript{16}Br\textsubscript{2}
Mol. Wt.: 296.05 g.mol\textsuperscript{-1}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm) 1.21 – 1.44 (m, 7H), 1.98 – 2.08 (m, 5H), 6.01 (dt, \( J = 13.5, 1.2 \) Hz, 2H), 6.15 (dd, \( J = 13.8, 6.7 \) Hz, 2H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm) 28.4, 28.6, 32.8, 104.1, 138.1. MS (ESI+) m/z: 297.2[M+H]\textsuperscript{+} · IR (NaCl, cm\textsuperscript{-1}) 2924, 2852, 1461, 1378, 722. Rf (Hexane) 0.38

(E)-1-bromo-5-chloro-1-pentene [95835-52-2] (E)-6h\textsuperscript{17}

\[
\begin{array}{c}
\text{Cl} \\
\text{H} \\
\end{array}
\]

(E)-7h was synthesized according to General Procedure G from 5-chloro-1-pentyne [14267-92-6] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (111.9 mg, 61%).

Ratio (Z:E) = 6:94
Formula: C\textsubscript{5}H\textsubscript{8}BrCl
Mol. Wt.: 183.47 g.mol\textsuperscript{-1}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm) 1.78 – 1.94 (m, 2H), 2.14 – 2.28 (m, 2H), 3.55 (td, \( J = 6.5, 4.3 \) Hz, 2H), 6.04 – 6.18 (m, 2H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) (ppm) 22.3, 29.9, 34.1, 105.7, 136.1. MS (ESI+) m/z: 297.2[M+H]\textsuperscript{+} · IR (NaCl, cm\textsuperscript{-1}) 2924, 2852, 1461, 1378, 722. Rf (Hexane) 0.38

Supporting information

m/z: 184.6[M+H]⁺ IR (NaCl, cm⁻¹) 3345, 2927, 2721, 2476, 1636, 1369, 1082, 803, 722, 649. \( R_f \) (Hexane) 0.50

1-(E)-2-bromoethenyl-cyclohexene [78463-06-6] (E)-6i¹⁸

\( (E)-7i \) was synthesized according to General Procedure G from 1-ethynyl-cyclohexene [931-49-7] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (115.9 mg, 62%).

Ratio \( (Z:E) > 1:99 \)

Formula: \( \text{C}_8\text{H}_{11}\text{Br} \)

Mol. Wt.: 187.08 g.mol⁻¹

\(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) (ppm) 1.51 – 1.78 (m, 4H), 2.01 – 2.14 (m, 4H), 5.76 (s, 1H), 6.14 (t, \( J = 10.5 \) Hz, 1H), 6.69 (d, \( J = 13.8 \) Hz, 1H).

\(^{13}\)C NMR (75 MHz, CDCl₃) \( \delta \) (ppm) 19.4, 22.1, 22.2, 24.1, 25.8, 102.6, 130.8, 139.5, 140.6. MS (ESI⁺) m/z: 188.3[M+H]⁺ IR (NaCl, cm⁻¹) 3421, 1640, 1406, 803, 790. \( R_f \) (Hexane) 0.40

(3E)-4-bromo-3-buten-1-yl-benzene [77208-20-9] (E)-6k¹⁸

\( (E)-7k \) was synthesized according to General Procedure G from 4-phenyl-1-butyne [16520-62-0] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (80.2 mg, 38%).

Ratio \( (Z:E) = 6:94 \)

Formula: \( \text{C}_{10}\text{H}_{11}\text{Br} \)

Mol. Wt.: 211.10 g.mol⁻¹

\(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) (ppm) 2.38 (dd, \( J = 14.9, 7.5 \) Hz, 2H), 2.73 (t, \( J = 7.7 \) Hz, 2H), 6.06 (dd, \( J = 13.5, 1.2 \) Hz, 1H), 6.14 – 6.30 (m, 1H), 7.26 (s, 3H), 7.27 – 7.36 (m, 2H).

\(^{13}\)C NMR (75 MHz, CDCl₃) \( \delta \) (ppm) 31.4, 34.2, 34.7, 35.0, 105.0, 108.4, 126.1, 128.4, 128.5, 133.9, 137.1, 140.9. MS (ESI⁺) m/z: 212.5[M+H]⁺ IR (NaCl, cm⁻¹) 3084, 3063, 3026, 2926, 2855, 1620, 1604, 1496, 1453, 1217, 934, 758, 699, 588. \( R_f \) (Hexane) 0.35

2-(E)-5-bromo-4-penten-1-yl-1H-isooindole-1,3(2H)-dione (E)-6l

(E)-7l was synthesized according to General Procedure G from 2-(4-pentyn-1-yl)-1H-isooindole-1,3(2H)-dione [6097-07-0] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (152.9 mg, 52%).

Ratio (Z:E) = 0:100
Formula: C_{13}H_{12}BrNO_{2}
Mol. Wt.: 294.15 g.mol^{-1}

$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 1.35 (dd, $J$ = 14.3, 7.3 Hz, 2H), 1.51 (dd, $J$ = 14.7, 7.0 Hz, 2H), 3.32 (t, $J$ = 6.9 Hz, 2H), 5.66 (d, $J$ = 13.5 Hz, 1H), 5.82 (dt, $J$ = 13.9, 6.9 Hz, 1H), 6.88 (dd, $J$ = 5.4, 3.0 Hz, 2H), 7.41 – 7.53 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) 27.1, 29.9, 36.8, 105.2, 122.7, 133.3, 136.3. MS (ESI+) m/z: 295.4[M+H]$^+$; HRMS m/z (ESI+, Orbitrap) [M+H]$^+$ calcd for C_{13}H_{13}BrNO$_2$ 294.0124; found 294.0124. IR (NaCl, cm$^{-1}$) 3365, 2977, 2930, 1770, 1713, 1366, 1145, 849, 721. Rf (EtOAc 2%:Hexane) 0.30

(E)-(2-bromo-1-ethenyl)(1,1-dimethylethyl)dimethyl-silane (E)-6m

(E)-7m was synthesized according to General Procedure G from tert-butyldimethylsilyl-acetylene [86318-61-8] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (90.7 mg, 41%).

Ratio (Z:E) = 5:95
Formula: C$_8$H$_{17}$BrSi
Mol. Wt.: 221.21 g.mol$^{-1}$

$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) 0.00 – 0.08 (m, 6H), 0.83 – 0.93 (m, 9H), 6.51 (d, $J$ = 6.8 Hz, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ (ppm) -6.21,16.6, 26.7, 29.7, 131.5, 136.5, 148.1. MS (ESI+) m/z: 222.5[M+H]$^+$; IR (NaCl, cm$^{-1}$) 2954, 2926, 2855, 1464, 1251, 833, 774. MS (ESI+) m/z: unstable on heating. Rf (EtOAc 5%/Hexane) 0.38
Procedure H for the synthesis of Z bromoalkenes

To a suspension of the desired alkyne (1.0 equiv.) in dry MTBE (1 mL/mmol) were added DIPOB (1.1 equiv.), Schwartz (12 mol%), MTBE, 70°C, 4h.

1. DIPOB (1.1 equiv.),
2. MeOH (3.0 equiv.), -78°C, 1h
3. Br₂ (1.1 equiv.), MTBE 0°C, 1h
4. MeONa (2.2 equiv.) 0°C, 2h

The reaction mixture was then heated to 70°C using an oil bath for 4h. After cooling to -78°C dry methanol (3.0 equiv.) was added and the mixture was left to stir for 1h. The mixture was then concentrated under vacuum. To a solution of the methyl alkenylborate (1.0 equiv., 1 mmol) in MTBE (1 mL/mmol) was added a solution of Br₂ (1.1 equiv.) in MTBE. The reaction was stirred for 1 hour at 0°C. In parallel MeONa was freshly prepared from methanol and sodium (2.2 equiv.) and finally added to the previous mixture. After 2h at 0°C the solution was warmed to room temperature, concentrated under vacuum and purified by column chromatography on silica gel to afford pure Z bromoalkene. The Z:E ratio was then determined based on ¹H NMR.

(Z)-1-bromo-1-octene [42843-49-2] (Z)-6b

(Z)-7b was synthesized according to General Procedure H from 1-octyne [629-05-0] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (149.0 mg, 78%).

Ratio (Z:E) > 99:1
Formula: C₈H₁₅Br
Mol. Wt.: 191.11 g.mol⁻¹

¹H NMR (300 MHz, C₆D₆) δ (ppm) 0.86 (t, J = 6.9 Hz, 3H), 1.12 – 1.26 (m, 7H), 2.01 – 2.14 (m, 3H), 5.60 – 5.76 (m, 1H), 5.85 (dt, J = 6.9, 1.4 Hz, 1H). ¹³C NMR (75 MHz, C₆D₆) δ (ppm) 14.0, 22.6, 28.1, 28.8, 29.7, 31.6, 107.5, 134.8. MS (ESI⁺) m/z: 192.3[M+H]⁺ IR (NaCl, cm⁻¹) 3374, 2924, 2848, 2472, 1709, 1376, 990, 830. Rf (Hexane) 0.35
Supporting information

(Z)-2-bromoethenyl]-benzene [588-73-8] (Z)-6d<sup>19</sup>

(Z)-7d was synthesized according to General Procedure H from 1-ethynyl-4-methyl-benzene [536-74-3] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (137.3 mg, 75%).

Ratio (Z:E) = 70:30
Formula: C<sub>8</sub>H<sub>7</sub>Br
Mol. Wt.: 183.05 g.mol⁻¹

**<sup>1</sup>H NMR (300 MHz, CDCl₃) δ (ppm) 6.44 (d, J = 8.1 Hz, 1H), 6.72 – 6.83 (m, 1H), 7.08 (d, J = 7.7 Hz, 1H), 7.28 – 7.46 (m, 2H), 7.47 – 7.57 (m, 1H), 7.69 (dt, J = 3.5, 2.2 Hz, 1H).**

**<sup>13</sup>C NMR (75 MHz, CDCl₃) δ (ppm) 103.0, 106.4, 121.3, 128.3, 128.8, 129.00, 129.4, 132.3.**

**MS (ESI+) m/z: 184.2[M+H]⁺**

**IR (NaCl, cm⁻¹) 3084, 3063, 3026, 2926, 2855, 1945, 1604, 1217, 935, 758, 699.**

**Rf (Hexane) 0.33**

1-(Z)-2-bromoethenyl-4-methyl-benzene [73839-44-8] and 1-(E)-2-bromoethenyl-4-methyl-benzene (50:50) [60655-80-3] (Z)-6e<sup>19</sup>

(Z)-7e was synthesized according to General Procedure H from 1-ethynyl-4-methyl-benzene [766-97-2] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (155.7 mg, 79%).

Ratio (Z:E) = 50:50
Formula: C<sub>9</sub>H<sub>9</sub>Br
Mol. Wt.: 197.08 g.mol⁻¹

**<sup>1</sup>H NMR [E] (300 MHz, C₆D₆) δ (ppm) 2.03 (s, 3H), 5.96 (d, J = 8.1 Hz, 1H), 6.60 (d, J = 8.1 Hz, 1H), 6.74 (d, J = 7.8 Hz, 2H), 7.33 (dd, J = 22.9, 8.1 Hz, 2H).**

**<sup>1</sup>H NMR [Z] (300 MHz, C₆D₆) δ (ppm) 2.02 (s, 3H), 6.31 – 6.39 (d, J = 14.0 Hz, 1H), 6.89 (d, J = 14.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 2H), 7.38 (s, 1H), 7.54 (d, J = 8.1 Hz, 1H).**

**<sup>13</sup>C NMR (75 MHz, C₆D₆) δ (ppm) 20.8, 20.9, 102.6, 105.1, 105.6, 116.6, 121.8, 126.1, 128.8, 128.9, 129.0, 129.1, 129.3, 132.1, 133.2, 133.7, 137.0, 137.8, 138.0.**

**MS (ESI+) m/z: 198.3[M+H]⁺**

**IR (NaCl, cm⁻¹) 3079, 3026, 2922, 2854, 1907, 1692, 1607, 1509, 1450, 1226, 1205, 1160, 948, 932, 876, 820, 769, 688.**

**Rf (Hexane) 0.33 (E), 0.38 (Z)**

(1Z,9Z)-1,10-dibromo-1,9-decadiene [863596-11-6] (Z)-6g

(Z)-7g was synthesized according to General Procedure H from 1,9-decadiyne [1720-38-3] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (248.7 mg, 84%).

Ratio (Z:E) = 96:4
Formula: C10H16Br2
Mol. Wt.: 296.05 g.mol⁻¹

¹H NMR (300 MHz, CDCl₃) δ (ppm) 1.30 – 1.48 (m, 8H), 2.19 (dt, J = 7.5, 3.6 Hz, 4H), 6.04 – 6.18 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 28.0, 28.8, 29.6, 107.6, 114.2, 134.9. MS (ESI⁺) m/z: 297.2[M+H⁺]⁺ IR (NaCl, cm⁻¹) 2922, 2850, 1454, 1372, 730. Rf (Hexane) 0.38

(Z)-1-bromo-5-chloro-1-pentene [88357-37-3] (Z)-6h

(Z)-7h was synthesized according to General Procedure H from 5-chloro-1-pentyne [14267-92-6] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (143.1 mg, 78%).

Ratio (Z:E) = 99:1
Formula: C₅H₈Br
Mol. Wt.: 183.47 g.mol⁻¹

¹H NMR (300 MHz, C₆D₆) δ (ppm) 1.34 (dq, J = 13.2, 6.6 Hz, 2H), 2.00 (ddd, J = 14.8, 7.4, 1.4 Hz, 2H), 2.96 (t, J = 6.7 Hz, 2H), 5.40 (q, J = 7.0 Hz, 1H), 5.77 (dt, J = 7.0, 1.4 Hz, 1H). ¹³C NMR (75 MHz, C₆D₆) δ (ppm) 26.9, 30.8, 43.6, 108.7, 132.8. MS (ESI⁺) m/z: 184.6[M+H⁺]⁺ IR (NaCl, cm⁻¹) 3345, 2927, 2853, 2721, 2476, 1636, 1369, 1082, 803, 722, 649. Rf (Hexane) 0.48

1-(E)-2-bromoethenyl-cyclohexene [218902-69-3] (Z)-6

\[ \text{CH}_2=\text{CHBr} \]

(Z)-7i was synthesized according to General Procedure H from 1-ethynyl-cyclohexene [931-49-7] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (164.6 mg, 88%).

Ratio \((Z:E) = 53:47\)

Formula: \(\text{C}_8\text{H}_{11}\text{Br}\)

Mol. Wt.: 187.08 g.mol\(^{-1}\)

\(^1\text{H} \text{NMR}\) (E) (300 MHz, \(\text{C}_6\text{D}_6\)) \(\delta\) (ppm) 1.51 – 1.78 (m, 4H), 2.01 – 2.14 (m, 4H), 5.76 (s, 1H), 6.14 (t, \(J = 10.5\) Hz, 1H), 6.69 (d, \(J = 13.8\) Hz, 1H).

\(^1\text{H} \text{NMR}\) (Z) (300 MHz, \(\text{C}_6\text{D}_6\)) \(\delta\) (ppm) 1.67 (dd, \(J = 3.4, 2.6\) Hz, 2H), 1.75 (d, \(J = 2.6\) Hz, 2H), 1.78 – 1.90 (m, 2H), 2.39 (dd, \(J = 8.3, 6.2\) Hz, 2H), 5.82 (s, 1H), 5.91 (dd, \(J = 13.8, 0.7\) Hz, 1H).

\(^{13}\text{C} \text{NMR}\) (75 MHz, \(\text{C}_6\text{D}_6\)) \(\delta\) (ppm) 22.0, 22.4, 23.8, 25.6, 28.0, 101.4, 129.0, 134.6.

MS (ESI+) \(m/z\): 188.3\([\text{M}+\text{H}]^+\)

IR (NaCl, cm\(^{-1}\)) 3421, 3409, 2978, 1714, 1640, 1454, 1406, 1372, 851, 803, 790.

Rf (Hexane) 0.40; 0.38

(Z)-4-bromo-3-buten-1-yl-benzene [77150-85-7] (Z)-6

(Z)-7k was synthesized according to General Procedure H from 4-phenyl-1-butyne [16520-62-0] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (156.2 mg, 74%).

Ratio \((Z:E) = 99:1\)

Formula: \(\text{C}_{10}\text{H}_{11}\text{Br}\)

Mol. Wt.: 211.10 g.mol\(^{-1}\)

\(^1\text{H} \text{NMR}\) (300 MHz, \(\text{C}_6\text{D}_6\)) \(\delta\) (ppm) 2.30 – 2.48 (m, 4H), 5.57 – 5.69 (m, 1H), 5.80 (dt, \(J = 7.0, 1.3\) Hz, 1H), 6.93 – 7.14 (m, 5H).

\(^{13}\text{C} \text{NMR}\) (75 MHz, \(\text{C}_6\text{D}_6\)) \(\delta\) (ppm) 31.3, 34.1, 108.1, 126.1, 128.4, 133.7, 141.0.

MS (ESI+) \(m/z\): 212.5\([\text{M}+\text{H}]^+\)

IR (NaCl, cm\(^{-1}\)) 3080, 3013, 2943, 2830, 1637, 1473, 1212, 922, 733, 622.

Rf (Hexane) 0.38

(Z)-(2-bromo-1-ethenyl)(1,1-dimethylethyl)dimethyl-silane (Z)-6m

(Z)-7m was synthesized according to General Procedure H from tert-butylidemethylsilyl-acetylene [86318-61-8] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (101.7 mg, 46%).

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Ratio (Z:E) = 99:1
Formula: C₈H₁₇BrSi
Mol. Wt.: 221.21 g.mol⁻¹

¹H NMR (300 MHz, C₆D₆) δ (ppm) 0.20 (s, 6H), 0.86 (s, 9H), 6.12 (d, J = 9.3 Hz, 1H), 6.68 (d, J = 9.3 Hz, 1H). ¹³C NMR (75 MHz, C₆D₆) δ (ppm) -5.37, 26.1, 123.1, 132.3. MS (ESI⁺) m/z: 222.5[M+H]⁺ IR (NaCl, cm⁻¹) 2954, 2926, 2855, 1464, 1252, 833, 775. MS (ESI⁺) m/z: unstable on heating. Rf (EtOAc 5%/Hexane) 0.41

(Z)-(4-bromobut-1-en-1-yl) (Z)-6n

(Z)-7n was synthesized according to General Procedure H from 4-bromobut-1-yne [86318-61-8] on a 1 mmol scale and obtained as a yellow oil after column chromatography [eluent: hexane] (141.2 mg, 66%).

Ratio (Z:E) = 94:6
Formula: C₄H₆Br₂
Mol. Wt.: 213.90 g.mol⁻¹

¹H NMR (300 MHz, C₆D₆) δ (ppm) 2.30 (qd, J = 6.8, 1.5 Hz, 2H), 2.75 (t, J = 6.7 Hz, 2H), 5.54 (q, J = 6.8 Hz, 1H), 5.78 (dt, J = 7.0, 1.5 Hz, 1H). ¹³C NMR (75 MHz, C₆D₆) δ (ppm) 29.9, 32.6, 109.7, 131.4. MS (ESI⁺) m/z: unstable on heating. IR (NaCl, cm⁻¹) 2932, 2817, 1512, 1462, 1318, 991, 951, 853. Rf (EtOAc 5%/Hexane) 0.41.
4. NMR spectra

Compound (2a) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (2a) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (2b) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (2b) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (2c) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (2c) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (2d) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (2d) $^{11}\text{B}$ NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (2e) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (2e) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (2f) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (2f) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (3a) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (3a) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

Compound (3a) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (3b) \(^1\)H NMR in CDCl\(_3\) at 25°C (300 MHz)
Supporting information

**Compound (3b) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)**

![Compound (3b) $^{13}$C NMR spectrum in CDCl$_3$ at 25°C (75 MHz)]
Supporting information

Compound (3b) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (3d) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (3d) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)

[Chemical structure diagram]
Supporting information

Compound (3d) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (3e) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

**Compound (3e) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)**

![Compound (3e) $^{13}$C NMR spectrum](image)
Supporting information

Compound (3e) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (3f) $^1$H NMR in CDCl$_3$ at 25°C (400 MHz)
Supporting information

**Compound (3f) $^{13}$C NMR in CDCl$_3$ at 25°C (100 MHz)**
Supporting information

**Compound (3f) \(^{11}\text{B} \)** NMR in CDCl\(_3\) at 25°C (128 MHz)
Supporting information

Compound (3f) $^{19}$F NMR in CDCl$_3$ at 25°C (376 MHz)
Supporting information

 Compound (3g) $^1$H NMR in CDCl$_3$ at 25°C (400 MHz)
Compound (3g) $^{13}$C NMR in CDCl$_3$ at 25°C (100 MHz)
Supporting information

Compound (3g) $^{11}$B NMR in CDCl$_3$ at 25°C (128 MHz)
Compound (3h) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (3h) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (3h) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (3i) \(^1\text{H NMR in CDCl}_3\) at 25°C (300 MHz)
Compound (3i) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

**Compound (3i) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)**
Compound (3j) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)

[Chemical structure image]
Supporting information

Compound (3j) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

**Compound (3j) \(^{11}\)B NMR in CDCl\(_3\) at 25°C (96 MHz)**

![NMR Spectrum]

**Image Description:**
- The spectrum shows a peak at a specific ppm value, indicating the chemical shift of the compound.
- The structure of compound (3j) is also shown, highlighting the chemical bonds and functional groups.

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74
Compound (3k) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (3k) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (3k) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (3I) $^1$H NMR in CDCl$_3$ at 25°C (400 MHz)
Supporting information

Compound (3I) $^{13}$C NMR in CDCl$_3$ at 25°C (100 MHz)
Supporting information

Compound (3l) $^{11}$B NMR in CDCl$_3$ at 25°C (128 MHz)
Compound (4a) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

**Compound (4a) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)**
Supporting information

Compound (4a) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (4b) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (4b) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (4b) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (4c) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (4c) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

Compound (4c) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (4d) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (4d) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (4d) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (4h) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (4h) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (4h) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

**Compound (4i) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)**
Supporting information

Compound (4i) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

**Compound (4i) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)**
Supporting information

Compound (4j) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

**Compound (4j) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)**

![NMR Spectrum](image)
Supporting information

Compound (4) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (4k) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (4k) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (4k) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (4I) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (4l) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (4) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (4m) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)

![NMR spectrum diagram](image)
Supporting information

**Compound (4m) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)**
Compound (4m) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (4n) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (4n) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (4n) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (4o) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (4o) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (4o) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (4p) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (4p) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (4p) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (5a) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (5a) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (5a) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (5d) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (5d) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (5d) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

**Compound (5h) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)**
Supporting information

Compound (5h) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

Compound (5h) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (5i) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (5i) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

Compound (5i) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Supporting information

Compound (5j) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (5) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

**Compound (5j) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)**
Compound (5k) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

**Compound (5k) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)**
Supporting information

Compound (5k) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (5i) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (5l) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (5l) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound (5n) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound (5n) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (5n) $^{11}$B NMR in CDCl$_3$ at 25°C (96 MHz)
Compound ((E)-6b) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound ([E]-6b) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

**Compound ((E)-6d) $^1$H NMR in C$_6$D$_6$ at 25°C (300 MHz)**

![NMR Spectrogram]

**Chemical Shifts:**
- 1.02 ppm
- 2.01 ppm
- 1.09 ppm
- 1.13 ppm

**Resonance Peaks:**
- Peaks at 1.02, 2.01, 1.09, and 1.13 ppm.
Supporting information

Compound ((E)-6d) $^{13}$C NMR in C$_6$D$_6$ at 25°C (75 MHz)
Compound (E)-6e $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound ((E)-6e) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

Compound ((E)-6g) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound \((E)-6g\) \(^{13}\text{C}\) NMR in \(\text{CDCl}_3\) at 25°C (75 MHz)
Compound (E)-6h $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound [(E)-6h] $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound ((E)-6i) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound [(E)-6i] $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

Compound ((E)-6k) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Compound \((E)-6k\) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Supporting information

Compound ([E]-6l) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

**Compound (\((E)-6\))^{13}C NMR in CDCl$_3$ at 25°C (75 MHz)**
Supporting information

Compound ((E)-6m) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (\((E)-6\)m) \(^{13}\)C NMR in CDCl\(_3\) at 25°C (75 MHz)
Compound (\((Z)-6b\)) \(^1\)H NMR in C\(_6\)D\(_6\) at 25°C (300 MHz)
Compound ((Z)-6b) $^{13}$C NMR in C$_6$D$_6$ at 25°C (75 MHz)
Supporting information

Compound ((Z)-6d) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound \((Z)-6d\) $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound (\((Z)-6e\)) $^1$H NMR in C$_6$D$_6$ at 25°C (300 MHz)
Supporting information

Compound ((Z)-6e) $^{13}$C NMR in C$_6$D$_6$ at 25°C (75 MHz)
Compound ((Z)-6g) $^1$H NMR in CDCl$_3$ at 25°C (300 MHz)
Supporting information

Compound (Z)-6g $^{13}$C NMR in CDCl$_3$ at 25°C (75 MHz)
Compound ((Z)-6h) $^1$H NMR in C$_6$D$_6$ at 25°C (300 MHz)
Supporting information

Compound \((Z\text{-}6h)\) $^{13}$C NMR in C$_6$D$_6$ at 25°C (75 MHz)
Compound (Z-6i) \(^1\)H NMR in C\(_6\)D\(_6\) at 25°C (300 MHz)
Compound ((Z)-6i) $^{13}$C NMR in C$_6$D$_6$ at 25°C (75 MHz)
Supporting information

Compound ( (Z)-6k ) $^1$H NMR in C$_6$D$_6$ at 25°C (300 MHz)
Supporting information

Compound ((Z)-6k) $^{13}$C NMR in C$_6$D$_6$ at 25°C (75 MHz)
Supporting information

**Compound ((Z)-6m) $^1$H NMR in C$_6$D$_6$ at 25°C (300 MHz)**
Supporting information

Compound (Z)-6m $^{13}$C NMR in C$_6$D$_6$ at 25°C (75 MHz)
Compound ([Z]-6n) $^1$H NMR in C$_6$D$_6$ at 25°C (300 MHz)
Supporting information

Compound ((Z)-6n) $^{13}$C NMR in C$_6$D$_6$ at 25°C (75 MHz)

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