Supporting Information for:

Enantioselective Synthesis of Imperanene, a Platelet Aggregation Inhibitor

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General Procedures

Proton and carbon-13 NMR spectra were obtained on a Bruker Avance-200 spectrometer. Chemical shifts were reported as δ scale in parts per million downfield from tetramethylsilane. Spectra were obtained in $CDCl_3$ and referenced to residual $CHCl_3$ at 7.24 ppm for proton and 77.23 ppm for carbon-13 NMR. Mass spectrometry was carried out with an HP 6890 gas chromatograph linked to an HP 6890 mass selective detector. Analytical thin-layer chromatography was performed on Baker-flex silica gel IB2-F pre-cut plates and visualized with ceric ammonium molybdenate reagent. Flash chromatography was carried out on Fisher Chemical Chromatographic Silica Gel (200-425 Mesh ASTM). Anhydrous solvents were used as purchased from Aldrich. Reactions were normally performed under an atmosphere of argon in flame-dried glassware.

Experimental Procedures

Protected Phenol 3. Eugenol (**2**) (2.40 g, 14.6 mmol), imidazole (2.04 g, 30.0 mmol), *t*-butyldimethylsilyl chloride (2.49 g, 16.5 mmol), and anhydrous DMF (20 mL) were combined and stirred overnight (19 h). Distilled water (25 mL) and ether (50 mL) were added to the solution. The ether layer was extracted with saturated aqueous sodium bicarbonate (50 mL), water (50 mL) and brine (50 mL). The ether layer was dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 95:5) to yield **3** (3.26 g, 11.7 mmol, 78%) as a colorless oil : ^{1}H NMR ($CDCl_3$) δ 6.75 (1H, d, J = 8 Hz), 6.62 (2H, m) 5.95 (1H, m), 5.07 (1H, m), 5.00 (1H, m), 3.77 (3H, s), 3.30 (2H, d, J = 6.7 Hz), 0.97 (9H, s), 0.12 (6H, s); ^{13}C NMR ($CDCl_3$) δ 151.02, 143.51, 138.05, 133.67, 120.94, 120.90, 115.70, 112.88, 55.71, 40.12, 25.98, 18.67, -4.42; EI *m/z* (relative intensity) 278 (1), 221 (84), 206 (100), 179 (23), 73 (23), 59 (23).

Aldehyde 4. To 2-methyl-2-butene (1.83 g, 26.1 mmol), borane-methyl sulfide complex (6.2 mL, 2.0M in ether, 12.4 mmol) was added at 0°C and stirred for 2 h. Protected phenol **3** (3.20 g, 11.5 mmol) was cooled to 0°C, added dropwise to the mixture, and stirred for 3h at 0°C. Solvent and methyl sulfide were removed and the resulting oil was added dropwise to pyridinium chlorochromate (20.87 g, 96.67 mmol) in CH_2Cl_2 (75 mL). The mixture was heated at reflux for 2h and then cooled to rt. Ether (30 mL) was added and the dark mixture was filtered through Florisil® (100-200 mesh) with ether rinses.

The solvent was removed and the product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **4** (2.54 g, 8.63 mmol, 75%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 9.80 (1H, t, *J* = 1.5 Hz), 6.74 (1H, d, *J* = 8 Hz), 6.63 (2H, m), 3.77 (3H, s), 2.87 (2H, m), 2.73 (2H, m), 0.96 (9H,s), 0.12 (6H, s); ^{13}C NMR ($CDCl_3$) δ 202.05, 151.13, 143.74, 133.95, 121.12, 120.55, 112.71, 55.76, 45.72, 28.11, 25.97, 18.67, -4.40; EI *m/z* (relative intensity) 294 (5), 237 (100), 222 (62), 194 (25), 179 (62), 163 (36).

***S*AMP Hydrazone 5.** (*S*)-1-amino-2-methoxymethylpyrrolidine (*S*AMP, 0.466 g, 3.58 mmol) was added to aldehyde **4** (1.05 g, 3.58 mmol) at 0°C. The solution was stirred for 30 min, then warmed to rt and stirred overnight (20h). Ether (120 mL) and water (20 mL) were added. The aqueous layer was extracted with ether (2 x 10 mL). The combined ether layers were dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **5** (1.22 g, 3.01 mmol, 84%) as a colorless oil : ^{1}H NMR ($CDCl_3$) δ 6.77-6.61 (4H, m), 3.78 (3H, s), 3.56-3.42 (1H, m), 3.40-3.34 (3H, m), 3.37 (3H, s), 2.76-2.63 (3H, m), 2.55-2.45 (2H, m), 1.95-1.84 (4H, m), 0.98 (9H, s), 0.14 (6H, s); ^{13}C NMR ($CDCl_3$) δ 150.90, 143.29, 138.18, 135.32, 120.85, 120.74, 112.81, 75.10, 63.68, 59.42, 55.70, 50.64, 35.15, 34.01, 26.85, 25.96, 22.39, 18.65, -4.43; EI *m/z* (relative intensity) 361(100), 179 (76), 155 (32), 109 (20), 73 (93).

***R*AMP Hydrazone 6.** The procedure for **5** was followed except (*R*)-1-amino-2-methoxymethylpyrrolidine (*R*AMP, 0.466 g, 3.58 mmol) was used in place of *S*AMP. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **6** (1.19 g, 2.93 mmol, 82%) as a colorless oil : ^{1}H NMR ($CDCl_3$) δ 6.77-6.61 (4H, m), 3.78 (3H, s), 3.56-3.42 (1H, m), 3.40-3.34 (3H, m), 3.37 (3H, s), 2.76-2.63 (3H, m), 2.55-2.45 (2H, m), 1.95-1.84 (4H, m), 0.98 (9H, s), 0.14 (6H, s); ^{13}C NMR ($CDCl_3$) δ 150.89, 143.28, 138.16, 135.31, 120.85, 120.73, 112.78, 75.09, 63.68, 59.43, 55.69, 50.63, 35.16, 34.02, 26.84, 25.96, 22.39, 18.65, -4.43; EI *m/z* (relative intensity) 361(96), 179 (80), 155 (34), 109 (22), 73 (100).

Alkylated *S*AMP Hydrazone 7. Anhydrous ether (1.2 mL) and diisopropylamine (0.42 mL, 3.2 mmol) were combined and cooled to 0°C under an argon atmosphere. *n*-Butyllithium (2.0 mL, 1.6M in hexanes, 3.2 mmol) was added dropwise and the solution was then stirred for 15 min. *S*AMP hydrazone **5** (0.88 g, 2.2 mmol) was dissolved in anhydrous ether (2.3 mL) and added dropwise. The reaction mixture was stirred for 5.5 h at 0°C and then cooled to -120°C in a pentane/liquid nitrogen bath. Benzyl chloromethyl ether (0.507 g, 3.2 mmol) was added dropwise. The temperature was maintained at -120°C for 20 min and then was allowed to warm to rt and stirred for 20h (overnight). The mixture was diluted with ether (100 mL) and water (20 mL). The aqueous layer was extracted with ether (2 x 10 mL). The combined ether layers were washed with brine (20 mL), dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **7** (0.892 g, 1.69 mmol, 77%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 7.33-7.26 (5H, m), 6.73-6.52 (4H, m), 4.46 (2H, s), 3.72 (3H, s), 3.54-3.19 (7H, m), 3.33 (3H, s), 2.87-2.60 (3H, m), 1.97-1.69 (4H, m), 0.96 (9H, s), 0.11 (6H, s); ^{13}C NMR ($CDCl_3$) δ 150.79, 143.27,

138.88, 133.58, 128.64, 128.50, 127.73, 127.66, 121.78, 120.68, 113.56, 74.94, 73.21, 71.94, 63.47, 59.39, 55.64, 50.26, 44.55, 36.53, 26.88, 25.95, 22.28, 18.63, -4.44; EI *m/z* (relative intensity) 526 (3), 481 (58), 373 (4), 275 (35), 179 (29), 160 (18), 91 (100), 73 (31).

Alkylated *R*AMP Hydrazone 8. The procedure for **7** was repeated with the following changes. Anhydrous ether (18 mL) was used instead of 1.2 mL. *R*AMP hydrazone **6** (0.88 g, 2.2 mmol) was used in place of **5**. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **8** (0.869 g, 1.65 mmol, 75%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 7.38-7.26 (5H, m), 6.75-6.52 (4H, m), 4.46 (2H, s), 3.72 (3H, s), 3.58-3.19 (7H, m), 3.33 (3H, s), 2.86-2.62 (3H, m), 1.97-1.71 (4H, m), 0.96 (9H, s), 0.11 (6H, s); ^{13}C NMR ($CDCl_3$) δ 150.79, 143.27, 138.88, 133.58, 128.64, 128.50, 127.73, 127.66, 121.78, 120.68, 113.56, 74.94, 73.21, 71.94, 63.47, 59.39, 55.64, 50.26, 44.55, 36.53, 26.88, 25.95, 22.28, 18.63, -4.44; EI *m/z* (relative intensity) 526 (2), 481 (52), 373 (12), 275 (26), 179 (51), 160 (16), 91 (100), 73 (38).

Aldehyde 9. Alkylated *S*AMP hydrazone **7** (0.288 g, 0.547 mmol) was dissolved in CH_2Cl_2 (5 mL) under a nitrogen atmosphere and cooled to -78°C in a dry ice/ethanol bath. Ozone was bubbled through the rapidly stirred solution until the reaction was complete as judged by TLC (~ 35 min). The solution was warmed to rt and the solvent was removed. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **9** (0.179 g, 0.432 mmol, 79%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 9.76 (1H, d, J = 1.4 Hz), 7.35-7.25 (5H, m), 6.71 (1H, d, J = 8 Hz), 6.64-6.53 (2H, m), 4.46 (2H, s), 3.72 (3H, s), 3.70-3.55 (2H, m), 2.98 (1H, m), 2.84-2.69 (2H, m), 0.97 (9H, s), 0.12 (6H, s); ^{13}C NMR ($CDCl_3$) δ 203.66, 151.08, 143.78, 138.10, 132.05, 128.64, 127.97, 127.81, 121.40, 121.03, 113.19, 73.57, 67.93, 55.68, 54.05, 31.72, 25.93, 18.63, -4.43; EI *m/z* (relative intensity) 414 (1), 357 (41), 249 (37), 234 (31), 205 (44), 193 (31), 179 (100), 105 (90), 91 (60).

Aldehyde 10. The procedure for **9** was repeated except alkylated *R*AMP hydrazone **8** (0.567 g, 1.08 mmol) was used in place of **7**. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **10** (0.334 g, 0.806 mmol, 75%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 9.76 (1H, d, J = 1.3 Hz), 7.38-7.25 (5H, m), 6.72 (1H, d, J = 8 Hz), 6.63-6.53 (2H, m), 4.46 (2H, s), 3.72 (3H, s), 3.69-3.54 (2H, m), 2.98 (1H, m), 2.84-2.69 (2H, m), 0.97 (9H, s), 0.12 (6H, s); ^{13}C NMR ($CDCl_3$) δ 203.66, 151.08, 143.78, 138.10, 132.05, 128.64, 127.97, 127.81, 121.40, 121.03, 113.19, 73.57, 67.93, 55.68, 54.05, 31.72, 25.93, 18.63, -4.43; EI *m/z* (relative intensity) 414 (1), 357 (36), 249 (17), 221 (25), 205 (45), 193 (32), 179 (100), 105 (61), 91 (51).

(*R*,*R*)-Diol Derivative 11. (2*R*, 3*R*)-2,3-butanediol (0.30 g, 3.3 mmol), triethylamine (1.34 g, 13.2 mmol) and THF (15 mL) were combined under an argon atmosphere at 0°C. Trimethylsilyl chloride (0.90 g, 8.3 mmol) was added dropwise to immediately form a thick white precipitate. The mixture was warmed to rt and stirred overnight (20h). The white suspension was poured into water (25 mL) and ether (50 mL). Saturated aqueous sodium bicarbonate (50 mL) was added and the mixture was extracted. The ether layer was separated, extracted with water (50 mL) and brine (50 mL), dried with $MgSO_4$,

filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 95:5) to yield **11** (0.712 g, 3.04 mmol, 92%) as a colorless oil : ^{1}H NMR ($CDCl_3$) δ 3.60 (2H, m), 1.04 (6H, d, *J* = 6 Hz), 0.09 (18H, s); ^{13}C NMR ($CDCl_3$) δ 72.30, 18.37, 0.44; EI *m/z* (relative intensity) 219 (2), 147 (44), 133 (15), 117 (100), 73 (86).

Chiral Acetal 12. Trimethylsilyl triflate (0.001 g, 0.004 mmol) was added to CH_2Cl_2 at -78°C under an argon atmosphere. (*R,R*)-diol derivative **11** (0.056 g, 0.24 mmol) and aldehyde **9** (0.10 g, 0.24 mmol) were added sequentially and the mixture was stirred for 3h at -78°C. The mixture was then warmed to 0°C and pyridine (a few drops) was added to quench the reaction. After pouring into saturated aqueous sodium bicarbonate (5 mL), the mixture was extracted with ether (3 x 5 mL). The ether layers were combined, dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **12** (0.089g, 0.18 mmol, 76%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 7.30 (5H, s (broad)), 6.77-6.59 (3H, m), 5.14 (1H, d, *J* = 4 Hz), 4.44 (2H, s), 3.73 (3H, s), 3.60 (2H, m), 3.46 (2H, d, *J* = 5 Hz), 2.84 (1H, dd, *J* = 13.8 Hz and 6 Hz), 2.65 (1H, dd, *J* = 13.6 Hz and 9 Hz), 2.15 (1H, m), 1.26 (6H, m), 0.99 (9H, s), 0.14 (6H, s); ^{13}C NMR ($CDCl_3$) δ 150.82, 143.23, 138.91, 133.84, 128.46, 127.63, 127.57, 121.73, 120.70, 113.49, 103.20, 79.90, 78.58, 73.25, 68.87, 55.64, 45.27, 32.20, 25.96, 18.64, 17.60, 17.11, -4.43; EI *m/z* (relative intensity) 486 (2), 429 (40), 283 (39), 193 (54), 179 (88), 105 (79), 101 (75), 91 (84), 73 (100).

Chiral Acetal 13. The procedure for **12** was repeated except aldehyde **10** was used instead of **9**. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 3:1) to yield **13** (0.084g, 0.17 mmol, 72%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 7.38-7.25 (5H, m), 6.76-6.60 (3H, m), 5.14 (1H, d, *J* = 4 Hz), 4.43 (2H, s), 3.73 (3H, s), 3.59 (2H, m), 3.47 (2H, d, *J* = 5.7 Hz), 2.82 (1H, dd, *J* = 13.8 Hz and 5.8 Hz), 2.65 (1H, dd, *J* = 13.6 Hz and 9 Hz), 2.15 (1H, m), 1.29 (3H, d, *J* = 5.7 Hz), 1.22 (3H, d, *J* = 5.7 Hz), 0.99 (9H, s), 0.14 (6H, s); ^{13}C NMR ($CDCl_3$) δ 150.81, 143.23, 138.90, 133.88, 128.44, 127.62, 127.56, 121.71, 120.70, 113.52, 103.13, 79.92, 78.55, 73.25, 68.94, 55.63, 45.19, 32.14, 25.96, 18.63, 17.60, 17.12, -4.43; EI *m/z* (relative intensity) 486 (3), 429 (56), 283 (37), 193 (47), 179 (74), 105 (77), 101 (74), 91 (83), 73 (100).

Protected Phenol 15. Imidazole (1.97 g, 28.9 mmol), *t*-butyldimethylsilyl chloride (2.41 g, 15.9 mmol), and 2-methoxy-4-methylphenol **14** (2.00 g, 14.5 mmol) were dissolved in DMF (20 mL) and stirred for 3h at rt. Ether (25 mL) was added and the mixture was extracted with saturated aqueous sodium bicarbonate (25 mL) and brine (25 mL). The ether layer was dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 95:5) to yield **15** (3.15 g, 12.5 mmol, 86%) as a colorless oil : ^{1}H NMR ($CDCl_3$) δ 6.73-6.56 (3H, m), 3.75 (3H, s), 2.25 (3H, s), 0.96 (9H, s), 0.11 (6H, s); ^{13}C NMR ($CDCl_3$) δ 150.83, 142.92, 131.45, 121.32, 120.86, 113.43, 55.68, 25.99, 21.32, 18.67, -4.45 ; EI *m/z* (relative intensity) 195 (50), 180 (100), 165 (15), 150 (10), 73 (15), 59 (17).

Brominated Protected Phenol 16. *N*-bromosuccinimide (2.22 g, 12.5 mmol) and benzoyl peroxide (0.300 g, 1.25 mmol) were dissolved in CCl_4 (25 mL). To this solution,

protected phenol **15** (3.09 g, 12.2 mmol) dissolved in CCl_4 (5 mL) was added and the mixture was refluxed for 3h. The reaction mixture was filtered to remove a solid impurity and ether (50 mL) was added to the filtrate. The ether layer was extracted with saturated aqueous sodium bicarbonate (50 mL) and brine (50 mL). The organic layer was then dried with $MgSO_4$, filtered and concentrated. The crude yellow oil was found to be unstable and therefore was used in the next step with no further purification. : ^{1}H NMR ($CDCl_3$) δ 6.87-6.71 (3H, m), 4.48 (2H, s), 3.85 (3H, s), 0.99 (9H, s) 0.15 (6H, s); ^{13}C NMR ($CDCl_3$) δ 151.24, 145.66, 131.27, 121.94, 121.07, 113.17, 55.88, 34.90, 26.09, 18.84, -4.21; EI *m/z* (relative intensity) 275 (14), 273 (14), 251 (19), 179 (100), 149 (18), 73 (15), 59 (10).

Wittig Reagent 17. Crude brominated phenol **16** (4.04 g, 12.2 mmol) was dissolved in toluene (30 mL), and triphenylphosphine (3.20 g, 12.2 mmol) was added. The mixture was heated to reflux for 19h and the crude solid product was isolated by filtration. The solid was dissolved in boiling CH_2Cl_2 (~ 100 mL) and then concentrated (~ 40 mL) until cloudy. After cooling to rt, hexane (~ 10 mL) was carefully layered above the CH_2Cl_2 solution and stored in the freezer overnight. The solid (impurity) was removed by filtration. The filtrate was again concentrated until cloudy and an equal volume of hexane was layered above the CH_2Cl_2 solution. After storing overnight in the freezer, pure white solid product **17** (3.62 g, 6.10 mmol, 50% from **15**) was isolated by filtration : ^{1}H NMR ($CDCl_3$) δ 7.80-7.54 (15H, m), 6.88 (1H, t, *J* = 2.1 Hz), 6.58 (1H, dd, *J* = 8 Hz and 0.5 Hz), 6.38 (1H, dt, *J* = 8 Hz and 2.5 Hz), 5.30 (2H, d, *J* = 13.7 Hz), 3.48 (3H, s), 0.93 (9H, s), 0.07 (6H, s); ^{13}C NMR ($CDCl_3$) δ 151.29, 145.35, 135.04, 134.78, 130.24, 123.63, 121.12, 120.22, 119.13, 117.43, 116.11, 55.82, 25.88, 18.64, -4.50.

***Trans*-alkene 18.** Wittig reagent **17** (0.29 g, 0.48 mmol) was mixed with THF (4 mL) and sealed in a flask purged with argon. After cooling to 0°C, *n*-butyllithium (0.30 mL, 1.6M in hexanes, 0.48 mmol) was added dropwise. The resulting red mixture was warmed to rt and stirred for 30 min. After cooling to 0°C, a solution of aldehyde **9** (0.10 g, 0.24 mmol) in THF (2 mL) was added dropwise to the red mixture. The resulting yellow mixture was warmed to rt and stirred overnight (19h). The reaction was quenched with water (2 mL) and then diluted with ether (5 mL) and additional water (2 mL). The two layers were separated and the aqueous layer was extracted with ether (2 x 10 mL). The combined organic layers were washed with water (2 x 5 mL), dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 95:5) to yield **18** (0.113 g, 0.174 mmol, 72%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 7.33 (5H, m), 6.80-6.58 (6H, m), 6.23 (1H, d, *J* = 16 Hz), 5.98 (1H, dd, *J* = 16 Hz and 7.7 Hz), 4.52 (2H, s), 3.79 (3H, s), 3.68 (3H, s), 3.47 (2H, d, *J* = 5.3 Hz), 2.89-2.61 (3H, m), 0.99 (9H, s), 0.98 (9H, s), 0.14 (6H, s), 0.13 (6H, s); ^{13}C NMR ($CDCl_3$) δ 151.12, 150.69, 144.69, 143.30, 138.80, 133.65, 131.85, 130.86, 129.61, 128.56, 127.83, 127.73, 121.79, 121.07, 120.73, 119.22, 113.79, 109.93, 73.29, 73.02, 55.67, 55.63, 45.19, 38.26, 25.96, 18.69, 18.65, -4.44; EI *m/z* (relative intensity) 397 (5), 379 (1), 291 (37), 251 (68), 179 (79), 105 (5), 91 (100), 73 (87).

***Trans*-alkene 19.** Wittig reagent **17** (0.212 g, 0.357 mmol) was mixed with THF (3 mL) and sealed in a flask purged with argon. After cooling to 0°C, *n*-butyllithium (0.22 mL,

1.6M in hexanes, 0.36 mmol) was added dropwise. The resulting red mixture was warmed to rt and stirred for 30 min. After cooling to 0°C, a solution of aldehyde **10** (0.074 g, 0.179 mmol) in THF (1.5 mL) was added dropwise to the red mixture. The resulting yellow mixture was warmed to rt and stirred overnight (19h). The reaction was quenched with water (2 mL) and then diluted with ether (5 mL) and additional water (3 mL). The two layers were separated and the aqueous layer was extracted with ether (2 x 10 mL). The combined organic layers were washed with water (2 x 5 mL), dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 95:5) to yield **19** (0.073 g, 0.11 mmol, 63%) as a yellow oil : ^{1}H NMR ($CDCl_3$) δ 7.33 (5H, m), 6.82-6.58 (6H, m), 6.24 (1H, d, *J* = 16 Hz), 5.98 (1H, dd, *J* = 16 Hz and 7.7 Hz), 4.52 (2H, s), 3.79 (3H, s), 3.69 (3H, s), 3.46 (2H, d, *J* = 5 Hz), 2.93-2.60 (3H, m), 0.99 (9H, s), 0.98 (9H, s), 0.14 (6H, s), 0.13 (6H, s); ^{13}C NMR ($CDCl_3$) δ 151.12, 150.68, 144.68, 143.29, 138.79, 133.64, 131.84, 130.86, 129.59, 128.55, 127.82, 127.72, 121.79, 121.06, 120.72, 119.22, 113.78, 109.92, 73.28, 73.01, 55.65, 55.61, 45.19, 38.25, 25.96, 18.68, 18.64, -4.44; EI *m/z* (relative intensity) 397 (17), 379 (6), 291 (29), 251 (62), 179 (98), 105 (14), 91 (100), 73 (41).

Trimethylsilyl ether 20. Alkene **18** (0.066 g, 0.092 mmol) was dissolved in 1,2-dichloroethane (1.8 mL). Zinc iodide (0.147 g, 0.462 mmol), *n*Bu_4NI (0.051 g, 0.139 mmol), and $PhSSiMe_3$ (0.169 g, 0.924 mmol) were sequentially added and the mixture was stirred for 2.5 h at rt. The mixture was poured into CH_2Cl_2 (30 mL) and extracted with saturated aqueous barium hydroxide (10 mL), water (10 mL) and brine (10 mL). The CH_2Cl_2 layer was dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 95:5) to yield **20** (0.038 g, 0.060 mmol, 65%) as a colorless oil : ^{1}H NMR ($CDCl_3$) δ 6.74 (4H, m), 6.63 (2H, m), 6.20 (1H, d, *J* = 16 Hz), 5.91 (1H, dd, *J* = 16 Hz and 7.6 Hz), 3.78 (3H, s), 3.70 (3H, s), 3.55 (2H, d (broad), *J* = 4.7 Hz), 2.81 (1H, m), 2.57 (2H, m), 0.97 (9H, s), 0.96 (9H, s), 0.12 (6H, s), 0.11 (6H, s), 0.09 (9H, s); ^{13}C NMR ($CDCl_3$) δ 151.11, 150.68, 144.64, 143.24, 133.96, 131.93, 130.96, 129.67, 121.76, 121.07, 120.72, 119.16, 113.77, 109.89, 65.56, 55.65, 47.40, 37.87, 25.96, 18.67, -0.16, -4.43; EI *m/z* (relative intensity) 379 (5), 289 (56), 251 (18), 217 (19), 179 (35), 73 (100).

Trimethylsilyl ether 21. Alkene **19** (0.041 g, 0.063 mmol) was dissolved in 1,2-dichloroethane (1.3 mL). Zinc iodide (0.101 g, 0.316 mmol), *n*Bu_4NI (0.035 g, 0.095 mmol), and $PhSSiMe_3$ (0.115 g, 0.63 mmol) were sequentially added and the mixture was stirred for 1 h at rt. The mixture was poured into CH_2Cl_2 (30 mL) and extracted with saturated aqueous barium hydroxide (10 mL), water (10 mL) and brine (10 mL). The CH_2Cl_2 layer was dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 95:5) to yield **21** (0.023 g, 0.037 mmol, 59%) as a colorless oil : ^{1}H NMR ($CDCl_3$) δ 6.74 (4H, m), 6.63 (2H, m), 6.20 (1H, d, *J* = 16 Hz), 5.91 (1H, dd, *J* = 16 Hz and 7.6 Hz), 3.78 (3H, s), 3.70 (3H, s), 3.55 (2H, d (broad), *J* = 4.7 Hz), 2.81 (1H, m), 2.57 (2H, m), 0.97 (9H, s), 0.96 (9H, s), 0.12 (6H, s), 0.11 (6H, s), 0.09 (9H, s); ^{13}C NMR ($CDCl_3$) δ 151.11, 150.67, 144.63, 143.24, 133.96, 131.92, 130.96, 129.67, 121.76, 121.07, 120.72, 119.15, 113.76, 109.89, 65.56, 55.64, 47.40, 37.87, 25.96, 18.68, -0.16, -4.43; EI *m/z* (relative intensity) 370 (3), 289 (100), 251 (42), 217 (36), 179 (58), 73 (59).

(*R*)-imperanene 1a. Trimethylsilyl ether **20** (0.021 g, 0.033 mmol) was dissolved in THF (1 mL) and TBAF (0.11 mL, 1.0M in THF, 0.11 mmol) was added dropwise at rt. The mixture initially turned cloudy and then became clear as it was stirred for 26 min. The solution was poured into ether (10 mL) and extracted with water (2 x 7 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 1:2) to yield **1a** (0.009 g, 0.027 mmol, 82%) as a pale yellow oil : $[\alpha]^{25.4}_D$ -633° (*c*=0.01 g/mL, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.83 (3H, s), 6.78 (1H, s), 6.67 (2H, m), 6.34 (1H, d, *J* = 16 Hz), 5.90 (1H, dd, *J* = 16 Hz and 8 Hz), 5.61 (1H, s (broad)), 5.48 (1H, s, (broad)), 3.87 (3H, s), 3.81 (3H, s), 3.64 (1H, m), 3.54 (1H, m), 2.68 (2H, m), 2.61 (1H, m); ^{13}C NMR ($CDCl_3$) δ 146.80, 146.51, 145.52, 144.12, 132.37, 131.73, 129.93, 128.61, 122.07, 119.95, 114.63, 114.37, 111.95, 108.39, 65.44, 56.11, 56.09, 47.84, 37.88; EI *m/z* (relative intensity) 330 (3), 193 (34), 175 (52), 143 (28), 137 (100), 115 (32).

(*S*)-imperanene 1b. Trimethylsilyl ether **21** (0.020 g, 0.032 mmol) was dissolved in THF (1 mL) and TBAF (0.11 mL, 1.0M in THF, 0.11 mmol) was added dropwise at rt. The mixture initially turned cloudy and then became clear as it was stirred for 20 min. The solution was poured into ether (10 mL) and extracted with water (2 x 7 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated. The product was purified by silica gel flash chromatography (hexane/ethyl acetate, 1:2) to yield **1b** (0.008 g, 0.024 mmol, 75%) as a pale yellow oil : $[\alpha]^{25.8}_D$ +610° (*c*=0.007 g/mL, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.83 (3H, s), 6.78 (1H, s), 6.67 (2H, m), 6.34 (1H, d, *J* = 16 Hz), 5.90 (1H, dd, *J* = 16 Hz and 8 Hz), 5.59 (1H, s (broad)), 5.46 (1H, s, (broad)), 3.88 (3H, s), 3.81 (3H, s), 3.64 (1H, m), 3.54 (1H, m), 2.68 (2H, m), 2.61 (1H, m); ^{13}C NMR ($CDCl_3$) δ 146.81, 146.53, 145.54, 144.14, 132.38, 131.74, 129.95, 128.63, 122.09, 119.96, 114.64, 114.39, 111.97, 108.42, 65.46, 56.12, 56.10, 47.85, 37.89; EI *m/z* (relative intensity) 330 (7), 193 (67), 175 (71), 143 (24), 137 (100), 115 (20).