Supporting Information

Synthesis of Functionalized Cyclic Boronates

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Table of Contents

General	SI-2
Experimental Procedures	SI-3
General Alkylation Procedure	SI-3
Ring Closing Metathesis Procedure 1	SI-10
Ring Closing Metathesis Procedure 2	SI-11
Intermolecular Cross Metathesis Procedure 1	SI-16
Intermolecular Cross Metathesis Procedure 2	SI-18
Conversion of 2c to vinyl ether	SI-19
Alkylation of 5	SI-20
Intramolecular (4 + 3) cycloaddition of 7	SI-21
LAH Reduction of 8	SI-22
Crystallographic Data	SI-23
Copies of NMR Spectra	SI-24

General

All glassware and needles were oven-dried and allowed to cool in a desiccator prior to use. Tetrahydrofuran (THF), diethyl ether and toluene were purchased from Fisher Scientific and distilled from sodium-benzophenone prior to use. Dichloromethane, diisopropylamine, triethylamine and methanol were distilled over calcium hydride prior to use. *n*Butyl lithium (nBuLi) was purchased from Aldrich and titrated with freshly recrystallized diphenylacetic acid prior to use. 2-isopropenylboronic acid pinacol ester was used as received from Frontier Scientific. All products were purified by flash chromatography using 230-400 mesh silica purchased from Aldrich and, if crystalline, were recrystallized from hexane-diethyl ether until a constant melting point was observed. All compounds were characterized by ¹H, and ¹³C Nuclear Magnetic Resonance (NMR) spectroscopy using a 500 MHz Bruker instrument. Proton spectra were reported in δ units, parts per million (ppm), relative to trimethylsilane internal standard (0.00 ppm). Carbon spectra were recorded in ppm relative to deuterated chloroform peak (77.16 ppm) or (39.52 ppm) where DMSO was used. Samples were further characterized using mass spectroscopy on a Bruker Apex-Qe instrument. Infrared spectra were recorded on a Thermo Nicolet NEXUS 670 FT-IR instrument.

Experimental Procedures

General Alkylation Procedure

To a solution of diisopropylamine (120 μ L , 0.84 mmol) in THF (4.0mL) was added *n*BuLi (2.04 M in THF, 380 μ L, 0.77mmol) at -78 °C and stirred for one hour. To the stirring solution of LDA was added **3** (200 mg, 0.648 mmol) in 2.0 mL THF and stirred for an additional hour before addition of iodide (0.712 mmol). After dropwise addition of the iodide, the reaction was removed from cold bath and allowed to warm to room temperature over 3 h. The reaction was quenched with a saturated solution of ammonium chloride and the mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated in *vacuo*. The residue was absorbed onto silica and purified via flash chromatography (20% EtOAc in Hexanes) affording the corresponding mono-alkylated product.



4,4,5,5-tetramethyl-2-(6-methyl-3-(phenylsulfonyl)hepta-1,6-dien-2-yl)-1,3,2-dioxaborolane (**1d**): ¹H NMR (500 MHz, CDCl₃) δ7.80 (d, *J* = 8 Hz, 2H), 7.59 (t, *J* = 7 Hz, 1H), 7.49 (t, *J* = 7 Hz, 2H), 6.15 (d, *J* = 2 Hz, 1H), 5.88 (s, 1H), 4.72 (s, 1H), 4.64 (s, 1H), 3.90 (dd, *J* = 3.5 Hz, *J* = 11.5 Hz, 1H), 2.37 – 2.31 (m, 1H), 2.18 – 2.10 (m, 1H), 2.08 – 2.03 (m, 1H), 1.97 – 1.91 (m, 1H), 1.68 (s, 3H), 1.14 (s, 6H), 1.13 (s, 6H)); ¹³C NMR (500 MHz, CDCl₃) δ 144.1, 138.3, 136.7, 133.3, 129.7, 128.7,111.4, 83.9, 67.6, 34.7, 24.9, 24.8, 24.6, 22.1; IR (film) $v_{max} = 3021$, 2979, 2930, 1447, 1423, 1305, 1216, 1145, 1085 cm⁻¹; HRMS calcd for (C₂₀H₂₉BO₄S)Na+ 399.1771; Found: 399.1766.



4,4,5,5-tetramethyl-2-(7-methyl-3-(phenylsulfonyl)octa-1,7-dien-2-yl)-1,3,2-dioxaborolane (**1e**): ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, J = 8 Hz, 2H), 7.58 (t, J = 7 Hz, 1H), 7.49 (t, J = 7 Hz, 2H), 6.14 (d, J = 2 Hz, 1H), 5.90 (s, 1H), 4.68 (s, 1H), 4.63 (s, 1H), 3.93 (dd, J = 12 Hz, J = 4 Hz, 1H), 2.18 – 2.12 (m, 1H), 2.05 – 1.93 (m, 3H), 1.66 (s, 3H), 1.52 – 1.44 (m, 1H), 1.41 – 1.32 (m, 1H), 1.14 (s, 12H); ¹³C NMR (500 MHz, CDCl₃) δ 145.2, 138.5, 136.6, 133.3, 129.8, 128.7, 110.5, 84.0, 67.8, 37.4, 26.6, 24.8, 24.8, 24.7, 22.4; IR (film) v_{max} = 3071, 2977, 2935, 1647, 1447, 1423, 1305, 1144, 1086 cm⁻¹; HRMS calcd for (C₂₁H₃₁BO₄S)Na+ 413.1928; Found: 413.1926.



4,4,5,5-tetramethyl-2-(6-methyl-3-(phenylsulfonyl)octa-1,7-dien-2-yl)-1,3,2-dioxaborolane (1f): ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, J = 7.5 Hz, 4H), 7.58 (t, J = 7.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 4H), 6.13 (dd, J = 2.5 Hz, 1.5 Hz, 2H), 5.87 (d, J = 1.5 Hz, 2H), 5.68 – 5.56 (m, 1H), 3.88 (td, J = 11 Hz, J = 3.5 Hz, 2H), 2.22 – 2.07 (m, 2H), 2.03 – 1.93 (m, 1H), 1.32 – 1.22 (m, 2H), 1.15(s, 6H), 1.14 (s, 6H), 0.96 (dd, J = 7 Hz, J = 3 Hz, 6H); ¹³C NMR (500 MHz, CDCl₃) δ 144.1, 143.7, 138.5, 138.4, 136.5, 136.5, 133.3, 129.7, 129.7, 128.7, 113.5, 113.1, 84.0, 68.2, 68.0, 37.7, 37.6, 33.6, 33.5, 24.8, 24.8, 24.7, 24.7, 20.5, 19.7; IR (film) v_{max} = 2976, 1447, 1422, 1380, 1372, 1305, 1143, 1084 cm⁻¹; HRMS calcd for (C₂₁H₃₁BO₄S)Na+ 413.1928; Found: 413.1927.



4,4,5,5-tetramethyl-2-(6-phenyl-3-(phenylsulfonyl)octa-1,7-dien-2-yl)-1,3,2-dioxaborolane (**1g**): d.r. $(1.00 : 0.36)^{1}$ H NMR (500 MHz, CDCl₃) δ 7.75 (d, J = 8 Hz, 4H), 7.56 (t, J = 7.5 Hz, 2H), 7.46 (t, J = 7.5 Hz, 4H), 7.30 – 7.25 (m, 4H), 7.17 (t, J = 7 Hz, 2H), 7.12 (t, J = 7.5 Hz, 4H), 6.13 (d, J = 2 Hz, 1H), 6.09 (d, J = 2 Hz, 1H), 5.93 – 5.83(m, 2H), 5.83 (s, 1H), 5.75 (s, 1H), 5.04 – 4.97 (m, 4H), 3.92 (dd, J = 12 Hz, J = 3.5 Hz, 1H), 3.90 (dd, J = 10.5 Hz, J = 5.5 Hz, 1H), 3.21 (q, J = 7.5 Hz, 2H), 2.18 – 2.06 (m, 2H), 1.91 – 1.83 (m, 2H), 1.76 – 1.61 (m, 4H), 1.15 – 1.14 (m, 24H); ¹³C NMR (500 MHz, CDCl₃) δ 144.1, 143.5, 141.8, 141.2, 138.3, 138.3, 136.6, 136.5, 133.3, 129.7, 129.6, 128.7, 128.6, 127.6, 127.5, 126.5, 126.4, 115.0, 114.5, 84.0, 67.9,49.7, 49.6, 32.5, 32.5, 25.2, 25.1, 24.8, 24.8, 24.7; IR (film) v_{max} = 3062, 3026, 2937, 1634, 1601, 1492, 1447, 1307, 1208, 1178, 1146, 1084, 1025 cm⁻¹; HRMS calcd for (C₂₆H₃₃BO₄S)Na+ 475.2085; Found: 475.2084.



2-(6,6-dimethyl-3-(phenylsulfonyl)octa-1,7-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (1h): ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 6.09 (d, *J* = 2.5 Hz, 1H), 5.80 (s, 1H), 5.69 (dd, *J* = 17.5 Hz, *J* = 11 Hz, 1H), 4.92 – 4.91 (m, 1H), 4.88 (dd, *J* = 10 Hz, *J* = 1.5 Hz, 1H), 3.80 (dd, *J* = 12 Hz, *J* = 3 Hz, 1H), 2.17 – 2.10 (m, 1H), 1.98 – 1.90 (m, 1H), 1.30 – 1.24 (m, 1H), 1.21 – 1.17 (m, 1H), 1.16 (s, 6H), 1.15 (s, 6H), 0.97 (s, 6H);¹³C NMR (500 MHz, CDCl₃) δ 147.7, 138.4, 136.4, 133.3, 129.7, 128.7, 111.1, 84.0, 69.0, 39.6, 36.7, 26.7, 26.7, 24.9, 24.7, 22.2; IR (film) v_{max} = 2973, 2930, 1447, 1423, 1305, 1216, 1145, 1085 cm⁻¹; HRMS calcd for (C₂₂H₃₃BO₄S)Na+427.2084; Found: 427.2084.



4,4,5,5-tetramethyl-2-(3-(phenylsulfonyl)-4-(2-vinylphenyl)but-1-en-2-yl)-1,3,2dioxaborolane (1i):¹H NMR (500 MHz, CDCl₃) δ 7.84 (d, *J* = 8 Hz, 2H), 7.58 (t, *J* = 8 Hz, 1H), 7.50 (t, *J* = 8 Hz, 2H), 7.40 (t, *J* = 8 Hz, 1H), 7.14 (t, *J* = 7 Hz, 1H), 7.11 – 7.06 (m, 2H), 6.92 (dd, *J* = 17.5 Hz, *J* = 11 Hz, 1H), 6.03 (d, *J* = 2 Hz, 1H), 5.92 (s, 1H), 5.59 (dd, *J* = 17.5 Hz, *J* = 1.5 Hz, 1H), 5.30 (dd, *J* = 11 Hz, *J* = 1 Hz, 1H), 4.19 (dd, *J* = 11.5 Hz, *J* = 3 Hz, 1H), 3.72 (dd, *J* = 14 Hz, *J* = 3 Hz, 1H), 3.32 (dd, *J* = 14 Hz, *J* = 12 Hz, 1H), 1.08 (s, 6H), 1.04 (s, 6H);¹³C NMR (500 MHz, CDCl₃) δ 138.6, 137.3, 137.2, 134.6, 134.4, 133.4, 130.7, 129.5, 128.8, 127.6, 127.0, 126.2, 116.5, 83.9, 68.1, 30.7, 24.8, 24.5; IR (film) v_{max} = 3066, 2978, 2932, 1481, 1447, 1424, 1390, 1372, 1306, 1215, 1145, 1085 cm⁻¹; HRMS calcd for (C₂₄H₂₉BO₄S)Na+ 447.1772; Found: 447.1766.



4,4,5,5-tetramethyl-2-(3-(phenylsulfonyl)-5-(2-vinylphenyl)pent-1-en-2-yl)-1,3,2dioxaborolane (1j):¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 8 Hz, 2H), 7.58 (t, *J* = 8 Hz, 1H),

7.49 – 7.45 (m, 3H), 7.21 – 7.15 (m, 2H), 7.10 – 7.08 (m, 1H), 6.89 (dd, J = 17 Hz, J = 11 Hz, 1H), 6.18 (d, J = 2 Hz, 1H), 5.89 (s, 1H), 5.60 (dd, J = 17 Hz, J = 2 Hz, 1H), 5.25 (dd, J = 11 Hz, J = 1 Hz, 1H), 3.94 (dd, J = 11 Hz, J = 3.5 Hz, 1H), 2.74 (ddd, J = 15 Hz, J = 11 Hz, J = 3 Hz, 1H), 2.56 (ddd, J = 13.5 Hz, J = 11 Hz, J = 6 Hz, 1H), 2.43 – 2.36 (m, 1H), 2.30 – 2.22 (m, 1H), 1.19 (s, 6H), 1.18 (s, 6H);¹³C NMR (500 MHz, CDCl₃) δ 138.3, 138.2, 136.7, 136.6, 134.4, 133.4, 129.7, 129.7, 128.7, 127.9, 126.8, 126.0, 116.0, 84.1, 68.3, 30.6, 28.2, 24.9, 24.7; IR (film) $v_{max} = 2977$, 1461, 1446, 1422, 1372, 1305, 1144 cm⁻¹; HRMS calcd for (C₂₄H₂₉BO₄S)Na+ 461.1928; Found: 461.1921.



N-allyl-4-methyl-N-(3-(phenylsulfonyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)benzenesulfonamide (1k):¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, 8 Hz, 2H), 7.65 (d, J = 8 Hz, 2H), 7.61 (t, J = 8 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 8 Hz, 2H), 6.12 (s, 1H), 5.79 (s, 1H), 5.56 (dddd, J = 16.5 Hz J = 10 Hz, J = 6.5 Hz, J = 6.5 Hz, 1H), 5.17 (d, J = 17 Hz, 1H), 5.12 (d, J = 10 Hz, 1H), 3.94 (dd, J = 10.5 Hz, J = 3.5 Hz, 1H), 3.77 (d, J = 6 Hz, 2H), 3.23 (ddd, J = 15 Hz, J = 8 Hz, J = 8 Hz, 1H), 3.12 (ddd, J = 13.5 Hz, J = 8.5 Hz, J = 4.5 Hz, 1H), 2.42 (s, 4H), 2.20 – 2.13 (m, 1H), 1.17 (s, 12H);¹³C NMR (500 MHz, CDCl₃) δ 143.5, 137.8, 137.0, 136.7, 133.6, 132.9, 129.9, 129.8, 128.8, 127.3, 119.4, 84.2, 65.8, 50.7, 44.8, 25.7, 24.9, 24.8, 21.7; IR (film) v_{max} = 3067, 3021, 2979, 2930, 2872, 1598, 1495, 1447, 1423, 1305, 1216, 1145, 1085, 1320, 998 cm⁻¹; HRMS calcd for (C₂₇H₃₆BNO₆S₂)Na+ 568.1969; Found: 568.1967.



2-(5-(allyloxy)-3-(phenylsulfonyl)pent-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11**): ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8 Hz, 2H), 7.59 (t, *J* = 6.5 Hz, 1H), 7.49 (t, *J* = 8 Hz, 2H), 6.12 (d, *J* = 2 Hz, 1H), 5.87 – 5.80 (m, 2H), 5.84 (s, 1H), 5.22 (dq, *J* = 17 Hz, *J* = 1Hz, 1H), 5.12 (dq, *J* = 10.5 Hz, *J* = 1.5 Hz, 1H), 4.12 (dd, *J* = 11.5 Hz, *J* = 4 Hz, 1H), 3.93 – 3.84 (m, 2H), 3.52 (ddd, *J* = 10 Hz, *J* = 6.5 Hz, *J* = 4.5 Hz, 1H), 3.38 – 3.33 (m, 1H), 2.53 – 2.47 (m, 1H), 2.26 – 2.19 (m, 1H), 1.15 (s, 12H);¹³C NMR (500 MHz, CDCl₃) δ 138.3, 136.7, 134.8, 133.3, 129.7, 128.7, 116.8, 83.9, 71.8, 66.7, 65.6, 27.2, 24.8, 24.7, 24.7; IR (film) v_{max} = 3069, 2978, 2933, 2865, 1479, 1460, 1447, 1423, 1372, 1306, 1216, 1141 cm⁻¹; HRMS calcd for (C₂₀H₂₉BO₅S)Na+ 415.1721; Found: 415.1720.



N-allyl-4-methyl-N-(4-(phenylsulfonyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl)benzenesulfonamide (1m): ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 6.09 (d, *J* = 2 Hz, 1H), 5.76 (s, 1H), 5.58 (dddd, *J* = 16.5 Hz, *J* = 10 Hz, *J* = 6.5 Hz, *J* = 6.5 Hz, 1H), 5.15 – 5.10 (m, 2H), 3.86 (dd, *J* = 11 Hz, *J* = 4 Hz, 1H), 3.79 – 3.70 (m, 2H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 2.12 – 2.06 (m, 1H), 1.98 – 1.90 (m, 1H), 1.62 – 1.56 (m, 1H), 1.55 – 1.47 (m, 1H), 1.16 (s, 12H);¹³C NMR (500 MHz, CDCl₃) δ 143.4, 138.0, 137.0, 136.7, 133.5, 133.2, 129.8, 129.8, 128.8, 127.3, 119.1, 84.1, 68.1, 50.9, 46.9, 25.9, 24.8, 24.8, 24.2, 21.6; IR (film) $v_{max} = 3062, 2978, 2933, 1627, 1601, 1492, 1447, 1410, 1379, 1315, 1304, 1143 cm⁻¹; HRMS$ calcd for (C₂₈H₃₈BNO₆S₂)Na+ 582.2125; Found: 582.2124.

Ring Closing Metathesis Procedure 1

Diene **1b** (36.0 mg, 95 μ mol) was dissolved in 700 μ L dry dichloromethane (0.1M) that was degassed with argon prior to use. The solution was added to a sealed tube under argon atmosphere and charged with Grubbs 2nd generation catalyst (4.1 mg, 5 mol %). The tube was sealed with Teflon coated cap and heated to 45 °C for 2 h. Solvent was evaporated and the crude residue was purified on a flash column (20% EtOAc/Hexanes) affording **2b** as a solid (23 mg, 70%).



4,4,5,5-tetramethyl-2-(6-(phenylsulfonyl)cyclohex-1-en-1-yl)-1,3,2-dioxaborolane (2b): ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, J = 7 Hz, 2H), 7.61 (t, J = 7 Hz, 1H), 7.53 (t, J = 7 Hz, 2H), 6.84 (t, J = 3 Hz, 1H), 4.03 (d, J = 5.5 Hz, 1H), 2.14 – 2.03 (m, 3H), 1.85 – 1.76 (m, 1H), 1.74 – 1.67 (m, 1H), 1.53 – 1.48 (m, 1H), 1.26 (s, 12H);¹³C NMR (500 MHz, CDCl₃) δ 149.0, 139.2, 133.4, 129.3, 129.0, 83.8, 61.4, 25.5, 25.0, 24.8, 22.4, 17.1; IR (film) v_{max} = 2959, 1628, 1447, 1409, 1373, 1317, 1304, 1145 cm⁻¹; HRMS calcd for (C₁₈H₂₅BO₄S)Na+ 371.1459; Found: 371.1459.

Ring Closing Metathesis Procedure 2

Diene **1d** (115 mg, 0.305 mmol) was dissolved in 60 mL dry toluene (0.005 M) that was degassed with argon prior to use. The solution was added to a sealed tube under argon atmosphere and treated with Hoveyda - Grubbs 2nd generation catalyst (19.1 mg, 10 mol %) and benzoquinone (66 mg, 0.610 mmol). The tube was sealed with a Teflon coated cap and heated to 110 °C for 24 h. Solvent was evaporated and the crude black residue was purified on a flash column (20% EtOAc/Hexanes) affording **2d** as a solid (83 mg, 78%).



4,4,5,5-tetramethyl-2-(5-(phenylsulfonyl)cyclopent-1-en-1-yl)-1,3,2-dioxaborolane (2d): ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, J = 8 Hz, 2H), 7.61 (t, J = 8 Hz, 1H), 7.50 (t, J = 8 Hz, 2H), 4.43 (d, J = 8.5 Hz, 1H), 2.27 (dd, J = 14.5 Hz, J = 9 Hz, 1H), 2.16 – 2.03 (m, 2H), 1.89 (s, 3H), 1.82 – 1.76 (m, 1H), 1.29 (s, 6H), 1.28 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) δ 165.6, 137.5, 133.3, 129.7, 128.6, 83.6, 76.1, 38.9, 26.3, 25.2, 24.7, 17.3; IR (film) v_{max} = 2978, 2932, 1638, 1446, 1386, 1372, 1315, 1302, 1143, 1130 cm⁻¹; HRMS calcd for (C₁₈H₂₅BO₄S)Na+ 371.1459; Found: 371.1455.



4,4,5,5-tetramethyl-2-(7-(phenylsulfonyl)cyclohept-1-en-1-yl)-1,3,2-dioxaborolane (2c):¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, J = 8 Hz, 2H), 7.59 (t, J = 8 Hz, 1H), 7.50 (t, J = 8 Hz, 2H), 7.11 (dd, J = 9 Hz, J = 4 Hz, 1H), 4.25 (t, J = 5 Hz, 1H), 2.81 – 2.74 (m, 1H), 2.56 – 2.53 (m, 1H), 2.34 – 2.27 (m, 2H), 1.84 – 1.82 (m, 2H), 1.71 – 1.64 (m, 1H), 1.30 – 1.25 (m, 1H), 1.05 (s, 6H), 1.01 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) δ 156.4, 140.2, 133.2, 129.4, 128.9, 83.8, 66.0, 30.1, 26.9, 26.3, 25.9, 25.0, 24.7; IR (film) v_{max} = 2978, 2928, 2859, 1629, 1446, 1409, 1331, 1305 cm⁻¹; HRMS calcd for (C₁₉H₂₇BO₄S)Na+ 385.1615; Found: 385.1611.



4,4,5,5-tetramethyl-2-(4-(phenylsulfonyl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)-1,3,2dioxaborolane (2g):d.r. $(1.00 : 0.34)^{1}$ H NMR (500 MHz, CDCl₃) δ 7.97 – 7.93 (m, 4H), 7.64 (t, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 4H), 7.29 – 7.16 (m, 6H), 7.06 (d, J = 7 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 2 Hz, 1H), 6.75 (s, 1H), 4.19 – 4.17 (m, 1H), 4.10 – 4.09 (m, 1H), 3.32 – 3.29 (m, 1H), 3.27 – 3.23 (m, 1H), 2.26 – 2.23 (m, 1H), 2.17 – 2.09 (m, 1H), 1.97 – 1.78 (m, 6H), 1.31 (s, 6H), 1.30 (s, 6H)), 1.28 (s, 6H), 1.27 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) δ 150.9, 150.1, 144.2, 144.1, 139.0, 138.4, 133.6, 133.5, 129.5, 129.4, 129.1, , 129.0, 128.6, 128.6, 128.0, 127.8, 126.6, 84.1, 84.0, 62.0, 61.3, 43.3, 40.7, 27.1, 26.6, 25.1, 24.8, 24.7, 22.9, 20.0; IR (film) $v_{max} = 2978, 2933, 1447, 1410, 1379, 1304, 1143, cm^{-1}$; HRMS calcd for (C₂₄H₂₉BO₄S)Na+ 447.1772; Found: 447.1771.



4,4,5,5-tetramethyl-2-(3-methyl-6-(phenylsulfonyl)cyclohex-1-en-1-yl)-1,3,2-dioxaborolane (**2f)**:d.r. (1.00 : 0.75) ¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.88 (m, 4H), 7.63 – 7.59 (m, 2H), 7.54 – 7.50 (m, 4H), 6.64 – 6.33 (m, 2H), 4.06 – 4.04 (m, 1H), 4.00 (d, *J* = 6 Hz, 1H), 2.20 – 2.14 (m, 1H), 2.14 – 2.07 (m, 1H), 2.06 – 1.98 (m, 1H), 1.92 – 1.82 (m, 1H), 1.78 – 1.69 (m, 1H), 1.57 – 1.50 (m, 1H), 1.29 (s, 24H), 1.26 – 1.25 (m, 1H) 1.24 – 1.19 (m, 1H), 1.19 – 1.10 (m, 2H), 0.94 (d, J = 7 Hz, 3H), 0.88 (d, J = 7 Hz, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 154.2, 153.9, 139.1, 138.4, 133.4, 133.4, 129.5, 129.4, 128.9, 128.9, 83.9, 62.2, 61.6, 31.1, 29.6, 26.2, 25.6, 25.1, 24.8, 24.7, 22.6, 20.6, 20.4, 20.4; IR (film) $\nu_{max} = 2978$, 2928, 1446, 1331, 105, 1142 cm⁻¹; HRMS calcd for (C₁₉H₂₇BO₄S)Na+ 385.1615; Found: 385.1615.



2h

2-(3,3-dimethyl-6-(phenylsulfonyl)cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (2h): ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, J = 8 Hz, 2H), 7.61 (t, J = 8 Hz, 1H), 7.52 (t, J = 8 Hz, 2H), 6.46 (s, 1H), 3.98 (d, J = 6 Hz, 1H), 2.07 – 2.02 (m, 1H), 1.88 – 1.80 (m, 1H), 1.42 (ddd, J = 13.5 Hz, J = 13.5 Hz, J = 4 Hz, 1H), 1.30 (s, 12H), 1.22 (ddd, J = 14 Hz, 4.5 Hz, 4.5 Hz, 1 H), 0.90 (s, 3H), 0.79 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 157.3, 138.8, 133.4, 129.5, 128.9, 83.9, 61.9, 32.1, 31.6, 29.0, 28.4, 25.1, 24.7, 20.1; IR (film) v_{max} = 2976, 2930, 1447, 1422, 1372, 1305, 1143, 1084 cm⁻¹; HRMS calcd for (C₂₀H₂₉BO₄S)Na+ 399.1771; Found: 399.1771.



4,4,5,5-tetramethyl-2-(3-(phenylsulfonyl)-3,4-dihydronaphthalen-2-yl)-1,3,2-dioxaborolane (2i):¹H NMR (500 MHz, CDCl₃) δ 7.55 (d, *J* = 8 Hz, 2H), 7.28 (t, *J* = 8 Hz, 1H), 7.18 (s, 1H), 7.13 (t, *J* = 8 Hz, 2H), 7.06 (t, *J* = 7 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 4.24 (d, *J* = 8 Hz, 1H), 3.60 (d, *J* = 18 Hz, 1H), 3.28 (dd, *J* = 18 Hz, *J* = 8.5 Hz, 1H),1.34 (s, 6H), 1.33 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) δ 145.0, 136.8, 133.2, 132.5, 131.8, 129.8, 129.4, 127.9, 127.8, 127.7, 126.9, 84.3, 61.2, 28.1, 25.1, 24.7; IR (film) v_{max} = 3062, 3026, 2937, 2867, 1634, 1601, 1585, 1492, 1447, 1307, 1208, 1149, 1084, 1025 cm⁻¹; HRMS calcd for (C₂₂H₂₅BO₄S)Na+ 419.1459; Found: 419.1456.



4,4,5,5-tetramethyl-2-(7-(phenylsulfonyl)-6,7-dihydro-5H-benzo[7]annulen-8-yl)-1,3,2dioxaborolane (2j):¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8 Hz, 2H), 7.50 (t, *J* = 8 Hz, 1H), 7.40 (t, *J* = 8 Hz, 2H), 7.34 (s, 1H), 7.12 – 7.08 (m, 3H), 7.03 – 7.02 (m, 1H), 4.61 (t, *J* = 7.5 Hz, 1H), 2.92 – 2.79 (m, 2H), 2.43 – 2.39 (m, 2H), 1.31 (s, 12H); ¹³C NMR (500 MHz, CDCl₃) δ 147.6, 141.7, 137.7, 135.3, 133.4, 132.0, 129.7, 128.7, 128.5, 126.4, 84.3, 67.5, 31.8, 31.3, 25.1, 24.9, 24.7; IR (film) v_{max} = 2978, 2932, 1638, 1446, 1386, 1372, 1315, 1302, 1143, 1130, 1085 cm⁻¹;HRMS calcd for (C₂₃H₂₇BO₄S)Na+ 433.1615; Found: 433.1615.



4-(phenylsulfonyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-2,3,4,7tetrahydro-1H-azepine (2k): ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8 Hz, 2H), 7.65 (d, *J* = 8 Hz, 2H), 7.62 (t, *J* = 8 Hz, 1H), 7.51 (t, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 Hz, 2H), 7.03 (dd, *J* = 8 Hz, *J* = 4 Hz, 1H), 4.33 – 4.28 (m, 2H), 3.98 – 3.92 (m, 2H), 3.70 (t, *J* = 12.5 Hz, 1H), 2.57 (ddd, *J* = 15 Hz, *J* = 3.5 Hz, *J* = 3.5 Hz, 1H), 2.41 (s, 3H), 2.14 – 2.06 (m, 1H), 1.04 (s, 6H), 1.00 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) δ 149.5, 143.5, 139.2, 136.5, 133.8, 129.9, 129.3, 129.2, 127.2, 84.3, 64.4, 47.5, 46.8, 27.6, 24.9, 24.7, 21.6; IR (film) v_{max} = 2977, 2925, 1636, 157, 1332, 1305, 1143, 1094 cm⁻¹; HRMS calcd for (C₂₅H₃₂BO₆S₂)Na+ 540.1656; Found: 540.1656.

Intermolecular Cross Metathesis Procedure 1

Vinyl boronate **3** (100 mg, 0.324 mmol), Grubbs 2^{nd} generation catalyst (13.7 mg, 16 µmol) and 1-hexene (80 µL, 0.648 mmol) were added to a flask under argon atmosphere. The starting materials were dissolved in 1.62 mL dry dichloromethane, which was degassed with argon prior to use. The flask was fitted with a reflux condenser and heated to reflux for 24 h. The solvent was removed and the crude was purified on a flash column (20% EtOAc/Hexanes) affording **14** as a solid (86 mg, 73%).



4,4,5,5-tetramethyl-2-(1-(phenylsulfonyl)hept-2-en-2-yl)-1,3,2-dioxaborolane (15): Z/E (1.00 : 0.18) ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8 Hz, 2H), 7.81 (d, *J* = 8 Hz, 2H), 7.60 (t, *J* = 8 Hz, 2H), 7.51 (t, *J* = 8 Hz, 4H), 6.58 (t, *J* = 7 Hz, 1H), 6.06 (t, *J* = 8 Hz, 1H), 4.03 (s, 2H), 3.87 (s, 2H), 2.32 (q, *J* = 2 Hz, 2H), 1.94 (q, *J* = 4 Hz, 2H), 1.28 – 1.21 (m, 8 H), 1.19 (s, 12H), 1.13 (s, 12H), 0.84 (t, *J* = 7 Hz, 6H); ¹³C NMR (500 MHz, CDCl₃) δ 157.6, 155.3, 139.4, 138.9,133.4, 133.3, 129.1, 129.0, 128.8, 83.9, 83.7, 62.6, 556.0, 31.5, 31.2, 30.7, 29.3, 24.9, 24.8, 24.8, 22.6, 22.2, 13.9, 13.9; IR (film) v_{max} = 2976, 2930, 2871, 1631, 1147, 1415, 1373, 1316 cm⁻¹; HRMS calcd for (C₁₉H₂₂BO₄S)Na+ 387.1772; Found: 387.1767.



4,4,5,5-tetramethyl-2-(5-phenyl-1-(phenylsulfonyl)pent-2-en-2-yl)-1,3,2-dioxaborolane (**16**):¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8 Hz, 2H), 7.60 (t, *J* = 8 Hz, 1H), 7.51 (t, *J* = 8 Hz, 2H), 7.28 – 7.25 (m, 2H), 7.18 (t, *J* = 8 Hz, 1H), 7.12 (d, *J* = 8 Hz, 2H), 6.67 (t, *J* = 7 Hz, 1H), 3.97 (s, 2H), 2.63 – 2.60 (m, 2H), 2.35 – 2.30 (m, 2H), 1.12 (s, 12H); ¹³C NMR (500 MHz, CDCl₃) δ 153.6, 141.2, 139.1, 133.2, 128.9, 128.8, 128.3, 128.2, 125.9, 83.7, 55.6, 34.5, 31.4, 24.5; IR (film) $v_{max} = 2977, 2934, 1447, 1423, 1372, 1316, 1305, 1145, 1084 \text{ cm}^{-1}$; HRMS calcd for (C₂₃H₂₉BO₄S)Na+ 435.1772; Found: 435.1772.

Intermolecular Cross Metathesis Procedure 2

Vinyl boronate **3** (50 mg, 0.162 mmol), Grubbs 2^{nd} generation catalyst (6.9 mg, 8 µmol) and 1hexene (80 µL, 0.648 mmol) were added to a sealed tube under argon atmosphere. The starting materials were dissolved in 1.62 mL dry toluene which was degassed with argon prior to use. The tube was fitted with a Teflon screw cap and heated to 135 °C for 12 h. The solvent was removed and the crude was purified on a flash column (20% EtOAc/Hexanes) affording **16** as a solid (16 mg, 30%).



(Z)-4,4,5,5-tetramethyl-2-(1-(phenylsulfonyl)but-2-en-2-yl)-1,3,2-dioxaborolane (17):¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 8 Hz, 2H), 7.61 (t, *J* = 8 Hz, 1H), 7.51 (t, *J* = 8 Hz, 2H), 6.72 (q, *J* = 7 Hz, 1H), 4.04 (s, 2H), 1.58 (s, 3H), 1.13 (s, 12H); ¹³C NMR (500 MHz, CDCl₃) δ 149.8, 139.3, 133.5, 133.4, 129.1, 129.0, 129.0, 83.9, 83.8, 55.6, 24.8, 24.7, 15.3 ; IR (film) v_{max} = 2978, 2932, 1638, 1446, 1386, 1302 cm⁻¹; HRMS calcd for (C₁₆H₂₃BO₄S)Na+ 345.1302; Found: 345.1298.

Conversion of 2c to vinyl ether 5

Vinyl boronate **2c** (1.02 g, 2.82 mmol) was dissolved in 21 mL (5:1 MeOH/DCM) solvent system (0.1 M), and to the solution was added triethylamine (1.6 mL, 11.2 mmol) and copper(II) acetate (1.02 mg, 5.60 mmol). The resulting mixture was heated to 40 °C and stirred for 6 days open to air. Over the course of the reaction additional solvent was added as needed due to evaporation. The mixture was diluted with ether and washed with water. The organic layer was separated, dried over magnesium sulfate and concentrated under reduced pressure resulting in a white solid which could be recrystallized from a 2:1 mixture of pentane/ether (672 mg, 75%).



4,4,5,5-tetramethyl-2-(7-(phenylsulfonyl)cyclohept-1-en-1-yl)-1,3,2-dioxaborolane (5): ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, J = 8 Hz, 2H), 7.61 (t, J = 7 Hz, 1H), 7.51 (t, J = 8 Hz, 2H), 5.01 (dd, J = 8.5 Hz, J = 4.5 Hz, 1H), 3.78 (t, J = 5 Hz, 1H), 3.06 (s, 3H), 2.61 – 2.54 (m, 1H), 2.51 – 2.46 (m, 1H), 2.28 – 2.20 (m, 1H), 2.09 – 2.03 (m, 1H), 1.91 – 1.74 (m, 3H), 1.38 – 1.31 (m, 1H); ¹³C NMR (500 MHz, CDCl₃) δ 151.3, 139.6, 133.4, 128.8, 128.7, 104.7, 70.8, 54.4, 27.4, 25.3, 24.7, 23.1; IR (film) $\nu_{max} = 2977$, 2935, 1447, 1305, 1144 cm⁻¹; HRMS calcd for (C₁₄H₁₈O₃S)Na+ 289.0869; Found: 289.0869.

Alkylation of 5

Sulfone **5** (564 mg, 2.11 mmol) was dissolved in 10.5mL dry THF (0.2 M), cooled to -78 °C, treated with *n*BuLi (1.53 M in THF, 1.10 mL, 2.53 mmol) and allowed to stir an additional 30 minutes before addition of iodide (564 mg, 2.53 mmol). The reaction was then allowed to reach room temperature over the course of 1 hour before being quenched with saturated ammonium chloride. The aqueous layer was extracted with dichloromethane (2 x 10 mL), and the organic layers were separated, dried over magnesium sulfate and concentrated under reduced pressure. The resulting crude residue was purified on a flash column (20% EtOAc/Hexanes) affording the product as a colorless oil (643 mg, 84%).



(E)-7-(hepta-4,6-dien-1-yl)-1-methoxy-7-(phenylsulfonyl)cyclohept-1-ene (7): ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, J = 8 Hz, 2H), 7.58 (t, J = 8 Hz, 1H), 7.47 (t, J = 8 Hz, 2H), 6.25 (ddd, J = 17 Hz, J = 10 Hz, J = 10 Hz, 1H), 5.98 (dd, J = 15 Hz, J = 10.5 Hz, 1H), 5.60 (dt, J = 15 Hz J = 7 Hz, 1H), 5.06 (d, J = 17 Hz, 1H), 5.00 (t, J = 7 Hz, 1H), 4.94 (d, J = 10 Hz, 1H), 3.20 (s, 3H), 2.43 – 2.36 (m, 2H), 2.12 – 2.07 (m, 1H), 2.05 – 1.97 (m 5H), 1.79 – 1.65 (m 3H), 1.52 – 1.43 (m, 2H), 1.28 – 1.20 (m, 1H); ¹³C NMR (500 MHz, CDCl₃) δ 151.5, 138.4, 137.2, 134.5, 133.2, 131.4, 130.3, 128.2, 115.1, 105.0, 76.4, 54.2, 35.5, 33.0, 29.1, 25.5, 24.3, 22.6, 21.6; IR (film) $v_{max} = 2978$. 2932. 1638. 1446. 1386. 1302. 1315. 1236. 1143. 1130. 1085 cm⁻¹; HRMS calcd for (C₂₁H₂₈O₃S)Na+ 383.1651; Found: 383.1651.

Intramolecular [4+3] Cycloaddition of 7

The enol ether 7 (643 mg, 1.78 mmol) was dissolved in 17.8 mL dry dichloromethane (0.1 M) and cooled to -78 °C. The solution was treated with titanium(IV) chloride (215 μ L, 1.95 mmol) and stirred 4 minutes before quenched with water. After warming to room temperature, the reaction was extracted with dichloromethane (3 x 5 mL) and the organic layers were combined, dried over magnesium sulfate, and concentrated under reduced pressure affording a colorless oil (293 mg, 81%).



(3aR,8S,11aR)-1,2,3,4,5,6,7,8,9,11a-decahydro-3a,8-methanocyclopenta[10]annulen-12-one (8): ¹H NMR (500 MHz, CDCl₃) δ 5.70 – 5.65 (m, 1H), 5.45 (dt, *J* = 11 Hz, *J* = 4.5Hz, 1H), 2.89 – 2.84 (m, 1H), 2.77 – 2.71 (m, 1H), 2.63 – 2.56 (m, 1H), 2.41 – 2.34 (m, 1H), 2.16 – 2.10 (m, 1H), 2.02 – 1.93 (m, 2H), 1.82 – 1.67 (m, 6H), 1.61 – 1.55 (m, 1H), 1.53 – 1.46 (m 1H), 1.44 – 1.38 (m, 1H), 1.35 – 1.30 (m 1H), 1.27 – 1.22 (m, 1H); ¹³C NMR (500 MHz, CDCl₃) δ 216.1, 135.0, 128.2, 62.6, 55.3, 47.8, 40.0, 35.9, 34.6, 31.2, 29.2, 26.8, 26.1, 22.9; IR (film) v_{max} = 3026, 2937, 1634, 1447, 1307, 1208, 1149, 1084 cm⁻¹; HRMS calcd for (C₁₄H₂₀O)Na+ 227.1406; Found: 227.1708.

LAH Reduction of 8

To a suspension of lithium aluminum hydride (20 mg, 0.543 mmol) in diethyl ether at 0 °C was added ketone **8** (74 mg, 0.362 mmol) as a solution in 1.0 mL diethyl ether. After dropwise addition, the reaction was allowed to warm to room temperature over the course of 1 hour. After the reaction was determined complete by TLC, it was cooled to 0 °C and 5 mL ethyl acetate was added slowly. The reaction was warmed back to room temperature, and a saturated solution of Rochelle's salt was added to the biphasic system which was stirred vigorously for one hour. The organic layer was separated from the mixture, dried over magnesium sulfate, and concentrated under reduced pressure. The crude residue was purified on a flash column in (2.5% EtOAc/Hexanes) giving two diastereomers; one of which could be recrystallized with ethanol.



(3aR,8S,11aR,12R)-1,2,3,4,5,6,7,8,9,11a-decahydro-3a,8-methanocyclopenta[10]annulen-12-ol (9): ¹H NMR (500 MHz, CDCl₃) δ 5.48 – 5.46 (m, 1H), 5.31 (d, *J* = 11 Hz, 1H), 3.81 (s, 1H), 2.71 (s, 1H), 2.35 – 2.10 (m, 3H), 1.99 – 1.88 (m, 2H), 1.86 – 1.84 (m, 1H), 1.67 – 1.48 (m, 12H); ¹³C NMR (500 MHz, CDCl₃) δ 134.1, 126.7, 80.9, 52.4, 44.9, 42.5, 40.9, 37.9, 34.9, 33.8, 31.6, 26.4, 26.1, 23.1; HRMS calcd for (C₁₄H₂₂O)Na+ 229.1562; Found: 229.1564.

Crystallographic Data



Compound 9



EA-VI-53B

	 20	- 4	- 09	- 00	120 1	140	160	180	200	220	240
F2 - Processing parameters SI 125.757791 MHz WDW EA SSB 125.757791 MHz M EA SSB 125.757791 MHz C 126 Hz C Hz C Hz C Hz C Hz C Hz C Hz C Hz C											
======= CHANNEL f2 ===================================											
====== CHANNEL fl ========= NUCl 13C Pl 12:00 usec PL1 0:30 dB PL1 125.7716224 MHz					-						
Time 11.23 INSTRUM 5 mm CPTCI 11.23 PULLROG 71424 SOLVENT 29930 71424 NS 71424 NS 71424 NS 71424 NS 71424 NS 71424 A2 2000100 Hz 700 Hz									PhO ₂ S O ^{-B} O	1d	
PROCNO 2 PROCNO 1 F2 - Acquisition Parameters Date_ 20120926	\rightarrow										
Current Data Parameters NAME EA-VI-53B	87.42 - 24.60 - 22.52	89.42 - 88.42 -	LG·L9 — I6·9L — 91·// —	19.88 – 24.77 –	56.111 - 89.821 -	02,051 — 78,851 — 78,851 — 26,851 — 20,451 —					
	2 0 8	8	L T 9	Z T	68 89	02 TE 29 EE 60					

13C NMR



EA-VII-16B



13C NMR



EA-VI-135B



13C NMR



EA-VI-167A



13C NMR



EA-VI-180A



13C NMR



EA-VI-78B



13C NMR



EA-VI-86C


13C



1H NMR



240



EA-VII-37A





EA-VII-51C





EA-IV-54-IC









EA-VI-138AA





EA-VI-182A





EA-VI-187B





EA-VI-80A





EA-VI-34B





EA-VI-91A





EA-VII-40B





EA-VI-55A





EA-VI-148C





EA-V-73CII





EA-VII-86A



TOCT



EA-VII-97B





EA-VII-108B


13C NMR



1H NMR



13C NMR