Supporting Information

A convergent fragment coupling strategy to access all-carbon quaternary stereocenters

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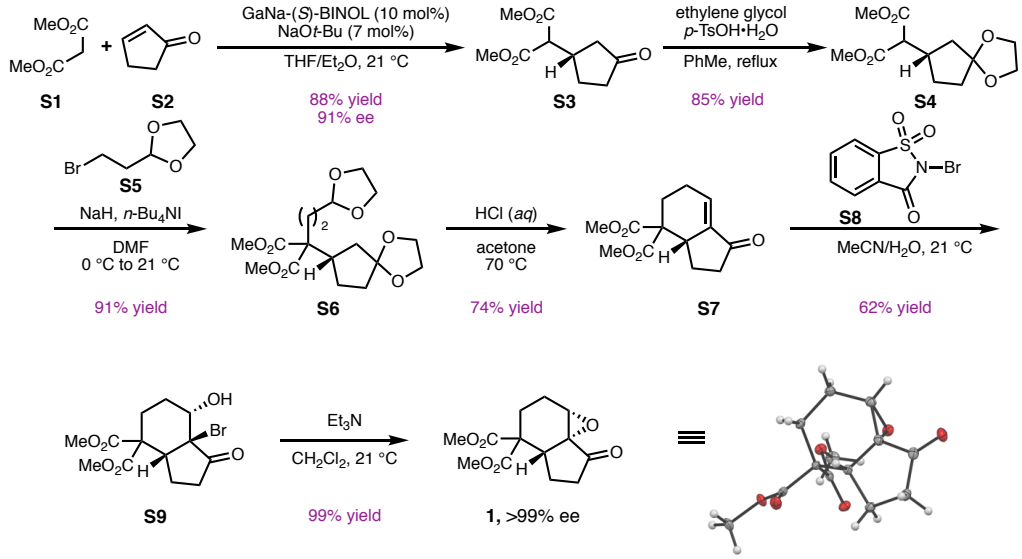
1. General Procedures

Unless otherwise stated, reactions were performed under an inert atmosphere (dry N_2) using freshly dried solvents and standard Schlenk techniques. Glassware was oven-dried at 120 °C for a minimum of four hours. Tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), acetonitrile (ACN), methanol (MeOH), benzene (PhH), and toluene (PhMe) were dried by passing through activated alumina columns. CH_2Cl_2 (D150-4), benzene (PhH, OmniSolv, BX0212-1), acetonitrile (A998-4), pentane (P399-4), acetone (A18-20), hexanes (H292-20), and *n*-butanol (A399-4) were purchased from Fisher and used as received. Anhydrous *N,N*-dimethylformamide (DMF) was purchased from VWR (EM-DX1727-6) and used as received. All reactions were monitored by thin-layer chromatography using EMD/Merck silica gel 60 F254 pre-coated plates (0.25 mm) and were visualized by UV or by staining with *p*-anisaldehyde or potassium permanganate ($KMnO_4$). Flash column chromatography was performed as described by Still et al.[1] using silica gel (particle size 0.032–0.063) purchased from MilliporeSigma. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD with Prodigy cryoprobe (at 400 MHz and 101 MHz, respectively), a Varian Inova 500 (at 500 MHz and 126 MHz, respectively), a Bruker 400 MHz Spectrometer with broadband iProbe, or a Varian Inova 600 (at 600 MHz and 150 MHz, respectively), and are reported relative to internal $CDCl_3$ (^1H, δ = 7.26; ^{13}C, δ = 77.16), CD_2Cl_2 (^1H, δ = 5.32; ^{13}C, δ = 53.84) or CD_3CN (^1H, δ = 1.94; ^{13}C, δ = 118.3). $CDCl_3$ was stored over anhydrous potassium carbonate (K_2CO_3). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS data were acquired using an Agilent 6230 Series time-of-flight (TOF) mass spectrometer with an Agilent G1978A ion trap or by LC-MS using a Waters LCT Premier XE Electrospray TOF mass spectrometer interfaced with Waters UPLC chromatography, or by GC-MS interfaced with a JEOL JMS-T2000 GC AccuTOF GC-Alpha with Field Ionization. Molecular formulas of the compounds [M] are given, with the observed ion fragment in brackets, e.g. $[M+H]^+$. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm. Melting points were determined using a Büchi B-545 capillary melting point apparatus, and the values reported are uncorrected. Unless otherwise stated, chemicals and

reagents were used as received. Stereochemistry of products was assigned analogous to compounds **2a-OH** (CCDC # 2083859) and **6** (CCDC # 2224814), both of which have had their absolute configuration confirmed via X-ray crystallography. The X-ray structure of **2a-OH** has been previously reported by Reisman and appears as S11 in their SI.[2]

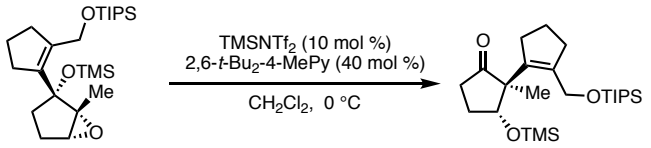
2. Synthetic Procedures

Preparation of enantiopure epoxyketone 1:



1 was prepared according to a six step procedure reported by Reisman, and ^{1}H NMR data matched their report.[2]

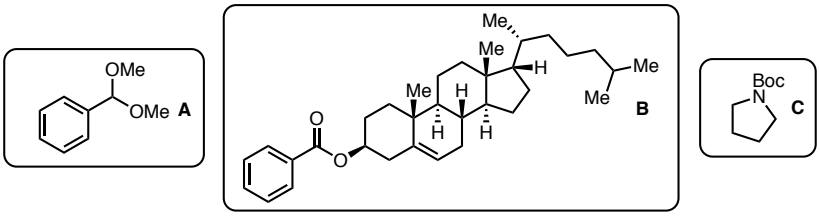
Protecting Group Compatibility Additive Screen



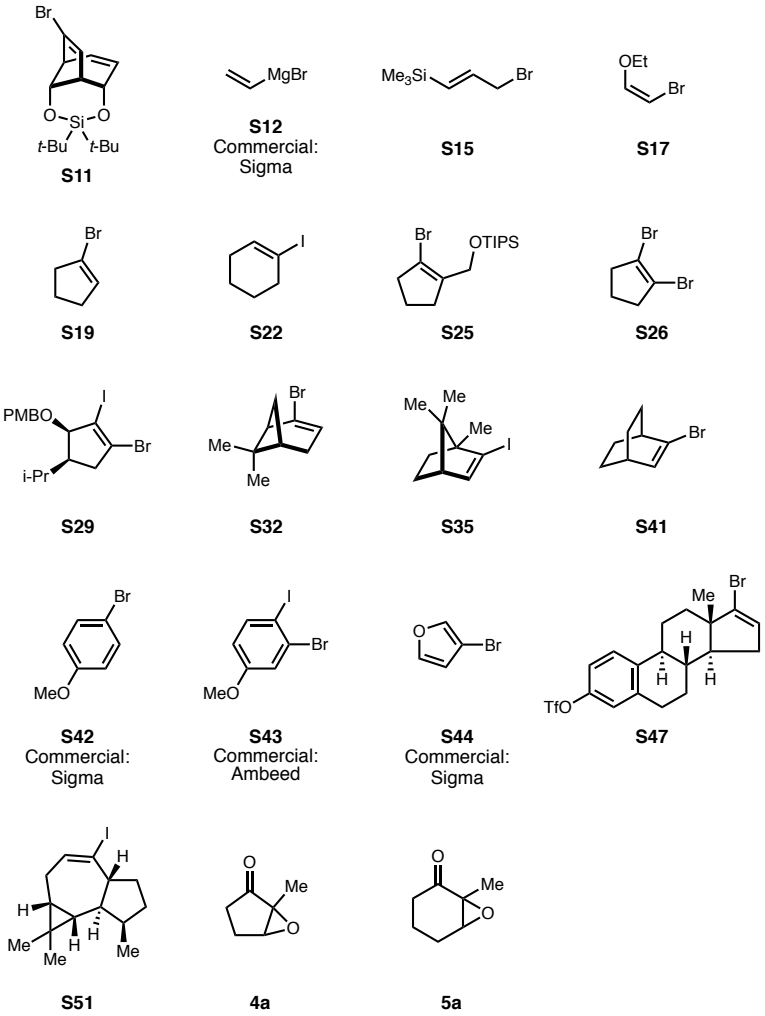
4a' **5a**

Additive	Reaction Yield	Recovered SM	Mass Balance	Additive Recovery
none	93%	0%	93%	N/A
A	86%	0%	86%	76% recovery
B	92%	0%	92%	93% recovery
C	20%	71%	91%	87% recovery

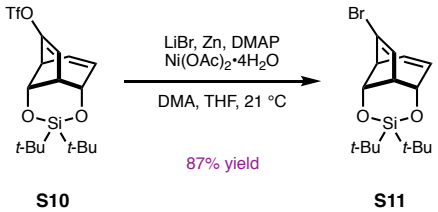
all yields in table are qNMR yields with pyrazine internal standard in $CDCl_3$



Preparation of alkenyl halides for 1,2-additions:



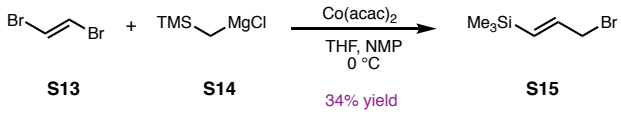
Preparation of S11:



Alkenyl triflate **S10** was prepared in 11 steps according to a procedure reported by Reisman,[2] and ^{1}H NMR characterization data matched their report.

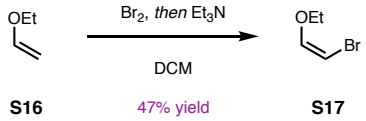
Alkenyl bromide **S11** were prepared according to a procedure reported by Reisman,[2] and ^{1}H NMR characterization data matched their report.

Preparation of S15:



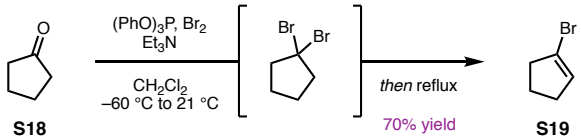
Allyl bromide **S15** was prepared according to a procedure reported by Okamoto.[3] ^{1}H NMR characterization data matched a report by Clayden.[4]

Preparation of S17:



Bromoethoxy ethene **S17** was prepared according a procedure reported by Valentí.[5] ^{1}H NMR characterization data matched a report by Stalick.[6]

Preparation of alkenyl bromide S19:

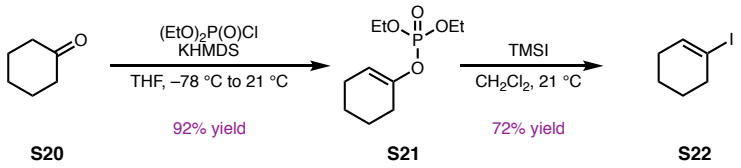


A 500 mL round bottom flask was charged with triphenyl phosphite (27.6 mL, 105 mmol, 1.1 equiv), CH_2Cl_2 (300 mL), and was cooled to –60 °C. Br_2 (5.9 mL, 115.5 mmol, 1.2 equiv) was added followed by Et_3N (17.6 mL, 126 mmol, 1.3 equiv). Cyclopentanone (**S18**, 8.53 mL, 96 mmol, 1.0 equiv) was added and the reaction was allowed to warm to ambient temperature. The reaction mixture was stirred until complete consumption of the starting material was observed by TLC (100% hexanes, $KMnO_4$ stain, *ca*. 6 hours). Upon completion, the flask was equipped with a reflux condenser and the reaction mixture was heated to reflux until complete consumption of the starting material was observed by TLC (100% hexanes, $KMnO_4$ stain, *ca*. 1 hour). The reaction was cooled to ambient temperature and the mixture was transferred to a separatory funnel. The organic layer was washed with aqueous 2 M HCl (2 x 300 mL), and the combined aqueous washes were extracted with pentane (2 x 150 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure on an ice bath due to the volatility of the product. Purification of the crude residue by column chromatography (silica, 100%

pentane) provided alkenyl bromide **S19** (10 g, 67.2 mmol, 70% yield) as a clear oil contaminated with some residual pentane.

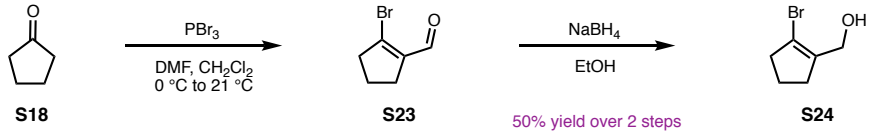
^{1}H NMR data agrees with characterization data reported by Hayashi.[7] This procedure was adapted from a procedure reported by Liang.[8]

Preparation of cyclohexenyl iodide S22:



Cyclohexenyl iodide **S22** was prepared according to a procedure by Wiemer.[9] ^{1}H NMR data agrees with characterization data reported by Prabhu.[10]

Preparation of allylic alcohol S24:

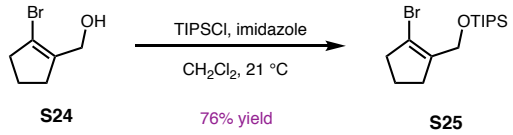


A 1 L round bottom flask was charged with DMF (14.0 mL, 181 mmol, 3.2 equiv) and CH_2Cl_2 (80 mL). The solution was cooled to 0 °C then PBr_3 (14.3 mL, 153 mmol, 2.7 equiv) was added dropwise via syringe. The reaction mixture was allowed to stir for 1 hour at 0 °C. A solution of cyclopentanone (**S18**, 5.0 mL, 56.5 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) was added dropwise via syringe. The reaction was allowed to warm to 21 °C and was stirred for an additional 21 h. The reaction was cooled to 0 °C and quenched *carefully* with sat. $NaHCO_3$ (500 mL). Solid $NaHCO_3$ was added periodically as needed until bubbling ceased and the aqueous layer tested to be slightly basic with pH paper. The resulting mixture was extracted with Et_2O (3 x 250 mL), and the combined organic extracts were washed with H_2O (2 x 500 mL), brine (500 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica, 15% EtOAc:85% hexanes) to afford bromoenal **S23** (*ca*. 5.8 g), which was used in the next step without rigorous removal of solvent. Spectroscopic data for bromoenal **S23** matched that reported in the literature.[11]

A 500 mL round bottom flask was charged with bromoenal **S23** (*ca.* 5.8 g) and EtOH (33 mL) followed by cooling the reaction to 0 °C. $NaBH_4$ (1.5 g, 39.8 mmol, 1.2 equiv) was added and the reaction was stirred for 1 hour at 0 °C. The reaction was quenched with H_2O (200 mL) and the mixture was partially concentrated under reduced pressure to remove ethanol. The resulting aqueous solution was extracted with Et_2O (3 x 200 mL), and the combined organic extracts were washed with brine (200 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography (silica, 15% EtOAc in hexanes) afforded allylic alcohol **S24** (5.05 g, 28.5 mmol, 50% yield over two steps) as a clear colorless oil. Allylic alcohol **S24** matched characterization reported in the literature.[12]

Caution: Bromoenal **S23** was found to decompose exothermically upon standing for several hours at 21 °C, or several days at –20 °C. It was found to be stable to storage at –78 °C at which temperature it solidifies into a crystalline solid. It was also found to be stable to storage as a 10% solution in diethyl ether at –20 °C for months.

Preparation of TIPS ether S25:



S24 76% yield **S25**

A 200 mL round bottom flask was charged with allylic alcohol **S24** (5.05 g, 28.5 mmol, 1.0 equiv), imidazole (4.66 g, 68.5 mmol, 2.4 equiv), DMF (57 mL), and TIPSCl (7.32 mL, 34.2 mmol, 1.2 equiv) sequentially. The reaction was stirred at 21 °C until complete consumption of the starting material was observed by TLC (*ca*. 12 hours). The reaction was quenched with sat. $NaHCO_3$ (100 mL) and H_2O (100 mL) then the reaction mixture was extracted with Et_2O (3 x 200 mL). The combined organic extracts were washed with H_2O (200 mL), brine (200 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude oil was purified by column chromatography (5% EtOAc:95% hexanes) to afford TIPS ether **S25** (7.27 g, 21.8 mmol, 76% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.35 (tq, J = 1.7, 0.9 Hz, 2H), 2.68 – 2.62 (m, 2H), 2.52 – 2.45 (m, 2H), 1.99 – 1.91 (m, 2H), 1.18 – 1.10 (m, 3H), 1.10 – 1.04 (m, 18H).

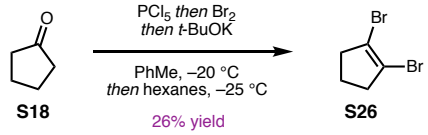
^{13}C NMR (126 MHz, $CDCl_3$): δ 140.7, 115.2, 61.4, 40.2, 32.3, 21.5, 18.0, 12.0.

FTIR (NaCl, thin film): 2960, 2941, 2892, 2866, 1657, 1463, 1383, 1369, 1104, 1066 cm^{-1}.

HRMS: (FAB) calc'd for $C_{15}H_{28}BrOSi$ $[M+H-H_2]^+$ 331.1093, found 331.1089.

TLC (10% EtOAc:90% Hexanes), R_f: 0.77 ($KMnO_4$ stain).

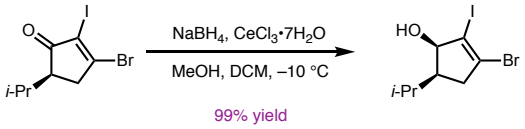
Preparation of S26:



S18 S26

Cyclopentenyl dibromide **S26** was prepared according a procedure reported by Feringa.[13] ^{1}H NMR data agrees with characterization data in their report.

Preparation of S28:



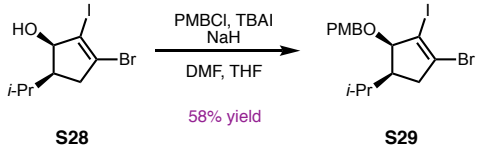
S27 S28

Ketone **S27** was prepared according to a five step procedure reported by Reisman, and ^{1}H NMR data matched their report.[14] Alcohol **S28** was prepared via a Luche reduction.

A 100 mL flask was charged with ketone **S27** (0.517 g, 1.57 mmol, 1.0 equiv), MeOH (15.7 mL), and CH_2Cl_2 (15.7 mL). The solution was cooled to –10 °C then cerium chloride heptahydrate (1.76 g, 4.71 mmol, 3.0 equiv) was added, followed by $NaBH_4$ (89.2 mg, 2.36 mmol, 2.0 equiv). The mixture was stirred at –10 °C until complete consumption of the starting material was observed by TLC (*ca*. 30 minutes). The reaction was quenched with 1 M NaOH (30 mL), diluted with Et_2O (100 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with brine (1 x 30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude product by column chromatography (silica, 10–20% Et_2O in hexanes gradient) afforded the product as a pale yellow crystalline solid (0.515 g, 99% yield). ^{1}H NMR

characterization data matched the data in Reisman's report with the exception that alcohol **S28** had the opposite optical rotation sign. $[\alpha]_D^{25}$ = +3.4° (c = 1.00, $CHCl_3$).

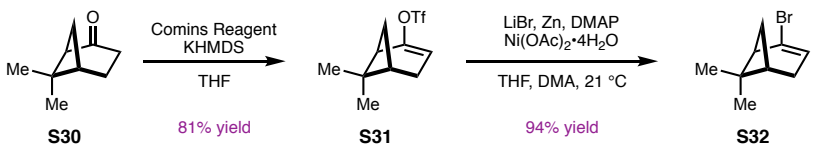
Preparation of S29:



S28 **S29**

PMB ether **S29** was prepared via a procedure reported by Reisman.[14] A 25 mL flask in a glovebox was charged with NaH (dry 95%, 71.4 mg, 2.83 mmol, 2.0 equiv) and DMF (3.54 mL). The flask was sealed with a rubber septa, removed from the glovebox, put under N_2 on a Schlenk line, and was cooled to 0 °C. A solution of alcohol **S28** (468 mg, 1.41 mmol, 1.0 equiv) in THF (3.54 mL) was cannulated into the NaH suspension. The reaction was stirred for 45 minutes, then 4-methoxybenzyl chloride (249 uL, 1.84 mmol, 1.3 equiv) was added dropwise. The reaction was warmed to 21 °C then tetrabutylammonium iodide (157 mg, 0.42 mmol, 0.30 equiv) was added in a single portion. The reaction was stirred at 21 °C until complete consumption of the starting material was observed by TLC (*ca.* 16 hours). The reaction was quenched by a dropwise addition of sat. NH_4Cl (15 mL) at 0 °C. The reaction mixture was diluted in Et_2O (20 mL), and the layers were separated. The aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic extracts were washed with water (1 x 20 mL), brine (1 x 20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by column chromatography (silica, 50% CH_2Cl_2:50% hexanes followed by a second column using a 7.5% EtOAc in hexanes to 15% EtOAc in hexanes gradient) afforded the product as a clear colorless oil (0.368 g, 58% yield). ^{1}H NMR characterization data matched the data in Reisman's report with the exception that PMB ether **S29** had the opposite optical rotation sign. $[\alpha]_D^{25}$ = +20.4° (c = 1.00, $CHCl_3$).

Preparation of S32:



S30 **S31** **S32**

S31 was prepared from (+)-nopinone (**S30**) according to a procedure reported by Fallis,[15] ^{1}H NMR characterization data matched their report.

S32 was prepared via a procedure adapted from Reisman.[16] A 25 mL flask equipped with a stir bar was brought into a glovebox. The flask was charged with nickel (II) acetate tetrahydrate (8.98 mg, 0.036 mmol, 0.05 equiv), 4-dimethylaminopyridine (8.81 mg, 0.072 mmol, 0.10 equiv), and lithium bromide (94.0 mg, 1.08 mmol, 1.5 equiv). Anhydrous THF (2.2 mL), and DMA (0.7 mL) were added. The alkenyl triflate **S31** (250 mg of a 78% solution in PhMe, 0.72 mmol, 1.0 equiv) was added. The flask was stirred at 600 RPM for 16 hours at 21 °C. The reaction was quenched with sat. NH_4Cl (10 mL), and water (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 25 mL). The combined organic layers were washed with brine (1 x 30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure (Caution! The product is volatile!). The crude product was purified by column chromatography (silica, 100% pentane) to yield **S32** as a clear colorless oil (145 mg, 94% yield).

^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.83 (tdd, *J* = 3.2, 1.8, 1.1 Hz, 1H), 2.47 (dt, *J* = 8.9, 5.7 Hz, 1H), 2.41 (td, *J* = 5.6, 1.9 Hz, 1H), 2.34 (dt, *J* = 17.5, 3.2 Hz, 1H), 2.25 (dt, *J* = 17.5, 3.0 Hz, 1H), 2.14 (ttd, *J* = 5.7, 2.8, 1.1 Hz, 1H), 1.37 (d, *J* = 8.9 Hz, 1H), 1.30 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 126.7, 123.5, 52.7, 40.2, 33.3, 32.8, 26.1, 20.8.

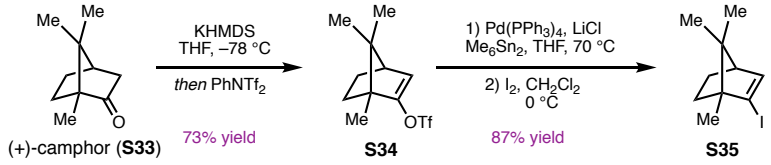
FTIR (NaCl, thin film): 3036, 2924, 2930, 2341, 2357, 1627, 1471, 1308, 1048, 1048, 971, 881 cm^{-1}.

HRMS: (FI-TOF) calc'd for $C_9H_{13}Br$ $[M]^+$ 200.0195, found 200.0199.

$[\alpha]_D^{25}$ = +53.9 (*c* = 1.00, $CHCl_3$).

TLC (100% Hexanes), R*f*: 0.77, ($KMnO_4$ stain).

Preparation of S35:



Preparation of enol triflate S34:

A 500 mL oven dried N_2 flushed flask was charged with (+)-camphor (**S33**) (4.58 g, 30 mmol, 1.0 equiv) and THF (250 mL). The solution was cooled to –78 °C then KHMDS (63 mL, 0.5 M in toluene, 31.5 mmol, 1.05 equiv) was added dropwise. The reaction was stirred for 45 minutes at –78 °C. A 100 mL oven dried N_2 flushed flask was charged with $PhNTf_2$ (11.25 g, 31.5 mmol, 1.05 equiv) and THF (50 mL). The $PhNTf_2$ solution was transferred via cannula into the enolate solution over the course of 30 minutes. The resulting mixture was allowed to warm to 21 °C and was allowed to react until complete consumption of the starting material was observed by TLC (*ca*. 12 hours). The reaction was quenched with sat. NH_4Cl (100 mL). The reaction mixture was extracted with Et_2O (3 x 200 mL) then the combined organic extracts were washed with aqueous 1 M NaOH (4 x 100 mL), brine (1 x 100 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by filtration through silica gel (eluting with hexanes) afforded alkenyl triflate **S34** (6.20 g, 21.9 mmol, 73% yield) as a clear colorless oil. ^1H NMR data matches a report by Fallis.[17]

Preparation of alkenyl iodide S35:

A 100 mL flask in a glovebox was charged with alkenyl triflate **S34** (1.00 g, 3.52 mmol, 1.0 equiv), LiCl (447 mg, 10.55 mmol, 3.0 equiv), and $Pd(PPh_3)_4$ (163 mg, 0.141 mmol, 0.04 equiv). THF (35 mL) was added, and once the contents dissolved Me_6Sn_2 (1.15 g, 3.52 mmol, 1.0 equiv) was added. The flask was sealed with a reflux condenser containing a septum, brought out of the glovebox, and was heated to reflux (bath temperature set to 70 °C) with vigorous stirring for 3 h. The reaction mixture was cooled to 21 °C then was diluted with hexanes (75 mL) and H_2O (25 mL). The reaction mixture was extracted with hexanes (3 x 75 mL). The combined organic extracts were washed with H_2O (25 mL), 10% NH_4OH (25 mL), H_2O (25 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure.

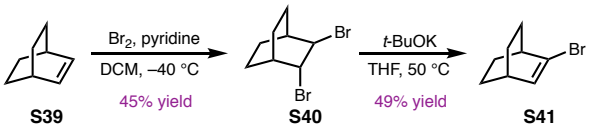
A 100 mL oven dried N_2 flushed flask was charged with the crude alkenyl stannane, CH_2Cl_2 (25 mL), then the solution was cooled to 0 °C. To the stannane was cannulated a solution of I_2 (0.938 g, 3.70 mmol, 1.05 equiv) in CH_2Cl_2 (10 mL). After stirring for 30 min at 0 °C the reaction was quenched with sat. $Na_2S_2O_3$ (50 mL) and was diluted with H_2O (25 mL) and CH_2Cl_2 (25 mL). The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 75 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude residue via filtration through silica gel (eluting with

hexanes) provided alkenyl iodide **S35** (800 mg, 3.06 mmol, 87% yield) as a clear oil. **Note**: alkenyl iodide **S35** is slightly volatile, and it should not be left under vacuum for extended periods of time. ^{1}H NMR data matched a report by Kollàr.[18]

Preparation of S39:

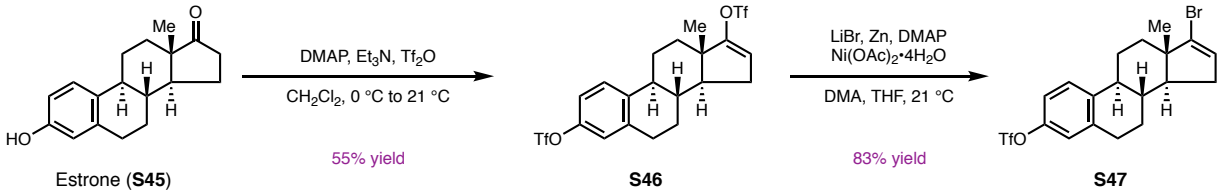
S39 was prepared according to a procedure reported by Paquette,[19] ^{1}H NMR characterization data matched their report.

Preparation of S41:



S41 was prepared from **S39** according to a procedure reported by Takeuchi,[20] ^{1}H NMR characterization data matched their report.

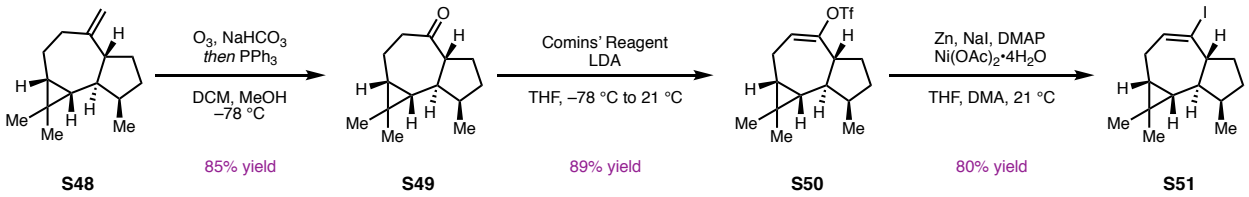
Preparation of S47:



Alkenyl triflate **S46** was prepared according to a procedure reported by Wang,[21] and ^{1}H NMR characterization data matched their report.

Alkenyl bromide **S47** was prepared according to a procedure reported by Reisman,[16] and ^{1}H NMR characterization data matched their report.

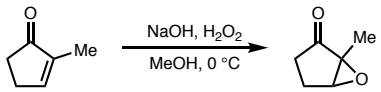
Preparation of S56:



Ketone **S49** was prepared according to a procedure reported by Barker,[22] and ^{1}H NMR characterization data matched their report.

Alkenyl triflate **S50** and alkenyl iodide **S51** was prepared according to a procedure reported by Reisman,[16] and ^{1}H NMR characterization data matched their report.

Preparation of 4a:



Epoxide **4a** was prepared according to a literature procedure by Berthold.[23]

^{1}H NMR (400 MHz, Chloroform-*d*): δ 3.77 (dt, *J* = 1.7, 0.8 Hz, 1H), 2.35 (dddd, *J* = 17.1, 9.0, 7.4, 0.9 Hz, 1H), 2.32 – 2.22 (m, 1H), 2.16 – 2.04 (m, 1H), 2.03 – 1.94 (m, 1H), 1.44 (s, 3H).

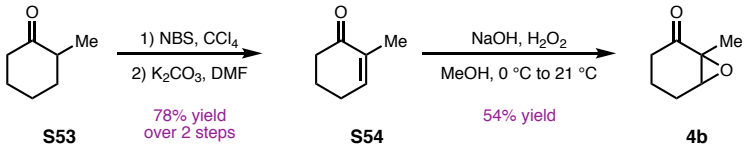
^{13}C NMR (101 MHz, $CDCl_3$): δ 211.0, 64.2, 61.1, 31.3, 22.4, 10.1.

FTIR (NaCl, thin film): 2973, 2936, 1746, 1446, 1072, 844 cm^{-1}.

HRMS: (FI-TOF) calc'd for $C_6H_8O_2$ $[M]^+$ 112.0519, found 112.0519.

TLC (20% EtOAc:80% Hexanes), R_f: 0.33 ($KMnO_4$ stain).

Preparation of 4b:



Enone **S54** was prepared according to a literature report by Maddaluno,[24] and ^{1}H NMR characterization data matched their report.

Epoxide **4b** was prepared according to a literature report by Berthold,[23] and ^{1}H NMR characterization data matched their report.

Preparative procedures for 1,2-additions followed by TMS trapping:

General Procedure A (Regular Addition)

A 50 mL round bottom flask was charged with epoxyketone **1** (0.30 mmol) and was dried via azeotropic removal of trace water by concentration under reduced pressure from anhydrous toluene (3 x 5 mL at 45 °C water bath temperature, 30 mbar pressure), followed by drying under vacuum on a Schlenk line (0.3 mbar) for 30 minutes. An oven dried 10 mL flask under N_2, sealed with a rubber septum, was charged with the alkenyl or aryl halide (0.36 mmol, 1.2 equiv) via syringe followed by THF (0.12 M). The alkenyl or aryl halide solution was cooled to –78 °C followed by a rapid addition of *t*-BuLi (1.7 M in pentane, 2.4–2.7 equiv) and was stirred for 20 minutes at this temperature. Epoxyketone **1** was dissolved in THF (0.05 M) and was cooled to –94 °C in an acetone/liq. N_2 bath. The alkenyl or aryl lithium solution was added via cannula to the epoxyketone solution over the course of 5 minutes then the solution was stirred at –94 °C for 20 minutes. The reaction was warmed to –78 °C on an acetone/CO_2 bath for 5 minutes, then TMSCl (2.4 equiv) was added. The cooling bath was removed, and the reaction was warmed to 21 °C. Upon reaching 21 °C the flask was stirred for an additional 10 minutes then the reaction was concentrated under reduced pressure and purified immediately by SiO_2 column chromatography.

General Procedure B (Inverse Addition)

A 25 mL round bottom flask was charged with epoxyketone **1** (0.30 mmol) and was dried via azeotropic removal of trace water by concentration under reduced pressure from anhydrous toluene (3 x 5 mL at 45 °C water bath temperature, 30 mbar pressure) followed by drying on a Schlenk line (0.3 mbar) for 30 minutes. An oven dried 10 mL flask under N_2, sealed with a rubber septum, was charged with the alkenyl or aryl halide (0.36 mmol, 1.2 equiv) via syringe followed by THF (0.12 M). The alkenyl or aryl halide solution was cooled to –78 °C followed by a rapid addition of *t*-BuLi (1.7 M in pentane, 2.4–2.7 equiv) and was stirred for 20 minutes at this temperature. The alkenyl or aryl lithium solution was cooled to –94 °C in an acetone/liq. N_2 bath. Epoxyketone **1** was dissolved in THF (6 mL, 0.05 M) and was cannulated into the alkenyl or aryl lithium solution over the course of 5 minutes. The flask was rinsed with THF (2 x 1 mL) then the solution was stirred at this temperature for 20 minutes. The reaction was warmed to –78 °C on an

acetone/CO_2 bath for 5 minutes, then TMSCl (2.4 equiv) was added. The cooling bath was removed, and the reaction was warmed to 21 °C. Upon reaching 21 °C the flask was stirred for an additional 10 minutes then the reaction was concentrated under reduced pressure and purified immediately by SiO_2 column chromatography.

Procedure C (LDA Lithiation of furan)

A 25 mL round bottom flask was charged with epoxyketone **1** (0.30 mmol) and was dried via azeotropic removal of trace water by concentration under reduced pressure from anhydrous toluene (3 x 5 mL at 45 °C water bath temperature, 30 mbar pressure) followed by drying on a Schlenk line (0.3 mbar) for 30 minutes. A 50 mL flask under N_2 was charged with *i*-Pr_2NH (1.25 equiv) and THF (0.13 M). The solution was cooled to –78 °C, followed by the addition of *n*-BuLi (1.25 equiv). The solution was stirred at –78 °C for 30 minutes. A 25 mL oven dried N_2 flushed round bottom flask was charged with 3-bromofuran (**S44**) (1.2 equiv) and THF (0.21 M). The bromofuran solution was cannulated into the LDA solution over the course of 5 minutes. The flask containing the bromofuran solution was rinsed into the reaction flask with THF (2 x 1 mL) to ensure quantitative reagent transfer. The resulting solution was stirred at –78 °C for 30 minutes followed by cooling the solution to –94 °C. Epoxyketone **1** was dissolved in THF (0.075 M) and was cannulated into the furan solution over the course of 5 minutes. The flask containing the epoxy ketone solution was rinsed into the reaction flask with THF (2 x 1 mL) to ensure quantitative reagent transfer. Once the addition was complete, the reaction was stirred at –94 °C for 20 minutes followed by warming the reaction to –78 °C with an acetone/CO_2 bath. The reaction was stirred at –78 °C for 5 minutes, followed by adding TMSCl (2.4 equiv). The reaction was allowed to warm to 21 °C and was stirred for 15 minutes. The reaction was concentrated under reduced pressure and was purified immediately by SiO_2 chromatography.

Procedure D (Grignard Addition)

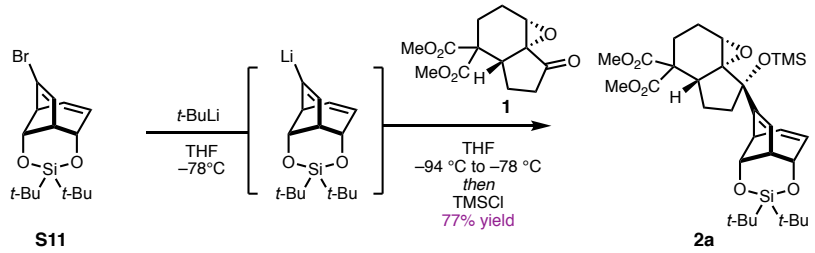
A 50 mL round bottom flask was charged with epoxyketone **1** (0.30 mmol) and was dried via azeotropic removal of trace water by concentration under reduced pressure from anhydrous toluene (3 x 5 mL at 45 °C water bath temperature, 30 mbar pressure) followed by drying on a Schlenk line (0.3 mbar) for 30 minutes. The epoxyketone was dissolved in THF (0.075 M) and was cooled to –94 °C. To the epoxyketone solution was added a solution of the Grignard reagent

(1.2 equiv) dropwise over the course of 5 minutes. The reaction was stirred at –94 °C for 20 minutes then –78 °C for 5 minutes. The reaction was quenched with sat. NH_4Cl at –78 °C. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The reaction was purified immediately by SiO_2 chromatography.

Notes

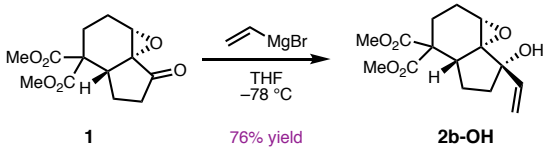
1. It is extremely important for this reaction to be rigorously dry. Trace water significantly diminishes the yield.
2. Before use, the alkenyl halides were dried by eluting them through a SiO_2 plug with pentane followed by concentration under reduced pressure. The purity of the alkenyl halides was quantified using qNMR (pyrazine internal standard).
3. It is important to run an SiO_2 column immediately following the concentration of the reaction because the product is unstable in the crude reaction mixture.
4. Scales larger than 0.30 mmol were quenched with sat. $NaHCO_3$, and an aqueous workup was performed. Specific details can be found in their respective procedures.

Preparation of 1,2-addition product 2a:



Prepared from **1** (2.13 g, 7.93 mmol, 1.3 equiv), and alkenyl bromide **S11** (2.18 g, 6.10 mmol, 1.0 equiv) according to method reported by Reisman, and [1]H NMR characterization data matched their report.[2]

Preparation of 1,2-addition product 2b-OH:



Prepared via General Procedure D, 76% yield.

Prepared from **1** (81.2 mg, 0.30 mmol, 1.0 equiv), and vinylmagnesium bromide (1.0 M in THF, 0.36 mL, 0.36 mmol, 1.2 equiv) according to method **D**. The crude reaction was purified by column chromatography (silica, 40% EtOAc:60% Hexanes) to yield **2b-OH** (68.6 mg, 76% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.89 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.34 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.13 (dd, *J* = 10.7, 1.4 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.29 (d, *J* = 4.0 Hz, 1H), 2.75 (dd, *J* = 10.8, 7.4 Hz, 1H), 2.52 (s, 1H), 2.51 – 2.43 (m, 1H), 2.40 – 2.27 (m, 2H), 2.09 – 1.90 (m, 4H), 1.59 – 1.50 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.0, 170.4, 140.2, 113.7, 75.8, 72.1, 56.4, 55.2, 53.1, 52.3, 44.0, 38.5, 29.5, 23.6, 21.7.

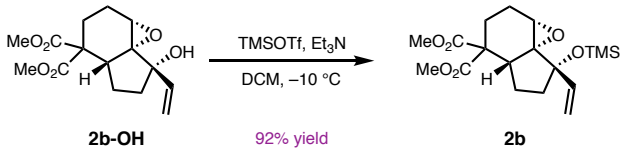
FTIR (NaCl, thin film): 3508, 3092, 2998, 2953, 1731, 1433, 1243, 1213, 1060 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{15}H_{21}O_6$ $[M+H]^+$, 297.1333 found 297.1327.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +21.4° (*c* = 0.50, $CHCl_3$).

TLC (40% EtOAc:60% Hexanes), R*f*: 0.39, (dark blue in *p*-anisaldehyde stain).

Preparation of silyl ether 2b:



2b-OH 92% yield **2b**

A 25 mL oven dried N_2 flushed round bottom flask was charged with alcohol **2b-OH** (68.6 mg, 0.23 mmol, 1.0 equiv) and CH_2Cl_2 (6 mL, 0.04 M). The solution was cooled to –10 °C then triethylamine (120 µL, 0.87 mmol, 3.8 equiv) was added followed by TMSOTf (50 µL, 0.28 mmol, 1.2 equiv). The reaction was stirred for 15 minutes at –10 °C followed by a quench with sat. $NaHCO_3$. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, 15% EtOAc:85% Hexanes) to yield the product **2b** (78.2 mg, 92% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.93 (ddd, *J* = 17.2, 10.6, 0.7 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.13 (dd, *J* = 10.6, 1.2 Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 3.20 (d, *J* = 3.7 Hz, 1H),

2.74 (t, J = 9.4 Hz, 1H), 2.59 (dddd, J = 12.8, 10.7, 9.5, 5.1 Hz, 1H), 2.43 – 2.24 (m, 2H), 2.16 – 1.98 (m, 2H), 1.97 – 1.82 (m, 2H), 1.53 – 1.44 (m, 1H), 0.08 (s, 8H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.3, 170.6, 141.9, 113.7, 78.9, 71.0, 55.2, 53.7, 52.9, 52.2, 42.3, 35.7, 29.9, 22.5, 21.5, 2.4.

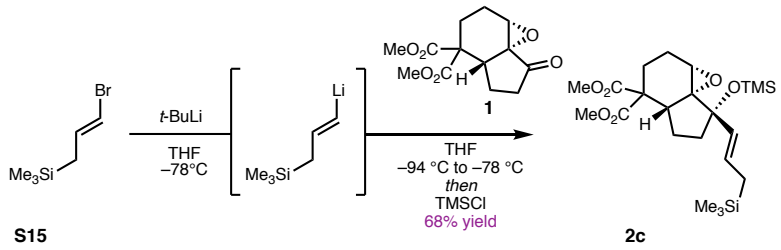
FTIR (NaCl, thin film): 3084, 2952, 1734, 1639, 1451, 1434, 1249, 1059, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{18}H_{28}O_6SiNa$ $[M+Na]^+$, 391.1547 found 391.1547.

$[\alpha]_D^{25}$ = +17.5° (c = 1.00, $CHCl_3$).

TLC (15% EtOAc:85% Hexanes), R_f: 0.33, (turquoise in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2c:



Prepared via General Procedure B, 68% yield.

Prepared from **1** (80.9, 0.30 mmol, 1.0 equiv), **S15** (77.2 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.45 mL, 0.74 mmol, 2.4 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4 equiv) according to method **B**. The reaction was directly subjected to column chromatography (silica, 10% Acetone:90% Hexanes) to yield **2c** (92.6 mg, 68% yield) as a white crystalline solid.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.67 (dt, J = 15.5, 8.2 Hz, 1H), 5.36 (dq, J = 15.5, 1.2 Hz, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.22 (dd, J = 3.6, 0.8 Hz, 1H), 2.78 (dd, J = 9.8, 9.0 Hz, 1H), 2.59 (dddd, J = 13.0, 11.2, 9.0, 4.0 Hz, 1H), 2.38 – 2.24 (m, 2H), 2.08 (ddd, J = 12.8, 8.8, 4.0 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.95 – 1.87 (m, 1H), 1.81 (dddd, J = 13.0, 9.9, 8.8, 7.4 Hz, 1H), 1.51 (dd, J = 8.2, 1.3 Hz, 2H), 1.49 – 1.41 (m, 1H), 0.06 (s, 9H), 0.03 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 170.6, 132.0, 127.0, 78.3, 71.3, 55.2, 53.6, 52.8, 52.2, 41.8, 35.6, 30.2, 23.0, 22.0, 21.6, 2.4, –1.7.

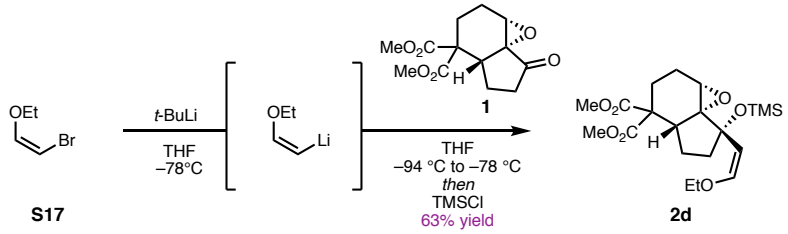
FTIR (NaCl, thin film): 2993, 2952, 2898, 1734, 1654, 1450, 1434, 1248, 888, 857, 841 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{22}H_{38}O_6Si_2Na$ $[M+Na]^+$, 477.2099 found 477.2098.

$[\alpha]_D^{25}$ = +36.7° (c = 1.00, $CHCl_3$).

TLC (10% Acetone:90% Hexanes), R*f*: 0.30, (blue in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2d:



Prepared via General Procedure B, 63% yield.

Prepared from **1** (81.0 mg, 0.30 mmol, 1.0 equiv), **S17** (54.4 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.48 mL, 0.82 mmol, 2.7 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4 equiv) according to method **B**. The reaction was directly subjected to column chromatography (silica, 20% EtOAc:80% Hexanes) to yield **2d** (79.0 mg, 63% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.90 (d, *J* = 7.1 Hz, 1H), 4.34 (dd, *J* = 7.1, 0.6 Hz, 1H), 3.82 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.68 (s, 3H), 3.33 (d, *J* = 3.6 Hz, 1H), 2.88 (dd, *J* = 9.9, 8.6 Hz, 1H), 2.49 (dddd, *J* = 12.6, 10.4, 8.5, 3.8 Hz, 1H), 2.34 – 2.25 (m, 2H), 2.12 (ddd, *J* = 12.1, 8.3, 3.8 Hz, 1H), 2.01 – 1.96 (m, 1H), 1.95 – 1.87 (m, 1H), 1.86 – 1.80 (m, 1H), 1.57 – 1.49 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.08 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.5, 170.7, 146.0, 109.6, 76.7, 70.9, 68.6, 55.3, 55.2, 52.6, 51.9, 42.1, 38.5, 29.8, 21.6, 21.5, 15.4, 2.3.

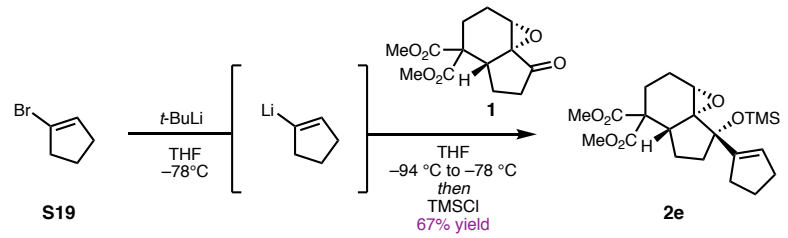
FTIR (NaCl, thin film): 2952, 1733, 1659, 1433, 1248, 1101, 841 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{20}H_{33}O_7Si$ $[M+H]^+$ 413.1990, found 413.2000.

$[\alpha]_D^{25}$ = +57.5° (*c* = 1.00, $CHCl_3$).

TLC (20% EtOAc:80% Hexanes), R*f*: 0.30, (pink in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2e:



Prepared via General Procedure A, 67% yield.

Prepared from **1** (81.3 mg, 0.30 mmol, 1.0 equiv), *t*-BuLi (1.7 M in pentane, 0.44 mL, 0.74 mmol, 2.5 equiv), TMSCl (90 µL, 0.63 mmol, 2.4 equiv), and **S19** (51.9 mg, 0.36 mmol, 1.2 equiv) according to method **A**. The reaction was directly subjected to column chromatography (silica, 10% EtOAc:90% Hexanes) to yield **2e** (82.8 mg, 67% yield) as a white crystalline solid.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.67 (p, *J* = 2.0 Hz, 1H), 3.74 (s, 3H), 3.68 (s, 3H), 3.28 (dd, *J* = 3.6, 0.8 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.43 – 2.18 (m, 7H), 2.04 – 1.79 (m, 5H), 1.54 – 1.44 (m, 1H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.3, 170.4, 146.1, 126.4, 77.5, 70.3, 55.0, 54.3, 52.7, 52.0, 41.7, 35.3, 32.4, 31.3, 29.8, 23.2, 22.0, 21.2, 1.9.

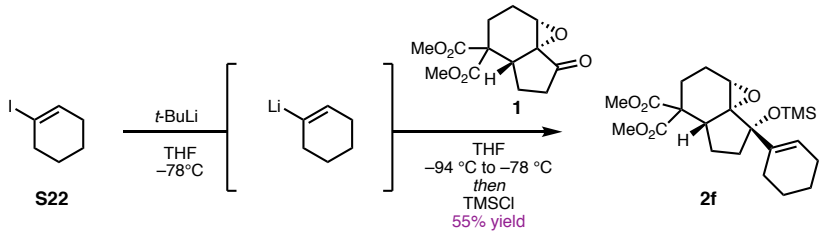
FTIR (NaCl, thin film): 2952, 2847, 1733, 1449, 1433, 1248, 840 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{21}H_{33}O_6Si$ $[M+H]^+$ 409.2041, found 409.2059.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +32.7° (*c* = 1.00, $CHCl_3$).

TLC (10% EtOAc:90% Hexanes), R*f*: 0.12, (navy blue in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2f:



Prepared via General Procedure A, 55% yield.

Prepared from **1** (80.5 mg, 0.30 mmol, 1.0 equiv), **S22** (77.3 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.47 mL, 0.80 mmol, 2.7 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4 equiv) according to method **A**. The reaction was directly subjected to column chromatography (silica, 10% EtOAc:90% Hexanes) to yield **2f** (70.1 mg, 55% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.76 – 5.73 (m, 1H), 3.74 (s, 3H), 3.68 (s, 3H), 3.31 (d, *J* = 3.8 Hz, 1H), 2.63 (dd, *J* = 9.7, 8.2 Hz, 1H), 2.55 (dddd, *J* = 12.7, 10.5, 8.2, 3.2 Hz, 1H), 2.37 – 2.27 (m, 2H), 2.21 (ddd, *J* = 12.7, 8.2, 3.2 Hz, 1H), 2.16 – 2.00 (m, 3H), 1.98 – 1.85 (m, 3H), 1.82 – 1.75 (m, 1H), 1.75 – 1.68 (m, 1H), 1.67 – 1.60 (m, 1H), 1.59 – 1.45 (m, 3H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.3, 170.5, 138.1, 122.5, 80.5, 70.3, 55.1, 55.0, 52.7, 52.0, 41.7, 34.1, 29.8, 25.3, 24.0, 22.8, 22.2, 21.9, 21.2, 2.0.

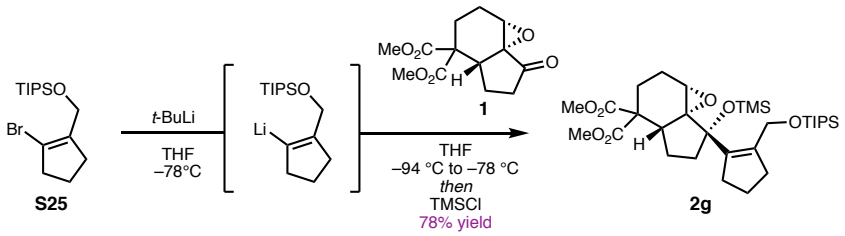
FTIR (NaCl, thin film): 2950, 2859, 1733, 1449, 1434, 1248, 841 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{22}H_{35}O_6Si$ $[M+H]^+$ 423.2197, found 423.2189.

$[\alpha]_D^{25}$ = +11.1° (*c* = 1.00, $CHCl_3$).

TLC (10% EtOAc:90% Hexanes), R_f: 0.40, (navy blue in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2g:



Prepared via General Procedure A, 78% yield.

Prepared from **1** (80.5 mg, 0.30 mmol, 1.0 equiv), **S25** (141.0 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.48 mL, 0.82 mmol, 2.7 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4 equiv) according to Method **A**. The reaction was directly subjected to column chromatography (silica, 10% EtOAc:90% Hexanes) to yield **2g** (140.1 mg, 78% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.58 (dt, *J* = 13.4, 1.6 Hz, 1H), 4.47 (dt, *J* = 13.9, 2.0 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.27 (d, *J* = 3.7 Hz, 1H), 2.67 (dd, *J* = 10.4, 8.5 Hz, 1H), 2.58 – 2.46 (m, 4H), 2.46 – 2.40 (m, 1H), 2.39 – 2.33 (m, 1H), 2.32 – 2.26 (m, 1H), 2.18 (ddd, *J* = 13.2, 8.2, 6.6 Hz, 1H), 2.03 (ddd, *J* = 13.3, 10.0, 5.4 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.77 (p, *J* = 7.5 Hz, 2H), 1.50 (ddd, *J* = 13.3, 10.3, 8.4 Hz, 1H), 1.10 – 1.05 (m, 21H), 0.07 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.2, 170.4, 140.3, 137.6, 79.3, 71.2, 61.3, 55.2, 55.1, 52.8, 52.1, 43.7, 38.0, 35.5, 35.1, 29.6, 23.1, 21.8, 21.4, 18.1, 12.0, 2.2.

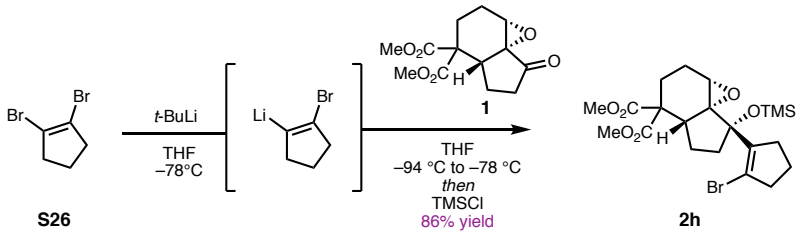
FTIR (NaCl, thin film): 2949, 2866, 1738, 1463, 1434, 1248, 1219, 881, 841 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{58}O_7Si_2N$ $[M+NH_4]^+$ 612.3746, found 612.3751.

$[\alpha]_D^{25}$ = +17.8° (*c* = 1.00, $CHCl_3$).

TLC (10% EtOAc:90% Hexanes), R_f: 0.30, (navy blue in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2h:



Prepared via General Procedure A, 86% yield.

Prepared from **1** (80.1 mg, 0.30 mmol, 1.0 equiv), **S26** (81.3 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.44 mL, 0.74 mmol, 2.5 equiv), and TMSCl (90 µL, 0.63 mmol, 2.4 equiv) according to method **A**. The reaction was directly subjected to column chromatography (silica, 20% EtOAc:80% Hexanes) to yield **2h** (125.5 mg, 86% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 3.75 (s, 3H), 3.69 (s, 3H), 3.42 (d, *J* = 3.6 Hz, 1H), 2.82 (t, *J* = 9.1 Hz, 1H), 2.78 – 2.62 (m, 2H), 2.55 – 2.39 (m, 4H), 2.36 – 2.26 (m, 2H), 2.04 – 1.96 (m, 2H), 1.94 – 1.83 (m, 3H), 1.62 – 1.54 (m, 1H), 0.08 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.2, 170.5, 141.1, 115.3, 78.9, 70.1, 56.5, 55.2, 52.8, 52.0, 43.3, 42.9, 36.8, 34.3, 29.4, 22.4, 21.5, 21.3, 2.0.

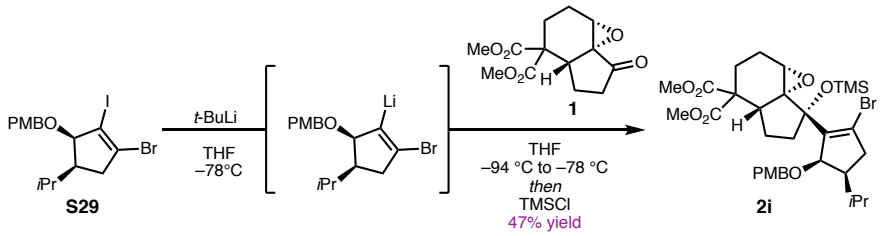
FTIR (NaCl, thin film): 2952, 2851, 1733, 1448, 1433, 1248, 840 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{21}H_{32}O_6SiBr$ $[M+H]^+$ 487.1146, found 487.1145.

$[\alpha]_D^{25}$ = +52.6° (*c* = 1.00, $CHCl_3$).

TLC (15% EtOAc:85% Hexanes), R*f*: 0.17, (dark blue in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2i:



Prepared via General Procedure B, 47% yield.

Prepared from **1** (81.1 mg, 0.30 mmol, 1.0 equiv), **S29** (164.0 mg, 0.36 mmol, 1.2 equiv), *n*-BuLi (2.6 M in hexanes, 0.45 mL, 0.38 mmol, 1.3 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4

equiv) according to method **B**. The reaction was directly subjected to column chromatography (silica, 15% EtOAc:85% Hexanes) to yield **2i** (95.1 mg, 47% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.27 – 7.22 (m, 2H), 6.89 – 6.84 (m, 2H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.51 (dd, *J* = 5.5, 1.0 Hz, 1H), 4.45 (d, *J* = 10.4 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.24 (d, *J* = 3.3 Hz, 1H), 3.15 (dd, *J* = 12.7, 5.4 Hz, 1H), 2.73 (ddd, *J* = 16.0, 9.3, 1.1 Hz, 1H), 2.55 (dd, *J* = 15.9, 7.3 Hz, 1H), 2.43 – 2.19 (m, 4H), 2.11 – 1.92 (m, 4H), 1.77 – 1.60 (m, 2H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.12 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.3, 170.8, 159.2, 146.7, 131.3, 129.3, 121.2, 113.9, 84.5, 81.1, 72.7, 71.1, 58.6, 55.4, 52.9, 52.3, 51.2, 46.6, 46.1, 43.8, 28.6, 26.9, 25.3, 22.1, 22.0, 21.3, 2.9.

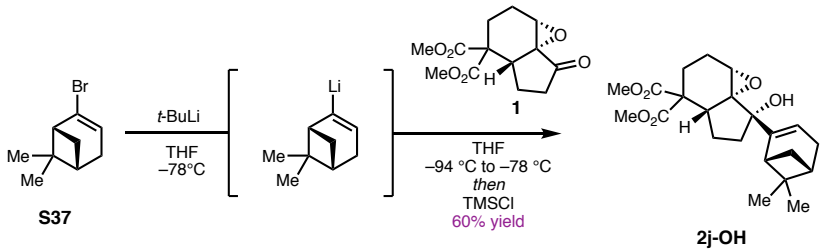
FTIR (NaCl, thin film): 2954, 2867, 1732, 1614, 1514, 1248, 835, 758, 752 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{32}H_{49}O_8SiBrN$ $[M+NH_4]^+$, 682.2405 found 682.2385.

$[\alpha]_D^{25}$ = +63.9° (*c* = 1.00, $CHCl_3$).

TLC (15% EtOAc:85% Hexanes), R_f: 0.32, (forest green in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2j-OH:



Prepared via General Procedure A, 60% yield.

Prepared from **1** (80.5 mg, 0.30 mmol, 1.0 equiv), **S37** (79.7 mg, 0.40 mmol, 1.3 equiv), *t*-BuLi (1.7 M in pentane, 0.44 mL, 0.72 mmol, 2.4 equiv) according to method **A**. The reaction was quenched with sat. NH_4Cl and was allowed to warm to 21 °C. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, 30% EtOAc:70% Hexanes) to yield **2j-OH** (70.0 mg, 60% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.51 (tt, *J* = 3.1, 1.5 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.38 (d, *J* = 3.8 Hz, 1H), 2.78 (dd, *J* = 10.5, 8.1 Hz, 1H), 2.51 – 2.30 (m, 7H), 2.26 (dt, *J* = 17.8,

2.8 Hz, 1H), 2.11 (ttd, *J* = 5.6, 2.7, 1.2 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.90 (dtd, *J* = 12.4, 7.9, 4.8 Hz, 1H), 1.82 (ddd, *J* = 13.4, 9.4, 4.8 Hz, 1H), 1.64 – 1.51 (m, 1H), 1.30 (s, 3H), 1.14 (d, *J* = 8.6 Hz, 1H), 0.85 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.1, 170.5, 148.7, 117.3, 77.2, 71.1, 56.8, 55.3, 53.0, 52.2, 44.8, 42.9, 40.9, 37.8, 37.3, 31.9, 31.4, 29.6, 26.4, 23.2, 21.6, 21.6.

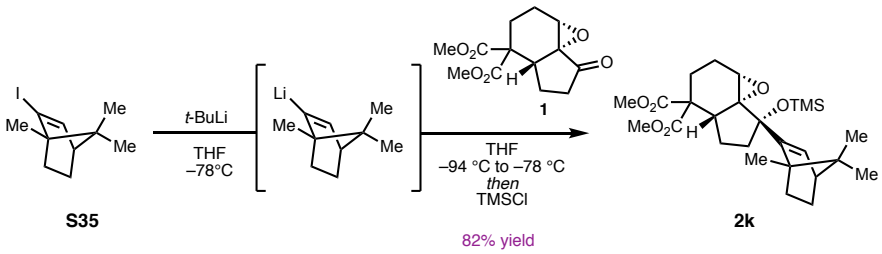
FTIR (NaCl, thin film): 3504, 2949, 2917, 1734, 1458, 1450, 1432, 1239, 1220, 1174 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{22}H_{31}O_6$ $[M+H]^+$, 391.2115 found 391.2113.

$[\alpha]_D^{25}$ = +29.4° (*c* = 1.00, $CHCl_3$).

TLC (30% EtOAc:70% Hexanes), R_f: 0.37, (purple in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2k:



Prepared via General Procedure B, 82% yield.

Prepared from **1** (81.1 mg, 0.30 mmol, 1.0 equiv), **S35** (94.6 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.45 mL, 0.74 mmol, 2.5 equiv), and TMSCl (90 μL, 0.63 mmol, 2.4 equiv) according to method **B**. The crude reaction mixture was purified by column chromatography (silica, 10% EtOAc:90% Hexanes) to yield **2k** (118.7 mg, 82% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.71 (d, *J* = 3.4 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.34 (d, *J* = 3.6 Hz, 1H), 2.78 (t, *J* = 9.3 Hz, 1H), 2.52 (dddd, *J* = 12.8, 10.8, 9.0, 4.6 Hz, 1H), 2.41 – 2.28 (m, 2H), 2.25 (t, *J* = 3.5 Hz, 1H), 2.19 (ddd, *J* = 13.0, 8.6, 4.6 Hz, 1H), 2.05 – 1.94 (m, 2H), 1.87 – 1.79 (m, 2H), 1.56 – 1.44 (m, 2H), 1.23 (ddd, *J* = 12.2, 9.2, 3.6 Hz, 1H), 1.10 (s, 3H), 1.01 (ddd, *J* = 11.6, 9.2, 3.7 Hz, 1H), 0.77 (s, 3H), 0.74 (s, 3H), 0.06 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.2, 170.6, 150.0, 128.7, 79.3, 70.1, 57.1, 55.3, 55.2, 55.0, 52.7, 51.9, 51.2, 42.4, 36.1, 32.9, 29.8, 25.4, 22.7, 21.2, 19.7, 19.5, 13.5, 2.4.

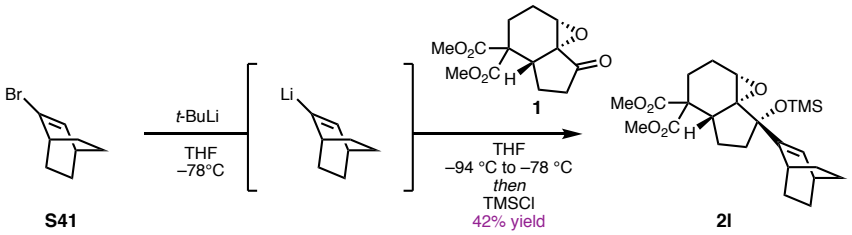
FTIR (NaCl, thin film): 2952, 2873, 1734, 1450, 1434, 1247, 839, 887 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{26}H_{41}O_6Si$ $[M+H]^+$ 477.2667, found 477.2673.

$[\alpha]_D^{25}$ = –11.8° (*c* = 1.00, $CHCl_3$).

TLC (10% EtOAc:90% Hexanes), R*f*: 0.29, (navy blue in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2l:



Prepared via General Procedure A, 42% yield.

Prepared from **1** (80.8, 0.30 mmol, 1.0 equiv), **S41** (67.6 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.45 mL, 0.74 mmol, 2.4 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4 equiv) according to method **A**. The reaction was directly subjected to column chromatography (silica, 15% EtOAc:85% Hexanes) to yield **2l** (56.5 mg, 42% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.14 (dd, *J* = 6.8, 1.7 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.36 (d, *J* = 3.6 Hz, 1H), 2.70 (br s, 1H), 2.67 (t, *J* = 9.4 Hz, 1H), 2.64 – 2.53 (m, 2H), 2.39 – 2.26 (m, 2H), 2.23 (ddd, *J* = 12.6, 8.6, 3.9 Hz, 1H), 2.01 (ddd, *J* = 12.7, 10.9, 7.4 Hz, 1H), 1.95 – 1.80 (m, 2H), 1.62 – 1.49 (m, 4H), 1.48 – 1.39 (m, 1H), 1.32 – 1.22 (m, 3H), 1.10 (ddt, *J* = 14.4, 8.8, 3.1 Hz, 1H), 0.06 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 170.7, 147.5, 127.2, 79.6, 70.4, 55.2, 54.6, 52.9, 52.1, 42.3, 34.3, 30.6, 30.3, 30.0, 26.9, 26.4, 26.4, 26.1, 22.5, 21.5, 2.3.

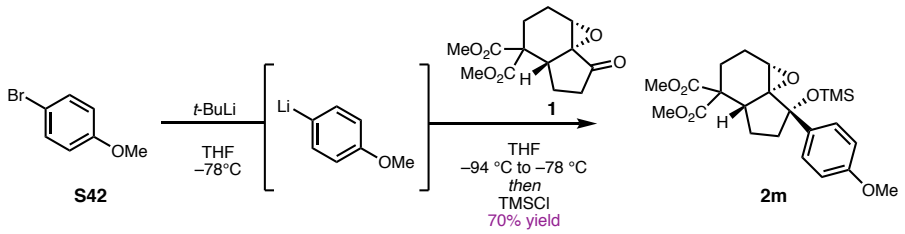
FTIR (NaCl, thin film): 2945, 2862, 1734, 1450, 1433, 1247, 841 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{24}H_{36}O_6SiK$ $[M+K]^+$, 487.1913 found 487.1921.

$[\alpha]_D^{25}$ = +16.8° (*c* = 1.00, $CHCl_3$).

TLC (15% EtOAc:85% Hexanes), R*f*: 0.54, (purple in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2m:



Prepared via General Procedure A, 70% yield.

Prepared from **1** (81.2 mg, 0.30 mmol, 1.0 equiv), **2m** (67.3 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.48 mL, 0.82 mmol, 2.7 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4 equiv) according to method **A**. The reaction was directly subjected to column chromatography (silica, 20% EtOAc:80% Hexanes) to yield **2m** (95.6 mg, 70% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.35 – 7.31 (m, 2H), 6.88 – 6.85 (m, 2H), 3.82 (s, 3H), 3.77 (s, 3H), 3.65 (s, 3H), 3.47 (d, *J* = 4.1 Hz, 1H), 2.73 (dddd, *J* = 13.1, 11.0, 8.7, 3.6 Hz, 1H), 2.55 (dd, *J* = 9.9, 8.8 Hz, 1H), 2.46 (ddd, *J* = 13.0, 8.4, 3.7 Hz, 1H), 2.33 (dddd, *J* = 15.4, 10.2, 8.1, 0.7 Hz, 1H), 2.27 – 2.17 (m, 2H), 1.98 – 1.87 (m, 2H), 1.35 (ddd, *J* = 13.3, 10.3, 8.5 Hz, 1H), –0.08 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.1, 170.4, 158.9, 136.7, 127.2, 113.6, 79.4, 72.2, 55.2, 55.0, 54.8, 52.7, 52.1, 41.7, 36.4, 29.6, 22.2, 21.3, 1.9.

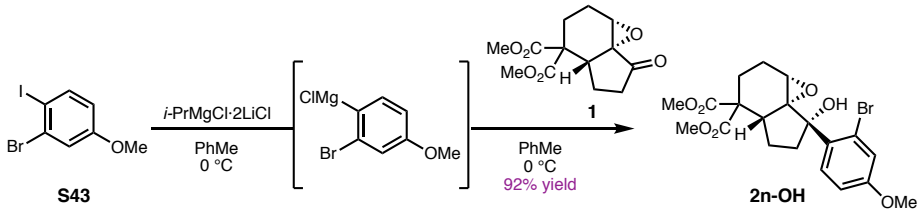
FTIR (NaCl, thin film): 2998, 2952, 2838, 1732, 1609, 1511, 1250, 887, 841 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{33}O_7Si$ $[M+H]^+$ 449.1990, found 449.1998.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +37.5° (*c* = 1.00, $CHCl_3$).

TLC (20% EtOAc:80% Hexanes), R*f*: 0.24, (dark blue in *p*-anisaldehyde stain).

Preparation of epoxy-alcohol 2n-OH:



A 250 mL round bottom flask was charged with aryl iodide **S43** (4.85 g, 15.49 mmol, 1.7 equiv), PhMe (27 mL, 0.54 M), and was cooled to 0 °C. To the solution was added *i*-PrMgCl·2LiCl (1.3 M in THF, 11.9 mL, 15.49 mmol, 1.7 equiv) dropwise via syringe, which was then allowed

to stir at 0 °C for 1 hour. A separate 100 mL flask was charged with epoxyketone **1** (2.54 g, 9.45 mmol, 1 equiv) and PhMe (48 mL, 0.2 M) under N_2 (to get the epoxyketone to dissolve, the PhMe solution was heated slightly in a warm water bath). To the aryl Grignard solution at 0 °C was added the epoxyketone solution dropwise via cannula. The epoxyketone flask was rinsed with PhMe (1 x 20 mL) to ensure quantitative transfer then the reaction was stirred for 30 minutes at 0 °C. **Caution**: the epoxyketone may crash out of solution, gentle heating will re-dissolve the epoxyketone. The reaction was quenched with H_2O (30 mL) and the reaction mixture was allowed to warm to 21 °C. The biphasic mixture was transferred to a 1 L Erlenmeyer flask, and aqueous sat. Rochelle's salt solution (150 mL) and Et_2O were added (150 mL). The biphasic mixture was allowed to vigorously stir for 30 minutes. The mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was extracted with Et_2O (4 x 150 mL). The combined organic extracts were washed with brine (2 x 100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica, 30% Ethyl acetate:70% Hexanes) to yield epoxy alcohol **2n-OH** (3.95 g, 8.70 mmol, 92% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.10 (d, *J* = 2.7 Hz, 1H), 6.83 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.78 (s, 6H), 3.73 (s, 3H), 3.43 (dd, *J* = 12.8, 6.1 Hz, 1H), 3.25 – 3.19 (m, 1H), 3.07 (d, *J* = 1.3 Hz, 1H), 2.67 – 2.52 (m, 1H), 2.42 – 2.30 (m, 2H), 2.25 (dtd, *J* = 15.7, 8.7, 1.2 Hz, 1H), 2.13 – 2.00 (m, 3H), 1.78 (dt, *J* = 13.4, 8.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 170.8, 159.1, 134.1, 129.9, 120.5, 119.7, 112.7, 78.1, 72.8, 61.1, 55.5, 55.2, 52.9, 52.0, 45.7, 40.1, 28.2, 25.7, 21.7.

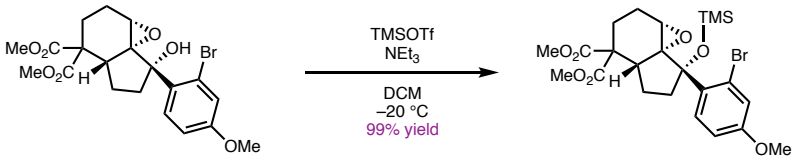
FTIR (NaCl, thin film): 3491, 2995, 2952, 2838, 2255, 1731, 1602, 1487, 1291, 1234, 1031, 917, 731 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{20}H_{25}O_8Br$ $[M+H_2O]^+$ 472.0727, found 472.0750.

$[\alpha]_D^{25}$ = +58.1° (*c* = 1.35, $CHCl_3$).

TLC (30% EtOAc:70% Hexanes), R_f: 0.40 (blue in *p*-anisaldehyde)

Preparation of silyl ether 2n:



2n-OH **2n**

A 500 mL round bottom flask was charged with epoxy alcohol **2n-OH** (3.95 g, 8.67 mmol, 1.0 equiv) and was dried via azeotropic removal of trace water by concentration under reduced pressure from anhydrous toluene (3 x 10 mL at 45 °C water bath temperature) followed by drying under vacuum on a Schlenk line (0.2 torr) for 30 minutes. The epoxy alcohol was dissolved in CH_2Cl_2 (87 mL, 0.1 M) and was cooled to –20 °C on an acetone/dry ice bath. Et_3N (3.63 mL, 26.0 mmol, 3.0 equiv) was added followed by TMSOTf (1.49 mL, 10.4 mmol, 1.2 equiv). The reaction was stirred for 30 minutes then was warmed to 0 °C on an ice bath. An additional portion of TMSOTf was added if needed (0.63 mL, 3.47 mmol, 0.4 equiv) to ensure complete consumption of starting material by TLC. The reaction was quenched with sat. $NaHCO_3$ (150 mL) and was allowed to warm to 21 °C. The biphasic mixture was transferred to a separatory funnel, and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 200 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, 10% to 15% to 20% ethyl acetate in hexanes) to afford silyl ether **2n** (4.52 g, 8.59 mmol, 99% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.30 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 2.7 Hz, 1H), 6.79 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.68 (s, 3H), 3.47 (d, *J* = 3.5 Hz, 1H), 2.93 (dd, *J* = 10.9, 7.7 Hz, 1H), 2.61 – 2.50 (m, 1H), 2.50 – 2.27 (m, 4H), 2.14 – 2.07 (m, 1H), 1.97 – 1.88 (m, 1H), 1.65 – 1.53 (m, 1H), 0.06 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 170.4, 158.8, 135.7, 128.1, 122.7, 121.0, 112.3, 82.1, 70.6, 56.7, 55.5, 55.2, 52.8, 52.1, 43.8, 40.3, 29.2, 24.1, 21.4, 2.4.

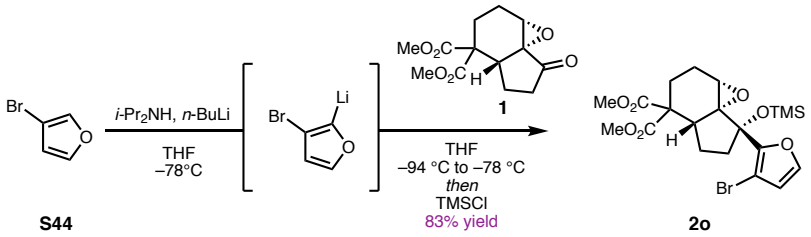
FTIR (NaCl, thin film): 2952, 2389, 1731, 1601, 1488, 1434, 1239, 1032, 883, 842, 734 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{35}O_7BrN$ $[M+NH_4]^+$ 544.1361, found 544.1359.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +34.4° (*c* = 1.30, $CHCl_3$).

TLC (20% EtOAc:80% Hexanes), R*f*: 0.40 (blue in *p*-anisaldehyde)

Preparation of 1,2-addition product 2o:



Prepared via General Procedure C, 83% yield.

Prepared from **1** (81.2 mg, 0.30 mmol, 1.0 equiv), *n*-BuLi (2.6 M in hexanes, 140 µL, 0.36 mmol, 1.3 equiv), *i*-Pr_2NH (60 µL, 0.43 mmol, 1.4 equiv), **S44** (52.9 mg, 0.36 mmol, 1.2 equiv) and TMSCl (90 µL, 0.87 mmol, 2.4 equiv) according to method **C**. The reaction was directly subjected to column chromatography (silica, 15% EtOAc:85% Hexanes) to yield **2o** (122.0 mg, 83% yield) as a pale yellow crystalline solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.34 (d, *J* = 1.9 Hz, 1H), 6.42 (d, *J* = 1.9 Hz, 1H), 3.76 (s, 3H), 3.68 (d, *J* = 3.7 Hz, 1H), 3.66 (s, 3H), 2.79 (ddd, *J* = 12.3, 8.2, 2.4 Hz, 1H), 2.65 (dddd, *J* = 12.4, 10.1, 7.8, 2.4 Hz, 1H), 2.57 (dd, *J* = 10.0, 7.8 Hz, 1H), 2.38 – 2.25 (m, 2H), 2.13 – 2.05 (m, 1H), 2.03 – 1.97 (m, 1H), 1.90 – 1.79 (m, 1H), 1.58 – 1.45 (m, 1H), –0.05 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 170.4, 150.9, 141.6, 116.0, 97.3, 76.6, 70.0, 56.2, 55.1, 52.7, 52.1, 41.4, 35.1, 29.7, 21.3, 21.1, 1.1.

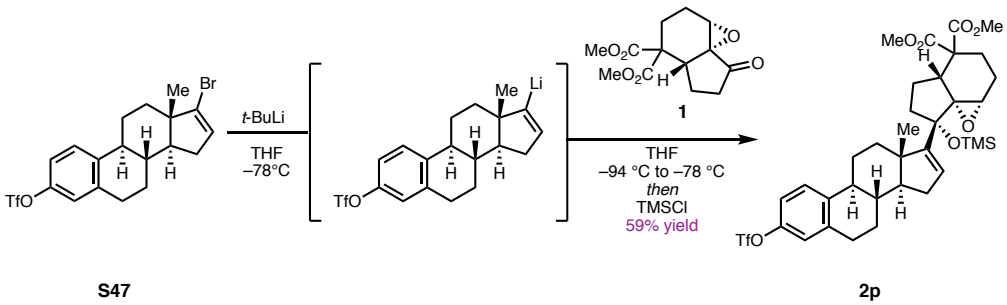
FTIR (NaCl, thin film): 3151, 2993, 2952, 2847, 1733, 1567, 1432, 1250, 873, 843 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{20}H_{28}O_7SiBr$ $[M+H]^+$ 487.0782, found 487.0780.

$[\alpha]_D^{25}$ = +57.4° (*c* = 1.00, $CHCl_3$).

TLC (15% EtOAc:85% Hexanes), R*f*: 0.29, (light brown in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2p:



Prepared via General Procedure B, 59% yield.

Prepared from **1** (80.5 mg, 0.30 mmol, 1.0 equiv), **S47** (187.0 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.46 mL, 0.75 mmol, 2.4 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4 equiv) according to method **B**. The reaction was directly subjected to repeated column chromatography (silica, 10% EtOAc:90% Hexanes) to yield **2p** (131.0 mg, 59% yield) as a white foam.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.31 (d, *J* = 8.5 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.97 (d, *J* = 2.6 Hz, 1H), 5.67 (dd, *J* = 3.3, 1.5 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.36 (d, *J* = 3.8 Hz, 1H), 2.96 – 2.90 (m, 2H), 2.83 (dd, *J* = 10.1, 8.2 Hz, 1H), 2.59 (dddd, *J* = 13.1, 11.2, 8.2, 3.3 Hz, 1H), 2.43 – 2.18 (m, 6H), 2.18 – 2.07 (m, 2H), 2.04 – 1.92 (m, 3H), 1.87 (ddt, *J* = 13.1, 10.2, 8.4 Hz, 1H), 1.67 – 1.38 (m, 6H), 1.00 (s, 3H), 0.10 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 170.8, 158.0, 147.6, 141.4, 139.7, 127.0, 125.8, 121.3, 120.2, 118.2, 117.7, 80.3, 70.9, 57.2, 55.8, 55.5, 52.9, 52.1, 48.0, 44.3, 41.9, 37.5, 36.8, 36.6, 31.1, 30.0, 29.6, 27.3, 26.6, 22.5, 21.3, 17.9, 2.7.

*Note: The peaks at 120.2 ppm, and 118.2 ppm are split due to C-F coupling. ^{1}J=320.8 Hz.

^{19}F NMR (376 MHz, $CDCl_3$): δ 73.0.

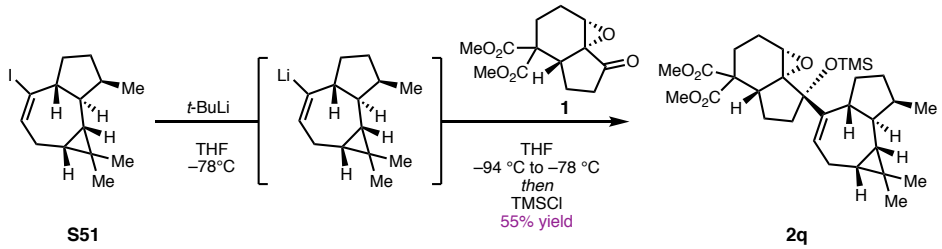
FTIR (NaCl, thin film): 2949, 2850, 1734, 1420, 1249, 1214, 1143, 919, 882, 839, 758 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{35}H_{46}F_3O_9SSi$ $[M+H]^+$, 727.2578 found 727.2582.

$[\alpha]_D^{25}$ = +22.5° (*c* = 1.00, $CHCl_3$).

TLC (10% EtOAc:90% Hexanes), R*f*: 0.46, (turquoise in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 2q:



Prepared via General Procedure B, 55% yield.

Prepared from **1** (80.5 mg, 0.30 mmol, 1.0 equiv), **S51** (127.0 mg, 0.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 0.45 mL, 0.74 mmol, 2.4 equiv), and TMSCl (90 µL, 0.71 mmol, 2.4

equiv) according to method **B**. The reaction was directly subjected to column chromatography (silica, 100% Pentane) to yield **2q** (88.5 mg, 55% yield) as a white foam.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.67 (ddd, *J* = 8.9, 4.2, 1.6 Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 3.29 (d, *J* = 3.7 Hz, 1H), 2.63 (dd, *J* = 10.3, 7.8 Hz, 1H), 2.49 – 2.29 (m, 4H), 2.20 – 1.94 (m, 7H), 1.94 – 1.74 (m, 3H), 1.62 – 1.49 (m, 1H), 1.26 (tt, *J* = 12.0, 9.6 Hz, 1H), 1.07 (s, 3H), 1.02 (s, 3H), 0.88 (d, *J* = 7.2 Hz, 3H), 0.85 (td, *J* = 10.2, 9.5, 6.7 Hz, 1H), 0.52 (dd, *J* = 11.4, 9.4 Hz, 1H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.4, 170.6, 145.6, 123.1, 83.9, 72.3, 56.6, 55.3, 52.8, 52.1, 46.4, 45.1, 42.8, 41.1, 33.1, 32.9, 32.3, 29.8, 28.6, 26.8, 25.4, 24.1, 23.0, 21.7, 18.8, 18.6, 15.4, 2.4.

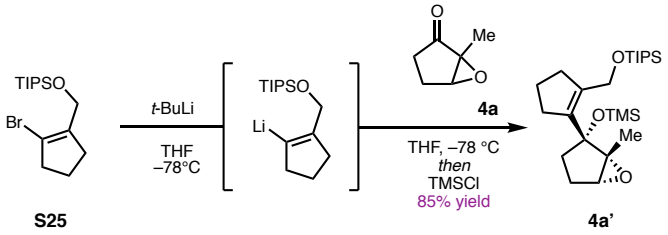
FTIR (NaCl, thin film): 2951, 2868, 1734, 1456, 1433, 1247, 1221, 838, 758 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{30}H_{50}O_6SiN$ $[M+NH_4]^+$, 548.3402 found 548.3398.

$[\alpha]_D^{25}$ = –40.0° (*c* = 1.00, $CHCl_3$).

TLC (10% EtOAc:90% Hexanes), R_f: 0.54, (blue in *p*-anisaldehyde stain).

Preparation of 1,2-addition product 4a':



Prepared via General Procedure A, 85% yield.

Prepared from **4a** (235 mg, 1.97 mmol, 1.0 equiv), **S25** (788 mg, 2.36 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 2.84 mL, 4.83 mmol, 2.45 equiv) and TMSCl (0.60 mL, 2.4 equiv) according to method **A**. The reaction was quenched with sat. $NaHCO_3$, and the reaction mixture was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, 1% EtOAc: 99% Hexanes) to yield the product **4a'** (737.4 mg, 85% yield) as a white crystalline solid.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.80 (dt, *J* = 14.0, 1.6 Hz, 1H), 4.60 (dt, *J* = 13.9, 2.0 Hz, 1H), 3.29 (s, 1H), 2.71 – 2.57 (m, 1H), 2.55 – 2.44 (m, 1H), 2.36 (dddt, *J* = 15.3, 8.8, 6.7, 2.2 Hz, 1H), 2.19 (dddd, *J* = 16.6, 9.0, 4.8, 2.0 Hz, 1H), 2.00 (td, *J* = 10.1, 3.4 Hz, 1H), 1.85 – 1.65 (m, 5H), 1.34 (s, 3H), 1.21 – 1.00 (m, 21H), 0.19 (s, 9H).

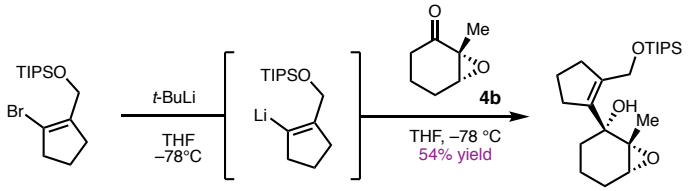
^{13}C NMR (126 MHz, $CDCl_3$): δ 139.3, 136.0, 86.1, 67.4, 63.7, 61.7, 35.1, 34.9, 34.4, 26.5, 22.1, 18.3, 18.3, 13.4, 12.2, 2.4.

FTIR (NaCl, thin film): 2934, 2866, 1652, 1463, 1248, 1098, 1056, 989, 839 cm^{-1}.

HRMS: (FI-TOF) calc'd for $C_{24}H_{46}O_3Si_2$ $[M]^+$ 438.2980, found 438.2985.

TLC (10% EtOAc:90% Hexanes), R_f: 0.67 (grey in *p*-anisaldehyde)

Preparation of 1,2-addition product 4b'-OH:



S25 **4b'-OH**

Prepared via General Procedure A, 54% yield.

Prepared from **4b** (229 mg, 1.82 mmol, 1.0 equiv), **S25** (726 mg, 2.18 mmol, 1.2 equiv), *t*-BuLi (1.7 M in pentane, 2.62 mL, 4.45 mmol, 2.45 equiv) according to method **A**. The reaction was quenched with MeOH (1 mL) and sat. NH_4Cl (5 mL) at –78 °C. The reaction mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, 15% EtOAc:85% Hexanes) then a second column (silica, 1% – 5% gradient of Et_2O in CH_2Cl_2) to yield the product **4b'-OH** (372.8 mg, 54% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 4.49 (d, *J* = 12.4 Hz, 1H), 4.44 (d, *J* = 12.5 Hz, 1H), 3.24 (t, *J* = 2.2 Hz, 1H), 3.05 (s, 1H), 2.62 – 2.38 (m, 4H), 2.02 (dt, *J* = 13.0, 6.0 Hz, 1H), 1.89 – 1.61 (m, 4H), 1.58 – 1.42 (m, 2H), 1.40 – 1.33 (m, 1H), 1.32 (s, 3H), 1.17 – 1.05 (m, 21H).

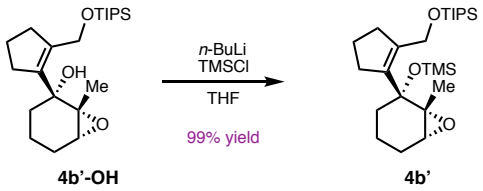
^{13}C NMR (126 MHz, $CDCl_3$): δ 139.4, 137.5, 74.9, 64.0, 63.0, 61.2, 36.2, 36.0, 30.4, 23.9, 22.3, 19.2, 18.2, 16.4, 12.1.

FTIR (NaCl, thin film): 3485, 2940, 2893, 2965, 1463, 1381, 1086, 996, 882 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{22}H_{41}O_3Si$ $[M+H]^+$ 381.2825, found 381.2808.

TLC (5% Et_2O:95% CH_2Cl_2), R_f: 0.47 (purple in *p*-anisaldehyde)

Preparation of silyl ether 4b':



4b'-OH **4b'**

A 25 mL oven dried N_2 flushed flask was charged with epoxy alcohol **4b'-OH** (100 mg, 0.26 mmol, 1.0 equiv) and THF (2.6 mL). The solution was cooled to –78 °C then *n*-BuLi (2.5 M in hexanes, 0.13 mL, 0.32 mmol, 1.2 equiv) was added and the reaction stirred for 20 minutes. Next, to the solution was added trimethylsilyl chloride (67 µL, 0.53 mmol, 2.0 equiv). The reaction was allowed to warm to 21 °C and stir at this temperature for 15 minutes. The reaction was quenched with sat. $NaHCO_3$, and the reaction mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, 2% EtOAc:98% Hexanes) to yield the product **4b'** (117.5 mg, 99% yield) as a clear colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 4.54 (dt, *J* = 12.7, 1.2 Hz, 1H), 4.35 (ddd, *J* = 12.6, 2.5, 1.2 Hz, 1H), 3.11 (d, *J* = 4.2 Hz, 1H), 2.72 – 2.60 (m, 1H), 2.59 – 2.34 (m, 3H), 1.95 – 1.59 (m, 5H), 1.50 (dt, *J* = 11.6, 3.3 Hz, 1H), 1.47 – 1.38 (m, 1H), 1.35 (dq, *J* = 10.5, 2.9 Hz, 1H), 1.31 (s, 3H), 1.18 – 1.00 (m, 21H), 0.17 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 139.1, 137.6, 80.1, 63.8, 62.5, 61.4, 36.7, 35.9, 32.9, 22.7, 21.8, 18.8, 18.5, 18.2, 12.2, 2.8.

FTIR (NaCl, thin film): 2934, 2863, 1463, 1378, 1250, 1100, 1013, 964, 883, 840 cm^{-1}.

HRMS: (FI-TOF) calc'd for $C_{25}H_{48}O_3Si_2$ $[M]^+$ 452.3137, found 452.3143.

TLC (10% EtOAc:90% Hexanes), R_f: 0.72 (dark purple in *p*-anisaldehyde)

Preparative procedures for semi-pinacol rearrangements:

General Procedure A:

A 25 mL round bottom flask was charged with the epoxide (1.0 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (0.40 equiv). The mixture was dried via azeotropic removal of trace water by concentration under reduced pressure from anhydrous toluene (3 x 5 mL, 45 °C water bath temperature) followed by drying under vacuum on a Schlenk line (0.3 torr) for 30 minutes. The flask was backfilled with N_2 and was charged CH_2Cl_2 (0.04 M). The resulting solution was cooled to –78 °C then *N*-(Trimethylsilyl)bis(trifluoromethanesulfonyl)imide ($TMSNTf_2$) (0.10 equiv) was added, which was weighed out in a glovebox in a 25 μL syringe. The reaction was stirred for 30 minutes at –78 °C and was then quenched with MeOH (0.1 mL) at this temperature. The reaction was warmed to 21 °C then the reaction was concentrated under reduced pressure. The crude product was purified directly by SiO_2 column chromatography.

General Procedure B:

A 25 mL round bottom flask was charged with the epoxide (1.0 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (1.1 equiv). The mixture was dried via azeotropic removal of trace water by concentration under reduced pressure from anhydrous toluene (3 x 5 mL, 45 °C water bath temperature) followed by drying under vacuum on a Schlenk line (0.3 torr) for 30 minutes. The flask was backfilled with N_2 and was charged CH_2Cl_2 (0.04 M). The resulting solution was cooled to –78 °C then *N*-(Trimethylsilyl)bis(trifluoromethanesulfonyl)imide ($TMSNTf_2$) (0.50 equiv) was added, which was weighed out in a glovebox in a 25 μL syringe. The reaction was stirred for 4 hours at –78 °C and was then quenched with MeOH (0.1 mL) at this temperature. The reaction was warmed to 21 °C then the reaction was concentrated under reduced pressure. The crude product was purified directly by SiO_2 column chromatography.

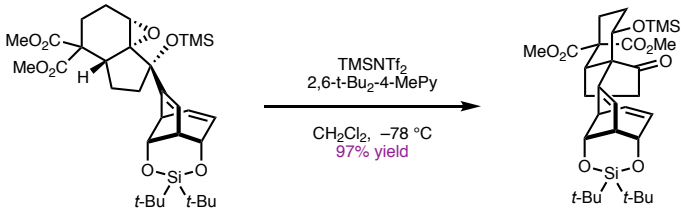
General Procedure C

A 25 mL round bottom flask was charged with the epoxide (1.0 equiv) and 2,6-di-*tert*-butyl-4-methylpyridine (1.0 equiv). The mixture was dried via azeotropic removal of trace water by concentration under reduced pressure from anhydrous toluene (3 x 5 mL, 45 °C water bath temperature) followed by drying under vacuum on a Schlenk line (0.3 torr) for 30 minutes. The flask was backfilled with N_2 and was charged CH_2Cl_2 (0.04 M). The resulting solution was cooled to –78 °C then *N*-(Trimethylsilyl)bis(trifluoromethanesulfonyl)imide ($TMSNTf_2$) (0.30 equiv) was added, which was weighed out in a glovebox in a 25 μL syringe. The reaction was stirred for 4 hours at –78 °C and was then quenched with MeOH (0.1 mL) at this temperature. The reaction was warmed to 21 °C then the reaction was concentrated under reduced pressure. The crude product was purified directly by SiO_2 column chromatography.

General Procedure D:

A 25 mL round bottom flask was charged with the epoxy alcohol (1.0 equiv), triethylamine (6.0 equiv), and CH_2Cl_2 (0.1 M). The solution was cooled to 0 °C then TMSOTf (5.0 equiv) was added, and the reaction was stirred for 1 hour at this temperature. The reaction was quenched with sat. NH_4Cl (5 mL), and 1 M HCl (1 mL) and was stirred vigorously for 1 hour at 21 °C. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by SiO_2 column chromatography.

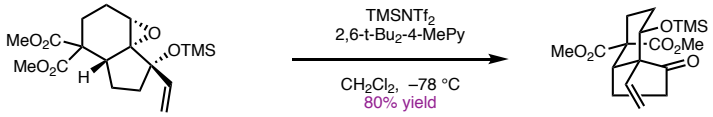
Preparation of semi-pinacol product 3a:



2a **3a**

Prepared from **2a** (4.27 g, 7.93 mmol, 1.0 equiv), according to method reported by Reisman, and ^1H NMR characterization data matched their report.[2]

Preparation of semi-pinacol product 3b:



2b **3b**

Prepared via General Procedure A, 80% yield.

Prepared from **2b** (79.1 mg, 0.22 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (17.6 mg, 0.086 mmol, 0.4 equiv), and $TMSNTf_2$ (7.6 mg, 0.022 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 15% Acetone:85% Hexanes) to yield **3b** (63.5 mg, 80% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.66 (dd, *J* = 17.8, 11.2 Hz, 1H), 5.21 (dd, *J* = 11.2, 0.6 Hz, 1H), 5.08 (dt, *J* = 17.8, 0.4 Hz, 1H), 4.19 (t, *J* = 2.9 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.18 (dd, *J* = 12.4, 7.2 Hz, 1H), 2.46 (td, *J* = 13.8, 4.0 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.23 – 2.07 (m, 3H), 1.78 – 1.68 (m, 1H), 1.64 – 1.50 (m, 2H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 218.2, 171.0, 170.9, 138.7, 116.1, 70.5, 58.1, 56.3, 52.8, 52.8, 45.6, 38.6, 27.0, 23.6, 19.4, 0.1.

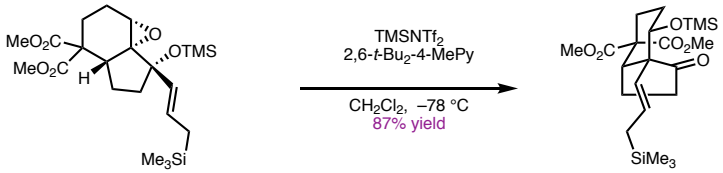
FTIR (NaCl, thin film): 3086, 2954, 1738, 1681, 1434, 1253, 1172, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{18}H_{28}O_6SiNa$ $[M+Na]^+$ 391.1547, found 391.1553.

$[\alpha]_D^{25}$ = +143.8° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R*f*: 0.34 (turquoise in *p*-anisaldehyde).

Preparation of semi-pinacol product 3c:



2c **3c**

Prepared via General Procedure A, 87% yield.

Prepared from **2c** (92.6 mg, 0.20 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (16.7 mg, 0.082 mmol, 0.4 equiv), and $TMSNTf_2$ (7.2 mg, 0.020 mmol, 0.1 equiv) at –78 °C for

30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 10% Acetone:90% Hexanes) to yield **3c** (80.2 mg, 87% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.59 (dt, *J* = 16.0, 8.1 Hz, 1H), 5.14 (dt, *J* = 15.9, 1.3 Hz, 1H), 4.07 (t, *J* = 2.7 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.16 (dd, *J* = 12.5, 6.8 Hz, 1H), 2.51 – 2.41 (m, 1H), 2.34 – 2.24 (m, 1H), 2.19 – 2.03 (m, 3H), 1.73 – 1.65 (m, 1H), 1.59 – 1.52 (m, 2H), 1.48 – 1.42 (m, 2H), 0.05 (s, 9H), –0.01 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 218.6, 171.1, 129.2, 128.3, 72.4, 57.4, 56.5, 52.8, 52.7, 45.6, 38.5, 26.9, 23.8, 23.6, 19.4, 0.1, –1.7.

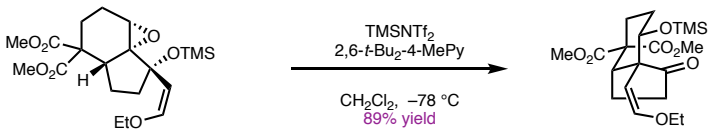
FTIR (NaCl, thin film): 2953, 1741, 1434, 1404, 1251, 1170, 844 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{22}H_{38}O_6Si_2Na$ $[M+Na]^+$ 477.2099, found 477.2098.

$[\alpha]_D^{25}$ = +130.6° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R_f: 0.40 (navy blue in *p*-anisaldehyde).

Preparation of semi-pinacol product 3d:



2d **3d**

Prepared via General Procedure A, 89% yield.

Prepared from **2d** (67.4 mg, 0.16 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (13.4 mg, 0.065 mmol, 0.4 equiv), and $TMSNTf_2$ (6.0 mg, 0.016 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 15% Acetone:85% Hexanes) to yield **3d** (60.9 mg, 89% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.92 (d, *J* = 6.1 Hz, 1H), 4.04 (d, *J* = 6.1 Hz, 1H), 3.93 (t, *J* = 2.8 Hz, 1H), 3.78 (dq, *J* = 9.9, 7.1 Hz, 1H), 3.73 (s, 3H), 3.74 – 3.67 (m, 1H), 3.68 (s, 3H), 3.52 (dd, *J* = 13.0, 7.0 Hz, 1H), 2.41 (td, *J* = 13.8, 3.8 Hz, 1H), 2.38 – 2.28 (m, 1H), 2.26 (ddd, *J* = 18.4, 8.7, 1.0 Hz, 1H), 2.17 – 2.01 (m, 2H), 1.79 (dddd, *J* = 11.4, 8.6, 7.0, 1.3 Hz, 1H), 1.67 (dddd, *J* = 14.4, 13.6, 3.2, 2.0 Hz, 1H), 1.60 (dq, *J* = 14.4, 3.7 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.04 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 220.6, 171.3, 145.1, 107.2, 72.1, 68.0, 56.2, 54.8, 52.7, 52.5, 43.7, 38.4, 26.6, 24.0, 19.4, 15.3, 0.1.

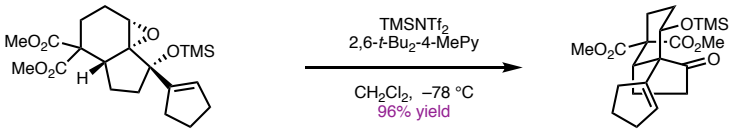
FTIR (NaCl, thin film): 2954, 2898, 1742, 1659, 1435, 1252, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{20}H_{32}O_7SiNa$ $[M+Na]^+$ 435.1810, found 435.1818.

$[\alpha]_D^{25}$ = +89.9° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R_f: 0.23 (brown in *p*-anisaldehyde).

Preparation of semi-pinacol product 3e:



2e **3e**

Prepared via General Procedure A, 96% yield.

Prepared from **2e** (77.9 mg, 0.19 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (15.7 mg, 0.076 mmol, 0.4 equiv), and $TMSNTf_2$ (6.7 mg, 0.019 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 15% Acetone:85% Hexanes) to yield **3e** (74.4 mg, 96% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.38 (p, *J* = 2.1 Hz, 1H), 4.33 (t, *J* = 2.9 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 3.37 (dd, *J* = 12.5, 6.9 Hz, 1H), 2.53 (dddd, *J* = 16.9, 9.6, 4.7, 2.0 Hz, 1H), 2.46 (td, *J* = 13.9, 3.9 Hz, 1H), 2.42 – 2.24 (m, 3H), 2.24 – 2.07 (m, 3H), 1.98 – 1.89 (m, 1H), 1.89 – 1.81 (m, 2H), 1.81 – 1.72 (m, 2H), 1.68 (dq, *J* = 14.3, 3.6 Hz, 1H), 0.06 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 219.4, 171.0, 170.7, 143.1, 127.5, 70.5, 58.0, 56.3, 52.7, 42.1, 39.3, 33.1, 32.9, 28.0, 23.7, 23.0, 19.7, 0.1.

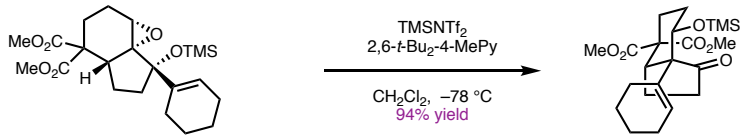
FTIR (NaCl, thin film): 2953, 2849, 1741, 1434, 1252, 1169, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{21}H_{32}O_6SiNa$ $[M+Na]^+$ 431.1860, found 431.1861.

$[\alpha]_D^{25}$ = +100.5° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R_f: 0.33 (dark green in *p*-anisaldehyde).

Preparation of semi-pinacol product 3f:



2f **3f**

Prepared via General Procedure A, 94% yield.

Prepared from **2f** (54.1 mg, 0.13 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (10.5 mg, 0.051 mmol, 0.4 equiv), and $TMSNTf_2$ (4.5 mg, 0.013 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 15% Acetone:85% Hexanes) to yield **3f** (50.9 mg, 94% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.32 (t, *J* = 3.8 Hz, 1H), 4.34 (s, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.46 (dd, *J* = 12.5, 7.2 Hz, 1H), 2.44 (td, *J* = 13.8, 4.0 Hz, 1H), 2.32 (dd, *J* = 17.8, 8.0 Hz, 1H), 2.27 – 2.03 (m, 5H), 2.03 – 1.93 (m, 1H), 1.80 – 1.69 (m, 2H), 1.69 – 1.54 (m, 4H), 1.54 – 1.42 (m, 2H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 220.5, 171.0, 170.7, 136.4, 124.3, 69.9, 60.6, 56.3, 52.8, 41.4, 39.9, 28.2, 26.9, 25.7, 23.6, 23.0, 22.1, 19.7, 0.2.

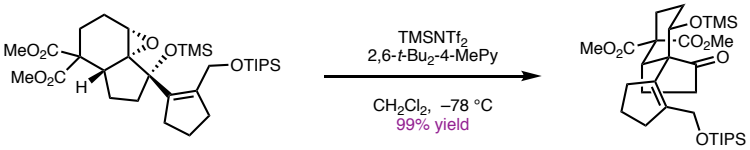
FTIR (NaCl, thin film): 2950, 2933, 2858, 2839, 1740, 1682, 1434, 1251, 1060, 1020, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{22}H_{34}O_6SiNa$ $[M+Na]^+$ 445.2017, found 445.2023.

$[\alpha]_D^{25}$ = +102.6° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R*f*: 0.37 (pistachio in *p*-anisaldehyde).

Preparation of semi-pinacol product 3g:



2g **3g**

Prepared via General Procedure A, 99% yield.

Prepared from **2g** (132.0 mg, 0.22 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (18.2 mg, 0.89 mmol, 0.4 equiv), and $TMSNTf_2$ (7.8 mg, 0.022 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 15% Acetone:85% Hexanes) to yield **3g** (130.0 mg, 99% yield) as a clear colorless oil.

^{1}H NMR (400 MHz, Acetonitrile-d_3): δ 4.27 (t, *J* = 2.9 Hz, 1H), 4.22 (d, *J* = 12.2 Hz, 1H), 4.05 (d, *J* = 12.7 Hz, 1H), 3.68 (s, 3H), 3.63 (s, 3H), 3.40 (dd, *J* = 12.6, 7.5 Hz, 1H), 2.63 – 2.51 (m, 1H), 2.51 – 2.39 (m, 2H), 2.38 – 2.30 (m, 1H), 2.30 – 2.16 (m, 3H), 2.15 – 2.03 (m, 2H), 1.90 – 1.77 (m, 2H), 1.77 – 1.67 (m, 3H), 1.20 – 1.04 (m, 21H), 0.05 (s, 9H).

^{13}C NMR (101 MHz, CD_3CN): δ 218.6, 170.8, 170.7, 138.4, 136.0, 70.5, 61.6, 57.5, 56.4, 52.0, 51.9, 45.2, 38.5, 36.5, 34.8, 28.2, 23.3, 21.4, 19.2, 17.4, 11.9, –1.1.

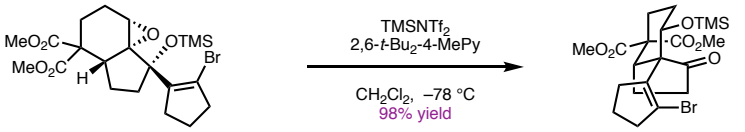
FTIR (NaCl, thin film): 2948, 2865, 1743, 1447, 1252, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{31}H_{54}O_7Si_2Na$ $[M+Na]^+$ 617.3300, found 617.3309.

$[\alpha]_D^{25}$ = +26.9° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R*f*: 0.49 (dark purple in *p*-anisaldehyde).

Preparation of semi-pinacol product 3h:



2h **3h**

Prepared via General Procedure A, 98% yield.

Prepared from **2h** (82.0 mg, 0.17 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (13.8 mg, 0.067 mmol, 0.4 equiv), and $TMSNTf_2$ (5.9 mg, 0.017 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 15% Acetone:85% Hexanes) to yield **3h** (80.1 mg, 98% yield) as a clear colorless oil.

^{1}H NMR (400 MHz, CD_3CN): δ 4.23 (s, 1H), 3.84 – 3.74 (m, 1H), 3.68 (s, 3H), 3.63 (s, 3H), 2.62 (dddd, *J* = 11.7, 7.8, 5.1, 2.4 Hz, 2H), 2.52 – 2.32 (m, 3H), 2.25 (dddd, *J* = 18.6, 9.2, 1.3, 0.7 Hz, 2H), 2.13 – 1.99 (m, 2H), 1.90 – 1.78 (m, 3H), 1.76 – 1.61 (m, 2H), 0.03 (s, 9H).

^{13}C NMR (101 MHz, CD_3CN): δ 217.3, 171.0, 170.7, 140.1, 116.8, 70.2, 57.2, 56.5, 52.1, 52.0, 42.2, 41.5, 39.3, 35.0, 28.2, 23.6, 21.7, 19.2, –1.0. *run at 70 °C to converge atropisomers.

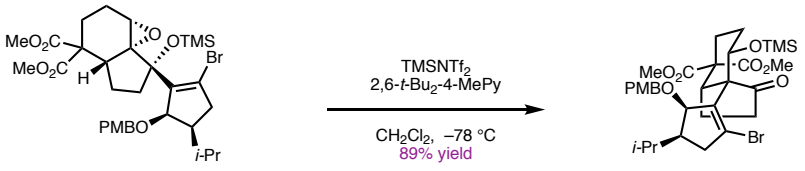
FTIR (NaCl, thin film): 2952, 2911, 2858, 1740, 1622, 1433, 1252, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{21}H_{31}O_6SiBrNa$ $[M+Na]^+$ 509.0965, found 509.0950.

$[\alpha]_D^{25}$ = +20.0° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R*f*: 0.31 (dark pistachio in *p*-anisaldehyde).

Preparation of semi-pinacol product 3i:



2i **3i**

Prepared via General Procedure B, 89% yield.

Prepared from **2i** (78.2 mg, 0.12 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (26.5 mg, 0.13 mmol, 1.1 equiv), and $TMSNTf_2$ (20.8 mg, 0.059 mmol, 0.5 equiv) at –78 °C for 4 hours according to method **B**. The reaction was purified by column chromatography (silica, 10 to 20% EtOAc gradient in hexanes) to yield **3i** (69.4 mg, 89% yield) as a white foam.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.40 – 7.32 (m, 2H), 6.89 – 6.80 (m, 2H), 5.17 (d, *J* = 10.3 Hz, 1H), 4.78 – 4.72 (m, 1H), 4.47 (d, *J* = 5.7 Hz, 1H), 4.23 (d, *J* = 10.3 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.66 (s, 3H), 2.68 (d, *J* = 8.2 Hz, 2H), 2.61 (ddd, *J* = 18.6, 10.8, 9.6 Hz, 1H), 2.48 (ddd, *J* = 14.0, 12.5, 5.1 Hz, 1H), 2.33 (ddt, *J* = 18.5, 9.3, 1.0 Hz, 1H), 2.13 (tdd, *J* = 12.5, 10.8, 9.6 Hz, 1H), 2.09 – 2.03 (m, 1H), 1.98 – 1.87 (m, 2H), 1.83 (dddd, *J* = 11.9, 9.5, 7.7, 1.2 Hz, 1H), 1.76 – 1.65 (m, 2H), 1.11 (d, *J* = 5.8 Hz, 3H), 0.96 (d, *J* = 6.0 Hz, 3H), –0.06 (d, *J* = 0.8 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 218.8, 171.4, 171.0, 159.0, 140.8, 131.5, 129.5, 125.6, 113.7, 81.9, 67.9, 66.0, 57.5, 56.7, 55.4, 52.8, 52.7, 50.3, 46.1, 43.1, 39.7, 29.1, 27.7, 24.1, 22.1, 21.7, 19.1, 0.2.

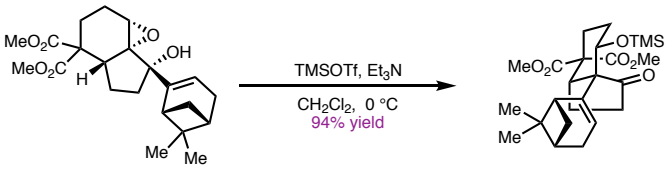
FTIR (NaCl, thin film): 2954, 1738, 1614, 1514, 1251, 1172, 1059, 866, 840 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{32}H_{49}O_8SiBrN$ $[M+NH_4]^+$ 682.2405, found 682.2403.

$[\alpha]_D^{25}$ = +12.3° (*c* = 1.00, $CHCl_3$).

TLC (20% EtOAc:80% Hexanes), R_f: 0.42 (dark blue in *p*-anisaldehyde).

Preparation of semi-pinacol product 3j:



2j-OH **3j**

Prepared via General Procedure D, 94% yield.

Prepared from **2j-OH** (60.0 mg, 0.15 mmol, 1.0 equiv), triethylamine (129 µL, 0.92 mmol, 6.0 equiv), and TMSOTf (139 µL, 0.77 mmol, 5.0 equiv) at 0 °C for 1 hour according to method **D**. The reaction was quenched with sat. NH_4Cl (5 mL), and 1 M HCl (1 mL) and was stirred vigorously for 1 hour. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, 100% CH_2Cl_2 to 10% Et_2O in CH_2Cl_2 gradient) to yield **3j** (66.9 mg, 94% yield) as a pale-yellow oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.18 (dq, *J* = 3.1, 1.6 Hz, 1H), 4.35 (t, *J* = 2.8 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.31 (dd, *J* = 11.9, 7.1 Hz, 1H), 2.45 (td, *J* = 13.9, 3.6 Hz, 1H), 2.39 (dt, *J* = 8.8, 5.7 Hz, 1H), 2.27 – 2.14 (m, 4H), 2.12 – 1.98 (m, 2H), 1.96 (dtd, *J* = 5.6, 2.8, 1.1 Hz, 1H), 1.88 (td, *J* = 5.6, 1.8 Hz, 1H), 1.85 – 1.72 (m, 2H), 1.69 (dq, *J* = 14.2, 3.6 Hz, 1H), 1.39 (d, *J* = 8.8 Hz, 1H), 1.22 (s, 3H), 0.88 (s, 3H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 217.8, 171.1, 170.7, 145.8, 119.7, 69.8, 60.0, 56.5, 53.0, 52.7, 45.8, 41.9, 40.3, 39.7, 38.7, 32.3, 31.4, 28.4, 26.7, 24.0, 21.2, 19.4, 0.2.

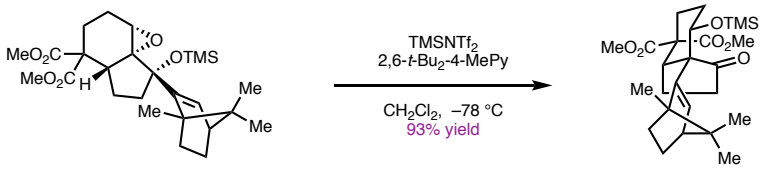
FTIR (NaCl, thin film): 2952, 2916, 2930, 1742, 1459, 1432, 1250, 1169, 1057, 844 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{25}H_{39}O_6Si$ $[M+H]^+$ 463.2510, found 463.2527.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +69.8° (*c* = 1.00, $CHCl_3$).

TLC (100% CH_2Cl_2), R_f: 0.54 (dark blue in *p*-anisaldehyde).

Preparation of semi-pinacol product 3k:



2k **3k**

Prepared via General Procedure A, 93% yield.

Prepared from **2k** (82.9 mg, 0.17 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (14.3 mg, 0.070 mmol, 0.4 equiv), and $TMSNTf_2$ (6.1 mg, 0.017 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 6% Acetone:94% Hexanes) to yield **3k** (77.2 mg, 93% yield) as a white crystalline solid.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.70 (d, *J* = 3.7 Hz, 1H), 4.31 (s, 1H), 3.74 (s, 3H), 3.63 (s, 3H), 3.27 (dd, *J* = 11.8, 8.1 Hz, 1H), 2.39 (td, *J* = 13.9, 3.4 Hz, 1H), 2.34 – 2.19 (m, 2H), 2.17 (t, *J* = 3.7 Hz, 1H), 2.12 (dt, *J* = 14.0, 3.1 Hz, 1H), 2.07 – 1.91 (m, 3H), 1.78 (ddt, *J* = 11.6, 9.0, 3.6 Hz, 1H), 1.69 (dq, *J* = 14.1, 3.5 Hz, 1H), 1.59 (ddd, *J* = 12.1, 9.2, 3.3 Hz, 1H), 1.37 (ddd, *J* = 11.9, 8.9, 4.0 Hz, 1H), 0.91 (d, *J* = 3.6 Hz, 6H), 0.71 (s, 3H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 219.9, 171.3, 170.7, 146.9, 133.4, 71.1, 59.0, 57.2, 56.5, 55.7, 52.7, 52.7, 51.5, 42.1, 38.9, 31.6, 28.5, 25.2, 24.6, 20.1, 19.9, 19.5, 14.3, 0.2.

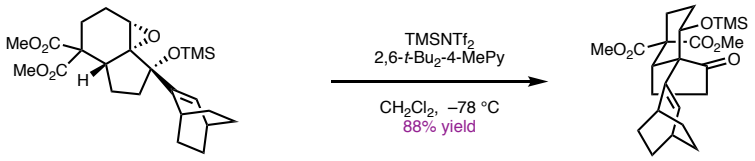
FTIR (NaCl, thin film): 3062, 2951, 2874, 1742, 1434, 1250, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{26}H_{40}O_6SiK$ $[M+K]^+$ 515.2226, found 515.2231.

$[\alpha]_D^{25}$ = +1.8° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R*f*: 0.41 (vibrant purple in *p*-anisaldehyde).

Preparation of semi-pinacol product 3l:



2l **3l**

Prepared via General Procedure A, 88% yield.

Prepared from **2l** (53.0 mg, 0.12 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (9.7 mg, 0.047 mmol, 0.4 equiv), and $TMSNTf_2$ (4.2 mg, 0.012 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 10% Acetone:90% Hexanes) to yield **3l** (50.7 mg, 88% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.85 (dd, *J* = 7.0, 1.9 Hz, 1H), 4.34 (t, *J* = 2.8 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 3.35 (dd, *J* = 12.3, 7.0 Hz, 1H), 2.50 – 2.41 (m, 2H), 2.29 (dd, *J* = 17.9,

8.1 Hz, 1H), 2.22 – 2.01 (m, 4H), 1.88 – 1.79 (m, 1H), 1.79 – 1.66 (m, 3H), 1.55 – 1.24 (m, 6H), 1.18 (dddd, *J* = 11.8, 9.1, 5.8, 2.5 Hz, 1H), 0.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 218.7, 171.2, 170.6, 143.8, 129.7, 69.9, 59.8, 56.5, 52.8, 52.7, 42.7, 39.5, 33.8, 30.7, 28.5, 27.4, 26.8, 26.4, 25.1, 24.1, 19.4, 0.2.

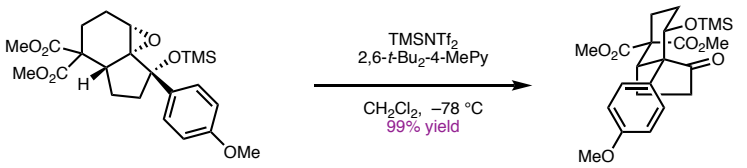
FTIR (NaCl, thin film): 2948, 2863, 1732, 1434, 1252, 860, 844 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{24}H_{36}O_6SiNa$ $[M+Na]^+$ 471.2173, found 471.2155.

$[\alpha]_D^{25}$ = +35.6° (*c* = 1.00, $CHCl_3$).

TLC (10% Acetone:90% Hexanes), R_f: 0.29 (bright red in *p*-anisaldehyde).

Preparation of semi-pinacol product 3m:



2m **3m**

Prepared via General Procedure A, 99% yield.

Prepared from **2m** (95.4 mg, 0.21 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (17.5 mg, 0.085 mmol, 0.4 equiv), and $TMSNTf_2$ (7.5 mg, 0.021 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 15% Acetone:85% Hexanes) to yield **3m** (94.5 mg, 99% yield) as a clear colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 6.99 – 6.94 (m, 2H), 6.85 – 6.79 (m, 2H), 4.64 (t, *J* = 3.1 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.57 (dd, *J* = 12.7, 6.6 Hz, 1H), 3.04 (s, 3H), 2.54 – 2.41 (m, 2H), 2.41 – 2.28 (m, 2H), 2.25 (dtd, *J* = 13.8, 3.5, 1.1 Hz, 1H), 2.02 (tdd, *J* = 13.9, 3.6, 2.2 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.84 (dq, *J* = 14.5, 3.5 Hz, 1H), 0.09 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 220.7, 170.9, 170.2, 158.0, 134.2, 128.9, 113.7, 69.4, 58.8, 56.1, 55.4, 52.8, 52.3, 48.1, 39.6, 28.2, 23.7, 19.4, 0.1.

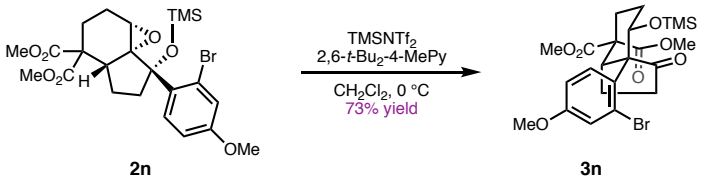
FTIR (NaCl, thin film): 2952, 2901, 2836, 2794, 1742, 1611, 1514, 1253, 1172, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{32}O_7SiNa$ $[M+Na]^+$ 471.1810, found 471.1811.

$[\alpha]_D^{25}$ = +72.7° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R_f: 0.15 (yellow in *p*-anisaldehyde).

Preparation of rearrangement product 3n:



A 500 mL flask was charged with silyl ether **2n** (4.52 g, 8.59 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (1.94 g, 9.45 mmol, 1.1 equiv) and CH_2Cl_2 (172 mL, 0.05 M), and the solution was cooled to 0 °C. To the flask was added *N*-(Trimethylsilyl)bis(trifluoromethanesulfonyl)imide ($TMSNTf_2$) (1.52, 4.30 mmol, 0.50 equiv) which had being weighed out in a glovebox in a 1 mL syringe. After stirring for an additional 30 minutes at 0 °C the reaction was quenched with sat. $NaHCO_3$ (200 mL) and the solution was allowed to warm to 21 °C. The biphasic mixture was separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 200 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, 10% to 12.5% to 15% acetone in hexanes gradient) to afford ketone **3n** (3.32 g, 6.27 mmol, 73% yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.17 (d, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 1H), 6.77 (dd, *J* = 8.9, 2.8 Hz, 1H), 4.55 – 4.53 (m, 1H), 4.32 (dd, *J* = 12.0, 8.1 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.07 (s, 3H), 2.75 (dt, *J* = 18.1, 9.6 Hz, 1H), 2.47 (td, *J* = 13.8, 3.8 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.32 – 2.18 (m, 2H), 2.05 – 1.95 (m, 2H), 1.84 (dq, *J* = 14.6, 3.5 Hz, 1H), 0.08 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 219.3, 170.7, 170.3, 158.3, 132.5, 130.1, 123.7, 120.6, 112.4, 70.6, 58.5, 56.1, 55.5, 52.7, 52.2, 41.7, 39.3, 28.4, 23.6, 19.1, –0.1.

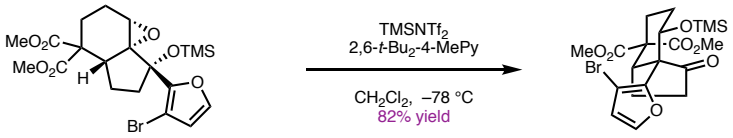
FTIR (NaCl, thin film): 3470, 3083, 2254, 1745, 1732, 1602, 1493, 1456, 1253, 1213, 1173, 1047, 1026, 869, 840, 731 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{32}O_7SiBr$ $[M+H]^+$ 527.1095, found 527.1093.

$[\alpha]_D^{25}$ = +52.6° (*c* = 1.40, $CHCl_3$).

TLC (20% EtOAc:80% Hexanes), R_f: 0.35 (yellow in *p*-anisaldehyde).

Preparation of semi-pinacol product 3o:



2o **3o**

Prepared via General Procedure A, 82% yield.

Prepared from **2o** (84.9 mg, 0.17 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (14.3 mg, 0.070 mmol, 0.4 equiv), and $TMSNTf_2$ (6.2 mg, 0.017 mmol, 0.1 equiv) at –78 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 15% Acetone:85% Hexanes) to yield **3o** (69.2 mg, 82% yield) as a clear colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.24 (d, *J* = 2.0 Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 4.65 (t, *J* = 2.7 Hz, 1H), 3.73 (s, 3H), 3.67 (dd, *J* = 12.9, 7.4 Hz, 1H), 3.43 (s, 3H), 2.62 – 2.35 (m, 4H), 2.32 – 2.11 (m, 3H), 1.98 (tdd, *J* = 14.4, 3.4, 2.1 Hz, 1H), 1.87 – 1.74 (m, 2H), 0.07 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 215.5, 170.8, 170.7, 150.6, 141.1, 115.1, 96.4, 68.9, 56.3, 56.2, 53.1, 52.8, 43.4, 39.0, 28.6, 23.8, 19.4, 0.1.

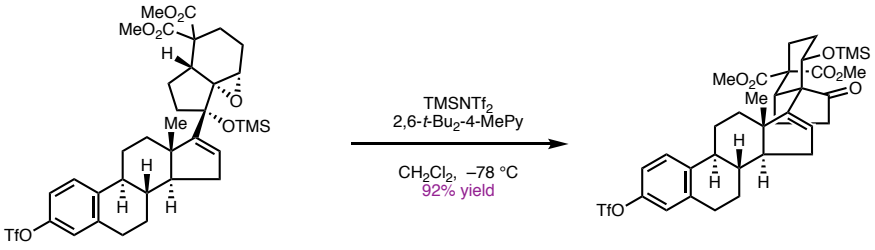
FTIR (NaCl, thin film): 3126, 2954, 1748, 1572, 1434, 1253, 1059, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{20}H_{28}O_7SiBr$ $[M+H]^+$ 487.0782, found 487.0798.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +16.7° (*c* = 1.00, $CHCl_3$).

TLC (15% Acetone:85% Hexanes), R*f*: 0.27 (purple in *p*-anisaldehyde).

Preparation of semi-pinacol product 3p:



2p **3p**

Prepared via General Procedure B, 92% yield.

Prepared from **2p** (66.3 mg, 0.091 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (20.6 mg, 0.10 mmol, 1.1 equiv), and $TMSNTf_2$ (16.1 mg, 0.046 mmol, 0.5 equiv) at –78 °C for 4 hours according to method **B**. The reaction was purified by column chromatography (silica, 15% EtOAc:85% Hexanes) to yield **3p** (60.8 mg, 92% yield) as a white foam.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.27 (d, *J* = 8.2 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.96 (d, *J* = 2.7 Hz, 1H), 5.56 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.40 (s, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 3.34 (t, *J* = 9.9 Hz, 1H), 2.93 – 2.87 (m, 2H), 2.44 – 2.36 (m, 1H), 2.35 – 2.29 (m, 2H), 2.29 – 2.18 (m, 3H), 2.18 – 2.03 (m, 4H), 1.99 – 1.89 (m, 2H), 1.76 (d, *J* = 10.6 Hz, 1H), 1.74 – 1.67 (m, 1H), 1.67 – 1.51 (m, 4H), 1.48 – 1.37 (m, 1H), 1.03 (s, 3H), 0.07 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 219.8, 171.3, 171.0, 154.1, 147.7, 141.2, 139.7, 129.4, 126.9, 121.3, 118.2, 70.6, 58.7, 56.5, 56.3, 52.6, 52.5, 48.5, 43.8, 43.7, 39.0, 36.8, 36.2, 31.2, 29.6, 28.1, 27.1, 26.5, 24.5, 20.0, 17.9, 0.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ 73.0.

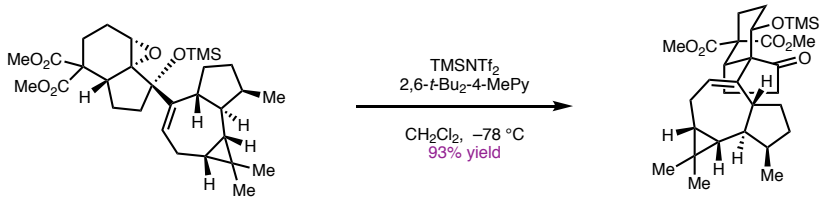
FTIR (NaCl, thin film): 2952, 1741, 1605, 1490, 1423, 1250, 1211, 1143, 919, 843, 756 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{35}H_{46}F_3O_9SSi$ $[M+H]^+$ 727.2578, found 727.2581.

$[\alpha]_D^{25}$ = +51.4° (*c* = 1.00, $CHCl_3$).

TLC (15% EtOAc:85% Hexanes), R*f*: 0.31 (dark blue in *p*-anisaldehyde).

Preparation of semi-pinacol product 3q:



2q **3q**

Prepared via General Procedure C, 93% yield.

Prepared from **2q** (62.4 mg, 0.12 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (24.1 mg, 0.12 mmol, 1.0 equiv), and $TMSNTf_2$ (12.5 mg, 0.035 mmol, 0.3 equiv) at –78 °C for 4 hours according to method **C**. The reaction was directly subjected to column chromatography (silica, 100% CH_2Cl_2) to yield **3q** (58.2 mg, 93% yield) as a white foam.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 5.35 (dt, *J* = 9.2, 2.9 Hz, 1H), 4.20 (s, 1H), 3.72 (s, 3H), 3.72 (dd, *J* = 12.1, 8.2 Hz, 1H), 3.63 (s, 3H), 2.55 – 2.45 (m, 0H), 2.43 – 2.08 (m, 6H), 2.07 – 1.96 (m, 3H), 1.93 – 1.80 (m, 3H), 1.73 (dq, *J* = 14.6, 3.4 Hz, 1H), 1.70 – 1.65 (m, 1H), 1.61 (dt, *J* = 11.4, 4.1 Hz, 1H), 1.02 (s, 3H), 1.01 (s, 3H), 0.89 (d, *J* = 7.1 Hz, 3H), 0.63 (dd, *J* = 11.5, 9.3 Hz, 1H), 0.06 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 219.8, 171.2, 170.6, 141.9, 127.1, 72.2, 61.2, 56.1, 52.8, 52.5, 49.7, 42.8, 42.5, 39.3, 33.8, 33.5, 33.2, 30.0, 28.4, 27.5, 26.2, 24.2, 23.2, 19.4, 19.0, 18.4, 15.5, 0.3.

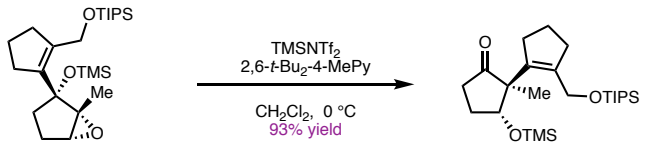
FTIR (NaCl, thin film): 2952, 2870, 1736, 1457, 1251, 1056, 836, 750 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{30}H_{46}O_6SiNa$ $[M+Na]^+$ 553.2956, found 553.2948.

$[\alpha]_D^{25}$ = –43.1° (*c* = 1.00, $CHCl_3$).

TLC (10% EtOAc:90% Hexanes), R*f*: 0.31 (navy blue in *p*-anisaldehyde).

Preparation of semi-pinacol product 5a:



4a' **5a**

Prepared via General Procedure A, 93% yield.

Prepared from **4a'** (52.7 mg, 0.12 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (9.9 mg, 0.048 mmol, 0.4 equiv), and $TMSNTf_2$ (4.2 mg, 0.012 mmol, 0.1 equiv) at 0 °C for 30 minutes according to method **A**. The reaction was purified by column chromatography (silica, 1.5% Acetone:98.5% Hexanes) to yield **5a** (48.8 mg, 93% yield) as a clear colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 4.32 (t, *J* = 5.2 Hz, 1H), 4.22 – 4.07 (m, 2H), 2.64 – 2.52 (m, 1H), 2.52 – 2.21 (m, 5H), 2.04 (dddd, *J* = 13.0, 9.4, 6.6, 4.9 Hz, 1H), 1.86 – 1.67 (m, 3H), 1.10 (s, 3H), 1.09 – 1.02 (m, 21H), 0.10 (s, 9H).

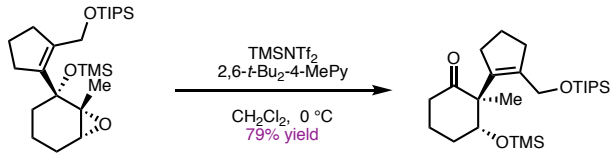
^{13}C NMR (101 MHz, $CDCl_3$): δ 219.6, 138.3, 136.1, 78.4, 60.8, 56.4, 36.2, 35.5, 35.1, 28.6, 21.4, 18.2, 15.6, 12.1, 0.1.

FTIR (NaCl, thin film): 2939, 2865, 1746, 1652, 1462, 1251, 1094, 1064, 880, 848, 842 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{24}H_{47}O_3Si_2$ $[M+H]^+$ 439.3064, found 439.3079.

TLC (10% EtOAc:90% Hexanes), R*f*: 0.58 (dark blue in *p*-anisaldehyde).

Preparation of semi-pinacol product 5b:



4b' **5b**

Prepared via General Procedure B, 79% yield.

Prepared from **4b'** (57.2 mg, 0.125 mmol, 1.0 equiv), 2,6-di-*tert*-butyl-4-methylpyridine (28.2 mg, 0.138 mmol, 1.1 equiv), and $TMSNTf_2$ (22.1 mg, 0.0625 mmol, 0.5 equiv) at 0 °C for 30 minutes according to method **B**. The reaction was purified by column chromatography (silica, 1.5% Acetone:98.5% Hexanes) to yield **5b** (44.7 mg, 79% yield) as a clear colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 4.17 (dt, *J* = 4.7, 1.5 Hz, 1H), 4.10 (dt, *J* = 12.6, 1.2 Hz, 1H), 4.00 (ddd, *J* = 12.5, 2.2, 1.1 Hz, 1H), 2.67 (ddd, *J* = 13.4, 12.0, 6.5 Hz, 1H), 2.61 – 2.31 (m, 4H), 2.26 (dddd, *J* = 13.4, 4.9, 3.5, 1.5 Hz, 1H), 2.04 (ddt, *J* = 24.1, 11.9, 4.8, 3.7 Hz, 1H), 1.90 (tdd, *J* = 12.1, 4.0, 1.8 Hz, 1H), 1.82 – 1.70 (m, 2H), 1.66 (dtt, *J* = 13.5, 5.3, 2.7 Hz, 1H), 1.08 (s, 3H), 1.06 – 0.99 (m, 21H), 0.19 – 0.11 (m, 1H), 0.06 (s, 9H).

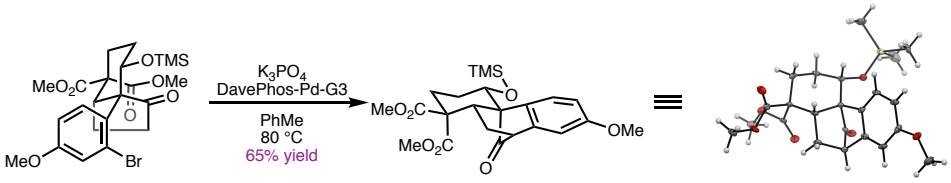
^{13}C NMR (101 MHz, $CDCl_3$): δ 214.5, 138.1, 137.3, 77.9, 60.0, 57.5, 39.3, 35.4, 34.9, 29.9, 21.6, 21.4, 19.4, 18.1, 12.1, 0.2.

FTIR (NaCl, thin film): 2943, 2893, 2867, 1714, 1660, 1463, 1251, 1103, 1079, 1067, 986, 840 cm^{-1}.

HRMS: (FI-TOF) calc'd for $C_{25}H_{48}O_3Si_2$ $[M]^+$ 452.3137, found 452.3137.

TLC (10% EtOAc:90% Hexanes), R_f: 0.58 (dark pink in *p*-anisaldehyde).

Preparation of aromatic intermediate 6:



3n **6**

A 40 mL vial was charged with aryl bromide **3n** (480 mg, 0.910 mmol, 1.0 equiv) and was brought into a glovebox. The vial was charged with K_3PO_4 (882 mg, 3.64 mmol, 4.0 equiv), DavePhos-Pd-G3 (69.5 mg, 0.091 mmol, 10 mol %), and lastly PhMe (23 mL, 0.04 M). The vial

was sealed, brought out of the glovebox, and placed inside an 80 °C oil bath. The reaction was allowed to stir for 15 hours. **Note**: it is extremely important to maintain vigorous stirring. A cross-shaped stir bar was used in this reaction. When the stirring was not vigorous incomplete conversion was observed. The reaction was cooled to 21 °C and filtered through a plug of silica gel that had pre-saturated with Et_2O. The crude product was purified by column chromatography (silica, 15% to 18% to 20% EtOAc in hexanes gradient) to afford **6** (264 mg, 0.592 mmol, 65% yield) as a white solid.

The material was recrystallized from Et_2O to afford crystals suitable for X-ray diffraction analysis.

Note: This reaction was initially developed and performed on racemic material and the X-ray structure was obtained was on racemic material. The route was repeated and fully characterized using enantiopure epoxyketone **1**.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.12 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.53 (dd, *J* = 10.0, 5.8 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.67 (s, 3H), 3.36 (d, *J* = 4.4 Hz, 1H), 2.58 (dt, *J* = 12.6, 4.6 Hz, 1H), 2.42 – 2.34 (m, 1H), 2.05 – 1.89 (m, 4H), 1.53 (dd, *J* = 12.4, 11.1 Hz, 1H), 0.11 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.5, 171.8, 170.4, 158.8, 142.4, 133.5, 121.5, 112.3, 107.1, 67.9, 56.8, 55.4 (two ^{13}C signals), 52.7, 52.3, 49.0, 43.1, 30.3, 28.7, 28.5, 0.7.

FTIR (NaCl, thin film): 2954, 1790, 1779, 1738, 1732, 1609, 1484, 1455, 1251, 1121, 1043, 908, 875, 842, 732 cm^{-1}.

HRMS: (ESI-TOF) calc'd for $C_{23}H_{31}O_7Si$ $[M+H]^+$ 447.1834, found 447.1824.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = +51.7° (*c* = 0.78, $CHCl_3$).

TLC (20% EtOAc:80% Hexanes), R*f*: 0.35 (UV, brown in I_2 stain) note: does not appear in *p*-anisaldehyde or CAM.

3. X-Ray Crystallographic Data

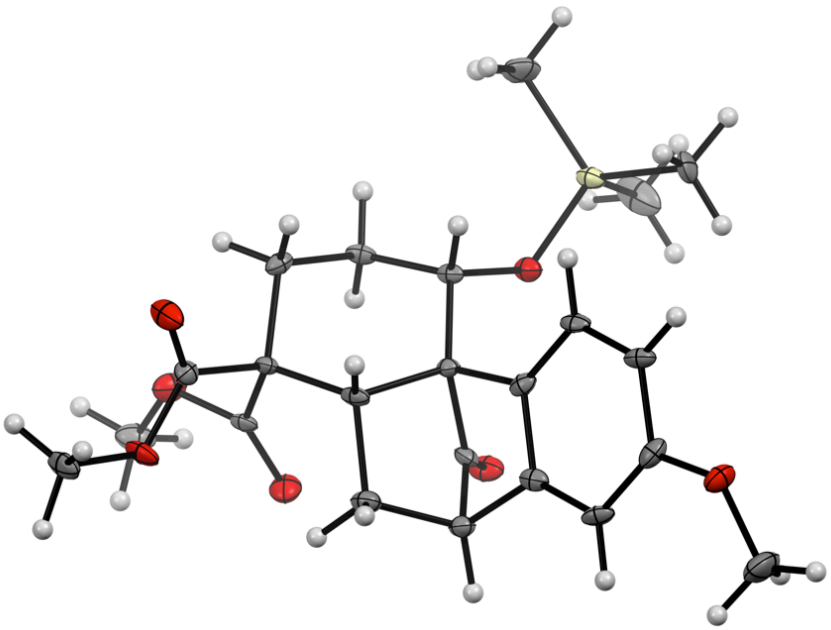
Low-temperature diffraction data (ϕ- and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to either a PHOTON 100 CMOS detector with Mo-$K\alpha$ radiation (λ = 0.71073 Å) or a PHOTON II CPAD detector with either Mo-$K\alpha$ radiation (λ = 0.71073 Å) or Cu-$K\alpha$ radiation (λ = 1.54178 Å) from a fine-focus sealed X-ray tube. All

diffractometer manipulations, including data collection integration, and scaling were carried out using the Bruker APEXII software.[1] Absorption corrections were applied using SADABS.[2] The structure was solved by intrinsic phasing using SHELXT[3] and refined against F^2 on all data by full-matrix least squares with SHELXL-2014[4] using established refinement techniques.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl and hydroxyl groups). Absolute configuration was determined by anomalous dispersion[6] and confirmed by Bayesian statistical analysis using the program PLATON.[7] Graphical representation of the structure with 50% probability thermal ellipsoids was generated using Mercury visualization software.

CRYSTALLOGRAPHIC ANALYSIS OF **6**

Special Refinement Details

Rendering of **6**.



Compound **6** crystallizes in the orthorhombic space group *P*bca with one molecule in the asymmetric unit. CCDC 2224814.

Crystallographic Tables

Crystal data and structure refinement for ***6***.

Identification code	P16149	
Empirical formula	$C_{23}H_{30}O_7Si$	
Formula weight	446.56	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 18.2041(15) Å	α = 90°.
	b = 12.7693(13) Å	β = 90°.
	c = 19.5076(18) Å	γ = 90°.
Volume	4534.6(7) $Å^3$	
Z	8	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	0.145 mm^{-1}	
F(000)	1904	
Crystal size	0.188 x 0.151 x 0.05 mm^3	
Theta range for data collection	2.210 to 32.037°.	
Index ranges	-27<=h<=27, -17<=k<=18, -29<=l<=26	
Reflections collected	135898	
Independent reflections	7877 [R(int) = 0.0810]	
Completeness to theta = 26.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7468 and 0.6970	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7877 / 0 / 287	
Goodness-of-fit on F^2	1.090	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0997	
R indices (all data)	R1 = 0.0621, wR2 = 0.1053	
Extinction coefficient	0.0014(3)	
Largest diff. peak and hole	0.412 and -0.287 $e.Å^{-3}$	

4. References

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5. NMR Spectra