Supporting Information

Experimental Procedure

Unless stated otherwise, reactions were performed in flame-dried or oven-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents (distilled or passed over a column of activated alumina). Commercially obtained reagents were used as received. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, potassium permanganate, or p-anisaldehyde staining. SiliaFlash P60 Academic Silica gel (particle size 0.040–0.063 mm) was used for flash chromatography.

Aldehyde 21

To a solution of ketone **10** (505 mg, 3.07 mmol) in toluene (25 mL) were added neopentyl glycol (1.92 g, 18.4 mmol) and PPTS (77 mg, 0.31 mmol). A Dean-Stark apparatus and condenser were affixed to the reaction flask and the reaction was heated to 140 °C for 3.5 h, at which point TLC indicated complete consumption of starting material. The reaction was diluted with CH_2Cl_2 (25 mL), SiO_2 (2 g) was added and the solvent was removed *in vacuo*. The resulting solid was dry-loaded and purified by flash chromatography (2.5 x 11 cm, 5:1 hexanes:Et_2O) to yield intermediate ketal (558 mg, 73%) as a colorless oil. A portion of this ketal (0.110 g, 0.439 mmol) was taken up in CH_2Cl_2 (8.75 mL) and cooled to –78 °C. Ozone was bubbled through the solution and the reaction was carefully monitored by TLC until all starting material was consumed (2 h). PPh_3 (288 mg, 1.01 mmol) was added and the reaction was allowed to slowly warm to 23 °C and stirred for 12 h. The crude product was concentrated *in vacuo* and purified by flash chromatography (1.5 x 15 cm SiO_2, 9:1 hexanes:EtOAc) to yield aldehyde **21** (107 mg, 97%) as a colorless oil.

Vinyl Iodide 9

A solution of iodomethyltriphenylphosphonium iodide (3.02 g, 5.70 mmol) in THF (20 mL) was cooled to 0 °C and NaHMDS (0.950 g, 5.18 mmol) was added in a single portion. The solution turned bright orange over one minute, was stirred for 5 minutes, was removed from the ice bath and a reflux condenser was affixed to the reaction flask. The reaction was heated to 40 °C, at which point a solution of aldehyde **21** (250 mg, 0.99 mmol) in THF (10 mL) was added via syringe by a rapid dropwise addition and the reaction was stirred for 30 minutes, at which point TLC analysis indicated complete consumption of starting material. The reaction was cooled to 23 °C, filtered through a pad of Celite and rinsed with additional benzene, quenched with 20 mL saturated aqueous NH_4Cl and extracted with 3 x 20 mL Et_2O. The combined organics were washed with brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography (5 x 8 cm SiO_2, 9:1 hexanes:Et_2O) to yield vinyl iodide **9** (245 mg, 66%) as a pale yellow oil in a 5:1 *Z*:*E* ratio by comparison of integration of the terminal alkene proton by ^1H NMR.

Ketal 22

A solution of THP ether **8** (315 mg, 1.42 mmol) in THF (1.6 mL) was cooled to 0 °C and a 2.5 M solution of *n*-BuLi in hexanes (0.67 mL, 1.68 mmol) was added dropwise. After 10 minutes, the ice bath was removed and the mixture was stirred for 30 minutes. The reaction was brought into a nitrogen-filled glove box, $ZnCl_2$ (264 mg, 1.93 mmol) was added, and the solution was stirred for 10 minutes, turning from pale yellow to clear.

$PdCl_2(PPh_3)_2$ (34 mg, 0.048 mmol) was added and the weighing vial was rinsed with an additional 0.5 mL THF, which was added to the solution. The reaction turned yellow and then olive-green. Vinyl iodide **9** (485 mg, 1.29 mmol) was added as an oil, and the weighing vial was rinsed with an additional 0.5 mL THF, which was added to the solution. The reaction turned brown and was stirred for 12 h, at which point TLC analysis indicated complete consumption of vinyl iodide **9**. The solvent was removed *in vacuo* and the crude reaction was purified by flash chromatography (2.5 x 12 cm SiO_2, 5:1 hexanes:Et_2O) to yield ketal **22** (572 mg, 95%) as a pale yellow oil.

Aryl Triflate 7

To a solution of ketal **22** (1.43 g, 3.04 mmol) in MeOH (30 mL) was added Montmorillonite K-10 (304 mg). The reaction was heated to 50 °C and stirred for 2 h, at which point complete consumption of starting material was observed by TLC. The reaction was cooled to 23 °C, filtered through a pad of Celite and rinsed with additional MeOH. The MeOH was removed *in vacuo* and the crude product was dissolved in CH_2Cl_2 (75 mL). DMAP (1.03 g, 9.2 mmol) was added in a single portion, followed by dropwise addition of Tf_2O (0.92 mL, 5.5 mmol). After stirring for 16 h, the reaction was incomplete by TLC. An additional portion of DMAP (500 mg, 4.6 mmol) and Tf_2O (0.46 mL, 2.8 mmol) were added. After an additional 1 h of stirring, complete consumption of starting material was observed by TLC. The reaction was quenched with 10 mL of saturated aqueous Na_2CO_3, diluted with 20 mL H_2O, and extracted with 2 x 50 mL CH_2Cl_2. The combined organics were washed with 30 mL 1 N HCl, and the resulting aqueous phase was extracted with an additional 2 x 50 mL CH_2Cl_2. The organic layers were combined and the solvent was removed *in vacuo*. The product was purified by flash chromatography (3.5 x 24 cm SiO_2, 8:1:1→4:1:1 hexanes:Et_2O:CH_2Cl_2) to yield aryl triflate **7** (863 mg, 65% over two steps) as a pale yellow oil.

Tricyclic Ketone 6

In a nitrogen-filled glove box, tetrabutylammonium acetate (140 mg, 0.46 mmol) and the Herrmann-Beller catalyst (**17**, 15 mg, 16 μmol) were weighed into a microwave vial and a solution of aryl triflate **7** (54 mg, 0.12 mmol) in DMA (2.4 mL) was added. The vial was sealed and heated to 120 °C in a microwave reactor for 2 h. The reaction was concentrated *in vacuo* and purified by flash chromatography (2.5 x 21 cm SiO_2, 8:1:1 hexanes:Et_2O:CH_2Cl_2) to yield tricyclic ketone **6** (31 mg, 88%) as a colorless oil.

Epoxide 24

To a solution of tricyclic ketone **6** (44 mg, 0.16 mmol) and (*R*,*R*)-Mn(salen) epoxidation catalyst **23** (13.5 mg, 0.021 mmol) in CH_2Cl_2 (1.35 mL) was added a 0.54 M, pH 11.2 NaOCl solution (0.45 mL). The reaction was stirred for 42 h, at which point TLC indicated complete consumption of starting material. The reaction was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (1 mL). The phases were separated and the aqueous phase was extracted with 3 x 5 mL CH_2Cl_2. The combined organic phases were concentrated *in vacuo* and purified by flash chromatography (3 x 12 cm SiO_2, 8:1:1→4:1:1→2:1:1 hexanes:Et_2O:CH_2Cl_2) to yield epoxide **24** (41 mg, 89%) as a pale yellow oil in a 10:1 mixture of inconsequential diastereomers by ^1H NMR integration.

Ketal 25

To a solution of epoxide **24** (12 mg, 0.04 mmol) in acetone (2 mL) was added $AuCl_3$ (1.2 mg, 4.0 μmol). The reaction was stirred for 1.5 h, at which point TLC analysis indicated incomplete consumption of starting material and an additional portion of $AuCl_3$ (1 mg, 3 μmol) was added. After an additional 1.5 h of stirring, complete consumption of starting material was indicated by TLC analysis. The crude reaction mixture was filtered through a short silica plug and eluted with Et_2O, and the solvent was removed *in vacuo*. The product was purified by flash chromatography (1 x 14 cm SiO_2, 79:10:10:1 hexanes:Et_2O:CH_2Cl_2:Me_2NEt) to yield ketal **25** (10.6 mg, 74%) as a pale yellow oil. This product was determined to be a single diastereomer by ^1H NMR analysis.

Alkene 26

To a solution of methyltriphenylphosphonium bromide (36.4 mg, 102 μmol) in benzene (0.7 mL) was added a 2.06 M solution of *n*-BuLi in hexanes (45 μL, 93 μmol), causing the reaction to turn yellow. The reaction was stirred for 20 minutes, at which point a solution of ketal **25** (6.6 mg, 19 μmol) in benzene (0.3 mL) was added. A reflux condenser was affixed to the reaction flask and the reaction was submerged in a pre-heated oil bath at 90 °C. After 1 h, TLC analysis indicated complete consumption of starting material. The reaction was cooled to 23 °C, diluted with 5 mL EtOAc, quenched with 2 mL saturated aqueous NH_4Cl and extracted with 2 x 5 mL EtOAc. The combined organic fractions were dried over $MgSO_4$, concentrated *in vacuo* and purified by flash chromatography (1.5 x 10 cm SiO_2, 4:1 hexanes:EtOAc) to yield alkene **26** (4.4 mg, 67%) as a colorless oil.