Supplemental materials for:

Convergent and Diastereoselective Synthesis of the Polycyclic Pyran Core of Saudin

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Table of Contents:

Materials and Methods S1

Preparative Procedures S2

Crystal Structure Analysis of 19a S16

Crystal Structure Analysis of 24c S25

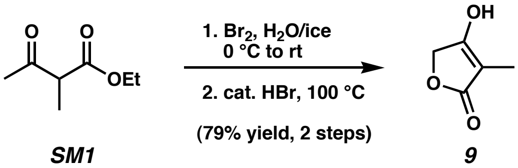
Crystal Structure Analysis of 43 S33

References S44

Spectral Data S45

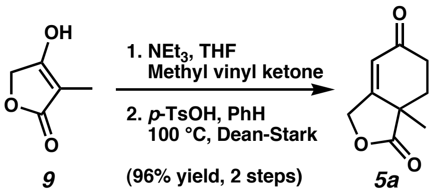
Materials and Methods. Unless stated otherwise, reactions were performed in flame-dried glassware sealed with rubber septa under a nitrogen atmosphere using anhydrous, deoxygenated solvents. Commercially obtained reagents were used as received. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. Reaction temperatures were controlled by a temperature modulator. Thin-layer chromatography (TLC) was performed using silica gel precoated plates (0.25 mm) and visualized using a combination of UV, anisaldehyde, ceric ammonium molybdate, and potassium permanganate staining. Silica gel (particle size 0.032 - 0.063 mm) was used for flash chromatography. ^{1}H NMR spectra were recorded at 300 or 500 MHz and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded at 75 or 125 MHz and are reported relative to Me_4Si (δ 0.0). Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra are reported in terms of frequency of absorption (cm^{-1}). High resolution mass spectra were obtained.

Preparative Procedures



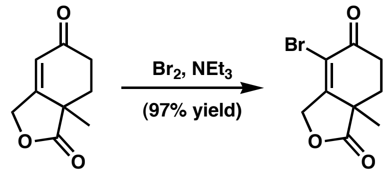
Methyl tetronic acid 9. This is a modification of a known literature procedure.[1] To a solution of ethylmethyl acetoacetate ***SM1*** (50 mL, 353 mmol) in deionized water (100 mL) cooled to 0 °C was slowly added bromine (18 mL, 353 mmol) in a dropwise fashion over 2 h. Following addition, the ice bath was allowed to warm to 23 °C, and the reaction mixture was stirred for 12 h. The organic layer was separated and dried over Na_2SO_4 and evaporated in vacuo to provide the desired bromoketone (81.08 g, 353 mmol) as a clear oil, which was used in the next step without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.28 (dq, J = 7.2, 0.9 Hz, 1H), 2.43 (s, 3H), 1.97 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H).

To the bromoketone from the previous step (81.08 g, 353 mmol) was added 12 drops of HBr (48% *w/v* in H_2O) in a dropwise fashion. Following addition, the reaction mixture was refluxed at 100 °C and allowed to stir for 12 h. The reaction was cooled to 23 °C. The precipitate was vacuum filtered and rinsed with ethyl acetate. The concentrated filtrate was resubmitted to the reaction conditions twice. The filtrates from the three reaction cycles were combined to yield methyl tetronic acid **9** (31.86 g, 79% yield) as a white solid: mp 185 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.74 (s, 1H), 4.55 (s, 2H), 1.57 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.3, 173.0, 94.5, 66.6, 6.0; IR (KBr pellet) 2984, 2695, 1598, 1448 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_5H_6O_3]^+$: *m/z* 114.0317, found 114.0313.



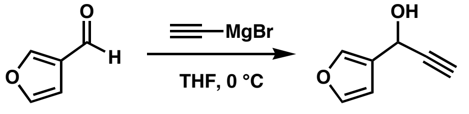
Enone 5a. To a cooled (0 °C) solution of methyl tetronic acid **9** (150 g, 1.31 mol) in THF (1.3 L) was added Et_3N (366 mL, 2.63 mol). Methyl vinyl ketone (131 mL, 1.58 mol) was then slowly added over 15 min. After stirring for 30 min, the reaction mixture was washed with 1 N HCl (1 L). The organic layer was separated, dried over Na_2SO_4, and evaporated in vacuo to provide the conjugate addition product (242.2 g, 1.31 mol) as a yellow oil, which was used without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73 (d, J = 16.8 Hz, 1H), 4.63 (d, J = 16.8 Hz, 1H), 2.56 (t, J = 7.2 Hz, 2H), 2.12 (s, 3H), 2.09-1.95 (m, 2H), 1.31 (s, 3H).

To a solution of this conjugate addition product (242.2 g, 1.31 mol) in benzene (650 mL) was added *p*-TsOH (24.9 g, 131 mol). The mixture was refluxed with azeotropic removal of H_2O (Dean-Stark trap). After stirring for 40 h, the reaction mixture was allowed to cool to 23 °C and concentrated in vacuo. The resulting oil was dissolved in CH_2Cl_2 (300 mL) and washed with water (200 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 40 mL). The combined organic layers were dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (2:1 hexanes/EtOAc eluent) provided enone **5a** (211 g, 96% yield over 2 steps) as a clear oil: R_F 0.40 (1:3 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (s, 1H), 5.01 (dd, *J* = 14.6, 2.1 Hz, 1H), 4.83 (d, *J* = 14.6 Hz, 1H), 2.60-2.36 (m, 2H), 2.22-1.92 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 177.5, 161.6, 122.2, 68.2, 41.3, 32.6, 29.5, 20.7; IR (thin film/NaCl) 2940, 1780, 1676 cm^{-1}; HRMS (EI$^+$) calc'd for $[C_9H_{10}O_3]^+$: *m/z* 166.0630, found 166.0629.



5a *5b*

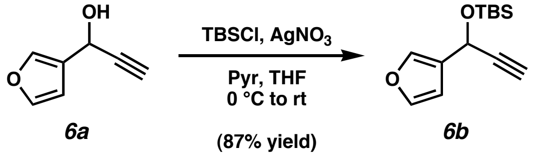
Bromoenone 5b. To a solution of enone **5a** (5.0 g, 30 mmol) in CH_2Cl_2 (60 mL) cooled to 0 °C was added a solution of Br_2 (1.7 mL, 33 mmol) in CH_2Cl_2 (30 mL) in a dropwise fashion over 15 min. When the addition was complete, Et_3N (4.6 mL, 33 mmol) was quickly added. After stirring for 5 min, the reaction mixture was washed with water (3 x 50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash chromatography (3:1 hexanes/EtOAc eluent) provided bromoenone **5b** (7.16 g, 97% yield) as a clear oil: R_F 0.30 (2:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.00 (s, 2H), 2.83-2.77 (m, 2H), 2.33-2.14 (m, 2H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.6, 176.7, 160.2, 117.8, 69.4, 45.2, 33.3, 29.5, 21.7; IR (thin film/NaCl) 2935, 1782, 1689, 1655 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_9H_9O_3Br]^+$: 243.9735, found 243.9732.



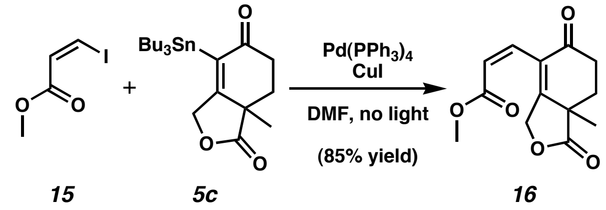
10 *6a*

Alcohol 6a. To a solution of 3-furaldehyde **10** (17.3 mL, 200 mmol) in THF (170 mL) cooled to 0 °C was added ethynyl magnesium bromide (0.5 M in Et_2O, 500 mL, 250 mmol) slowly via an addition funnel over 2 h. Following addition, the ice bath was allowed to warm to 23 °C, and the mixture was stirred for 5 h. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (500 mL) and extracted with Et_2O (2 x 400 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by flash chromatography (2:1 hexanes/EtOAc eluent) provided alcohol **6a** (25.41 g, 99% yield) as a clear oil: R_F 0.25 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, *J* = 0.8 Hz, 1H), 7.37 (t, *J* = 1.7 Hz, 1H), 6.48 (d, *J* = 0.8 Hz, 1H), 5.35 (d, *J* = 1.3 Hz, 1H), 3.14 (s, 1H), 2.58 (d, *J* = 2.4 Hz, 1H);

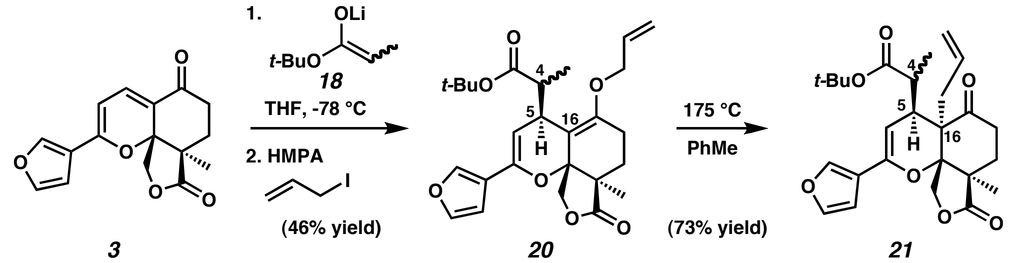
^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 140.4, 126.0, 109.2, 83.2, 73.5, 57.0; IR (thin film/NaCl) 3293, 1505, 1158, 1021 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_7H_6O_2]^+$: 122.0368, found 122.0367.



TBS-ether 6b. To a cooled (0 °C) solution of alcohol **6a** (235.2 mg, 2.00 mmol) in THF (9.6 mL) were added $AgNO_3$ (491 mg, 2.89 mmol), Pyridine (623 µl, 7.70 mmol), and TBSCl (435 mg, 2.89 mmol). After 5 min, the reaction mixture was warmed to 23 °C. The reaction was stirred for 10 h and then passed through a short pad of Celite (Et_2O eluent). The solution was washed with water (15 mL). The aqueous layer was extracted with Et_2O (2 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash chromatography (10:1 hexanes/EtOAc eluent) provided TBS-ether **6b** (411.6 mg, 87% yield) as a clear oil: R_F 0.68 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 0.8 Hz, 1H), 7.20 (t, *J* = 1.7 Hz, 1H), 6.28 (d, *J* = 1.1 Hz, 1H), 5.28 (d, *J* = 1.1 Hz, 1H), 2.35 (d, *J* = 2.1 Hz, 1H), 0.77 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 139.8, 127.2, 109.3, 84.0, 72.9, 58.2, 25.9, 18.5, -4.4, -4.8; IR (thin film/NaCl) 3309, 2957, 2931, 2858, 1254, 1087, 1062 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_{13}H_{20}O_2Si]^+$: 236.1233, found 236.1232.



Enone 16. To a mixture of $Pd(PPh_3)_4$ (14 mg, 0.012 mmol), vinyl stannane **5c** (50 mg, 0.12 mmol), and vinyl iodide **15**^{2} (30 mg, 0.12 mmol) was added DMF (2.5 mL). CuI (17.5 mg, 0.09 mmol) was added, and the flask was protected from ambient light. After stirring for 9 h, the mixture was diluted with water (10 mL) and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (1:1 hexanes/EtOAc eluent) provided enone **16** (25.5 mg, 85% yield): R_F 0.25 (1:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.62 (ddd, *J* = 12.2, 1.9, 0.8 Hz, 1H), 6.15 (d, *J* = 12.2 Hz, 1H), 5.02 (dd, *J* = 15.0, 2.0 Hz, 1H), 4.72 (dd, *J* = 15.0, 0.7 Hz, 1H), 3.69 (s, 3H), 2.77-2.53 (m, 2H), 2.32-2.11 (m, 2H), 1.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 177.9, 165.5, 158.7, 136.0, 128.7, 125.6, 77.7, 68.6, 51.9, 42.0, 33.0, 29.9, 21.0; IR (thin film/NaCl) 2952, 1781, 1722, 1675, 1197, 1179 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_{13}H_{14}O_5]^+$: 250.0841, found 250.0844.

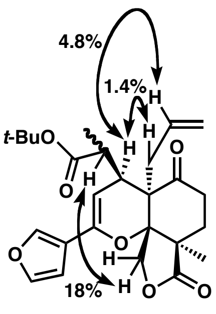


Claisen Product 21. To a solution of HN(*i*-Pr)$_2$ (130 μL, 0.933 mmol) in THF (1.8 mL) cooled to 0 °C was added *n*-butyllithium (2.5 M in hexanes, 375 μL, 0.933 mmol). After 5 min the mixture was cooled to -78 °C, and a solution of *t*-butyl propionate (140 μL, 0.933 mL) in THF (1.8 mL) was slowly added along the sides of the flask in a dropwise fashion. Following addition, the mixture was stirred for 25 min, and then a solution of polycycle **3** (50 mg, 0.175 mmol) in THF (1.8 mL) was slowly added over 2 min. After 15 min the reaction was transferred via cannula into a 23 °C solution of allyl iodide (900 μL) and HMPA (900 μL). Following addition, the mixture was stirred for 80 min and then quenched with H_2O (15 mL). The mixture was extracted with Et_2O (3 x 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by flash chromatography (10:1 hexanes/EtOAc eluent) provided enol ether **20** (37.1 mg, 46% yield) as a clear oil, which was used immediately in the next step.

Enol ether **20** (32.6 mg, 0.0714 mmol) in toluene (4 mL) was transferred to a sealable flask. The flask was sealed, and the reaction vessel was heated to 175 °C behind a blast shield. After 2.5 h the mixture was cooled to 23 °C and concentrated in vacuo. The 2.7:1 diastereomeric mixture (Diastereomer 1 : Diastereomer 2) of Claisen products **21** was purified and separated by preparatory thin layer chromatography on silica gel (0.5 mm, 3:1 hexanes/EtOAc eluent) to provide Diastereomer 1 (17.4 mg, 53% yield) and Diastereomer 2 (6.4 mg, 20% yield) as two clear oils (23.8 mg combined, 73% yield).

Diastereomer 1: R_F 0.31 (2:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 7.26 (s, 1H), 6.93 (t, *J* = 1.7 Hz, 1H), 6.10 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.77-5.60 (m, 1H), 4.98-4.86 (m, 2H), 4.82 (d, *J* = 5.8 Hz, 1H), 3.93 (d, *J* = 10.5 Hz, 1H), 3.52 (t, *J* = 6.5 Hz, 1H), 3.30 (d, *J* = 10.5 Hz, 1H), 2.33 (t, *J* = 6.5 Hz, 1H), 2.17 (t, *J* = 7.4 Hz, 1H), 2.12-1.98 (m, 1H), 1.78-1.69 (m, 1H), 1.63 (s, 9H), 1.37 (s, 3H), 1.30-1.27 (m, 1H), 1.01 (d, *J* = 7.7 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 206.1, 178.6, 175.8, 143.9, 143.0, 140.1, 132.4, 122.4, 119.1, 107.8, 99.0, 86.0, 80.2, 69.9, 56.7, 46.0, 41.5, 38.9, 36.5, 35.3, 30.2, 28.6, 17.5, 17.0; IR (thin film/NaCl) 2977, 1784, 1722, 1156 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{26}H_{31}O_7]^+$: 455.2070, found 455.2089.

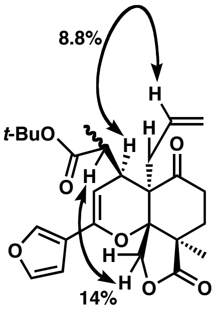
Claisen product **21** *(Diastereomer 1)* was assigned the indicated relative stereochemistry based on the shown nOe interactions.



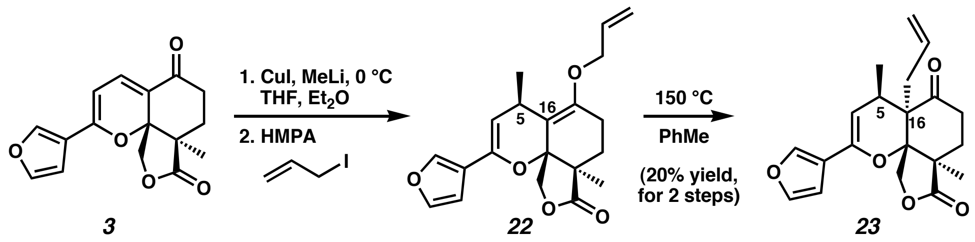
21 (Diastereomer 1)

Diastereomer 2: R_F 0.38 (2:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 7.27 (s, 1H), 6.91 (t, *J* = 1.8 Hz, 1H), 6.17 (dd, *J* = 1.7, 0.8 Hz, 1H), 5.50-5.36 (m, 1H), 5.32 (d, *J* = 5.5 Hz, 1H), 4.94-4.74 (m, 3H), 3.88 (d, *J* = 11.6 Hz, 1H), 2.54-2.41 (m, 2H), 2.36-2.15 (m, 2H), 2.07-1.95 (m, 1H), 1.69 (d, *J* = 6.6 Hz, 3H), 1.55-1.41 (m, 1H), 1.37 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 206.3, 179.4, 174.3, 144.0, 142.7, 140.4, 132.1, 122.4, 119.8, 107.7, 99.4, 85.0, 80.9, 72.7, 57.2, 46.2, 43.2, 41.7, 38.5, 36.1, 30.5, 28.3, 21.8, 18.4; IR (thin film/NaCl) 2977, 1782, 1719, 1150 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{26}H_{33}O_7]^+$: 457.2226, found 457.2213.

Claisen product **21** *(Diastereomer 2)* was assigned the indicated relative stereochemistry based on the shown nOe interactions.



21 (Diastereomer 2)

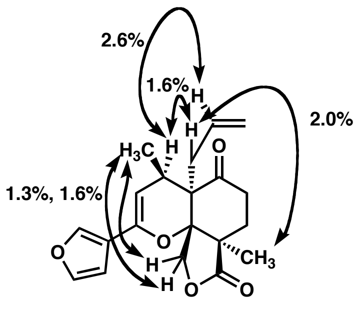


Methyl Claisen Product 23. A solution of MeLi in Et_2O (1.29 mL, 2.07 mmol) was slowly added to a mixture of CuI (197 mg, 1.03 mmol) in Et_2O (2.5 mL) at 0 °C in a dropwise fashion. Following addition, the mixture was stirred for 10 min at 0 °C, and then a solution of polycycle **3** (60 mg, 0.210 mmol) in THF (2 mL) was added. After 30 min the reaction was transferred via cannula into a flask at 23 °C containing allyl iodide (500 µL) and HMPA (500 µL). Following addition the mixture was stirred for 2 h and then quenched with brine

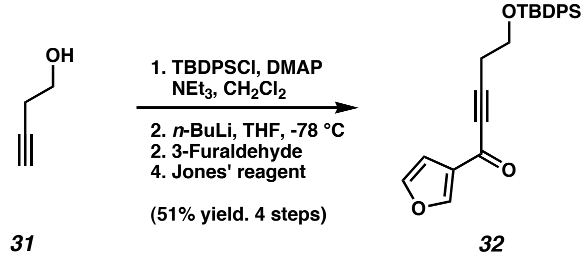
(10 mL). The mixture was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by flash chromatography (8:1 hexanes/EtOAc eluent) provided enol ether **22** (14.1 mg, 20% yield) as a clear oil, which was used immediately in the next step.

Enol ether **22** (14.1 mg, 0.412 mmol) in toluene (1 mL) was transferred to a sealable flask. The flask was sealed, and the reaction vessel was heated at 150 °C behind a blast shield. After 4.5 h, the mixture was cooled to 23 °C and concentrated under reduced pressure to provide Claisen product **23** (14.1 mg, 100% yield) as a clear oil: R_F 0.67 (1:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 7.29 (s, 1H), 6.98 (t, J = 2.0 Hz, 1H), 6.16-6.14 (m, 1H), 5.55-5.46 (m, 1H), 4.96-4.92 (m, 1H), 4.84-4.78 (m, 1H), 4.73 (d, J = 5.4 Hz, 1H), 4.10 (d, J = 10.7 Hz, 1H), 3.42 (d, J = 10.7 Hz, 1H), 2.53-2.46 (m, 1H), 2.28 (d, J = 7.3 Hz, 2H), 2.05-1.97 (m, 1H), 1.73-1.65 (m, 1H), 1.60-1.52 (m, 1H), 1.41-1.37 (m, 1H), 1.36 (s, 3H), 0.91 (d, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 206.0, 179.5, 143.9, 142.3, 140.2, 132.7, 122.6, 119.2, 107.8, 103.5, 85.1, 72.6, 55.4, 46.0, 38.0, 36.0, 31.7, 30.5, 18.9, 17.3; IR (thin film/NaCl) 2944, 1779, 1712, 1113 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_{20}H_{22}O_5]^+$: 342.1467, found 342.1462.

Methyl Claisen product **23** was assigned the indicated relative stereochemistry based on the shown nOe interactions.



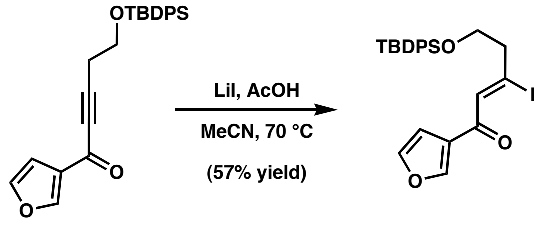
23



Ynone 32. To a solution of alcohol **31** (1.73 mL, 22.9 mmol), *t*-butyldiphenylsilyl chloride (5.72 g, 22 mmol), and DMAP (98 mg, 0.8 mmol) in CH_2Cl_2 (20 mL) was added Et_3N (3.1 mL, 22 mmol). After stirring for 1 h, the reaction was washed with H_2O (20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was dissolved in benzene (10 mL) and concentrated in vacuo to azeotropically remove water, and the resulting protected alcohol was taken on to the next step without further purification.

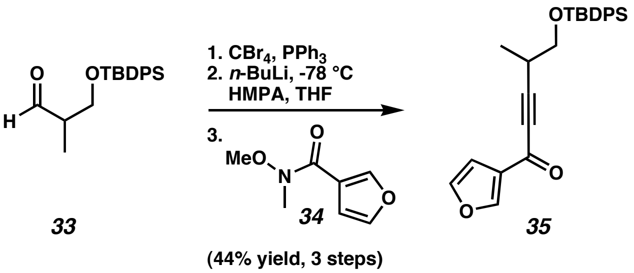
The product from the previous step was dissolved in THF (40 mL) and cooled to –78 °C. To this solution was slowly added *n*-butyllithium (2.5 M in hexanes, 8.8 mL, 22 mmol). After 20 min 3-furaldehyde (1.9 mL, 22 mmol) was slowly added. Following addition, the mixture was warmed to 23 °C and stirred for 10 min. The reaction was quenched with 1 N HCl (40 mL). The mixture was concentrated in vacuo to remove THF, and the resulting solution was extracted with ether (2 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure, and the resulting coupled alcohol was taken onto the next step without further purification.

The crude product from the previous step was dissolved in acetone (40 mL) and cooled to 0 °C. To this solution was added Jones' reagent[3] (2.67 M, 15 mL, 40 mmol). After stirring for 10 min, *i*-PrOH (5 mL) was added to quench the remaining oxidant. The reaction was diluted with ether (100 mL) and extracted with a 1:1 mixture of brine and saturated aqueous $NaHCO_3$ (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (30:1 hexanes/EtOAc eluent) provided ynone **32** (4.47 g, 51% yield): R_F 0.56 (3:1 hexanes/EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 1.3, 0.8 Hz, 1H), 7.75-7.66 (m, 5H), 7.48-7.35 (m, 6H), 6.81 (dd, *J* = 1.9, 0.8 Hz, 1H), 3.88 (t, *J* = 6.6 Hz, 2H), 2.68 (t, *J* = 6.5 Hz, 2H), 1.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 150.6, 144.6, 135.7, 135.0, 133.4, 130.1, 129.8, 129.4, 128.0, 127.9, 108.6, 90.6, 80.8, 61.7, 27.0, 26.8, 23.4, 19.4; IR (thin film/NaCl) 2931, 2858, 2217, 1642, 1428, 1308, 1164, 1112 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_{25}H_{26}O_3Si]^+$: 402.1651, found 402.1664.



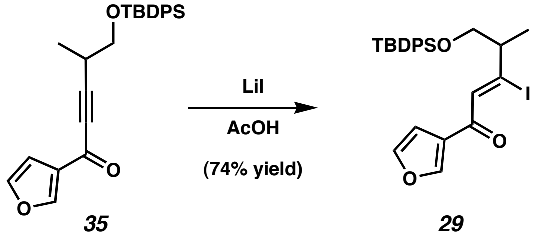
32 **28**

Vinyl Iodide 28. To a solution of ynone **32** (402 mg, 1.0 mmol) and LiI (147 g, 1.1 mmol) in MeCN (1.0 mL) was added glacial AcOH (63 µL, 1.1 mmol). Following addition, the mixture was refluxed for 20 h. The mixture was concentrated in vacuo and purified by flash chromatography (50:1 to 4:1 hexanes/EtOAc eluent) to provide vinyl iodide **28** (302 mg, 57% yield): R_F 0.45 (3:1 hexanes/EtOAc); ^1H NMR (300 MHz, C_6D_6) δ 7.75-7.68 (m, 4H), 7.45 (dd, *J* = 1.3, 0.8 Hz, 1H), 7.25-7.19 (m, 6H), 6.77 (t, *J* = 1.7 Hz, 1H), 6.72 (t, *J* = 1.1 Hz, 1H), 6.68 (dd, *J* = 1.9, 0.8 Hz, 1H), 3.71 (t, *J* = 6.0 Hz, 2H), 2.61 (dt, *J* = 5.9, 0.9 Hz, 2H), 1.10 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 182.5, 147.4, 144.7, 136.4, 136.3, 135.6, 134.1, 132.0, 130.5, 130.2, 129.2, 128.5, 128.2, 113.6, 109.6, 62.7, 51.2, 27.4, 27.3, 27.1, 19.8, 19.6; IR (thin film/NaCl) 2930, 2857, 1662, 1591, 1428, 1157, 1112 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{25}H_{28}O_3SiI]^+$: 531.0853, found 531.0856.



Ynone 35. To a solution of PPh_3 (8.53 g, 32.5 mmol) in CH_2Cl_2 (10 mL) cooled to 0 °C was added a solution of CBr_4 (5.4 g, 16.3 mmol) in CH_2Cl_2 (4 mL). After 10 min, aldehyde **33**[4] (2.66 g, 8.13 mmol) in CH_2Cl_2 (6 mL) was slowly added. Following addition, the reaction was stirred for 4 h at 0 °C. A small scoop of Celite was added to the reaction mixture, which was then slowly poured onto a stirring solution of Celite in petroleum ether (500 mL). The mixture was filtered, and the filtrate was concentrated in vacuo and purified by flash chromatography on silica gel (20:1 petroleum ether/EtOAc eluent) to provide the vinyl dibromide (3.46 g, 91% yield) as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (m, 4H), 7.41 (m, 6H), 6.27 (d, *J* = 8.7 Hz, 1H), 3.55 (m, 2H), 2.69 (m, 1H), 1.06 (s, 9H), 1.04 (d, *J* = 6.9 Hz, 3H).

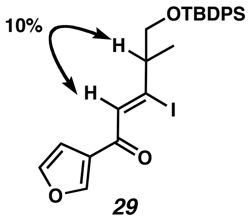
To a solution of the resulting vinyl dibromide (2.29 mg, 4.91 mmol) in THF (25 mL) cooled to -78 °C was slowly added *n*-butyllithium (2.5 M in hexanes, 4.3 mL, 10.8 mmol). After 15 min, the mixture was warmed to 0 °C. The reaction was stirred for 30 min at this temperature and then cooled back to -78 °C. HMPA (2.5 mL) was added, and the mixture was stirred for 20 min. The reaction was then warmed to -40 °C, and a solution of Weinreb amide **34**[5] (1.73 g, 11.1 mmol) in THF (12.5 mL) was slowly added. The cold bath was allowed to warm to 23 °C, and after 2.5 h the reaction was quenched with saturated aqueous NH_4Cl (50 mL). The mixture was extracted with ether (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification by flash chromatography (15:1 hexanes/EtOAc eluent) provided ynone **35** (989.2 mg, 48% yield, 44% yield over 2 steps) as a clear oil: R_F 0.54 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 1.3, 0.8 Hz, 1H), 7.70-7.65 (m, 4H), 7.47-7.34 (m, 7H), 6.80 (dd, *J* = 1.9, 0.8 Hz, 1H), 3.78 (dd, *J* = 9.8, 6.1 Hz, 1H), 3.67 (dd, *J* = 9.7, 6.5 Hz, 1H), 2.95-2.82 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 150.6, 144.6, 135.8, 133.4, 133.4, 130.1, 129.4, 128.0, 108.6, 95.1, 80.6, 77.4, 67.0, 29.7, 27.0, 19.5, 16.7; IR (thin film/NaCl) 2932, 2858, 2215, 1643, 1113 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_{26}H_{27}O_3Si]^+$: 415.1730, found 415.1727.



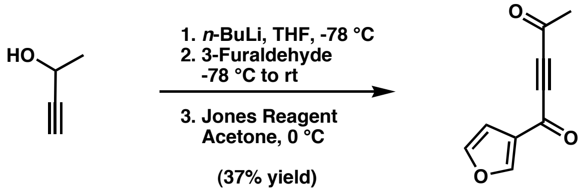
Vinyl Iodide 29. To a solution of ynone **35** (387 mg, 0.929 mmol) in glacial AcOH (10 mL) was added LiI (250 mg, 1.86 mmol). Following addition, the mixture was stirred for 10 h and then poured onto ice water

(50 mL). Solid K_2CO_3 was added until bubbling ceased, and the mixture was extracted with Et_2O (4 x 50 mL). The combined organic layers were dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by flash chromatography (20:1 hexanes/EtOAc eluent) provided vinyl iodide **29** (373.5 mg, 74% yield) as a yellow oil: R_F 0.50 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 7.78-7.71 (m, 4H), 7.54 (dd, *J* = 1.3, 0.8 Hz, 1H), 7.27-7.20 (m, 6H), 6.83 (d, *J* = 0.8 Hz, 1H), 6.79 (t, *J* = 1.7 Hz, 1H), 6.70 (dd, *J* = 1.9, 0.8 Hz, 1H), 3.68 (dd, *J* = 10.2, 7.6 Hz, 1H), 3.51 (dd, *J* = 10.1, 5.1 Hz, 1H), 2.31-2.19 (m, 1H), 1.12 (s, 9H), 0.82 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 183.4, 147.7, 144.7, 136.5, 136.3, 136.3, 134.3, 134.1, 131.1, 130.5, 130.5, 130.5, 129.0, 128.5, 123.4, 109.6, 67.9, 51.2, 27.4, 27.4, 19.9, 17.9; IR (thin film/NaCl) 2931, 2858, 1664, 1590, 1156, 1112 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{26}H_{30}O_3SiI]^+$: 545.1009, found 545.0997.

Vinyl iodide **29** was assigned the (Z) stereochemistry based on a 10% nOe interaction between the vinyl hydrogen and the allylic hydrogen.



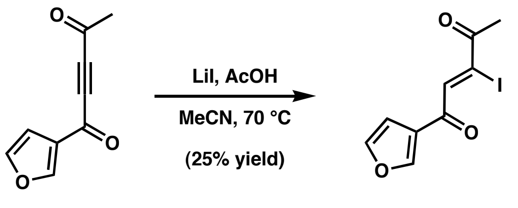
29



36 *37*

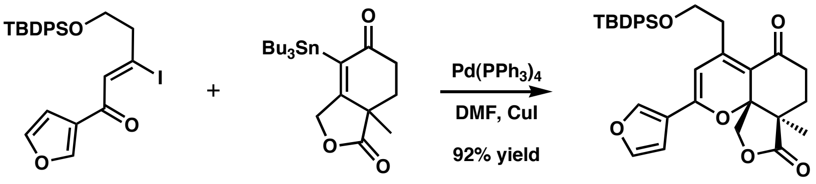
Ynone 37. Alcohol **36** (3.14 mL, 40 mmol) was dissolved in THF (80 mL) and cooled to -78 °C. To this solution was slowly added *n*-butyllithium (2.5 M in hexanes, 32 mL, 80 mmol) over 5 min. After 20 min, 3-furaldehyde (3.63 mL, 42 mmol) was slowly added. Following addition, the mixture was warmed to 23 °C and stirred for 10 min. The reaction was quenched with 1 N HCl (100). The mixture was concentrated in vacuo to remove THF, and the resulting solution was extracted with ether (2 x 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting coupled alcohol was taken onto the next step without further purification.

The product from the previous step was dissolved in acetone (100 mL) and cooled to 0 °C. To this solution was added Jones' reagent (2.67 M, 35 mL, 93 mmol). After stirring for 10 min, *i*-PrOH (5 mL) was added to quench the remaining oxidant. The reaction was diluted with ether (150 mL) and extracted with a 1:1 mixture of brine and saturated aqueous $NaHCO_3$ (150 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash chromatography (9:1 hexanes/EtOAc eluent) provided ynone **37** (2.37 g, 37% yield): R_F 0.37 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.49 (t, *J* = 1.7 Hz, 1H), 6.83 (dd, *J* = 1.9, 0.8 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.1, 169.4, 151.4, 145.4, 128.6, 108.3, 83.6, 83.0, 32.8; IR (thin film/NaCl) 3133, 1681, 1641, 1556, 1510, 1305, 1200, 1156 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_9H_6O_3]^+$: 162.0317, found 162.0321.



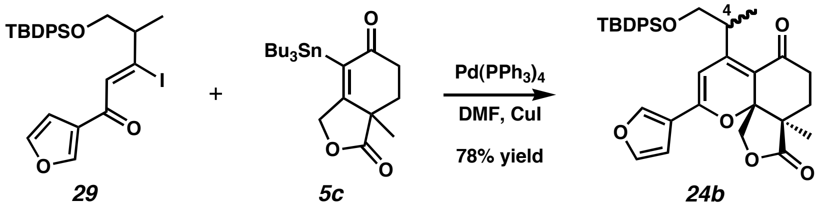
37 *30*

Vinyl Iodide 30. To a solution of ynone **37** (2.37 g, 14.6 mmol) and LiI (2.15 g, 16.1 mmol) in MeCN (160 mL) was added glacial AcOH (922 µL, 1.1 mmol). Following addition, the mixture was refluxed for 20 h. The mixture was concentrated in vacuo and purified by flash chromatography (6:1 hexanes/EtOAc eluent) to provide vinyl iodide **30** (1.0 g, 25% yield): R_F 0.27 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 6.86 (dd, *J* = 1.3, 0.8 Hz, 1H), 6.65 (dd, *J* = 2.0, 1.5 Hz, 1H), 6.50 (s, 1H), 6.41 (dd, *J* = 2.1, 0.8 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 198.8, 180.7, 148.5, 144.8, 135.4, 127.4, 118.1, 109.2, 25.6; IR (thin film/NaCl) 3134, 1706, 1654, 1576, 1512, 1156 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_9H_7O_3I]^+$: 289.9440, found 289.9432.



28 *5c* *24a*

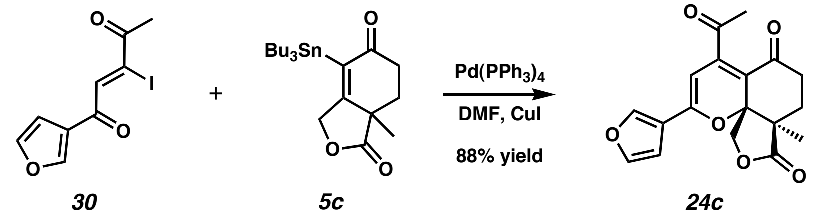
Polycycle 24a. Vinyl stannane **5c** (1.78 g, 3.90 mmol) and vinyl iodide **28** (2.07 g, 3.90 mmol) were subjected to the tandem Stille-oxa-electrocyclization conditions, as described previously for the synthesis of polycycle **3**. Purification by flash chromatography (3:1 hexanes/EtOAc eluent) provided polycycle **24a** (2.05 g, 3.59 mmol) as an orange solid: R_F 0.26 (3:1 hexanes/EtOAc); mp 85-86 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.66-7.61 (m, 4H), 7.45-7.32 (m, 7H), 6.46 (d, *J* = 2.1 Hz, 1H), 5.82 (s, 1H), 4.74 (d, *J* = 11.1 Hz, 1H), 3.97-3.88 (m, 3H), 3.10 (dt, *J* = 2.4, 6 Hz, 2H), 2.68-2.37 (m, 2H), 2.04-2.00 (m, 2H), 1.54 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 179.2, 151.5, 144.3, 143.1, 135.6, 133.7, 133.6, 129.7, 127.7, 120.7, 113.9, 107.3, 105.5, 86.5, 71.5, 63.3, 44.9, 36.6, 35.0, 27.8, 26.9, 19.3, 14.9; IR (thin film/NaCl) 2932, 2858, 1785, 1659, 1112 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $[C_{34}H_{37}O_6Si]^+$: 569.2359, found 569.2346.



Polycycle 24b. Vinyl stannane **5c** (611 mg, 1.34 mmol) and vinyl iodide **29** (665 mg, 1.22 mmol) were subjected to the tandem Stille-oxa-electrocyclization conditions, as described previously for the synthesis of polycycle **3**. Purification by flash chromatography (3:1 hexanes/EtOAc eluent) provided a 1:1 diastereomeric mixture of polycycle **24b** (554 mg, 78% yield) as an orange oil.

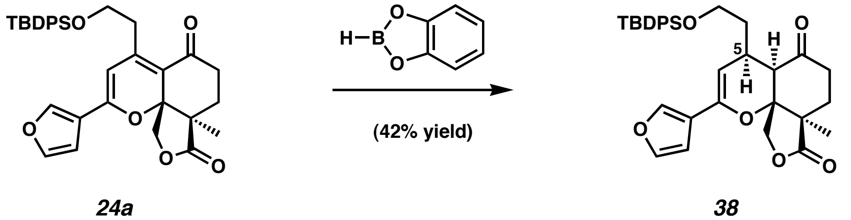
Diastereomer 1: R_F 0.27 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 7.71-7.63 (m, 4H), 7.28 (d, *J* = 0.8 Hz, 1H); 7.21-7.18 (m, 6H), 6.85 (t, *J* = 1.7 Hz, 1H), 6.15 (s, 1H), 6.06 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.74 (s, 1H), 4.80-4.66 (m, 1H), 4.28 (d, *J* = 11.0 Hz, 1H), 3.69-3.55 (m, 2H), 3.30 (d, *J* = 11.0 Hz, 1H), 2.31-2.04 (m, 2H), 1.54-1.43 (m, 2H), 1.40 (s, 3H), 1.18-1.10 (m, 2H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 195.2, 178.8, 153.7, 152.3, 144.5, 143.4, 136.3, 136.2, 134.3, 134.2, 130.4, 130.3, 128.7, 128.5, 128.4, 128.3, 121.7, 116.5, 107.9, 99.8, 87.3, 71.0, 67.6, 45.5, 36.2, 36.0, 28.4, 27.3, 19.8, 15.6, 15.4; IR (thin film/NaCl) 2930, 1784, 1654, 1522, 1110 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{35}H_{39}O_6Si]^+$: 583.2516, found 583.2534.

Diastereomer 2: R_F 0.23 (3:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, C_6D_6) δ 7.84-7.75 (m, 4H), 7.28-7.20 (m, 6H), 6.83 (t, *J* = 1.8 Hz, 1H), 6.14 (s, 1H), 6.07 (t, *J* = 1.1 Hz, 1H), 5.93 (s, 1H), 4.72-4.62 (m, 1H), 4.47 (d, *J* = 11.0 Hz, 1H), 3.91 (d, *J* = 5.8 Hz, 2H), 3.48 (d, *J* = 11.0 Hz, 1H), 2.15-1.99 (m, 2H), 1.44-1.36 (m, 2H), 1.30 (s, 3H), 1.16 (s, 9H), 1.05 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 194.7, 178.7, 155.2, 152.3, 144.6, 143.5, 136.5, 136.4, 134.3, 134.3, 130.5, 121.7, 115.2, 107.7, 101.0, 87.5, 74.9, 71.1, 68.6, 45.3, 36.2, 35.8, 33.4, 28.0, 27.6, 27.5, 20.0, 15.9, 15.2; IR (thin film/NaCl) 2931, 1784, 1657, 1515, 1112 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{35}H_{39}O_6Si]^+$: 583.2516, found 583.2533.



Polycycle 24c. Vinyl stannane **5c** (1.57 g, 3.45 mmol) and vinyl iodide **30** (1.0 g, 3.45 mmol) were subjected to the tandem Stille-oxa-electrocyclization conditions, as described previously for the synthesis of polycycle **3**. Purification by flash chromatography (2:1 hexanes/EtOAc eluent) provided polycycle **24c** (1.0 g, 88% yield) as an orange solid. Suitable crystals for X-ray diffraction were grown from 1:1 hexanes/EtOAc by slow evaporation: R_F 0.24 (1:1 hexanes/EtOAc); mp 142 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 6.78 (t, *J* = 1.7 Hz, 1H), 6.18 (s, 1H), 5.90 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.36 (s, 1H), 4.19 (d, *J* = 11.4 Hz, 1H), 3.20 (d, *J* = 11.2 Hz, 1H), 2.17 (s, 3H), 1.95-1.88 (m, 2H), 1.40-1.22 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 201.9, 192.8, 178.1, 154.9, 149.9, 145.1, 144.8, 144.2, 107.7, 98.3, 86.3, 70.5, 44.8, 33.4, 29.1, 27.7, 26.6, 14.4; IR

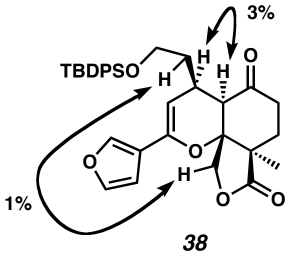
(thin film/NaCl) 3135, 2918, 1782, 1705, 1668, 1560, 1519, 1499, 1161 cm^{-1}; HRMS (EI$^+$) *m/z* calc'd for $[C_{18}H_{16}O_6]^+$: 328.0947, found 328.0946.



24a 38

Ketone 38. To a solution of enone **24a** (36.7 mg, 0.0645 mmol) in THF (500 mL) was added catecholborane (20 mL, 0.194 mmol). The mixture was stirred for 90 min and then quenched with MeOH (500 mL). The mixture was diluted with Et_2O (20 mL) and extracted with a 2:1 mixture of 1 N NaOH and saturated aqueous NH_4Cl (4 x 7 mL). The combined aqueous layers were extracted with Et_2O (10 mL). The combined organic layers were washed with brine (15 mL) and dried over Na_2SO_4. After filtration, the residue was concentrated under reduced pressure. Purification by preparatory thin layer chromatography on silica gel (0.5 mm, 3:1 hexanes/EtOAc eluent) provided ketone **38** (15.5 mg, 42% yield) as a clear oil: R_F 0.27 (2:1 hexanes/EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.67 (m, 5H), 7.48-7.34 (m, 7H), 6.32 (s, 1H), 5.31 (d, *J* = 5.5 Hz, 1H), 4.37 (d, *J* = 11.0 Hz, 1H), 4.09 (d, *J* = 10.4 Hz, 1H), 3.86 (t, *J* = 6.0 Hz, 2H), 3.00 (d, *J* = 4.9 Hz, 1H), 2.91-2.82 (m, 1H), 2.69-2.54 (m, 1H), 2.50-2.28 (m, 2H), 2.10-1.97 (m, 3H), 1.51 (s, 3H), 1.09 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 203.4, 178.3, 143.8, 143.2, 140.2, 136.5, 136.4, 134.6, 134.5, 130.5, 130.5, 122.9, 107.8, 101.6, 84.8, 78.0, 71.3, 63.5, 49.7, 45.9, 36.2, 35.0, 30.2, 27.9, 27.5, 19.9, 13.8; IR (thin film/NaCl) 2931, 1784, 1719, 1105 cm^{-1}; HRMS (FAB$^+$) *m/z* calc'd for $[C_{34}H_{39}O_6Si]^+$: 571.2516, found 571.2492.

Ketone **38** was assigned the indicated relative stereochemistry based on the shown nOe interactions.



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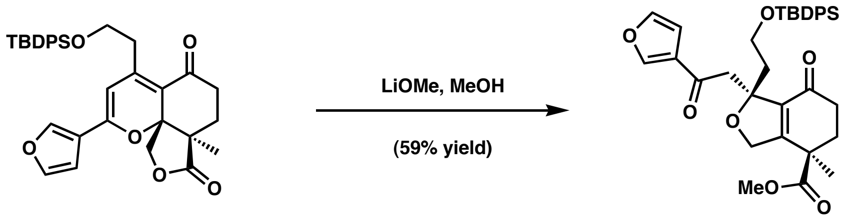
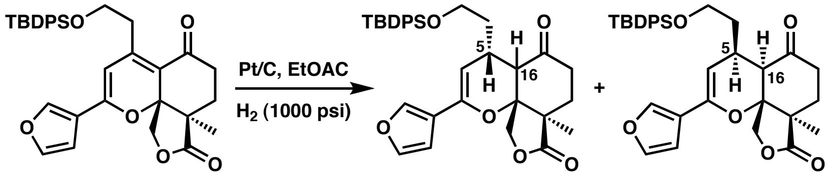


24a 42

Diketone 42. To a solution of lactone **24a** (75.7 mg, 0.133 mmol) in MeOH (1.75 mL) was added LiOH (32 mg, 1.33 mmol). The mixture was stirred for 30 min and then quenched with saturated aqueous

NH_4Cl (5 mL). The mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over Na_2SO_4. After filtration the residue was concentrated under reduced pressure. Purification by flash chromatography (4:1 hexanes/EtOAc eluent) provided diketone **42** (47.0 mg, 59% yield) as a clear oil: R_F 0.52 (1:1 hexanes/EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 1.5, 0.7 Hz, 1H), 7.69-7.60 (m, 5H), 7.42-7.35 (m, 6H), 6.69 (dd, *J* = 1.9, 0.8 Hz, 1H), 4.58 (d, *J* = 16.0 Hz, 1H), 4.47 (d, *J* = 15.7 Hz, 1H), 3.86-3.73 (m, 1H), 3.52-3.44 (m, 1H), 3.37 (s, 3H), 3.24-3.20 (m, 3H), 2.38-2.20 (m, 4H), 1.92-1.81 (m, 1H), 1.29 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.9, 192.9, 173.6, 159.4, 148.4, 144.2, 135.7, 133.9, 129.7, 129.0, 127.9, 108.7, 90.2, 74.2, 60.0, 52.6, 48.7, 43.9, 42.4, 35.7, 35.0, 27.0, 26.9, 23.0, 19.3; IR (thin film/NaCl) 2930, 1735, 1675, 1111 cm^{-1}; HRMS (FAB^+) *m/z* calc'd for $[C_{35}H_{41}O_7Si]^+$: 601.2622, found 601.2631.



24a

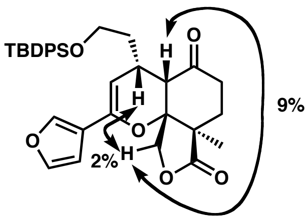
43 *(65%, 1.4:1 @ C(16))*

38 *(13%)*

Ketone 43. Two batches of enone **24a** (2.33 g, 4.105 mmol each) were separately dissolved in EtOAc (11 mL each). To these mixtures were added 10% Pt/C (560 mg in each mixture). The mixtures were then transferred to a H_2 bomb and stirred for 9 h under an atmosphere of pressurized H_2 (1000 psi). The two mixtures were then combined and passed through a short pad of silica gel to remove the Pt/C (EtOAc eluent). Purification by flash chromatography (5:1 hexanes/EtOAc eluent) provided the C(16) β-H epimer of ketone **43** (1.29 g, 27.5% yield) as a white solid, the C(16) α-H epimer of ketone **43** (1.75 g, 37.2% yield) as a clear oil,[6] and ketone **38** (0.627 g, 13.4% yield) as a clear oil. For the C(16) β-H epimer of **43**, suitable crystals for X-ray diffraction were grown from Et_2O by slow evaporation.

Ketone ***43*** *C(16) β-H:* R_F 0.45 (2:1 hexanes/EtOAc); mp 131 °C; ^1H NMR (300 MHz, C_6D_6) δ 7.79-7.71 (m, 5H), 7.32-7.21 (m, 6H), 6.97 (t, *J* = 1.7 Hz, 1H), 6.15-6.12 (m, 1H), 4.94 (s, 1H), 3.93 (d, *J* = 9.6 Hz, 1H), 3.82-3.72 (m, 1H), 3.67-3.57 (m, 2H), 3.26 (q, *J* = 7.0 Hz, 2H), 2.75-2.65 (m, 1H), 2.47 (d, *J* = 4.3 Hz, 1H), 2.26-2.16 (m, 2H), 1.92-1.83 (m, 2H), 1.18 (s, 9H), 0.98 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 205.6, 177.9, 143.8, 143.6, 139.5, 136.4, 136.3, 134.2, 134.1, 130.6, 130.5, 122.9, 107.9, 101.2, 84.5, 73.3, 62.7, 47.1, 46.3, 37.3, 34.2, 30.9, 28.2, 27.5, 27.3, 19.8, 18.8; IR (thin film/NaCl) 2931, 2858, 1784, 1727, 1111 cm^{-1}; HRMS (FAB^+) *m/z* calc'd for $[C_{34}H_{39}O_6Si]^+$: 571.2516, found 571.2502.

The C(16) β-H epimer of ketone **43** was assigned the indicated relative stereochemistry based on the shown nOe interactions.



43
C(16) β-H

Crystal Structure Analysis of 19a

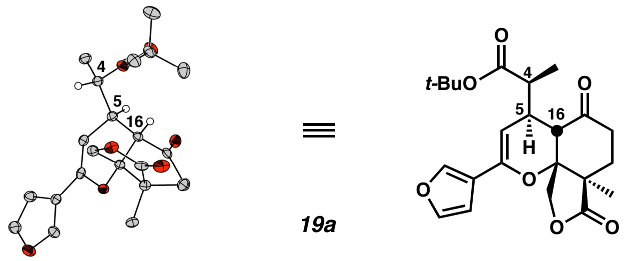


Figure S1 Ketone **19a** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 175515.

Table S1 Crystal data and structure refinement for **19a** (CCDC 175515).

Empirical formula	$C_{23}H_{28}O_7$	
Formula weight	416.45	
Crystallization Solvent	Ether	
Crystal Habit	Irregular fragment	
Crystal size	Not measured	
Crystal color	Colorless	

Data Collection

Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	98(2) K	
θ range for 12296 reflections used in lattice determination	2.22 to 28.17°	
Unit cell dimensions	a = 8.2333(6) Å b = 25.9013(19) Å c = 9.8295(7) Å	β= 95.7760(10)°
Volume	2085.5(3) Å^3	
Z	4	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Density (calculated)	1.326 Mg/m^3	

F(000)	888
Data collection program	Bruker SMART v5.054
θ range for data collection	1.57 to 28.23°
Completeness to θ = 28.23°	95.1 %
Index ranges	$-10 \le h \le 10$, $-32 \le k \le 34$, $-12 \le l \le 12$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.22
Reflections collected	30345
Independent reflections	4886 [R_{int}= 0.0543]
Absorption coefficient	0.098 mm^{-1}
Absorption correction	None

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	4886 / 0 / 383
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.845
Final R indices [$I>2\sigma(I)$, 3765 reflections]	R1 = 0.0418, *w*R2 = 0.0643
R indices (all data)	R1 = 0.0574, *w*R2 = 0.0657
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Largest diff. peak and hole	0.404 and -0.295 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **19a** (CCDC 175515). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	8639(1)	3834(1)	4601(1)	29(1)
O(2)	8194(1)	4245(1)	2608(1)	22(1)
O(3)	11695(1)	2720(1)	142(1)	21(1)
O(4)	7428(1)	3279(1)	66(1)	16(1)
O(5)	3617(1)	3010(1)	-2777(1)	24(1)
O(6)	13803(1)	4143(1)	617(1)	26(1)
O(7)	11834(1)	4617(1)	1480(1)	19(1)
C(1)	8369(2)	3813(1)	3377(1)	20(1)
C(2)	8169(2)	3333(1)	2491(1)	17(1)
C(3)	6399(2)	3144(1)	2504(1)	20(1)
C(4)	9385(2)	2914(1)	3023(1)	21(1)
C(5)	9899(2)	2586(1)	1863(1)	20(1)
C(6)	10710(2)	2902(1)	842(1)	16(1)
C(7)	10239(2)	3476(1)	740(1)	15(1)
C(8)	8477(1)	3547(1)	1078(1)	15(1)
C(9)	7933(2)	4112(1)	1170(1)	18(1)
C(10)	7624(2)	3422(1)	-1270(1)	15(1)
C(11)	6141(2)	3297(1)	-2143(1)	16(1)
C(12)	5839(2)	3328(1)	-3601(1)	22(1)
C(13)	4324(2)	3153(1)	-3926(1)	25(1)
C(14)	4762(2)	3105(1)	-1705(1)	19(1)
C(15)	9002(2)	3622(1)	-1634(1)	16(1)
C(16)	10525(2)	3693(1)	-674(1)	15(1)
C(17)	11219(2)	4255(1)	-723(1)	17(1)
C(18)	12034(2)	4328(1)	-2041(1)	22(1)
C(19)	12456(2)	4333(1)	509(1)	18(1)
C(20)	12799(2)	4717(1)	2823(1)	22(1)
C(21)	14328(2)	5015(1)	2589(2)	33(1)
C(22)	11655(2)	5045(1)	3566(2)	27(1)
C(23)	13149(2)	4212(1)	3576(2)	30(1)

Table S3 Bond lengths [Å] and angles [°] for **19a** (CCDC 175515).

O(1)-C(1)	1.2027(14)
O(2)-C(1)	1.3503(15)
O(2)-C(9)	1.4497(14)
O(3)-C(6)	1.2103(14)
O(4)-C(10)	1.3887(13)
O(4)-C(8)	1.4295(14)
O(5)-C(14)	1.3640(14)
O(5)-C(13)	1.3722(15)
O(6)-C(19)	1.2084(14)
O(7)-C(19)	1.3457(14)
O(7)-C(20)	1.4939(14)
C(1)-C(2)	1.5174(17)
C(2)-C(4)	1.5313(18)
C(2)-C(3)	1.5387(17)
C(2)-C(8)	1.5399(16)
C(3)-H(3A)	0.985(12)
C(3)-H(3B)	0.995(13)
C(3)-H(3C)	1.001(13)
C(4)-C(5)	1.5171(18)
C(4)-H(4A)	0.996(13)
C(4)-H(4B)	0.981(12)
C(5)-C(6)	1.5033(17)
C(5)-H(5A)	0.959(13)
C(5)-H(5B)	0.979(13)
C(6)-C(7)	1.5372(17)
C(7)-C(8)	1.5312(16)
C(7)-C(16)	1.5394(16)
C(7)-H(7)	0.954(12)
C(8)-C(9)	1.5374(17)
C(9)-H(9A)	0.992(12)
C(9)-H(9B)	0.978(12)
C(10)-C(15)	1.3289(16)
C(10)-C(11)	1.4572(16)
C(11)-C(14)	1.3491(17)
C(11)-C(12)	1.4314(17)
C(12)-C(13)	1.3354(18)
C(12)-H(12)	0.956(13)
C(13)-H(13)	0.971(13)
C(14)-H(14)	0.958(12)
C(15)-C(16)	1.5030(17)
C(15)-H(15)	0.926(11)
C(16)-C(17)	1.5649(16)
C(16)-H(16)	1.004(11)
C(17)-C(19)	1.5158(17)
C(17)-C(18)	1.5292(17)
C(17)-H(17)	1.001(12)
C(18)-H(18A)	0.999(13)
C(18)-H(18B)	0.956(13)
C(18)-H(18C)	1.004(13)
C(20)-C(22)	1.5102(19)
C(20)-C(21)	1.5142(19)

C(20)-C(23)	1.5169(19)
C(21)-H(21A)	1.015(15)
C(21)-H(21B)	0.987(15)
C(21)-H(21C)	0.973(16)
C(22)-H(22A)	0.996(15)
C(22)-H(22B)	0.953(14)
C(22)-H(22C)	0.990(15)
C(23)-H(23A)	0.988(14)
C(23)-H(23B)	1.033(15)
C(23)-H(23C)	0.977(15)

C(1)-O(2)-C(9)	110.26(9)
C(10)-O(4)-C(8)	114.18(9)
C(14)-O(5)-C(13)	105.68(10)
C(19)-O(7)-C(20)	121.01(9)
O(1)-C(1)-O(2)	121.41(11)
O(1)-C(1)-C(2)	127.58(12)
O(2)-C(1)-C(2)	111.01(10)
C(1)-C(2)-C(4)	110.80(11)
C(1)-C(2)-C(3)	107.69(10)
C(4)-C(2)-C(3)	111.03(11)
C(1)-C(2)-C(8)	101.83(10)
C(4)-C(2)-C(8)	113.66(10)
C(3)-C(2)-C(8)	111.35(10)
C(2)-C(3)-H(3A)	110.4(7)
C(2)-C(3)-H(3B)	111.8(7)
H(3A)-C(3)-H(3B)	109.0(10)
C(2)-C(3)-H(3C)	111.1(7)
H(3A)-C(3)-H(3C)	106.1(10)
H(3B)-C(3)-H(3C)	108.2(10)
C(5)-C(4)-C(2)	111.27(11)
C(5)-C(4)-H(4A)	108.8(7)
C(2)-C(4)-H(4A)	109.3(7)
C(5)-C(4)-H(4B)	109.8(7)
C(2)-C(4)-H(4B)	108.9(7)
H(4A)-C(4)-H(4B)	108.7(10)
C(6)-C(5)-C(4)	111.88(11)
C(6)-C(5)-H(5A)	109.2(8)
C(4)-C(5)-H(5A)	110.9(8)
C(6)-C(5)-H(5B)	106.3(7)
C(4)-C(5)-H(5B)	109.4(7)
H(5A)-C(5)-H(5B)	109.1(11)
O(3)-C(6)-C(5)	122.32(12)
O(3)-C(6)-C(7)	121.28(11)
C(5)-C(6)-C(7)	116.39(10)
C(8)-C(7)-C(6)	109.85(10)
C(8)-C(7)-C(16)	112.76(10)
C(6)-C(7)-C(16)	110.59(10)
C(8)-C(7)-H(7)	108.3(7)
C(6)-C(7)-H(7)	103.6(7)
C(16)-C(7)-H(7)	111.3(7)
O(4)-C(8)-C(7)	108.07(9)
O(4)-C(8)-C(9)	110.07(10)
C(7)-C(8)-C(9)	114.49(10)

O(4)-C(8)-C(2)	108.12(9)
C(7)-C(8)-C(2)	113.49(10)
C(9)-C(8)-C(2)	102.37(9)
O(2)-C(9)-C(8)	105.54(10)
O(2)-C(9)-H(9A)	105.0(7)
C(8)-C(9)-H(9A)	115.9(7)
O(2)-C(9)-H(9B)	108.0(6)
C(8)-C(9)-H(9B)	110.3(7)
H(9A)-C(9)-H(9B)	111.4(9)
C(15)-C(10)-O(4)	122.84(11)
C(15)-C(10)-C(11)	128.00(11)
O(4)-C(10)-C(11)	109.11(10)
C(14)-C(11)-C(12)	105.87(11)
C(14)-C(11)-C(10)	125.18(11)
C(12)-C(11)-C(10)	128.91(11)
C(13)-C(12)-C(11)	106.55(12)
C(13)-C(12)-H(12)	128.2(8)
C(11)-C(12)-H(12)	125.3(8)
C(12)-C(13)-O(5)	110.94(12)
C(12)-C(13)-H(13)	134.9(8)
O(5)-C(13)-H(13)	114.1(8)
C(11)-C(14)-O(5)	110.96(11)
C(11)-C(14)-H(14)	134.4(8)
O(5)-C(14)-H(14)	114.6(7)
C(10)-C(15)-C(16)	124.02(11)
C(10)-C(15)-H(15)	116.5(7)
C(16)-C(15)-H(15)	119.3(7)
C(15)-C(16)-C(7)	109.17(10)
C(15)-C(16)-C(17)	112.24(10)
C(7)-C(16)-C(17)	117.18(10)
C(15)-C(16)-H(16)	108.1(6)
C(7)-C(16)-H(16)	106.5(6)
C(17)-C(16)-H(16)	103.0(6)
C(19)-C(17)-C(18)	110.08(11)
C(19)-C(17)-C(16)	108.54(10)
C(18)-C(17)-C(16)	109.53(10)
C(19)-C(17)-H(17)	107.9(6)
C(18)-C(17)-H(17)	110.9(6)
C(16)-C(17)-H(17)	109.9(7)
C(17)-C(18)-H(18A)	110.3(7)
C(17)-C(18)-H(18B)	111.1(7)
H(18A)-C(18)-H(18B)	108.5(10)
C(17)-C(18)-H(18C)	111.2(7)
H(18A)-C(18)-H(18C)	106.8(10)
H(18B)-C(18)-H(18C)	108.7(10)
O(6)-C(19)-O(7)	124.86(12)
O(6)-C(19)-C(17)	123.54(11)
O(7)-C(19)-C(17)	111.53(10)
O(7)-C(20)-C(22)	102.87(10)
O(7)-C(20)-C(21)	109.31(11)
C(22)-C(20)-C(21)	110.83(12)
O(7)-C(20)-C(23)	109.84(10)
C(22)-C(20)-C(23)	110.28(12)
C(21)-C(20)-C(23)	113.22(13)

C(20)-C(21)-H(21A)	108.3(8)
C(20)-C(21)-H(21B)	108.3(8)
H(21A)-C(21)-H(21B)	105.0(12)
C(20)-C(21)-H(21C)	112.3(9)
H(21A)-C(21)-H(21C)	113.3(12)
H(21B)-C(21)-H(21C)	109.4(12)
C(20)-C(22)-H(22A)	108.9(8)
C(20)-C(22)-H(22B)	110.6(8)
H(22A)-C(22)-H(22B)	107.8(11)
C(20)-C(22)-H(22C)	110.4(8)
H(22A)-C(22)-H(22C)	108.7(11)
H(22B)-C(22)-H(22C)	110.4(11)
C(20)-C(23)-H(23A)	107.6(8)
C(20)-C(23)-H(23B)	109.3(8)
H(23A)-C(23)-H(23B)	109.6(11)
C(20)-C(23)-H(23C)	111.1(9)
H(23A)-C(23)-H(23C)	109.6(11)
H(23B)-C(23)-H(23C)	109.6(12)

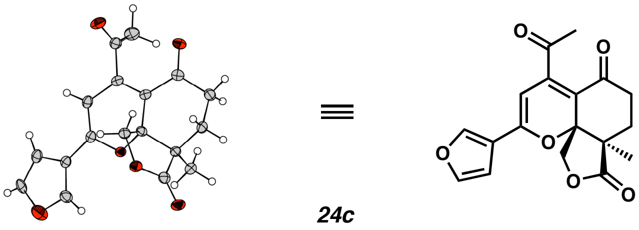
Table S4 Anisotropic displacement parameters ($Å^2$x 10^4) for **19a** (CCDC 175515). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	359(6)	331(6)	178(5)	-64(4)	65(4)	-105(5)
O(2)	270(5)	198(5)	213(5)	-44(4)	69(4)	-27(4)
O(3)	213(5)	210(5)	222(5)	7(4)	44(4)	44(4)
O(4)	162(5)	186(5)	133(4)	-1(4)	13(4)	-35(4)
O(5)	191(5)	320(6)	211(5)	-10(4)	-1(4)	-60(4)
O(6)	162(5)	292(6)	312(5)	-56(4)	5(4)	25(4)
O(7)	165(5)	185(5)	225(5)	-37(4)	2(4)	0(4)
C(1)	167(7)	234(7)	217(7)	-31(6)	71(6)	-49(6)
C(2)	178(7)	182(7)	148(6)	-10(5)	29(5)	-20(5)
C(3)	214(8)	207(8)	191(7)	3(6)	62(6)	-33(6)
C(4)	219(8)	246(8)	165(7)	41(6)	25(6)	-11(6)
C(5)	198(7)	178(7)	235(7)	46(6)	15(6)	35(6)
C(6)	131(7)	183(7)	167(6)	-12(5)	-33(5)	-6(5)
C(7)	136(7)	160(7)	139(6)	-14(5)	-4(5)	-19(5)
C(8)	146(7)	152(7)	151(6)	-13(5)	9(5)	-12(5)
C(9)	169(7)	182(7)	193(7)	-10(6)	40(6)	4(6)
C(10)	196(7)	116(6)	135(6)	3(5)	20(5)	32(5)
C(11)	175(7)	132(6)	165(6)	-12(5)	20(5)	8(5)
C(12)	225(8)	242(8)	188(7)	5(6)	28(6)	-33(6)
C(13)	269(8)	295(8)	175(7)	11(6)	-19(6)	-46(6)
C(14)	179(7)	217(7)	174(7)	-26(6)	3(6)	-9(5)
C(15)	186(7)	153(7)	129(6)	4(5)	28(5)	11(5)
C(16)	149(7)	142(7)	166(6)	-2(5)	36(5)	0(5)
C(17)	148(7)	141(7)	229(7)	12(5)	38(6)	0(5)
C(18)	202(8)	199(8)	254(8)	30(6)	61(6)	-14(6)
C(19)	164(7)	133(7)	258(7)	10(5)	50(6)	-34(5)
C(20)	187(7)	212(7)	234(7)	-53(6)	-43(6)	-7(6)
C(21)	260(9)	359(10)	372(10)	-110(8)	20(7)	-86(8)
C(22)	255(9)	265(9)	282(9)	-66(7)	-2(7)	5(7)
C(23)	361(10)	263(9)	261(8)	-40(7)	-58(7)	58(7)

Table S5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **19a** (CCDC 175515).

	x	y	z	U_{iso}
H(3A)	6160(14)	3071(5)	3447(13)	19(3)
H(3B)	5599(15)	3402(5)	2092(12)	23(4)
H(3C)	6220(15)	2812(5)	1989(13)	26(4)
H(4A)	10372(16)	3080(5)	3503(12)	26(4)
H(4B)	8875(14)	2696(5)	3677(12)	17(3)
H(5A)	10626(16)	2316(5)	2205(13)	26(4)
H(5B)	8931(16)	2431(5)	1363(12)	21(3)
H(7)	10949(15)	3634(5)	1448(12)	18(3)
H(9A)	8579(15)	4368(5)	702(12)	19(3)
H(9B)	6765(15)	4144(4)	879(11)	11(3)
H(12)	6599(16)	3449(5)	-4201(13)	26(4)
H(13)	3621(16)	3110(5)	-4773(13)	29(4)
H(14)	4421(15)	3026(5)	-825(12)	22(4)
H(15)	9019(14)	3702(4)	-2550(12)	12(3)
H(16)	11412(14)	3478(4)	-1018(11)	12(3)
H(17)	10319(14)	4511(4)	-665(11)	14(3)
H(18A)	12311(15)	4700(5)	-2164(12)	26(4)
H(18B)	13014(16)	4130(5)	-2023(12)	25(4)
H(18C)	11283(16)	4225(5)	-2864(13)	27(4)
H(21A)	13993(17)	5336(6)	2039(14)	37(4)
H(21B)	14823(17)	5145(5)	3480(15)	39(4)
H(21C)	15119(19)	4804(6)	2172(15)	47(5)
H(22A)	12173(17)	5117(5)	4507(15)	39(4)
H(22B)	10658(17)	4866(5)	3648(13)	28(4)
H(22C)	11439(17)	5378(6)	3083(13)	37(4)
H(23A)	13729(16)	4295(5)	4480(14)	32(4)
H(23B)	12061(19)	4029(6)	3706(14)	43(4)
H(23C)	13828(18)	3986(6)	3074(15)	44(5)

Crystal Structure Analysis of 24c



24c

Figure S2 Polycycle **24c** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 201414.

Table S6 Crystal data and structure refinement for 24c (CCDC 201414).

Empirical formula	$C_{18}H_{16}O_6$
Formula weight	328.31
Crystallization Solvent	Hexanes/ethylacetate
Crystal Habit	Fragment
Crystal size	0.28 x 0.22 x 0.15 mm^3
Crystal color	Yellow

Data Collection

Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	98(2) K	
θ range for 7975 reflections used in lattice determination	2.26 to 28.15°	
Unit cell dimensions	a = 12.3799(11) Å b = 7.2521(7) Å c = 17.2138(15) Å	 β= 101.892(2)°
Volume	1512.3(2) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Density (calculated)	1.442 Mg/m^3	
F(000)	688	
Data collection program	Bruker SMART v5.054	

θ range for data collection	1.86 to 28.22°
Completeness to θ = 28.22°	94.4 %
Index ranges	$-15 \le h \le 16$, $-9 \le k \le 9$, $-22 \le l \le 21$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	21320
Independent reflections	3525 [R_{int}= 0.0530]
Absorption coefficient	0.109 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9838 and 0.9701

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	3525 / 0 / 281
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.948
Final R indices [$I>2\sigma(I)$, 2658 reflections]	R1 = 0.0425, *w*R2 = 0.0689
R indices (all data)	R1 = 0.0606, *w*R2 = 0.0710
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Largest diff. peak and hole	0.376 and -0.393 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table S7 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **24c** (CCDC 201414). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
O(1)	7557(1)	-202(1)	-1544(1)	32(1)
O(2)	9763(1)	1794(1)	-583(1)	23(1)
O(3)	9007(1)	2746(1)	3057(1)	27(1)
O(4)	8289(1)	483(1)	2230(1)	22(1)
O(5)	7079(1)	2940(1)	971(1)	18(1)
O(6)	3873(1)	3651(2)	1211(1)	39(1)
C(1)	6423(1)	1692(2)	-309(1)	20(1)
C(2)	7531(1)	1661(2)	-435(1)	18(1)
C(3)	8392(1)	1951(2)	179(1)	17(1)
C(4)	9524(1)	2132(2)	62(1)	18(1)
C(5)	10385(1)	2853(2)	743(1)	22(1)
C(6)	10145(1)	2438(2)	1559(1)	21(1)
C(7)	8975(1)	3043(2)	1635(1)	17(1)
C(8)	8765(1)	2161(2)	2391(1)	21(1)
C(9)	8083(1)	134(2)	1380(1)	20(1)
C(10)	8135(1)	2030(2)	997(1)	17(1)
C(11)	6232(1)	2420(2)	372(1)	18(1)
C(12)	5164(1)	2845(2)	541(1)	18(1)
C(13)	4133(1)	2958(2)	1(1)	22(1)
C(14)	3386(1)	3403(2)	410(1)	23(1)
C(15)	4958(1)	3270(2)	1271(1)	25(1)
C(16)	7661(1)	1354(2)	-1282(1)	22(1)
C(17)	7785(2)	2990(2)	-1776(1)	29(1)
C(18)	8853(1)	5134(2)	1645(1)	22(1)

Table S8 Bond lengths [Å] and angles [°] for **24c** (CCDC 201414).

O(1)-C(16)	1.2118(16)
O(2)-C(4)	1.2302(15)
O(3)-C(8)	1.2008(15)
O(4)-C(8)	1.3562(17)
O(4)-C(9)	1.4550(16)
O(5)-C(11)	1.3639(15)
O(5)-C(10)	1.4564(16)
O(6)-C(15)	1.3551(18)
O(6)-C(14)	1.3979(19)
C(1)-C(11)	1.3495(19)
C(1)-C(2)	1.433(2)
C(1)-H(1)	0.947(14)
C(2)-C(3)	1.3548(18)
C(2)-C(16)	1.5151(19)
C(3)-C(4)	1.4630(19)
C(3)-C(10)	1.5061(18)
C(4)-C(5)	1.507(2)
C(5)-C(6)	1.5238(19)
C(5)-H(5A)	1.013(14)
C(5)-H(5B)	0.982(15)
C(6)-C(7)	1.5453(19)
C(6)-H(6A)	0.963(14)
C(6)-H(6B)	1.007(14)
C(7)-C(8)	1.5191(19)
C(7)-C(10)	1.5352(18)
C(7)-C(18)	1.524(2)
C(9)-C(10)	1.5325(19)
C(9)-H(9A)	0.956(15)
C(9)-H(9B)	1.028(14)
C(11)-C(12)	1.4439(19)
C(12)-C(15)	1.367(2)
C(12)-C(13)	1.4186(19)
C(13)-C(14)	1.313(2)
C(13)-H(13)	0.963(14)
C(14)-H(14)	0.706(15)
C(15)-H(15)	0.951(15)
C(16)-C(17)	1.487(2)
C(17)-H(17A)	0.951(18)
C(17)-H(17B)	1.000(17)
C(17)-H(17C)	0.990(17)
C(18)-H(18A)	1.024(15)
C(18)-H(18B)	0.972(15)
C(18)-H(18C)	0.986(15)
C(8)-O(4)-C(9)	109.86(10)
C(11)-O(5)-C(10)	116.28(10)
C(15)-O(6)-C(14)	105.53(12)
C(11)-C(1)-C(2)	118.85(14)
C(11)-C(1)-H(1)	118.0(8)
C(2)-C(1)-H(1)	122.5(8)

C(3)-C(2)-C(1)	120.16(13)
C(3)-C(2)-C(16)	123.44(13)
C(1)-C(2)-C(16)	116.37(12)
C(2)-C(3)-C(4)	121.86(12)
C(2)-C(3)-C(10)	116.87(12)
C(4)-C(3)-C(10)	121.25(12)
O(2)-C(4)-C(3)	121.49(13)
O(2)-C(4)-C(5)	120.57(13)
C(3)-C(4)-C(5)	117.86(12)
C(4)-C(5)-C(6)	114.14(12)
C(4)-C(5)-H(5A)	105.8(8)
C(6)-C(5)-H(5A)	110.0(8)
C(4)-C(5)-H(5B)	108.1(8)
C(6)-C(5)-H(5B)	109.9(8)
H(5A)-C(5)-H(5B)	108.6(11)
C(5)-C(6)-C(7)	112.68(12)
C(5)-C(6)-H(6A)	109.4(8)
C(7)-C(6)-H(6A)	108.0(8)
C(5)-C(6)-H(6B)	107.4(8)
C(7)-C(6)-H(6B)	110.9(8)
H(6A)-C(6)-H(6B)	108.5(11)
C(8)-C(7)-C(10)	101.65(11)
C(8)-C(7)-C(18)	111.96(12)
C(10)-C(7)-C(18)	115.50(12)
C(8)-C(7)-C(6)	106.35(11)
C(10)-C(7)-C(6)	108.23(11)
C(18)-C(7)-C(6)	112.29(12)
O(3)-C(8)-O(4)	121.56(13)
O(3)-C(8)-C(7)	128.07(13)
O(4)-C(8)-C(7)	110.30(11)
O(4)-C(9)-C(10)	105.25(11)
O(4)-C(9)-H(9A)	107.7(9)
C(10)-C(9)-H(9A)	111.4(9)
O(4)-C(9)-H(9B)	111.4(8)
C(10)-C(9)-H(9B)	110.5(8)
H(9A)-C(9)-H(9B)	110.5(11)
O(5)-C(10)-C(3)	110.50(10)
O(5)-C(10)-C(7)	106.03(10)
C(3)-C(10)-C(7)	116.40(11)
O(5)-C(10)-C(9)	107.60(11)
C(3)-C(10)-C(9)	113.81(11)
C(7)-C(10)-C(9)	101.72(11)
C(1)-C(11)-O(5)	121.35(13)
C(1)-C(11)-C(12)	126.13(13)
O(5)-C(11)-C(12)	112.43(11)
C(15)-C(12)-C(13)	106.02(13)
C(15)-C(12)-C(11)	125.81(13)
C(13)-C(12)-C(11)	128.15(13)
C(14)-C(13)-C(12)	107.52(14)
C(14)-C(13)-H(13)	124.6(9)
C(12)-C(13)-H(13)	127.9(9)
C(13)-C(14)-O(6)	110.62(15)
C(13)-C(14)-H(14)	136.8(13)
O(6)-C(14)-H(14)	112.3(13)

O(6)-C(15)-C(12)	110.27(14)
O(6)-C(15)-H(15)	117.5(9)
C(12)-C(15)-H(15)	132.2(9)
O(1)-C(16)-C(2)	118.03(13)
O(1)-C(16)-C(17)	123.07(14)
C(2)-C(16)-C(17)	118.53(13)
C(16)-C(17)-H(17A)	108.8(10)
C(16)-C(17)-H(17B)	111.6(9)
H(17A)-C(17)-H(17B)	108.0(14)
C(16)-C(17)-H(17C)	112.2(9)
H(17A)-C(17)-H(17C)	107.1(13)
H(17B)-C(17)-H(17C)	108.9(13)
C(7)-C(18)-H(18A)	109.3(8)
C(7)-C(18)-H(18B)	111.6(8)
H(18A)-C(18)-H(18B)	110.3(12)
C(7)-C(18)-H(18C)	108.4(8)
H(18A)-C(18)-H(18C)	109.7(12)
H(18B)-C(18)-H(18C)	107.5(12)

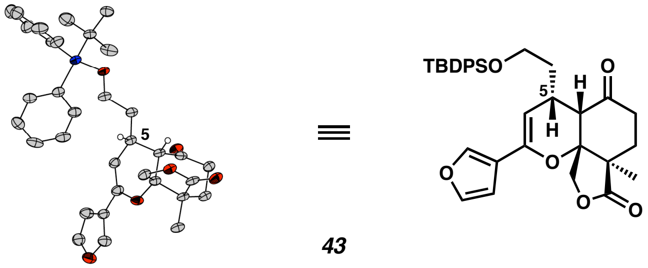
Table S9 Anisotropic displacement parameters (Å^2x 10^4) for **24c** (CCDC 201414). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	418(7)	297(6)	249(6)	-92(5)	72(5)	-20(5)
O(2)	260(6)	276(6)	180(6)	23(4)	93(5)	30(5)
O(3)	301(6)	360(6)	136(6)	-24(5)	30(5)	22(5)
O(4)	269(6)	256(6)	146(5)	28(4)	46(4)	-23(5)
O(5)	162(5)	229(5)	155(5)	-18(4)	26(4)	11(4)
O(6)	329(7)	498(8)	371(7)	25(6)	133(6)	42(6)
C(1)	194(8)	211(8)	173(8)	14(6)	1(7)	-24(6)
C(2)	248(8)	126(7)	164(8)	9(6)	48(6)	5(6)
C(3)	213(8)	148(7)	151(7)	7(6)	39(6)	16(6)
C(4)	236(8)	154(7)	168(8)	44(6)	59(6)	28(6)
C(5)	194(9)	256(9)	220(8)	8(7)	61(7)	-4(7)
C(6)	186(8)	250(9)	167(8)	1(6)	13(7)	-14(7)
C(7)	167(8)	212(8)	135(7)	-3(6)	22(6)	0(6)
C(8)	167(8)	257(8)	195(8)	10(6)	34(6)	40(6)
C(9)	216(9)	234(8)	152(8)	7(6)	42(7)	-15(7)
C(10)	154(7)	188(7)	165(7)	7(6)	45(6)	26(6)
C(11)	197(8)	162(7)	161(7)	31(6)	19(6)	-21(6)
C(12)	206(8)	160(7)	184(8)	13(6)	40(6)	-20(6)
C(13)	241(9)	205(8)	216(9)	33(6)	25(7)	-47(7)
C(14)	113(9)	313(9)	256(9)	79(7)	35(7)	21(7)
C(15)	195(9)	326(9)	236(9)	5(7)	47(7)	30(7)
C(16)	189(8)	270(9)	177(8)	-14(6)	15(6)	19(7)
C(17)	360(11)	336(10)	175(9)	44(7)	42(8)	8(9)
C(18)	228(9)	234(8)	207(9)	-31(7)	36(7)	-18(7)

Table S10 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **24c** (CCDC 201414).

	x	y	z	U_{iso}
H(1)	5805(11)	1389(18)	-713(8)	19(4)
H(5A)	10412(11)	4230(20)	661(8)	28(4)
H(5B)	11101(12)	2324(19)	701(8)	25(4)
H(6A)	10670(12)	3082(19)	1959(8)	23(4)
H(6B)	10250(11)	1070(20)	1653(8)	19(4)
H(9A)	7364(13)	-399(19)	1229(8)	28(4)
H(9B)	8668(12)	-733(19)	1235(8)	22(4)
H(13)	3987(12)	2801(19)	-567(9)	28(4)
H(14)	2817(13)	3610(20)	328(9)	27(5)
H(15)	5430(12)	3399(19)	1778(9)	27(4)
H(17A)	7096(15)	3620(20)	-1906(10)	47(5)
H(17B)	8001(13)	2630(20)	-2283(10)	44(5)
H(17C)	8333(13)	3880(20)	-1492(9)	38(5)
H(18A)	8984(11)	5666(19)	1121(9)	26(4)
H(18B)	8131(13)	5499(19)	1731(8)	25(4)
H(18C)	9410(12)	5627(19)	2091(9)	27(4)

Crystal Structure Analysis of 43 (C(16) β-H)



43

Figure S3 Ketone **43** is shown with 50% probability ellipsoids. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 197200.

Table S11 Crystal data and structure refinement for 43 (C(16) β-H) (CCDC 197200).

Empirical formula	$C_{34}H_{38}O_6Si$
Formula weight	570.73
Crystallization Solvent	Benzene
Crystal Habit	Fragment
Crystal size	0.30 x 0.26 x 0.24 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation	
Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	98(2) K	
θ range for 12272 reflections used in lattice determination	2.41 to 27.51°	
Unit cell dimensions	a = 10.3188(7) Å b = 10.5705(8) Å c = 27.269(2) Å	β= 92.9410(10)°
Volume	2970.5(4) Å^3	
Z	4	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Density (calculated)	1.276 Mg/m^3	

F(000)	1216
Data collection program	Bruker SMART v5.054
θ range for data collection	1.50 to 28.26°
Completeness to θ = 28.26°	93.9 %
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 13$, $-35 \leq l \leq 35$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	49441
Independent reflections	6912 [R_{int}= 0.0683]
Absorption coefficient	0.124 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9709 and 0.9638

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	6912 / 0 / 522
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.686
Final R indices [$I>2\sigma(I)$, 4526 reflections]	R1 = 0.0491, *w*R2 = 0.0689
R indices (all data)	R1 = 0.0835, *w*R2 = 0.0712
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Largest diff. peak and hole	0.534 and -0.364 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table S12 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **43** (CCDC 197200). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Si(1)	2828(1)	9991(1)	2058(1)	24(1)
O(1)	4132(1)	6866(1)	133(1)	33(1)
O(2)	51(1)	4263(1)	-799(1)	36(1)
O(3)	-763(1)	6000(1)	-466(1)	30(1)
O(4)	1492(1)	8495(1)	-683(1)	31(1)
O(5)	2833(1)	11714(1)	-1323(1)	39(1)
O(6)	2483(1)	8760(1)	1706(1)	26(1)
C(1)	1069(2)	7330(2)	-477(1)	24(1)
C(2)	1800(2)	7014(2)	17(1)	23(1)
C(3)	3127(2)	6442(2)	-55(1)	26(1)
C(4)	3089(2)	5294(2)	-380(1)	29(1)
C(5)	2507(2)	5661(2)	-886(1)	28(1)
C(6)	1184(2)	6286(2)	-870(1)	25(1)
C(7)	146(2)	5373(2)	-720(1)	29(1)
C(8)	-396(2)	7321(2)	-413(1)	30(1)
C(9)	756(2)	6771(2)	-1385(1)	31(1)
C(10)	1766(2)	8152(2)	364(1)	25(1)
C(11)	2258(2)	9287(2)	100(1)	30(1)
C(12)	2051(2)	9419(2)	-384(1)	30(1)
C(13)	2508(2)	10459(2)	-680(1)	27(1)
C(14)	3375(2)	11462(2)	-530(1)	37(1)
C(15)	3529(2)	12177(2)	-922(1)	36(1)
C(16)	2225(2)	10654(2)	-1160(1)	33(1)
C(17)	2423(2)	7959(2)	873(1)	26(1)
C(18)	1803(2)	8820(2)	1236(1)	27(1)
C(19)	1354(2)	10465(2)	2386(1)	25(1)
C(20)	187(2)	9866(2)	2284(1)	36(1)
C(21)	-939(2)	10165(2)	2533(1)	42(1)
C(22)	-853(2)	11039(2)	2901(1)	44(1)
C(23)	306(2)	11618(2)	3031(1)	47(1)
C(24)	1383(2)	11359(2)	2769(1)	41(1)
C(25)	3332(2)	11291(2)	1640(1)	25(1)
C(26)	4203(2)	11045(2)	1272(1)	30(1)
C(27)	4499(2)	11948(2)	929(1)	35(1)
C(28)	3931(2)	13125(2)	942(1)	39(1)
C(29)	3075(2)	13413(2)	1300(1)	35(1)
C(30)	2782(2)	12501(2)	1645(1)	29(1)
C(31)	4151(2)	9415(2)	2501(1)	28(1)
C(32)	3668(2)	8237(2)	2761(1)	32(1)
C(33)	5347(2)	9070(3)	2216(1)	43(1)
C(34)	4556(3)	10399(2)	2891(1)	46(1)

Table S13 Bond lengths [Å] and angles [°] for **43** (CCDC 197200).

Si(1)-O(6)	1.6437(12)
Si(1)-C(19)	1.8717(18)
Si(1)-C(25)	1.8745(18)
Si(1)-C(31)	1.8779(18)
O(1)-C(3)	1.2182(19)
O(2)-C(7)	1.197(2)
O(3)-C(7)	1.365(2)
O(3)-C(8)	1.452(2)
O(4)-C(12)	1.3799(19)
O(4)-C(1)	1.4312(19)
O(5)-C(15)	1.368(2)
O(5)-C(16)	1.371(2)
O(6)-C(18)	1.432(2)
C(1)-C(8)	1.531(2)
C(1)-C(2)	1.544(2)
C(1)-C(6)	1.547(2)
C(2)-C(3)	1.519(2)
C(2)-C(10)	1.533(2)
C(2)-H(2)	0.977(14)
C(3)-C(4)	1.502(2)
C(4)-C(5)	1.526(2)
C(4)-H(4A)	0.969(16)
C(4)-H(4B)	0.967(16)
C(5)-C(6)	1.519(2)
C(5)-H(5A)	0.937(16)
C(5)-H(5B)	0.971(16)
C(6)-C(7)	1.513(2)
C(6)-C(9)	1.540(2)
C(8)-H(8A)	0.987(16)
C(8)-H(8B)	1.003(17)
C(9)-H(9A)	1.004(17)
C(9)-H(9B)	0.988(18)
C(9)-H(9C)	0.999(18)
C(10)-C(11)	1.501(2)
C(10)-C(17)	1.526(2)
C(10)-H(10)	0.995(15)
C(11)-C(12)	1.333(2)
C(11)-H(11)	0.946(15)
C(12)-C(13)	1.456(2)
C(13)-C(16)	1.341(2)
C(13)-C(14)	1.433(2)
C(14)-C(15)	1.326(3)
C(14)-H(14)	0.949(17)
C(15)-H(15)	0.923(18)
C(16)-H(16)	0.969(17)
C(17)-C(18)	1.511(2)
C(17)-H(17A)	0.962(16)
C(17)-H(17B)	0.931(16)
C(18)-H(18A)	1.025(14)
C(18)-H(18B)	0.965(15)
C(19)-C(20)	1.376(2)

C(19)-C(24)	1.407(2)
C(20)-C(21)	1.412(3)
C(20)-H(20)	0.955(17)
C(21)-C(22)	1.363(3)
C(21)-H(21)	0.900(18)
C(22)-C(23)	1.374(3)
C(22)-H(22)	0.92(2)
C(23)-C(24)	1.380(3)
C(23)-H(23)	1.08(2)
C(24)-H(24)	1.02(2)
C(25)-C(30)	1.399(2)
C(25)-C(26)	1.407(2)
C(26)-C(27)	1.381(3)
C(26)-H(26)	0.992(16)
C(27)-C(28)	1.376(3)
C(27)-H(27)	0.975(17)
C(28)-C(29)	1.385(3)
C(28)-H(28)	0.915(16)
C(29)-C(30)	1.389(3)
C(29)-H(29)	0.923(14)
C(30)-H(30)	0.949(15)
C(31)-C(32)	1.529(3)
C(31)-C(34)	1.530(3)
C(31)-C(33)	1.535(3)
C(32)-H(32A)	0.965(19)
C(32)-H(32B)	0.962(17)
C(32)-H(32C)	0.989(17)
C(33)-H(33A)	0.99(2)
C(33)-H(33B)	0.98(2)
C(33)-H(33C)	1.05(2)
C(34)-H(34A)	0.962(19)
C(34)-H(34B)	0.981(19)
C(34)-H(34C)	1.06(2)

O(6)-Si(1)-C(19)	109.50(7)
O(6)-Si(1)-C(25)	106.52(7)
C(19)-Si(1)-C(25)	110.59(8)
O(6)-Si(1)-C(31)	104.27(7)
C(19)-Si(1)-C(31)	111.17(8)
C(25)-Si(1)-C(31)	114.41(8)
C(7)-O(3)-C(8)	109.54(14)
C(12)-O(4)-C(1)	120.28(13)
C(15)-O(5)-C(16)	105.20(15)
C(18)-O(6)-Si(1)	124.65(11)
O(4)-C(1)-C(8)	111.89(15)
O(4)-C(1)-C(2)	112.50(14)
C(8)-C(1)-C(2)	109.92(14)
O(4)-C(1)-C(6)	107.80(13)
C(8)-C(1)-C(6)	100.70(14)
C(2)-C(1)-C(6)	113.46(14)
C(3)-C(2)-C(10)	116.14(15)
C(3)-C(2)-C(1)	112.18(14)
C(10)-C(2)-C(1)	110.10(14)
C(3)-C(2)-H(2)	106.4(8)

C(10)-C(2)-H(2)	108.5(8)
C(1)-C(2)-H(2)	102.5(9)
O(1)-C(3)-C(4)	122.83(17)
O(1)-C(3)-C(2)	123.55(16)
C(4)-C(3)-C(2)	113.61(16)
C(3)-C(4)-C(5)	109.00(16)
C(3)-C(4)-H(4A)	109.7(9)
C(5)-C(4)-H(4A)	108.5(10)
C(3)-C(4)-H(4B)	109.3(9)
C(5)-C(4)-H(4B)	113.0(9)
H(4A)-C(4)-H(4B)	107.3(13)
C(6)-C(5)-C(4)	113.43(15)
C(6)-C(5)-H(5A)	110.5(10)
C(4)-C(5)-H(5A)	106.7(10)
C(6)-C(5)-H(5B)	108.6(10)
C(4)-C(5)-H(5B)	110.0(10)
H(5A)-C(5)-H(5B)	107.5(13)
C(7)-C(6)-C(5)	112.31(16)
C(7)-C(6)-C(9)	106.55(15)
C(5)-C(6)-C(9)	109.58(15)
C(7)-C(6)-C(1)	100.75(13)
C(5)-C(6)-C(1)	115.55(15)
C(9)-C(6)-C(1)	111.52(15)
O(2)-C(7)-O(3)	121.04(17)
O(2)-C(7)-C(6)	128.96(17)
O(3)-C(7)-C(6)	110.00(15)
O(3)-C(8)-C(1)	104.39(15)
O(3)-C(8)-H(8A)	105.9(9)
C(1)-C(8)-H(8A)	111.7(9)
O(3)-C(8)-H(8B)	111.9(9)
C(1)-C(8)-H(8B)	110.7(9)
H(8A)-C(8)-H(8B)	111.9(13)
C(6)-C(9)-H(9A)	108.0(9)
C(6)-C(9)-H(9B)	110.6(10)
H(9A)-C(9)-H(9B)	110.3(13)
C(6)-C(9)-H(9C)	114.1(10)
H(9A)-C(9)-H(9C)	106.2(14)
H(9B)-C(9)-H(9C)	107.5(14)
C(11)-C(10)-C(17)	113.45(16)
C(11)-C(10)-C(2)	108.15(15)
C(17)-C(10)-C(2)	115.73(15)
C(11)-C(10)-H(10)	106.1(9)
C(17)-C(10)-H(10)	107.1(9)
C(2)-C(10)-H(10)	105.6(9)
C(12)-C(11)-C(10)	121.20(18)
C(12)-C(11)-H(11)	118.3(9)
C(10)-C(11)-H(11)	120.3(9)
C(11)-C(12)-O(4)	123.46(17)
C(11)-C(12)-C(13)	126.02(17)
O(4)-C(12)-C(13)	110.13(14)
C(16)-C(13)-C(14)	105.43(17)
C(16)-C(13)-C(12)	126.59(17)
C(14)-C(13)-C(12)	127.95(17)
C(15)-C(14)-C(13)	106.89(19)

C(15)-C(14)-H(14)	125.6(10)
C(13)-C(14)-H(14)	127.5(10)
C(14)-C(15)-O(5)	111.17(19)
C(14)-C(15)-H(15)	132.6(12)
O(5)-C(15)-H(15)	116.1(12)
C(13)-C(16)-O(5)	111.29(18)
C(13)-C(16)-H(16)	130.8(10)
O(5)-C(16)-H(16)	117.9(10)
C(18)-C(17)-C(10)	109.36(16)
C(18)-C(17)-H(17A)	106.5(9)
C(10)-C(17)-H(17A)	111.1(9)
C(18)-C(17)-H(17B)	111.4(10)
C(10)-C(17)-H(17B)	109.2(10)
H(17A)-C(17)-H(17B)	109.3(13)
O(6)-C(18)-C(17)	110.81(15)
O(6)-C(18)-H(18A)	109.6(8)
C(17)-C(18)-H(18A)	110.0(8)
O(6)-C(18)-H(18B)	108.3(9)
C(17)-C(18)-H(18B)	109.0(9)
H(18A)-C(18)-H(18B)	109.1(12)
C(20)-C(19)-C(24)	116.33(18)
C(20)-C(19)-Si(1)	120.30(14)
C(24)-C(19)-Si(1)	123.19(15)
C(19)-C(20)-C(21)	122.3(2)
C(19)-C(20)-H(20)	119.8(11)
C(21)-C(20)-H(20)	117.7(11)
C(22)-C(21)-C(20)	118.8(2)
C(22)-C(21)-H(21)	123.7(12)
C(20)-C(21)-H(21)	117.5(12)
C(21)-C(22)-C(23)	121.0(2)
C(21)-C(22)-H(22)	118.6(13)
C(23)-C(22)-H(22)	120.1(13)
C(22)-C(23)-C(24)	119.4(2)
C(22)-C(23)-H(23)	123.7(12)
C(24)-C(23)-H(23)	116.9(12)
C(23)-C(24)-C(19)	122.1(2)
C(23)-C(24)-H(24)	118.0(12)
C(19)-C(24)-H(24)	119.9(12)
C(30)-C(25)-C(26)	116.67(17)
C(30)-C(25)-Si(1)	122.66(14)
C(26)-C(25)-Si(1)	120.39(14)
C(27)-C(26)-C(25)	121.8(2)
C(27)-C(26)-H(26)	117.0(10)
C(25)-C(26)-H(26)	121.2(10)
C(28)-C(27)-C(26)	119.9(2)
C(28)-C(27)-H(27)	120.8(10)
C(26)-C(27)-H(27)	119.3(10)
C(27)-C(28)-C(29)	120.3(2)
C(27)-C(28)-H(28)	121.7(11)
C(29)-C(28)-H(28)	118.1(11)
C(28)-C(29)-C(30)	119.6(2)
C(28)-C(29)-H(29)	122.0(10)
C(30)-C(29)-H(29)	118.3(10)
C(29)-C(30)-C(25)	121.74(19)

C(29)-C(30)-H(30)	118.1(9)
C(25)-C(30)-H(30)	120.1(9)
C(32)-C(31)-C(34)	108.36(17)
C(32)-C(31)-C(33)	109.37(17)
C(34)-C(31)-C(33)	108.35(19)
C(32)-C(31)-Si(1)	108.58(13)
C(34)-C(31)-Si(1)	112.96(14)
C(33)-C(31)-Si(1)	109.17(13)
C(31)-C(32)-H(32A)	111.1(10)
C(31)-C(32)-H(32B)	109.1(10)
H(32A)-C(32)-H(32B)	110.5(14)
C(31)-C(32)-H(32C)	110.1(10)
H(32A)-C(32)-H(32C)	107.6(14)
H(32B)-C(32)-H(32C)	108.3(14)
C(31)-C(33)-H(33A)	110.3(11)
C(31)-C(33)-H(33B)	111.8(12)
H(33A)-C(33)-H(33B)	106.9(16)
C(31)-C(33)-H(33C)	108.3(11)
H(33A)-C(33)-H(33C)	110.2(15)
H(33B)-C(33)-H(33C)	109.4(16)
C(31)-C(34)-H(34A)	114.2(12)
C(31)-C(34)-H(34B)	110.1(11)
H(34A)-C(34)-H(34B)	101.4(16)
C(31)-C(34)-H(34C)	109.4(11)
H(34A)-C(34)-H(34C)	112.9(16)
H(34B)-C(34)-H(34C)	108.4(16)

Table S4 Anisotropic displacement parameters (Å^{2}x 10^4) for **43** (CCDC 197200). The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2} U^{11}$ + ... + 2 h k a* b* U^{12}].

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	236(3)	306(3)	166(3)	-13(2)	11(2)	-33(2)
O(1)	279(8)	449(8)	263(8)	-59(6)	-6(6)	-61(7)
O(2)	462(9)	375(8)	249(8)	-81(6)	78(6)	-163(7)
O(3)	278(8)	389(8)	241(7)	-41(6)	36(6)	-103(6)
O(4)	406(8)	307(7)	199(7)	8(6)	-43(6)	-130(6)
O(5)	466(9)	398(8)	313(8)	87(7)	15(7)	-48(7)
O(6)	314(7)	328(7)	136(7)	-24(6)	-3(5)	-36(6)
C(1)	249(11)	294(11)	171(10)	0(8)	-3(8)	-59(8)
C(2)	263(11)	290(11)	143(10)	-8(8)	21(8)	-93(9)
C(3)	327(12)	296(11)	168(10)	43(8)	-2(9)	-74(9)
C(4)	290(12)	317(13)	254(11)	-35(9)	22(9)	-43(10)
C(5)	297(12)	362(13)	196(11)	-53(10)	37(9)	-76(10)
C(6)	267(11)	324(11)	155(10)	-23(8)	17(8)	-84(9)
C(7)	299(11)	427(13)	130(10)	-40(9)	5(8)	-86(10)
C(8)	320(12)	370(13)	221(12)	-45(10)	8(10)	-59(10)
C(9)	296(13)	437(14)	184(11)	-29(10)	6(9)	-89(11)
C(10)	267(11)	301(11)	179(10)	-21(8)	12(9)	-37(9)
C(11)	403(13)	262(11)	231(11)	-42(9)	22(9)	-61(10)
C(12)	386(12)	306(11)	206(11)	-40(9)	-5(9)	-104(9)
C(13)	329(11)	294(11)	193(10)	-2(9)	8(8)	-33(9)
C(14)	455(14)	371(13)	265(13)	13(10)	-52(10)	-114(11)
C(15)	435(14)	307(13)	327(13)	-1(10)	13(11)	-94(11)
C(16)	354(12)	367(12)	259(12)	31(10)	-21(9)	-80(10)
C(17)	295(13)	296(12)	192(11)	-2(9)	25(9)	-73(10)
C(18)	251(12)	390(13)	180(11)	-5(9)	7(9)	-67(10)
C(19)	284(11)	270(11)	203(10)	32(8)	1(8)	-4(9)
C(20)	316(12)	501(14)	260(11)	-37(11)	3(9)	34(11)
C(21)	295(13)	665(17)	305(12)	67(12)	-30(10)	-48(12)
C(22)	441(15)	509(15)	394(14)	53(12)	146(12)	154(12)
C(23)	598(17)	377(14)	435(15)	-2(11)	166(13)	43(12)
C(24)	500(15)	386(13)	349(13)	-22(10)	151(11)	-36(11)
C(25)	217(10)	338(11)	198(10)	-23(9)	-39(8)	-71(9)
C(26)	292(12)	377(13)	223(11)	4(10)	-15(9)	-86(10)
C(27)	326(13)	487(15)	228(12)	12(10)	-4(10)	-134(11)
C(28)	364(13)	502(15)	277(13)	158(11)	-101(10)	-176(12)
C(29)	326(13)	340(14)	357(13)	47(11)	-133(10)	-30(11)
C(30)	221(11)	419(13)	227(11)	25(10)	-58(9)	-44(10)
C(31)	258(11)	364(11)	204(10)	16(9)	-11(8)	-53(9)
C(32)	265(13)	426(14)	253(12)	65(11)	-11(10)	3(10)
C(33)	232(12)	674(18)	388(15)	199(14)	10(11)	5(12)
C(34)	533(17)	465(16)	369(15)	26(12)	-159(13)	-115(13)

Table S5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **43** (CCDC 197200).

	x	y	z	U_{iso}
H(2)	1269(14)	6339(13)	147(5)	15(4)
H(4A)	2545(15)	4651(15)	-243(6)	27(5)
H(4B)	3953(16)	4944(15)	-391(6)	29(5)
H(5A)	3101(15)	6208(14)	-1025(6)	24(5)
H(5B)	2426(15)	4918(15)	-1094(6)	32(5)
H(8A)	-608(15)	7565(14)	-77(6)	24(5)
H(8B)	-856(16)	7867(15)	-668(6)	31(5)
H(9A)	748(15)	6032(15)	-1617(6)	34(5)
H(9B)	1355(17)	7431(16)	-1493(6)	38(5)
H(9C)	-140(18)	7133(15)	-1409(6)	39(6)
H(10)	831(16)	8316(14)	412(6)	25(5)
H(11)	2661(14)	9960(14)	278(5)	24(5)
H(14)	3790(16)	11587(15)	-215(7)	35(5)
H(15)	4040(18)	12875(17)	-976(7)	45(6)
H(16)	1708(16)	10161(15)	-1397(6)	37(5)
H(17A)	2301(14)	7109(15)	987(6)	23(5)
H(17B)	3307(16)	8122(14)	859(6)	22(5)
H(18A)	1800(13)	9734(14)	1110(5)	15(4)
H(18B)	919(16)	8551(14)	1273(5)	23(5)
H(20)	141(16)	9170(16)	2061(6)	37(6)
H(21)	-1667(18)	9728(17)	2450(7)	47(6)
H(22)	-1570(19)	11186(17)	3078(7)	56(7)
H(23)	440(20)	12270(20)	3335(8)	84(8)
H(24)	2220(20)	11840(20)	2859(8)	79(8)
H(26)	4631(15)	10209(16)	1246(6)	35(5)
H(27)	5122(16)	11746(15)	684(6)	36(5)
H(28)	4105(16)	13738(15)	718(6)	29(5)
H(29)	2716(14)	14207(14)	1328(5)	16(5)
H(30)	2168(15)	12708(13)	1879(6)	15(4)
H(32A)	4317(18)	7919(15)	2996(7)	40(6)
H(32B)	3437(16)	7601(16)	2520(7)	35(6)
H(32C)	2888(17)	8444(15)	2941(6)	33(5)
H(33A)	6017(19)	8670(17)	2438(7)	51(6)
H(33B)	5747(19)	9821(19)	2075(7)	61(7)
H(33C)	5054(19)	8444(18)	1932(8)	63(7)
H(34A)	3867(19)	10662(18)	3092(7)	48(7)
H(34B)	4779(18)	11198(18)	2733(7)	51(6)
H(34C)	5390(20)	10069(18)	3099(8)	75(7)

References

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[1] For an earlier synthesis of **9**, see: Knight, D. W.; Pattenden, G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 635-640.

[2] For the synthesis of **15**, see: Piers, E.; Wong, T.; Coish, P.; Rogers, C. *Can. J. Chem.* **1994**, *72*, 1816-1819.

[3] For a synthesis of of Jones' reagent, see: Kashima, C.; Shimizu, M.; Omote, Y. *Chem. Pharm. Bull.* **1987**, *35*, 2694-2697.

[4] For the synthesis of **33**, see: Kiyooka, S; Shahid, K. A.; Goto, F.; Okazaki, M.; Shuto, Y. *J. Org. Chem.* **2003**, *68*, 7967-7978.

[5] For the synthesis of **34**, see: Kinoshita, T.; Ichinari, D.; Sinya, J. *J. Heterocycl. Chem.* **1996**, *33*, 1313-1317.

[6] The C(16) α-H epimer of ketone **43** (i.e., ***ii***) was easily converted to the C(16) β-H epimer of ketone **43** by simple bases such as NaH: