Palladium-Catalyzed Intramolecular Cyclization of Vinyl and Aryl Triflates. Associated Regioselectivity of the β-Hydride Elimination Step

Shaowo Liang and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210 USA

The Pd(0)-catalyzed intramolecular olefination of vinyl and aryl triflates has been studied with a view to gaining insight into the question of kinetically preferred reductive elimination when at least two options are available. In either series, a non-activated alkene participant was found to be converted most readily into the non-conjugated cyclization product. This trend is seen despite the more forcing conditions necessary to engage the less reactive aryl triflates in ring closure. On the other hand, when the pendant chain is terminated by an α-methyl acrylate unit, the conjugated diene is kinetically preferred. The two reactions appear to be closely balanced energetically since product distributions are not greatly disparate. Nevertheless, their complementarity could be utilized to advantage in the synthesis of polycyclic molecules possessing multiple stereogenic centers.

Dedicated to Professor Lars Skattebøl on the occasion of his 65th birthday.

The ability of palladium catalysts to effect the regioselective coupling of aryl, vinyl and benzyl halides to alkenes has been known for some time.[1] More recently, the scope and utility of this olefination has been extended to include aryl[2] and vinyl triflates[3] as reaction partners and to encompass intramolecular variants.[4] In the great majority of examples studied, however, the substitution patterns of the alkene participants have been quite simple. In somewhat more elaborate systems typified by 1, cyclization can be reliably assumed to involve initial oxidative addition by Pd(0) into the triflate C–O bond to generate 2, which subsequently experiences carbon–carbon bond insertion to deliver 3 (Scheme 1).

In cases such as this, the directionality of β-hydride elimination takes on significance. One of the possibilities that emerges involves loss of the allylic proton to generate the conjugated diene 4. This pathway likely requires a synplanar arrangement of the allylic C–H and adjoining
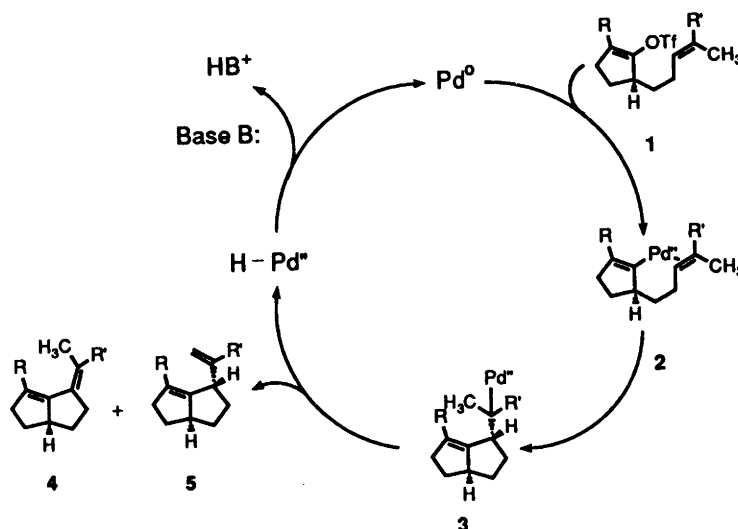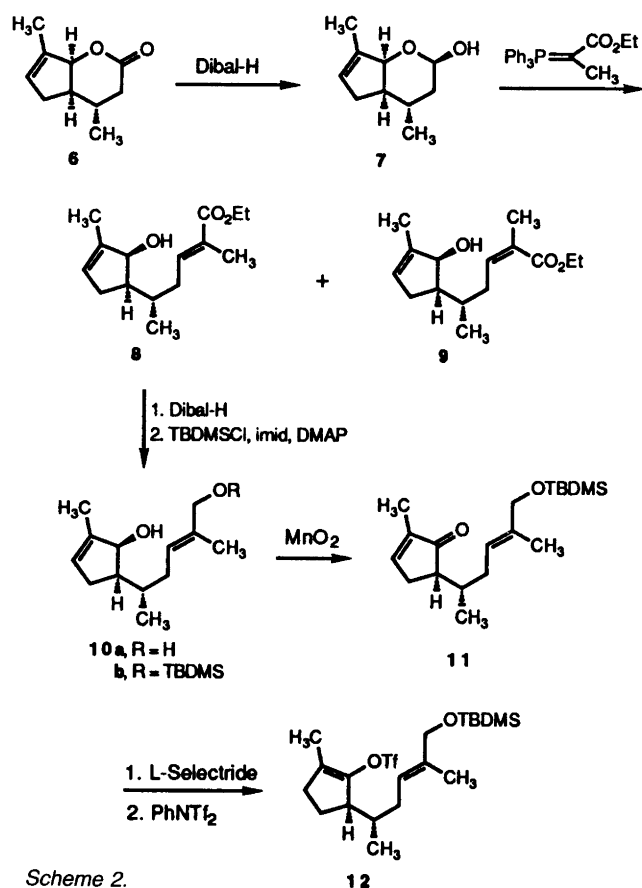

Scheme 1.

* To whom correspondence should be addressed.

C–Pd bonds. The steric congestion associated with attaining this alignment could increase the energy requirements of the transition state. The associated reaction rate would in turn be ameliorated. The stage could then be set for competing hydrogen atom loss from methyl to give 5. Since three hydrogens are available at this site, probability factors are more favorable. However, product 5 does not profit from the extended conjugation available to 4.

Some understanding of the regioselectivities involved in these potentially useful cyclizations was considered desirable as a prelude to their possible implementation in several natural product syntheses. For this reason, we undertook to examine a small group of cyclopentenyl and aryl triflates. Both mechanistic options were found to operate at levels that differ appreciably from one substrate to another.

Results and discussion

Dibal-H reduction of the lactone 6[5] in toluene at −78 °C afforded the lactol 7 as a single stereoisomer. The assignment of stereochemistry rests on the assumption that hydride attack proceeds more rapidly from the less hindered α-face of the carbonyl group to position the hydroxy group β (axial). Wittig reaction[6] of 7 with (ethoxycarbonyl-ethylidene)triphenylphosphorane[7] in refluxing benzene for 20 h resulted in the formation of a mixture of the E- and

Scheme 2.
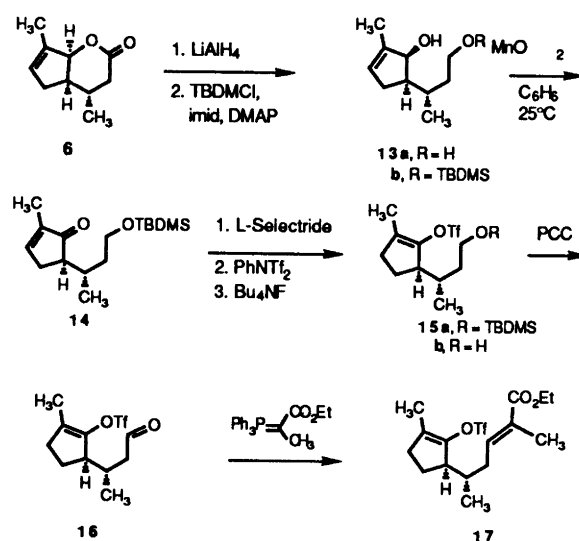
Z-esters 8 (88 %) and 9 (5 %) (Scheme 2). These isomers were easily distinguished on the basis of their ^{1}H NMR spectra. Thus, the β-vinyl proton in 8 (δ 6.87 in CDCl$_3$) experiences considerable deshielding relative to that in 9 (δ 6.15) because of its spatial proximity to the carbonyl group. For the same reason, one of the allylic protons in 9 (δ 2.98) is shifted more downfield than that in 8 (δ 2.53).

Following reduction of 8 with Dibal-H, the terminal hydroxy group in 10a was protected as its tert-butyl-dimethylsilyl ether. Subsequently, the secondary allylic hydroxyl was oxidized with manganese dioxide in benzene at room temperature.[8] Cyclopentenone 11 was thereby produced smoothly in 90 % yield without epimerization at C-5. This was not the case with chromium-based oxidants,[9] especially when prolonged reaction times were required. Treatment of 11 with L-Selectride at −78 °C and direct trapping of the resultant regiospecifically generated enolate with N-phenyltriflimide[10] provided vinyl triflate 12 in 84 % yield.

In order to position an electron-withdrawing substituent on the sidechain double bond, the lactone 6 was reduced with lithium aluminum hydride and regioselectively silylated to give 13b (Scheme 3). Following conversion into the enol triflate 15a as before, the protecting group was removed and conversion into the aldehyde effected via PCC oxidation. Wittig condensation in the prediscribed manner furnished 17 along with trace amounts of the Z-isomer.

Exposure of 12 to tetrakis(triphenylphosphine)palladium in the presence of lithium chloride and lithium carbonate at the reflux temperature of THF for 3 h resulted in smooth and efficient conversion into 18 (91 %) (Scheme 4). Analogous processing of 17 led, in less than 3 h, to a 5:1 mixture of 19 and 20. The stereochemical assignments to 18–20 were confirmed by appropriate NOE measurements (Fig. 1).

The exclusive formation of 18 suggests that β-hydride elimination to form the conjugated diene suffers from

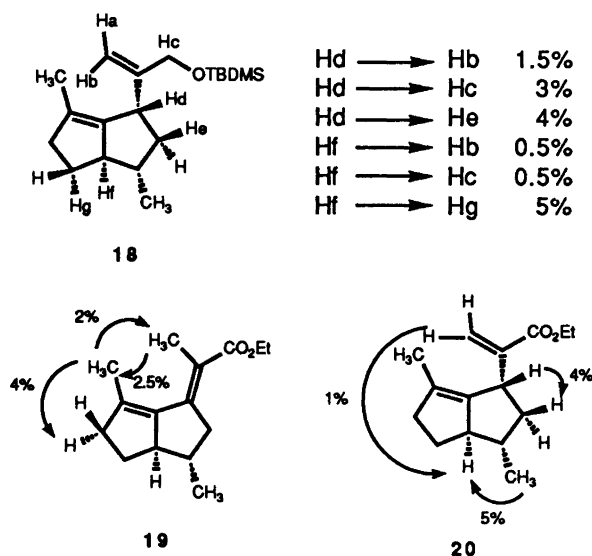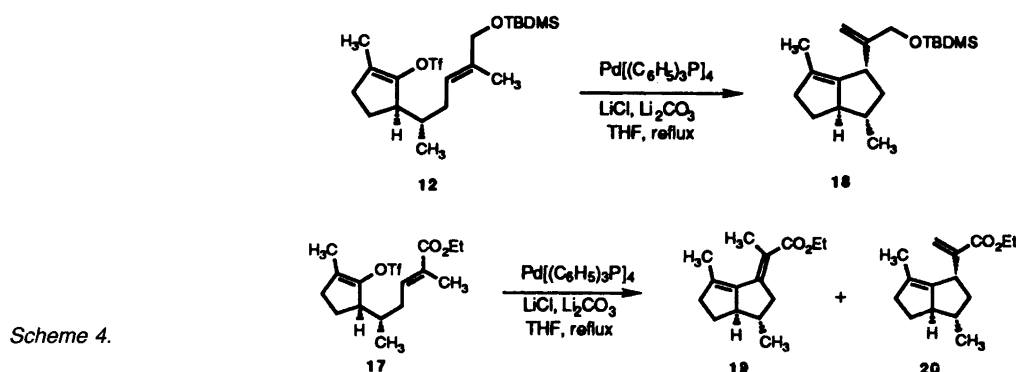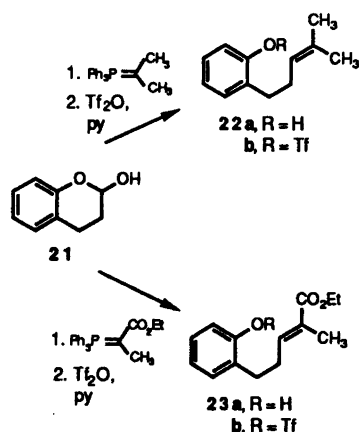Scheme 3.

Scheme 4.

Fig. 1. NOE Studies of 18–20.

Hd	⟶	Hb	1.5%
Hd	⟶	Hc	3%
Hd	⟶	He	4%
Hf	⟶	Hb	0.5%
Hf	⟶	Hc	0.5%
Hf	⟶	Hg	5%

modest steric inhibition. The unfavorable energetics associated with this regiochemical outcome do not appear to be excessively elevated, since they can be offset to a substantial degree when extended conjugation to an ester carbonyl can develop as in **19**.

Longer reaction times (up to 24 h in refluxing THF) did not alter isomer ratios. Nor did resubmission of pure samples of **19** and **20** to the reaction conditions induce isomerization. Accordingly, the product distributions give evidence of being under kinetic control.
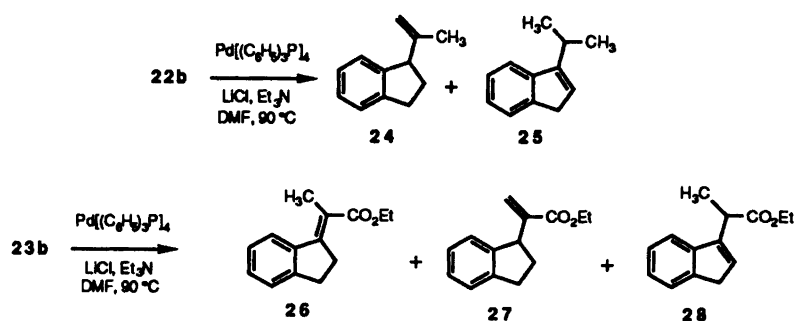
Scheme 5.

Further insight into these trends was gained by investigating the intramolecular cyclization of the aryl triflates **22b** and **23b**. Reduction of dihydrocoumarin with Dibal-H in ether at −78 °C afforded 2-chromanol (**21**) in 87 % yield according to precedent.[11] Wittig reaction of **21** with isopropyltriphenylphosphonium bromide in the presence of KHMDS gave the phenol **22a** (69 %), which underwent ready conversion into the triflate **22b** (Scheme 5). The standard (ethoxycarbonylethylidene)triphenylphosphorane procedure was utilized to produce **23a**, from which **23b** was derived (82 %) by reaction with triflic anhydride in pyridine.

Palladium-catalyzed intramolecular cyclization of **22b** afforded the hydrocarbons **24** and **25** (1:1) inefficiently in refluxing THF with lithium carbonate as base. When the ring closure was performed instead in DMF at 90 °C with triethylamine as a base, a good yield of **24** and **25** (ratio now 6:1) was realized (Scheme 6), along with trace amounts of unidentified isomers. Cyclization of **23b** in like fashion gave **26** and **27** in major amounts (combined yield of 80 %, ratio 1.5:1) together with **28** (2 %).

The following observations are worthy of emphasis. While the vinyl triflates undergo ready cyclization in THF under catalysis by Pd(0) in the presence of lithium chloride and lithium carbonate, the lower intrinsic reactivity of aryl triflates requires higher reaction temperatures and a solvent of increased polarity to drive ring closure to completion. Further, with an unactivated alkene participant as in **22b**, a larger amount of catalyst is needed to attain a reasonable reaction rate. Double-bond migration was not observed under the first set of conditions, but was noted in the aryl series.

Notwithstanding these differences, a common general trend surfaces across the two series. A non-activated alkene double bond is transformed in either case preferentially into the non-conjugated annulation product. Contrariwise, when the pendant chain is terminated by an α-methylacrylate ester, reductive elimination to give the conjugated product is kinetically preferred. The pair of regioselective processes appear, however, to be rather closely balanced since no dramatically disparate product distributions were uncovered.

Scheme 6.

Experimental

Infrared spectra were recorded with a Perkin-Elmer 1320 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were determined on Bruker WP-300 and AC-300 FT instruments. Combustion analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Exact high resolution mass measurements were determined at The Ohio State University Chemical Instrumentation Center with a Kratos MS-30 mass spectrometer. Capillary gas chromatography analyses were performed with a Carlo Erba Strumentazione Fractovap 4130 unit fitted with a 30 m × 0.25 mm Durabond column set for a flow rate of 2 ml min^{-1}. The column chromatographic purifications were performed with Woelm silica gel (63–200 mesh).

(2R,4S,4aR,7aS)-2,3,4,4a,5,7a-Hexahydro-4,7-dimethyl-cyclopenta[b]pyran-2-ol (7). A solution of the lactone 6[5] (1.58 g, 9.5 mmol) in toluene (50 ml) was treated with Dibal-H (10.5 ml of a 1 M solution in cyclohexane, 10.5 mmol) at −78 °C under nitrogen. The resulting mixture was stirred for 2 h at this temperature before being quenched with methanol (2 ml), and allowed to warm to room temperature. To this mixture was added brine (4 ml), followed by ether (500 ml) and anhydrous magnesium sulfate (8 g). After 1 h of stirring, the solids were separated by filtration and the filter cake was rinsed with ether. The combined organic phases were evaporated under reduced pressure. The crude lactol 7 was obtained as white solid (1.67 g) and used directly in the next step without further purification; IR (KBr): 3360 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.54 (dd, J = 1.2, 1.0 Hz, 1 H), 5.22–5.15 (m, 1 H), 4.61 (d, J = 7.3 Hz, 1 H), 2.94 (d, J = 3.8 Hz, 1 H), 2.52–2.42 (m, 1 H), 2.09–2.00 (m, 1 H), 1.95–1.87 (m, 1 H), 1.82–1.72 (m, 1 H), 1.74 (dd, J = 0.7, 1.5 Hz, 3 H), 1.43–1.07 (m, 2 H), 0.96 (d, J = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 138.90, 128.97, 92.88, 79.04, 45.33, 38.54, 37.06, 31.14, 20.12, 14.08; MS: *m/z* (*M*$^+$) calc. for C$_{10}$H$_{16}$O$_2$: 168.1150, obsd. 168.1159.

Ethyl (2E,5S)- and (2Z,5S)-5-[1R,2S)-2-hydroxy-3-methyl-3-cyclopenten-1-yl]-2-methyl-2-hexenoate (8 and 9). The crude lactol 7 (1.67 g) was dissolved in benzene (200 ml), (ethoxycarbonylthylidene)triphenylphosphorane[7] (5.18 g, 14.3 mmol) was added, and the solution was heated to reflux for 20 h. After cooling, the solvent was removed under reduced pressure, the products were up taken in 15 % ethyl acetate in petroleum ether and separated by column chromatography (silica gel, elution with 15 % ethyl acetate in petroleum ether) to give 2.13 g (88 % overall) of 8 and 125 mg (5 % overall) of 9, both as colorless oils.

For 8: IR (neat): 3470, 1710, 1640 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.87 (m, 1 H), 5.56 (t, J = 1.3 Hz, 1 H), 4.29 (dd, J = 6.2, 6.1 Hz, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 2.57–2.49 (m, 1 H), 2.33–2.25 (m, 1 H), 2.17–2.05 (m, 2 H), 2.00–1.75 (m, 2 H), 1.86 (s, 3 H), 1.81 (s, 3 H), 1.29 (t, J = 7.1 Hz, 3 H), 1.15–0.80 (m, 1 H), 0.94 (d, J = 6.2 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.30, 142.58, 141.00, 128.85, 128.58, 78.99, 60.33, 49.81, 35.00, 34.61, 32.91, 18.13, 14.30 (2 C), 12.51; MS: *m/z* (*M*$^+$ −H$_2$O) calc. 234.1619, obsd. 234.1620. Anal. Calc. for C$_{15}$H$_{24}$O$_3$: C, 71.39; H, 9.59. Found: C, 71.12; H, 9.61.

For 9: IR (neat): 3450, 1700 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.16 (m, 1 H), 5.57 (t, J = 1.3 Hz, 1 H), 4.41 (dd, J = 5.0, 4.0 Hz, 1 H), 4.20 (dq, J = 1.2, 7.2 Hz, 2 H), 2.97 (dd, J = 8.9, 12.5 Hz, 1 H), 2.67 (d, J = 5.1 Hz, 1 H), 2.30–1.95 (series of m, 3 H), 1.92 (d, J = 1.1 Hz, 3 H), 1.90–1.71 (m, 2 H), 1.82 (dd, J = 1.8, 3.9 Hz, 3 H), 1.29 (t, J = 7.1 Hz, 3 H), 0.96 (d, J = 6.1 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.13, 142.95, 142.16, 128.71, 127.47, 78.21, 60.31, 50.97, 35.51, 34.91, 33.71, 20.74, 18.20, 14.68, 14.22; MS: *m/z* (*M*$^+$) calc. 252. 1725, obsd. 252.1764. Anal. Calc. for C$_{15}$H$_{24}$O$_3$: C, 71.39; H, 9.59. Found: C, 71.21; H, 9.61.

(1S,5R)-5-[(1S,3E)-5-Hydroxy-1,4-dimethyl-3-pentenyl]-2-methyl-2-cyclopenten-1-ol (10a). A solution of 8 (900 mg, 3.57 mmol) in dichloromethane (25 ml) and hexane (50 ml) was treated with diisobutylaluminum hydride (14.28 ml of a 1 M solution in hexane, 14.28 mmol) at −78 °C under nitrogen. The mixtue was stirred for 40 min at this temperature, treated with methanol (2.5 ml), and allowed to warm to room temperature. The mixture was treated with brine (5 ml), followed by ether (600 ml) and anhydrous magnesium sulfate (12 g), then stirred for 1 h and filtered. After the removal of solvents, the crude diol 10a (800 mg, colorless oil) was obtained and used directly in the next step; IR (neat): 3340 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ

5.53–5.46 (m, 2 H), 4.26 (br s, 1 H), 3.97 (br s, 2 H), 2.37–2.15 (m, 2 H), 2.07 (br s, 2 H), 2.02–1.83 (m, 1 H), 1.82–1.70 (m, 2 H), 1.78 (br s, 3 H), 1.66 (s, 3 H), 1.44 (br s, 1 H), 0.88 (d, J = 6.0 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.44, 135.58, 128.69, 124.69, 78.84, 68.81, 49.94, 34.98, 33.65, 33.09, 18.07, 14.33, 13.79; MS: m/z (M^+ −H$_2$O) calc. 192.1514, obsd. 192.1503.

(1S,5R)-5-[(1S,3E)-5-(tert-Butyldimethylsiloxy)-1,4-di-methyl-3-pentenyl]-2-methyl-2-cyclopenten-1-ol (10b). The crude diol 10a was subjected to high vacuum for 2 h, then dissolved in DMF (10 ml). To this solution was added imidazole (490 mg, 7.2 mmol), TBDMSCl (603 mg, 4.0 mmol), and DMAP (22 mg, 0.18 mmol). The resulting mixture was stirred for 2 days at room temperature, poured into a precooled (1:1) mixture of ether and saturated sodium hydrogen carbonate solution, and extracted with ether. The combined ethereal phases were washed with saturated sodium hydrogen carbonate solution and brine, then dried. After the removal of solvent, the crude product was purified by column chromatography (silica gel, elution with 5 % ethyl acetate in petroleum ether) to give 948 mg (82 % overall) of 10b as a colorless oil; IR (neat): 3350 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.55–5.49 (m, 2 H), 4.29 (dd, J = 5.3, 5.5 Hz, 1 H), 4.03 (s, 2 H), 2.40–1.67 (series of m, 6 H), 1.80 (d, J = 2.0 Hz, 3 H), 1.63 (s, 3 H), 1.11 (d, J = 7.5 Hz, 1 H), 0.92 (d, J = 5.8 Hz, 3 H), 0.91 (s, 9 H), 0.06 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.51, 135.33, 128.72, 123.20, 78.94, 68.72, 50.10, 35.08, 33.69, 33.22, 25.94 (3 C), 18.40, 18.24, 14.42, 13.63, −5.28 (2 C); MS: m/z (M^+ −H$_2$O) calc. 306.2379, obsd. 306.2417. Anal. Calc. for C$_{19}$H$_{36}$O$_2$Si: C, 70.31; H, 11.18. Found: C, 70.33; H, 11.18.

(5R)-5-[(1S,3E)-5-(tert-Butyldimethylsiloxy)-1,4-dimethyl-3-pentenyl]-2-methyl-2-cyclopentenone (11). A mixture of 10b (700 mg, 2.16 mmol) and manganese dioxide (3.76 g, 43.2 mmol, 20 equiv.) in dry benzene (70 ml) was stirred for 2 days at room temperature under nitrogen. After filtration through Celite and rinsing of the filter cake with ether, the combined organic phases were evaporated and the crude product was purified by column chromatography (silica gel, elution with 5 % ethyl acetate in petroleum ether) to give 626 mg (90 %) of 11 as a colorless oil; IR (neat): 1700, 1640 cm^{-1}; ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 6.57 (dd, J = 1.4, 1.6 Hz, 1 H), 5.44 (qt, J = 1.4, 7.5 Hz, 1 H), 3.98 (s, 2 H), 2.32–2.23 (m, 2 H), 2.10–1.84 (m, 4 H), 1.64 (m, 3 H), 1.58 (s, 3 H), 0.98 (s, 9 H), 0.69 (d, J = 6.7 Hz, 3 H), 0.07 (s, 6 H); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 209.89, 155.56, 142.38, 136.09, 123.40, 68.96, 48.77, 34.24, 33.29, 28.48, 26.10 (3 C), 18.54, 14.64, 13.65, 10.25, −5.12 (2 C); MS: m/z (M^+ −C$_4$H$_9$) calc. 265.1624, obsd. 265.1675. Anal. Calc. for C$_{19}$H$_{34}$O$_2$Si: C, 70.75; H, 10.62. Found: C, 70.79; H, 10.60.

PCC oxidation of 10b. A solution of 10b (34 mg, 0.1 mmol) in dichloromethane (10 ml) was treated with PCC on

neutral alumina (220 mg) and mechanically stirred under nitrogen at room temperature. After 16 h of stirring (starting alcohol all consumed), ether (10 ml) was added and the mixture was filtered through Celite. The filter cake was rinsed with ether, the combined organic phases were evaporated, and the residue was purified by column chromatography (silica gel, elution with 5 % ethyl acetate in petroleum ether) to give 8.6 mg (27 %) of the enone 11 (spectroscopically identical with the product obtained above) and 12.8 mg (40 %) of the epimerized enone as a colorless oil; IR (neat): 1710, 1635 cm^{-1}; ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 6.61 (dd, J = 1.3, 1.4 Hz, 1 H), 5.41 (qt, J = 1.4, 7.5 Hz, 1 H), 4.00 (s, 2 H), 2.38–2.30 (m, 1 H), 2.12 (dd, J = 6.4, 18.6 Hz, 1 H), 1.93–1.80 (m, 1 H), 1.92 (dd, J = 2.4, 18.6 Hz, 1 H), 1.72 (m, 1 H), 1.67 (dd, J = 1.8, 1.6 Hz, 3 H), 1.53 (s, 3 H), 1.41–1.32 (m, 1 H), 1.00 (s, 9 H), 0.59 (d, J = 6.8 Hz, 3 H), 0.09 (s, 6 H); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 207.26, 159.33, 142.02, 135.96, 122.73, 68.71, 43.48, 37.62, 36.89, 32.89, 26.09 (3 C), 18.54, 15.93, 13.66, 10.18, −5.15 (2 C); MS: m/z (M^+ −C$_4$H$_9$) calc. 265.1624, obsd. 265.1594. Anal. Calc. for C$_{19}$H$_{34}$O$_2$Si: C, 70.75; H, 10.62. Found: C, 70.48; H, 10.58.

(5R)-5-[(1S,3E)-5-(tert-Butyldimethylsiloxy)-1,4-dimethyl-3-pentenyl]-2-methyl-1-cyclopentenyl   trifluoromethanesul-fonate (12). To a solution of L-Selectride (1.36 ml of a 1 M solution in THF, 1.36 mmol) in THF (10 ml) was added a solution of 11 (400 mg, 1.24 mmol) in THF (2 ml) dropwise at −78 °C via syringe under nitrogen. After 30 min of stirring, solid N-phenyltriflimide (443 mg, 1.24 mmol) was added and the mixture was warmed to room temperature and stirred for 16 h before being poured into cold brine. The aqueous phase was extracted with petroleum ether, the combined organic phases were dried and evaporated, and the crude product was purified by chromatography (silica gel, elution with 2 % ethyl acetate in petroleum ether) to give 473 mg (84 %) of 12 as a colorless oil; IR (neat): 1470, 1420, 1215, 1150, 1120, 925, 860, 780, 670 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.39 (qt, J = 1.3, 6.1 Hz, 1 H), 4.01 (s, 2 H), 3.02 (br s, 1 H), 2.32–2.22 (m, 2 H), 1.99–1.83 (m, 4 H), 1.78–1.67 (m, 1 H), 1.73 (s, 3 H), 1.59 (s, 3 H), 0.91 (s, 9 H), 0.78 (d, J = 6.5 Hz), 3 H), 0.06 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 144.60, 135.72, 129.36, 122.55, 118.48 (q, J = 319.9 Hz, CF$_3$), 68.49, 46.82, 33.57, 32.63, 32.20, 25.90 (3 C), 20.24, 18.38, 13.85, 13.45, 12.30, −5.33, −5.36; MS: m/z (M^+ −C$_4$H$_9$) calc. 399.1273, obsd. 399.1292. Anal. Calc. for C$_{20}$H$_{35}$F$_3$O$_4$SSi: C, 52.61; H, 7.73. Found: C, 52.87; H, 7.78.

(3S)-3-[(1R,2S)-2-Hydroxy-3-methyl-3-cyclopentenyl]butan-1-ol (13a). To a suspension of lithium aluminium hydride (807 mg, 21.27 mmol) in ether (80 ml) was added a solution of 6 (2.76 g, 16.36 mmol) dropwise over a period of 20 min at 0 °C under nitrogen. After 90 min of stirring at 5–10 °C, the mixture was quenched with 10 ml of saturated sodium sulfate solution. The organic layer was decanted and the

solid was washed several times with ether. The combined organic phases were dried over magnesium sulfate. After removal of the solvent, 2.60 g (93 %) of **13a** were obtained as white crystals, m.p. 88–89 °C (from ethyl acetate); IR (KBr): 3220 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.56 (m, 1 H), 4.35 (br d, J = 4.7 Hz, 1 H), 3.80–3.60 (m, 2 H), 3.40 (br s, 1 H), 2.78 (br s, 1 H), 2.35–2.22 (m, 1 H), 2.14–2.00 (m, 1 H), 1.92–1.70 (m, 3 H), 1.80 (dd, J = 1.3, 2.6 Hz, 3 H), 1.44–1.25 (m, 1 H), 0.95 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.03, 129.09, 78.85, 61.04, 50.61, 39.05, 35.35, 29.26, 19.01, 14.46; MS m/z (M^+) calc. 170.1307, obsd. 170.1328. Anal. Calc. for C$_{10}$H$_{18}$O$_2$: C, 70.55; H, 10.66. Found: C, 70.68; H, 10.71.

(1S,5R)-5-[(1S)-3-(tert-Butyldimethylsiloxy)-1-methyl-propyl]-2-methyl-2-cyclopenten-1-ol (**13b**). A solution of **13a** (345 mg, 2 mmol), imidazole (272.4 mg, 4 mmol), DMAP (4.9 mg, 0.04 mmol) and TBDMSCl (310.4 mg, 2 mmol) in DMF (10 ml) was stirred at room temperature under nitrogen for 24 h before being poured into a cold 1:1 mixture of ether and saturated sodium hydrogen carbonate solution. The aqueous layer was extracted with ether and the combined organic phases were washed with saturated sodium hydrogen carbonate solution and brine, then dried over magnesium sulfate. After the removal of solvent, the residue was purified by column chromatography (silica gel, elution with 2.5 % ethyl acetate in petroleum ether) to give 523 mg (92 %) of **13b** as a colorless oil, which solidified upon standing: m.p. 44–45 °C (from petroleum ether); IR (neat): 3400 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.57 (m, 1 H), 4.36 (ddd, J = 4.5, 4.7, 1.1 Hz, 1 H), 3.80–3.72 (m, 1 H), 3.69–3.60 (m, 1 H), 2.30 (d, J = 4.6 Hz, 1 H), 2.28–2.15 (m, 1 H), 2.14–2.04 (m, 1 H), 1.90–1.70 (m, 3 H), 1.80 (d, J = 1.2 Hz, 3 H), 1.42–1.30 (m, 1 H), 0.94 (d, J = 6.3 Hz, 3 H), 0.90 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 142.03, 128.91, 78.53, 61.77, 50.86, 39.21, 35.21, 29.12, 26.00 (3 C), 19.03, 18.38, 14.69, −5.37, −5.42; MS: m/z (M^+ −CH$_3$) calc. 269.1937, obsd. 269.1952. Anal. Calc. for C$_{16}$H$_{32}$O$_2$Si: C, 67.55; H, 11.34. Found: C, 67.63; H, 11.41.

(5R)-5-[(1S)-3-(tert-Butyldimethylsiloxy)-1-methylpropyl]-2-methyl-2-cyclopentenone (**14**). A mixture of **13b** (452 mg, 1.49 mmol) and manganese dioxide (20 equiv.) in dry benzene (50 ml) was stirred for 2 days at room temperature under nitrogen, then filtered through Celite. The filter cake was rinsed with ether, the combined organic phases were evaporated, and the crude product was purified by column chromatography (silica gel, elution with 2.5 % ethyl acetate in petroleum ether) to give 400 mg (95 %) of **14** as a colorless oil; IR (neat): 1700, 1640 cm^{-1}; ^{1}H NMR (300 MHz, C$_6$H$_6$): δ 6.63 (dd, J = 1.2, 2.6 Hz, 1 H), 3.52 (dt, J = 2.2, 6.5 Hz, 2 H), 2.35 (m, 1 H), 2.20 (m, 1 H), 2.08–1.84 (m, 2 H), 1.62 (dd, J = 2.1, 3.6 Hz, 3 H), 1.50–1.27 (m, 2 H), 0.94 (s, 9 H), 0.67 (d, J = 6.8 Hz, 3 H), 0.03 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 209.62, 115.69, 142.39, 61.48, 49.08, 37.96, 30.50, 28.67, 26.13

(3 C), 18.43, 14.84, 10.24, −5.21, −5.24; MS: m/z (M^+ −C$_4$H$_9$) calc. 225.1311, obsd. 225.1369. Anal. Calc. for C$_{16}$H$_{30}$O$_2$Si: C, 68.03; H, 10.70. Found: C, 68.22; H, 10.81.

(5R)-5-[(1S)-3-(tert-Butyldimethylsiloxy)-1-methylpropyl]-2-methyl-1-cyclopentenyl trifluoromethanesulfonate (**15a**). To a solution of L-Selectride (4.25 ml of a 1 M solution, 4.25 mmol) in THF (50 ml) was added a solution of **14** (1.00 g, 3.54 mmol) in THF (5 ml) via cannula at −78 °C under argon. After 30 min, solid N-phenyltriflimide (1.52 g, 4.25 mmol) was added and the mixture was allowed to warm to room temperature. After 16 h, the mixture was poured into cold saturated sodium hydrogen carbonate solution, the aqueous phase was extracted with petroleum ether, and the combined organic phases were washed with saturated sodium hydrogen carbonate solution and brine prior to drying over magnesium sulfate. After solvent removal, chromatography of the residue (silica gel, elution with 1.25 % ethyl acetate in petroleum ether) gave 1.21 g (82 %) of **15a** as a colorless oil; IR (neat): 1460, 1420, 1380, 1250, 1210, 1145, 1105, 1055, 1000, 940, 900, 850, 780 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.63 (m, 2 H), 3.01 (br s, 1 H), 2.35–2.17 (m, 2 H), 2.03–1.88 (m, 2 H), 1.73 (s, 3 H), 1.72–1.63 (m, 1 H), 1.56–1.32 (m, 2 H), 0.89 (s, 9 H), 0.78 (d, J = 6.9 Hz, 3 H), 0.04 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 144.47, 129.49, 118.48 (q, J = 319.9 Hz, CF$_3$), 61.24, 47.55, 37.66, 32.19, 29.75, 25.88 (3 C), 20.46, 18.25, 13.74, 12.31, −5.40, −5.45; MS: m/z (M^+ −C$_4$H$_9$) calc. 359.0961, obsd. 359.0973. Anal. Calc. for C$_{17}$H$_{31}$F$_3$O$_4$SSi: C, 49.02; H, 7.50. Found: C, 48.67; H, 7.38.

(5R)-5-[(1S)-3-Hydroxy-1-methylpropyl]-2-methyl-1-cyclopentenyl trifluoromethanesulfonate (**15b**). A solution of **15a** (145 mg, 0.348 mmol) in THF (10 ml) was treated with tetrabutylammonium fluoride (1.05 ml of a 1 M solution in THF, 1.05 mmol) at 0 °C under nitrogen. The resulting mixture was stirred for 1.5 h at room temperature, diluted with ether and poured into brine. The aqueous phase was extracted with ether and the combined organic phases were dried and evaporated. Purification of the residue by chromatography (silica gel, elution with 15 % ethyl acetate in petroleum ether) gave 100 mg (95 %) of **15b** as a colorless oil; IR (neat): 3330, 1460, 1415, 1380, 1245, 1210, 1140, 990, 920, 850 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.76–3.62 (m, 2 H), 3.03 (br s, 1 H), 2.40–2.15 (m, 2 H), 2.05–1.89 (m, 2 H), 1.74 (dd, J = 0.8, 0.9 Hz, 3 H), 1.76–1.64 (m, 1 H), 1.60–1.25 (series of m, 3 H), 0.82 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 144.18, 129.64, 118.45 (q, J = 320.4 Hz, CF$_3$), 61.03, 47.23, 37.37, 32.14, 29.73, 20.42, 13.95, 12.30; MS: m/z (M^+ +H) calc. 303.0878, obsd. 303.0924. Anal. Calc. for C$_{11}$H$_{17}$F$_3$O$_4$S: C, 43.70; H, 5.67. Found: C, 44.08; H, 5.67.

Ethyl (2E,5S)- and (2Z,5S)-2-methyl-5-[(1R)-3-methyl-2-trifluoromethylsulfonyloxy-2-cyclopentenyl]-2-hexenoate (**17** and isomer). To a solution of **15b** (65 mg, 0.215 mmol)

in dichloromethane (20 ml) was added PCC on alumina (560 mg). The mixture was stirred for 2 h at room temperature under nitrogen, diluted with ether, and filtered through Celite. The filter cake was rinsed with ether, the combined organic phases were dried over magnesium sulfate, and the solvent was evaporated. The crude aldehyde was dissolved in benzene (20 ml), treated with (ethoxy-carbonylethylidene)triphenylphosphorane (72 mg, 0.22 mmol), and heated at 80 °C for 16 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography (silia gel, 5 % ethyl acetate in petroleum ether) to give 44 mg (53 % overall) of 17 and 1.6 mg (2 % overall) of the Z-isomer, both as colorless oils.

For 17: IR (neat): 1700, 1640 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.74 (ddq, J = 7.3, 7.5, 1.4 Hz, 1 H), 4.19 (dq, J = 0.9, 7.1 Hz, 2 H), 3.00 (br s, 1 H), 2.40–2.20 (m, 2 H), 2.15–2.07 (m, 2 H), 2.05–1.90 (m, 2 H), 1.82 (d, J = 1.2 Hz, 3 H), 1.77–1.67 (m, 1 H), 1.74 (dd, J = 0.8, 0.9 Hz, 3 H), 1.29 (t, J = 7.1 Hz, 3 H), 0.82 (d, J = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.98, 144.04, 140.12, 129.95, 128.94, 118.44 (q, J = 319.8 Hz, CF$_3$), 60.46, 47.11, 33.72, 32.26, 32.14, 20.36, 14.22, 19.92, 12.45, 12.35; MS: m/z (M^+) calc. for C$_{16}$H$_{23}$F$_3$O$_5$S: 384.1218, obsd. 384.1225. Anal. Calc. for C$_{16}$H$_{23}$F$_3$O$_5$S: C, 49.99; H, 6.03. Found: C, 50.37; H, 6.05.

For the Z-isomer: IR (neat): 1710, 1640 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.88 (dt, J = 1.4, 7.5 Hz, 1 H), 4.19 (q, J = 7.1 Hz, 2 H), 3.02 (br s, 1 H), 2.51–2.16 (m, 4 H), 2.00–1.88 (m, 2 H), 1.91 (d, J = 1.3 Hz, 3 H), 1.82–1.65 (m, 1 H), 1.73 (s, 3 H), 1.30 (t, J = 7.1 Hz, 3 H), 0.80 (d, J = 3.6 Hz, 3 H); MS: m/z (M^+) calc. for C$_{16}$H$_{23}$F$_3$O$_5$S: 384.1218 obsd. 384.1208.

tert-Butyl{2-[(1S,3S,3aR)-1,2,3,3a,4,5-hexahydro-3,6-dimethyl-1-pentalenyl]allyloxy}dimethylsilane (18). A mixture of 12 (46 mg, 0.1 mmol), lithium chloride (25.4 mg, 0.6 mmol), lithium carbonate (14.8 mg, 0.2 mmol) and Pd(Ph$_3$P)$_4$ (11.6 mg, 0.01 mmol) in THF (10 ml) was deoxygenated for 30 min with argon, then gently refluxed for 3 h. After cooling, petroleum ether was added followed by saturated sodium hydrogen carbonate solution. The aqueous phase was extracted with petroleum ether, and the combined organic layers were washed with saturated sodium hydrogen carbonate solution and brine prior to being dried over sodium sulfate. After solvent removal, the product was up taken in petroleum ether and purified by chromatography (silica gel, elution with petroleum ether) to give 28 mg (91 %) of 18 as a colorless oil; IR (neat): 1645 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.96 (m, 1 H), 4.80 (m, 1 H), 4.09 (s, 2 H), 3.10 (m, 1 H), 2.78–2.62 (m, 1 H), 2.56–2.48 (m, 1 H), 2.47–2.24 (m, 2 H), 2.06–1.95 (m, 1 H), 1.54 (dd, J = 2.0, 2.2 Hz, 3 H), 1.45–1.15 (m, 3 H), 0.96 (d, J = 6.0 Hz, 3 H), 0.92 (s, 9 H), 0.07 (s, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 151.06, 146.15, 128.61, 106.49, 64.65, 59.94, 46.49, 42.44, 41.61, 39.75, 29.57, 25.97 (3 C), 18.43, 18.17, 14.03, −5.36, −5.38; MS: m/z

(M^+) calc. 306.2379, obsd. 306.2377. Anal. Calc. for C$_{19}$H$_{34}$OSi: C, 74.44; H, 11.18. Found: C, 74.73; H, 11.14.

(E)-Ethyl 2-[(3S,3aR)-1,2,3,3a,4,5-hexahydro-3,6-dimethylpentalen-1-ylidene]propanoate (19) and ethyl 2-[1S,3S,3aR)-1,2,3,3a,4,5-hexahydro-3,6-dimethylpentalen-1-yl]propenoate (20). A mixture of 17 (20 mg, 0.052 mmol), lithium chloride (13 mg, 0.312 mmol), lithium carbonate (8 mg, 0.104 mmol), and Pd(Ph$_3$P)$_4$ (6 mg, 0.005 mmol) in THF (5 ml) was deoxygenated for 30 min with argon and gently refluxed for 3 h. After cooling, ether was added followed by brine, and the aqueous phase was extracted with ether. The combined organic phases were dried over sodium sulfate and evaporated. Purification of the residue by chromatography (silica gel, 0.5 % ethyl acetate in petroleum ether) gave first 2 mg (16 %) of 20 followed by 10 mg (82 %) of 19.

For 19: IR (neat): 1705, 1650 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.19 (q, J = 7.1 Hz, 2 H), 3.27 (dd, J = 19.0, 8.6 Hz, 1 H), 2.86 (m, 1 H), 2.64–2.43 (m, 2 H), 2.39 (dddd, J = 16.5, 9.9, 2.5, 2.5 Hz, 1 H), 2.17–2.06 (m, 1 H), 1.96 (s, 3 H), 1.74 (s, 3 H), 1.61–1.40 (m, 2 H), 1.30 (t, J = 7.1 Hz, 3 H), 1.01 (d, J = 6.6 Hz, 3 H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 168.88, 149.26, 144.08, 135.48, 117.81, 59.84, 59.21, 44.62, 43.83, 40.54, 28.70, 19.08, 18.74, 17.67, 14.42; MS: m/z (M^+) calc. 234.1619, obsd. 234.1607.

For 20: IR (neat): 1720, 1625 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.04 (dd, J = 1.6, 0.7 Hz, 1 H), 5.45 (dd, J = 1.7, 1.6 Hz, 1 H), 4.22 (dq, J = 7.2, 3.0 Hz, 2 H), 3.47 (m, 1 H), 2.78–2.50 (m, 3 H), 2.35 (dd, J = 15.2, 9.5 Hz, 1 H), 2.03 (dtd, J = 12.3, 7.4, 0.7 Hz, 1 H), 1.52 (s, 3 H), 1.50–1.17 (m, 3 H), 1.31 (t, J = 7.2 Hz, 3 H), 0.96 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (300 MHz, CDCl$_3$): δ 167.35, 145.52, 143.59, 129.38, 122.14, 60.49, 59.58, 47.46, 42.42, 41.73, 38.41, 29.53, 18.14, 14.24, 14.06; MS: m/z (M^+) calc. 234.1619, obsd. 234.1637.

o-(4-Methyl-3-pentenyl)phenol (22a). Isopropyltriphenylphosphonium bromide (2.14 g, 5.5 mmol) was dried at 60 °C under high vacuum for 16 h and allowed to cool under argon. Dry THF (100 ml) was added, the solution was cooled to −78 °C and KHMDS (11 ml of a 0.5 M solution in toluene, 5.5 mmol) was introduced. After 30 min at −78 °C and 2 h at room temperature (deep red color), a solution of 2-chromanol (21)[11] (552 mg, 3.7 mmol) in THF (5 ml) was added at −78 °C, and the reaction mixture was allowed to warm to room temperature, stirred for 4 h, and poured into saturated sodium hydrogen carbonate solution. The aqueous phase was extracted with ether, and the combined organic phases were washed with brine and dried. After solvent removal, purification of the residue by column chromatography (silica gel, elution with 2.5 % ethyl acetate in petroleum ether) gave 450 mg (69 %) of 22a as a colorless oil; IR (neat): 3430, 1605 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.71–7.01 (m, 2 H), 6.84

(dt, J = 1.1, 7.4 Hz, 1 H), 6.71 (dd, J = 0.9, 7.9 Hz, 1 H), 5.22–5.18 (m, 1 H), 5.20 (s, 1 H), 2.62 (dd, J = 7.2, 8.1 Hz, 2 H), 2.30 (dd, J = 7.5, 15.0 Hz, 2 H), 1.67 (d, J = 0.7 Hz, 3 H), 1.55 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.43, 132.85, 130.23, 128.31, 127.07, 123.76, 120.76, 115.36, 30.29, 28.28, 25.57, 17.51; MS: m/z (M^+) calc. 176.1201, obsd. 176.1231. Anal. Calc. for C$_{12}$H$_{16}$O: C, 81.77; H, 9.15. Found: C, 81.67; H, 9.21.

o-(4-Methyl-3-pentenyl)phenyl trifluoromethanesulfonate (22b). To a solution of 22a (176 mg, 1 mmol) in pyridine (10 ml) was added triflic anhydride (339 mg, 1.2 mmol) at 0 °C. The mixture was allowed to warm to room temperature, stirred for 16 h under nitrogen, diluted with ether (50 ml), and washed with water (3×). The combined aqueous layers were back-extracted with petroleum ether. The combined organic phases were dried over magnesium sulfate and evaporated. The crude product was subjected to high vacuum to remove the remaining pyridine, then purified by column chromatography (silica gel, elution with 2.5 % ethyl acetate in petroleum ether). There was isolated 49 mg (28 %) of unchanged 22a and 206 mg (67 %) of 22b as a colorless oil; IR (neat): 1575, 1490, 1450, 1420, 1380, 1250, 1220, 1145, 1110, 1080, 1045, 900, 845, 800, 770, 710, 650, 630 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.35–7.15 (m, 4 H), 5.14 (m, 1 H), 2.72 (dd, J = 7.5, 9.4 Hz, 2 H), 2.31 (dd, J = 7.5, 15.3 Hz, 2 H), 1.68 (d, J = 0.8 Hz, 3 H), 1.54 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 148.14, 134.94, 133.06, 131.36, 128.19, 127.68, 122.69, 121.17, 118.75 (q, J = 319.8 Hz, CF$_3$), 30.16, 28.43, 25.61, 17.46; MS: m/z (M^+) calc. 308.0694, obsd. 308.0674. Anal. Calc. for C$_{13}$H$_{15}$F$_3$O$_3$S: C, 50.64; H, 4.90. Found: C, 51.05; H, 5.01.

Ethyl (E)-5-(o-Hydroxyphenyl)-2-methyl-2-pentenoate (23a). A solution of 21 (751 mg, 5 mmol) and (ethoxycarbonylethylidene)triphenylphosphorane (2.174 mg, 6 mmol) in benzene (50 ml) was refluxed for 16 h under argon. After cooling, the solvent was removed under reduced pressure and the residue was purified chromatographically (silica gel, elution with 20 % ethyl acetate in petroleum ether) to give 1.076 g (92 %) of 23a as colorless crystals, m.p. 45–46 °C (from ether–petroleum ether); IR (film): 3400, 1700, 1680, 1640, 1605 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.20–7.05 (m, 2 H), 6.94 (tq, J = 7.4, 1.3 Hz, 1 H), 6.87 (m, 2 H), 6.50 (br s, 1 H), 4.24 (q, J = 7.1 Hz, 2 H), 2.80 (dd, J = 7.2, 8.3 Hz, 2 H), 2.54 (dd, J = 7.6, 5.2 Hz, 2 H), 1.84 (s, 3 H), 1.33 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 168.92, 154.00, 142.33, 130.02, 127.91, 127.53, 127.22, 120.25, 115.19, 60.67, 29.06, 28.85, 14.09, 12.10; MS: m/z (M^+) calc. 234.1256, obsd. 234.1293. Anal. Calc. for C$_{14}$H$_{18}$O$_3$: C, 71.77; H, 7.74. Found: C, 71.75; H, 7.78.

Ethyl (E)-2-methyl-5-(o-trifluoromethylsulfonyloxy)-2-pentenoate (23b). To a solution of 23a (234.3 mg, 1 mmol) in pyridine (10 ml) was added triflic anhydride (339 mg, 1.2 mmol) at 0 °C. The mixture was warmed to room tem-

perature, stirred for 16 h under nitrogen, diluted with ether (50 ml), and washed with water (3×). The combined aqueous layers were back-extracted with ether. The combined organic phases were dried over magnesium sulfate and evaporated. The crude product was subjected to high vacuum to remove the remaining pyridine, then purified by column chromatography (silica gel, elution with 2.5 % ethyl acetate in petroleum ether) to give 300 mg (82 %) of 23b as a colorless oil; IR (neat): 1710, 1645 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.34 (m, 4 H), 6.76 (tq, J = 1.4, 7.6 Hz, 1 H), 4.18 (q, J = 7.0 Hz, 2 H), 2.85 (dd, J = 7.2, 9.2 Hz, 2 H), 2.51 (dd, J = 7.6, 15.4 Hz, 2 H), 1.78 (s, 3 H), 1.29 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.88, 147.94, 139.40, 133.86, 131.20, 129.33, 128.42, 128.18, 121.38, 118.57 (q, J = 319.9 Hz, CF$_3$), 60.47, 28.91, 28.86, 14.18, 12.17; MS: m/z (M^+) calc. 366.0748, obsd. 366.0724. Anal. Calc. for C$_{15}$H$_{17}$F$_3$O$_5$S: C, 49.18; H, 4.68. Found: C, 49.25; H, 4.75.

Intramolecular cyclization of 22b. A mixture of 22b (120 mg, 0.39 mmol), lithium chloride (51 mg, 1.2 mmol), triethylamine (0.17 ml, 1.2 mmol), and Pd(Ph$_3$P)$_4$ (451 mg, 0.39 mmol) in DMF (5 ml) was deoxygenated for 30 min with argon and heated at 90 °C for 18 h. After cooling, ether and brine were added, the aqueous phase was extracted with ether, and the combined organic phases were washed with water and dried over sodium sulfate. After solvent removal, purification of the residue by column chromatography (silica gel, elution with petroleum ether) gave 38 mg (62 %) of 1-isopropenylindane (24) and 6.3 mg (10 %) of 3-isopropylindene (25), along with 18 mg (15 %) of recovered 22b.

For 24: colorless oil; IR (neat, cm^{-1}): 3080, 3030, 2980, 2960, 2870, 1650, 1480, 1460, 1440, 1380, 900, 750; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.30–7.00 (m, 4 H), 4.84–4.80 (m, 2 H), 3.87 (dd, J = 7.5, 7.5 Hz, 1 H), 3.05–2.80 (m, 2 H), 2.35–2.15 (m, 1 H), 2.05–1.85 (m, 1 H), 1.64 (dd, J = 1.3, 0.9 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 147.33, 145.21, 144.30, 126.47, 126.11, 124.49, 124.36, 111.60, 53.38, 31.75, 31.27, 19.20; MS: m/z (M^+ −1) calc. 157.1018, obsd. 157.0946.

For 25: colorless oil; IR (neat, cm^{-1}): 3080, 3000, 2960, 2940, 2860, 1460, 1380, 1100; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.50–7.10 (m, 4 H), 6.19 (br s, 1 H), 3.31 (br s, 2 H), 2.93 (m, 1 H), 1.28 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 147.34, 145.22, 144.31, 126.48, 124.50, 124.50, 124.37, 111.61, 53.38, 31.75, 31.27, 19.21; MS: m/z (M^+) calc. 158.1095, obsd. 158.1085.

Intramolecular cyclization of 23b. A mixture of 23b (160 mg, 0.437 mmol), lithium chloride (56 mg, 1.32 mmol), triethylamine (0.2 ml, 1.32 mmol), and Pd(Ph$_3$P)$_4$ (25 mg, 0.022 mmol) in DMF (5 ml) was deoxygenated for 30 min with argon, and heated at 90 °C for 72 h. After cooling, ether and brine were added, the aqueous layer was extracted with ether, and the combined organic phases were washed with water and dried over sodium sulfate. After

solvent removal, purification of the residue by column chromatography (silica gel, elution with 2.5 % ethyl acetate in petroleum ether) gave 45 mg (48%) of (E)-ethyl 2-indan-2-ylidenepropanoate (**26**), 30 mg (32%) of ethyl 2-indan-2-ylpropenoate (**27**), 2 mg (2%) of ethyl 2-(1H-indan-3-yl)propanoate (**28**), and 16 mg (10%) of unchanged **23b**.

For **26**: colorless oil; IR (neat): 1700, 1610, 1590 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.75 (dd, J = 6.8, 1.8 Hz, 1 H), 7.37–7.23 (m 3 H), 4.26 (1, J = 7.2 Hz, 2 H), 3.24–3.18 (m, 2 H), 3.00 (dd, J = 7.0, 6.0 Hz, 2 H), 2.32 (t, J = 1.9 Hz, 3 H), 1.35 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 169.61, 153.70, 150.16, 141.10, 129.09, 126.96, 126.24, 125.35, 119.91, 60.24, 33.81, 30.83, 16.42, 14.39; MS: m/z (M^+) calc. 216.1150, obsd. 216.1163. Anal. Calc. for C$_{14}$H$_{16}$O$_2$: C, 77.75; H, 7.46. Found: C, 77.86; H, 7.55.

For **27**: colorless oil; IR (neat): 1710, 1620 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.26–7.09 (m, 4 H), 6.22 (d, J = 1.2 Hz, 1 H), 5.33 (t, J = 1.2 Hz, 1 H), 4.33–4.20 (m, 3 H), 2.96–2.86 (m, 2 H), 2.53–2.41 (m, 1 H), 1.98–1.87 (m, 1 H), 1.30 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 167.27, 144.59, 144.51, 144.03, 126.71, 126.65, 124.83, 124.51, 124.36, 60.70, 46.66, 33.52, 31.13, 14.19; MS: m/z (M^+) calc. 216.1150, obsd. 216.1153. Anal. Calc. for C$_{14}$H$_{16}$O$_2$: C, 77.75; H, 7.46. Found: C, 77.86; H, 7.62.

For **29**: ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.44 (dd, J = 7.2, 7.1 Hz, 2 H), 7.35–7.15 (m, 2 H), 6.39 (br s, 1 H), 4.15 (dq, J = 7.1, 0.8 Hz, 2 H), 3.80 (dq, J = 7.1, 1.3 Hz, 1 H), 3.36 (br s. 2 H), 1.54 (d, J = 7.1 Hz, 3 H), 1.22 (5, J = 7.1 Hz, 3 H).

References and notes

1. (a) Heck, R. F. *Org. React. (NY) 27* (1982) 345; (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*, Academic Press, New York 1985; (c) Tsuji, J. *Organic Synthesis with Palladium Compounds*, Springer-Verlag, New York, 1980; (d) Hegedus, L. S. *Angew. Chem., Int. Ed. Engl. 27* (1988) 1113.

2. (a) Cacchi, S., Morera, E. and Ortar, G. *Tetrahedron Lett. 25* (1984) 2271; (b) Scott, W. J., Peña, M. R., Swärd, K., Stoessel, S. J. and Stille, J. K. *J. Org. Chem. 50* (1985) 2302.

3. Chen, Q.-Y. and Yang, Z.-Y. *Tetrahedron Lett. 27* (1986) 1171.

4. (a) Mori, M., Kanada, N., Oda, L. and Ban, Y. *Tetrahedron 41* (1985) 5465; (b) Harrington, P. J., Hegedus, L. S. and McDaniel, K. F. *J. Am. Chem. Soc. 109* (1987) 4335; (c) Larock, R. C. and Babu, S. *Tetrahedron Lett. 28* (1987) 5291; (d) Iwasaki, M., Li, J. P., Kobayashi, T., Matsuzaka, H., Ishii, Y. and Hidai, M. *Tetrahedron Lett. 30* (1989) 95.

5. Liang, S. Ph.D. Thesis, The Ohio State University, 1991. Details for the preparation of **6** will be reported elsewhere.

6. (a) Johnson, M. R., Nakata, T. and Kishi, Y. *Tetrahedron Lett. 20* (1979) 4343; (b) Thomas, E. J. and Whitehead, W. J. *J. Chem. Soc., Perkin Trans. 1* (1989) 507.

7. Isler, O., Gutmann, H., Montavon, M., Ruegg, R., Ryser, G. and Zeller, P. *Helv. Chim. Acta 40* (1957) 1243.

8. (a) Gritter, R. J. and Wallace, T. J. *J. Org. Chem. 24* (1959) 1051; (b) Papodopoulos, E. P., Jarrar, A. and Issidorides, C. H. *J. Org. Chem. 31* (1966), 615; (c) Dollimore, D. and Tonge, K. J. *J. Chem. Soc. B* (1967) 1380.

9. (a) Adams, L. L. and Luzzio, F. A. *J. Org. Chem. 54* (1989) 5387; (b) Cheng, Y. S., Liu, W.-L. and Chen, S.-H. *Synthesis* (1980) 223.

10. (a) Crisp, G. T., Scott, W. J. and Stille, J. K. *J. Am. Chem. Soc. 106* (1984) 7500; (b) Crisp, G. T. and Scott, W. J. *Synthesis* (1985) 335.

11. Yates, P. and Macas, T. S. *Can. J. Chem. 66* (1988) 1.