# Total Synthesis of (+)-Superstolide A 

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General Experimental Details. All reaction solvents were purified before use. Tetrahydrofuran, dichloromethane, diethyl ether, and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of nitrogen using flame-dried or oven-dried $\left(140^{\circ} \mathrm{C}\right)$ glassware. Triethylamine and diisopropylethylamine were dried by distillation over calcium hydride. Acetone was dried by distillation from anhydrous calcium sulfate.
${ }^{1} \mathrm{H}$ NMR spectra were recorded on commercial instruments at 400 MHz or $500 \mathrm{MHz} .{ }^{13} \mathrm{C}$ NMR spectra were recorded at 100 MHz or 125 MHz . The proton signal for residual non-deuterated solvent ( $\delta$ 7.26 for $\mathrm{CHCl}_{3}, 7.16$ for $\mathrm{C}_{6} \mathrm{H}_{6}$ ) was used as an internal reference for ${ }^{1} \mathrm{H}$ NMR spectra. For ${ }^{13} \mathrm{C}$ NMR spectra, chemical shifts are reported relative to the $\delta 77.0$ resonance of $\mathrm{CDCl}_{3}$ and 128.0 resonance of $\mathrm{C}_{6} \mathrm{D}_{6}$. Infrared (IR) spectra were recorded as films on commercial FTIR instrument. Optical rotations were measured on a polarimeter using a quartz cell with 1 mL capacity and a 10 cm path length. Melting points were determined on a hot stage melting point apparatus and are uncorrected. Mass spectra were measured on commercially available instruments.

Analytical thin layer chromatography (TLC) was performed on Kieselgel $60 \mathrm{~F}_{254}$ glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid). Column chromatography was generally performed using Kieselgel 60 (230-400 mesh) silica gel or, when noted, silica gel Davisil ${ }^{\mathrm{TM}}$, grade 645, 60-100 mesh, $150 \AA$.

Compounds 3-5, 19, 20, 23, 24, 38, 47-49, 54 and SI-6-SI-12 showed a dynamic mixture of conformational isomers and/or Boc rotamers evidenced by doubling of ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ resonances for many protons and carbons.

Many of the polyene intermediates generated in this work are extremely sensitive to light. Therefore, flasks were covered with aluminum foil whenever possible for intermediates $\mathbf{4}, \mathbf{5}, \mathbf{1 9}, \mathbf{2 0}, \mathbf{3 6 b}$, 43a-b, 47-49 and SI-8 - SI-10.


Diol 10. A solution of salt-free bis(d-isopinocampheyl)allyl borane ( 75 mmol ) in $\mathrm{Et}_{2} \mathrm{O}(100 \mathrm{~mL})$ was cooled to $-105^{\circ} \mathrm{C}$ in a diethyl ether/pentane/liquid nitrogen bath. A solution of (4S)-2,2-diethyl-1,3-dioxolane-4-acetaldehyde $(9){ }^{1}(8.49 \mathrm{~g}, 49.3 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(40 \mathrm{~mL})$ was cooled to $-78{ }^{\circ} \mathrm{C}$ and added via cannula over 30 min to the allylboron reagent while maintaining the reaction temperature below $-100^{\circ} \mathrm{C}$. After 1 h more, the reaction was then slowly warmed to $-72^{\circ} \mathrm{C}$ over 1.5 h . After the addition of MeOH $(6 \mathrm{~mL})$, the reaction was warmed to $0^{\circ} \mathrm{C}$. A solution of $2 \mathrm{~N} \mathrm{NaOH}(40 \mathrm{~mL})$ and hydrogen peroxide $(35 \%$ $\mathrm{aq}, 60 \mathrm{~mL}$ ) was added dropwise over 30 min . The mixture was stirred for 18 h at room temperature. After extraction of the product with diethyl ether ( $2 \times 200 \mathrm{~mL}$ ), the combined organic layers were washed with brine, dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated to a crude oil ( 31.33 g ) consisting of the desired allylation product (10:1 d.r.) and isopinocampheol.

The product mixture ( $\sim 182 \mathrm{mmol}$ total) was dissolved in THF ( 150 mL ) and cooled to $0{ }^{\circ} \mathrm{C}$. Sodium hydride ( $95 \%$ purity, $6.11 \mathrm{~g}, 254 \mathrm{mmol}$ ) was added in portions to control the exothermic release of hydrogen. Methyl iodide ( $20.4 \mathrm{~mL}, 327 \mathrm{mmol}$ ) was then added and the mixture was gradually warmed to room temperature (the release of hydrogen was controlled by placing of the reaction vessel in an ice bath). After 40 h , the reaction was carefully poured into a 2 L -Erlenmeyer flask which contained sat aq $\mathrm{NH}_{4} \mathrm{Cl}(400 \mathrm{~mL})$ and ice. The mixture was extracted with $\mathrm{Et}_{2} \mathrm{O}(2 \times 300 \mathrm{~mL})$. The combined organic layers were washed with sat. aq. $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$, brine, dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated to a crude colorless oil ( 22.80 g ).

The crude was dissolved in a mixture of $\mathrm{MeOH}(40 \mathrm{~mL})$ and $1 \mathrm{~N} \mathrm{HCl}(\mathrm{aq})(20 \mathrm{~mL})$. After 40 h , the reaction was poured carefully into an Erlenmeyer flask which contained $\mathrm{NaHCO}_{3}(7.0 \mathrm{~g})$ and then partitioned between brine $(30 \mathrm{~mL})$ and $\operatorname{EtOAc}(100 \mathrm{~mL})$. After separation of the layers, the aqueous phase was extracted once more with EtOAc ( 100 mL ). The combined organic layers were dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated. Purification of the crude product by flash column chromatography ( $40 \% \mathrm{EtOAc} /$ hexanes $\rightarrow 5 \% \mathrm{MeOH} / \mathrm{EtOAc} \rightarrow 15 \% \mathrm{MeOH} / \mathrm{EtOAc}$ ) afforded pure 10 $(4.22 \mathrm{~g}, 26.4 \mathrm{mmol}, 53 \%$ over 3 steps $)$ as a colorless oil: $[\alpha]^{25}{ }_{\mathrm{D}}=+65.0^{\circ}\left(c 1.50, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 5.76(\mathrm{ddt}, J=14.3,10.6,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.13-5.11(\mathrm{~m}, 2 \mathrm{H}), 3.90(\mathrm{~m}, 1 \mathrm{H}), 3.72(\mathrm{br} \mathrm{s}$, $1 \mathrm{H}), 3.60(\mathrm{dd}, J=11.1,3.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.55(\mathrm{~m}, 1 \mathrm{H}), 3.47$ (dd, $J=11.1,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.41$ (s, 3H), 2.41-2.26 (m, 2H), $2.16(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 1.69(\mathrm{ddd}, J=14.8,9.8,9.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.60(\operatorname{app} \mathrm{dt}, J=14.8,3.0 \mathrm{~Hz}, 1 \mathrm{H}){ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 133.5,117.7,80.0,71.3,66.4,56.1,37.2,36.5$; IR (film) 3391, 3078, 2978,

2933, 2829, 1643, 1418, $1089 \mathrm{~cm}^{-1}$; HRMS (CI, $\left.\mathrm{NH}_{3}\right) m / z$ for $\mathrm{C}_{8} \mathrm{H}_{17} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+}$calcd 161.1178, found 161.1174.


Triether 11. A solution of diol $10(3.76 \mathrm{~g}, 24.7 \mathrm{mmol})$ and pyridine ( $2.70 \mathrm{~mL}, 33.3 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(90 \mathrm{~mL})$ was treated with $\mathrm{TrCl}(8.27 \mathrm{~g}, 29.7 \mathrm{mmol})$. After 16 h , the reaction mixture was poured into sat. aq. $\mathrm{NaHCO}_{3}(200 \mathrm{~mL})$. The aqueous phase was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 100 \mathrm{~mL})$. The combined organic layers were washed with sat. aq. $\mathrm{Na}_{2} \mathrm{CO}_{3}(100 \mathrm{~mL})$, dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated to a crude oil ( 13.88 g ). This product was combined with imidazole ( 3.36 g , 49.4 mmol ), 4-(dimethylamino)pyridine ( $300 \mathrm{mg}, 2.47 \mathrm{mmol}$ ), and DMF ( 20 mL ). The solution was cooled to $0{ }^{\circ} \mathrm{C}$ and treated with TBDPSCl ( $8.03 \mathrm{~mL}, 30.9 \mathrm{mmol}$ ). The reaction mixture was stirred at room temperature for 21 h and quenched with sat. aq. $\mathrm{NaHCO}_{3}(150 \mathrm{~mL})$. The aqueous phase was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 100 \mathrm{~mL})$. The combined organic layers were washed with water ( $2 \times 150 \mathrm{~mL}$ ), brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated. Purification of the crude product by flash column chromatography ( $2-5 \%$ EtOAc/hexanes) afforded $11\left(15.7 \mathrm{~g}, 24.5 \mathrm{mmol}, 99 \%\right.$ ) as a viscous oil: $[\alpha]^{25}{ }_{\mathrm{D}}=$ $-11.0^{\circ}\left(c 2.10, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.63(\mathrm{~m}, 4 \mathrm{H}), 7.44-7.28(\mathrm{~m}, 12 \mathrm{H}), 7.26-7.17(\mathrm{~m}$, $9 \mathrm{H}), 5.63(\mathrm{ddt}, J=13.9,10.3,7.0 \mathrm{~Hz} 1 \mathrm{H}), 4.97(\mathrm{~m}, 1 \mathrm{H}), 4.92(\mathrm{~m}, 1 \mathrm{H}), 3.98(\mathrm{~m}, 1 \mathrm{H}), 3.21-3.04(\mathrm{~m}, 3 \mathrm{H})$, $3.03(\mathrm{~s}, 3 \mathrm{H}), 2.01(\mathrm{~m}, 2 \mathrm{H}), 1.85(\mathrm{app} \mathrm{t}, J=14.0,6.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.70(\mathrm{app} \mathrm{dt}, J=14.0,6.7 \mathrm{~Hz}, 1 \mathrm{H}), 1.05(\mathrm{~s}$, $9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 144.4,136.3,136.2,134.9,134.5,134.3,129.9,129.7,129.3,129.1$, $127.9,127.8,127.7,127.1,117.1,86.7,77.2,70.8,67.4,56.2,38.7,38.0,27.4,19.6$; IR (film) 3069 , 2930, 2857, 2821, 1960, 1897, 1822, 1640, 1597, 1490, 1472, 1449, 1389, 1361, 1111, $1022 \mathrm{~cm}^{-1} ;$ HRMS (ESI) $m / z$ for $\mathrm{C}_{43} \mathrm{H}_{48} \mathrm{NaO}_{3} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+} 663.3270$, found 663.3274; Anal. calcd for $\mathrm{C}_{43} \mathrm{H}_{48} \mathrm{O}_{3} \mathrm{Si}$ : C, 80.58; H, 7.55. Found: C 80.26; H 7.51 .


Aldehyde 12. A solution of $\mathbf{1 1}(12.7 \mathrm{~g}, 19.8 \mathrm{mmol})$ and Sudan III dye in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(119 \mathrm{~mL})$ and $\mathrm{MeOH}(36 \mathrm{~mL})$ was cooled to $-78^{\circ} \mathrm{C}$. Ozone gas was bubbled through the solution until the pink color disappeared ( 2 h ). Triphenylphosphine ( $8.0 \mathrm{~g}, 29.7 \mathrm{mmol}$ ) was added and the reaction was stirred for 16 h at room temperature. The reaction mixture was poured into 100 mL half-saturated brine and extracted
with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 100 \mathrm{~mL})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated. Purification of the crude product by flash chromatography ( $5-10 \% \mathrm{EtOAc} /$ hexanes ) afforded aldehyde $12(10.09 \mathrm{~g}, 16.96 \mathrm{mmol}, 76 \%)$ as a viscous oil: $[\alpha]^{25}{ }_{\mathrm{D}}=-14.0^{\circ}\left(c 3.10, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 9.50(\mathrm{dd}, J=3.0,1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.65-7.61(\mathrm{~m}, 2 \mathrm{H}), 7.59-7.56(\mathrm{~m}, 2 \mathrm{H}), 7.47-$ $7.31(\mathrm{~m}, 12 \mathrm{H}), 7.25-7.20(\mathrm{~m}, 9 \mathrm{H}), 3.89(\mathrm{~m}, 1 \mathrm{H}), 3.60(\mathrm{~m}, 1 \mathrm{H}), 3.15(\mathrm{~m}, 2 \mathrm{H}), 3.08(\mathrm{~s}, 3 \mathrm{H}), 2.25(\mathrm{ddd}, J=$ $16.2,7.9,3.1 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.14 (ddd, $J=16.2,4.1,1.8 \mathrm{~Hz} 1 \mathrm{H}$ ), 1.91 (app dt, $J=14.0,6.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 1.90 (ddd, $J=12.8,7.3,5.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.05(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 201.4,143.9,135.9,135.8,133.8$, 133.6, 129.8, 129.6, 128.7, 127.7, 127.5, 126.9, 86.5, 73.1, 69.9, 66.7, 56.2, 48.0, 38.3, 27.0, 19.2; IR (neat) $3056,2930,2858,2822,2724,1726,1590,1490,1449,1428,1116 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{42} \mathrm{H}_{46} \mathrm{NaO}_{4} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 665.3063, found 665.3087.


Enoate 13. A solution of ethyl 2-(bis(2,2,2-trifluoroethoxy)phosphoryl)propanoate (11.5 g, 33.4 $\mathrm{mmol})$ and 18 -crown-6 $(21.0 \mathrm{~g}, 79.5 \mathrm{mmol})$ in THF $(110 \mathrm{~mL})$ was cooled to $-78^{\circ} \mathrm{C}$ and treated dropwise over 30 min with a solution of potassium bis(trimethylsilyl)amide ( $6.33 \mathrm{~g}, 31.8 \mathrm{mmol}$ ) in toluene ( 64 mL ). After an additional 30 min , a solution of aldehyde $\mathbf{1 2}(10.2 \mathrm{~g}, 15.9 \mathrm{mmol})$ in THF ( 20 mL ) was transferred to the reaction mixture via cannula over 1.5 h . After the reaction was stirred an additional 6 h at $-78{ }^{\circ} \mathrm{C}$, sat. aq. $\mathrm{NH}_{4} \mathrm{Cl}(40 \mathrm{~mL})$ was added. The mixture was warmed to $23^{\circ} \mathrm{C}$, and extracted with $\mathrm{Et}_{2} \mathrm{O}(2 \times 100 \mathrm{~mL})$. The combined organic layers were dried over anhydrous $\mathrm{MgSO}_{4}$, filtered, and concentrated. Purification of the crude product by flash chromatography ( $10 \% \mathrm{EtOAc} /$ hexanes ) furnished $13(11.2 \mathrm{~g}, 15.6 \mathrm{mmol}, 98 \%)$ as a pale yellow oil: $[\alpha]^{25}{ }_{\mathrm{D}}=+6.0^{\circ}\left(c 3.40, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 400\right.$ $\mathrm{MHz}) \delta 6.61(\mathrm{~m}, 4 \mathrm{H}), 7.43-7.28(\mathrm{~m}, 12 \mathrm{H}), 7.25-7.18(\mathrm{~m}, 9 \mathrm{H}), 5.78(\mathrm{app} \mathrm{td}, J=6.6 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.14$ $(\mathrm{q}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}), 4.08(\mathrm{~m}, 1 \mathrm{H}), 3.21(\mathrm{~m}, 1 \mathrm{H}), 3.18(\mathrm{dd}, J=9.5,5.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.02(\mathrm{dd}, J=9.5,4.5 \mathrm{~Hz}$, $1 \mathrm{H}), 3.03(\mathrm{~s}, 3 \mathrm{H}), 2.62-2.49(\mathrm{~m}, 2 \mathrm{H}), 1.89(\mathrm{~d}, J=1.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.86(\mathrm{~m}, 1 \mathrm{H}), 1.75(\mathrm{ddd}, J=13.9,7.5,5.9$ $\mathrm{Hz}, 1 \mathrm{H}), 1.28(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}), 1.09(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 167.8,144.1,138.5$, $136.0,135.8,134.2,134.0,129.5,129.4,128.7,128.5,127.6,127.5,127.4,126.7,86.3,70.4,66.9,60.0$, 55.6, 38.4, 32.9, 27.0, 20.7, 19.3, 14.3; IR (neat) 3054, 2930, 2317, 1960, 1900, 1822, 1732, 1715, 1652, $1645,1590,1488,1455,1372 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{47} \mathrm{H}_{54} \mathrm{NaO}_{5} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 749.3638 , found 749.3639 .


Alcohol SI-1. Camphorsulfonic acid ( $0.14 \mathrm{~g}, 0.61 \mathrm{mmol})$ was added to a solution of the trityl ether $13(4.40 \mathrm{~g}, 6.05 \mathrm{mmol})$ in $\mathrm{EtOH}(20 \mathrm{~mL}) / \mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ at $23{ }^{\circ} \mathrm{C}$. After 36 h , the mixture was poured into an Erlenmeyer flask which contained $\mathrm{NaHCO}_{3}(7 \mathrm{~g})$, filtered, and concentrated. Purification of the crude product by flash chromatography (5-10\% EtOAc/hexanes to elute trityl alcohol, then 40\% EtOAc/hexanes) afforded the deprotected alcohol SI-1 ( $2.84 \mathrm{~g}, 5.86 \mathrm{mmol}, 96 \%$ ) as a pale yellow oil: $[\alpha]_{\mathrm{D}}^{25}=+33.0^{\circ}\left(c 3.20, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.65(\mathrm{~m}, 4 \mathrm{H}), 7.45-7.35(\mathrm{~m}, 6 \mathrm{H}), 5.82$ (app dt, $J=7.3,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.18(\mathrm{q}, ~ J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 3.99(\mathrm{ddd}, J=11.7,5.9,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.56(\mathrm{~m}, 1 \mathrm{H})$, $3.50(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.28(\mathrm{~s}, 3 \mathrm{H}), 2.70(\mathrm{~m}, 1 \mathrm{H}), 2.61(\mathrm{br} \mathrm{s}, 3 \mathrm{H}), 2.55(\mathrm{ap} \mathrm{td}, J=15.8,7.0 \mathrm{~Hz}, 1 \mathrm{H})$, $1.87(\mathrm{~s}, 3 \mathrm{H}), 1.74(\mathrm{ddd}, J=14.8,8.5,3.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.64(\mathrm{ddd}, J=14.8,6.1,3.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.28(\mathrm{t}, J=7.1$ $\mathrm{Hz}, 3 \mathrm{H}), 1.06(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 167.7,137.6,135.8,135.7,133.9,133.7,129.8$, $127.7,127.6,94.4,76.4,70.9,65.4,60.1,55.9,37.7,32.7,27.0,20.8,19.2,14.3$; IR (neat) 3469 (br), 3072, 2931, 2889, 2858, 1713, 1645, 1590, 1462, 1428, 1373, $1110 \mathrm{~cm}^{-1}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ for $\mathrm{C}_{28} \mathrm{H}_{40} \mathrm{NaO}_{5} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 507.2543, found 507.2565; Anal. calcd for $\mathrm{C}_{28} \mathrm{H}_{40} \mathrm{O}_{5} \mathrm{Si}$ : C, 69.38; H, 8.32. Found: C 69.24; H 8.26.


Aldehyde 14. To a solution of SI-1 $(6.60 \mathrm{~g}, 13.6 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(109 \mathrm{~mL})$ was added DMSO $(6.80 \mathrm{~mL}, 95.5 \mathrm{mmol})$ and diisopropylethylamine $(11.9 \mathrm{~mL}, 68.2 \mathrm{mmol})$. The mixture was cooled to $0^{\circ} \mathrm{C}$ and charged with $\mathrm{SO}_{3} \bullet$ pyridine $(6.51 \mathrm{~g}, 40.9 \mathrm{mmol})$. After 30 min , sat. aq. $\mathrm{NaHCO}_{3}(50 \mathrm{~mL})$ was added and the aqueous phase was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 30 \mathrm{~mL})$. The combined organic layers were washed with brine, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $20 \% \mathrm{EtOAc} /$ hexanes) afforded $14(6.20 \mathrm{~g}, 12.8 \mathrm{mmol}, 94 \%)$ as a viscous oil: $[\alpha]^{25}{ }_{\mathrm{D}}=+38.3^{\circ}\left(c 1.16, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 9.53(\mathrm{~s}, 1 \mathrm{H}), 7.64(\mathrm{~m}, 4 \mathrm{H}), 7.46-7.41(\mathrm{~m}$, $2 \mathrm{H}), 7.39-7.34(\mathrm{~m}, 4 \mathrm{H}), 5.85(\mathrm{tq}, J=7.5,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.18(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 4.09(\mathrm{dd}, J=6.4,2.3 \mathrm{~Hz}$, $1 \mathrm{H}), 3.71(\mathrm{~m}, 1 \mathrm{H}), 3.30(\mathrm{~s}, 3 \mathrm{H}), 2.80-2.72(\mathrm{~m}, 1 \mathrm{H}), 2.58(\mathrm{~m}, 1 \mathrm{H}), 1.94-1.87(\mathrm{~m}, 1 \mathrm{H}), 1.90(\mathrm{~d}, J=1.3 \mathrm{~Hz}$, $3 \mathrm{H}), 1.69(\mathrm{ddd}, J=14.5,6.4,2.7 \mathrm{~Hz}, 1 \mathrm{H}), 1.29(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}), 1.12(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100\right.$ $\mathrm{MHz}) \delta 202.4,167.7,137.2,135.7,135.6,133.2,132.7,130.0,129.3,127.8,127.7,75.3,75.2,60.1,56.3$, 39.0, 32.3, 26.9, 20.8, 19.3, 14.3; IR (neat) $3072,3050,2958,2932,2894,2858,2826,2713,1963,1895$,
$1825,1732,1715,1648,1590,1473,1463,1428,1372,1228,1193,1112 \mathrm{~cm}^{-1} ;$ HRMS $m / z$ for $\mathrm{C}_{28} \mathrm{H}_{38} \mathrm{NaO}_{5} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 505.2386, found 505.2367.


Allylic Alcohol 7a. To a slurry of anhydrous chromium (II) chloride ( $15.8 \mathrm{~g}, 128.6 \mathrm{mmol}$ ) in THF ( 26 mL ) was added a solution of $\mathbf{1 4}(6.20 \mathrm{~g}, 12.9 \mathrm{mmol})$ and iodoform ( $15.2 \mathrm{~g}, 38.6 \mathrm{mmol}$ ) in dioxane ( 219 mL ). The resulting brown suspension was stirred at room temperature for 12 h , then diluted with $\mathrm{Et}_{2} \mathrm{O}(200 \mathrm{~mL})$ and poured into 200 mL of water. The aqueous phase was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \mathrm{x}$ 100 mL ). The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $20-80 \% \mathrm{CH}_{2} \mathrm{Cl}_{2}$-hexanes) afforded iodide SI-2 ( $6.46 \mathrm{~g}, 10.6 \mathrm{mmol}, 82 \%$ ) as a yellow oil.

To a $-78{ }^{\circ} \mathrm{C}$ solution of $\mathbf{S I - 2}(6.46 \mathrm{~g}, 10.6 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(64 \mathrm{~mL})$, was added DIBAL-H ( 26.6 mL of a 1.0 M solution in hexanes, 26.6 mmol ) dropwise. The mixture was allowed to warm up to -20 ${ }^{\circ} \mathrm{C}$ and then quenched with sat. aq. sodium potassium tartrate (Rochelle's salt, 50 mL ) and diluted with $\mathrm{Et}_{2} \mathrm{O}$. The mixture was stirred at room temperature for 12 h . The aqueous phase was extracted with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 30 \mathrm{~mL}$ ), dried over anhydrous $\mathrm{MgSO}_{4}$, filtered and concentrated to provide pure allylic alcohol $7 \mathbf{a}$ $(5.83 \mathrm{~g}, 10.3 \mathrm{mmol}, 94 \%)$ as a viscous oil: $[\alpha]^{25}{ }_{\mathrm{D}}=-41.0^{\circ}\left(c 3.20, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right)$ $\delta 7.65-7.60(\mathrm{~m}, 4 \mathrm{H}), 7.45-7.36(\mathrm{~m}, 6 \mathrm{H}), 6.49(\mathrm{dd}, J=14.4,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.94(\mathrm{dd}, J=14.1,1.0 \mathrm{~Hz}, 1 \mathrm{H})$, $5.17(\operatorname{app} \mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.23(\mathrm{~m}, 1 \mathrm{H}), 3.99(\mathrm{~d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.92(\mathrm{~d}, J=11.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.21(\mathrm{~m}$, $1 \mathrm{H}), 3.18(\mathrm{~s}, 3 \mathrm{H}), 2.09(\mathrm{~m}, 2 \mathrm{H}), 1.9(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 1.79(\mathrm{~s}, 3 \mathrm{H}), 1.77$ (ddd, $J=14.0,7.4,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.49$ (ddd, $J=14.1,6.9,5.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.06(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 148.0,138.0,135.9,135.8$, 133.6, 133.3, 129.8, 129.8, 127.6, 127.6, 123.2, 76.7, 73.7, 61.3, 56.6, 41.2, 31.8, 27.0, 22.1, 19.3; IR (neat) 3435 (br), $3071,3045,2931,2857,1713,1606,1471,1427,1111 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{27} \mathrm{H}_{37} \mathrm{INaO}_{3} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 587.1454, found 587.1462.


Boronic Ester SI-3. A mixture of anhydrous chromium(II) chloride ( $0.80 \mathrm{~g}, 6.50 \mathrm{mmol}$ ) and lithium iodide ( $0.16 \mathrm{~g}, 5.67 \mathrm{mmol}$ ) was cooled to $0{ }^{\circ} \mathrm{C}$ and suspended in degassed THF ( 8 mL ). A degassed solution of aldehyde $\mathbf{1 4}(0.39 \mathrm{~g}, 0.81 \mathrm{mmol})$ and dichloromethyl pinacol boronate ${ }^{2}(0.34 \mathrm{~g}, 1.6$ $\mathrm{mmol})$ in THF ( 4 mL ) was transferred via cannula to the suspension. After 16 h , the dark mixture was poured into water $(50 \mathrm{~mL})$ and extracted with diethyl ether ( $3 \times 50 \mathrm{~mL}$ ). The combined ethereal layers were washed with water ( 10 mL ), dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated to furnish vinyl boronate SI-3 $(0.45 \mathrm{~g}, 0.74 \mathrm{mmol}, 92 \%)$ as a pale yellow oil: $[\alpha]^{25}{ }_{\mathrm{D}}=-5.7^{\circ}\left(c 4.40, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right.$, $400 \mathrm{MHz}) \delta 7.63(\mathrm{~m}, 4 \mathrm{H}), 7.41-7.30(\mathrm{~m}, 6 \mathrm{H}), 6.57(\mathrm{dd}, J=17.9,5.5 \mathrm{~Hz}, 1 \mathrm{H}), 5.80(\mathrm{app} \mathrm{td}, J=6.9,1.2$ $\mathrm{Hz}, 1 \mathrm{H}), 5.49(\mathrm{dd}, J=17.9,11.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.38(\mathrm{~m}, 1 \mathrm{H}), 4.16(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 3.29(\mathrm{~m}, 1 \mathrm{H}), 3.12(\mathrm{~s}$, $3 \mathrm{H}), 2.55(\mathrm{~m}, 2 \mathrm{H}), 1.86(\mathrm{~d}, J=1.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.78$ (ddd, $J=14.0,8.2,5.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.47$ (ddd, $J=14.0,7.0$, $4.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.26(\mathrm{~m}, 15 \mathrm{H}), 1.07(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 125 \mathrm{MHz}\right) \delta 167.7 .154 .8,138.3,135.9$, $135.8,134.1,133.8,129.5,129.4,128.5,127.4,127.3,83.0,76.1,59.5,55.6,41.7,33.1,27.0,24.8,24.7$, 24.6, 24.3, 20.7, 19.3, 14.2 [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ${ }^{11}$ B nucleus]; IR (film) 3072, 3049, 2978, 2932, 2858, 1715, 1642, 1590, 1472, $1463,1428,1371,1338,1216,1145,1105 \mathrm{~cm}^{-1} ;$ HRMS (ES) calcd for $\mathrm{C}_{35} \mathrm{H}_{51} \mathrm{BNaO}_{6} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+}$ 629.3446, found 629.3459.


Allylic Alcohol 7b. A solution of ethyl ester SI-3 ( $0.42 \mathrm{~g}, 0.69 \mathrm{mmol}$ ) in diethyl ether ( 7 mL ) was cooled to $-78{ }^{\circ} \mathrm{C}$ and treated with DIBAL-H ( 1.0 M in hexanes, $2.08 \mathrm{~mL}, 2.08 \mathrm{mmol}$ ). The dry ice/acetone bath was replaced with an ice bath and the reaction was stirred for an additional 30 min . The reaction was quenched by sequential addition of water $(0.3 \mathrm{~mL}), 2 \mathrm{~N} \mathrm{NaOH}(0.6 \mathrm{~mL})$, and water $(0.3 \mathrm{~mL})$. After the mixture was stirred for 1 h at $23^{\circ} \mathrm{C}$, the white precipitate was filtered through a pad of Celite. The product was eluted with diethyl ether, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated to furnish $\mathbf{7 b}$ $(0.38 \mathrm{~g}, 0.67 \mathrm{mmol}, 97 \%)$ as a transparent oil: $[\alpha]^{25}{ }_{\mathrm{D}}=-7.0^{\circ}\left(c 2.00, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400\right.$ $\mathrm{MHz}) \delta 7.64(\mathrm{~m}, 4 \mathrm{H}), 7.44-7.31(\mathrm{~m}, 6 \mathrm{H}), 6.57(\mathrm{dd}, J=18.0,5.5 \mathrm{~Hz}, 1 \mathrm{H}), 5.51(\mathrm{dd}, J=18.0,1.3 \mathrm{~Hz}, 1 \mathrm{H})$, 5.13 (app t, $J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.34(\mathrm{app} \mathrm{q}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.96(\mathrm{dd}, J=11.7,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{dd}, J=$ $11.6,6.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.15(\mathrm{~m}, 1 \mathrm{H}), 3.13(\mathrm{~s}, 3 \mathrm{H}), 2.40(\mathrm{~m}, 1 \mathrm{H}), 2.12-1.95(\mathrm{~m}, 2 \mathrm{H}), 1.80-1.73(\mathrm{~m}, 1 \mathrm{H}), 1.77$ $(\mathrm{s}, 3 \mathrm{H}), 1.43(\mathrm{dt}, J=14.1,5.7 \mathrm{~Hz}, 1 \mathrm{H}), 1.26(\mathrm{~s}, 6 \mathrm{H}), 1.25(\mathrm{~s}, 6 \mathrm{H}), 1.07(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100\right.$
$\mathrm{MHz}) \delta 154.7,138.0,136.0,135.9,134.1,133.6,129.7,129.5,127.5,127.4,123.4,83.1,76.7,72.7,61.2$, 56.6, 41.1, 32.1, 27.1, 24.8, 24.6, 22.3, 19.3; IR (film) 3445 (br), 3072, 3049, 2976, 2932, 2859, 1643, $1472,1428,1391,1371,1338,1272,1146,1112 \mathrm{~cm}^{-1} ; ~ H R M S(E S)$ calcd for $\mathrm{C}_{33} \mathrm{H}_{49} \mathrm{BNaO}_{5} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+}$ 587.3340, found 587.3348.


Allylic Bromide 17. Methane sulfonic anhydride ( $0.98 \mathrm{~g}, 5.62 \mathrm{mmol}$ ) was added to a cold solution ( $0^{\circ} \mathrm{C}$ ) of (2E,4E)-5-tributylstannyl-2-methylpenta-2,4-dien-1-ol $\mathbf{1 6}^{3}$ ( $1.50 \mathrm{~g}, 4.32 \mathrm{mmol}$ ) and triethylamine $(0.90 \mathrm{~mL}, 6.48 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(9 \mathrm{~mL})$. After 15 min , the reaction was diluted with acetone ( 9 mL ) and charged with anhydrous lithium bromide ( $2.25 \mathrm{~g}, 25.9 \mathrm{mmol}$ ). After the mixture was stirred for 2 h at $23^{\circ} \mathrm{C}$, the solvents were removed in vacuo. The concentrate was then rinsed out of the flask and partitioned between sat. aq. $\mathrm{NH}_{4} \mathrm{Cl}(100 \mathrm{~mL})$ and hexanes $(100 \mathrm{~mL})$. The aqueous layer was extracted twice more with hexanes $(100 \mathrm{~mL})$. The combined organic layers were dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated to an oil. After trituration with pentane and filtration through a pad of Celite, the filtrate was concentrated to furnish the desired dienylic bromide $17(1.44 \mathrm{~g}, 3.20 \mathrm{mmol}, 81 \%)$ as a yellow oil: ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 500 \mathrm{MHz}\right) \delta 6.71(\mathrm{dd}, J=18.6,10.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.38 \mathrm{~Hz}(\mathrm{~d}, J=18.6 \mathrm{~Hz}, 1 \mathrm{H})$, $6.16(\mathrm{br} \mathrm{d}, J=10.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.05(\mathrm{~s}, 2 \mathrm{H}), 1.93(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.51(\mathrm{~m}, 6 \mathrm{H}), 1.30(\mathrm{~m}, 6 \mathrm{H}), 0.91(\mathrm{~m}$, $15 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 142.1,137.9,132.9,132.2,42.0,29.1,27.3,15.2,13.7,13.6,9.5$; IR (film) 2956, 2925, 2871, 2853, 1558, 1463, 1203, $985 \mathrm{~cm}^{-1}$.


Phosphonium Salt 8a. A deoxygenated solution of dienyl bromide $17(1.52 \mathrm{~g}, 3.71 \mathrm{mmol})$ in 3:2 MeCN:THF ( 10 mL ) was cooled to $-10^{\circ} \mathrm{C}$ and treated with tributylphosphine ( $0.88 \mathrm{~mL}, 3.52 \mathrm{mmol}$ ). The reaction was then warmed to $23{ }^{\circ} \mathrm{C}$ over 10 minutes, at which point the solvent was removed first by evaporation under a stream of argon, then in vacuo. The oily residue was triturated with pentane and cooled to $-20^{\circ} \mathrm{C}$ in a freezer. The oily orange solid was collected by filtration through a pad of Celite topped by a layer of sea sand. After removal of the filtrate, the product was dissolved and eluted using $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and then concentrated in vacuo to provide the phosphonium salt $\mathbf{8 a}(1.88 \mathrm{~g}, 2.88 \mathrm{mmol}, 80 \%)$ as an oily orange solid: ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3} / \mathrm{CH}_{2} \mathrm{Cl}_{2}, 500 \mathrm{MHz}\right) \delta 6.62(\mathrm{dd}, J=18.5,10.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.32(\mathrm{~d}, J=$
$18.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.12(\mathrm{~m}, 1 \mathrm{H}), 3.52(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 2 \mathrm{H}), 2.43(\mathrm{~m}, 6 \mathrm{H}), 1.94(\mathrm{~s}, 3 \mathrm{H}), 1.65-1.37(\mathrm{~m}, 18 \mathrm{H})$, $1.31(\mathrm{~m}, 6 \mathrm{H}), 0.93(\mathrm{~m}, 9 \mathrm{H}), 0.87(\mathrm{~m}, 15 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 140.5,140.4,137.4,137.4$, $135.7,135.6,122.5,122.3,30.2,29.7,28.6,28.5,27.9,27.5,27.0,26.9,26.7,26.5,26.4,23.8,23.7,23.6$, $23.5,23.4,23.4,23.3,23.3,21.2,19.1,18.7,13.3,13.2,13.0,10.0,9.1$ (note: spectrum is not ${ }^{31} \mathrm{P}$ decoupled); IR (film) 3391, 2958, 2928, 2873, 2181, 1827, 1771, 1633, 1557, 1464, 1456, 1417, 1379, $923 \mathrm{~cm}^{-1} ;$ HRMS (ES) calcd for $\mathrm{C}_{30} \mathrm{H}_{62} \mathrm{PSn}[\mathrm{M}-\mathrm{Br}]^{+} 573.3611$, found 573.3625 .


Trienyl Stannane 19. A solution of azeotropically dried phosphonium salt 8a (1.11 g, 1.81 mmol) and 18 -crown-6 ( $2.26 \mathrm{~g}, 8.56 \mathrm{mmol}$ ) in THF $(12 \mathrm{~mL})$ was cooled to $-45^{\circ} \mathrm{C}$ and treated with a potassium bis(trimethylsilyl)amide ( 1.0 M in toluene, $1.77 \mathrm{~mL}, 1.77 \mathrm{mmol}$ ). The dark orange/brown solution was then cooled to $-78^{\circ} \mathrm{C}$. A solution of aldehyde $\mathbf{1 8}^{4}(0.474 \mathrm{~g}, 1.07 \mathrm{mmol})$ in THF $(2 \mathrm{~mL})$ was slowly transferred via cannula to the cooled ylide solution. The reaction was stirred at $-78^{\circ} \mathrm{C}$ for 10 min , then gradually warmed to $-10^{\circ} \mathrm{C}$ over 2 h . The mixture was treated with sat. aq. $\mathrm{NH}_{4} \mathrm{Cl}(20 \mathrm{~mL})$ and extracted with a 1:1 hexanes:diethyl ether $(2 \times 60 \mathrm{~mL})$. The combined organic extracts were washed with sat. aq. $\mathrm{NaHCO}_{3}$, then dried over $\mathrm{MgSO}_{4}$. Filtration of the solution through a pad of basic alumina (diethyl ether as eluant) and concentration of the filtrate furnished the product $19(0.83 \mathrm{~g}, 1.04 \mathrm{mmol}$, $92 \%,>10: 1 \mathrm{E}: Z \mathrm{Z})$ as a yellow oil. $[\alpha]^{25}{ }_{\mathrm{D}}=+9.3^{\circ}\left(c 6.30, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 500 \mathrm{MHz}\right) \delta 6.88$ (ddd, $J=18.5,10.6,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.26(\mathrm{~d}, J=18.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.07(\mathrm{~d}, J=15.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.00(\mathrm{~d}, J=10.3$ $\mathrm{Hz}, 1 \mathrm{H}), 5.76(\mathrm{ddd}, J=15.7,7.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.07$ and $4.03(2 \mathrm{~d}, J=4.9 \mathrm{~Hz}, 1 \mathrm{H}$ combined), $3.97(\mathrm{~m}, 1 \mathrm{H})$, $3.78(\mathrm{~m}, 2 \mathrm{H}), 2.42(\mathrm{~m}, 1 \mathrm{H}), 1.89(\mathrm{~d}, J=1.5 \mathrm{~Hz}, 3 \mathrm{H}), 1.76(\mathrm{~m}, 1 \mathrm{H}), 1.56-1.46(\mathrm{~m}, 21 \mathrm{H}), 1.31(\mathrm{~m}, 6 \mathrm{H})$, $1.08-1.03(\mathrm{~m}, 6 \mathrm{H}), 0.90(\mathrm{~m}, 24 \mathrm{H}), 0.79$ and $0.78(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}$ combined $), 0.06(2 \mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 125 \mathrm{MHz}\right) \delta 151.8,151.5,143.1,134.2,134.2,134.1,134.1,133.5,133.5,132.3,92.7$, 79.7, $79.1,78.0,77.7,73.5,73.4,54.8,54.7,43.8,35.7,35.7,29.2,29.2,29.1,29.0,28.6,28.5,28.3,27.5,27.4$, $27.3,27.1,26.1,26.1,25.6,24.5,18.6,18.4,17.0,16.9,13.8,13.7,13.2,12.8,10.4,10.3,10.2,9.5,-3.8,-$ 3.8, -4.0; IR (film) 2957, 2929, 2856, 1699, 1600, 1388, 1374, 1253, $1105 \mathrm{~cm}^{-1}$; HRMS (ES) calcd for $\mathrm{C}_{41} \mathrm{H}_{79} \mathrm{NNaO}_{4} \mathrm{SiSn}[\mathrm{M}+\mathrm{Na}]^{+}$820.4698, found 820.4706. Anal. Calcd for $\mathrm{C}_{41} \mathrm{H}_{79} \mathrm{NO}_{4} \mathrm{SiSn}: \mathrm{C}, 61.80$; H , 9.99; N 1.76, found: C 61.59; H 10.17; N 1.72.


Trienyl Iodide 20. A solution of trienyl stannane 19 ( $227 \mathrm{mg}, 0.270 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( 4 mL ) was cooled to $0{ }^{\circ} \mathrm{C}$ and treated with a solution of iodine ( $65 \mathrm{mg}, 0.26 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(1.2 \mathrm{~mL})$. The iodine solution (dark magenta in color) was added dropwise to the reaction (yellow) until the endpoint was just reached (slight orange/purple tint). [Note: Any excess of iodine was found to cause olefin isomerization.] A solution of sat. aq. $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}(1 \mathrm{~mL})$ was then immediately added, followed by sat. aq. KF ( 4 mL ) and diethyl ether ( 5 mL ). The biphasic mixture was stirred for 1 h and then filtered through a pad of Celite $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ as eluant). The aqueous layer was extracted with diethyl ether ( $2 \times 10 \mathrm{~mL}$ ), and the combined organic layers were stirred over $\mathrm{MgSO}_{4}$ and KF on Celite for $1 \mathrm{~h} .{ }^{5}$ Filtration through a pad of basic alumina and concentration furnished pure trienyl iodide 20 ( $161 \mathrm{mg}, 0.250 \mathrm{mmol}, 95 \%$ ) as a bright yellow oil/foam: $[\alpha]^{25}{ }_{\mathrm{D}}=+13.0^{\circ}\left(c 1.80, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.37$ (ddd, $J=14.1$, $11.4,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.26(\mathrm{~d}, J=14.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.03(\mathrm{~d}, J=16.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.90(\mathrm{~d}, J=11.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.83$ (ddd, $J=15.9,7.4,3.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.05$ and $4.01(2 \mathrm{~d}, J=5.9 \mathrm{~Hz}, 1 \mathrm{H}$ combined), 3.97 and $3.80(2 \mathrm{~m}, 1 \mathrm{H}$ combined), $3.77(\mathrm{~m}, 1 \mathrm{H}), 2.38(\mathrm{~m}, 1 \mathrm{H}), 1.82(\mathrm{~s}, 3 \mathrm{H}), 1.73(\mathrm{~m}, 1 \mathrm{H}), 1.55$ and $1.50(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.48 and $1.46(2 \mathrm{~s}, 12 \mathrm{H}$ combined), 1.06-1.02 (m, 6 H$), 0.90$ and $0.89(2 \mathrm{~s}, 9 \mathrm{H}$ combined), 0.79 and 0.78 ( $2 \mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}$ combined), $0.06,0.05,0.04,0.03\left(4 \mathrm{~s}, 6 \mathrm{H}\right.$ combined); ${ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right)$ $\delta 151.5,141.8,135.8,135.0,133.0,128.2,92.4,79.5,78.8,77.9,77.6,77.4,73.0,54.4,43.5,35.4,28.2$, $28.2,28.0,27.1,25.8,25.3,24.2,18.1,16.6,13.5,12.9,12.7,9.9,-4.1,-4.3$; IR (film) 2972, 2956, 2929, $2856,1698,1462,1388,1374,1253,1178,1105 \mathrm{~cm}^{-1}$; HRMS calcd for $\mathrm{C}_{29} \mathrm{H}_{52} \mathrm{INNaO}_{4} \mathrm{Si}[\mathrm{M}+\mathrm{Na}]^{+}$ 656.2608 , found 656.2626 .


Enal 5. To a solution of vinyl boronate $7 \mathbf{b}(0.163 \mathrm{~g}, 0.289 \mathrm{mmol})$ and vinyl iodide $20(0.183 \mathrm{~g}$, 0.289 mmol ) in THF ( 3 mL ) was added thallium(I) carbonate ( $0.34 \mathrm{~g}, 0.72 \mathrm{mmol}$ ) and degassed by three freeze-pump-thaw cycles. An aliquot of degassed water ( 1 mL ) was then added, followed by a solution of $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(20.0 \mathrm{mg}, 0.017 \mathrm{mmol})$ in degassed THF $(0.4 \mathrm{~mL})$. After 2.5 h , the reaction was complete by TLC ( $4: 1$ hexanes:EtOAc). The reaction mixture was filtered through a pad of Celite and eluted with diethyl ether. The resulting filtrate was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered through a thin layer of basic alumina, and concentrated to afford $22(0.260 \mathrm{~g}, 0.27 \mathrm{mmol}, 95 \%)$ as an orange oil. Attempted purification of samples of $\mathbf{2 2}$ by flash column chromatography resulted in decomposition.

A solution of alcohol $22(0.207 \mathrm{~g}, 0.219 \mathrm{mmol})$, DMSO ( $0.11 \mathrm{~mL}, 1.5 \mathrm{mmol})$, and diisopropyl ethylamine $(0.17 \mathrm{~mL}, 0.99 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(1 \mathrm{~mL})$ was cooled to $0^{\circ} \mathrm{C}$ and $\mathrm{SO}_{3} \cdot$ pyridine $(0.105 \mathrm{~g}, 0.658$ mmol) was added. After 40 min , the reaction was quenched with sat. aq. $\mathrm{NaHCO}_{3}$. The mixture was partitioned between hexanes and half-saturated brine. The hexanes layer was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered, and concentrated to furnish the enal $5(0.20 \mathrm{~g}, 0.21 \mathrm{mmol}, 97 \%)$ as an orange oil: $[\alpha]^{25}{ }_{\mathrm{D}}=-38.0^{\circ}(c 2.7$, $\left.\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 9.96(\mathrm{~s}, 1 \mathrm{H}), 7.67-7.61(\mathrm{~m}, 4 \mathrm{H}), 7.45-7.32(\mathrm{~m}, 6 \mathrm{H}), 6.40(\mathrm{~m}$, $2 \mathrm{H}), 6.14-6.00(\mathrm{~m}, 2 \mathrm{H}), 5.99(\mathrm{~d}, J=12.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.96(\mathrm{dd}, J=15.1,10.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.75(\mathrm{app} \mathrm{dt}, J=15.6$, $7.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.62(\mathrm{dd}, J=15.1,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.33(\mathrm{~m}, 1 \mathrm{H}), 4.07$ and $4.06(2 \mathrm{~d}, J=5.1 \mathrm{~Hz}, 1 \mathrm{H}$ combined $)$, 3.98 and $3.90(2 \mathrm{~m}, 1 \mathrm{H}$ combined), $3.78(\mathrm{~m}, 1 \mathrm{H}), 3.33(\mathrm{~m}, 1 \mathrm{H}), 3.17(\mathrm{~s}, 3 \mathrm{H}), 2.58(\mathrm{~m}, 2 \mathrm{H}), 2.42(\mathrm{~m}, 1 \mathrm{H})$, $1.87(\mathrm{~m}, 1 \mathrm{H}), 1.86(\mathrm{~s}, 3 \mathrm{H}), 1.75(\mathrm{~m}, 4 \mathrm{H}), 1.60-1.46(\mathrm{~m}, 16 \mathrm{H}), 1.11-1.04(\mathrm{~m}, 6 \mathrm{H}), 1.06(\mathrm{~m}, 9 \mathrm{H}), 0.90(2 \mathrm{~s}$, 9 H combined), $0.77(\mathrm{~m}, 6 \mathrm{H}), 0.07,0.06,0.05$ and $0.04(4 \mathrm{~s}, 6 \mathrm{H}$ combined); IR (film) $3072,2957,2930$, $2857,2733,1958,1816,1697,1590,1472,1462,1428,1388,1374,1301,1255,1106 \mathrm{~cm}^{-1}$; HRMS calcd for $\mathrm{C}_{56} \mathrm{H}_{87} \mathrm{NNaO}_{7} \mathrm{Si}_{2}[\mathrm{M}+\mathrm{Na}]^{+} 964.5919$, found 964.5939 .


IMDA Cycloadduct 23. A solution of pentaene $5(0.20 \mathrm{~g}, 0.22 \mathrm{mmol})$ and BHT (one small crystal) in 2,2,2-trifluoroethanol ( $16 \mathrm{ml}, 0.01 \mathrm{M}$ ) was heated to $70-75{ }^{\circ} \mathrm{C}$ for 9 h . The solvent was removed under reduced pressure, affording the crude product as an orange oil ( $\geq 6: 1: 1$ d.s. by $\left.{ }^{1} \mathrm{H}-\mathrm{NMR}\right)$ which was purified by flash column chromatography on silica gel (10:1 hexanes:EtOAc). The cyclized adduct $23(0.13 \mathrm{~g}, 0.14 \mathrm{mmol}, 65 \%)$ was isolated as a yellow oil. HPLC purification ( 21 mm column, 91:9 hexanes:EtOAc, r.t. 16.5 min$)$ provided an analytical sample: $[\alpha]^{25}{ }_{\mathrm{D}}=-29.0^{\circ}\left(c 0.60, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 500 \mathrm{MHz}\right) \delta 9.42(\mathrm{~d}, J=1.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.68(\mathrm{~m}, 4 \mathrm{H}), 7.45-7.35(\mathrm{~m}, 6 \mathrm{H}), 6.04(\mathrm{br} \mathrm{d}, J=10.3$ $\mathrm{Hz}, 1 \mathrm{H}), 5.97(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.63(\mathrm{ddd}, J=15.9,7.3,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.55(\mathrm{app} \mathrm{dt}, J=10.2,3.6 \mathrm{~Hz}$, $1 \mathrm{H}), 5.36(\mathrm{~d}, J=10.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.02$ and $4.00(2 \mathrm{~d}, J=5.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.98$ and $3.80(2 \mathrm{~m}, 1 \mathrm{H}$ combined), 3.77 and $3.69(\mathrm{~m}, 2 \mathrm{H}), 3.21(\mathrm{~s}, 3 \mathrm{H}), 3.11(\mathrm{brd}, J=10.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.85(\mathrm{~m}, 1 \mathrm{H}), 2.35(\mathrm{~m}, 1 \mathrm{H}), 2.30(\mathrm{~m}$, $1 \mathrm{H}), 2.02(\mathrm{br} \mathrm{d}, J=11.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.86(\mathrm{brd}, J=12.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.81(\mathrm{~d}, J=0.7 \mathrm{~Hz}, 3 \mathrm{H}), 1.74(\mathrm{~m}, 1 \mathrm{H})$, $1.61(\mathrm{~m}, 1 \mathrm{H}), 1.55$ and $1.51(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.51 and $1.48(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.48 and $1.47(2 \mathrm{~s}, 9 \mathrm{H}$ combined), $1.35(\mathrm{~m}, 1 \mathrm{H}), 1.25(\mathrm{~m}, 1 \mathrm{H}), 1.09(\mathrm{~s}, 9 \mathrm{H}), 1.09$ and $1.05(2 \mathrm{~d}, J=6.1 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 1.02 and $1.01(2 \mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}), 0.91(\mathrm{~s}, 3 \mathrm{H}), 0.89$ and $0.88(2 \mathrm{~s}, 9 \mathrm{H}$ combined $), 0.78(2 \mathrm{~d}, J=6.5 \mathrm{~Hz}, 3 \mathrm{H})$, $0.06,0.05,0.03,0.03\left(4 \mathrm{~s}, 6 \mathrm{H}\right.$ combined); ${ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 204.4,151.8,151.5,136.2$, $135.7,134.0,133.7,132.7,129.8,129.7,128.3,127.9,127.6,123.9,92.6,92.2,79.7,79.1,77.9,77.7$,
$77.4,73.4,71.2,55.9,54.8,50.4,43.4,41.2,38.2,37.4,35.5,35.2,29.1,28.6,28.5,28.5,27.0,26.1,25.7$, $24.5,22.8,19.2,18.4,16.9,13.3,12.7,10.2,-3.8,-4.0 ;$ IR (film) 3065, 2956, 2931, 2858, 2708, 1725, 1698, 1472, 1428, 1388, 1254, 1178, $1111 \mathrm{~cm}^{-1}$; HRMS (ES) calcd for $\mathrm{C}_{56} \mathrm{H}_{97} \mathrm{NNaO}_{7} \mathrm{Si}_{2}[\mathrm{M}+\mathrm{Na}]^{+}$ 964.5919, found 964.5917.


Boronic Ester 24. A solution of aldehyde $23(52.0 \mathrm{mg}, 0.056 \mathrm{mmol})$ and dichloromethyl pinacol boronate $^{2}(23 \mathrm{mg}, 0.11 \mathrm{mmol})$ in THF ( 1 mL ) was degassed by three freeze-pump-thaw cycles. Chromium(II) chloride ( $54 \mathrm{mg}, 0.44 \mathrm{mmol}$ ) and lithium iodide ( $48 \mathrm{mg}, 0.36 \mathrm{mmol}$ ) were cooled to $-78{ }^{\circ} \mathrm{C}$ in a dry flask. The THF solution was transferred by cannula to the salts and then warmed to $23^{\circ} \mathrm{C}$. After 18 h , the reaction was diluted with water $(10 \mathrm{~mL})$ and diethyl ether $(5 \mathrm{~mL})$. The product was extracted with diethyl ether ( $3 \times 20 \mathrm{~mL}$ ). The combined ethereal layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered and concentrated to afford $24(56 \mathrm{mg}, 0.055 \mathrm{mmol}, 95 \%)$ as a yellow oil: $[\alpha]^{25}{ }_{\mathrm{D}}=-42.0^{\circ}(c 1.80$, $\left.\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 500 \mathrm{MHz}\right) \delta 7.68(\mathrm{~m}, 4 \mathrm{H}), 7.47-7.35(\mathrm{~m}, 6 \mathrm{H}), 6.71(\mathrm{dd}, J=18.5,1.9 \mathrm{~Hz}, 1 \mathrm{H})$, $6.01(\mathrm{dd}, J=15.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}), 5.96(\mathrm{~d}, J=10.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.63-5.57(\mathrm{~m}, 2 \mathrm{H}), 5.40(\mathrm{dd}, J=5.3,9.0 \mathrm{~Hz}$, $1 \mathrm{H}), 5.34(\mathrm{~d}, J=18.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.06$ and $4.04(2 \mathrm{~d}, J=4.6 \mathrm{~Hz}, 1 \mathrm{H}$ combined), 3.96-3.90 ( $2 \mathrm{~m}, 1 \mathrm{H}$ combined), $3.77(\mathrm{~m}, 1 \mathrm{H}), 3.66(\mathrm{~m}, 1 \mathrm{H}), 3.18(2 \mathrm{~s}, 3 \mathrm{H}$ combined), $2.85(\mathrm{~m}, 1 \mathrm{H}), 2.74(\mathrm{~m}, 1 \mathrm{H}), 2.41(\mathrm{~m}$, $1 \mathrm{H}), 2.35(\mathrm{~m}, 1 \mathrm{H}), 1.98(\mathrm{br} \mathrm{d}, J=12.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.82(\mathrm{~m}, 1 \mathrm{H}), 1.74(\mathrm{~m}, 1 \mathrm{H}), 1.69(\mathrm{~d}, J=3.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.56$ and $1.51(2 \mathrm{~s}, 3 \mathrm{H}$ combined $), 1.55(\mathrm{~m}, 1 \mathrm{H}), 1.51$ and $1.48(2 \mathrm{~s}, 3 \mathrm{H}$ combined $), 1.48$ and $1.46(2 \mathrm{~s}, 9 \mathrm{H}$ combined), 1.31-1.24 (m, 2H), $1.28(\mathrm{~s}, 12 \mathrm{H}), 1.21$ and $1.20(2 \mathrm{~s}, 9 \mathrm{H}$ combined), 1.10 and $1.05(2 \mathrm{~d}, J=$ $6.2 \mathrm{~Hz}, 3 \mathrm{H}$ combined $), 1.03(2 \mathrm{~d}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}$ combined $), 0.92(\mathrm{~s}, 3 \mathrm{H}), 0.91(2 \mathrm{~s}, 9 \mathrm{H}$ combined $), 0.79$ $(2 \mathrm{~d}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H}), 0.06$ and $0.05(2 \mathrm{~s}, 6 \mathrm{H}$ combined $) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 160.7,151.8$, $151.5,135.2,134.3,130.5,129.7,129.6,127.6,127.5,122.5,92.6,92.2,84.2,82.8,77.7,73.6,73.3,71.5$, $55.7,54.8,44.3,43.8,43.6,42.3,39.4,38.8,36.9,36.2,30.3,29.6,28.5,28.5,27.9,27.4,27.0,26.1,25.6$, $24.7,24.7,24.4,19.2,18.4,13.9,13.3,12.6,10.2,-3.7,-4.1$ [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ${ }^{11} \mathrm{~B}$ nucleus]; IR (film) 3072, 2978, 2932, 2858, $1698,1628,1472,1428,1389,1348,1326,1255,1215,1146,1111 \mathrm{~cm}^{-1} ; M S(E S)$ calcd for $\mathrm{C}_{63} \mathrm{H}_{100} \mathrm{BNNaO}_{8} \mathrm{Si}_{2}[\mathrm{M}+\mathrm{Na}]^{+} 1089$, found 1089.


Vinyl Iodide 6. A solution of 2-butyn-1-ol ( $1.81 \mathrm{~mL}, 24.2 \mathrm{mmol}$, in THF ( 25 mL ) at $-78{ }^{\circ} \mathrm{C}$ was treated with Red-Al ( $65 \mathrm{wt} . \%$ in toluene, $8.0 \mathrm{~mL}, 27 \mathrm{mmol}$ ) dropwise by syringe. The reaction was then warmed to $23^{\circ} \mathrm{C}$ and stirred for 18 h . After cooling the mixture back to $-78^{\circ} \mathrm{C}$, tributyltin chloride ( $13.1 \mathrm{~mL}, 48.4 \mathrm{mmol}$ ) was added dropwise by addition funnel. The reaction was then warmed to $23{ }^{\circ} \mathrm{C}$ for 1 h and poured into a solution of sodium potassium tartrate (Rochelle's salt, aq). Potassium fluoride (sat. aq.) and diethyl ether were added and the biphasic mixture was stirred for 3 h and then filtered through a pad of Celite. The filtrate was extracted with diethyl ether ( $2 \times 100 \mathrm{~mL}$ ), and the combined organic layers were stirred over a mixture of $\mathrm{MgSO}_{4}$ and KF on Celite for 1.5 h . The solids were filtered by flushing the mixture through a pad of basic alumina and the filtrate was concentrated to a transparent oil. Purification of the crude product by flash chromatography ( $10 \%$ EtOAc-hexanes) furnished (Z)-3-tributystannyl-2-buten-1-ol ( $6.24 \mathrm{~g}, 17.28 \mathrm{mmol}, 71 \%$ ) as a pale oil.
(Z)-3-tributystannyl-2-buten-1-ol ( $1.52 \mathrm{~g}, 4.31 \mathrm{mmol}$ ), DMSO ( $2.1 \mathrm{~mL}, 29.4 \mathrm{mmol}$ ), and diisopropyl ethylamine ( $3.31 \mathrm{~mL}, 18.9 \mathrm{mmol}$ ) were dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ and cooled to $0{ }^{\circ} \mathrm{C}$. $\mathrm{SO}_{3} \cdot$ pyridine $(2.01 \mathrm{~g}, 12.6 \mathrm{mmol})$ was added in one portion. After 40 min , the reaction was diluted with diethyl ether and sat. aq. sodium bicarbonate. The product was extracted with diethyl ether ( $3 \times 30 \mathrm{~mL}$ ). The combined organic extracts were washed with half-saturated brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated to afford enal $\mathbf{2 7}^{6}(1.45 \mathrm{~g}, 4.04 \mathrm{mmol}, 96 \%)$.

Phosphonate reagent $\mathbf{2 8}^{7}(0.81 \mathrm{~g}, 2.58 \mathrm{mmol})$ was dissolved in THF ( 3 mL ) and cooled to $0{ }^{\circ} \mathrm{C}$. A solution of $n-\operatorname{BuLi}(2.2 \mathrm{M}$ in hexanes, $1.05 \mathrm{~mL}, 2.31 \mathrm{mmol})$ was added dropwise and the reaction was warmed to $23^{\circ} \mathrm{C}$ for 15 min . After cooling the mixture to $0^{\circ} \mathrm{C}$, a solution of enal $27(0.31 \mathrm{~g}, 0.86 \mathrm{mmol})$ in THF ( 1 mL ) was added dropwise over 5 min . After 20 min , the reaction was complete by TLC ( $4 \%$ EtOAc-hexanes). The solvent was removed under reduced pressure and the crude product was partitioned between diethyl ether and sat. aq. ammonium chloride. The ethereal layer was washed with half-saturated brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated to afford the vinyl stannane TMSE ester 29 ( 0.33 g , $0.66 \mathrm{mmol}, 77 \%$ ) as a pale yellow oil

Finally, the vinyl stannane TMSE ester 29 ( $0.83 \mathrm{~g}, 1.66 \mathrm{mmol}$ ) was dissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( 5 mL ) and cooled to $-78{ }^{\circ} \mathrm{C}$. A solution of iodine $(0.40 \mathrm{~g}, 1.57 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ was added dropwise by syringe. The mixture was warmed to $0{ }^{\circ} \mathrm{C}$ and then quenched with sat. aq. $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$. The reaction was diluted with diethyl ether ( 6 mL ) and sat. aq. potassium fluoride solution. After vigorously stirring the mixture for 1 h , it was filtered through a pad of Celite. The ethereal layer was separated and stirred over $\mathrm{MgSO}_{4}$ and KF on Celite for 1 h . The mixture was filtered and concentrated to a crude orange oil. The
crude product was purified by flash column chromatography on silica gel ( $5 \% \mathrm{Et}_{2} \mathrm{O}$-hexanes) to furnish the dienyl iodide $6(0.34 \mathrm{~g}, 1.01 \mathrm{mmol}, 61 \%)$ as a pale yellow oil: ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 500 \mathrm{MHz}\right) \delta 7.20$ $(\mathrm{dd}, J=15.4,10.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.15(\mathrm{dq}, J=10.3,0.5 \mathrm{~Hz}, 1 \mathrm{H}), 5.89(\mathrm{dd}, J=15.4,0.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.17(\operatorname{app} \mathrm{~d}, J$ $=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.16(\operatorname{appd}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.58(\mathrm{~s}, 3 \mathrm{H}), 0.95(\operatorname{appd}, J=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 0.93(\operatorname{app} \mathrm{~d}, J=$ 8.1 Hz, 1H), -0.04 (s, 9H); ${ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 166.8,145.7,132.7,123.6,111.6,62.7,34.8$, 17.3, -1.4; IR (film) 2954, 2926, 1714, 1631, 1457, 1377, 1314, $12511180,1139,837 \mathrm{~cm}^{-1}$; HRMS (ES) calcd for $\mathrm{C}_{12} \mathrm{H}_{23} \mathrm{INaO}_{3}\left[\mathrm{M}+\mathrm{Na}+\mathrm{CH}_{3} \mathrm{OH}\right]^{+} 393.0359$, found 393.0358.


TMSE Ester 3. A solution of vinyl boronate $24(53 \mathrm{mg}, 0.05 \mathrm{mmol})$ and vinyl iodide $6(34 \mathrm{mg}$, 0.01 mmol ) in THF ( 1 mL ) was treated with thalium( I ) carbonate ( $58 \mathrm{mg}, 0.12 \mathrm{mmol}$ ) and degassed by three freeze-pump-thaw cycles. Water $\left(0.4 \mathrm{~mL}\right.$, degassed) and a solution of $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ (cat.) in THF (0.2 mL , degassed) were added consecutively to the reaction mixture. After 4.5 h , the reaction was diluted with diethyl ether and filtered through a plug of silica gel. Concentration of the ethereal solution yielded a crude yellow oil which was purified by flash column chromatography on silica gel (5-10\% EtOAchexanes) to provided $3(38.0 \mathrm{mg}, 0.033 \mathrm{mmol}, 66 \%)$ as a bright yellow oil: $[\alpha]^{25}{ }_{\mathrm{D}}=+22.0^{\circ}(c 0.50$, $\left.\mathrm{CH}_{2} \mathrm{Cl}_{2}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.72(\mathrm{~m}, 5 \mathrm{H}), 7.41(\mathrm{~m}, 6 \mathrm{H}), 6.64(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.17(\mathrm{~d}, J$ $=15.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.03(\mathrm{~m}, 2 \mathrm{H}), 5.98(\mathrm{~d}, J=10.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.76(\mathrm{~d}, J=15.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.61(\mathrm{~m}, 2 \mathrm{H}), 5.40(\mathrm{~d}$, $J=11.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.25(\operatorname{app} \mathrm{t}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.24$ and $3.96(2 \mathrm{~m}, 1 \mathrm{H}$ combined $), 4.04(2 \mathrm{~d}, J=4.0 \mathrm{~Hz}$, 1 H combined $), 3.75(\mathrm{~m}, 3 \mathrm{H}), 3.18(\mathrm{~s}, 3 \mathrm{H}), 2.86(\mathrm{~m}, 1 \mathrm{H}), 2.78(\mathrm{~m}, 1 \mathrm{H}), 2.48(\mathrm{~m}, 1 \mathrm{H}), 2.36(\mathrm{~m}, 1 \mathrm{H}), 2.00$ $(\mathrm{m}, 1 \mathrm{H}), 1.85(\mathrm{~m}, 1 \mathrm{H}), 1.80(\mathrm{~d}, J=3.7 \mathrm{~Hz}, 3 \mathrm{H}), 1.73(\mathrm{~m}, 2 \mathrm{H}), 1.67(\mathrm{~s}, 3 \mathrm{H}), 1.54-1.50(2 \mathrm{~s}, 3 \mathrm{H}), 1.48$ and $1.47(2 \mathrm{~s}, 12 \mathrm{H}), 1.31(\mathrm{~m}, 2 \mathrm{H}), 1.11-1.03(\mathrm{~m}, 17 \mathrm{H}), 0.90(\mathrm{~s}, 12 \mathrm{H}), 0.77(\mathrm{~m}, 3 \mathrm{H}), 0.06(\mathrm{~s}, 15 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 167.7,151.8,143.2,143.0,139.2,135.8,135.4,134.3,134.1,134.0,132.3,132.2$, $131.5,131.4,130.7,129.8,129.7,128.6,128.4,127.7,127.6,125.4,122.8,119.6,92.6,92.2,79.7,79.1$, $77.1,77.8,77.6,73.6,71.4,62.4,55.7,54.8,44.9,43.8,41.1,38.8,36.8,36.1,30.1,29.7,28.6,28.5,28.3$, $27.4,27.0,26.1,25.6,24,5,21.2,19.3,18.5,17.5,17.3,13.9,13.2,12.8,10.2,-1.4,-3.7,-4.0 ;$ IR (film) $3065,2957,2930,2884,2858,1700,1616,1472,1428,1389,1302,1252,1163,1109 \mathrm{~cm}^{-1} ;$ HRMS calcd for $\mathrm{C}_{68} \mathrm{H}_{107} \mathrm{NNaO}_{8} \mathrm{Si}_{3}[\mathrm{M}+\mathrm{Na}]^{+}$1172.7202, found 1172.7175 .



Boronic Ester 33. To a solution of 7a ( $100 \mathrm{mg}, 0.180 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{~mL})$ was added DMSO ( $90 \mu \mathrm{~L}, 1.26 \mathrm{mmol}$ ) and diisopropylethylamine ( $0.16 \mathrm{~mL}, 0.90 \mathrm{mmol}$ ). The mixture was cooled to $0{ }^{\circ} \mathrm{C}$ and charged with $\mathrm{SO}_{3} \cdot$ pyridine ( $86 \mathrm{mg}, 0.54 \mathrm{mmol}$ ). After 30 min , sat. aq. $\mathrm{NaHCO}_{3}(50 \mathrm{~mL})$ was added and the aqueous phase was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 5 \mathrm{~mL})$. The combined organic layers were washed with brine, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. The crude product ( $90 \mathrm{mg}, 0.16 \mathrm{mmol}$, $90 \%$ ) was used in the next step without further purification: ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 0.96(\mathrm{~s}, 1 \mathrm{H})$, 7.65-7.60 (m , 4H), 7.46-7.36 (m, 6H), $6.50(\mathrm{dd}, J=14.4,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.37$ (tq, $J=8.0,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.98$ (dd, $J=14.4,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.27(\mathrm{~m}, 1 \mathrm{H}), 3.35(\mathrm{~m}, 1 \mathrm{H}), 3.19(\mathrm{~s}, 3 \mathrm{H}), 2.59(\operatorname{app} \mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.78$ (ddd, $J=14.0,8.1,5.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.76(\mathrm{~s}, 3 \mathrm{H}), 1.48(\mathrm{ddd}, J=14.0,7.0,4.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.06(\mathrm{~s}, 9 \mathrm{H})$.

A solution of LiI ( $385 \mathrm{mg}, 2.88 \mathrm{mmol}$ ) in degassed THF ( 4 mL ) was added to a suspension of $\mathrm{CrCl}_{2}$ ( $708 \mathrm{mg}, 5.76 \mathrm{mmol}$ ) in degassed THF ( 7 mL ). Then, a solution of aldehyde $\mathbf{3 2}$ and boronic ester 15 in degassed THF was added dropwise. The mixture was stirred for 16 h and then quenched with $\mathrm{H}_{2} \mathrm{O}$ $(20 \mathrm{~mL})$. The aqueous phase was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 20 \mathrm{~mL})$. The combined organic phases were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $5 \%$ EtOAc-hexanes) afforded 33 ( $368 \mathrm{mg}, 0.56 \mathrm{mmol}, 78 \%$ ) as a yellow oil: $[\alpha]^{25}{ }_{\mathrm{D}}=-40.5^{\circ}\left(c 5.20, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.65-7.60(\mathrm{~m}, 4 \mathrm{H}), 7.44-7.36$ (m, 6H), $7.04(\mathrm{~d}, J=18.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.48(\mathrm{dd}, J=14.4,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.91(\mathrm{dd}, J=14.4,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.58$ (t, $J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.47(\mathrm{~d}, J=18.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.25(\mathrm{~m}, 1 \mathrm{H}), 3.27(\mathrm{~m}, 1 \mathrm{H}), 3.17(\mathrm{~s}, 3 \mathrm{H}), 2.32-2.19(\mathrm{~m}, 2 \mathrm{H})$, 2.32-2.19 (m, 2H), $1.74(\mathrm{~m}, 1 \mathrm{H}), 1.69(\mathrm{~s}, 3 \mathrm{H}), 1.50(\mathrm{ddd}, J=14.0,7.5,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.29(\mathrm{~s}, 12 \mathrm{H}), 1.06(\mathrm{~s}$, 9H); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 154.3,148.0,136.8,135.9,135.8,133.7,133.4,132.3,129.8,129.7$, $127.6,127.5,83.0,76.7,76.5,73.7,56.1,41.6,32.4,27.0,24.8,19.2,11.8$ [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ${ }^{11}$ B nucleus]; IR (neat) 2978, 2857, 1607, 1465, 1426, 1374, 1344, 1267, 1193, 1144, 1111, 998, 965, 847, 823, 738, $705 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{34} \mathrm{H}_{48} \mathrm{O}_{4} \mathrm{BISiNa}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 709.2357, found 709.2339.


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Enyne 45. To a $-78^{\circ} \mathrm{C}$ solution of trimethylsilyldiazomethane ( 21.1 mL of a 2.0 M solution in hexanes, 42.2 mmol ) was added $n-\mathrm{BuLi}(14.6 \mathrm{~mL}$ of a 2.5 M solution in hexanes, 36.6 mmol ). After being stirred for 30 min , a solution of $\mathbf{4 4}^{6}(10.1 \mathrm{~g}, 28.1 \mathrm{mmol})$ in THF $(56 \mathrm{~mL})$ was added. The mixture was stirred for 1 h at $-7{ }^{\circ} \mathrm{C}, 30 \mathrm{~min}$ at $0{ }^{\circ} \mathrm{C}$ and then quenched with sat. aq. $\mathrm{NHCl}_{4}(100 \mathrm{~mL})$. The aqueous phase was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 50 \mathrm{~mL})$. The combined organic phases were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography (hexanes $+2 \% \mathrm{Et}_{3} \mathrm{~N}$ ) afforded $45(8.0 \mathrm{~g}, 22.5 \mathrm{mmol}, 80 \%)$ as a yellow oil: ${ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 5.64\left(\operatorname{app} q u i n t, J=1.8 \mathrm{~Hz},{ }^{3} J_{\mathrm{Sn}-\mathrm{H}}=55.8 \mathrm{~Hz}, 1 \mathrm{H}\right), 3.14(\operatorname{app} \mathrm{dt}, J=2.0,0.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.14$ $\left(\mathrm{dd}, J=1.8,0.5 \mathrm{~Hz},{ }^{3} J_{\mathrm{Sn}-\mathrm{H}}=40.8 \mathrm{~Hz}, 1 \mathrm{H}\right), 1.53-1.45(\mathrm{~m}, 6 \mathrm{H}), 1.31(\mathrm{sext}, J=7.3 \mathrm{~Hz}, 6 \mathrm{H}), 0.92(\mathrm{~m}, 6 \mathrm{H})$, $0.89(\mathrm{t}, J=7.3 \mathrm{~Hz}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.6,117.0,80.5,77.2,29.0\left({ }^{3} J_{\mathrm{Sn}-\mathrm{C}}=20.3 \mathrm{~Hz}\right)$, $27.3\left({ }^{2} J_{\text {Sn-C }}=55.6\right), 22.9,13.7,9.3\left({ }^{1} J_{\text {Sn-C }}=330.0 \mathrm{~Hz}\right)$; IR (neat) $3312,2957,2926,2872,2873,1463$, 1376, 1072, 1013, 970, $874 \mathrm{~cm}^{-1}$; HRMS (GC-CI) $m / z$ for $\mathrm{H}_{17} \mathrm{H}_{33} \mathrm{Sn}[\mathrm{M}+\mathrm{H}]^{+}$calcd 357.1604, found 357.1567.


Bimetallic Lichpin 36b. To a $0{ }^{\circ} \mathrm{C}$ solution of 2,5-dimethyl-2,4-hexadiene ( $1.4 \mathrm{~mL}, 9.6 \mathrm{mmol}$ ) in THF ( 0.8 mL ) was added $\mathrm{BH}_{3} \bullet$ THF ( 4.8 mL of a 1.0 M solution in THF, 4.8 mmol ) dropwise. The solution was stirred for 3 h at $0^{\circ} \mathrm{C}$ and then a solution of $45(1.42 \mathrm{~g}, 4.00 \mathrm{mmol})$ in THF ( 4 mL ) was added dropwise. The reaction mixture was stirred at $0^{\circ} \mathrm{C}$ for 1 h and then was allowed to warm to room temperature. Water was added $(0.8 \mathrm{~mL})$, the reaction mixture was stirred for 30 min and then treated with an aqueous solution of formaldehyde ( 0.45 mL of a $37 \mathrm{wt} \%$ solution, 6.00 mmol ). After being stirred for 1 h , pinacol ( $567 \mathrm{mg}, 4.80 \mathrm{mmol}$ ) was added. The reaction mixture was stirred at room temperature for 24 h before water $(20 \mathrm{~mL})$ and $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ were added. The aqueous phase was extracted with $\mathrm{Et}_{2} \mathrm{O}(3$ x 15 mL ) and the combined organic layers were washed with water ( $2 \times 15 \mathrm{~mL}$ ) and brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography (hexanes-15\% EtOAc/hexanes) afforded 36b ( $970 \mathrm{mg}, 2.00 \mathrm{mmol}, 50 \%$ ) as a pale yellow oil: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.40(\mathrm{dd}, J=17.4,10.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.28(\mathrm{dqd}, J=10.8,2.0,0.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.46(\mathrm{~d}, J=$ $17.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.08\left(\mathrm{~d}, J=1.6 \mathrm{~Hz},{ }^{3} J_{\mathrm{Sn}-\mathrm{H}}=46.6 \mathrm{~Hz}, 3 \mathrm{H}\right), 1.55-1.40(\mathrm{~m}, 6 \mathrm{H}), 1.35-1.25(\mathrm{~m}, 6 \mathrm{H}), 1.27(\mathrm{~s}$, $12 \mathrm{H}), 0.95-0.89(\mathrm{~m}, 6 \mathrm{H}), 0.88(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 150.7,143.3$, 141.1,
83.1, $29.1\left({ }^{3} J_{\mathrm{Sn}-\mathrm{C}}=20.0 \mathrm{~Hz}\right), 27.3\left({ }^{2} J_{\mathrm{Sn}-\mathrm{C}}=53.4\right), 24.7,20.4,13.7,9.2\left({ }^{1} J_{\mathrm{Sn}-\mathrm{C}}=329.0 / 322.0 \mathrm{~Hz}\right)$, [note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ${ }^{11} \mathrm{~B}$ nucleus]; IR (neat) 2957, 2926, 2872, 2854, 1610, 1572, 1455, 1379, 1354, 1328, 1271, 1146, 990, 971, $850 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{23} \mathrm{H}_{45} \mathrm{O}_{2} \mathrm{BSnNa}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 507.2435, found 507.2478.


Allylic Bromide SI-4. To a $0{ }^{\circ} \mathrm{C}$ solution of $7 \mathrm{a}(1.00 \mathrm{~g}, 1.77 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(15 \mathrm{~mL})$ was added triethylamine ( $0.74 \mathrm{~mL}, 5.31 \mathrm{mmol}$ ) followed by a solution of methanesulfonic anhydride ( 462 mg , $2.65 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \mathrm{~mL})$. After being stirred for 15 min , the reaction mixture was diluted with acetone ( 18 mL ) and charged with anhydrous lithium bromide ( $769 \mathrm{mg}, 8.85 \mathrm{mmol}$ ). The reaction was stirred for 1 h at room temperature and then quenched with water $(15 \mathrm{~mL})$ and extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \mathrm{x}$ $15 \mathrm{~mL})$. The combined organic layers were washed with brine, dried over anhydrous $\mathrm{MgSO}_{4}$, filtered and concentrated. Then hexanes ( 30 mL ) were added and the mixture was filtered through a pad of Celite. The filtrate was concentrated to furnish the desired allylic bromide SI-4 ( $1.09 \mathrm{~g}, 1.74 \mathrm{mmol}, 98 \%$ ) as a colorless oil: $[\alpha]^{25}=-53.0^{\circ}\left(c 3.82, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.66-7.60(\mathrm{~m}, 4 \mathrm{H}), 7.46-$ $7.36(\mathrm{~m}, 6 \mathrm{H}), 6.49(\mathrm{dd}, J=14.4,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.93(\mathrm{dd}, J=14.4,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.28(\mathrm{td}, J=7.3,1.4 \mathrm{~Hz}$, $1 \mathrm{H}), 4.25(\mathrm{~m}, 1 \mathrm{H}), 3.88(\mathrm{~d}, J=9.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.85(\mathrm{~d}, J=9.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.28(\mathrm{~m}, 1 \mathrm{H}), 3.17(\mathrm{~s}, 3 \mathrm{H}), 2.12(\mathrm{t}, J$ $=6.31 \mathrm{~Hz}, 1 \mathrm{H}), 1.82(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.75(\mathrm{ddd}, J=14.0,8.4,5.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.51(\mathrm{ddd}, J=14.0,7.3$, $4.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.06(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 148.0,135.9,135.8,133.7,133.6,133.4,129.8$, 129.7, 127.63, 127.56, 126.6, 76.8, 76.2, 73.6, 56.2, 41.5, 32.1, 31.7, 27.0, 22.0, 19.3; IR (neat) 3071, 3043, 2931, 2858, 1607, 1471, 1428, 1362, 1205, 1111, 944, $822 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{27} \mathrm{H}_{36} \mathrm{BrIO}_{2} \mathrm{SiNa}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 651.0589, found 651.0573.


Phosphonium Salt 35a. To a $0^{\circ} \mathrm{C}$ solution of SI-4 ( $1.09 \mathrm{~g}, 1.74 \mathrm{mmol}$ ) in MeCN:THF (3:2, 15 mL ) was added tributylphosphine ( $0.46 \mathrm{~mL}, 1.86 \mathrm{mmol}$ ). After being stirred for 1 h at room temperature the solution was concentrated and the crude product was washed with hexanes ( x 3 ) to remove the excess of tributylphosphine. The phosphonium salt $\mathbf{3 5 a}$ was obtained as a viscous colorless oil $(1.30 \mathrm{~g}, 1.57$ $\mathrm{mmol}, 89 \%$ ) and was used without further purification: $[\alpha]^{25}{ }_{\mathrm{D}}=-31.8^{\circ}\left(c \quad 3.58, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR (400
$\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.62-7.57(\mathrm{~m}, 4 \mathrm{H}), 7.44-7.34(\mathrm{~m}, 6 \mathrm{H}), 6.46(\mathrm{dd}, J=14.3,7.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.92(\mathrm{dd}, J=14.4$, $0.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.38(\mathrm{~m}, 1 \mathrm{H}), 4.24(\mathrm{~m}, 1 \mathrm{H}), 3.38(\mathrm{~m}, 1 \mathrm{H}), 3.25(\mathrm{~m}, 1 \mathrm{H}), 3.14(\mathrm{~s}, 3 \mathrm{H}), 2.46(\mathrm{~m}, 6 \mathrm{H}), 2.11(\mathrm{~m}$, $1 \mathrm{H}), 1.19(\mathrm{~s}, 3 \mathrm{H}), 1.77(\mathrm{ddd}, J=14.0,8.2,5.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.59-1.39(\mathrm{~m}, 13 \mathrm{H}), 1.05(\mathrm{~s}, 9 \mathrm{H}), 0.96(\mathrm{t}, J=7.1$ $\mathrm{Hz}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 147.0,135.1,135.0,129.1,128.6,128.5,127.5,126.9,126.8,124.3$, $124.3,124.2,76.7$ (overlapping $\mathrm{w} /$ chloroform), $75.4,72.9,55.7,40.7,32.4,26.3,25.0,23.3,23.2,23.1$, $23.0,19.3,18.8,18.5,12.8$ [note: spectrum is not ${ }^{31} \mathrm{P}$ decoupled]; IR (neat) 3071, 2956, 2931, 2868, $2459,2149,1825,1463,1428,1192,1111,822,752 \mathrm{~cm}^{-1} ;$ HRMS (ESI) $m / z$ for $\mathrm{C}_{39} \mathrm{H}_{64} \mathrm{IO}_{2} \mathrm{PSi}[\mathrm{M}+\mathrm{H}]^{+}$ calcd 750.3453 , found 750.3452 .


Carboxylic Acid 41a. To a $0{ }^{\circ} \mathrm{C}$ solution of $40(0.210 \mathrm{~mL}, 1.43 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(14 \mathrm{~mL})$ was added a solution of $\mathrm{NaOMe}(141 \mathrm{mg}, 2.60 \mathrm{mmol})$ in $\mathrm{MeOH}(2.6 \mathrm{~mL})$. The reaction mixture was stirred for 5 min at this temperature followed by addition of a solution of $\mathbf{3 9}^{8}(150 \mathrm{mg}, 1.30 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}$ (5 $\mathrm{mL})$. The ice bath was removed and the mixture was stirred for 1 h at room temperature. Water ( 10 mL ) was added and the aqueous phase was acidified $(\mathrm{pH}=1)$ with $\mathrm{H}_{2} \mathrm{SO}_{4}(1 \mathrm{M} \mathrm{aq}$.$) . The organic phase was$ then washed with sat. aq. $\mathrm{K}_{2} \mathrm{CO}_{3}(3 \mathrm{x} 10 \mathrm{~mL})$. The basic aqueous layer was acidified with $\mathrm{H}_{2} \mathrm{SO}_{4}(1 \mathrm{M}$ aq.) and extracted with EtOAc ( $3 \times 10 \mathrm{~mL}$ ). The combined organic phases were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. The crude product was recrystallized from hexanes to afford the known carboxylic acid $\mathbf{4 1 a}{ }^{9}(195 \mathrm{mg}, 1.15 \mathrm{mmol}, 88 \%)$ as a white solid.


Allylic Alcohol 42a. To a $0^{\circ} \mathrm{C}$ solution of $41 \mathrm{a}(488 \mathrm{mg}, 2.87 \mathrm{mmol})$ in THF ( 6 mL ) was added triethylamine $(0.790 \mathrm{~mL}, 5.74 \mathrm{mmol})$ followed by ethyl chloroformate $(0.400 \mathrm{~mL}, 3.73 \mathrm{mmol})$. The reaction mixture was stirred for 1 h at room temperature and then filtered through a pad of Celite and concentrated. The crude product was dissolved in $\mathrm{MeOH}(15 \mathrm{~mL})$, cooled to $-78{ }^{\circ} \mathrm{C}$ and $\mathrm{NaBH}_{4}(271 \mathrm{mg}$, 7.17 mmol ) was added in portions. The mixture was stirred for 30 min at this temperature and then carefully quenched with sat. aq. $\mathrm{NH}_{4} \mathrm{Cl}(10 \mathrm{~mL})$. The aqueous phase was extracted with EtOAc (3 x 20 $\mathrm{mL})$. The combined organic layers were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $20-50 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded 42a(358 mg, $2.29 \mathrm{mmol}, 80 \%$ ) as a white solid: $\mathrm{mp}=45-47{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $7.56(\mathrm{dd}, J=15.1,11.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.99(\mathrm{~d}, J=11.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.75(\mathrm{~d}, J=15.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.27(\mathrm{~s}, 2 \mathrm{H}), 3.67$
(s, 3H), 3.14 (br s, 1H), $1.90(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.7,147.0,139.4,125.4,120.3$, $61.6,51.6,21.9$; IR (neat) $3356,2946,1711,1633,1603,1428,1347,1307,1279,1206,1148,1120$, 1003, 988, 912, $882 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{8} \mathrm{H}_{13} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+}$calcd 157.0859, found 157.0852



Ester 43a. To a $0^{\circ} \mathrm{C}$ solution of 42a ( $64 \mathrm{mg}, 0.41 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(4 \mathrm{~mL})$ was added DessMartin periodinane ( $262 \mathrm{mg}, 0.62 \mathrm{mmol}$ ). The reaction mixture was stirred for 1 h at room temperature and then cooled again to $0^{\circ} \mathrm{C}$. Hexanes were added ( 4 mL ) and the resulting suspension was filtered through a Davisil ${ }^{\mathrm{TM}}$ column using a $1: 1 \mathrm{Et}_{2} \mathrm{O}$ :hexanes mixture as eluent. The filtrate was concentrated to give aldehyde 37 ( $54 \mathrm{mg}, 0.35 \mathrm{mmol}, 85 \%$ ) as a white solid. Compound $\mathbf{3 7 a}$ was used immediately in the next step to avoid isomerization of the trisubstituted double bond: $\mathrm{mp}=82-83{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 10.37(\mathrm{~s}, 3 \mathrm{H}), 8.13(\mathrm{dd}, J=15.0,12.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.98(\mathrm{~d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.08(\mathrm{~d}, J=$ $15.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 1.92(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 189.8,166.5,141.5,140.8,135.7$, $126.7,51.9,16.8 ;$ IR (neat) $2916,1710,1663,1639,1626,1597,1435,1308,1291,1227,1195,1006$, $984,920,856,719 \mathrm{~cm}^{-1}$.

To a $-78^{\circ} \mathrm{C}$ solution of $\mathbf{3 5 a}(174 \mathrm{mg}, 0.209 \mathrm{mmol})$, in THF ( 2 mL ) was added NaHDMS ( 0.54 mL of a 0.50 M solution in THF, freshly prepared, 0.27 mmol ). After being stirred for 10 min , a solution of $\mathbf{3 7 a}(38 \mathrm{mg}, 0.25 \mathrm{mmol})$ in THF $(0.6 \mathrm{~mL})$ was added. The reaction mixture was allowed to warm up to $-10{ }^{\circ} \mathrm{C}$ over 2 h and quenched with sat. aq. $\mathrm{NH}_{4} \mathrm{Cl}(1 \mathrm{~mL})$. The aqueous phase was extracted with EtOAc ( $3 \times 3 \mathrm{~mL}$ ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( 2 g of Davisil ${ }^{\mathrm{TM}}$ pretreated with hexanes $+2 \%$ of $\mathrm{Et}_{3} \mathrm{~N}, 5 \% \mathrm{EtOAc}$ as eluent) afforded 43a ( $119 \mathrm{mg}, 0.17 \mathrm{mmol}, 81 \%$ ) as a colorless oil, which was immediately used in the next reaction: $[\alpha]^{25}{ }_{\mathrm{D}}=-22.9^{\circ}\left(c 2.33, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.85(\mathrm{dd}, J=15.0,12.0 \mathrm{~Hz}, 1 \mathrm{H})$, 7.65-7.60 (m, 4H), 7.44-7.34 (m, 6H), $6.90(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.72(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.49(\mathrm{dd}, J=$ $14.4,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.12(\mathrm{~d}, J=12.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.91(\mathrm{dd}, J=14.4,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.86(\mathrm{~d}, J=15.0 \mathrm{~Hz}, 1 \mathrm{H})$, $5.40(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.27(\mathrm{~m}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.30(\mathrm{~m}, 1 \mathrm{H}), 3.20(\mathrm{~s}, 3 \mathrm{H}), 2.33(\mathrm{~m}, 2 \mathrm{H}), 2.01(\mathrm{~s}, 3 \mathrm{H})$, $1.92(\mathrm{~s}, 3 \mathrm{H}), 1.76(\mathrm{~m}, 1 \mathrm{H}), 1.56(\mathrm{ddd}, J=14.1,7.5,3.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.06(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\mathrm{CDCl}_{3}$ ) $\delta 167.9,148.0,143.1,139.3,135.9,135.8,134.2,133.7,133.5,129.80,129.76,129.3,128.9$,
127.63, 127.58, 127.2, 124.6, 119.6, 73.8, 56.2, 51.5, 41.7, 31.5, 27.1, 21.2, 20.7, 19.3; IR (neat) 2934, 2857, 1706, 1607, 1434, 1305, 1270, 1226, 1163, 1133, 1108, 976, 949, 908, 823, $732 \mathrm{~cm}^{-1}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ for $\mathrm{C}_{35} \mathrm{H}_{45} \mathrm{IO}_{4} \mathrm{SiNa}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 707.2029, found 707.2032.



Aldehyde SI-6. To a $0{ }^{\circ} \mathrm{C}$ solution of $\mathbf{4 6}^{4}(4.82 \mathrm{~g}, 14.7 \mathrm{mmol})$ in THF $(103 \mathrm{~mL})$ was added triethylamine ( $10.2 \mathrm{~mL}, 73.6 \mathrm{mmol}$ ) followed by TESOTf ( $4.33 \mathrm{~mL}, 19.1 \mathrm{mmol}$ ). The mixture was stirred for 1 h at room temperature and quenched with sat. aq. $\mathrm{NaHCO}_{3}(50 \mathrm{~mL})$. The aqueous phase was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 50 \mathrm{~mL})$. The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $10 \%$ EtOAc/hexanes) afforded the protected alcohol SI-5 ( $5.74 \mathrm{~g}, 13.0 \mathrm{mmol}, 88 \%$ ) as a colorless oil.

To a $-78{ }^{\circ} \mathrm{C}$ solution of SI-5 $(5.00 \mathrm{~g}, 11.3 \mathrm{mmol})$ and Sudan III dye in $4: 1 \mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{MeOH}(112$ mL ) was bubbled ozone gas until the pink color of Sudan III disappeared ( 45 min ). Then $\mathrm{Ph}_{3} \mathrm{P}$ ( 3.65 g , 13.6 mmol ) was added and the mixture was stirred at room temperature for 3 h . Water ( 50 mL ) was added and the aqueous phase was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 30 \mathrm{~mL})$. The combined organic phases were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $30-80 \% \mathrm{CH}_{2} \mathrm{Cl}_{2} /$ hexanes ) afforded SI-6 ( $4.76 \mathrm{~g}, 10.7 \mathrm{mmol}, 95 \%$ ) as a colorless oil: $[\alpha]^{25}{ }_{\mathrm{D}}=+7.6^{\circ}\left(c 2.05, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 9.75$ and $9.74(2 \mathrm{~d}, J=2.7$ $\mathrm{Hz}, 1 \mathrm{H}$ combined), 4.34 and $4.30(2 \mathrm{dd}, J=7.0,1.9 \mathrm{~Hz}, 1 \mathrm{H}$ combined), 4.01 and 3.84 ( $2 \mathrm{qd}, J=6.3,4.8$ $\mathrm{Hz}, 1 \mathrm{H}$ combined), 3.79 and $3.76(2 \mathrm{~d}, J=4.7 \mathrm{~Hz}, 1 \mathrm{H}$, combined), $2.54(\mathrm{~m}, 1 \mathrm{H}), 1.75(2 \mathrm{qd}, J=6.8,2.0$ $\mathrm{Hz}, 1 \mathrm{H}$, combined), 1.56 and 1.52 ( $2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.52 and $1.48(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.48 and 1.47 ( 2 s, 9 H combined), 1.11 and $1.08(2 \mathrm{~d}, J=6.3 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 1.06 and $1.05(2 \mathrm{~d}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 0.96 and $0.95(2 \mathrm{t}, J=7.9 \mathrm{~Hz}, 9 \mathrm{H}$ combined), $0.84(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 0.64 and 0.63 ( $2 \mathrm{q}, J=7.9 \mathrm{~Hz}, 6 \mathrm{H}$ combined); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 204.6,151.7,151.3,93.0,92.5$, $79.8,79.2,76.9,72.4,72.3,54.8,54.7,51.5,51.4,35.9,35.8,28.44,28.36,28.3,27.4,25.5,24.3,13.8$, $13.1,11.2,11.1,9.43,9.38,6.89,6.88,5.3$; IR (neat) $2978,2878,1731,1698,1456,1392,1302,1255$, 1178, 1109, 1066, 1043, 1012, $869 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{23} \mathrm{H}_{45} \mathrm{NO}_{5} \mathrm{SiNa}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 466.2962, found 466.2977.



SI-6
38
Vinyl Iodide 38. To a slurry of anhydrous chromium (II) chloride ( $5.53 \mathrm{~g}, 4.50 \mathrm{mmol}$ ) in THF ( 9 mL ) was added a solution of SI-6 ( $2.0 \mathrm{~g}, 4.5 \mathrm{mmol}$ ) and iodoform ( $5.32 \mathrm{~g}, 13.5 \mathrm{mmol}$ ) in dioxane ( 76 $\mathrm{mL})$. The resulting brown suspension was stirred at room temperature for 12 h , then diluted with $\mathrm{Et}_{2} \mathrm{O}$ $(100 \mathrm{~mL})$ and poured into 100 mL of water. The aqueous phase was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 50 \mathrm{~mL})$. The combined organic layers were washed with brine, dried over anhydrous $\mathrm{MgSO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $20-50 \% \mathrm{CH}_{2} \mathrm{Cl}_{2}$-hexanes) afforded iodide SI-7 ( $1.90 \mathrm{~g}, 4.32 \mathrm{mmol}, 96 \%$ ) as a pale yellow solid.

To a $0{ }^{\circ} \mathrm{C}$ solution of SI-7 $(1.85 \mathrm{~g}, 3.26 \mathrm{mmol})$ in THF ( 33 mL ) was added TBAF ( 4.9 mL of a 1.0 M solution in THF freshly prepared, 4.9 mmol ). After 1 h at room temperature the solution was quenched with water $(15 \mathrm{~mL})$ and diluted with $\operatorname{EtOAc}(15 \mathrm{~mL})$. The aqueous phase was extracted with EtOAc ( $3 \times 15 \mathrm{~mL}$ ). The combined organic layers were washed with brine, dried over anhydrous $\mathrm{MgSO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography (5-30\% EtOAchexanes) afforded $38(1.36 \mathrm{~g}, 3.19 \mathrm{mmol}, 95 \%)$ as a viscous colorless oil: $[\alpha]^{25}{ }_{\mathrm{D}}=+10.9^{\circ}(c 1.34$, $\left.\mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.53(2 \mathrm{dd}, J=14.4,8.9 \mathrm{~Hz}, 1 \mathrm{H}$, combined), $6.13(2 \mathrm{~d}, J=14.4$ $\mathrm{Hz}, 1 \mathrm{H}$ combined), 4.00 and $3.84(2 \mathrm{~m}, 1 \mathrm{H}), 3.98(\mathrm{~m}, 1 \mathrm{H}), 3.63(\mathrm{~m}, 1 \mathrm{H}), 2.36$ and 2.34 (2 quint, $J=7.0$ $\mathrm{Hz}, 1 \mathrm{H}$ combined), $1.99(\mathrm{t}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.88$ and $1.83(2 \mathrm{qd}, J=6.8,2.6 \mathrm{~Hz}, 1 \mathrm{H}$ combined), 1.56 and $1.52(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.50 and $1.48(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.47 and $1.45(2 \mathrm{~s}, 9 \mathrm{H}$ combined), 1.11 and $1.07(2 \mathrm{~d}, J=6.2 \mathrm{~Hz}, 3 \mathrm{H}$ combined), $1.00(2 \mathrm{~d}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}$ combined), 0.81 and $0.80(2 \mathrm{~d}, J=6.4 \mathrm{~Hz}$, 3 H combined); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 151.7,151.4,149.3,92.8,92.4,79.8,79.2,77.2,75.7$, $73.2,73.1,54.6,54.5,44.2,44.1,34.1,34.0,28.5,28.4,28.2,27.3,25.2,24.0,16.42,16.36,13.9,13.2$, 8.9; IR (neat) 3481, 2977, 2937, 2880, 1693, 1455, 1392, 1375, 1253, 1177, 1106, 1059, 1006, 982, 870 $\mathrm{cm}^{-1} ;$ HRMS (ESI) $m / z$ for $\mathrm{C}_{18} \mathrm{H}_{32} \mathrm{NO}_{4} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 476.1268 , found 476.1260 .



Synthesis of IMDA Cyclization of SI-10: Synthesis of Cycloadduct Adduct 26. ${ }^{10}$ To a solution of SI-7 ( $62 \mathrm{mg}, 0.11 \mathrm{mmol}$ ) and $\mathbf{3 6 b}(82 \mathrm{mg}, 0.17 \mathrm{mmol})$ in anhydrous DMF $(1 \mathrm{~mL})$ was added a solution of $\mathrm{Pd}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2} \mathrm{Cl}_{2}(3.0 \mathrm{mg}, 0.012 \mathrm{mmol})$ in DMF $(0.2 \mathrm{~mL})$. The resulting brown solution was stirred at room temperature for 16 h . The mixture was diluted with EtOAc $(2 \mathrm{~mL})$ and poured into water ( 2 mL ). The organic phase was washed with water $(3 \times 2 \mathrm{~mL})$ and brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $0-5 \% \mathrm{EtOAc} / \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) afforded SI-8 ( $50 \mathrm{mg}, 0.079 \mathrm{mmol}, 72 \%$ ) as a pale yellow foam: ${ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.37$ (ddd, $J=17.4,11.2,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.09(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.07(\mathrm{~d}, J=11.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.80(\operatorname{app} \mathrm{ddd}, J=15.7$, 8.0, 4.1 Hz, 1H), $5.54(\mathrm{~d}, J=17.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.97$ and $3.80(2 \mathrm{~m}, 1 \mathrm{H}$ combined), 3.96 and $3.93(2 \mathrm{~m}, 1 \mathrm{H}$ combined), $3.74(\mathrm{~m}, 1 \mathrm{H}), 2.35(\mathrm{~m}, 1 \mathrm{H}), 1.93(\mathrm{~s}, 3 \mathrm{H}), 1.74(\mathrm{~m}, 1 \mathrm{H}), 1.55$ and $1.50(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.50 and $1.47(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.47 and $1.46(2 \mathrm{~s}, 9 \mathrm{H}$ combined), $1.27(\mathrm{~s}, 12 \mathrm{H}), 1.08$ and $1.04(2 \mathrm{~d}, J$ $=6.3 \mathrm{~Hz}, 3 \mathrm{H}$ combined $), 0.99$ and $0.98(2 \mathrm{~d}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}$ combined $), 0.93$ and $0.92(2 \mathrm{t}, J=8.1 \mathrm{~Hz}, 9 \mathrm{H}$ combined), 0.77 ( $2 \mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 0.60-0.53 (m, 6H).

To a solution of $7 \mathbf{a}(31.0 \mathrm{mg}, 0.055 \mathrm{mmol})$ and SI-8 $(42.0 \mathrm{mg}, 0.066 \mathrm{mmol})$ in degassed THF: $\mathrm{H}_{2} \mathrm{O}(3: 1)\left(1 \mathrm{~mL}, 3\right.$ freeze-pump-thaw cycles) was added a solution of $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(7 \mathrm{mg}, 6 \mu \mathrm{~mol})$ in THF ( 0.5 mL ) followed by TlOEt $(8.0 \mu \mathrm{~L}, 0.11 \mathrm{mmol})$. After 2 h , the reaction was filtered through Celite and poured into water $(5 \mathrm{~mL})$. The aqueous phase was extracted with EtOAc ( 3 x 10 mL ). The combined organic layers were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. The crude product was filtered through a short pad of Davisil ${ }^{\mathrm{TM}}$ (5\% EtOAc $+2 \% \mathrm{Et}_{3} \mathrm{~N}$ ) to afford SI-19 (32 $\mathrm{mg}, 0.033 \mathrm{mmol}, 60 \%$ ), which was immediately used in the next reaction without further purification: ${ }^{1} \mathrm{H}$ NMR (400 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 7.68-7.62(\mathrm{~m}, 4 \mathrm{H}), 7.45-7.32(\mathrm{~m}, 6 \mathrm{H}), 6.38(\mathrm{dd}, J=14.2,11.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.13-$ $6.07(\mathrm{~m}, 2 \mathrm{H}), 5.99(\mathrm{~d}, J=11.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.92(\mathrm{dd}, J=15.0,10.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.71$ (ddd, $J=15.6,8.0,4.2 \mathrm{~Hz}$, $1 \mathrm{H}), 5.61(\mathrm{dd}, J=15.0,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 5.18(\mathrm{app} \mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.32(\mathrm{~m}, 1 \mathrm{H}), 4.00-3.88(\mathrm{~m}, 2), 3.95$ and
$3.80(2 \mathrm{~m}, 1 \mathrm{H}$ combined $), 3.78(\mathrm{~m}, 1 \mathrm{H}), 3.20(\mathrm{~m}, 1 \mathrm{H}), 3.17(\mathrm{~s}, 3 \mathrm{H}), 2.35(\mathrm{~m}, 1 \mathrm{H}), 2.25(\mathrm{~m}, 1 \mathrm{H}), 2.10(\mathrm{~m}$, $2 \mathrm{H}), 1.86(\mathrm{~s}, 3 \mathrm{H}), 1.85(\mathrm{~m}, 1 \mathrm{H}), 1.79(\mathrm{~s}, 3 \mathrm{H}), 1.78(\mathrm{~m}, 1 \mathrm{H}), 1.64(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 1.57$ and $1.52(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.52 and $1.49(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.49 and $1.47(2 \mathrm{~s}, 9 \mathrm{H}$ combined), 1.10 and $1.07(2 \mathrm{~d}, J=$ $6.3 \mathrm{~Hz}, 3 \mathrm{H}$ combined), $1.06(\mathrm{~s}, 9 \mathrm{H}), 1.02$ and $1.00(2 \mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}$ combined), $0.94(2 \mathrm{t}, J=7.9 \mathrm{~Hz}$, 9 H combined), 0.79 and $0.78(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}), 0.62-0.55(\mathrm{~m}, 6 \mathrm{H})$.

To a solution of SI-9 ( $32.0 \mathrm{mg}, 0.033 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(1 \mathrm{~mL})$ was added DMSO ( $12.0 \mu \mathrm{~L}$, 0.165 mmol ) and diisopropylethylamine ( $30.0 \mu \mathrm{~L}, 0.165 \mathrm{mmol}$ ). The mixture was cooled to $0{ }^{\circ} \mathrm{C}$ and charged with $\mathrm{SO}_{3} \bullet$ pyridine ( $16.0 \mathrm{mg}, 0.099 \mathrm{mmol}$ ). After 30 min , sat. aq. $\mathrm{NaHCO}_{3}(2 \mathrm{~mL})$ was added and the aqueous phase was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 5 \mathrm{~mL})$. The combined organic layers were washed with brine, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Aldehyde SI-10 ( $28.0 \mathrm{mg}, 0.030 \mathrm{mmol}, 90 \%$ ) was immediately used in the next reaction without further purification: ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta$ $9.96(\mathrm{~s}, 1 \mathrm{H}), 7.67-7.61(\mathrm{~m}, 4 \mathrm{H}), 7.45-7.32(\mathrm{~m}, 6 \mathrm{H}), 6.43-6.37(\mathrm{~m}, 2 \mathrm{H}), 6.12(\mathrm{dd}, J=14.5,11.2 \mathrm{~Hz}, 1 \mathrm{H})$, $6.10(\mathrm{~d}, J=15.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.01-5.92(\mathrm{~m}, 2 \mathrm{H}), 5.72(\mathrm{ddd}, J=15.6,8.1,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.62(\mathrm{dd}, J=15.0,7.1$ $\mathrm{Hz}, 1 \mathrm{H}), 4.35(\mathrm{~m}, 1 \mathrm{H}), 3.99$ and $3.80(2 \mathrm{~m}, 1 \mathrm{H}$ combined), 3.98 and $3.94(2 \mathrm{~d}, J=6.3 \mathrm{~Hz}, 1 \mathrm{H}$ combined), $3.72(\mathrm{~m}, 1 \mathrm{H}), 3.34(\mathrm{~m}, 1 \mathrm{H}), 3.17(\mathrm{~s}, 3 \mathrm{H}), 2.58(\mathrm{~m}, 2 \mathrm{H}), 2.36(\mathrm{~m}, 1 \mathrm{H}), 1.90-1.83(\mathrm{~m}, 1 \mathrm{H}), 1.87(\mathrm{~m}, 3 \mathrm{H})$, 1.79-1.73 (m, 1H), $1.75(\mathrm{~d}, J=1.0 \mathrm{~Hz}, 3 \mathrm{H}), 1.58(\mathrm{~m}, 1 \mathrm{H}), 1.57$ and $1.52(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.52 and $1.49(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.49 and $1.47(2 \mathrm{~s}, 9 \mathrm{H}$ combined), 1.10 and $1.07(2 \mathrm{~d}, J=6.3 \mathrm{~Hz}, 3 \mathrm{H}$ combined), $1.06(\mathrm{~s}, 9 \mathrm{H}), 1.01$ and $1.07(2 \mathrm{~d}, 3 \mathrm{H}$ combined), $1.06(\mathrm{~s}, 9 \mathrm{H}), 1.01$ and $1.00(2 \mathrm{~d}, J=6.8 \mathrm{~Hz}$, 3 H combined), 0.95 and $0.94(2 \mathrm{t}, J=7.9 \mathrm{~Hz}, 9 \mathrm{H}$ combined), 0.79 and $0.78(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 0.59-0.55 (m, 6H).

A solution of pentaene $\mathbf{S I - 1 0}(28.0 \mathrm{mg}, 0.030 \mathrm{mmol})$ and BHT (one small crystal) in 2,2,2trifluoroethanol ( $3 \mathrm{ml}, 0.01 \mathrm{M}$ ) was heated to $70-75^{\circ} \mathrm{C}$ for 9 h . The solvent was removed under reduced pressure, affording the crude product as an orange oil ( $\geq 6: 1: 1$ d.s. by ${ }^{1} \mathrm{H}-\mathrm{NMR}$ ) which was purified by flash column chromatography on silica gel ( $10-20 \%$ EtOAc-hexanes). The cyclized adduct 26 ( 17.0 mg , $0.018 \mathrm{mmol}, 60 \%)$ was isolated as a yellow oil: ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 9.42(\mathrm{~s}, 1 \mathrm{H}), 7.73-7.66(\mathrm{~m}$, $4 \mathrm{H}), 7.44-7.35(\mathrm{~m}, 6 \mathrm{H}), 6.05(\mathrm{br} \mathrm{d}, J=10.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.98(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.63-5.53(\mathrm{~m}, 2 \mathrm{H}), 5.38$ (br d, $J=10.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.98$ and $3.81(2 \mathrm{~m}, 1 \mathrm{H}$ combined), 3.93 and $3.90(2 \mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.78-3.69$ $(\mathrm{m}, 2 \mathrm{H}), 3.21(\mathrm{~s}, 3 \mathrm{H}), 3.12(\mathrm{~m}, 1 \mathrm{H}), 2.85(\mathrm{tt}, J=11.4,3.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.31$ and $3.26(\mathrm{~m}, 2 \mathrm{H}), 2.02(\mathrm{~m}, 1 \mathrm{H})$, $1.87(\mathrm{~m}, 1 \mathrm{H}), 1.82(\mathrm{~s}, 3 \mathrm{H}), 1.74(\mathrm{~m}, 1 \mathrm{H}), 1.62(\mathrm{~m}, 1 \mathrm{H}), 1.56$ and $1.51(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.51 and 1.48 $(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.48 and $1.47(2 \mathrm{~s}, 9 \mathrm{H}$ combined), 1.35-1.25 (m, 2 H$), 1.10-1.06(\mathrm{~m}, 6 \mathrm{H}), 1.07(\mathrm{~s}$, $9 \mathrm{H}), 0.95-0.91(\mathrm{~m}, 9 \mathrm{H}), 0.78$ and $0.77(2 \mathrm{~d}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H}$ combined), $0.63-0.53(\mathrm{~m}, 6 \mathrm{H})$.


Boronic Ester 47. To a solution of $\mathbf{3 8}(515 \mathrm{mg}, 1.17 \mathrm{mmol})$ and $\mathbf{3 6 b}(850 \mathrm{mg}, 1.76 \mathrm{mmol})$ in anhydrous DMF ( 10 mL ) was added a solution of $\operatorname{Pd}\left(\mathrm{CH}_{3} \mathrm{CN}\right)_{2} \mathrm{Cl}_{2}(31 \mathrm{mg}, 0.12 \mathrm{mmol})$ in DMF ( 2 mL ). The resulting brown solution was stirred at room temperature for 16 h . The mixture was diluted with EtOAc ( 12 mL ) and poured into water $(12 \mathrm{~mL})$. The organic phase was washed with water ( $3 \times 12 \mathrm{~mL}$ ) and brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $0-5 \% \mathrm{EtOAc} / \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ) afforded $47(304 \mathrm{mg}, 0.585 \mathrm{mmol}, 50 \%)$ as a pale yellow foam: $[\alpha]^{25}{ }_{\mathrm{D}}=-21.7^{\circ}\left(c 0.70, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.35(\mathrm{dd}, J=17.4,11.4 \mathrm{~Hz}, 1 \mathrm{H})$, $6.22(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.10(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.74(\mathrm{app} \mathrm{ddd}, J=15.6,8.8,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.57(\mathrm{~d}, J=$ $17.6 \mathrm{~Hz}, 1 \mathrm{H}$ ), 4.04-3.98 and 3.90-3.80 ( $2 \mathrm{~m}, 2 \mathrm{H}$ combined), 3.64 (tt, $J=8.8,2.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.35 (app sext, $J=7.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.94(\mathrm{~s}, 3 \mathrm{H}), 1.87(\mathrm{~m}, 1 \mathrm{H}), 1.77(\mathrm{dd}, J=9.8,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.58$ and $1.53(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.50 and $1.47(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.48 and 1.46 ( $2 \mathrm{~s}, 9 \mathrm{H}$ combined), 1.13 and 1.09 ( $2 \mathrm{~d}, J=$ $6.1 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 1.03 and $1.01(2 \mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 0.84 and $0.83(2 \mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}$ combined); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 151.7,151.4,145.3,138.33,138.29,135.9,134.44,134.42$, 132.1, 120.9, 92.6, 92.2, 83.0, 79.7, 79.0, 77.1, 76.9, 73.30, 73.27, 54.6, 54.5, 41.23, 41.21, 33.9, 33.8, $28.5,28.4,28.2,27.3,24.9,24.7,23.7,17.1,14.1,13.8,13.2,13.0,8.6,8.5$; IR (neat) $3468,2979,2937$, $2885,1691,1608,1579,1453,1391,1376,1341,1267,1174,1145,1106,1057,969,869,852,738 \mathrm{~cm}^{-1}$; HRMS (ESI) $m / z$ for $\mathrm{C}_{29} \mathrm{H}_{50} \mathrm{BNO}_{6} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 542.3629 , found 542.3629.


Ester 48. To a solution of $\mathbf{4 3 a}(23.0 \mathrm{mg}, 0.032 \mathrm{mmol})$ and $47(20.0 \mathrm{mg}, 0.038 \mathrm{mmol})$ in degassed THF: $\mathrm{H}_{2} \mathrm{O}$ (3:1) ( $0.4 \mathrm{~mL}, 3$ freeze-pump-thaw cycles) was added a solution of $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(7 \mathrm{mg}, 6 \mu \mathrm{~mol})$ in THF ( 0.2 mL ) followed by TlOEt $(7.0 \mu \mathrm{~L}, 0.01 \mathrm{mmol})$. After 2 h , the reaction was filtered through Celite and poured into water ( 2 mL ). The aqueous phase was extracted with EtOAc ( $3 \times 5 \mathrm{~mL}$ ). The combined organic layers were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. The crude product was filtered through a short pad of Davisil ${ }^{\mathrm{TM}}\left(5 \% \mathrm{EtOAc}^{2}+2 \% \mathrm{Et}_{3} \mathrm{~N}\right)$ to afford 48 ( $20 \mathrm{mg}, 0.02 \mathrm{mmol}, 62 \%$ ) which was immediately used in the next reaction: $[\alpha]^{25}{ }_{\mathrm{D}}=-131.3^{\circ}(c$ $\left.0.70, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.84(\mathrm{dd}, J=15.0,12.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.66-7.61(\mathrm{~m}, 4 \mathrm{H}), 7.42-$
$7.30(\mathrm{~m}, 6 \mathrm{H}), 6.88(\mathrm{~d}, J=15.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.72(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.32(\mathrm{dd}, J=14.6,11.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.21$ (d, $J=15.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.14-6.08(\mathrm{~m}, 2 \mathrm{H}), 6.00(\mathrm{~d}, J=11.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.89(\mathrm{dd}, J=15.1,10.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.84$ (d, $J=15.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.65 .5 .58(\mathrm{~m}, 2 \mathrm{H}), 5.41(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.35(\mathrm{~m}, 1 \mathrm{H}), 4.06-3.99$ and 3.88-3.86 (2 $\mathrm{m}, 2 \mathrm{H}$ combined), $3.76(\mathrm{~s}, 3 \mathrm{H}), 3.31-3.25(\mathrm{~m}, 1 \mathrm{H}), 3.17(\mathrm{~s}, 3 \mathrm{H}), 2.38-2.26(\mathrm{~m}, 3 \mathrm{H}), 2.00(\mathrm{~m}, 1 \mathrm{H}$ overlapped), 1.99 (s, 3H), $1.91(\mathrm{~s}, 3 \mathrm{H}), 1.91-1.88(\mathrm{~m}, 1 \mathrm{H}$ overlapped), $1.84(\mathrm{~s}, 3 \mathrm{H}), 1.84-1.80(\mathrm{~m}, 2 \mathrm{H})$, 1.58 and $1.54(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.50 and $1.48(2 \mathrm{~s}, 3 \mathrm{H}$ combined), 1.48 and $1.46(2 \mathrm{~s}, 9 \mathrm{H}$ combined), 1.13 and $1.10(2 \mathrm{~d}, J=6.3 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 1.05 (s, 9 H ), 1.02 and 1.01 ( $2 \mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}$ combined), 0.85 and $0.83\left(2 \mathrm{~d}, J=6.4 \mathrm{~Hz}, 3 \mathrm{H}\right.$ combined); ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.9,151.9,151.5,143.2$, $139.4,136.4,136.3,136.0,135.9,135.8,135.0,134.9,134.3,134.1,134.0,132.6,132.51,132.48,131.0$, $130.44,130.42,129.6,129.5,129.4,128.9,127.6,127.5,127.4,127.1,124.4,119.5,92.8,92.4,79.8$, $79.2,77.24,77.19,73.4,73.3,72.1,56.1,54.72,54.69,51.5,42.5,41.4,33.9,33.8,31.6,28.6,28.5,28.3$, $27.4,27.1,25.0,23.9,21.2,20.7,19.3,17.3,17.2,14.0,13.3,12.8,8.7,8.6$ IR (neat) $3480,2976,2935$, $1693,1612,1454,1428,1391,1376,1367,1310,1265,1230,1168,1133,1106,1066,986,871,822$, $738,703 \mathrm{~cm}^{-1}$.


Acid 41b. To a $0^{\circ} \mathrm{C}$ solution of $\mathbf{2 8}^{7}(3.20 \mathrm{~g}, 10.2 \mathrm{mmol})$ in THF $(41 \mathrm{~mL})$ was added $n-\mathrm{BuLi}(3.90$ mL of a 2.5 M solution in hexanes, 9.84 mmol ). The reaction mixture was stirred for 30 min at this temperature followed by addition of a solution of $\mathbf{3 9}{ }^{8}(468 \mathrm{mg}, 4.10 \mathrm{mmol})$ in THF $(8 \mathrm{~mL})$. The ice bath was removed and the mixture was stirred for 1 h at room temperature. Water $(30 \mathrm{~mL})$ was added and the aqueous phase was acidified $(\mathrm{pH}=1)$ with $\mathrm{H}_{2} \mathrm{SO}_{4}(1 \mathrm{M} \mathrm{aq}$.). The organic phase was then washed with sat. aq. $\mathrm{K}_{2} \mathrm{CO}_{3}(3 \times 20 \mathrm{~mL})$. The basic aqueous layer was acidified with $\mathrm{H}_{2} \mathrm{SO}_{4}$ ( 1 M aq.) and extracted with EtOAc ( $3 \times 20 \mathrm{~mL}$ ). The combined organic phases were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. The crude product was recrystallized from hexanes to afford 41b (804 $\mathrm{mg}, 3.11 \mathrm{mmol}, 76 \%)$ as a white solid: $\mathrm{mp}=77-78{ }^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.18(\mathrm{dd}, J=15.4$, $11.7 \mathrm{~Hz}, 1 \mathrm{H}), 6.59$ (dqd, $J=11.7,1.5,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.01$ (app dt, $J=15.4,0.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.28(\mathrm{~m}, 2 \mathrm{H}), 2.09$ (app dt, $J=1.4,0.7 \mathrm{~Hz}, 3 \mathrm{H}), 1.05(\mathrm{~m}, 2 \mathrm{H}), 0.06(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.9,166.7$, 139.7, 138.1, 133.4, 127.2, 63.0, 21.0, 17.3, -1.48; IR (neat) 2953, 2895, 1706, 1680, 1627, 1597, 1455, 1297, 1250, 1198, 1148, 1118, 1064, 987, 931, $857 \mathrm{~cm}^{-1} ;$ HRMS (ESI) $m / z$ for $\mathrm{C}_{12} \mathrm{H}_{20} \mathrm{O}_{4} \mathrm{SiNa}[\mathrm{M}+\mathrm{Na}]^{+}$ calcd 279.1023 , found 279.1029.


Allylic alcohol 42b. To a $0^{\circ} \mathrm{C}$ solution of $\mathbf{4 1 b}(800 \mathrm{mg}, 3.12 \mathrm{mmol})$ in THF ( 12 mL ) was added triethylamine $(1.70 \mathrm{~mL}, 12.5 \mathrm{mmol})$ followed by ethyl chloroformate $(0.45 \mathrm{~mL}, 4.7 \mathrm{mmol})$. The reaction mixture was stirred for 1 h at room temperature and then filtered through a pad of Celite and concentrated. The crude product was dissolved in $\mathrm{MeOH}(16 \mathrm{~mL})$, cooled to $-78^{\circ} \mathrm{C}$ and $\mathrm{NaBH}_{4}(354 \mathrm{mg}$, 9.36 mmol ) was added in portions. The mixture was stirred for 30 min at this temperature and then carefully quenched with sat. aq. $\mathrm{NH}_{4} \mathrm{Cl}(10 \mathrm{~mL})$. The aqueous phase was extracted with $\mathrm{EtOAc}(3 \mathrm{x} 20$ mL ). The combined organic layers were washed with brine, dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( $20-50 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded 42b ( $676 \mathrm{mg}, 2.79 \mathrm{mmol}, 89 \%$ ) as a colorless oil: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.59(\mathrm{dd}, J=$ $15.1,11.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.07(\mathrm{~d}, J=11.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.81(\mathrm{~d}, J=15.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.37(\mathrm{~d}, J=5.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.24(\mathrm{~m}$, $2 \mathrm{H}), 1.97(\mathrm{~s}, 3 \mathrm{H}), 1.41(\mathrm{t}, J=5.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.02(\mathrm{~m}, 2 \mathrm{H}), 0.05(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.5,146.8,139.0,125.4,120.9,62.5,61.4,21.9,17.3,-1.5$; IR (neat) $3427,2954,2898,1710,1638$, $1612,1451,1432,1379,1305,1281,1154,981,860,838 \mathrm{~cm}^{-1} ; \operatorname{HRMS}(E S I) m / z$ for $\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{SiNa}[\mathrm{M}+$ $\mathrm{Na}]^{+}$calcd 265.1230, found 265.1230.


Aldehyde 37b. To a $0{ }^{\circ} \mathrm{C}$ solution of $\mathbf{4 2 b}(200 \mathrm{mg}, 0.820 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(6 \mathrm{~mL})$ was added Dess-Martin periodinane ( $525 \mathrm{mg}, 1.24 \mathrm{mmol}$ ). The reaction mixture was stirred for 1 h at room temperature and then cooled again to $0^{\circ} \mathrm{C}$. Hexanes were added $(6 \mathrm{~mL})$ and the resulting suspension was filtered through a Davisil ${ }^{\mathrm{TM}}$ column using a $1: 1 \mathrm{Et}_{2} \mathrm{O}$ :hexanes mixture as eluent. The filtrate was concentrated to give aldehyde $\mathbf{3 7 b}(190 \mathrm{mg}, 0.79 \mathrm{mmol}, 96 \%)$ as a white solid. Compound $\mathbf{3 7 b}$ was used immediately in the next step to avoid isomerization of the trisubstituted double bond: $\mathrm{mp}=51-52{ }^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 9.94(\mathrm{~s}, 1 \mathrm{H}), 8.12(\mathrm{dd}, J=15.1,12.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.22(\mathrm{br} \mathrm{d}, J=12.4 \mathrm{~Hz}, 1 \mathrm{H})$, 5.93 (br d, $J=15.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.41(\mathrm{~m}, 2 \mathrm{H}), 1.65(\mathrm{~s}, 3 \mathrm{H}), 1.04(\mathrm{~m}, 2 \mathrm{H}), 0.04(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{C}_{6} \mathrm{D}_{6}\right) \delta 188.8,165.9,141.3,140.0,135.9,127.1,62.9,17.5,16.7,-1.6$; IR (neat) $2978,2878,1728$, $1698,1456,1392,1302,1255,1178,1109,1066,1043,1012,869 \mathrm{~cm}^{-1} ;$ HRMS (ESI) $m / z$ for $\mathrm{C}_{12} \mathrm{H}_{20} \mathrm{O}_{3} \mathrm{SiNa}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 263.1074 , found 263.1061 .


Ester 43b. To a $-78{ }^{\circ} \mathrm{C}$ solution of $\mathbf{3 5 a}(200 \mathrm{mg}, 0.240 \mathrm{mmol})$, in THF ( 2 mL ) was added NaHMDS ( 0.62 mL of a 0.5 M solution in THF, freshly prepared, 0.31 mmol ). After being stirred for 10 min, a solution of $\mathbf{3 7 b}(69 \mathrm{mg}, 0.29 \mathrm{mmol})$ in THF $(1 \mathrm{~mL})$ was added. The reaction mixture was allowed to warm up to $-10{ }^{\circ} \mathrm{C}$ over 2 h and quenched with sat. aq. $\mathrm{NH}_{4} \mathrm{Cl}(1 \mathrm{~mL})$. The aqueous phase was extracted with EtOAc ( $3 \times 3 \mathrm{~mL}$ ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated. Purification of the crude product by flash chromatography ( 2 g of Davisil ${ }^{\mathrm{TM}}$ pretreated with hexanes $+2 \%$ of $\mathrm{Et}_{3} \mathrm{~N}, 5 \%$ EtOAc as eluent) afforded $\mathbf{4 3 b}(167 \mathrm{mg}, 0.21 \mathrm{mmol}, 87 \%)$ as a colorless oil, which was immediately used in the next reaction: $[\alpha]^{25}=-17.7^{\circ}\left(c 1.03, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right) \delta 8.27(\mathrm{dd}, J=15.2$, $12.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.75-7.68(\mathrm{~m}, 4 \mathrm{H}), 7.25-7.18(\mathrm{~m}, 6 \mathrm{H}), 7.01(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H})$, $6.56(\mathrm{dd}, J=14.4,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.06(\mathrm{~d}, J=14.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.95(\mathrm{dd}, J=14.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.94(\mathrm{~d}, J=$ $10.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.31(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.39-4.33(\mathrm{~m}, 1 \mathrm{H}), 4.33(\mathrm{t}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.22-3.16(\mathrm{~m}, 1 \mathrm{H})$, $2.96(\mathrm{~s}, 3 \mathrm{H}), 2.30-2.15(\mathrm{~m}, 2 \mathrm{H}), 1.83(\mathrm{ddd}, J=14.0,9.2,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.80(\mathrm{~s}, 3 \mathrm{H}), 1.66(\mathrm{~s}, 3 \mathrm{H}), 1.56$ $(\mathrm{ddd}, J=14.0,7.6,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.35(\mathrm{~s}, 9 \mathrm{H}), 0.95(\mathrm{t}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}),-0.06(\mathrm{~s}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) $\delta 167.0,148.5,142.5,138.8,136.3,136.2,134.5,134.1,133.8,130.1,129.4,129.0,128.5$, $128.1,128.0,127.9,127.8,125.0,121.4,77.0,76.9,74.3,62.3,56.0,42.2,31.6,27.2,21.0,20.5,19.5$, $17.5,-1.5$; IR (neat) $3072,2953,2858,1704,1614,1472,1428,1380,1251,1161,1130,977,949,836$ $\mathrm{cm}^{-1} ;$ HRMS (ESI) $m / z$ for $\mathrm{C}_{39} \mathrm{H}_{55} \mathrm{IO}_{4} \mathrm{Si}_{2} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+}$calcd 793.2576, found 793.2575.

Comparison of ${ }^{1} H$ NMR Data for Synthetic and Natural Superstolide A

| Position | Natural (500 MHz) ${ }^{11}$ | Synthetic (400 MHz) |
| :---: | :---: | :---: |
| 1 | ------ | ------ |
| 2 | $5.70 \mathrm{~d}(J=15.3)$ | $5.70 \mathrm{~d}(J=14.9)$ |
| 3 | $7.21 \mathrm{dd}(J=15.3,11.2)$ | $7.21 \mathrm{dd}(J=15.2,11.0)$ |
| 4 | $5.92 \mathrm{~d}(J=11.2)$ | $5.91 \mathrm{~d}(J=11.0)$ |
| 5 | ------ | ------ |
| 6 | $6.88 \mathrm{~d}(J=16.3)$ | $6.87 \mathrm{~d}(J=16.4)$ |
| 7 | $5.60 \mathrm{~d}(J=16.3)$ | $5.60 \mathrm{~d}(J=16.4)$ |
| 8 | ------ | ----- |
| 9 | 1.48 m | 1.48 m |
| 10 | $1.45 \mathrm{~m}, 1.80 \mathrm{~m}$ | $1.45 \mathrm{~m}, 1.80 \mathrm{~m}$ |
| 11 | 3.10 m | 3.10 m (overlapped) |
| 12 | $1.31 \mathrm{~m}, 2.24 \mathrm{br} \mathrm{d}(J=10.5)$ | $1.30 \mathrm{~m}, 2.24$ br d ( $J=10.5$ ) |
| 13 | 4.76 br t ( $J=9.8$ ) | 4.77 m |
| 14 | 2.88 br s | 2.89 br s |
| 15 | $5.52 \mathrm{dt}(J=9.8,3.4)$ | $5.52 \mathrm{dt}(J=10.1,3.3)$ |
| 16 | $5.68 \mathrm{~d}(J=9.8)$ | $5.68 \mathrm{~d}(J=9.6)$ |
| 17 | 3.10 br d (overlapped) | 3.10 m (overlapped) |
| 18 | $5.78 \mathrm{~d}(J=10.8)$ | $5.79 \mathrm{~d}(J=10.7)$ |
| 19 | ------ | ------ |
| 20 | $6.29 \mathrm{~d}(J=15.3)$ | $6.29 \mathrm{~d}(J=15.2)$ |
| 21 | $5.32 \mathrm{dd}(J=15.3,9.8)$ | $5.32 \mathrm{dd}(J=15.2,9.6)$ |
| 22 | 2.71 m | 2.71 m |
| 23 | $4.79 \mathrm{dd}(J=10.5,2.0)$ | $4.79 \mathrm{~d}(J=10.5)$ |
| 24 | 1.82 m | 1.80 m |
| 25 | $3.16 \mathrm{dd}(J=10.5,2.7)$ | $3.16 \mathrm{dd}(J=10.5,2.4)$ |
| 26 | 4.18 m | 4.19 m |
| 27 | ------ | ------ |
| 28 | 1.96 s | 1.97 s |
| 29 | 1.92 s | 1.92 s |
| 30 | 1.15 s | 1.15 s |
| 31 | ------ | ------ |
| 32 | 1.77 s | 1.77 s |
| 33 | $1.07 \mathrm{~d}(J=6.9)$ | $1.08 \mathrm{~d}(J=6.8)$ |
| 34 | $0.90 \mathrm{~d}(J=6.9)$ | $0.90 \mathrm{~d}(J=6.8)$ |
| 35 | $1.05 \mathrm{~d}(J=6.9)$ | $1.05 \mathrm{~d}(J=6.9)$ |
| NH | $6.22 \mathrm{~d}(J=8.8)$ | $6.23 \mathrm{~d}(J=8.8)$ |
| $\mathrm{OCH}_{3}$ | 3.35 s | 3.35 s |
| $\mathrm{CONH}_{2}$ | 4.66 br s | 4.63 br s |
| OH (25) | 3.32 d (overlapped) | 3.33 (overlapped) |

## Comparison of ${ }^{13} \mathbf{C}$ NMR Data for Synthetic and Natural Superstolide A

| Position | Natural ( 500 MHz$)^{11}$ | Synthetic (400 MHz) |
| :---: | :---: | :---: |
| 1 | $167.0^{\text {a }}$ | 169.0 |
| 2 | 121.3 | 121.3 |
| 3 | 139.2 | 139.3 |
| 4 | 125.5 | 125.5 |
| 5 | 142.5 | 142.6 |
| 6 | 125.8 | 125.8 |
| 7 | 142.7 | 142.7 |
| 8 | 40.4 | 40.4 |
| 9 | 41.3 | 41.8 |
| 10 | 30.7 | 30.8 |
| 11 | 77.0 (under $\mathrm{CDCl}_{3}$ ) | 77.0 (under $\mathrm{CDCl}_{3}$ ) |
| 12 | 33.7 | 33.7 |
| 13 | 72.6 | 72.8 |
| 14 | 36.0 | 36.0 |
| 15 | 120.3 | 120.3 |
| 16 | 130.3 | 130.2 |
| 17 | 42.9 | 42.9 |
| 18 | $132.2^{\text {a }}$ | 133.1 |
| 19 | 132.4 | 132.4 |
| 20 | 137.1 | 137.1 |
| 21 | 129.4 | 129.4 |
| 22 | 40.7 | 40.9 |
| 23 | 77.0 (under $\mathrm{CDCl}_{3}$ ) | 77.0 (under $\mathrm{CDCl}_{3}$ ) |
| 24 | 37.5 | 37.6 |
| 25 | 73.1 | 73.1 |
| 26 | 45.4 | 45.5 |
| 27 | 169.7 | 169.7 |
| 28 | 23.5 | 23.5 |
| 29 | 20.7 | 20.7 |
| 30 | $29.7{ }^{\text {b }}$ | 31.3 |
| 31 | 156.0 | 156.1 |
| 32 | 12.0 | 12.0 |
| 33 | 18.0 | 18.0 |
| 34 | 8.8 | 8.8 |
| 35 | 12.7 | 12.6 |
| NH | ------ | ------ |
| $\mathrm{OCH}_{3}$ | 56.1 | 56.1 |
| $\mathrm{CONH}_{2}$ | ------ | ------ |
| OH (25) | ------ | ------ |

a: Appear to have been recorded incorrectly in tabulated data in the isolation paper, as the peaks in the spectra of synthetic and natural superstolide A are in perfect agreement.
b: This peak was misassigned in the isolation paper due to the presence of an impurity at 29.7 ppm . The correct peak was also present at 31.3 ppm in the spectrum of the natural product but was not reported by the isolation authors.

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