Enantioselective Carbocycle Formation through Intramolecular Pd-Catalyzed Allyl-Aryl Cross-Coupling

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General Information

$^1$H NMR spectra were measured using a Varian Gemini-500 (500 MHz) spectrometer or a Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl$_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet, app = apparent), and coupling constants (Hz). $^{13}$C($^1$H)NMR spectra were measured using a Varian Inova 500 (126 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl$_3$: 77.0 ppm). $^{31}$P($^1$H)NMR spectra were measured using a Varian Inova 500 (202 MHz) spectrometer. Chemical shifts are reported in ppm using phosphoric acid as the external standard (H$_3$PO$_4$: 0.0 ppm). Infrared (IR) spectra were measured using a Bruker α-P Spectrometer. Frequencies are reported in wavenumbers (cm$^{-1}$) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (HRMS) was performed at Boston College, Chestnut Hill, MA.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO$_2$, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA), potassium permanganate (KMnO$_4$), and Seebach’s “magic” stain (phosphomolybdic acid, Ce(SO$_4$)$_2$, sulfuric acid). Analytical chiral gas-liquid chromatography (GLC) was also performed on an Agilent Technologies 6850 Series chromatograph with a flame ionization detector, and a Supelco β –Dex 120 column with helium as the carrier gas. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Thar Supercritical Chromatograph equipped with auto sampler and a Waters photodiode array detector with methanol as the modifier.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran, dichloromethane and diethyl ether were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after being purged with argon. Dimethylformamide was dispensed from a Glass Contour Solvent Purification System (SG Water, USA LLC). Triethylamine was purchased from Aldrich and refluxed over calcium hydride prior to use. Palladium acetate (Pd(OAc)$_2$), rhodium cyclooctadiene chloride dimer ([RhCl(COD)]$_2$), phosphorus trichloride, and triisopropyl phosphine were purchased from Strem Chemicals and used as received. Catechol borane, (R,R)-tartaric acid, 2,2’-bipyridine, and 3,5-diterbutylbromobenzene were purchased from Alfa Aesar and used as received. B$_2$(pin)$_2$ was obtained from AllyChem and recrystallized from pentane prior to use. 2-Iodobromobenzene and 2-Iodochlorobenzene were purchased from Matrix Scientific and used as received. All other reagents were obtained from Aldrich or Fisher and used as received.
Experimental Procedures

(I) Preparation of phosphoramidite ligands

Ligands $\text{L}1$, $\text{L}2$, and $\text{L}3$ were prepared according to the general reaction scheme shown below. All spectral data are in accordance with the literature.

\[
\begin{align*}
\text{Me} & \quad \text{Ar} & \quad \text{OH} & \quad + & \quad \text{PCl}_3 & \quad \xrightarrow{i) \text{NEt}_3, \text{THF}} & \quad 0 \ ^\circ \text{C} \text{ to RT} & \quad \xrightarrow{\text{ii) HNR}_2} \\
\text{Me} & \quad \text{Ar} & \quad \text{OH} & \quad & & & & \\
\end{align*}
\]

$(R, R)$-$\text{L}1$: Ar = 3,5-dimethylphenyl, $R$ = Me
$(R, R)$-$\text{L}2$: Ar = 3,5-difluorophenyl, $R$ = Me
$(R, R)$-$\text{L}3$: Ar = 3,5-difluorophenyl, $R$ = -$(\text{CH}_2)_5$-

(II) Representative procedures for preparation of starting materials

Unless otherwise noted, allyl boronate starting materials were prepared according to the general method shown below.

\[
\begin{align*}
\text{R} & \quad \text{X} & \quad + & \quad \text{CH}_2\text{OH} & \quad \xrightarrow{\text{Pd(OAc)}_2 (2\%), \text{NBu}_4\text{Cl}} & \quad \text{NaHCO}_3, \text{DMF, 40 }^\circ\text{C} & \quad \text{R} & \quad \text{X} & \quad \text{CH}_2\text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{X} & \quad + & \quad \text{Cl} & \quad \xrightarrow{\text{SOCl}_2} & \quad \text{DCM, 0 }^\circ\text{C to RT} & \quad \text{R} & \quad \text{X} & \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{X} & \quad \xrightarrow{\text{PdCl}_2 (1\%), \text{B}_2(\text{pin})_2} & \quad \text{THF, 60 }^\circ\text{C} & \quad \text{R} & \quad \text{X} & \quad \text{B(\text{pin})} \\
\end{align*}
\]

1. Boele, M. D. K.; Kamer, P. C. J.; Lutz, M.; Spek, A. L.; de Vries, J. G.; van Leeuwen, P. W. N. M.; van Strijdonck, G. P. F. Chem. Eur. J. 2004, 10, 6232.
2. Woodward, A. R.; Burks, H. E.; Chan, L. M.; Morken, J. P. Org. Lett., 2005, 7, 5505.
3. Sieber, J. D.; Morken, J. P. J. Am. Chem. Soc. 2008, 130, 4978.
General procedure for aldehyde synthesis

To a flame-dried round-bottomed flask equipped with magnetic stir bar in the glovebox was added Pd(OAc)$_2$ (0.02 equiv.). The flask was removed from the glovebox, charged with tetrabutylammonium chloride (1.00 equiv.) and sodium bicarbonate (2.50 equiv.) and sealed with a septum. The flask was evacuated and back-filled with nitrogen (3x) followed by addition of dimethylformamide (0.5 M). After stirring at room temperature for 10 minutes, aryl iodide (1.00 equiv.) followed by allyl alcohol (1.50 equiv.) were added and the resulting mixture was heated to 40 °C for 12 hours. The resulting dark reaction mixture was cooled to room temperature, diluted with diethyl ether (50 mL) and water (50 mL) and the layers separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL) and the combined organic layers washed with a 50/50 water/brine solution (2 x 50 mL). The organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure. The pure aldehyde products were isolated after SiO$_2$ chromatography unless otherwise noted.

General procedure for allylic alcohol synthesis

To a flame-dried round-bottomed flask equipped with magnetic stir bar under nitrogen was added vinyl magnesium bromide (1.0 M in THF, 2.00 equiv.). The solution was cooled to 0 °C (ice/water bath) and treated dropwise with aldehyde (0.5 M in THF, 1.00 equiv.). After stirring at room temperature for 1 hour, the resulting yellow solution was returned to 0 °C and excess vinyl magnesium bromide was carefully quenched with water (5 mL) followed by addition of saturated aqueous ammonium chloride (20 mL). The resulting mixture was diluted with ethyl acetate (50 mL) and water (20 mL) and the layers separated. The aqueous layer was extracted with ethyl acetate (3 x 50 mL) and the combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The pure allylic alcohol products were isolated after SiO$_2$ chromatography.

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4 Kuwabe, S.; Torraca, K. E.; Buchwald, S. L. J. Am. Chem. Soc. 2001, 123, 12202.
General procedure for allylic chloride synthesis

To a flame-dried round-bottomed flask equipped with magnetic stir bar under nitrogen was added thionyl chloride (10.00 equiv.). The flask was cooled to 0 °C (ice/water bath) and an outlet line was installed in order to allow continuous nitrogen flow from the inlet through the outlet line which was bubbled through a 90/10 saturated aqueous sodium bicarbonate/water solution. Allylic alcohol (0.25 M in DCM, 1.00 equiv.) was then added dropwise and stirred at 0 °C for 30 minutes. After stirring at room temperature for 2 hours, the reaction mixture was diluted with DCM and poured over solid ice (75 mL) in a separatory funnel. The layers were separated and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layers were washed with brine (75 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure. The resulting crude material was purified via SiO\(_2\) chromatography to give a mixture of internal and terminal chloride products.

General procedure for allyl-boronate synthesis\(^5\)

To an oven-dried vial equipped with magnetic stir bar in the glovebox was added PdCl\(_2\) (0.01 equiv.) followed by B\(_2\)(pin)\(_2\) (1.00 equiv.) and THF (1.0 M). The resulting mixture was stirred for approximately 1 minute followed by addition of allyl chloride (mixture of regio isomers, 1.00 equiv.). The vial was sealed with a cap, removed from the glovebox and heated to 60 °C for 12 hours with vigorous stirring. After cooling to room temperature, the reaction mixture was passed through a plug of SiO\(_2\), eluding with 10% ethyl acetate in hexane (200 mL). The resulting solution was concentrated under reduced pressure to give the crude material which was subsequently purified via SiO\(_2\) chromatography. (NOTE: the allyl-boronate products suffer slow decomposition on SiO\(_2\) and purification is best carried out in an expedient fashion.)

\(^5\) Zhang, P.; Roundtree, I. A.; Morken, J. P. *Org. Lett.* 2012, 14, 1416.
(III) Preparation of starting materials

3-(2-bromophenyl)propanal (S1). Prepared according to the general procedure utilizing \( \text{Pd(OAc)}_2\) (47.6 mg, 0.212 mmol), tetrabutylammonium chloride (2.95 g, 10.6 mmol), sodium bicarbonate (2.23 g, 26.5 mmol), dimethylformamide (21 mL), 2-bromiodobenzene (1.36 mL, 10.6 mmol), and allyl alcohol (1.10 mL, 15.9 mmol). The crude material was purified (SiO\(_2\), 6% ethyl acetate in hexane) to give the desired product as a clear, yellow oil (1.99 g, 88%). \( R_f = 0.29 \) (5% ethyl acetate in hexane, UV/magic stain). All spectral data are in accordance with the literature.\(^6\)

5-(2-bromophenyl)pent-1-en-3-ol (S2). Prepared according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 18.7 mL, 18.7 mmol), 3-(2-bromophenyl)propanal (1.99 g, 9.34 mmol), and THF (19 mL). The crude material was purified (SiO\(_2\), 12% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (1.94 g, 86%). \( R_f = 0.24 \) (10% ethyl acetate in hexane, UV/magic stain). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.53 (1H, dd, \( J = 7.8, 1.0 \) Hz), 7.26-7.21 (2H, m), 7.07-7.04 (1H, m), 5.93 (1H, ddd, \( J = 17.1, 10.3, 5.9 \) Hz), 5.28 (1H, ddd (app dt’s), \( J = 17.1, 1.5, 1.5 \) Hz), 5.16 (1H, ddd (app dt’s), \( J = 10.3, 1.5, 1.5 \) Hz), 4.17 (1H, ddd (app q), \( J = 6.4 \) Hz), 2.88 (1H, ddd, \( J = 13.7, 9.3, 5.9 \) Hz), 2.81 (1H, ddd, \( J = 13.7, 9.3, 6.9 \) Hz), 1.91-1.80 (2H, m), 1.73 (1H, br s); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 141.2, 140.8, 132.8, 130.4, 127.6, 127.4, 124.4, 115.0, 72.4, 36.9, 32.0; IR (neat): 3359.9 (br), 3066.8 (w), 2931.3 (m), 2864.0 (m), 1643.6 (w), 1566.8 (w), 1470.6 (s), 1438.7 (m), 1045.4 (m), 1022.1 (s), 990.6 (m), 658.5 (m) cm\(^{-1}\); HRMS-(DART) for: C\(_{11}\)H\(_{12}\)Br \([\text{M+H-H}_2\text{O}]^+\): calculated: 223.0122, found: 223.0118.

(E)-1-bromo-2-(5-chloropent-3-en-1-yl)benzene (S3). Prepared according to the general procedure utilizing thionyl chloride (2.27 mL, 31.3 mmol), 5-(2-bromophenyl)pent-1-en-3-ol (750 mg, 3.11 mmol), and DCM (12.4 mL). The crude material was purified (SiO\(_2\), 12% ethyl acetate in hexane) to give the desired product as a 10:1 mixture of the title compound: 1-bromo-2-(3-chloropent-4-en-1-yl)benzene (clear, colorless oil (650.4 mg, 81%). \( R_f = 0.78 \) (10% ethyl acetate in hexane, UV/magic stain). \(^1\)H NMR (500 MHz, CDCl\(_3\)): (major isomer) \( \delta \) 7.54 (1H, dd, \( J = 8.3, 1.0 \) Hz), 7.26-7.19 (2H, m), 7.07 (1H, ddd (app dt’s), \( J = 7.3, 7.3, 2.0 \) Hz), 5.84 (1H, dt’s, \( J = 15.2, 6.9, 6.9 \) Hz), 5.66 (1H, dtt’s, \( J = 15.2, 6.9, 6.9, 1.5, 1.5 \) Hz), 4.04 (2H, d, \( J = 6.8 \) Hz), 2.84 (2H, t, \( J = 7.3 \) Hz), 2.40 (2H, dt’s (app q), \( J = 7.8 \) Hz); (minor isomer) \( \delta \) 7.54 (1H, d, \( J = 8.3 \) Hz), 7.26-7.19 (2H, m), 7.10-7.05 (1H, m), 5.96 (1H, ddd, \( J = 17.1, 10.3, 7.8 \) Hz), 5.32 (1H, d, \( J = 17.1 \) Hz), 5.19 (1H, d, \( J = 10.3 \) Hz), 4.38 (1H, ddd (app q), \( J = 7.8 \) Hz), 2.95 (1H, ddd, \( J = 13.7, 9.3, 5.9 \) Hz), 2.89-2.82 (1H, m), 2.18-2.08 (2H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): (both isomers (one overlapping signal)) \( \delta \) 140.6, 140.1, 134.5, 132.9, 132.8, 130.4, 127.9, 127.7, 127.5, 127.4, 126.8, 124.4, 116.9, 62.2, 45.2, 37.9, 35.5, 33.1, 32.1; IR (neat): 3054.3 (w), 3037.0 (w), 3011.4 (w), 2950.5 (m), 2931.3 (m), 2860.6 (w), 1665.2 (m), 1592.5 (w), 1566.8 (m), 1470.6 (s), 1438.7 (s), 1249.7 (m), 1023.5 (s), 965.1 cm\(^{-1}\)

\(^6\) Kuwabe, S.; Torracca, K. E.; Buchwald, S. L. J. Am. Chem. Soc. 2001, 123, 12202.
(s), 747.9 (s), 676.1 (s), 657.4 (s), 444.3 (m) cm⁻¹; HRMS-(DART) for: C₁₁H₁₂Br [M+H-HCl]⁺: calculated: 223.0122, found: 223.0121.

(E)-2-(5-(2-bromophenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 1, Table 1). Prepared according to the general procedure utilizing PdCl₂ (4.2 mg, 0.024 mmol), B₂(pin)₂ (599.6 mg, 2.36 mmol), THF (2.4 mL), and (E)-1-bromo-2-(5-chloropent-3-en-1-yl)benzene (10:1 with regio-isomeric allyl chloride, 612.9 mg, 2.36 mmol). The crude material was purified (SiO₂, 4% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (538.0 mg, 65%). Rf = 0.36 (5% ethyl acetate in hexane, UV/magic stain). ¹H NMR (500 MHz, CDCl₃): δ 7.51 (1H, d, J = 7.8 Hz), 7.23-7.19 (2H, m), 7.06-7.01 (1H, m), 5.55-5.43 (2H, m), 2.77 (2H, t, J = 7.8 Hz), 2.30 (2H, dt (app q), J = 5.9 Hz), 1.65 (2H, d, J = 6.8 Hz), 1.25 (12H, s); ¹³C NMR (126 MHz, CDCl₃): 141.4, 132.7, 130.4, 129.5, 127.4, 127.2, 125.9, 124.5, 83.1, 36.4, 32.8, 24.8; IR (neat): 3057.0 (w), 2977.3 (m), 2930.1 (m), 2862.4 (w), 1664.3 (w), 1591.9 (w), 1469.8 (m), 1438.8 (m), 1359.7 (s), 1323.1 (s), 1271.9 (m), 1213.7 (m), 1164.4 (m), 1142.3 (s), 1022.7 (m), 966.1 (s), 846.6 (s), 747.4 (s), 657.5 (m), 444.9 (w) cm⁻¹; HRMS-(DART) for: C₁₇H₂₅BBrO₂ [M+H]⁺: calculated: 351.1131, found: 351.1136.

3-(2-chlorophenyl)propanal (S4). Prepared according to the general procedure utilizing Pd(OAc)₂ (44.9 mg, 0.20 mmol), tetrabutylammonium chloride (2.78 g, 10.0 mmol), sodium bicarbonate (2.10 g, 25.0 mmol), dimethylformamide (20 mL), 2-chloroiodobenzene (1.22 mL, 10.0 mmol), and allyl alcohol (1.02 mL, 15.0 mmol). The crude material was purified (SiO₂, 6% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (1.5592 g, 92%). Rf = 0.40 (10% ethyl acetate in hexane, UV/magic stain). All spectral data are in accordance with the literature.⁷

5-(2-chlorophenyl)pent-1-en-3-ol (S5). Prepared according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 8.00 mL, 8.00 mmol), 3-(2-chlorophenyl)propanal (674.5 mg, 4.00 mmol), and THF (8.0 mL). The crude material was purified (SiO₂, 12% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (675 mg, 86%). Rf = 0.22 (10% ethyl acetate in hexane, UV/magic stain). ¹H NMR (500 MHz, CDCl₃): δ 7.34 (1H, dd, J = 7.8, 1.5 Hz), 7.25 (1H, dd, J = 7.3, 2.0 Hz), 7.18 (1H, ddd (app dt’s), J = 7.8, 7.8, 1.5 Hz), 7.14 (1H, ddd (app dt’s), J = 7.8, 7.8, 2.0 Hz), 5.93 (1H, ddd, J = 17.1, 10.3, 5.9 Hz), 5.28 (1H, ddd (app dt’s), J = 17.1, 1.5, 1.5 Hz), 5.15 (1H, ddd (app dt’s), J = 10.3, 1.0, 1.0 Hz), 4.16 (1H, ddd (app q), J = 5.9 Hz), 2.88 (1H, ddd, J = 13.7, 9.3, 6.5 Hz), 2.80 (1H, ddd, J = 13.7, 9.8, 6.9 Hz), 1.91-1.80 (2H, m), 1.75 (1H, br s); ¹³C NMR (126 MHz, CDCl₃): δ 140.8, 139.5, 133.9, 130.4, 129.5, 127.3, 126.8, 115.0, 72.5, 36.7, 29.5; IR (neat): 3374.8 (br), 3072.8 (w), 2929.1 (m), 2863.2 (w), 1643.6 (w), 1571.6 (w), 1474.3 (s), 1443.0 (m), 1133.3 (w), 1051.5 (s), 1031.5 (m), 990.9 (m), 923.9 (s), 750.2 (s), 679.7 (m) cm⁻¹; HRMS-(DART) for: C₁₁H₁₂Cl [M+H-H₂O]⁺: calculated: 179.0628, found: 179.0631.

⁷ Kuwabe, S.; Torraca, K. E.; Buchwald, S. L. J. Am. Chem. Soc. 2001, 123, 12202.
(E)-1-chloro-2-(5-chloropent-3-en-1-yl)benzene (S6). Prepared according to the general procedure utilizing thionyl chloride (2.27 mL, 31.1 mmol), 5-(2-chlorophenyl)pent-1-en-3-ol (750 mg, 3.11 mmol), and DCM (12.4 mL). The crude material was purified (SiO₂, 2% ethyl acetate in hexane) to give the desired product as a 9:1 mixture of the title compound: 1-chloro-2-(3-chloropent-4-en-1-yl)benzene (clear, colorless oil (650.4 mg, 81%)). Rf = 0.77 (10% ethyl acetate in hexane, UV/magic stain). 

1H NMR (500 MHz, CDCl₃): (major isomer) δ 7.35 (1H, d, J = 7.8 Hz), 7.22-7.20 (2H, m), 7.18-7.13 (1H, m), 5.84 (1H, dt’s, J = 15.2, 7.3, 7.3 Hz), 4.04 (2H, d, J = 7.3 Hz), 2.84 (2H, t, J = 7.3 Hz), 2.40 (2H, dt’s (app q), J = 7.3 Hz); (minor isomer) δ 7.35 (1H, d, J = 7.8 Hz), 7.27-7.25 (1H, m), 7.18-7.13 (2H, m), 5.96 (1H, ddd, J = 16.6, 10.3, 8.3 Hz), 5.32 (1H, d, J = 16.6 Hz), 5.19 (1H, d, J = 10.3 Hz), 4.37 (1H, ddd (app q), J = 6.9 Hz), 2.96 (1H, ddd, J = 14.2, 8.8, 6.4 Hz), 2.89-2.82 (1H, m), 2.17-2.11 (2H, m); 13C NMR (126 MHz, CDCl₃): (both isomers) δ 138.9, 138.4, 138.2, 134.6, 133.9, 133.9, 130.5, 130.4, 129.6, 129.5, 127.7, 127.4, 126.8, 126.7, 126.7, 126.7, 116.8, 62.2, 45.1, 37.8, 32.9, 32.0, 30.5; IR (neat): 3063.8 (w), 3035.5 (w), 2933.5 (m), 2861.0 (w), 1665.3 (w), 1593.9 (w), 1571.8 (w), 1474.2 (s), 1441.7 (s), 1349.0 (w), 1250.1 (s), 1122.7 (w), 1069.0 (w), 1051.3 (s), 1036.2 (s), 749.3 (s), 675.2 (s), 445.4 (m) cm⁻¹; HRMS-(DART) for: C₁₁H₁₂Cl [M+H-HCl]⁺: calculated: 179.0628, found: 179.0620.

(E)-2-(5-(2-chlorophenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 3, Table 2). Prepared according to the general procedure utilizing PdCl₂ (3.8 mg, 0.021 mmol), B₂(pin)₂ (544.7 mg, 2.15 mmol), THF (2.1 mL), and (E)-1-chloro-2-(5-chloropent-3-en-1-yl)benzene (9:1 with regio-isomeric allyl chloride, 500 mg, 2.15 mmol). The crude material was purified (SiO₂, 5% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (525.7 mg, 80%). Rf = 0.36 (10% ethyl acetate in hexane, UV/magic stain). 

1H NMR (500 MHz, CDCl₃): δ 7.32 (1H, dd, J = 7.8, 1.0 Hz), 7.20 (1H, dd, J = 7.8, 2.0 Hz), 7.16 (1H, ddd (app dt’s), J = 7.8, 7.8, 2.0 Hz), 7.11 (1H, ddd (app dt’s), J = 7.8, 7.8, 2.0 Hz), 5.58-5.42 (2H, m), 2.77 (2H, t, J = 7.8 Hz), 2.31 (2H, dt’s (app q), J = 5.9 Hz), 1.65 (2H, d, J = 6.8 Hz), 1.25 (12H, s); 13C NMR (126 MHz, CDCl₃): δ 139.7, 133.9, 130.4, 129.6, 129.3, 127.0, 126.5, 125.8, 83.1, 33.8, 32.6, 24.7; IR (neat): 3063.8 (w), 2978.3 (m), 2931.5 (m), 1641.2 (w), 1572.0 (w), 1473.9 (m), 1443.2 (m), 1361.1 (s), 1326.0 (s), 1272.7 (m), 1214.3 (w), 1143.6 (s), 1051.7 (w), 967.3 (s), 882.3 (w), 847.9 (s), 750.4 (s), 675.7 (m), 578.5 (w) cm⁻¹; HRMS-(DART) for: C₁₇H₂₅ClO₂ [M+H⁺]: calculated: 307.1636, found: 307.1631.

3-(2-chloro-4-methylphenyl)propanal (S7). Prepared according to the general procedure utilizing Pd(OAc)₂ (112 mg, 0.500 mmol), tetrabutylammonium chloride (6.95 g, 25.0 mmol), sodium bicarbonate (5.25 g, 62.5 mmol), dimethylformamide (50 mL), 2-chloro-1-iodo-4-methylbenzene (6.31 mL, 25.0 mmol), and allyl alcohol (2.55 mL, 37.5 mmol). The crude material was purified (SiO₂, 5% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (2.20 g, 38%). Rf = 0.40 (10% ethyl acetate in hexane, UV/magic stain). 

1H NMR (500 MHz, CDCl₃): δ 9.82 (1H, s), 7.18 (1H, d, J = 1.0 Hz), 7.12 (1H, d, J = 8.0
Hz), 6.99 (1H, dd, \( J = 8.0, 1.5 \) Hz), 3.02 (2H, t, \( J = 7.5 \) Hz), 2.77 (2H, td, \( J = 7.5, 7.5, 1.0 \) Hz), 2.30 (3H, s); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 201.2, 137.9, 134.7, 133.4, 130.2, 130.0, 127.7, 43.6, 25.7, 20.6; IR (neat): 2923.8 (w), 2821.7 (w), 2722.7 (w), 1722.8 (s), 1610.3 (w), 1494.3 (s), 1446.8 (m), 1406.4 (m), 1214.7 (w), 1052.6 (s), 878.3 (s), 818.9 (s), 687.3 (m), 563.8 (m), 490.9 (m) cm\(^{-1}\); HRMS-(DART) for: C\(_{10}\)H\(_{10}\)ClO \([\text{M-H}]^+\): calculated: 181.0420, found: 181.0426.

5-(2-chloro-4-methylphenyl)pent-1-en-3-ol (S8). Prepared according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 11.0 mL, 11.0 mmol), 3-(2-chloro-4-methylphenyl)propanal (1.00 g, 5.74 mmol), and THF (11.0 mL). The crude material was purified (SiO\(_2\), 10% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (1.05 g, 91%). \( R_f = 0.31 \) (10% ethyl acetate in hexane, UV/magic stain). \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.12 (1H, d, \( J = 7.5 \) Hz), 6.99 (1H, dd, \( J = 8.0, 1.0 \) Hz), 5.92 (1H, ddd (app dt’s), \( J = 17.0, 1.5, 1.5 \) Hz), 5.15 (1H, ddd (app dt’s), \( J = 11.0, 1.0, 1.0 \) Hz), 4.15 (1H, ddd (app q), \( J = 6.5 \) Hz), 2.83 (1H, ddd, \( J = 15.0, 9.0, 6.0 \) Hz), 2.76 (1H, ddd, \( J = 14.5, 9.5, 7.0 \) Hz), 2.30 (3H, s), 1.86-1.81 (2H, m), 1.77 (1H, br s); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta \) 134.8, 137.3, 136.2, 133.5, 130.1, 129.9, 127.6, 114.9, 72.5, 36.9, 29.0, 20.6; IR (neat): 3348.7 (br), 2979.6 (s), 2923.4 (m), 2864.6 (m), 1610.5 (s), 1500.4 (m), 1452.4 (m), 1425.5 (m), 1311.6 (s), 1180.4 (s), 1109.5 (s), 1109.5 (s), 1048.3 (s), 990.4 (s), 923.1 (m), 820.2 (s), 687.4 (m) cm\(^{-1}\); HRMS-(DART) for: C\(_{12}\)H\(_{14}\)Cl \([\text{M+H-HCl}]^+\): calculated: 193.0784, found: 193.0774.

\((E)\)-2-chloro-1-(5-chloropent-3-en-1-yl)-4-methylbenzene (S9). Prepared according to the general procedure utilizing thionyl chloride (3.44 mL, 47.5 mmol), 5-(2-chloro-4-methylphenyl)pent-1-en-3-ol (1.00 g, 4.75 mmol), and DCM (14.4 mL). The crude material was purified (SiO\(_2\), 2% ethyl acetate in hexane) to give the desired product as a 6.7:1 mixture of the title compound: 2-chloro-1-(3-chloropent-4-en-1-yl)-4-methylbenzene (997 mg, 90%). \( R_f = 0.38 \) (4% DCM in hexane, UV/magic stain). \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): (major isomer) \( \delta \) 7.16 (1H, s), 7.06 (1H, d, \( J = 7.5 \) Hz), 6.98 (1H, d, \( J = 7.0 \) Hz), 5.81 (1H, dt’s, \( J = 15.5, 6.5, 6.5 \) Hz), 5.64 (1H, dt’s, \( J = 15.0, 7.0, 7.0 \) Hz), 4.02 (2H, d, \( J = 7.5 \) Hz), 2.77 (2H, t, \( J = 7.5 \) Hz), 2.40 (2H, dt’s (app q), \( J = 7.0 \) Hz), 2.29 (3H, s); (minor isomer) \( \delta \) 7.16 (1H, s), 7.12 (1H, d, \( J = 7.5 \), 7.07-6.97 (1H, m), 5.93 (1H, ddd, \( J = 17.0, 10.0, 8.0 \) Hz), 5.29 (1H, d, \( J = 16.5 \) Hz), 5.17 (1H, d, \( J = 10.0 \) Hz), 4.34 (1H, ddd (app q), \( J = 7.5 \) Hz), 2.89 (1H, ddd, \( J = 14.5, 9.0, 6.5 \) Hz), 2.83-2.76 (1H, m), 2.29 (3H, s), 2.16-2.06 (2H, m); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): (both isomers, one overlapping signal) \( \delta \) 138.3, 137.7, 137.4, 135.7, 135.2, 134.8, 133.6, 133.5, 130.3, 130.2, 130.1, 129.9, 127.6, 127.5, 126.7, 116.8, 62.3, 45.2, 37.9, 32.5, 32.1, 30.1, 20.7; IR (neat): 3033.1 (w), 2924.7 (m), 2831.3 (w), 1665.8 (w), 1610.1 (w), 1494.1 (s), 1441.2 (m), 1250.1 (m), 1214.6 (w), 1049.7 (s), 966.0 (s), 930.9 (w), 875.0 (s), 817.9 (s), 686.6 (s), 573.2 (m), 446.5 (w) cm\(^{-1}\); HRMS-(DART) for: C\(_{12}\)H\(_{14}\)Cl \([\text{M+H-HCl}]^+\): calculated: 193.0784, found: 193.0788.
(E)-2-(5-(2-chloro-4-methyl-phenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S10).

Prepared according to the general procedure utilizing PdCl$_2$ (7.0 mg, 0.039 mmol), B$_2$(pin)$_2$ (997 mg, 3.93 mmol), THF (3.9 mL), and (E)-2-chloro-1-(5-chloropent-3-en-1-yl)-4-methylbenzene (6.67:1 with regio-isomeric allyl chloride, 900 mg, 3.93 mmol). The crude material was purified (SiO$_2$, 5% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.08 g, 85%). R$_f$ = 0.42 (5% ethyl acetate in hexane, UV/magic stain).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.08 (1H, d, $J$ = 7.5 Hz), 6.96 (1H, dd, $J$ = 7.5, 1.0 Hz), 5.53-5.42 (2H, m), 2.72 (2H, t, $J$ = 8.0 Hz), 2.30-2.26 (2H, m), 2.28 (3H, s), 1.65 (2H, d, $J$ = 6.5 Hz), 1.25 (12H, s);

$^{13}$C NMR (126 MHz, CDCl$_3$): δ 136.9, 136.5, 133.5, 130.1, 129.8, 129.7, 127.3, 125.7, 83.1, 33.4, 32.8, 24.7, 20.6; IR (neat): 2977.8 (m), 2928.3 (w), 2862.9 (w), 1610.5 (w), 1451.3 (w), 1360.2 (s), 1325.1 (s), 1272.4 (w), 1214.2 (w), 1164.8 (s), 1050.1 (w), 1004.5 (s), 882.2 (m), 847.2 (m), 818.1 (m), 686.3 (w), 673.9 (w), 575.9 (w), 449.9 (w) cm$^{-1}$; HRMS-(DART) for: C$_{18}$H$_{27}$BClO$_2$ [M+H]$^+$: calculated: 321.1793, found: 321.1797.

2-chloro-3-methylaniline (S11). To a solution of 2-chloro-1-methyl-3-nitrobenzene (5.00 g, 29.1 mmol) in ethanol (48 mL) was added Fe(0) (4.88 g, 87.4 mmol) and conc. HCl (2.43 mL) at room temperature. The reaction mixture was heated to reflux for 1.5 hours and then cooled to room temperature. The solvent was removed under reduced pressure and the residue was diluted with sat. aq. NH$_4$Cl and extracted with ethyl acetate (3 x 75 mL). The organic layers were combined and washed with DI H$_2$O (75 mL), brine (75 mL), dried over sodium sulfate, and concentrated under reduced pressure. The crude material was purified (SiO$_2$, 5% ethyl acetate in hexane) to give the product as a clear, yellow oil (2.78 g, 67%). $^1$H NMR (500 MHz, CDCl$_3$): δ 6.96 (1H, dd (app t), $J$ = 8.0 Hz), 6.65-6.63 (2H, m), 4.07 (2H, br s), 2.35 (3H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 143.0, 136.8, 126.7, 120.3, 119.8, 113.3, 20.4; IR (neat): 3471.2 (br), 3381.2 (br), 3060.8 (w), 3026.1 (w), 2979.9 (w), 2950.3 (w), 1611.3 (s), 1469.5 (s), 1313.1 (m), 1167.7 (w), 1095.2 (w), 1048.0 (s), 943.9 (w), 764.9 (s), 708.5 (m), 598.2 (s) cm$^{-1}$; HRMS-(DART) for: C$_7$H$_9$ClN [M]$^+$: calculated: 142.0424, found: 142.0426.

2-chloro-1-iodo-3-methylbenzene (S12). To a 250 mL round-bottomed flask equipped with a magnetic stir bar was added 2-chloro-3-methylaniline (2.25 g, 15.9 mmol) in DI H$_2$O (41 mL) and conc. HCl (8.1 mL). The reaction mixture was cooled to 0 $^\circ$C (ice/water bath) and treated dropwise with a solution of sodium nitrite (1.42 g, 20.6 mmol) in DI H$_2$O (10 mL), maintaining the reaction temperature to less than 10 $^\circ$C. After completing addition, the reaction mixture was allowed to stir at 0 $^\circ$C for 30 minutes. To the mixture was added dropwise a solution of potassium iodide (4.22 g, 25.4 mmol) in DI H$_2$O (10 mL). The mixture rapidly turned to a deep black solution. After the addition was complete, the mixture was heated to 60 $^\circ$C and allowed to stir for 1 h. The cooled solution was washed with 10% sodium bicarbonate (50 mL), 1M sodium thiosulfate (50 mL), 10% hydrochloric acid (50 mL), water (50 mL), and brine (50 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified (SiO$_2$, 100% hexanes), to give the product as a clear, slightly yellow oil (2.51 g, 63%).
5-(2-chloro-3-methylphenyl)pent-1-en-3-ol (S13). To a flame-dried round-bottomed flask equipped with magnetic stir bar in the glovebox was added Pd(OAc)$_2$ (71.3 mg, 0.32 mmol). The flask was removed from the glovebox, charged with tetrabutylammonium chloride (5.29 g, 19.0 mmol) and sodium bicarbonate (3.33 g, 39.7 mmol) and sealed with a septum. The flask was evacuated and back-filled with nitrogen (3x) followed by addition of dimethylformamide (32 mL). After stirring at room temperature for 10 minutes, 2-chloro-1-iodo-3-methylbenzene (2.50 g, 9.90 mmol) followed by allyl alcohol (2.16 mL, 31.7 mmol) were added and the resulting mixture was heated to 40 °C for 12 hours. The resulting dark reaction mixture was cooled to room temperature, diluted with diethyl ether (50 mL) and water (50 mL) and the layers separated. The aqueous layer was extracted with diethyl ether (3 x 50 mL) and the combined organic layers washed with a 50/50 water/brine solution (2 x 50 mL). The organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude reaction mixture was partially purified using flash chromatography (SiO$_2$, 10% ethyl acetate in hexane) to give a clear, yellow oil (crude, 1.21 g) which was used in the next step without any further purification.

The title compound was prepared according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 13.3 mL, 13.3 mmol), 3-(2-chloro-3-methylphenyl)propanal (1.21 g, 6.63 mmol), and THF (13.3 mL). The crude material was purified (SiO$_2$, 10% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (1.12 g, 54% over 2 steps). H$_r$ = 0.37 (10% ethyl acetate in hexane, UV/magic stain). H NMR (500 MHz, CDCl$_3$): δ 7.40-7.05 (3H, m), 5.93 (1H, ddd, J = 17.0, 11.0, 6.5 Hz), 5.28 (1H, ddd (app dd’s), J = 17.0, 1.5, 1.5 Hz), 5.15 (1H, ddd (app dd’s), J = 10.5, 1.5, 1.5 Hz), 4.14 (1H, ddd (app qq), J = 6.0 Hz), 2.89 (1H, ddd, J = 14.5, 9.5, 6.0 Hz), 2.61 (1H, ddd, J = 14.0, 9.5, 6.5 Hz), 2.39 (3H, s), 1.91-1.80 (2H, m), 1.66 (1H, br s); C NMR (126 MHz, CDCl$_3$): δ 140.9, 139.6, 136.6, 134.2, 128.7, 127.9, 126.1, 114.9, 72.5, 36.7, 30.0, 20.8; IR (neat): 3334.1 (br), 2979.4 (w), 2925.2 (w), 2862.9 (w), 1466.2 (m), 1453.7 (m), 1419.2 (m), 1380.5 (w), 1166.6 (w), 1043.2 (s), 989.5 (s), 922.4 (s), 770.2 (s), 725.1 (s) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{12}$ClI$^+$: calculated: 251.9203, found: 251.9213.

$(E)$-2-chloro-1-(5-chloropent-3-en-1-yl)-3-methylbenzene (S14). Prepared according to the general procedure utilizing thionyl chloride (2.53 mL, 34.5 mmol), 5-(2-chloro-3-methylphenyl)pent-1-en-3-ol (734 mg, 3.48 mmol), and DCM (12.4 mL). The crude material was purified (SiO$_2$, 2% ethyl acetate in hexane) to give the desired product as a 6.7:1 mixture of the title compound: 2-chloro-1-(3-chloropent-4-en-1-yl)-3-methylbenzene (655 mg, 82%). H$_r$ = 0.38 (4%}
DCM in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): (major isomer) $\delta$ 7.11-7.04 (3H, m), 5.85 (1H, dt’s, $J = 15.0$, 7.0, 7.0 Hz), 5.66 (1H, dt’s, $J = 15.5$, 7.0, 7.0 Hz), 4.04 (2H, d, $J = 7.0$ Hz), 2.84 (2H, t, $J = 7.0$ Hz), 2.42-2.37 (2H, m), 2.40 (3H, s); (minor isomer) $\delta$ 7.11-7.04 (3H, m), 5.95 (1H, ddd (app dt’s), $J = 16.5$, 10.0, 10.0 Hz), 5.31 (1H, d, $J = 17.0$ Hz), 5.19 (1H, d, $J = 10.5$ Hz), 4.37 (1H, ddd (app q), $J = 7.5$ Hz), 2.96 (1H, ddd (app dt’s), $J = 15.0$, 9.0, 9.0 Hz), 2.89-2.83 (1H, m), 2.40 (3H, s), 2.16-2.11 (2H, m);

$^{13}$C NMR (126 MHz, CDCl$_3$): (both isomers) $\delta$ 139.1, 138.6, 138.3, 136.8, 136.6, 134.9, 134.2, 134.2, 129.0, 128.8, 128.0, 127.8, 126.6, 126.2, 126.1, 116.8, 62.4, 45.2, 37.8, 33.5, 32.0, 31.1, 20.8, 20.8; IR (neat): 3054.7 (w), 2951.7 (m), 2858.6 (w), 1665.6 (w), 1466.7 (s), 1453.9 (s), 1249.7 (m), 1044.8 (s), 965.2 (s), 771.4 (s), 679.0 (m), 630.0 (s), 566.0 (w) cm$^{-1}$; HRMS-(DART) for: C$_{18}$H$_{27}$BClO$_2$ [M+H]+: calculated: 321.1793, found: 321.1785.

(E)-2-(5-(2-chloro-3-methylphenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S15). Prepared according to the general procedure utilizing PdCl$_2$ (5.1 mg, 0.029 mmol), B$_2$(pin)$_2$ (726 mg, 2.86 mmol), THF (2.9 mL), and (E)-2-chloro-1-(3-chloropent-4-en-1-yl)-3-methylbenzene (6.7:1 with regio-isomeric allyl chloride, 655 mg, 2.86 mmol). The crude material was purified (SiO$_2$, 5% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (789 mg, 86%). $R_f$ = 0.38 (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.07-7.04 (3H, m), 5.54-5.43 (2H, m), 2.78 (2H, t, $J = 8.0$ Hz), 2.38 (3H, s), 2.30 (2H, dt’s (app q), $J = 6.5$ Hz), 1.65 (2H, d, $J = 6.0$ Hz), 1.25 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 139.9, 136.3, 134.2, 129.8, 128.4, 127.8, 125.9, 125.6, 83.1, 34.4, 32.6, 24.7, 20.8; IR (neat): 2977.6 (m), 2930.3 (s), 1466.8 (w), 1359.3 (s), 1323.6 (s), 1213.8 (s), 1164.8 (s), 1107.7 (m), 882.7 (w), 846.6 (m), 770.6 (m), 724.2 (s), 673.7 (s) cm$^{-1}$; HRMS-(DART) for: C$_{18}$H$_{27}$BClO$_2$ [M+H]+: calculated: 321.1793, found: 321.1785.

3-(2-chloro-5-methoxyphenyl)propanal (S16). Prepared according to the general procedure utilizing Pd(OAc)$_2$ (33.4 mg, 0.149 mmol), tetrabutylammonium chloride (2.07 g, 7.45 mmol), sodium bicarbonate (1.56 g, 18.6 mmol), dimethylformamide (15 mL), 1-chloro-2-iodo-4-methoxybenzene (2.00 g, 7.45 mmol), and allyl alcohol (0.76 mL, 11.2 mmol). The crude material was purified (SiO$_2$, 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear, slightly yellow oil (1.25 g, 84%). $R_f$ = 0.49 (30% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.82 (1H, s), 7.23 (1H, d, $J = 9.0$ Hz), 6.78 (1H, d, $J = 2.0$ Hz), 6.70 (1H, dd, $J = 8.5$, 3.0 Hz), 3.77 (3H, s), 3.01 (2H, t, $J = 7.5$ Hz), 2.78 (2H, t, $J = 7.5$ Hz); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 200.9, 158.3, 138.8, 130.0, 125.0, 116.0, 113.1, 55.3, 43.3, 26.3; IR (neat): 3003.4 (w), 2938.8 (w), 2836.1 (w), 2723.9 (w), 1721.6 (s), 1597.3 (m), 1575.8 (m), 1476.3 (s), 1408.5 (m), 1298.2 (s), 1278.3 (s), 1241.1 (s), 1191.1 (s), 1021.7 (s), 868.8 (w), 805.4 (m), 630.9 (s), 858.7 (w) cm$^{-1}$; HRMS-(DART) for: C$_{10}$H$_{15}$ClNO$_2$ [M+NH$_4$]+: calculated: 216.0791, found: 216.0788.
5-(2-chloro-5-methoxyphenyl)pent-1-en-3-ol (S17).
Prepared according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 12.0 mL, 12.0 mmol), 3-(2-chloro-5-methoxyphenyl)propanal (1.20 g, 6.04 mmol), and THF (12.0 mL). The crude material was purified (SiO$_2$, 10% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (1.22 g, 89%). $R_f = 0.22$ (10% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.23 (1H, d, $J$ = 9.0 Hz), 6.79 (1H, d, $J$ = 3.0 Hz), 6.69 (1H, dd, $J$ = 3.0, 8.5 Hz), 5.92 (1H, ddd, $J$ = 16.5, 10.0, 5.5 Hz), 5.27 (1H, ddd (app dt’s), $J$ = 17.0, 1.5, 1.5 Hz), 5.16 (1H, d (app dt’s), $J$ = 10.5, 1.5, 1.5 Hz), 4.16 (1H, ddd (app q), $J$ = 6.5 Hz), 3.77 (3H, s), 2.83 (1H, ddd, $J$ = 14.0, 9.5, 6.5 Hz), 2.75 (1H, ddd, $J$ = 14.0, 9.5, 6.5 Hz), 1.90-1.79 (2H, m), 1.69 (1H, br s); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 150.3, 125.3, 115.9, 115.0, 112.8, 72.4, 55.4, 36.7, 29.8; IR (neat): 3360.6 (br), 3003.1 (w), 2936.2 (m), 2864.5 (s), 2836.7 (s), 1597.0 (m), 1575.3 (m), 1476.0 (s), 1419.8 (s), 1277.2 (s), 1161.7 (s), 1023.3 (s), 923.9 (m), 855.2 (s), 631.7 (s), 460.6 (s) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{14}$ClO [M+H-H$_2$O]+: calculated: 209.0733, found: 209.0731.

(E)-1-chloro-2-(5-chloropent-3-en-1-yl)-4-methoxybenzene (S18).
Prepared according to the general procedure utilizing thionyl chloride (3.52 mL, 48.5 mmol), 5-(2-chloro-5-methoxyphenyl)pent-1-en-3-ol (1.10 g, 4.85 mmol), and DCM (16 mL). The crude material was purified (SiO$_2$, 2% ethyl acetate in hexane) to give the desired product as a 5:1 mixture of the title compound: 1-chloro-2-(3-chloropent-4-en-1-yl)-4-methoxybenzene (clear, colorless oil (1.08 g, 91%)). $R_f = 0.65$ (10% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.5 Hz), 6.84 (1H, d, $J$ = 3.5 Hz), 6.70 (1H, dd, $J$ = 8.5, 3.0 Hz), 5.83 (1H, dt’$s$, $J$ = 15.0, 7.0, 7.0 Hz), 5.66 (1H, dtt’$s$, $J$ = 15.0, 7.5, 7.5, 1.0, 1.0 Hz), 4.03 (2H, d, $J$ = 7.0 Hz), 3.78 (3H, s), 2.78 (2H, t, $J$ = 8.0 Hz), 2.38 (2H, dt’$s$, $J$ = 10.0 Hz) (minor isomer) $\delta$ 7.24 (1H, d, $J$ = 8.5 Hz), 6.79 (1H, dd, $J$ = 3.5 Hz), 6.71 (1H, dd, $J$ = 8.5, 3.5 Hz), 5.94 (1H, ddd, $J$ = 17.0, 10.0, 7.5 Hz), 5.31 (1H, ddd (app dt’$s$), $J$ = 17.0, 1.0, 1.0 Hz), 5.18 (1H, d, $J$ = 10.5 Hz), 4.36 (1H, ddd (app q), $J$ = 7.5 Hz), 3.79 (3H, s), 2.89 (1H, ddd, $J$ = 13.5, 9.5, 6.0 Hz), 2.83-2.76 (2H, m), 2.17-2.07 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$): (both isomers) $\delta$ 159.3, 158.2, 139.8, 139.4, 138.2, 134.6, 130.2, 130.0, 126.8, 125.3, 116.9, 116.1, 116.0, 115.9, 113.0, 112.8, 62.2, 55.4, 45.2, 37.7, 36.6, 33.2, 31.9, 30.8; IR (neat): 3003.5 (w), 2939.1 (w), 2836.7 (w), 2723.3 (w), 1723.4 (s), 1597.8 (m), 1576.2 (m), 1477.5 (s), 1420.4 (m), 1356.3 (m), 1299.0 (m), 1279.1 (s), 1063.9 (m), 1022.5 (m), 936.3 (w), 870.0 (m), 631.3 (m cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{14}$ClO [M+] calculated: 244.0422, found: 244.0422.

(E)-2-[5-(2-chloro-5-methoxyphenyl)pent-2-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S19).
Prepared according to the general procedure utilizing PdCl$_2$ (5.3 mg, 0.030 mmol), B$_2$(pin)$_2$ (259 mg, 3.00 mmol), THF (3.0 mL), and (E)-1-chloro-2-(5-chloropent-3-en-1-yl)-4-methoxybenzene (5:1 with regio-isomeric allyl chloride, 733 mg, 3.00 mmol). The crude material was purified (SiO$_2$, 5% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.10 g, 88%). $R_f = 0.22$ (10% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.23 (1H, d, $J$ = 9.0 Hz), 6.79 (1H, d, $J$ = 3.0 Hz), 6.69 (1H, dd, $J$ = 3.0, 8.5 Hz), 5.92 (1H, ddd, $J$ = 16.5, 10.0, 5.5 Hz), 5.27 (1H, ddd (app dt’s), $J$ = 17.0, 1.5, 1.5 Hz), 5.16 (1H, d (app dt’s), $J$ = 10.5, 1.5, 1.5 Hz), 4.16 (1H, ddd (app q), $J$ = 6.5 Hz), 3.77 (3H, s), 2.83 (1H, ddd, $J$ = 14.0, 9.5, 6.5 Hz), 2.75 (1H, ddd, $J$ = 14.0, 9.5, 6.5 Hz), 1.90-1.79 (2H, m), 1.69 (1H, br s); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 150.3, 125.3, 115.9, 115.0, 112.8, 72.4, 55.4, 36.7, 29.8; IR (neat): 3360.6 (br), 3003.1 (w), 2936.2 (m), 2864.5 (s), 2836.7 (s), 1597.0 (m), 1476.0 (s), 1419.8 (s), 1277.2 (s), 1161.7 (s), 1023.3 (s), 923.9 (m), 855.2 (s), 631.7 (s), 460.6 (s) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{14}$ClO [M+] calculated: 244.0422, found: 244.0422.
5-chloro-6-iodobenzo[d][1,3]dioxole (S20).  To an oven-dried 250 mL RBF equipped with a stir bar was added a solution of 5-chlorobenzo[d][1,3]dioxole (2.00 g, 12.8 mmol) in acetonitrile (60 mL). To the flask was added trifluoroacetic acid (2.90 g, 25.4 mmol) followed by N-iodosuccinimide (8.60 g, 38.2 mmol), and the mixture was allowed to stir in the dark at room temperature under nitrogen for 24 hours. The dark brown solution was concentrated under reduced pressure and the crude residue was purified (SiO$_2$, 0-4% ethyl acetate in hexane) to give the desired product as a slightly yellow oil (1.80 g, 50%). $R_f = 0.52$ (5% ethyl acetate in hexane, UV/magic stain). All spectral data are in accordance with the literature.$^8$

3-(6-chlorobenzo[d][1,3]dioxol-5-yl)propanal (S21). Prepared according to the general procedure utilizing Pd(OAc)$_2$ (28.6 mg, 0.128 mmol), tetrabutylammonium chloride (1.77 g, 6.37 mmol), sodium bicarbonate (1.34 g, 15.9 mmol), dimethylformamide (20 mL), 5-chloro-6-iodobenzo[d][1,3]dioxole (1.80 g, 6.37 mmol), and allyl alcohol (0.65 mL, 9.6 mmol). The crude material was purified (SiO$_2$, 6% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (771 mg, 57%). $R_f = 0.42$ (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.81 (1H, t, $J=1.5$ Hz), 6.82 (1H, s), 6.71 (1H, s), 5.94 (2H, s), 2.96 (2H, t, $J=1.5$ Hz); $^1^C$ NMR (126 MHz, CDCl$_3$): $\delta$ 210.1, 146.8, 146.7, 130.9, 125.2, 110.0, 109.9, 101.7, 43.8, 26.1; IR (neat): 2898.4 (w), 2826.2 (w), 2726.4 (w), 1721.7 (s), 1503.7 (s), 1477.2 (s), 1413.2 (m), 1237.7 (s), 1160.0 (w), 1119.7 (s), 1035.4 (s), 931.7 (s), 863.3 (m), 838.6 (m), 433.0 (w) cm$^{-1}$; HRMS-(DART) for: C$_{10}$H$_{10}$ClO $[M]^+$: calculated: 212.0240, found: 212.0237.

5-(6-chlorobenzo[d][1,3]dioxol-5-yl)pent-1-en-3-ol (S22). Prepare according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 7.2 mL, 7.2 mmol), 3-(6-chlorobenzo[d][1,3]dioxol-5-yl)propanal (765 mg, 3.60 mmol), and THF (36 mL). The crude material was purified (SiO$_2$, 10% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (726 mg, 84%). $R_f = 0.24$ (10% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.81 (1H, s), 6.71 (1H, s), 5.96-5.87 (1H, m), 5.93 (2H, s), 5.26 (1H, ddd (app
(E)-5-chloro-6-(5-chloropent-3-en-1-yl)benzo-[d][1,3]dioxole (S23). Prepared according to the general procedure utilizing thionyl chloride (2.19 mL, 30.1 mmol), 5-(6-chlorobenzo-[d][1,3]dioxol-5-yl)pent-1-en-3-ol (726 mg, 3.01 mmol), and DCM (8.5 mL). The crude material was purified (SiO2, 2% ethyl acetate in hexane) to give the desired product as a 11:1 mixture of the title compound: 5-chloro-6-(3-chloropent-4-en-1-yl)benzo[d][1,3]dioxole (701 mg, 90%).

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\begin{align*}
\text{H NMR (500 MHz, CDCl}_3\text{):} & \quad \delta 6.82 (1H, s), 6.04 (1H, ddt, J = 17.5, 7.5, 7.5 Hz), 5.59 (1H, ddt, J = 17.5, 7.0, 7.0 Hz), 4.04 (2H, d, J = 7.0 Hz), 2.72 (2H, t, J = 7.5 Hz), 2.33 (2H, dtt's, J = 10.0 Hz), 2.14 (2H, m); \\
\text{IR (neat):} & \quad 2977.8 (w), 2929.2 (w), 1503.8 (m), 1476.7 (s), 1358.0 (s), 1324.0 (s), 1253.2, 1169.1, 110.0, 109.9, 109.8, 101.5, 101.4, 83.2, 33.7, 32.8, 24.7; \\
\text{HRMS-(DART) for:} & \quad C_{18}H_{24}BClO_4 [M]^+; \text{ calculated: 350.1456, found: 350.1458.}
\end{align*}
\]
3-(2-chloro-5-(trifluoromethyl)phenyl)propanal (S25).
Prepared according to the general procedure utilizing Pd(OAc)$_2$ (22.5 mg, 0.100 mmol), tetrabutylammonium chloride (1.39 g, 5.00 mmol), sodium bicarbonate (1.05 g, 12.5 mmol), dimethylformamide (10 mL), 4-chloro-3-iodobenzotrifluoride (0.78 mL, 5.00 mmol), and allyl alcohol (0.51 mL, 7.50 mmol). The crude material was purified (SiO$_2$, 6% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (922.5 mg, 78%). $R_f = 0.42$ (5% ethyl acetate in hexane, UV/magic stain).$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.82 (1H, d, $J = 1.0$ Hz), 7.51 (1H, d, $J = 1.5$ Hz), 7.46 (1H, d, $J = 8.3$ Hz), 7.41 (1H, d, $J = 8.8$ Hz), 3.10 (2H, t, $J = 7.3$ Hz), 2.83 (2H, t, $J = 7.3$ Hz); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 200.1, 139.1, 137.6, 130.1, 129.4 (q, $J_{C-F} = 32.4$ Hz), 127.3 (q, $J_{C-F} = 3.8$ Hz), 126.6 (q, $J_{C-F} = 271.8$ Hz), 43.0, 26.0; IR (neat): 2942.7 (w), 2901.9 (w), 2826.4 (w), 2728.2 (w), 1724.5 (s), 1610.3 (m), 1583.2 (w), 1412.4 (m), 1325.2 (s), 1276.6 (m), 1165.4 (s), 1119.2 (s), 1080.9 (s), 1056.0 (s), 904.1 (s), 825.5 (s), 728.7 (m), 507.5 (m), 458.1 (m), 439.6 (m), 386.3 (w) cm$^{-1}$; HRMS-(DART) for: C$_{10}$H$_7$ClF$_3$O [M-H]$^+$: calculated: 235.0138, found: 235.0140.

5-(2-chloro-5-(trifluoromethyl)phenyl)pent-1-en-3-ol (S26).
Prepared according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 31.0 mL, 31.0 mmol), 3-(2-chloro-5-(trifluoromethyl)phenyl)propanal (3.6552 g, 15.5 mmol), and THF (30 mL). The crude material was purified (SiO$_2$, 12% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear, colorless oil (3.6363 g, 90%). $R_f = 0.26$ (10% ethyl acetate in hexane, UV/magic stain).$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.51 (1H, d, $J = 2.0$ Hz), 7.45 (1H, d, $J = 8.3$ Hz), 7.39 (1H, d, $J = 8.3$ Hz), 5.92 (1H, ddd, $J = 17.1$, 10.3, 6.4 Hz), 5.28 (1H, d, $J = 17.1$ Hz), 5.17 (1H, d, $J = 10.3$ Hz), 4.17 (1H, ddd (app q), $J = 6.4$ Hz), 2.96-2.90 (1H, m), 2.87-2.81 (1H, m), 1.96-1.77 (3H, m); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 140.6, 137.7, 137.7, 129.9, 129.2 (q, $J_{C-F} = 32.4$ Hz), 127.2 (q, $J_{C-F} = 3.8$ Hz), 124.2 (q, $J_{C-F} = 3.8$ Hz), 123.8 (q, $J_{C-F} = 271.8$ Hz), 115.3, 72.4, 36.3, 29.5; IR (neat): 3348.4 (br), 3082.8 (w), 2937.1 (w), 2870.9 (w), 1644.9 (m), 1482.4 (m), 1412.0 (m), 1362.2 (s), 1274.4 (m), 1166.2 (s), 1121.0 (s), 1080.3 (s), 1042.0 (s), 990.0 (m), 924.9 (s), 823.9 (s), 730.3 (m), 513.3 (m), 441.0 (m), 385.7 (m) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{11}$ClF$_3$ [M+H-H$_2$O]$^+$: calculated: 247.0501, found: 247.0504.

(E)-1-chloro-2-(5-chloropent-3-en-1-yl)-4-(trifluoromethyl)benzene (S27).
Prepared according to the general procedure utilizing thionyl chloride (8.36 mL, 115 mmol), 5-(2-chloro-5-(trifluoromethyl)phenyl)pent-1-en-3-ol (2.8113 g, 10.7 mmol), and DCM (45 mL). The crude material was purified (SiO$_2$, 2% ethyl acetate in hexane) to give the desired product as a 10:1 mixture of the title compound: 1-chloro-2-(3-chloropent-4-en-1-yl)-4-(trifluoromethyl)benzene (clear, colorless oil (2.1999 g, 72%). $R_f = 0.51$ (5% ethyl acetate in hexane, UV/magic stain).$^1$H NMR (500 MHz, CDCl$_3$): (major isomer) $\delta$ 7.51-7.38 (3H, m), 5.81 (1H, dt’s, $J = 15.1$, 6.8, 6.8 Hz), 5.65 (1H, dtt’s, $J = 15.1$, 6.8, 6.8, 1.5, 1.5 Hz), 4.02 (2H, dd, $J = 6.8$, 1.0 Hz), 2.88 (2H, t, $J = 7.3$ Hz), 2.41 (2H, dt’s (app q), $J = 7.3$ Hz); (minor isomer) $\delta$ 7.51-7.38 (3H, m), 5.94 (1H, ddd, $J = 17.1$, 10.2, 7.8 Hz), 5.32 (1H, ddd (app dt’s), $J = 17.1$, 1.0, 1.0 Hz), 5.21 (1H, d, $J = 9.8$ Hz), 4.37 (1H, ddd
$^{1}{H}$ NMR (500 MHz, CDCl$_3$): δ 7.46-7.41 (2H, m), 7.37 (1H, dd, $J = 8.3, 2.0$ Hz), 5.54-5.48 (1H, m), 5.45-5.40 (1H, m), 2.81 (2H, t, $J = 7.8$ Hz), 2.32 (2H, dtd's, $J = 7.8, 7.8, 1.5$ Hz), 1.64 (2H, d, $J = 7.3$ Hz), 1.24 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 140.7, 137.7, 129.8, 129.0 (q, $J_{C-F} = 33.4$ Hz), 128.8, 127.2 (q, $J_{C-F} = 3.8$ Hz), 126.6, 123.9 (q, $J_{C-F} = 3.8$ Hz), 123.9 (q, $J_{C-F} = 271.9$ Hz), 83.2, 33.8, 32.3, 24.6; IR (neat): 2979.7 (m), 2932.5 (w), 2868.1 (w), 1609.2 (w), 1480.9 (w), 1453.9 (w), 1326.6 (m), 1271.1 (s), 1082.3 (s), 967.3 (m), 847.0 (m), 824.9 (m), 674.0 (w), 513.3 (w) cm$^{-1}$; HRMS-(DART) for: C$_{18}$H$_{24}$BClF$_3$O$_2$ [M+H]$^+$: calculated: 375.1510, found: 375.1519.

5-(2-chlorophenyl)-2-methylpent-1-en-3-ol (S29). To a flame-dried, two-neck round-bottomed flask equipped with magnetic stir bar was added freshly ground magnesium turnings (326.2 mg, 13.4 mmol). The flask was equipped with a reflux condenser and the apparatus placed under vacuum and flame-dried once more. After cooling to room temperature, the apparatus was back-filled with nitrogen and the magnesium turnings were vigorously stirred for 1 hour. THF (12 mL) was added followed by 2-bromopropene (1.08 mL, 12.2 mmol). After approximately 5 minutes, the reaction mixture became a slightly cloudy brown color and began to reflux. After refluxing under the heat of the reaction approximately 10 minutes, the reaction was returned to reflux for an additional 30 minutes, and the resulting light brown mixture was cooled to 0 °C (ice/water bath) and treated dropwise with a solution of 3-(2-chlorophenyl)propanal (1.03 g, 6.10 mmol) in THF (12 mL). After stirring at room temperature for 1 hour, the resulting brown, cloudy mixture was returned to 0 °C and excess Grignard reagent was carefully quenched with water (5 mL) followed by addition of saturated aqueous ammonium chloride (20 mL). The resulting mixture was diluted with ethyl acetate (50 mL) and water (20 mL) and the layers separated. The aqueous layer was extracted with ethyl acetate (3 x 50 mL) and the combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified (SiO$_2$, 12% ethyl acetate in hexane) to give the desired product as a clear, slightly yellow oil (1.1141 g, 87%). $R_f = 0.23$ (10% ethyl acetate in hexane, UV/magic

(E)-2-(5-(2-chloro-5-(trifluoromethyl)phenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S28). Prepared according to the general procedure utilizing PdCl$_2$ (10.6 mg, 0.060 mmol), B$_2$(pin)$_2$ (1.52 g, 6.00 mmol), THF (6.0 mL), and (E)-1-chloro-2-(5-chloropent-3-en-1-yl)-4-(trifluoromethyl)benzene (10:1 with regioisomeric allyl chloride, 1.699 g, 6.00 mmol). The crude material was purified (SiO$_2$, 5% ethyl acetate in hexane) to give the desired product as a clear, colorless and viscous oil (1.96 g, 87%). $R_f = 0.35$ (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.46-7.41 (2H, m), 7.37 (1H, dd, $J = 8.3, 2.0$ Hz), 5.54-5.48 (1H, m), 5.45-5.40 (1H, m), 2.81 (2H, t, $J = 7.8$ Hz), 2.32 (2H, dtd's, $J = 7.8, 7.8, 1.5$ Hz), 1.64 (2H, d, $J = 7.3$ Hz), 1.24 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 139.9, 133.7, 130.0, 129.2 (q, $J_{C-F} = 32.4$ Hz), 127.4, 127.2 (q, $J_{C-F} = 3.8$ Hz), 124.3 (q, $J_{C-F} = 3.8$ Hz), 123.8 (q, $J_{C-F} = 271.8$ Hz), 117.1, 44.9, 32.9, 31.6; IR (neat): 3039.3 (w), 2946.3 (m), 2866.1 (w), 1666.7 (w), 1609.5 (w), 1412.5 (m), 1325.3 (s), 1275.9 (m), 1166.7 (s), 1121.5 (s), 1080.0 (s), 1047.6 (m), 966.5 (m), 894.8 (m), 825.4 (s), 679.5 (m), 514.3 (w), 442.3 (w) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{11}$ClF$_3$ [M-Cl]$^+$: calculated: 247.0501, found: 247.0508.
(E)-1-chloro-2-(5-chloro-4-methylpent-3-en-1-yl)benzene (S30). Prepared according to the general procedure utilizing thionyl chloride (2.84 mL, 39.4 mmol), 5-(2-chlorophenyl)-2-methylpent-1-en-3-ol (830.4 mg, 3.94 mmol), and DCM (20 mL). The crude material was purified (SiO₂, 2% ethyl acetate in hexane) to give the desired product as a 5:1 mixture of the title compound: 1-chloro-2-(3-chloro-4-methylpent-4-en-1-yl)benzene (clear, colorless oil, 758.7 mg, 84%). Rᵢ = 0.48 (5% ethyl acetate in hexane, UV/magic stain). ¹H NMR (500 MHz, CDCl₃): (major isomer) δ 7.36-7.32 (1H, m), 7.20-7.12 (3H, m), 5.60 (1H, t, J = 7.3 Hz), 4.01 (2H, s), 2.79 (2H, t, J = 7.8 Hz), 1.67 (3H, s); (minor isomer) δ 7.36-7.32 (1H, m), 7.26-7.22 (1H, m), 7.20-7.12 (2H, m), 5.05 (1H, s), 4.94 (1H, q, J = 1.0 Hz), 4.40 (1H, dd (app t), J = 7.7 Hz), 2.92-2.84 (1H, m), 2.81-2.74 (1H, m), 2.19-2.11 (2H, m), 1.85 (3H, d, J = 1.0 Hz); ¹³C NMR (126 MHz, CDCl₃): (both isomers, one overlapping signal) δ 144.1, 139.0, 138.4, 133.9, 132.8, 130.5, 129.6, 129.4, 129.3, 127.7, 127.4, 1126.8, 1267, 114.4, 66.0, 52.2, 36.2, 33.1, 31.1, 28.1, 17.1, 14.0; IR (neat): 3064.4 (w), 2944.9 (w), 2861.4 (w), 1474.2 (s), 1442.0 (s), 1372.1 (m), 1324.3 (m), 1147.8 (m), 1052.2 (w), 966.6 (w), 850.9 (w), 751.0 (m), 673.6 (m), 455.9 (w), 443.4 (w) cm⁻¹; HRMS-(DART) for: C₁₂H₁₄Cl [M+H]⁺: calculated: 193.0784, found: 193.0788.

(E)-2-(5-(2-chlorophenyl)-2-methylpent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S31). Prepared according to the general procedure utilizing PdCl₂ (5.8 mg, 0.033 mmol), B₂(pin)₂ (840.8 mg, 3.31 mmol), THF (3.3 mL), and (E)-1-chloro-2-(5-chloro-4-methylpent-3-en-1-yl)benzene (5:1 with regio-isomeric allyl chloride, 758.7 mg, 3.31 mmol). The crude material was purified (SiO₂, 2% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.0045 g, 95%). Rᵢ = 0.40 (5% ethyl acetate in hexane, UV/magic stain). ¹H NMR (500 MHz, CDCl₃): δ 7.32 (1H, dd, J = 7.8, 1.5 Hz), 7.21 (1H, dd, J = 7.8, 2.0 Hz), 7.16 (1H, ddd (app dt’s), J = 7.3, 7.3, 1.5 Hz), 7.11 (1H, ddd (app dt’s), J = 7.3, 7.3, 2.0 Hz), 5.18 (1H, t, J = 6.9 Hz), 2.74 (2H, t, J = 7.8 Hz), 2.31 (2H, dt’s (app q), J = 7.8 Hz), 1.67 (2H, s), 1.61 (3H, s), 1.25 (12H, s); ¹³C NMR (126 MHz, CDCl₃): δ 139.9, 133.9, 132.9, 130.5, 129.3, 127.1, 126.5, 123.0, 83.1, 33.9, 28.3, 24.7, 17.8; IR (neat): 3070.6 (w), 2977.3 (m), 2931.9 (w), 2864.3 (w), 1475.0 (s), 1440.3 (s), 1372.1 (m), 1324.3 (m), 1147.8 (m), 1052.2 (w), 966.6 (w), 850.9 (w), 751.0 (m), 673.6 (m) cm⁻¹; HRMS-(DART) for: C₁₈H₂₇BClO₂ [M+H]⁺: calculated: 321.1793, found: 321.1794.
4-(2-chlorophenyl)butanal (S32). Prepared according to the general procedure utilizing Pd(OAc)$_2$ (46.5 mg, 0.21 mmol), tetrabutylammonium chloride (22.88 g, 10.4 mmol), sodium bicarbonate (2.18 g, 25.9 mmol), dimethylformamide (21 mL), 2-chloroiodobenzene (2.47 g, 10.4 mmol), and but-3-en-1-ol (1.12 g, 15.5 mmol). The crude material was purified (SiO$_2$, 6% ethyl acetate in hexane) to give the desired product as a 11:1 mixture of the title compound: 3-(2-chlorophenyl)butanal (clear, slightly yellow oil (1.64 g, 87%)). $R_f = 0.40$ (10% ethyl acetate in hexane, UV/magic stain). All spectral data are in accordance with the literature.

6-(2-chlorophenyl)hex-1-en-3-ol (S33). Prepared according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 18.0 mL, 18.0 mmol), 4-(2-chlorophenyl)butanal (1.64 g, 8.99 mmol), and THF (50 mL). The crude material was purified (SiO$_2$, 10% ethyl acetate in hexane) to give the desired product as a 15:1 mixture of the title compound: 5-(2-chlorophenyl)hex-1-en-3-ol (clear, slightly yellow oil (1.80 g, 87%)). $R_f = 0.39$ (10% ethyl acetate in hexane, UV/magic stain).

(E)-1-chloro-2-(6-chlorohex-4-en-1-yl)benzene (S34). Prepared according to the general procedure utilizing thionyl chloride (3.44 mL, 47.5 mmol), 6-(2-chlorophenyl)hex-1-en-3-ol (1.00 g, 4.75 mmol), and DCM (13.4 mL). The crude material was purified (SiO$_2$, 2% DCM in hexane) to give the desired product as a 40:8:1 mixture of the title compound: 1-chloro-2-(4-chlorohex-5-en-1-yl)benzene; (E)-1-chloro-2-(6-chlorohex-4-en-2-yl)benzene (691 mg, 59%). $R_f = 0.56$ (5% DCM in hexane, UV/magic stain).

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9 Kuwabe, S.; Torraca, K. E.; Buchwald, S. L. *J. Am. Chem. Soc.* 2001, 123, 12202.
(w), 1076.9 (s), 965.8 (s), 928.0 (s), 750.2 (s), 679.0 (s), 441.6 (w) cm⁻¹;
HRMS-(DART) for: C₁₂H₁₄Cl [M+H-HCl]+: calculated: 193.0784, found: 193.0778.

(E)-2-(6-(2-chlorophenyl)hex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S35). Prepared according to the general procedure utilizing PdCl₂ (16.9 mg, 0.0955 mmol), Bₓ(pin)₂ (2.43 mg, 9.55 mmol), THF (9.6 mL), and (E)-1-chloro-2-(6-chlorohex-4-en-1-yl)benzene (5:1 with regio-isomeric allyl chloride, 2.06 g, 9.55 mmol). The crude material was purified (SiO₂, 0-10% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (2.32 g, 79%). R_f = 0.35 (5% ethyl acetate in hexane, UV/magic stain).

1H NMR (500 MHz, CDCl₃): δ 7.32 (1H, dd, J = 7.5, 1.5 Hz), 7.21 (1H, dd, J = 7.5, 2.0 Hz), 7.16 (1H, ddd (appt d’s), J = 7.5, 7.5, 1.0 Hz), 7.11 (1H, ddd (appt d’s), J = 7.5, 7.5, 2.0 Hz), 5.53-5.39 (2H, m), 2.71 (2H, t, J = 8.0 Hz), 2.06 (2H, dt’s (app q), J = 7.0 Hz), 1.70-1.64 (4H, m), 1.25 (12H, s); 13C NMR (126 MHz, CDCl₃): δ 140.2, 139.9, 130.4, 130.2, 129.4, 127.0, 126.6, 125.5, 83.1, 33.0, 32.3, 29.5, 24.8; IR (neat): 2977.7 (w), 2928.5 (w), 2860.1 (w), 1473.9 (m), 1442.5 (w), 1359.6 (s), 1323.4 (s), 1272.1 (m), 1213.7 (w), 1143.0 (s), 1052.5 (m), 965.8 (s), 883.1 (w), 846.2 (s), 780.9 (s), 675.2 (m), 578.0 (w), 457.9 (w) cm⁻¹; HRMS-(DART) for: C₁₈H₂₇BClO₂ [M+H]⁺: calculated: 321.1793, found: 321.1786.

5-(2-chlorophenyl)pent-4-yn-1-ol (S36). Prepared according to the literature procedure¹⁰ utilizing CuI (28.6 mg, 0.150 mmol), PdCl₂(PPh₃)₂ (105.3 mg, 0.150 mmol), triethylamine (12.5 mL), 2-chloroiodobenzene (0.61 mL, 5.00 mmol), and pent-4-yn-1-ol (0.56 mL, 6.00 mmol). The crude material was purified (SiO₂, 20% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (924.1 mg, 95%). R_f = 0.29 (25% ethyl acetate in hexane, UV/KMnO₄). All spectral data are in accordance with the literature.¹⁰

5-(2-chlorophenyl)pentan-1-ol (S37). To a 50 mL round-bottomed flask equipped with magnetic stir bar was added PtO₂ (22.7 mg, 0.100 mmol) followed by methanol (20 mL) and 5-(2-chlorophenyl)pent-4-yn-1-ol (973.3 mg, 5.00 mmol). The flask was sealed with a septum and a three-way inlet equipped with vacuum line and hydrogen balloon was added. The flask was briefly evacuated until the reaction mixture began to boil, then backfilled with hydrogen. After repeating this sequence three additional times, the reaction mixture was vigorously stirred under positive hydrogen pressure (balloon) at room temperature for 24 hours. The resulting dark reaction mixture was diluted with 25% ethyl acetate in hexane (20 mL) and eluted through a small plug of SiO₂ with additional 25% ethyl acetate in hexane (150 mL). The resulting clear, colorless solution was concentrated under reduced pressure. The crude material was purified (SiO₂, 20% ethyl acetate in hexane) to give the desired product and a small amount (>5%) of inseparable de-chlorinated by-product. R_f = 0.30 (25% ethyl acetate in hexane). ¹H NMR (500 MHz, CDCl₃): δ 7.33 (1H, dd, J = 7.8, 1.0 Hz), 7.21 (1H, dd, J = 7.8, 2.0 Hz), 7.17 (1H, ddd (app dt’s), J = 7.3, 7.3, 1.5 Hz), 7.12 (1H, ddd (app dt’s), J = 7.3, 7.3, 2.0

¹⁰ Gericke, K. M.; Chai, D. I.; Lautens, M. Tetrahedron 2008, 64, 6002.
Hz), 3.65 (2H, t, $J = 6.9$ Hz), 2.74 (2H, t, $J = 7.8$ Hz), 1.69-1.59 (4H, m), 1.47-1.41 (2H, m); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 140.0, 133.8, 130.3, 129.4, 127.1, 126.6, 62.8, 33.5, 32.5, 29.5, 25.5; IR (neat): 3324.8 (br), 3063.4 (w), 3017.3 (w), 2931.5 (s), 2859.2 (m), 1594.0 (w), 1571.5 (w), 1473.3 (s), 1441.9 (m), 1069.9 (s), 1049.8 (s), 1031.4 (s), 746.9 (s), 678.8 (s), 456.9 (m), 444.0 (m) cm$^{-1}$; HRMS-(DART) for: C$_{11}$H$_{14}$Cl [M+H-H$_2$O]$^+$: calculated: 181.0784, found: 181.0775.

5-(2-chlorophenyl)pentanal (S38). Prepared according to the literature procedure.$^{11}$ To a 50 mL round-bottomed flask equipped with magnetic stir bar was added tetrakis(acetonitrile) copper(I) hexafluorophosphate (37.3 mg, 0.100 mmol) followed bipyridine (15.6 mg, 0.100 mmol) as a solution in acetonitrile (2 mL), resulting in immediate formation of a brown reaction mixture. TEMPO (15.6 mg, 0.100 mmol) as a solution in acetonitrile (2 mL) was added followed by N-methylimidazole (16.4 mg, 0.200 mmol) as a solution in acetonitrile (2 mL). After stirring at room temperature open to air for approximately 5 minutes, 5-(2-chlorophenyl)pentan-1-ol (397.4 mg, 2.00 mmol) was added as a solution in acetonitrile (2 mL). The resulting brown reaction mixture was vigorously stirred at room temperature open to air until the reaction became blue/green in color and TLC analysis indicated consumption of starting material (5 hours). The reaction mixture was concentrated under reduced pressure, and the resulting residue was taken up in 10% ethyl acetate in hexane (10 mL) and eluted through a short plug of SiO$_2$ with additional 10% ethyl acetate in hexane solution (150 mL). The resulting clear, slightly yellow solution was concentrated under reduced pressure and the crude material was purified (SiO$_2$, 6% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (385.6 mg, 98%). $R_f = 0.27$ (5% ethyl acetate in hexane, UV/KMnO$_4$). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.83 (1H, s), 7.40 (1H, d, $J = 7.3$ Hz), 7.28-7.23 (2H, m), 7.20 (1H, ddd (app dt’s), $J = 7.8$, 7.8, 2.0 Hz), 2.82 (2H, t, $J = 7.8$ Hz), 2.54 (2H, t, $J = 6.8$ Hz), 1.81-1.71 (4H, m); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 201.4, 138.5, 132.9, 129.4, 128.5, 126.4, 125.8, 42.7, 32.3, 28.2, 20.7; IR (neat): 3063.5 (w), 2935.7 (m), 2862.9 (w), 2822.0, (w), 2718.3 (w), 1722.4 (s), 1594.1 (w), 1571.5 (w), 1474.0 (m), 1442.8 (m), 1072.7 (m), 1050.7 (m), 1030.9 (m), 751.4 (s), 678.8 (m), 459.9 (w) cm$^{-1}$; HRMS-(DART) for: C$_{11}$H$_{14}$ClO [M+H]$^+$: calculated: 197.0733, found: 197.0738.

7-(2-chlorophenyl)hept-1-en-3-ol (S39). Prepared according to the general procedure utilizing vinyl magnesium bromide (1.0 M in THF, 7.80 mL, 7.80 mmol), 5-(2-chlorophenyl)pentanal (761.2 mg, 3.87 mmol), and THF (8.0 mL). The crude material was purified (SiO$_2$, 12% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (692.8 mg, 80%). $R_f = 0.28$ (10% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.33 (1H, dd, $J = 6.4$, 1.5 Hz), 7.21 (1H, dd, $J = 7.8$, 2.0 Hz), 7.17 (1H, ddd (app dt’s), $J = 6.8$, 6.8, 1.5 Hz), 7.12 (1H, ddd (app dt’s), $J = 7.3$, 7.3, 2.0 Hz), 5.87 (1H, ddd, $J = 17.1$, 10.3, 6.4 Hz), 5.22 (1H, ddd (app dt’s), $J = 17.1$, 1.5, 1.5 Hz), 5.11 (1H, ddd (app dt’s), $J = 10.3$, 1.5, 1.5 Hz), 4.12 (1H, ddd (app q), $J = 6.4$ Hz), 2.75-2.72 (2H, m), 1.70-1.38 (7H, m); $^{13}$C NMR (126

$^{11}$ Hoover, J. M.; Stahl, S. S. J. Am. Chem. Soc. 2011, 133, 16901.
MHz, CDCl$_3$: $\delta$ 141.2, 140.0, 133.8, 130.2, 129.4, 127.1, 126.6, 114.6, 73.1, 36.7, 33.5, 29.6, 25.1; IR (neat): 3361.9 (br), 3068.9 (w), 2933.6 (m), 2859.9 (m), 1643.7 (w), 1571.6 (w), 1474.0 (m), 1442.4 (m), 1131.2 (w), 1051.3 (m), 1032.1 (m), 990.6 (m), 921.4 (m), 750.1 (s), 680.2 (w) cm$^{-1}$; HRMS-(DART) for: C$_{13}$H$_{21}$ClNO [M+NH$_4^+$]: calculated: 242.1312, found: 242.1311.

(E)-1-chloro-2-(7-chlorohept-5-en-1-yl)benzene (S40). Prepar- ed according to the general procedure utilizing thionyl chloride (2.13 mL, 29.2 mmol), 7-(2-chlorophenyl)hept-1-en-3-ol (655.7 mg, 2.92 mmol), and DCM (12 mL). The crude material was purified (SiO$_2$, 2% ethyl acetate in hexane) to give the desired product as a 5:1 mixture of the title compound: 1-chloro-2-(5-chlorohept-6-en-1-yl)benzene (clear, colorless oil, 619.0 mg, 87%). R$_f$ = 0.51 (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): (major isomer) $\delta$ 7.34 (1H, dd, $J$ = 7.8, 1.0 Hz), 7.22-7.16 (2H, m), 7.13 (1H, ddd (app dt’s), $J$ = 7.8, 7.8, 2.0 Hz), 5.78 (1H, dt’s, $J$ = 15.2, 6.4, 6.4 Hz), 5.63 (1H, dt’s, $J$ = 15.2, 7.3, 7.3, 1.5, 1.5 Hz), 4.03 (2H, dd, $J$ = 6.4, 1.0 Hz), 2.74 (2H, t, $J$ = 7.8 Hz), 2.12 (2H, dt (app q), $J$ = 7.3 Hz), 1.68-1.61 (2H, m), 1.48 (2H, tt’s (app q), $J$ = 7.3 Hz); (minor isomer) $\delta$ 7.34 (1H, dd, $J$ = 7.8, 1.0 Hz), 7.22-7.11 (3H, m), 5.89 (1H, ddd, $J$ = 15.2, 6.9, 6.9 Hz), 5.26 (1H, d, $J$ = 16.6 Hz), 5.14 (1H, d, $J$ = 9.8 Hz), 4.35 (1H, ddd (app q), $J$ = 7.3 Hz), 2.76-2.72 (2H, m), 1.93-1.80 (2H, m), 1.70-1.45 (4H, m); $^{13}$C NMR (126 MHz, CDCl$_3$): (both isomers) $\delta$ 140.0, 139.8, 138.7, 135.8, 133.9, 130.3, 129.5, 129.4, 127.2, 127.2, 126.7, 126.7, 126.1, 116.4, 63.0, 45.4, 38.0, 33.4, 33.4, 31.8, 29.2, 29.1, 28.5, 26.2; IR (neat): 3064.8 (w), 3016.2 (w), 2932.6 (m), 2858.7 (m), 1737.4 (w), 1665.6 (w), 1595.0 (w), 1571.5 (w), 1474.0 (m), 1441.9 (m), 1348.6 (w), 1249.8 (m), 1052.1 (w), 966.3 (m), 750.8 (s), 678.9 (m) cm$^{-1}$; HRMS-(DART) for: C$_{13}$H$_{16}$ClO$_2$ [M]+: calculated: 242.0629, found: 242.0628.

(E)-2-(7-(2-chlorophenyl)hept-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S41). Prepared according to the general procedure utilizing PdCl$_2$ (4.2 mg, 0.024 mmol), B$_2$(pin)$_2$ (606.9 mg, 2.39 mmol), THF (2.4 mL), and (E)-1-chloro-2-(7-chlorohept-5-en-1-yl)benzene (5:1 with regio-isomeric allyl chloride, 581.2 mg, 2.39 mmol). The crude material was purified (SiO$_2$, 6% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (604.4 mg, 76%). R$_f$ = 0.40 (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.32 (1H, dd, $J$ = 7.8, 1.5 Hz), 7.20 (1H, dd, $J$ = 7.8, 2.0 Hz), 7.16 (1H, ddd (app dt’s), $J$ = 7.3, 7.3, 1.5 Hz), 7.11 (1H, ddd (app dt’s), $J$ = 7.3, 7.3, 2.0 Hz), 5.46 (1H, dt’s, $J$ = 15.2, 7.8, 7.8 Hz), 5.39 (1H, dt’s, $J$ = 15.2, 6.9, 6.9 Hz), 2.71 (2H, t, $J$ = 7.8 Hz), 2.03 (2H, dt’s (app q), $J$ = 6.9 Hz), 1.64 (2H, d, $J$ = 6.9 Hz), 1.62-1.58 (2H, m), 1.42 (2H, tt’s (app p), $J$ = 7.8 Hz), 1.24 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 140.3, 133.9, 130.6, 130.3, 129.3, 127.0, 126.6, 125.0, 83.1, 33.4, 32.5, 29.3, 29.2, 24.7; IR (neat): 3061.1 (w), 2978.1 (m), 2928.6 (m), 2857.6 (w), 1474.1 (m), 1442.6 (m), 1359.0 (s), 1325.4 (s), 1272.4 (w), 1144.3 (s), 966.7 (s), 846.9 (m), 750.4 (s), 676.4 (w) cm$^{-1}$; HRMS-(DART) for: C$_{19}$H$_{28}$BCIO$_2$ [M+H]$^+$: calculated: 335.1949, found: 335.1945.
1-(but-3-yn-1-yl)-2-chlorobenzene (S42). Prepared according to the literature procedure. To a flame-dried 250 mL round-bottomed flask equipped with magnetic stir bar was added K$_2$CO$_3$ (1.382 g, 10.0 mmol). The flask was sealed with a septum and evacuated, then back-filled with nitrogen (3x). Dry methanol (25 mL) was added, followed by 3-(2-chlorophenyl)propanal (843.1 mg, 5.00 mmol) as a solution in dry methanol (12.5 mL), and diethyl (1-diazo-2-oxopropyl)phosphonate (Ohira-Bessman reagent 1.321 g, 6.00 mmol) as a solution in dry methanol (12.5 mL). The resulting cloudy, yellow reaction mixture was stirred at room temperature for 12 hours. The reaction was diluted with diethyl ether (75 mL) and 5% aqueous sodium bicarbonate and the layers separated. The aqueous layer was extracted with diethyl ether (2 x 50 mL) and the combined organic layers were washed with brine (75 mL), dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified (SiO$_2$, 100% hexane) to give the desired product as a clear, colorless oil (548.6 mg, 67%). R$_f$ = 0.55 (100% hexane, UV/KMnO$_4$). $^1$H NMR (500 MHz, CDCl$_3$); δ 7.36 (1H, dd, $J = 7.8$ Hz), 7.29 (1H, dd, $J = 7.3$, 2.0 Hz), 7.08 (1H, t, $J = 7.3$ Hz), 2.98 (2H, t, $J = 7.8$ Hz), 1.99 (1H, t, $J = 2.9$ Hz); $^{13}$C NMR (126 MHz, CDCl$_3$); δ 137.8, 133.9, 130.7, 129.5, 126.7, 83.4, 69.0, 32.6, 18.6; IR (neat): 3300.0 (m), 2362.7 (w), 2322.4 (w), 1474.7 (w), 1444.3 (w), 1053.3 (w), 1038.7 (w), 750.0 (s), 637.6 (m) cm$^{-1}$; HRMS-(DART) for: C$_{10}$H$_{10}$Cl [M+H]$^+$: calculated: 165.0471, found: 165.0469.

(Z)-2-(4-(2-chlorophenyl)but-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S43). Prepared according to the literature procedure. To an oven-dried scintillation vial in the glovebox equipped with magnetic stir bar was added chloro(1,5-cyclooctadiene)rhodium(I) dimer (19.3 mg, 0.039 mmol), triisopropylphosphine (25.1 mg, 0.157 mmol), cyclohexane (7.0 mL), triethylamine (0.37 mL, 2.62 mmol), and catecholborane (0.28 mL, 2.62 mmol). The reaction mixture was stirred for 30 minutes followed by addition of 1-(but-3-yn-1-yl)-2-chlorobenzene (516.7 mg, 3.14 mmol). After stirring at room temperature for 2 hours, pinacol (463.5 mg, 3.92 mmol) was added in one portion and the vial was removed from the glovebox and stirred at room temperature for 12 hours. The resulting dark reaction mixture was diluted with 10% ethyl acetate in hexane (10 mL) and eluted through a short plug of SiO$_2$ with additional 10% ethyl acetate in hexane (150 mL). The resulting clear, yellow solution was concentrated under reduced pressure and the crude material was purified (SiO$_2$, 5% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (>40:1 Z:E, 586.8 mg, 77%). R$_f$ = 0.37 (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$); δ 7.33 (1H, dd, $J = 7.8$, 1.5 Hz), 7.29 (1H, dd, $J = 7.3$, 2.0 Hz), 7.08 (1H, t, $J = 7.3$ Hz), 2.84-2.81 (2H, m), 2.76-2.71 (2H, m), 1.25 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$); δ 153.3, 139.4, 134.0, 130.6, 129.3, 127.2, 126.5, 82.8, 33.5, 32.2, 24.8; IR (neat): 3066.8 (w), 2978.5 (m), 2929.2 (w), 2862.2 (w), 1628.6 (w), 1474.4 (w), 1444.3 (w), 1053.3 (w), 1038.7 (w), 750.0 (s), 637.6 (m) cm$^{-1}$; HRMS-(DART) for: C$_{10}$H$_{10}$Cl [M+H]$^+$: calculated: 165.0471, found: 165.0469.

12 Gung, B. W.; Dickson, H. Org. Lett. 2002, 4, 2517.
13 Ohmura, T.; Yamamoto, Y.; Miyaura, N. J. Am. Chem. Soc. 2000, 122, 4990.
1439.5 (m), 1422.5 (m), 1321.4 (m), 1261.7 (s), 1144.3 (s), 1053.4 (w), 968.8 (w), 749.2 (w), 677.8 (w) cm$^{-1}$; HRMS-(DART) for: C$_{16}$H$_{23}$BClO$_2$ [M+H]$^+$: calculated: 293.1480, found: 293.1478.

(Z)-2-(5-(2-chlorophenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S44). To a flame-dried 50 mL round-bottomed flask equipped with magnetic stir bar under nitrogen was added (Z)-2-(5-(2-chlorophenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (522.5 mg, 1.79 mmol), followed by THF (18 mL) and bromochloromethane (0.15 mL, 2.32 mmol). The resulting clear, colorless solution was cooled to -78 °C (dry ice/acetone bath) and treated dropwise with n-butyllithium (2.5 M in hexane, 0.93 mL, 2.32 mmol). After stirring at -78 °C for 20 minutes, the cooling bath was removed and the reaction mixture was allowed to slowly warm to room temperature and stirred an additional 3 hours. The resulting slightly cloudy reaction mixture was cooled to 0 °C (ice/water bath) and water (10 mL) was slowly added. The mixture was diluted with ethyl acetate (50 mL) and additional water (20 mL) and the layers separated. The aqueous layer was extracted with ethyl acetate (3 x 30 mL) and the combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified (SiO$_2$, 6% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (339.6 mg, 62%). $R_f = 0.35$ (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.33 (1H, dd, $J = 7.8, 1.5$, Hz), 7.23 (1H, dd, $J = 7.3, 1.5$, Hz), 7.17 (1H, ddd (app dt’s), $J = 7.3, 7.3, 1.5$, Hz), 7.12 (1H, ddd (app dt’s), $J = 7.8, 7.8, 2.0$, Hz), 5.58-5.52 (1H, m), 5.48-5.42 (1H, m), 2.78 (2H, t, $J = 7.8$, Hz), 2.36 (2H, dt’s (app q), $J = 7.8$, Hz), 1.67 (2H, d, $J = 7.8$, Hz), 1.24 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 139.7, 133.9, 130.4, 129.3, 128.3, 127.2, 126.6, 125.3, 83.2, 33.5, 27.1, 24.7; IR (neat): 3059.7 (w), 2978.2 (m), 2930.9 (s), 2864.6 (w), 1473.9 (w), 1443.5 (w), 1324.7 (s), 1272.5 (w), 1214.1 (w), 1143.8 (s), 1052.6 (w), 967.8 (w), 882.9 (w), 847.3 (w), 749.1 (m) cm$^{-1}$; HRMS-(DART) for: C$_{17}$H$_{25}$BClO$_2$ [M+H]$^+$: calculated: 307.1636, found: 307.1645.

5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-1-en-3-ol (S45). To a flame-dried two-neck 250 mL round-bottomed flask equipped with magnetic stir bar in the glovebox was added sodium hydride (576.0 mg, 24.0 mmol). The flask was sealed with septa, removed from the glovebox and equipped with a reflux condenser. THF (50 mL) was added and the resulting mixture was cooled to 0 °C (ice/water bath). To the cooled, stirring mixture was added 5-(2-bromophenyl)pent-1-en-3-ol (2.900 g, 12.0 mmol) as a solution in THF (10 mL). The resulting slightly yellow reaction mixture was then removed from the bath, warmed to room temperature, then heated to 80 °C in an oil bath. After 2.5 hours the resulting yellow-orange reaction mixture was cooled to room temperature, then to -78 °C (dry ice/acetone bath) and treated dropwise with n-butyllithium (2.51 M in hexane, 5.3 mL, 13.2 mmol), resulting in a slight darkening of the reaction mixture. After stirring for approximately 5 minutes at -78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.93 mL, 19.2 mmol) was added dropwise. The reaction was stirred at -78 °C for an additional 10 minutes, then warmed to room temperature. After 2 hours, the reaction was cooled to 0 °C (ice/water
bath) and slowly quenched with the dropwise addition of water (6 mL). The reaction was
diluted with ethyl acetate (75 mL) and additional water (50 mL) and the layers separated.
The aqueous layer was extracted with ethyl acetate (3 x 50 mL) and the combined
organic layers were dried over sodium sulfate, filtered and concentrated under reduced
pressure. The crude material was purified (SiO$_2$, 20% ethyl acetate in hexane) to give the
desired product as an inseparable mixture of the title compound and proto-debrominated
starting material (5:1 respectively), (clear, slightly yellow, viscous oil, 2.8722 g, 83%).
$R_f$ = 0.28 (25% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$
7.81 (1H, d, $J$ = 6.9 Hz), 7.37 (1H, ddd (app dt’s), $J$ = 7.8, 7.8, 1.5 Hz), 7.24-7.18 (2H, m),
5.89 (1H, d, $J$ = 17.1, 10.5, 5.4 Hz), 5.25 (1H, ddd (app dt’s), $J$ = 17.1, 1.5, 1.5 Hz), 5.08 (1H, ddd (app dt’s), $J$ = 10.7, 1.5, 1.5 Hz), 4.11-4.07 (1H, m), 3.04-2.93 (3H, m), 1.90-1.76 (2H, m), 1.37 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$
148.8, 141.1, 136.4, 131.2, 129.3, 125.2, 113.9, 83.8, 71.5, 40.7, 31.2, 24.9, 24.6; IR (neat): 3445.3
(br), 3067.2 (w), 2978.2 (m), 2931.0 (w), 2868.6 (w), 1644.3 (w), 1599.5 (m), 1568.8
(w), 1442.0 (m), 1381.1 (s), 1346.8 (s), 1311.7 (s), 1144.5 (s), 1071.4 (m), 861.6 (m),
661.1 (m) cm$^{-1}$; HRMS-(DART) for: C$_{17}$H$_{24}$BO$_2$ [M+H-H$_2$O]$^+$: calculated: 271.1869, found: 271.1871.

(E)-2-(2-(5-chloropent-3-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S46). Prepared according to the general
procedure utilizing thionyl chloride (1.10 mL, 15.0 mmol), 5-(2-
(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-1-en-3-ol (as a 5:1 mixture with proto-debrominated material described above) (432.3 mg,
1.50 mmol), and DCM (6.0 mL). The crude material was purified (SiO$_2$, 6% ethyl
acetate in hexane) to give the desired product as a 9:1 mixture of the title compound: 2-
(2-(3-chloropent-4-en-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (clear,
colorless oil, 368.8 mg, 80%). $R_f$ = 0.38 (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): (major isomer) $\delta$
7.84-7.78 (1H, m), 7.39-7.32 (1H, m), 7.24-7.14 (2H, m), 5.97 (1H, ddd, $J$ = 17.1, 10.3, 8.3 Hz), 5.30 (1H, d, $J$ = 17.1 Hz), 5.17 (1H, d, $J$ = 10.3 Hz), 4.41 (1H, ddd (app q), $J$ = 7.3 Hz), 3.10-2.92 (2H, m), 2.14-2.06 (2H, m), 1.36 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): (both isomers) $\delta$
148.5, 148.0, 138.8, 136.4, 136.2, 135.7, 131.0, 130.9, 129.4, 129.2, 126.0, 125.4, 125.2, 116.3, 83.5, 83.4, 63.0, 45.5, 41.4, 35.7, 35.3, 33.0, 24.9, 24.9; IR (neat): 3065.6 (w), 2977.4 (m), 2932.4 (m), 2867.3 (w), 1664.7 (w), 1599.3 (m),
1569.1 (w), 1488.3 (m), 1441.5 (s), 1380.5 (s), 1344.6 (s), 1311.5 (s), 1261.7 (s), 1213.8
(s), 1142.9 (s), 1115.2 (s), 1075.5 (s), 1039.7 (m), 962.0 (s), 862.0 (s), 759.9 (s), 673.5
(s) cm$^{-1}$; HRMS-(DART) for: C$_{17}$H$_{25}$BClO$_2$ [M+H]$^+$: calculated: 307.1636, found: 307.1636.
To a flame-dried 50 mL round-bottomed flask equipped with magnetic stir bar was added 4-dimethylaminopyridine (18.3 mg, 0.150 mmol). The flask was sealed with a septum, evacuated, and back-filled with nitrogen followed by addition of DCM (7.5 mL), triethylamine (0.63 mL, 4.50 mmol), and acetic anhydride (0.28 mL, 3.00 mmol). 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-1-en-3-ol (as a 5:1 mixture with proto-debrominated material described above) (432.3 mg, 1.50 mmol) as a solution in DCM (7.5 mL). After stirring at room temperature for 3 hours, TLC analysis indicated consumption of starting material and the reaction mixture was diluted with DCM (20 mL) and water (20 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 25 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude material was purified (SiO$_2$, 8% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (437.2 mg, 88%). $R_f$ = 0.24 (5% ethyl acetate in hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.79 (1H, d, $J = 7.3$ Hz), 7.35 (1H, dd (app t), $J = 7.3$ Hz), 7.20-7.16 (2H, m), 5.86 (1H, ddd, $J = 17.1$, 10.3, 6.4 Hz), 5.34 (1H, ddd (app q), $J = 5.9$ Hz), 5.28 (1H, d, $J = 17.1$ Hz), 5.19 (1H, d, $J = 10.8$ Hz), 2.96-2.86 (2H, m), 2.08 (2H, s), 1.96-1.84 (2H, m), 1.35 (12H, s); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 170.3, 148.6, 136.6, 136.3, 131.0, 129.2, 125.2, 116.4, 83.4, 74.9, 37.4, 31.7, 24.9, 24.8, 21.2; IR (neat): 3066.0 (w), 2977.8 (m), 2934.7 (w), 2871.7 (w), 1736.1 (s), 1646.9 (w), 1599.5 (m), 1569.5 (w), 1488.5 (m), 1442.1 (m), 1371.2 (s), 1345.2 (s), 1312.8 (s), 1233.3 (s), 1144.1 (s), 1110.7 (m), 1079.8 (m), 1021.5 (s), 962.5 (m), 861.5 (m), 755.8 (m), 661.2 (s) cm$^{-1}$; HRMS-(DART) for: C$_{19}$H$_{31}$BNO$_4$ [M+NH$_4^+$]: calculated: 348.2346, found: 348.2362.

(IV) Representative procedure for intramolecular coupling

To an oven-dried 2-dram vial equipped with magnetic stir bar in the glovebox was added (R,R)-L2 (0.07 equiv.), followed by cesium fluoride (3.00 equiv.), 1,3,5-trimethoxy benzene (internal standard, 10.0 mg), substrate (1.00 equiv.) and Pd(OAc)$_2$ (0.05 equiv.) as a solution in THF (0.2 M in substrate) resulting in a yellow-orange reaction mixture. The vial was sealed with a cap, removed from the glovebox and heated to 70 °C with vigorous stirring for 14 hours. The resulting grey, cloudy reaction mixture was cooled to room temperature, diluted with diethyl ether (2 mL) and passed through a short plug of SiO$_2$, eluding with additional diethyl ether (10 mL). The resulting clear, yellow solution was concentrated under reduced pressure and the crude reaction material analyzed for conversion and yield by $^1$H NMR analysis. The pure cyclized products were isolated after SiO$_2$ chromatography.
(V) Full characterization and proof of stereochemistry

(R)-1-vinyl-2,3-dihydro-1H-indene (compound 2, Scheme 2). Prepared according to the general procedure utilizing (R,R)-L2 (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), (E)-2-(5-(2-chlorophenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (76.7 mg, 0.250 mmol), Pd(OAc)$_2$ (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO$_2$, 100% pentane) to give the desired product as a clear, colorless oil (27.5 mg, 76%). $R_f$ = 0.34 (100% hexane, UV/KMnO$_4$). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.27-7.25 (1H, m), 7.20-7.17 (3H, m), 5.89 (1H, ddd, $J$ = 17.1, 9.3, 8.3 Hz), 5.18 (1H, dd, $J$ = 17.1, 1.0 Hz), 5.12 (1H, dd, $J$ = 9.8, 1.0 Hz), 3.78 (1H, ddd (app q), $J$ = 8.3 Hz), 2.99-2.86 (2H, m), 2.36 (1H, dddd (app ddd’s), $J$ = 11.7, 7.8, 7.8, 3.9 Hz), 1.88 (1H, dddd (app dq’s), $J$ = 12.7, 8.8, 8.8, 8.8 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 145.6, 143.9, 141.1, 126.5, 126.2, 124.4, 124.3, 114.8, 49.8, 33.1, 31.6; IR (neat): 3070.7 (w), 2954.6 (m), 2939.3 (m), 2926.2 (m), 2848.2 (m), 1638.4 (w), 1474.6 (m), 1457.7 (m), 1437.5 (w), 991.7 (m), 913.0 (s), 768.2 (m), 742.2 (s) cm$^{-1}$; HRMS-(DART) for: C$_{11}$H$_{13}$ [M+H]$^+$: calculated: 145.1017, found: 145.1024. [α]$_{20}^D$ = -69.233 (c = 1.360, CHCl$_3$, l = 50 mm).

Proof of stereochemistry:

The title compound was subjected to tandem ozonolysis/reduction as shown below to give (S)-(2,3-dihydro-1H-inden-1-yl)methanol and the specific rotation was measured ([α]$_{20}^D$ = -11.452 (c = 0.550, benzene, l = 50 mm). This value was compared to the known literature value$^{14}$ ([α]$_{20}^D$ = -14.3 (benzene, 85% ee material) for (S)-(2,3-dihydro-1H-inden-1-yl)methanol.

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$^{14}$ Caro, Y.; Torrado, M.; Masaguer, C. F.; Raviña, E. Tetrahedron Asymm. 2003, 14, 3689.
Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing (E)-2-(5-(2-chlorophenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl$_2$ as the pre-catalyst.

Chiral GLC ($eta$-dex, Supelco, 80 °C for 5 min, ramp 1 °C/min to 150 °C, 20 psi) – analysis of 1-vinyl-2,3-dihydro-1H-indene.

| Racemic Material | Standard Conditions |
|------------------|---------------------|
|                  |                     |
| **Peak RetTime** | **Type** | **Width** | **Area** | **Height** | **Area** |
| 27.5             | 27.702   | 0.1490    | 277.63089| 31.05666  | 49.77444 |
|                  | 28.116   | 0.1676    | 280.14709| 27.85743  | 50.22556 |
| **Totals:**      |          |           |          |            | 557.77790| 58.91699 |

| **Standard Conditions + NBu$_4$Cl** |
| **Peak RetTime** | **Type** | **Width** | **Area** | **Height** | **Area** |
| 27.5             | 27.702   | 0.1311    | 81.34442 | 10.3570   | 90.02866 |
|                  | 28.199   | 0.1293    | 8.99840  | 1.15978   | 9.97132  |
| **Totals:**      |          |           |          |            | 90.24252 | 11.49548 |

| **Peak RetTime** | **Type** | **Width** | **Area** | **Height** | **Area** |
| 27.5             | 27.846   | 0.1373    | 174.06595| 21.19496  | 92.82700 |
|                  | 28.357   | 0.1373    | 12.45055 | 1.63501   | 7.17300  |
| **Totals:**      |          |           |          |            | 187.51650| 22.76797 |
(R)-6-methyl-1-vinyl-2,3-dihydro-1H-indene (compound 4, Scheme 2). Prepared according to the general procedure utilizing (R,R)-L2 (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), (E)-2-(5-(2-chloro-4-methylphenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80.2 mg, 0.250 mmol), Pd(OAc)$_2$ (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO$_2$, 100% pentane) to give the desired product as a clear, colorless oil (27.0 mg, 68%). $R_f = 0.38$ (100% hexane, UV/magic stain).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.13 (1H, d, $J$ = 7.5 Hz), 6.98 (1H, d, $J$ = 11.5 Hz), 6.97 (1H, s), 5.85 (1H, ddd (app dt’s), $J$ = 17.0, 8.5, 8.5 Hz), 5.16 (1H, d, $J$ = 17.0 Hz), 5.09 (1H, d, $J$ = 10.0 Hz), 3.72 (1H, ddd (app q), $J$ = 8.5 Hz), 2.99 (1H, ddd, $J$ = 15.0, 9.0, 3.5 Hz), 2.83 (1H, ddd (app dt’s), $J$ = 15.5, 8.0, 8.0 Hz), 2.36-2.30 (1H, m), 2.33 (3H, s), 1.85 (1H, dddd (app dq’s), $J$ = 12.5, 8.5, 8.5, 8.5 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 145.8, 141.3, 140.9, 135.8, 127.3, 125.0, 124.1, 114.7, 49.8, 33.3, 31.2, 21.2; IR (neat): 3004.3 (w), 2922.8 (s), 2855.7 (m), 1732.8 (w), 1612.5 (m), 1491.0 (s), 1452.4 (m), 1439.4 (m), 1230.3 (w), 1119.4 (w), 1037.3 (s), 911.4 (s), 885.6 (w), 808.4 (s), 687.3 (w), 447.8 (w), 422.7 (w) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{15}$ [M+H]$^+$: calculated: 159.1174, found: 159.1177. $[\alpha]_D^{20} = -73.635$ (c = 0.535, CHCl$_3$, $l$ = 50 mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing (E)-2-(5-(2-chloro-4-methylphenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(OAc)$_2$ / PCy$_3$ as the pre-catalyst. The title compound was subjected to tandem ozonolysis/reduction as shown below to give (S)-(6-methyl-2,3-dihydro-1H-inden-1-yl)methanol. Further analysis of stereochemistry was performed on (S)-(6-methyl-2,3-dihydro-1H-inden-1-yl)methanol. Absolute stereochemistry was assigned by analogy.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{O} & \quad \text{O} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me}
\end{align*}
\]

i) O$_3$, MeOH:DCM (1:1) -78 $^\circ$C

ii) NaBH$_4$, -78 $^\circ$C to RT
Chiral SFC (Chiracel OJ-H, 3% IPA/hexane, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (S)-(6-methyl-2,3-dihydro-1H-inden-1-yl)methanol

Racemic Material

| Peak No | % Area | Area      | RT (min) |
|---------|--------|-----------|----------|
| 1       | 48.9441| 2975.2647 | 6.59     |
| 2       | 51.0559| 3103.6356 | 8.28     |
| Total:  | 100    | 6078.9003 |          |

Standard Conditions

| Peak No | % Area | Area      | RT (min) |
|---------|--------|-----------|----------|
| 1       | 7.4501 | 313.4004  | 6.61     |
| 2       | 92.5499| 3893.2675 | 8.28     |
| Total:  | 100    | 4205.6679 |          |
(R)-7-methyl-1-vinyl-2,3-dihydro-1H-indene (compound 5, Scheme 2).
Prepared according to the general procedure utilizing (R,R)-L2 (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), (E)-2-(5-(2-chloro-3-methylphenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80.2 mg, 0.250 mmol), Pd(OAc)$_2$ (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO$_2$, 100% pentane) to give the desired product as a clear, colorless oil (28.9 mg, 73%). R$_f$ = 0.36 (100% hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.10-7.06 (2H, m), 6.96-6.95 (1H, m), 5.87 (1H, ddd, J = 17.0, 10.0, 8.0 Hz), 4.97-4.90 (2H, m), 3.82 (1H, ddd (app td’s), J = 8.0, 8.0, 2.0 Hz), 3.00 (1H, ddd (app dt’s), J = 16.5, 9.0, 9.0 Hz), 2.82 (1H, ddd, J= 16.0, 9.0, 3.0 Hz) 2.33-2.25 (1H, m), 2.26 (3H, s), 1.94 (1H, dddd (app ddt’s), J = 13.0, 5.5, 3.0, 3.0 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 143.9, 143.4, 140.0, 134.8, 127.5, 126.9, 121.9, 113.3, 48.3, 32.5, 31.2, 18.8; IR (neat): 3017.9 (w), 2939.6 (m), 2847.7 (m), 1633.9 (w), 1596.6 (w), 1474.6 (m), 1459.4 (m), 1377.6 (w) 991.9 (m), 908.6 (s), 811.1 (s), 686.1 (m) 603.5 (w) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{15}$ [M+H]$^+$: calculated: 159.1174, found: 159.1176. [a]$_D^{20}$ = -7.307 (c = 0.950, CHCl$_3$, l = 50 mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing (E)-2-(5-(2-chloro-3-methylphenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl$_2$ as the pre-catalyst. The title compound was subjected to tandem hydroboration/oxidation as shown below to give (R)-2-(7-methyl-2,3-dihydro-1H-inden-1-yl)ethanol. Further analysis of stereochemistry was performed on (R)-2-(7-methyl-2,3-dihydro-1H-inden-1-yl)ethanol. Absolute stereochemistry was assigned by analogy.
Chiral SFC (Chiracel OJ-H, 3% IPA/hexane, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (R)-2-(7-methyl-2,3-dihydro-1H-inden-1-yl)ethanol.

### Racemic Material

| Peak No | % Area | Area   | RT (min) |
|---------|--------|--------|----------|
| 1       | 50.4504| 2741.4917| 19.14    |
| 2       | 49.5496| 2692.5384| 20.6     |
| Total:  | 100    | 5434.0301|          |

### Standard Conditions

| Peak No | % Area | Area   | RT (min) |
|---------|--------|--------|----------|
| 1       | 32.1948| 6062.9513| 20.61    |
| 2       | 67.8052| 12769.151| 21.92    |
| Total:  | 100    | 18832.1023|         |
(R)-5-methoxy-1-vinyl-2,3-dihydro-1H-indene (compound 6, Scheme 2). Prepared according to the general procedure utilizing (R,R)-L2 (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), (E)-2-(5-(2-chloro-5-methoxy-phenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (84.2 mg, 0.250 mmol), Pd(OAc)$_2$ (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO$_2$, 100% pentane) to give the desired product as a clear, colorless oil (40.2 mg, 77%). $R_f$ = 0.18 (100% hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.05 (1H, d, $J$= 8.0 Hz), 6.90 (1H, s), 6.74 (1H, dd, $J$ = 8.5, 2.5 Hz), 5.84 (1H, ddd, $J$ = 17.5, 10.0, 8.5 Hz), 5.12 (1H, ddd (app dq’s), $J$ = 17.0, 1.0 Hz), 5.07 (1H, ddd (app dq’s), $J$ = 10.0, 1.0 Hz), 3.80 (3H, s), 3.70 (1H, ddd (app q), $J$ = 8.0 Hz), 2.91 (1H, ddd, $J$ = 15.5, 8.5, 3.5 Hz), 2.84 (1H, ddd (app dt’s), $J$ = 16.0, 8.0, 8.0 Hz), 2.34 (1H, ddd (app dtd’s), $J$= 12.5, 8.0, 8.0, 4.0 Hz), 1.86 (1H, ddd (app dq’s), $J$ = 12.5, 8.5, 8.5, 8.5 Hz); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 159.0, 145.5, 141.6, 137.8, 124.8, 114.4, 112.0, 109.9, 55.4, 49.0, 33.5, 31.8; IR (neat): 3077.1 (w), 2996.4 (w), 2940.1 (m), 2833.3 (w), 1605.4 (m), 1584.9 (w), 1487.5 (s), 1378.3 (m), 1253.6 (m), 1240.7 (s), 1118.1 (s), 1032.9 (s), 991.9 (m), 864.9 (s), 839.9 (m), 806.6 (m), 697.8 (w), 627.1 (w), 435.7 (m) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{15}$O $[M+H]^+$: calculated: 175.1123, found: 175.1127. [$\alpha$]$_{D}^{20}$ = -83.999 (c = 1.040, CHCl$_3$, $l$ = 50 mm).

**Analysis of stereochemistry:**

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing (E)-2-(5-(2-chloro-5-methoxy-phenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl$_2$ as the pre-catalyst. Absolute stereochemistry was assigned by analogy.

**Chiral GLC** (β-dex, Supelco, 90 °C for 5 min, ramp 1 °C/min to 140 °C, 20 psi) – analysis of (R)-5-methoxy-1-vinyl-2,3-dihydro-1H-indene.

| Racemic Material | Standard Conditions |
|------------------|---------------------|
| **Peak RetTime** | **Peak RetTime** |
| Type # | Width | Area | Height | Area | Type # | Width | Area | Height | Area |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| [min] | [min] | [pA*s] | [pA] | % | [min] | [min] | [pA*s] | [pA] | % |
| 1 | 50.445 NM | 0.1587 | 265.7156 | 30.38396 | 90.06891 | 1 | 50.139 NM | 0.2294 | 2594.67226 | 166.71036 | 89.76009 |
| 2 | 50.910 NM | 0.1585 | 265.4725 | 30.03351 | 49.94969 | 2 | 50.897 NM | 0.1855 | 261.74902 | 23.51253 | 10.23991 |
| Totals : | 571.39041 | 60.42647 | | | 2356.16626 | 190.22289 | | | |
(R)-5-vinyl-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxole (compound 7, Scheme 2). Prepared according to the general procedure utilizing (R,R)-L2 (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), (E)-2-(5-(6-chlorobenzo[d][1,3]dioxol-5-yl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (87.7 mg, 0.250 mmol), Pd(OAc)$_2$ (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO$_2$, 100% pentane) to give the desired product as a clear, colorless oil (25.4 mg, 54%). $R_f = 0.08$ (100% hexane, UV/magic stain). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.69 (1H, s), 6.61 (1H, s), 6.74 (1H, dd, $J = 8.5, 2.5$ Hz), 5.91 (2H, dd, $J = 3.5, 1.0$ Hz), 5.80 (1H, ddd, $J = 17.0, 10.0, 8.0$ Hz), 5.12 (1H, ddd (app dq’s), $J = 17.0, 1.0$ Hz), 5.06 (1H, ddd (app dq’s), $J = 9.0, 1.0$ Hz), 3.64 (1H, ddd (app q), $J = 8.0$ Hz), 2.83 (1H, ddd, $J = 15.0, 8.0, 3.5$ Hz), 2.76 (1H, ddd (app dt’s), $J = 15.5, 9.0, 9.0$ Hz), 2.33 (1H, ddd (app ddd’s), $J = 12.0, 7.0, 7.0, 3.5$ Hz), 1.86 (1H, ddd (app dq’s), $J = 13.0, 8.5, 8.5, 8.5$ Hz); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 146.7, 146.4, 141.4, 138.5, 136.6, 114.7, 105.0, 105.0, 100.9, 49.7, 33.6, 31.4; IR (neat): 3076.4 (w), 2929.0 (m), 2850.1 (m), 2805.1 (w), 1768.3 (w), 1637.7 (w), 1470.6 (s), 1351.5 (m), 1294.2 (s), 1268.1 (s), 1170.5 (s), 1038.1 (s) 992.7 (m), 940.0 (s), 913.4 (s), 855.8 (s), 823.1 (m), 775.1 (w), 682.1 (w), 419.2 (m) cm$^{-1}$; HRMS-(DART) for: C$_{12}$H$_{12}$O$_2$[M+H]$^+$: calculated: 188.0837, found: 188.0834. $[\alpha]_D^{20} = -69.201$ (c = 0.590, CHCl$_3$, $l = 50$ mm).

**Analysis of stereochemistry:**

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing (E)-2-(5-(6-chlorobenzo[d][1,3]dioxol-5-yl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl$_2$ as the pre-catalyst. The title compound was subjected to tandem hydroboration/oxidation as shown below to give (R)-2-(6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-yl)ethanol. Further analysis of stereochemistry was performed on (R)-2-(6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-yl)ethanol. Absolute stereochemistry was assigned by analogy.
Chiral SFC (Chiracel ODR-H, 1% IPA/hexane, 2 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (R)-2-(6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-yl)ethanol.

| Racemic Material | Percentage | Area       | RT (min) |
|------------------|------------|------------|----------|
| 1                | 48.9109    | 7937.4771  | 4.06     |
| 2                | 51.0891    | 8290.8498  | 5.13     |
| Total:           | 100        | 16228.3269 |          |

| Standard Conditions | Percentage | Area       | RT (min) |
|---------------------|------------|------------|----------|
| 1                   | 91.3767    | 14223.3138 | 4.93     |
| 2                   | 8.6233     | 1342.274   | 5.31     |
| Total:              | 100        | 15565.5878 |          |
(R)-5-(trifluoromethyl)-1-vinyl-2,3-dihydro-1H-indene (compound 8, Scheme 2). Prepared according to the general procedure utilizing (R,R)-L2 (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), (E)-2-(5-(2-chloro-5-(trifluoromethyl)phenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (93.7 mg, 0.250 mmol), Pd(OAc)₂ (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO₂, 100% pentane) to give the desired product as a clear, colorless oil (30.7 mg, 58%). R_f = 0.64 (100% hexane, UV/KMnO₄). ^{1}H NMR (500 MHz, CDCl₃): δ 7.48 (1H, s), 7.43 (1H, dd, J = 7.8, 1.0 Hz), 7.24 (1H, d, J = 7.8 Hz), 5.84 (1H, ddd, J = 17.1, 10.3, 7.8 Hz), 5.17 (1H, ddd (app dt’s), J = 17.1, 1.0, 1.0 Hz), 5.14 (1H, ddd (app dt’s), J = 10.3, 1.0, 1.0 Hz), 3.79 (1H, ddd (app q), J = 8.3 Hz), 2.99 (1H, ddd, J = 15.7, 8.8, 3.4 Hz), 2.91 (1H, ddd (app dt’s), J = 16.1, 8.3, 8.3 Hz), 2.40 (1H, dddd (app dtd’s), J = 12.7, 7.8, 7.8, 3.4 Hz), 1.91 (1H, dddd (app dq’s), J = 12.7, 8.3, 8.3, 8.3 Hz); ^{13}C NMR (126 MHz, CDCl₃): δ 149.7, 144.7, 140.1, 129.1 (q, J_{C-F} = 32.4 Hz), 124.5 (q, J_{C-F} = 272.8 Hz), 124.5, 123.4 (q, J_{C-F} = 3.8 Hz), 121.3 (q, J_{C-F} = 3.8 Hz), 115.7, 49.6, 33.1, 31.4; IR (neat): 3079.6 (w), 2939.1 (m), 2858.8 (w), 1433.4 (w), 1333.1 (s), 1290.3 (m), 1121.9 (s), 1061.1 (m), 992.2 (w), 918.6 (m), 889.8 (m), 851.1 (w), 830.1 (m) cm⁻¹; HRMS-(DART) for: C₁₂H₁₂F₃[M+H]⁺: calculated: 213.0891, found: 213.0890. [α]_D^{20} = -40.342 (c = 0.960, CHCl₃, l = 50 mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing (E)-2-(5-(2-chloro-5-(trifluoromethyl)phenyl)pent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl₂ as the pre-catalyst. Absolute stereochemistry was assigned by analogy.

Chiral GLC (β-dex, Supelco, 80 °C for 5 min, ramp 1 °C/min to 150 °C, 20 psi) – analysis of 5-(trifluoromethyl)-1-vinyl-2,3-dihydro-1H-indene.

| Racemic Material | Standard Conditions |
|------------------|---------------------|
|                  |                     |

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**(R)-1-(prop-1-en-2-yl)-2,3-dihydro-1H-indene (compound 9, Scheme 2).** Prepared according to the general procedure utilizing \((R,R)-L_2\) (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), \((E)-2-(5-(2-chlorophenyl)-2-methylpent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80.2 mg, 0.250 mmol), Pd(OAc)\(_2\) (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO\(_2\), 100% pentane) to give the desired product as a clear, colorless oil (31.5 mg, 80%). \(R_f = 0.43\) (100% hexane, UV/KMnO\(_4\)). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.26-7.22\) (1H, m), 7.20-7.11 (3H, m), 4.86-4.85 (1H, m), 4.84-4.83 (1H, m), 3.87 (1H, dd (app t), \(J = 8.3\) Hz), 2.98 (1H, dd (app dt’s), \(J = 15.7, 8.8, 4.4\) Hz), 2.89 (1H, ddd (app dt’s), \(J = 15.7, 7.8, 7.8\) Hz), 2.32-2.25 (1H, m), 2.02-1.94 (1H, m), 1.66 (3H, s); \(^1^3\)C NMR (126 MHz, CDCl\(_3\)): \(\delta 147.3, 145.2, 144.3, 126.5, 126.1, 124.5, 124.3, 111.6, 53.3, 31.7, 31.2, 19.2\); IR (neat): 3069.8 (w), 3021.2 (w), 2957.4 (m), 2944.1 (m), 2848.0 (w), 1644.2 (m), 1477.0 (m), 1457.1 (m), 1437.0 (w), 1373.5 (w), 891.1 (s), 742.2 (s) cm\(^{-1}\); HRMS-(DART) for: C\(_{12}\)H\(_{15}\) [M+H]\(^+\): calculated: 159.1174, found: 159.1176. \([\alpha]_D^{20} = -25.43\) (\(c = 1.050,\) CHCl\(_3\), \(l = 50\) mm).

**Analysis of stereochemistry:**

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing \((E)-2-(5-(2-chlorophenyl)-2-methylpent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl\(_2\) as the pre-catalyst. Absolute stereochemistry was assigned by analogy.

**Chiral GLC (β-dex, Supelco, 80 °C for 5 min, ramp 1 °C/min to 150 °C, 20 psi) – analysis of 1-(prop-1-en-2-yl)-2,3-dihydro-1H-indene.**

| Racemic Material | Standard Conditions |
|------------------|---------------------|
|                  |                     |

**Analysis of stereochemistry:**

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing \((E)-2-(5-(2-chlorophenyl)-2-methylpent-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl\(_2\) as the pre-catalyst. Absolute stereochemistry was assigned by analogy.

**Chiral GLC (β-dex, Supelco, 80 °C for 5 min, ramp 1 °C/min to 150 °C, 20 psi) – analysis of 1-(prop-1-en-2-yl)-2,3-dihydro-1H-indene.**

| Racemic Material | Standard Conditions |
|------------------|---------------------|
|                  |                     |
(R)-1-vinyl-1,2,3,4-tetrahydronaphthalene (compound 10, Scheme 2). Prepared according to the general procedure utilizing \((R,R)\)-L2 (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), \((E)\)-2-(6-(2-chlorophenyl)hex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (80.2 mg, 0.250 mmol), Pd(OAc)$_2$ (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO$_2$, 100% pentane) to give the desired product as a clear, colorless oil (21.8 mg, 55%). $R_f$ = 0.38 (100% hexane, UV/magic stain). All spectral data are in accordance with the literature.$^{15}$ HRMS-(DART) for: C$_{12}$H$_{15}$[M+H]$^+$: calculated: 159.1174, found: 159.1181. $[\alpha]_D^{20} = -21.636 \, (c = 0.610, \text{CHCl}_3, l = 50 \, \text{mm})$.

**Analysis of stereochemistry:**

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing \((E)\)-2-(6-(2-chlorophenyl)hex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl$_2$ as the pre-catalyst. Absolute stereochemistry was assigned by analogy.

**Chiral GLC** ($\beta$-dex, Supelco, 80 °C for 5 min, ramp 1 °C/min to 150 °C, 20 psi) – analysis of (R)-1-vinyl-1,2,3,4-tetrahydronaphthalene.

| Racemic Material | Standard Conditions |
|------------------|---------------------|
|                  |                     |
| Peak RetTime Type | Width [min] | Area [pA] | Height [pA] | Area % |
| ---              | ---              | ---       | ---        | ---   |
| 1                | 44.994 s        | 289.6195  | 29.82614   | 56.53628 |
| 2                | 44.533 s        | 283.16623 | 29.25908   | 49.43672 |

*Totals: 572.78520 59.08522*

| Peak RetTime Type | Width [min] | Area [pA] | Height [pA] | Area % |
| ---              | ---              | ---       | ---        | ---   |
| 1                | 43.503 s        | 3059.7414 | 0.3270     | 155.59407 |
| 2                | 44.390 s        | 507.38211 | 0.2460     | 34.37797 |

*Totals: 3567.12357 190.33204* 

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$^{15}$ Namba, K.; Yamamoto, H.; Sasaki, I.; Mori, K.; Imagawa, H.; Nishizawa, M. *Org. Lett.* **2008**, *10*, 1767.
(R)-5-vinyl-6,7,8,9-tetrahydro-5H-benzo[7]annulene (compound 11, Scheme 2). Prepared according to the general procedure utilizing (R,R)-L2 (17.3 mg, 0.0175 mmol), cesium fluoride (113.9 mg, 0.750 mmol), (E)-2-(7-(2-chlorophenyl)hept-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (83.7 mg, 0.250 mmol), Pd(OAc)2 (2.8 mg, 0.0125 mmol), and THF (1.25 mL). The crude material was purified (SiO2, 100% pentane) to give the desired product as a clear, colorless oil (21.6 mg, 50%). \( R_f = 0.40 \) (100% hexane, UV/KMnO4). \(^1\)H NMR (500 MHz, CDCl3): \( \delta \) 7.14-7.12 (2H, m), 7.11-7.09 (2H, m), 6.16 (1H, ddd, \( J = 17.6, 10.3, 6.4 \) Hz), 5.12 (1H, ddd (app dt’s), \( J = 10.3, 1.5, 1.5 \) Hz), 4.92 (1H, d, \( J = 17.6 \) Hz), 3.64-3.61 (1H, m), 2.88-2.83 (1H, m), 2.81-2.76 (1H, m), 1.96-1.84 (2H, m), 1.81-1.69 (2H, m), 1.68-1.58 (2H, m); \(^{13}\)C NMR (126 MHz, CDCl3): \( \delta \) 144.0, 142.8, 141.1, 129.7, 128.1, 126.1, 125.9, 114.4, 48.8, 36.2, 33.2, 28.9, 28.0; IR (neat): 3071.2 (w), 3014.7 (w), 2922.5 (s), 2852.5 (m), 1639.3 (w), 1489.4 (w), 1474.1 (w), 1444.7 (w), 1053.1 (w), 1001.2 (w), 913.6 (m), 746.8 (s) cm\(^{-1}\); HRMS-(DART) for: C\(_{13}\)H\(_7\) [M+H]\(^+\): calculated: 173.1330, found: 173.1331. \([\alpha]_D^{20} = -6.752 \) (c = 0.385, CHCl3, \( l = 50 \) mm).

**Analysis of stereochemistry:**

Racemic compound was prepared according to the general procedure for intramolecular coupling utilizing (E)-2-(7-(2-chlorophenyl)hept-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pd(dppf)Cl2 as the pre-catalyst. Absolute stereochemistry was assigned by analogy.

**Chiral GLC (β-dex, Supelco, 80 °C for 5 min, ramp 1 °C/min to 150 °C, 20 psi) – analysis of 5-vinyl-6,7,8,9-tetrahydro-5H-benzo[7]annulene.**

| Racemic Material | Standard Conditions |
|------------------|---------------------|
| Peak RetTime | Type | Width | Area | Height | Area | Peak RetTime | Type | Width | Area | Height | Area |
| # | (min) | (min) | (pA*s) | (pA) | | # | (min) | (min) | (pA*s) | (pA) |
| 1 | 53.774 | HPLC | 0.2081 | 1084.7857 | 0.0930 | 50.27924 | 1 | 53.786 | HPLC | 0.1567 | 207.03444 | 22.09879 | 37.55123 |
| 2 | 54.663 | HPLC | 0.2209 | 1072.7365 | 0.92230 | 49.72076 | 2 | 54.652 | HPLC | 0.1719 | 345.63385 | 33.20714 | 62.44872 |
| Totals : | 2157.52234 | 167.81540 | | | | Totals : | 553.46829 | 55.60593 |
Compound S2
Compound S5
Compound S5
Compound S6
Compound 3
Compound 3
Compound S7
Compound S7

[Chemical structure image]
Compound S8
Compound S10
Compound S11
Compound S12

\[ \text{Diagram of Compound S12} \]
Compound S12
Compound S13
Compound S14
Compound S16

S-70
Compound S17
Compound S18

\[
\begin{align*}
&\text{MeO} \quad \text{MeO} \\
&\text{Cl} \quad \text{Cl} \\
&\text{Cl} \quad \text{Cl} \\
\end{align*}
\]
Compound S19
Compound 22
Compound S24
Compound S26
Compound S27
Compound S28
Compound S29
Compound S30
Compound S31
Compound S33
Compound S34
Compound S35
Compound S35
Compound S38
Compound S38
Compound S39
Compound S39
Compound S40
Compound S40
Compound S41
Compound S42
Compound S43

S-118
Compound S44
Compound S44
Compound S45
Compound S47

[Chemical Structure Image]
Compound 2

\[
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\]
Compound 7
Compound 8
Compound 9
