Supplemental Materials for:

Non Carbonyl-Stabilized Metallocarbenoids in Synthesis: The Development of a Tandem Rhodium-Catalyzed Bamford-Stevens/Thermal Aliphatic Claisen Rearrangement Sequence

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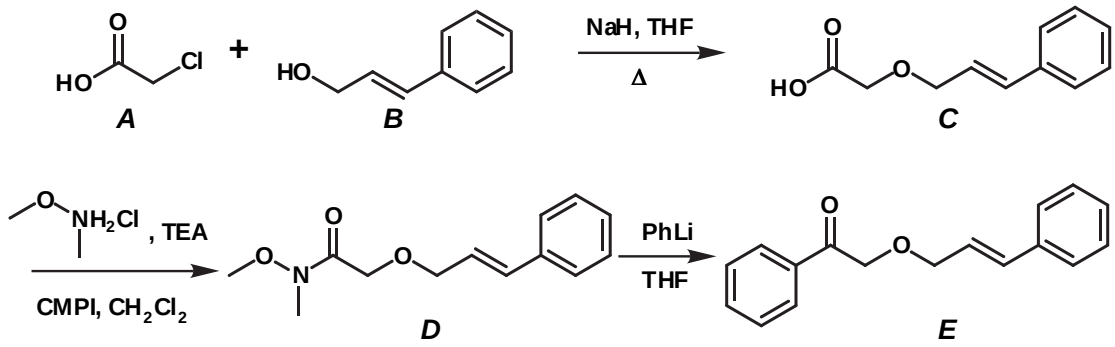
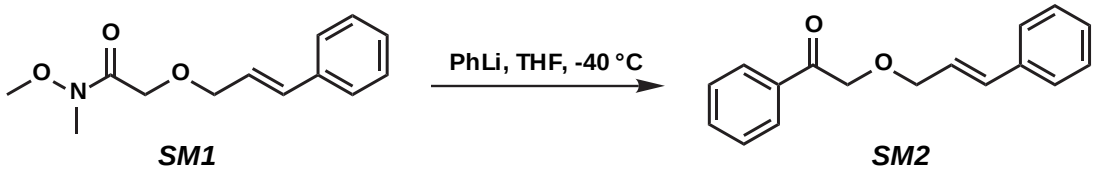
General Information: Reactions were performed in flame-dried glassware under a nitrogen atmosphere. *N*-Methyl 2-pyrrolidinone (NMP) was distilled from P_2O_5 and dichloroethane (DCE) was freshly distilled from CaH_2. Other solvents were dried and purified using activated alumina columns. All other reagents were used as received from commercial sources. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25mm) and visualized by UV, *p*-anisaldehyde staining, or ceric ammonium molybdate staining (CAM). ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz and 75 MHz, respectively) in $CDCl_3$ and are internally referenced to the residual chloroform peak (7.27 ppm and 77.23 ppm, respectively) relative to Me_4Si. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the UC Irvine Mass Spectral Facility. **CAUTION!** 1-Amino-2-phenyl-aziridinium acetate is explosive, and proper precautions should be taken whenever it is used (see Müller, Felix, Schreiber, Wintner, and Eschenmoser, *Org. Synth. Coll. Vol.* **1988**, *6*, 56).

Starting Material Preparation



α-Alloxy ketones **E** were obtained via a three step protocol using established procedures. Treatment of α-chloro acetic acid (**A**) with the appropriate allylic alcohols (i.e., **B**) produced the corresponding α-alloxy acids **C**.[1] Transformation of acids **C** to the Weinreb amide[2] and treatment with either alkyl-lithium or alkyl-magnesium bromides produced the desired keto-ethers **E**.

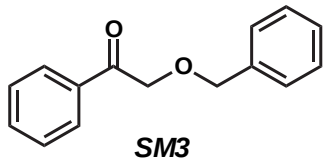
Representative Nucleophilic Addition to a Weinreb Amide



Ketone SM2. To a flame-dried flask (100 mL) equipped with a magnetic stirbar was added Weinreb amide **SM1** (2.85 g, 12.11 mmol) followed by THF (50 mL). This solution was cooled to -40 °C for 5 min, and then a PhLi solution (8.4 mL of a 1.8 M solution in cyclohexane/ether, 15.12 mmol) was added dropwise over 10 min. The mixture was stirred for 10 min and then quenched by the addition of MeOH (8 mL). Et_2O (20 mL) and H_2O (40 mL) were then added, the layers were separated, and the aqueous phase was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The ketone was

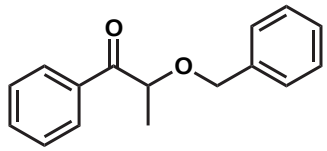
(1) Sibi, M. P.; Stessman, C. C.; Schultz, J. A.; Christensen, J. W.; Lu, J; Marvin, M. *Synth. Comm.* 1995, **25**, 1255
(2) Oh, T.; Wrobel, Z.; Rubenstein, S. M. *Tetrahedron Lett.* **1991**, 32, 4647.

purified by flash column chromatography (15:1 hexanes:ethyl acetate eluent) to provide **SM2** as a white crystalline solid (2.60 g, 10.29 mmol, 85% yield) that was spectroscopically identical to that previously reported.[3] Ketone **SM2** could be further purified by recrystalization from boiling hexanes. R_F 0.33 (15:1 hexanes:ethyl acetate eluent).



SM3

Keto-ether SM3. The general procedure outlined above was followed (using 2.87 g, 13.72 mmol of the corresponding Weinreb amide) to provide keto-ether **SM3** (2.14 g, 9.54 mmol, 70% yield) as a yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). The spectroscopic data were identical to those previously reported.[4] R_F 0.51 (3:1 hexanes:ethyl acetate eluent).



SM4

Keto-ether SM4. The general procedure outlined above was followed (using 4.01 g, 17.96 mmol of the corresponding Weinreb amide) to provide keto-ether **SM4** (3.43 g, 14.27 mmol, 79% yield) as a yellow oil. Flash chromatographic purification (9:1 hexanes:ethyl acetate eluent). The spectroscopic data were identical to those previously reported.[5] R_F 0.74 (1:1 hexanes:ethyl acetate eluent)

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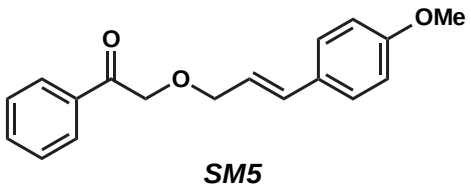
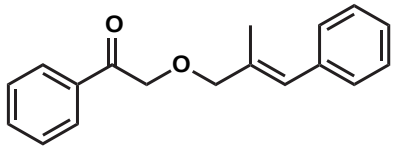
(3) Kachinski, J. L. C.; Salomon, R. G. *J. Org. Chem.* 1986, **51**, 1393
(4) Aitken, R. A.; Thomas, A. W. *Synlett* 1998, **1**, 102
(5) Sarko, C. R.; Guch, I. C.; Dimare, M. *J. Org. Chem.* 1994, **59**, 705



SM5

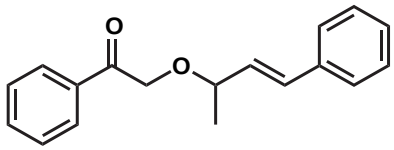
Keto-ether SM5. The general procedure outlined above was followed (using 2.96 g, 11.15 mmol of the corresponding Weinreb amide) to provide keto-ether **SM5** (1.97 g, 6.98 mmol, 63% yield) as a white solid. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). m.p. 70.0-73.0°; R_F 0.61 (1:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 6.6, 15.9 Hz, 1H), 4.81 (s, 2H), 4.31 (d, *J* = 6.6 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 159.2, 134.7, 133.4, 133.2, 129.0, 128.5, 127.7, 127.7, 122.6, 113.8, 72.3, 72.2, 55.3; IR (neat) 2999, 2931, 1700 cm^{-1}. HRMS (EI) m/z calcd for 236.1775, found 236.1776. HRMS (EI) m/z calcd for $[C_{18}H_{18}O_3]^+$ 282.1256, found 282.1256.



SM6

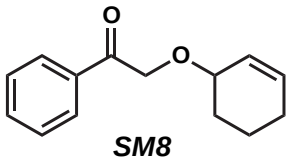
Keto-ether SM6. The general procedure outlined above was followed (using 2.28 g, 15.57 mmol of the corresponding Weinreb amide) to provide keto-ether **SM6** (2.90 g, 10.90 mmol, 70% yield) as a colorless oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). m.p. 51.5-52.5; R_F 0.32 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 6.57 (s, 1H), 4.81 (s, 2H), 4.23 (s, 2H), 1.96 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.3, 137.2, 134.9, 134.3, 133.5, 128.9, 128.6, 128.1, 128.0, 127.9, 126.6,

77.6, 72.3; IR (neat) 3059, 3023, 2908, 1699 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{18}O_2]^+$ 266.1307, found 266.1309.



SM7

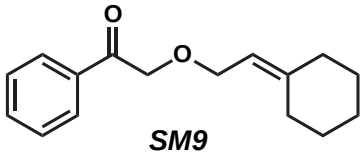
Keto-ether SM7. The general procedure outlined above was followed (using 1.81 g, 7.26 mmol of the corresponding Weinreb amide) to provide keto-ether **SM7** (1.42 g, 5.33 mmol, 73% yield) as a white solid. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.25 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.1 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47-7.26 (m, 7H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.14 (dd, *J* = 8.0, 15.9 Hz, 1H), 4.83 (d, *J* = 17.0 Hz, 1H), 4.73 (d, *J* = 17.0 Hz, 1H), 4.19 (dq, *J* = 6.3, 8.0 Hz, 1H), 1.47 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 136.0, 134.9, 133.2, 132.2, 130.4, 128.5, 128.5, 127.8, 127.7, 126.4, 77.5, 70.9, 21.7; IR (neat) 3060, 3028, 2975, 1699 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{18}O_2]^+$ 266.1307, found 266.1312.



SM8

Keto-ether SM8. The general procedure outlined above was followed (using 2.65 g, 13.30 mmol of the corresponding Weinreb amide) to provide keto-ether **SM8** (2.40 g, 11.08 mmol, 83% yield) as a pale yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.26 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.94-5.82 (comp.m, 2H), 4.80 (s, 2H), 4.04 (br.s, 1H,), 2.19-1.51 (comp.m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 134.8, 133.1, 131.4, 128.3, 127.8, 126.8, 73.5, 71.0,

28.1, 25.1, 19.0; IR (neat) 3062, 3028, 2934, 1702 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{18}O_2\text{-}2H]^+$ 242.1307, found 242.1313.



SM9

Keto-ether SM9. The general procedure outlined above was followed (using 328.0 mg, 1.14 mmol of the corresponding Weinreb amide) to provide keto-ether **SM9** (295.1 mg, 1.21 mmol, 84% yield) as a pale yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.38 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.47 (t, *J* = 7.1 Hz, 2H), 5.34 (t, *J* = 7.1 Hz, 1H), 4.72 (s, 2H), 4.16 (d, *J* = 7.14 Hz, 2H), 2.19-2.13 (comp.m, 2H), 1.57-1.54 (comp.m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 145.7, 134.5, 132.9, 128.1, 127.4, 116.5, 71.9, 66.3, 36.7, 28.6, 28.1, 27.5, 26.3; IR (neat) 3523, 3385, 2927, 1703, 1699, 1695 cm^{-1}. HRMS (EI) m/z calcd for $[C_{16}H_{20}O_2\text{-}2H]^+$ 214.0994, found 214.1001.

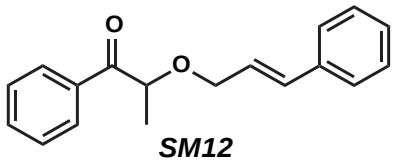
SM10

Keto-ether SM10. The general procedure outlined above was followed (using 2.39 g, 13.84 mmol of the corresponding Weinreb amide) to provide keto-ether **SM10** (1.84 g, 9.69 mmol, 70% yield) as a pale yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.45 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.0 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.81-5.58 (comp.m, 2H), 4.75 (s, 2H), 4.23 (d, *J* = 7.0 Hz, 2H), 1.68 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1, 134.7, 133.2, 128.9, 128.4, 127.6, 125.7,

72.4, 66.3, 13.2; IR (neat) 3063, 3026, 2920, 1701 cm^{-1}. HRMS (EI) m/z calcd for $[C_{12}H_{14}O_2\text{-}20H]^+$ 172.0888, found 172.0888.

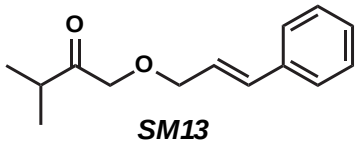
SM11

Keto-ether SM11. The general procedure outlined above was followed (using 6.23 g, 33.27 mmol of the corresponding Weinreb amide) to provide keto-ether **SM11** (3.50 g, 17.14 mmol, 52% yield) as a yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). The spectroscopic data were identical to those previously reported.[3] R_F 0.34 (9:1 hexanes:ethyl acetate eluent).



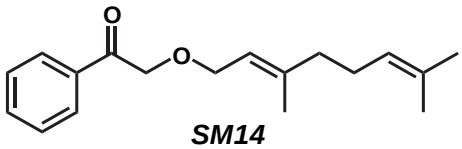
SM12

Keto-ether SM12. The general procedure outlined above was followed (using 426 mg, 1.71 mmol of the corresponding Weinreb amide) to provide keto-ether **SM12** (412 mg, 1.55 mmol, 91% yield) as a pale yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.59 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.38-7.25 (comp.m, 5H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 6.1, 15.9 Hz, 1H), 4.84 (q, *J* = 6.9 Hz, 1H), 4.28 (dd, *J* = 5.8, 12.4 Hz, 1H), 4.14 (dd, *J* = 6.6, 12.4 Hz, 1H), 1.55 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 136.5, 134.9, 133.5, 133.2, 128.9, 128.7, 128.6, 127.9, 126.6, 125.5, 78.2, 70.6, 19.2; IR (neat) 3060, 3027, 2983, 1694 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{18}O_2]^+$ 266.1307, found 266.1301.



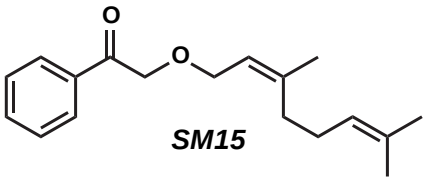
SM13

Keto-ether SM13. The general procedure outlined above was followed (using 2.00 g, 8.49 mmol of the corresponding Weinreb amide) to provide keto-ether **SM13** (1.10 g, 5.02 mmol, 59% yield) as a yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.51 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.24 (comp.m, 5H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 6.0, 15.9 Hz, 1H), 4.23 (d, *J* = 6.6 Hz, 2H), 4.21 (s, 2H), 2.78 (sept, *J* = 7.2 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.9, 136.4, 133.5, 128.7, 128.0, 126.7, 125.2, 73.5, 72.2, 37.4, 18.4; IR (neat) 3027, 2971, 1728 cm^{-1}. HRMS (EI) m/z calcd for $[C_{14}H_{18}O_2+H]^+$ 218.1307, found 218.1308.



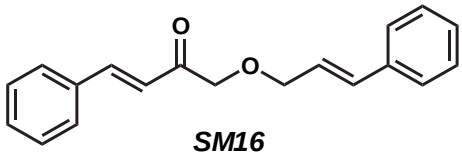
SM14

Keto-ether SM14. The general procedure outlined above was followed (using 5.10 g, 19.96 mmol of the corresponding Weinreb amide) to provide keto-ether **SM14** (3.96 g, 14.53 mmol, 73% yield) as a yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.36 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.0 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.41 (t, *J* = 7.0 Hz, 1H), 5.09 (t, *J* = 4.8 Hz, 1H), 4.73 (s, 2H), 4.17 (d, *J* = 7.0 Hz, 2H), 2.12-2.02 (comp.m, 4H), 1.68 (s, 6H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 141.4, 134.7, 133.2, 131.4, 128.4, 127.6, 123.6, 119.8, 72.2, 67.5, 39.5, 26.2, 25.6, 17.6, 16.4; IR (neat) 2968, 1702 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{24}O_2]^+$ 272.1776, found 272.1780.



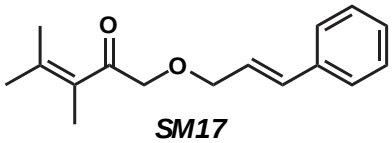
SM15

Keto-ether SM15. The general procedure outlined above was followed (using 3.82 g, 14.92 mmol of the corresponding Weinreb amide) to provide keto-ether **SM15** (2.14 g, 7.86 mmol, 53% yield) as a yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.35 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.42 (t, *J* = 7.2 Hz, 1H), 5.07 (m, 1H), 4.73 (s, 2H), 4.14 (d, *J* = 7.1 Hz, 2H), 2.13-2.02 (comp.m, 4H), 1.77 (s, 3H), 1.67 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 141.5, 134.8, 133.3, 131.9, 128.5, 127.8, 123.5, 120.9, 72.5, 67.4, 32.2, 26.7, 25.7, 23.6, 17.7; IR (neat) 2967, 2917, 1702 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{24}O_2]^+$ 272.1776, found 272.1785.



SM16

Keto-ether SM16. The general procedure outlined above was followed (using 1.29 g, 5.47 mmol of the corresponding Weinreb amide) to provide keto-ether **SM16** (1.39 g, 5.01 mmol, 92% yield) as a yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.21 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.2 Hz, 1H), 7.59 (dd, *J* = 3.6, 6.0 Hz, 2H), 7.43-7.24 (comp.m, 8H), 7.00 (d, *J* = 16.2 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 6.0, 15.9 Hz, 1H), 4.37 (s, 2H), 4.30 (d, *J* = 6.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0, 143.4, 136.2, 134.2, 133.5, 130.7, 128.8, 128.5, 128.4, 127.8, 126.5, 124.9, 121.5, 74.5, 72.1; IR (neat) 3026, 2957, 1695 cm^{-1}.

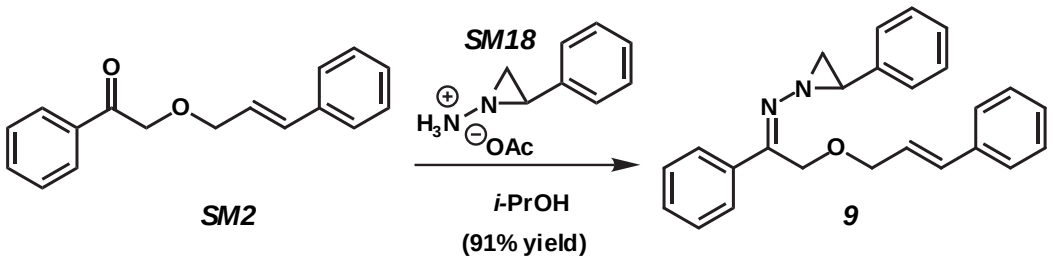


SM17

Keto-ether SM17. The general procedure outlined above was followed (using 1.58 g, 6.71 mmol of the corresponding Weinreb amide) to provide keto-ether **SM17** (658.5 mg, 2.70 mmol, 40% yield) as a yellow oil. Flash chromatographic purification (15:1 hexanes:ethyl acetate eluent). R_F 0.29 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.27 (comp.m, 5H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 6.1, 15.9 Hz, 1H), 4.3 (s, 2H), 4.25 (d, *J* = 6.1 Hz, 2H), 1.88 (s, 3H), 1.84 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.0, 140.0, 136.5, 133.4, 128.9, 128.7, 128.0, 126.7, 125.4, 74.3, 72.2, 26.6, 22.8, 21.9; IR (neat) 2922, 1693 cm^{-1}. HRMS (EI) m/z calcd for $[C_{16}H_{20}O_2+H]^+$ 245.1541, found 245.1544.

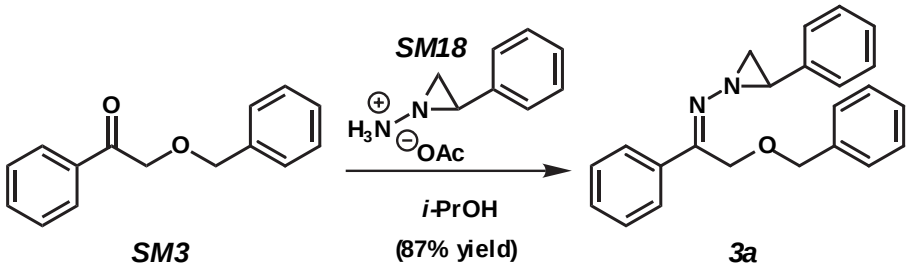
Representative Procedure for Aziridinyl Imine Formation

CAUTION! 1-Amino-2-phenyl-aziridinium acetate is explosive, and proper precautions should be taken whenever it is used (see Müller, Felix, Schreiber, Wintner, and Eschenmoser, *Org. Synth. Coll. Vol.* **1988**, *6*, 56).



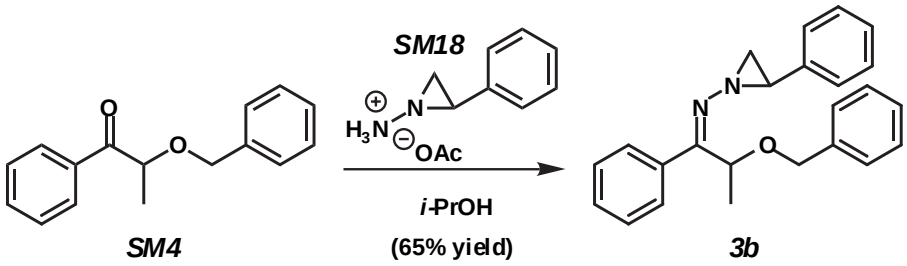
Aziridinyl Imine 9. A flame-dried flask (100 mL) was equipped with a magnetic stirbar and charged with a solution of ketone **SM2** (1.28 g, 5.09 mmol) in 2-propanol (50 mL). Finally, 1-amino-2-phenyl aziridinium hydrochloride (**SM18**; 1.52 g, 7.83 mmol) was added and the reaction was allowed to stir at room temperature until the starting material had been consumed as shown by TLC (3:1 hexanes:ethyl acetate eluent, usually

4-12 h, depending on substrate). The reaction was quenched with powdered $KHCO_3$, and then filtered through celite to remove the base. Removal of solvent under reduced pressure yielded a yellow oil, which was subsequently purified by flash column chromatography (15:1 → 9:1 hexanes:ethyl acetate gradient eluent) to yield α-alloxy aziridinyl imine **9** (1.39 g of the isomer shown (*E*) and 0.321 g of the (*Z*) hydrazone isomer for a total yield of 4.65 mmol, 91%) as a yellow oil. R_F 0.55 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.41-7.28 (m, 13H), 6.46 (dt, *J* = 1.5, 15.9 Hz, 1H), 6.12 (dt, *J* = 6.0, 15.6 Hz, 1H), 4.87 (d, *J* = 12.3 Hz, 1H), 4.80 (d, *J* = 12.6 Hz, 1H), 4.01 (dt, *J* = 4.5, 1.8 Hz, 2H), 3.06 (dd, *J* = 7.5, 4.8 Hz, 1H), 2.69 (d, *J* = 7.8 Hz, 1H), 2.46 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 138.2, 136.2, 136.3, 135.9, 132.7, 129.4, 128.3, 128.1, 128.0, 127.5, 127.0, 126.3, 126.1, 125.2, 71.3, 64.2, 45.0, 41.6; IR (neat) 3060, 3022, 1604 cm^{-1}. HRMS (EI) m/z calcd for $[C_{25}H_{24}N_2O+Na]^+$ 391.1786, found 391.1788.

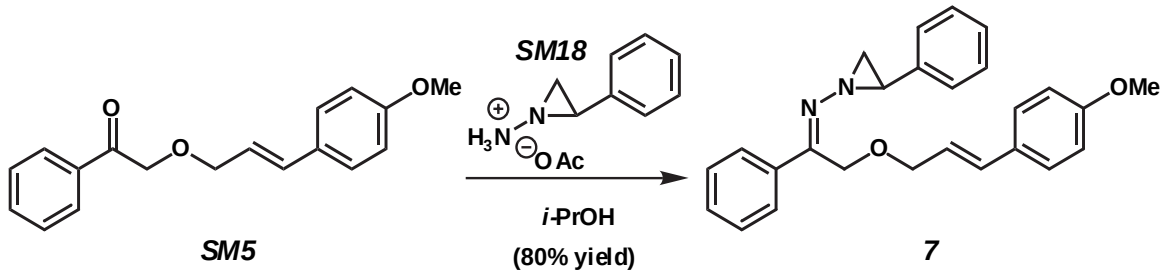


Hydrazone 3a. The general procedure outlined above was followed (using 2.14 g, 9.45 mmol of the corresponding keto-ether **SM3**) to provide **3a** (2.81 g, 8.19 mmol, 87% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.74 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.41-7.26 (comp.m, 11H), 7.17-7.14 (m, 2H), 4.88 (d, *J* = 12.6 Hz, 1H), 4.81 (d, *J* = 12.6 Hz, 1H), 4.36 (s, 2H), 3.05 (dd, *J* = 4.9, 7.7 Hz, 1H), 2.65 (d, *J* = 7.7 Hz, 1H), 2.43 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 138.2, 137.4, 135.8, 129.4, 128.2, 128.1, 128.0, 127.8, 127.5, 127.1, 127.1, 126.1, 72.7,

64.4, 45.0, 41.6; IR (neat) 3062, 3030, 1605 cm^{-1}. HRMS (EI) m/z calcd for $[C_{23}H_{22}N_2O+Na]^+$ 365.1630, found 365.1634.

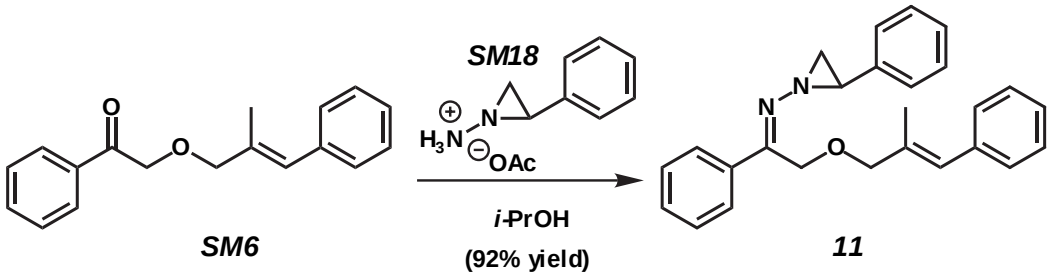


Hydrazone 3b. The general procedure outlined above was followed (using 3.04 g, 14.15 mmol of the corresponding keto-ether **SM4**) to provide **3b** (3.28 g, 9.19 mmol, 65% yield) as a yellow oil in a 1:1 mixture of diastereomers. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.29 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.91 (m, 2H), 7.45-7.06 (comp.m, 13H), 5.69 (q, *J* = 7.0 Hz, 1H), 4.36 (d, *J* = 11.4 Hz, 1H), 4.23 (d, *J* = 11.4 Hz, 1H), 3.19 (dd, *J* = 4.8, 7.3 Hz, 1H), 2.73 (d, *J* = 7.7 Hz, 1H), 2.45 (d, *J* = 4.4 Hz, 1H), 1.62 (d, *J* = 6.6 Hz, 3H), 1.43 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 138.0, 135.2, 129.6, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.7, 127.4, 126.3, 72.2, 71.7, 45.1, 42.3, 19.9; IR (neat) 3087, 3063, 3031, 1698, 1604 cm^{-1}. HRMS (EI) m/z calcd for $[C_{24}H_{24}N_2O+H]^+$ 357.1967, found 357.1971.

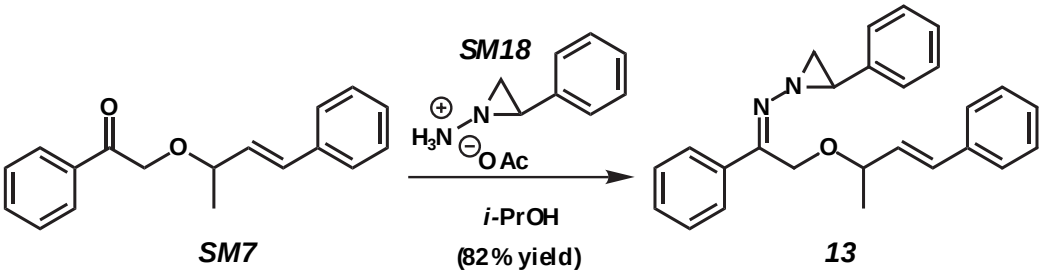


Hydrazone 7. The general procedure outlined above was followed (using 1.50 g, 5.32 mmol of the corresponding keto-ether **SM5**) to provide **7** (1.68 g, 4.24 mmol, 80% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl

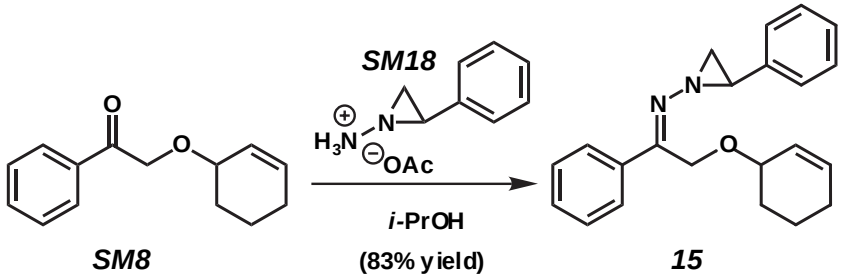
acetate gradient eluent). R_F 0.45 (99:1 CH_2Cl_2:MeOH eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.67 (m, 2H), 7.42-7.24 (comp.m, 13H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 15.9 Hz, 1H), 5.98 (dt, *J* = 6.3, 15.9 Hz, 1H), 4.85 (d, *J* = 12.4 Hz, 1H), 4.79 (d, *J* = 12.4 Hz, 1H), 3.98 (d, *J* = 6.3 Hz, 2H), 3.82 (s, 3H), 3.05 (dd, *J* = 4.7, 7.7 Hz, 1H), 2.67 (d, *J* = 7.7 Hz, 1H), 2.45 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 159.3, 138.6, 136.2, 132.9, 129.7, 129.4, 128.5, 128.3, 127.8, 127.4, 127.3, 126.4, 123.2, 114.0, 71.9, 64.5, 55.5, 45.3, 41.9; IR (neat) 3032, 2934, 1607 cm^{-1}. HRMS (EI) m/z calcd for $[C_{26}H_{26}N_2O_2+H]^+$ 399.2072, found 399.2069.



Hydrazone 11. The general procedure outlined above was followed (using 987.4 mg, 3.71 mmol of the corresponding keto-ether **SM6**) to provide **11** (1.31 g, 3.41 mmol, 92% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent) as a yellow oil. R_F 0.48 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (m, 2H), 7.42-7.23 (comp.m, 13H), 6.39 (s, 1H), 4.90 (d, *J* = 12.5 Hz, 1H), 4.82 (d, *J* = 12.5 Hz, 1H), 3.91 (s, 2H), 3.08 (dd, *J* = 4.7, 7.7 Hz, 1H), 2.69 (d, *J* = 7.7 Hz, 1H), 2.47 (d, *J* = 4.7 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 138.4, 137.4, 136.1, 134.6, 129.6, 128.9, 128.4, 128.2, 128.0, 127.5, 127.3, 126.5, 126.3, 77.1, 45.0, 41.7, 15.4; IR (neat) 3059, 3026, 2986, 1603 cm^{-1}.

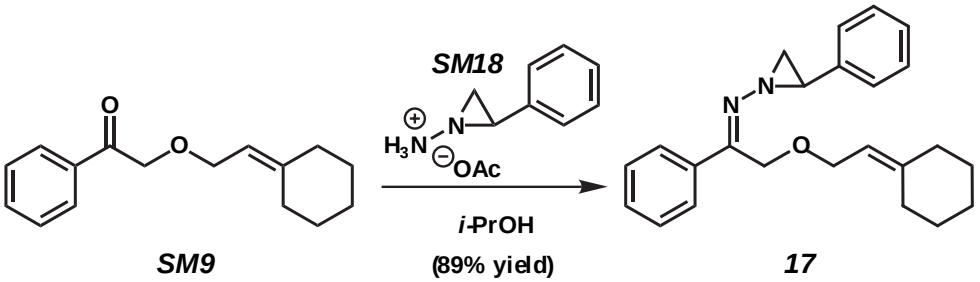


Hydrazone 13. The general procedure outlined above was followed (using 1.41 g, 5.29 mmol of the corresponding keto-ether **SM7**) to provide **13** (1.66 g, 4.34 mmol, 82% yield) as a yellow oil in a 1:1 mixture of diastereomers. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.47 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.75 (m, 4H), 7.40-7.24 (comp.m, 26H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.02 (dd, *J* = 7.7, 15.9 Hz, 1H), 5.86 (dd, *J* = 8.0, 15.9 Hz, 1H), 4.87 (d, *J* = 12.9 Hz, 1H), 4.80 (s, 2H), 4.69 (d, *J* = 12.9 Hz, 1H), 4.00-3.79 (comp.m, 2H), 3.08 (dd, *J* = 4.7, 7.4 Hz, 1H), 2.98 (dd, *J* = 4.7, 7.4 Hz, 1H), 2.68 (d, *J* = 7.4 Hz, 1H), 2.60 (d, *J* = 7.4 Hz, 1H), 2.49 (d, *J* = 4.7 Hz, 2H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 166.7, 138.4, 138.3, 136.3, 136.1, 136.0, 131.9, 131.7, 130.6, 130.6, 129.3, 128.4, 128.3, 128.2, 128.0, 127.6, 127.5, 127.2, 127.1, 126.4, 126.4, 126.1, 77.0, 77.0, 62.8, 44.9, 44.9, 41.8, 41.7, 21.5, 21.5; IR (neat) 3060, 3026, 2976, 1605 cm^{-1}. HRMS (EI) m/z calcd for $[C_{26}H_{26}N_2O+Na]^+$ 405.1943, found 405.1953.

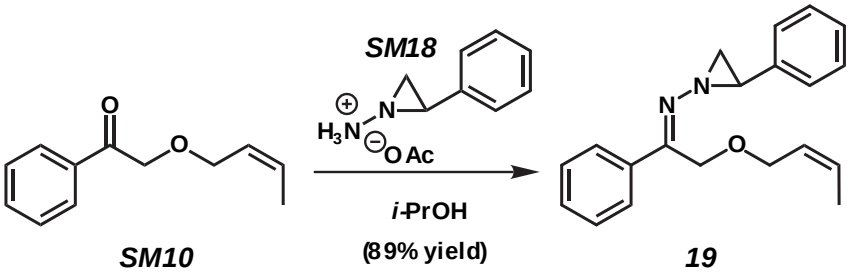


Hydrazone 15. The general procedure outlined above was followed (using 2.40 g, 11.08 mmol of the corresponding keto-ether **SM8**) to provide **15** (3.06 g, 9.21 mmol, 83% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl

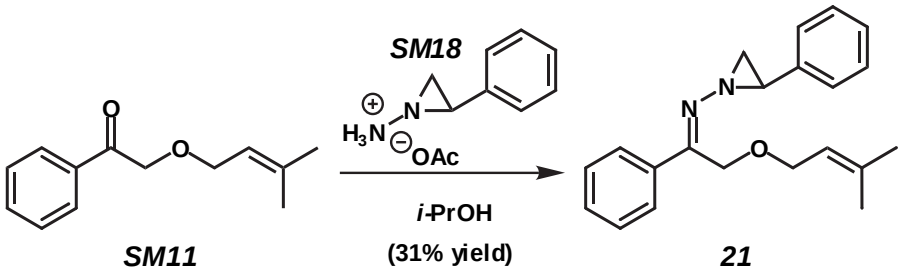
acetate gradient eluent). R_F 0.37 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2H), 7.46-7.29 (comp.m, 8H), 5.84-5.77 (m, 1H), 5.64-5.54 (m, 1H), 4.95 (d, *J* = 12.8 Hz, 1H), 4.84 (d, *J* = 12.8 Hz, 1H), 3.81 (br.s, 1H), 3.10 (dd, *J* = 4.8, 7.4 Hz, 1H), 2.69 (d, *J* = 7.7 Hz, 1H), 2.48 (d, *J* = 4.8 Hz, 1H), 2.05-1.87 (comp.m, 2H), 1.76-1.41 (comp.m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 138.6, 136.3, 131.2, 129.5, 128.4, 128.2, 127.4, 127.4, 127.4, 126.3, 72.9, 62.6, 45.1, 42.0, 28.1, 25.4, 19.3; IR (neat) 3062, 3028, 2987, 1650, 1605 cm^{-1}. HRMS (EI) m/z calcd for $[C_{22}H_{24}N_2O+H]^+$ 333.1967, found 333.1968.



Hydrazone 17. The general procedure outlined above was followed (using 295 mg, 1.21 mmol of the corresponding keto-ether **SM9**) to provide **17** (385.7 mg, 1.07 mmol, 89% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.44 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.43-7.27 (comp.m, 8H), 5.15 (t, *J* = 7.1 Hz, 1H), 4.81 (d, *J* = 12.6 Hz, 1H), 4.74 (d, *J* = 12.9 Hz, 1H), 3.83 (d, *J* = 7.1 Hz, 2H), 3.04 (dd, *J* = 4.7, 7.4 Hz, 1H), 2.65 (d, *J* = 7.7 Hz, 1H), 2.45 (d, *J* = 4.7 Hz, 1H), 2.05 (br.s, 2H), 1.96 (t, *J* = 5.5 Hz, 2H), 1.53-1.41 (comp.m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 145.6, 138.3, 135.9, 129.4, 128.2, 128.0, 127.1, 127.1, 126.1, 116.9, 66.2, 64.2, 45.0, 41.7, 37.0, 28.8, 28.3, 27.7, 26.6; IR (neat) 3061, 3031, 2927, 1667, 1605 cm^{-1}. HRMS (EI) m/z calcd for $[C_{24}H_{28}N_2O+Na]^+$ 383.2099, found 383.2082.

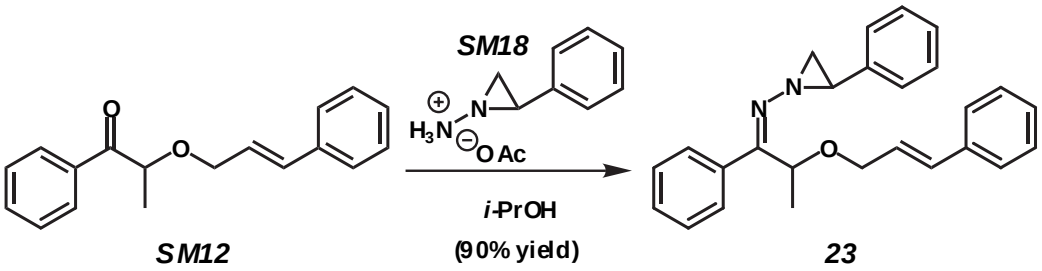


Hydrazone 19. The general procedure outlined above was followed (using 1.84 g, 9.67 mmol of the corresponding keto-ether **SM10**) to provide **19** (2.65 g, 8.65 mmol, 89% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.47 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.39-7.27 (comp.m, 8H), 5.65-5.55 (m, 1H), 5.46-5.38 (m, 1H), 4.82 (d, *J* = 12.3 Hz, 1H), 4.75 (d, *J* = 12.3 Hz, 1H), 3.90 (d, *J* = 6.6 Hz, 2H), 3.05 (dd, *J* = 4.8, 7.7 Hz, 1H), 2.67 (d, *J* = 7.7 Hz, 1H), 2.46 (d, *J* = 4.8 Hz, 1H), 1.49 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 138.2, 135.8, 129.3, 128.2, 128.1, 127.9, 127.0, 126.9, 126.0, 126.0, 65.8, 64.3, 44.9, 41.5, 12.9; IR (neat) 3062, 3026, 2986, 1605 cm^{-1}.

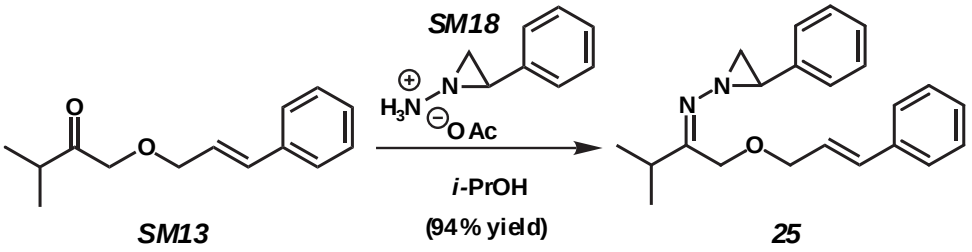


Hydrazone 21. The general procedure outlined above was followed (using 3.50 g, 17.14 mmol of the corresponding keto-ether **SM11**) to provide **21** (1.71 g, 5.34 mmol, 31% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.52 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7.38-7.24 (m, 8H), 5.20-5.14 (m, 1H), 4.78 (d, *J* = 22.8 Hz, 1H), 4.72 (d, *J* = 7.14 Hz, 1H), 3.80 (d, *J* = 7.1 Hz, 2H), 3.01 (dd, *J* = 7.7, 4.7 Hz, 1H), 2.64 (d, *J* = 22.5 Hz, 1H), 2.43 (d, *J* = 4.6 Hz, 1H), 1.66 (d, *J* = 0.8 Hz, 3H), 1.46 (d, *J* =

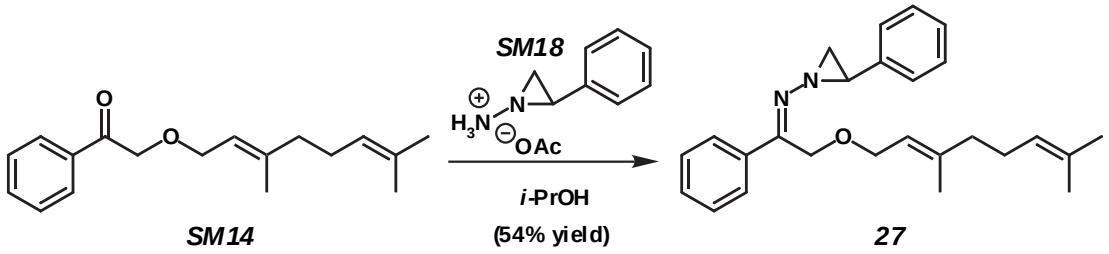
0.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 138.3, 137.7, 135.9, 129.4, 128.2, 128.0, 127.1, 127.1, 126.1, 120.3, 67.0, 64.3, 45.0, 41.7, 25.8, 17.8; IR (neat) 3062, 3030, 2975, 1605 cm^{-1}. HRMS (EI) m/z calcd for $[C_{21}H_{24}N_2O+H]^+$ 321.1967, found 321.1968.



Hydrazone 23. The general procedure outlined above was followed (using 387.3 mg, 1.45 mmol of the corresponding keto-ether **SM12**) to provide **23** (495.4 mg, 1.30 mmol, 90% yield) as a yellow oil as a 1:1 mixture of diastereomers. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.68 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.86 (m, 4H), 7.41-7.23 (comp.m, 26H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 6.16 (dt, *J* = 6.0, 15.9 Hz, 1H), 6.07 (dt, *J* = 6.0, 15.9 Hz, 1H), 5.69 (q, *J* = 6.6 Hz, 1H), 5.66 (q, *J* = 6.6 Hz, 1H), 4.08 (d, *J* = 6.0 Hz, 2H), 3.94 (m, 2H), 3.15 (dd, *J* = 4.4, 7.1 Hz, 1H), 2.96 (dd, *J* = 4.4, 7.7 Hz, 1H), 2.71 (d, *J* = 7.7 Hz, 1H), 2.55 (d, *J* = 7.7 Hz, 1H), 2.43 (d, *J* = 4.4 Hz, 1H), 2.40 (d, *J* = 4.9 Hz, 1H), 1.58 (d, *J* = 6.6 Hz, 3H), 1.39 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 138.7, 135.2, 132.9, 132.6, 129.5, 128.6, 128.5, 128.2, 128.0, 127.8, 127.7, 127.4, 127.3, 126.6, 126.4, 126.3, 125.7, 72.0, 71.7, 70.2, 45.3, 44.9, 42.3, 20.0, 19.7; IR (neat) 3027, 2983, 1602 cm^{-1}. HRMS (EI) m/z calcd for $[C_{26}H_{26}N_2O+H]^+$ 383.2123, found 383.2125.

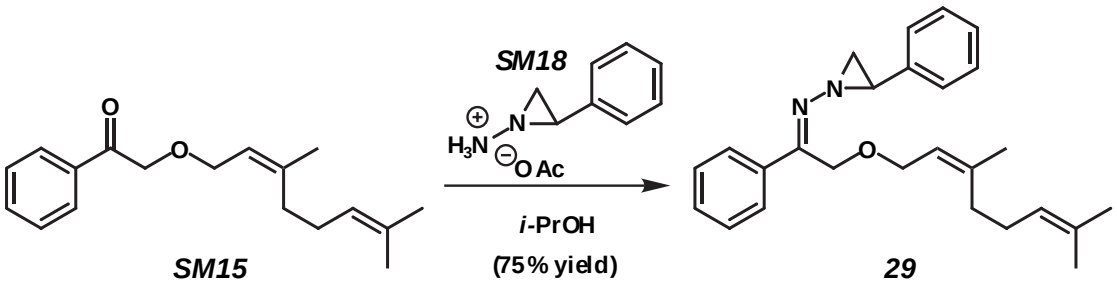


Hydrazone 25. The general procedure outlined above was followed (using 821.1 mg, 3.76 mmol of the corresponding keto-ether **SM13**) to provide **25** (251.2 mg, 3.54 mmol, 94% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.35 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.22 (comp.m, 10H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 6.0, 15.9 Hz, 1H), 4.52 (d, *J* = 14.3 Hz, 1H), 4.39 (d, *J* = 14.3 Hz, 1H), 4.06 (d, *J* = 6.0 Hz, 2H), 2.92-2.78 (comp.m, 2H), 2.42 (d, *J* = 7.7 Hz, 1H), 2.27 (d, *J* = 5.0 Hz, 1H), 1.15 (d, *J* = 3.3 Hz, 3H), 1.13 (d, *J* = 2.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 138.9, 136.7, 132.8, 128.6, 128.4, 127.8, 127.2, 126.6, 126.2, 125.7, 72.0, 66.6, 44.4, 41.4, 31.7, 20.6, 20.3; IR (neat) 3028, 2967, 1605 cm^{-1}. HRMS (EI) m/z calcd for $[C_{22}H_{26}N_2O+H]^+$ 335.2123, found 335.2122.

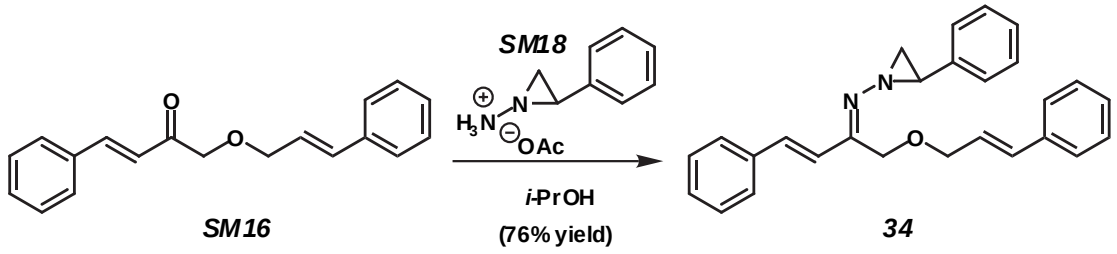


Hydrazone 27. The general procedure outlined above was followed (using 3.96 g, 14.54 mmol of the corresponding keto-ether **SM14**) to provide **27** (3.06 g, 7.87 mmol, 54% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.47 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.44-7.26 (comp.m, 8H), 5.21 (t, *J* = 6.9 Hz, 1H), 5.07 (t, *J* = 6.9 Hz, 1H), 4.81 (d, *J* = 12.6 Hz, 1H), 4.73 (d, *J* = 12.6 Hz, 1H), 3.84 (d, *J* = 6.9 Hz, 2H), 3.04 (dd, *J* = 4.7, 7.4 Hz, 1H), 2.66 (d, *J* = 7.7 Hz, 1H), 2.45 (d, *J* = 4.7 Hz, 1H),

2.06-1.95 (comp.m, 4H), 1.68 (s, 3H), 1.59 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 141.0, 138.3, 135.9, 131.5, 129.4, 128.3, 128.1, 127.2, 127.1, 126.1, 123.8, 120.0, 67.1, 64.3, 45.0, 41.7, 39.6, 26.4, 25.8, 17.8, 16.3; IR (neat) 3062, 3031, 2967, 1605 cm^{-1}.

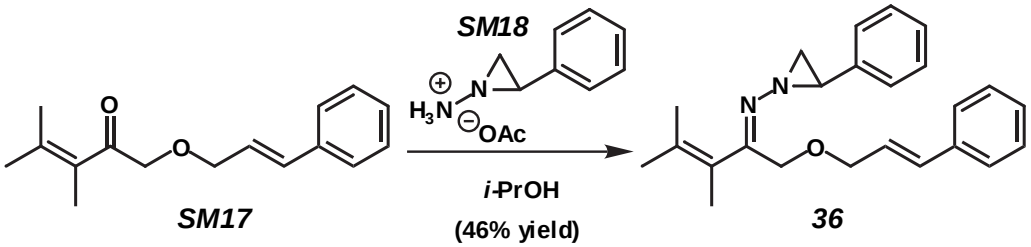


Hydrazone 29. The general procedure outlined above was followed (using 2.14 g, 7.86 mmol of the corresponding keto-ether **SM15**) to provide **29** (2.30 g, 5.93 mmol, 75% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.44 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.49-7.26 (m, 8H), 5.21 (t, *J* = 6.9 Hz, 1H), 5.01 (t, *J* = 6.6 Hz, 1H), 4.81 (d, *J* = 12.6 Hz, 1H), 4.73 (d, *J* = 12.6 Hz, 1H), 3.83 (d, *J* = 6.87 Hz, 2H), 3.05 (dd, *J* = 4.7, 7.7 Hz, 1H), 2.66 (d, *J* = 7.7 Hz, 1H), 2.45 (d, *J* = 4.7 Hz, 1H), 1.98-1.88 (m, 4H), 1.69 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 140.5, 138.2, 135.7, 131.3, 129.2, 128.0, 127.8, 126.9, 126.8, 125.9, 123.6, 121.0, 66.6, 64.1, 44.8, 41.5, 31.8, 26.5, 25.6, 23.3, 17.5; IR (neat) 2966, 1605 cm^{-1}. HRMS (EI) m/z calcd for $[C_{26}H_{32}N_2O+Na]^+$ 411.2412, found 411.2395.



Hydrazone 34. The general procedure outlined above was followed (using 807.8 mg, 2.90 mmol of the corresponding keto-ether **SM16**) to provide **34** (873.4 mg, 2.21

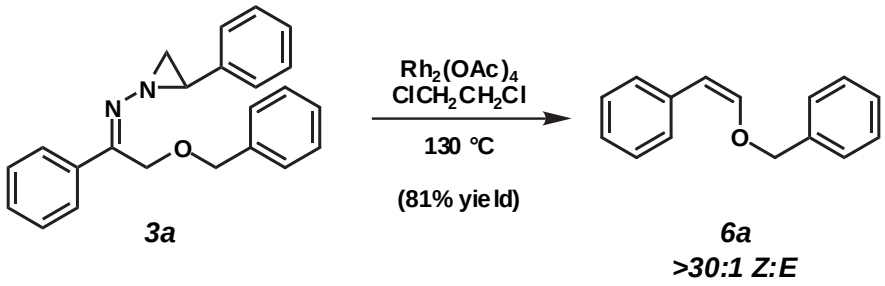
mmol, 76% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.29 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.9 Hz, 2H), 7.39-7.24 (m, 14H), 6.9 (d, *J* = 16.5 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 6.0, 15.9 Hz, 1H), 4.7 (d, *J* = 12.6 Hz, 1H), 4.62 (d, *J* = 12.6 Hz, 1H), 4.07 (d, *J* = 6.0 Hz, 2H), 5.99 (dd, *J* = 4.7, 7.4 Hz, 1H), 2.63 (d, *J* = 7.4 Hz, 1H), 2.46 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 136.4, 135.5, 133.0, 128.6, 128.5, 128.4, 128.3, 127.6, 127.2, 126.4, 126.1, 125.3, 125.1, 71.5, 64.2, 45.4, 41.9; IR (neat) 3058, 3026, 1622 cm^{-1}. HRMS (EI) m/z calcd for $[C_{27}H_{26}N_2O+Na]^+$ 417.1943, found 417.1946.



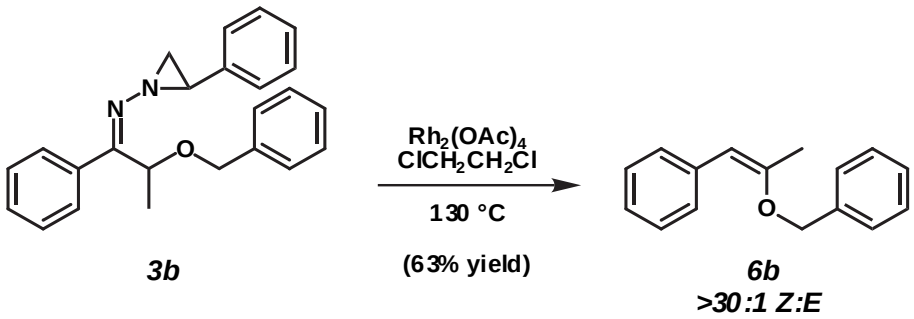
Hydrazone 36. The general procedure outlined above was followed (using 621.2 g, 2.54 mmol of the corresponding keto-ether **SM17**) to provide **36** (418.4 mg, 1.16 mmol, 46% yield) as a yellow oil. Flash chromatographic purification (15:1 → 9:1 hexanes:ethyl acetate gradient eluent). R_F 0.62 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.26 (comp.m, 10H), 6.51 (d, *J* = 15.9, 1H), 6.18 (dt, *J* = 6.0, 15.9 Hz, 1H), 4.67 (d, *J* = 15.4, 1H), 4.52 (d, *J* = 15.4 Hz, 1H), 4.07 (d, *J* = 6.0 Hz, 2H), 2.94 (dd, *J* = 4.4, 7.7 Hz, 1H), 2.52 (d, *J* = 7.1 Hz, 1H), 2.34 (d, *J* = 5.0 Hz, 1H), 1.87 (s, 3H), 1.80 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 138.6, 136.7, 132.6, 131.6, 128.6, 128.4, 127.8, 127.3, 126.6, 126.2, 126.2, 125.7, 72.0, 67.3, 44.3, 41.2, 22.2, 20.6, 17.7; IR (neat) 3061, 3028, 2987, 1604 cm^{-1}. HRMS (EI) m/z calcd for $[C_{24}H_{28}N_2O+H]^+$ 361.2280, found 361.2280.

Bamford-Stevens Reactions

Representative Procedure for the Rhodium-Catalyzed Bamford-Stevens Reaction:



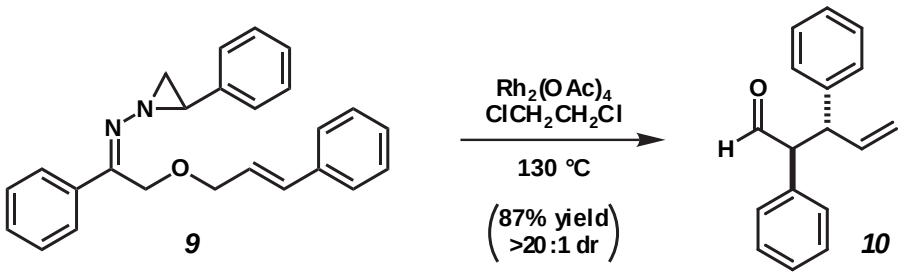
Enolether 6a. A flame-dried sealable schlenk tube (25 mL) was equipped with magnetic stirbar and charged with $Rh_2(OAc)_4$ (2.5 mg, 0.0057 mmol) under stream of nitrogen. DCE (3 mL) was added via syringe, followed by addition of **3a** (101.6 mg, 0.297 mmol). The tube was then sealed under nitrogen and stirred at 130 °C. The reaction was monitored by TLC (18:1 pentane:ether eluent) and discontinued by removal from heat after the starting material was consumed (3 h). The crude reaction mixture was then passed through a pad of silica to remove the catalyst, and the solvent was removed under reduced pressure. A ^{1}H NMR spectrum was taken of this crude product to determine the isomeric ratio, and then the product **3a** was purified via flash column chromatography (25:1 pentane:ether eluent) producing pure *Z*-enolether (50.2 mg, 0.239 mmol, 81% yield) as a yellow oil. R_F 0.45 (18:1 pentane:Et_2O eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.1 Hz, 2H), 7.46-7.35 (comp.m, 7H), 7.24 (q, *J* = 7.4 Hz, 1H), 6.35 (d, *J* = 6.9 Hz, 1H), 5.35 (d, *J* = 6.9 Hz, 1H), 5.05 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 137.0, 135.7, 128.1, 128.1, 127.9, 127.1, 125.6, 106.1, 74.8; IR (neat) 3031, 2932, 1651 cm^{-1}. HRMS (EI) m/z calcd for $[C_{15}H_{14}O]^+$ 210.1045, found 210.1042 .



Enolether 6b. The general procedure outlined above was followed (using 200.6 mg, 0.561 mmol of the corresponding hydrazone **3b**) to provide **6b** (83.0 mg, 0.370 mmol, 66% yield) as a yellow oil. Flash chromatographic purification (25:1 pentane:ether eluent). R_F 0.50 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 2H), 7.44-7.27 (comp.m, 6H), 7.16 (t, J = 7.7 Hz, 2H), 5.44 (s, 1H), 5.07 (s, 2H), 2.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 137.9, 136.7, 128.6, 128.2, 128.1, 127.8, 127.1, 125.4, 107.9, 69.7, 19.7; IR (neat) 3088, 3064, 3029, 2989, 1656 cm^{-1}. HRMS (EI) m/z calcd for $[C_{16}H_{16}O]^+$ 224.1201, found 224.1197.

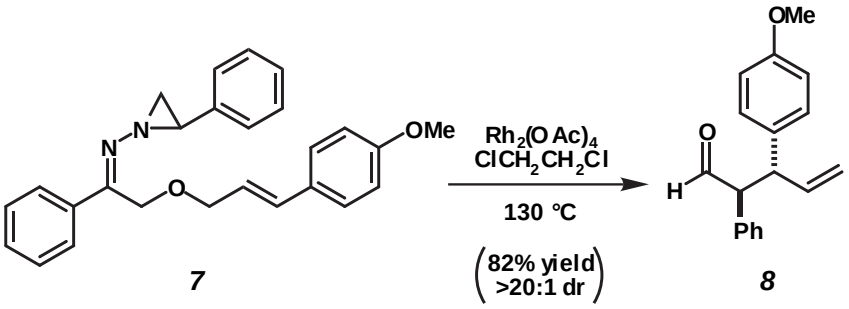
Rhodium-Catalyzed Tandem Bamford-Stevens/Claisen Reactions

Representative Procedure for the Rhodium-Catalyzed Bamford-Stevens/Claisen Rearrangement



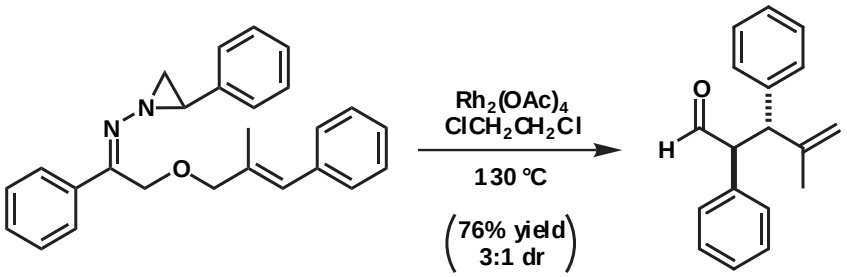
Aldehyde 10. A flame-dried sealable schlenk tube (25 mL) was equipped with magnetic stirbar and charged with $Rh_2(OAc)_4$ (2.5 mg, 0.0057 mmol) under stream of nitrogen. DCE (3 mL) was added via syringe, followed by addition of **9** (101.9 mg, 0.277 mmol). The tube was then sealed under nitrogen and stirred at 130 °C. The reaction was monitored by TLC (18:1 pentane:ether eluent) and discontinued by removal from heat

after the starting material (R_f= 0.15, green by p-anisaldehyde stain) and Bamford-Stevens intermediate (R_f= 0.2, blue by stain) were consumed (usually 3-5 h). The crude reaction mixture was then passed through a pad of silica to remove the catalyst, and the solvent was removed under reduced pressure. A ^{1}H NMR spectrum was taken of this crude product to determine the diastereomeric ratio, and then the product was purified via flash column chromatography (25:1 pentane:ether eluent) to give pure aldehyde **10** (57.1 mg, 0.242 mmol, 87% yield) as a white solid that could be recrystalized from pentane. mp 101.0-103.5; R_F 0.26 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (d, *J* = 2.4 Hz, 1H), 7.43-7.23 (m, 10H), 5.81 (ddd, *J* = 2.7, 10.2, 17.1 Hz, 1H), 4.94 (d, *J* = 9.9 Hz, 1H), 4.87 (d, *J* = 16.8 Hz, 1H), 4.18 (app.t, *J* = 8.1, 1H), 4.04 (dd, *J* = 3.0, 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 140.9, 138.1, 134.3, 129.5, 128.9, 128.7, 128.1, 127.7, 126.9, 116.7, 68.9, 50.4; IR (neat) 3060, 3028, 1712 cm^{-1}. HRMS (EI) m/z calcd for $[C_{17}H_{16}O]^+$ 236.1201, found 236.1207.



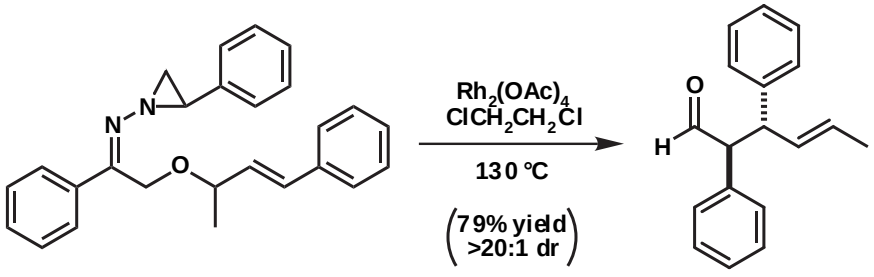
Aldehyde 8. The general procedure outlined above was followed (using 145.9 mg, 0.369 mmol of the corresponding hydrazone **7**) to provide aldehyde **8** (80.6 mg, 0.303 mmol, 82% yield) as a white solid. Flash chromatographic purification (25:1 pentane:ether eluent). R_F 0.15 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (d, *J* = 2.8 Hz, 1H), 7.42-7.18 (comp.m, 7H), 6.89 (d, *J* = 8.2 Hz, 2H), 5.79 (ddd, *J* = 7.7, 10.4, 17.0 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 4.85 (d, *J* = 17.0 Hz, 1H), 4.13 (dd, *J* = 7.7, 10.4 Hz, 1H), 3.98 (dd, *J* = 3.3, 10.4 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 158.5, 138.6, 138.6, 134.6, 133.1, 129.7, 129.4, 129.1, 127.9,

116.6, 114.3, 64.2, 55.5, 49.8; IR (neat) 2934, 1716 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{18}O_2]^+$ 266.1307, found 266.1312.



11 ***12***

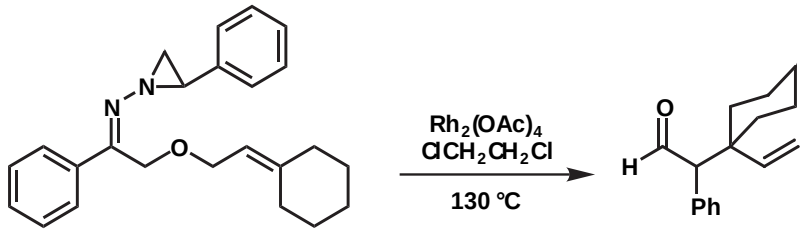
Aldehyde 12. The general procedure outlined above was followed (using 103.4 mg, 0.270 mmol of the corresponding hydrazone **11**) to provide aldehyde **12** (51.5 mg, 0.206 mmol, 76% yield) as a yellow oil. Flash chromatographic purification (25:1 pentane:ether eluent). R_F 0.22 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.53 (d, *J* = 3.3 Hz, 1H), 7.42-7.27 (comp.m, 10H), 4.83 (s, 1H), 4.69 (s, 1H), 4.29 (dd, *J* = 3.3, 12.1 Hz, 1H), 4.20 (d, *J* = 12.1 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 143.9, 140.0, 134.5, 129.0, 128.9, 128.5, 128.0, 127.6, 127.0, 113.3, 61.1, 52.9, 20.6; IR (neat) 3066, 3029, 2959, 1717 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{18}O]^+$ 250.1358, found 250.1360.



13 ***14***

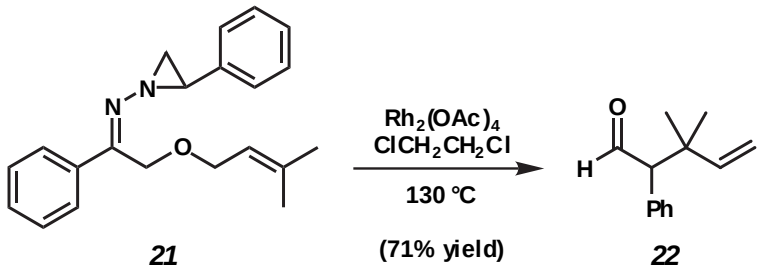
Aldehyde 14. The general procedure outlined above was followed (using 96.9 mg, 0.253 mmol of the corresponding hydrazone **13**) to provide aldehyde **14** (50.1 mg, 0.200 mmol, 79% yield) as a white solid. Flash chromatographic purification (25:1 pentane:ether eluent). Aldehyde **14** could be further purified by recrystalization from

pentane. R_F 0.34 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (d, *J* = 2.8 Hz, 1H), 7.41-7.20 (comp.m, 10H), 5.46-5.38 (m, 1H), 5.33-5.24 (m, 1H), 4.10 (dd, *J* = 7.7, 9.9 Hz, 1H), 3.96 (dd, *J* = 2.9, 9.9 Hz, 1H), 1.49 (d, *J* = 2.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 141.8, 134.5, 130.7, 129.5, 128.7, 128.6, 128.0, 127.5, 126.7, 64.2, 49.5, 18.0; IR (neat) 3062, 3024, 2956, 1711 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{18}O]^+$ 250.1358, found 250.1361.

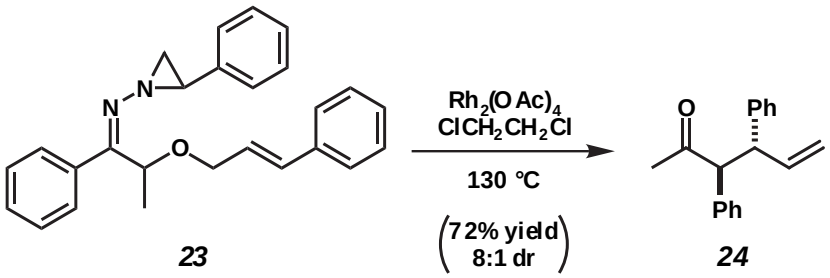


17 ***18***

Aldehyde 18. The general procedure outlined above was followed (using 98.9 mg, 0.274 mmol of the corresponding hydrazone **17**) to provide aldehyde **18** (53.9 mg, 0.236 mmol, 86% yield) as a yellow oil. Flash chromatographic purification (25:1 pentane:ether eluent). R_F 0.54 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.94 (d, *J* = 4.1 Hz, 1H), 7.34-7.26 (comp.m, 5H), 5.78 (dd, *J* = 11.0, 17.9 Hz, 1H), 5.37 (d, *J* = 11.0 Hz, 1H), 5.02 (d, *J* = 18.1 Hz, 1H), 3.38 (d, *J* = 3.9 Hz, 1H), 1.91 (s, 1H), 1.59-1.27 (comp.m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4, 141.7, 134.2, 130.3, 128.0, 127.2, 116.6, 67.8, 43.2, 39.7, 34.3, 26.1, 21.8, 21.7; IR (neat) 3030, 2932, 1720 cm^{-1}. HRMS (EI) m/z calcd for $[C_{16}H_{20}O]^+$ 228.1514, found 228.1514.



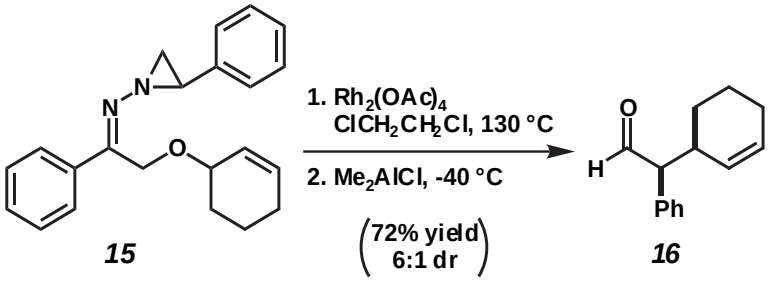
Aldehyde 22. The general procedure outlined above was followed (using 101.0 mg, 0.315 mmol of the corresponding hydrazone **21**) to provide aldehyde **22** (41.9 mg, 0.223 mmol, 71% yield) as a yellow oil. Flash chromatographic purification (25:1 pentane:ether eluent). R_F 0.35 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.93 (d, *J* = 3.3 Hz, 1H), 7.38-7.20 (comp.m, 5H), 6.02 (dd, *J* = 11.0, 17.6 Hz, 1H), 5.10 (d, *J* = 10.6 Hz, 1H), 5.00 (d, *J* = 17.6 Hz, 1H), 3.36 (d, *J* = 3.7 Hz, 1H), 1.14 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 144.5, 134.5, 130.3, 128.1, 127.3, 113.1, 67.6, 40.0, 26.5, 24.8; IR (neat) 3085, 3029, 2966, 1722 cm^{-1}. HRMS (EI) m/z calcd for $[C_{13}H_{16}O]^+$ 188.1201, found 188.1197.



Aldehyde 24. The general procedure outlined above was followed (using 46.9 mg, 0.123 mmol of the corresponding hydrazone **23**) to provide aldehyde **24** (22.2 mg, 0.089 mmol, 72% yield) as a pale yellow oil. Flash chromatographic purification (25:1 pentane:ether eluent). R_F 0.28 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.19 (comp.m, 10H), 5.71 (ddd, *J* = 7.1, 10.3, 17.1 Hz, 1H), 4.83 (d, *J* = 10.2 Hz, 1H), 4.74 (d, *J* = 17.3 Hz, 1H), 4.22-4.11 (comp.m, 2H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.9, 142.3, 139.1, 136.6, 129.2, 128.9, 128.7, 128.1, 127.7, 126.7,

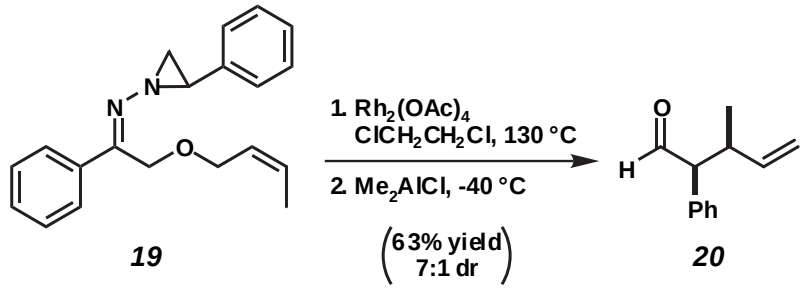
116.5, 64.5, 52.1, 30.8; IR (neat) 3028, 1707 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{18}O+NH_4]^+$ 268.1702, found 268.1700.

Representative Procedure for the Me_2AlCl-Mediated Bamford-Stevens/Claisen Rearrangement (Table 1, entries 5 and 7)



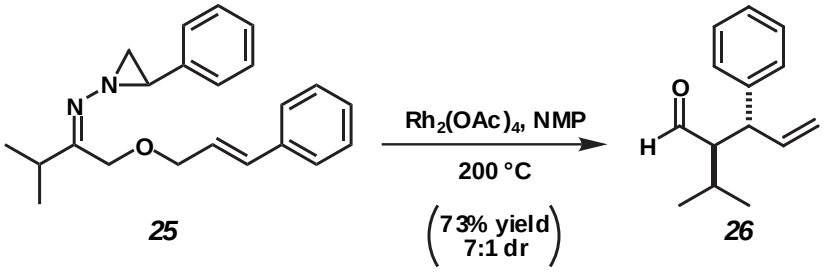
Aldehyde 16. A flame-dried sealable schlenk tube (25 mL) was equipped with magnetic stirbar and charged with $Rh_2(OAc)_4$ (1.9 mg, 0.0043 mmol) under stream of nitrogen. DCE (4.5 mL) was added via syringe, followed by addition of **15** (153.1 mg, 0.461 mmol). The tube was then sealed under nitrogen and stirred at 130 °C. The reaction was continued until the starting material had reacted (typically 2-3 h), and then CH_2Cl_2 (1 mL) was added to suppress freezing and the mixture was cooled to —40 °C. Me_2AlCl in hexanes (480 µl of a 1.0 M solution, 0.480 mmol) was then added over 0.5 min via syringe. TLC analysis (18:1 pentane:ether eluent) usually showed the reaction to be complete within 2 min. 5% HCl (aq) (10 mL) was then added dropwise to quench the excess reagent and dissolve the aluminates. The layers were separated and the aqueous layer was extracted three times with Et_2O (5 mL). The organic layers were combined and dried over $MgSO_4$. After removal of solvent under reduced pressure, the diastereomeric ratio was determined by ^1H NMR. Flash column chromatographic purification of the crude mixture (25:1 pentane:ether eluent) provided pure aldehyde **16** (66.5 mg, 0.332 mmol, 72% yield) as a yellow oil**.** R_F 0.32 (18:1 pentane:ether eluent); ^1H NMR (300 MHz, $CDCl_3$) δ 9.77 (d, *J* = 2.8 Hz, 1H), 7.41-7.18 (comp.m, 5H), 5.83-5.69 (comp.m, 2H), 3.43 (dd, *J* = 2.8, 9.9 Hz, 1H), 2.97-2.89 (m, 1H), 2.00-1.97 (m, 2H), 1.70-1.44

(comp.m, 3H), 1.18-1.07 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.6, 134.9, 129.4, 129.3, 129.1, 128.6, 127.7, 64.8, 35.8, 26.6, 25.5, 21.2; IR (neat) 3426, 3062, 3027, 1723 cm^{-1}. HRMS (EI) m/z calcd for $[C_{14}H_{16}O]^+$ 200.1201, found 200.1203.



Aldehyde 20. The general procedure outlined above was followed (using 150.3 mg, 0.490 mmol of the corresponding hydrazone **19**) to provide aldehyde **20** (53.8 mg, 0.309 mmol, 63% yield) as a yellow oil. Flash chromatographic purification (25:1 pentane:ether eluent). R_F 0.33 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (d, *J* = 2.8 Hz, 1H), 7.41-7.19 (comp.m, 5H), 5.81 (ddd, *J* = 8.3, 10.4, 17.6 Hz, 1H), 5.13 (d, *J* = 17.0 Hz, 1H), 5.08 (d, *J* = 10.1 Hz, 1H), 3.39 (dd, *J* = 3.3, 9.34 Hz, 1H), 3.00 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.5, 141.2, 134.9, 129.4, 129.0, 127.7, 115.3, 64.7, 38.9, 17.9; IR (neat) 3082, 3030, 2976, 1725 cm^{-1}. HRMS (EI) m/z calcd for $[C_{12}H_{14}O+NH_4]^+$ 192.1389, found 192.1395.

Representative Procedure for the Rhodium Catalyzed Bamford-Stevens/Claisen rearrangement using NMP (Table 1, entry 10)

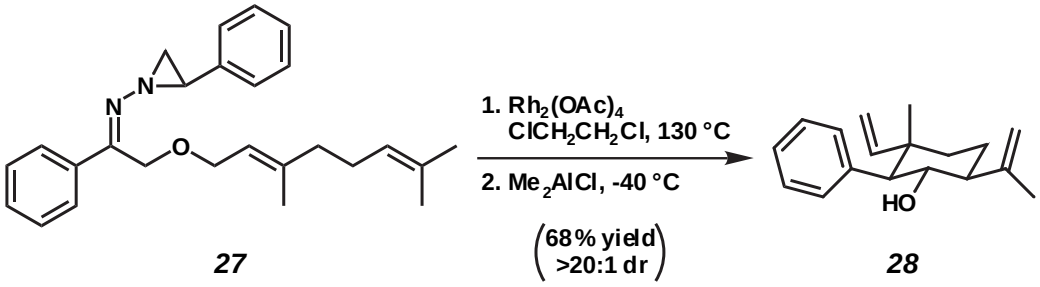


Aldehyde 26. A flame-dried sealable schlenk tube (25 mL) was equipped with magnetic stirbar and charged with $Rh_2(OAc)_4$ (1.4 mg, 0.0032 mmol) under stream of

nitrogen. NMP (3 mL) was added via syringe and followed by addition of **25** (102.1 mg, 0.305 mmol). The tube was then sealed under nitrogen and stirred at 200 °C. The reaction was monitored by TLC (18:1 pentane:ether eluent) and discontinued by removal from heat after the starting material and Bamford-Stevens intermediate were consumed (1 h). The crude reaction mixture was purified by direct flash column chromatography of the reaction mixture (25:1 pentane:ether eluent) to give pure aldehyde **26** (45.3 mg, 0.224 mmol, 73% yield) as a pale yellow oil. R_F 0.28 (18:1 pentane:ether eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.54 (d, *J* = 4.4 Hz, 1H), 7.35-7.17 (comp.m, 5H), 5.90 (ddd, *J* = 9.3, 10.2, 17.0 Hz, 1H), 5.17 (d, *J* = 17.0 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 3.81 (dd, *J* = 9.9, 9.9 Hz, 1H), 2.65 (ddd, *J* = 4.4, 4.4, 10.7 Hz, 1H), 2.16 (d sept., *J* = 4.1, 7.1 Hz, 1H), 1.11 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.3, 141.5, 139.5, 128.9, 128.1, 126.9, 116.1, 60.9, 49.1, 28.5, 22.0, 17.2; IR (neat) 3062, 3029, 2962, 1722 cm^{-1}. HRMS (EI) m/z calcd for the acetal form $[C_{14}H_{20}O_2\text{-}H]^+$ 219.1385, found 219.1385.

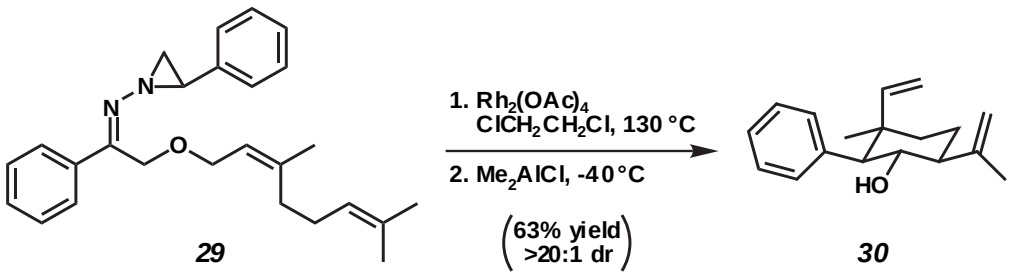
Cascade Reactions

Representative Procedure for the Me_2AlCl Mediated Bamford-Stevens/Claisen/Carbonyl-ene Rearrangement (Table 2, entries 1 and 2)



Alcohol 28. A flame-dried sealable schlenk tube (25 mL) was equipped with magnetic stirbar and charged with $Rh_2(OAc)_4$ (1.9 mg, 0.0043 mmol) under stream of nitrogen. DCE (4 mL) was added via syringe, followed by addition of **27** (150.5 mg, 0.387 mmol). The tube was then sealed under nitrogen and stirred at 130 °C. The

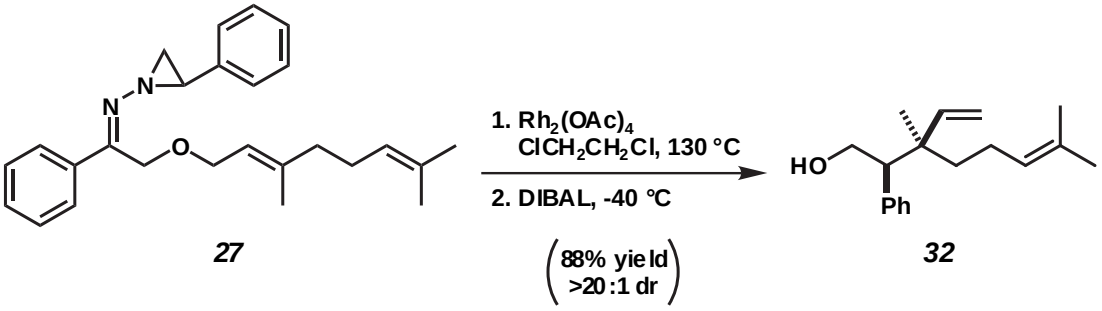
reaction was continued until the starting material had reacted (typically 2 h), and then 1 mL of CH_2Cl_2 was added to suppress freezing and the mixture was cooled to —40 °C. Me_2AlCl in hexanes (400 µl of a 1.0 M solution, 0.400 mmol) was then added at a moderate rate via syringe. TLC analysis (9:1 hexanes:ethyl acetate eluent) usually showed the reaction to be complete within 2 min. 5% HCl (aq) (15 mL) was then added dropwise to quench the excess reagent and dissolve the aluminates. The layers were separated and the aqueous layer was extracted three times with Et_2O (5 mL). The organic layers were then combined and dried over $MgSO_4$. After removal of solvent under reduced pressure, the diastereomeric ratio was determined by ^1H NMR. Flash column chromatographic purification of **28** (9:1 hexanes:ethyl acetate eluent) yielded pure alcohol (67.5 mg. 0.263 mmol, 68% yield) as a colorless oil. R_F 0.28 (9:1 hexanes:ethyl acetate eluent); ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.18 (comp.m, 5H), 5.69 (dd, *J* = 11.0, 17.6 Hz, 1H), 4.93 (s, 2H), 4.81 (d, *J* = 11.0 Hz, 1H), 4.70 (d, *J* = 18.1 Hz, 1H), 4.15 (t, *J* = 10.4 Hz, 1H), 2.57 (d, *J* = 11.0 Hz, 1H), 2.62-2.18 (m, 1H), 1.85-1.54 (comp.m, 4H), 1.84 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 146.9, 138.8, 130.1, 127.9, 126.8, 112.8, 111.0, 69.5, 59.6, 54.3, 42.0, 38.6, 26.4, 19.8, 18.3; IR (neat) 3583, 3461, 3082, 3029, 2969 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{24}O+H]^+$ 257.1905, found 257.1905.



Alcohol 30. The general procedure outlined above was followed (using 102.6 mg, 0.254 mmol of the corresponding hydrazone **29**) to provide **30** (41.0 mg, 0.160 mmol, 63% yield) as a colorless oil. Flash chromatographic purification (9:1 hexanes:ethyl acetate eluent). R_F 0.27 (9:1 hexanes:ethyl acetate eluent); ^1H NMR (300 MHz, $CDCl_3$)

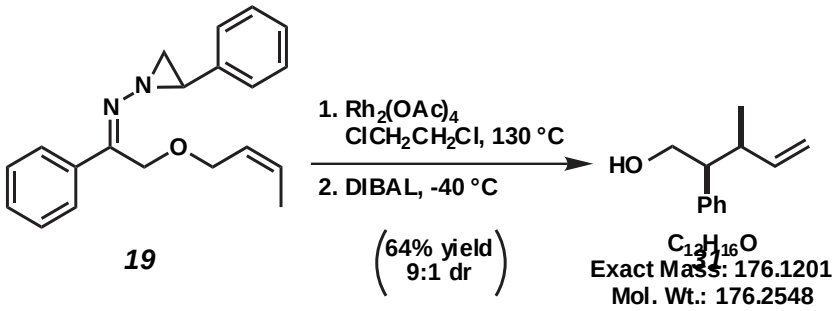
δ 7.34-7.21 (comp.m, 5H), 6.18 (dd, *J* = 11.0, 17.6 Hz, 1H), 5.07 (d, *J* = 11.0 Hz, 1H), 4.92 (s, 1H), 4.91 (s, 1H), 4.82 (d, *J* = 17.6 Hz, 1H), 4.05 (t, *J* = 10.4 Hz, 1H), 2.55 (d, *J* = 10.7 Hz, 1H), 2.30-2.21 (m, 1H), 1.89-1.79 (m, 1H), 1.82 (s, 3H), 1.68-1.53 (comp.m, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 141.0, 138.5, 130.2, 127.8, 126.8, 114.1, 112.7, 69.7, 61.9, 54.5, 42.0, 39.4, 28.3, 26.3, 19.7; IR (neat) 3564, 3083, 3029 cm^{-1}. HRMS (EI) m/z calcd for $[C_{18}H_{24}O+H]^+$ 257.1905, found 257.1907.

Representative Procedure for the DIBAL-Mediated Bamford-Stevens/Claisen Reductive Rearrangement (Table 2, entries 3-5)

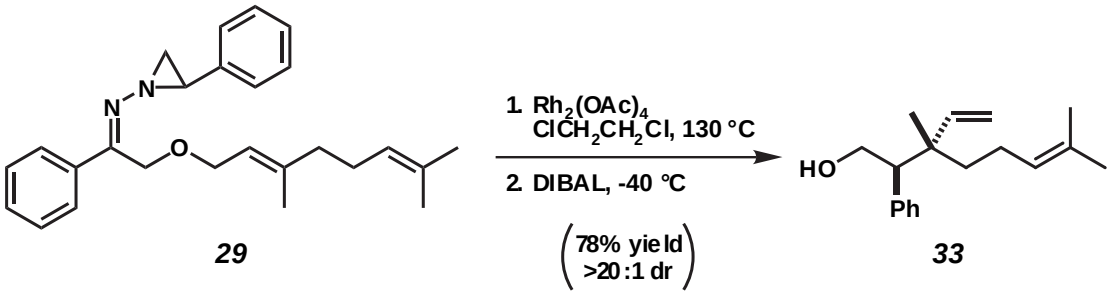


Alcohol 32. A flame-dried sealable schlenk tube (25 mL) was equipped with magnetic stirbar and charged with $Rh_2(OAc)_4$ (1.9 mg, 0.0043 mmol) under stream of nitrogen. DCE (4 mL) was added via syringe, followed by addition of **27** (151.9 mg, 0.391 mmol). The tube was then sealed under nitrogen and stirred at 130 °C. The reaction was continued until the starting material had reacted (typically 2 h), and then CH_2Cl_2 (1 mL) was added to suppress freezing and the mixture was cooled to —40 °C. DIBAL in hexanes (800 µl of a 1.0 M solution in hexanes, 0.800 mmol) was then added over 0.5 min via syringe. TLC analysis (3:1 hexanes:ethyl acetate eluent) usually showed the reaction to be complete within 20 min for aromatic substituted allyl ethers. Aliphatic substituted allyl ethers were allowed to warm to room temperature in order to completely react. 5% HCl (aq) (15 mL) was then added dropwise to quench the excess reagent and dissolve the aluminates. The layers were separated and the aqueous layer was extracted

three times with Et_2O (5 mL). The organic layers were then combined and dried over $MgSO_4$. After removal of solvent under reduced pressure, the diastereomeric ratio was determined by ^1H NMR. Flash column chromatographic purification of the crude mixture (9:1 hexanes:ethyl acetate eluent) furnished pure alcohol **32** (88.4 mg, 0.344 mmol, 88% yield). R_F 0.67 (3:1 hexanes:ethyl acetate eluent); ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.21 (comp.m, 5H), 5.79 (dd, *J* = 11.0, 17.6 Hz, 1H), 5.08 (d, *J* = 10.7 Hz, 1H), 4.98 (t, *J* = 7.2 Hz, 1H), 4.90 (d, *J* = 17.6 Hz, 1H), 4.06-3.91 (comp.m, 2H), 2.81 (dd, *J* = 5.0, 10.2 Hz, 1H), 1.97-1.73 (m, 2H), 1.64 (s, 3H), 1.54 (s, 3H), 1.35-1.15 (comp.m, 2H), 1.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 139.1, 131.1, 130.0, 128.0, 126.8, 124.5, 113.3, 62.9, 57.9, 41.9, 39.0, 25.8, 22.6, 21.3, 17.7; IR (neat) 3561, 3377, 3061, 2969 cm^{-1}.



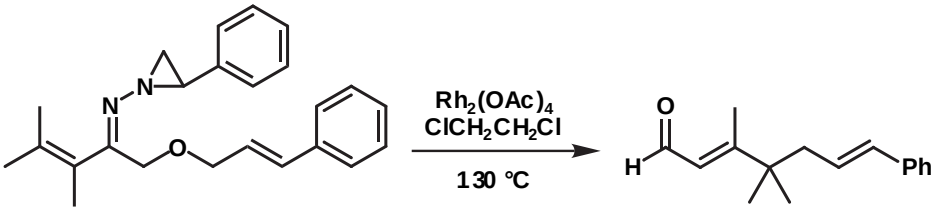
Alcohol 31. The general procedure outlined above was followed (using 49.6 mg, 0.325 mmol of the corresponding hydrazone **19**) to provide alcohol **31** (36.7 mg, 0.208 mmol, 64% yield) as a pale yellow oil. Flash chromatographic purification (9:1 hexanes:ethyl acetate eluent). R_F 0.15 (9:1 hexanes:ethyl acetate eluent); ^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.19 (comp.m, 5H), 5.79 (ddd, *J* = 8.5, 9.9, 17.0 Hz, 1H), 5.12 (d, *J* = 17.0 Hz, 1H), 5.04 (d, *J* = 10.2 Hz, 1H), 3.92-3.86 (m, 1H), 3.77-3.71 (m, 1H), 2.64-2.56 (m, 1H), 2.50-2.44 (m, 1H), 0.82 (d, *J* = 3.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 141.1, 128.5, 128.5, 126.7, 14.3, 66.1, 54.0, 41.3, 19.4; IR (neat) 3559, 3384, 3084, 2970 cm^{-1}. HRMS (EI) m/z calcd for $[C_{12}H_{16}O]^+$ 176.1201, found 176.1204.



29 ***33***

Alcohol 33. The general procedure outlined above was followed (using 99.3 mg, 0.256 mmol of the corresponding hydrazone **29**) to provide alcohol **33** (51.6 mg, 0.200 mmol, 78% yield) as a yellow oil. Flash chromatographic purification (9:1 hexanes:ethyl acetate eluent). R_F 0.14 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.23 (m, 5H), 5.82 (dd, *J* = 11.1, 6.6 Hz, 1H), 5.16 (dd, *J* = 1.2, 11.1 Hz, 1H), 5.03-4.93 (m, 2H), 4.00-3.89 (m, 2H), 2.81 (dd, *J* = 5.1, 4.8 Hz, 1H), 1.84 (m, 2H), 1.65 (s, 3H), 1.55 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 139.1, 131.1, 129.9, 128.0, 124.5, 113.6, 63.1, 57.1, 42.4, 40.0, 25.7, 22.5, 18.5, 17.7; IR (neat) 3383, 2969 cm^{-1}.

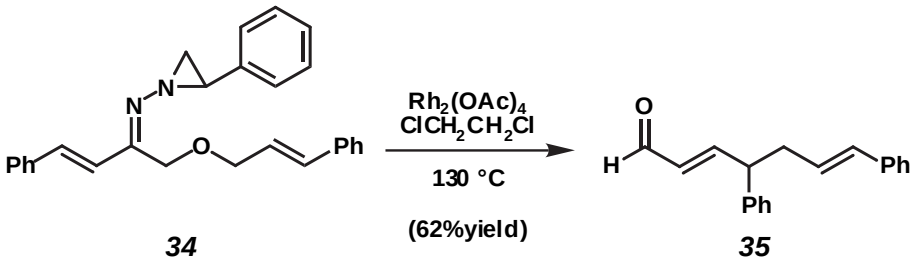
Representative Procedure for the Rhodium-Catalyzed Bamford-Stevens/Claisen/Cope Rearrangement (Table 2, entries 6 and 7)



36 ***37***

Aldehyde 37. A flame-dried sealable schlenk tube (25 mL) was equipped with magnetic stirbar and charged with $Rh_2(OAc)_4$ (1.9 mg, 0.0043 mmol) under stream of nitrogen. DCE (4 mL) was added via syringe, followed by addition of **36** (73.0 mg, 0.203 mmol). The tube was then sealed under nitrogen and stirred at 130 °C. The reaction was monitored by TLC (9:1 hexanes:ethyl acetate eluent) and discontinued by removal from heat after the starting material and intermediates were transformed to leave one product

visible by TLC (9:1 hexanes:ethyl acetate eluent, 3-8 h reaction time). The crude reaction mixture was then passed through a pad of silica to remove the catalyst, and the solvent was removed under reduced pressure. A ^{1}H NMR spectrum was taken of this crude product to determine the diastereomeric ratio, and then the crude mixture was purified via flash column chromatography (9:1 hexanes:ethyl acetate eluent) to yield aldehyde **37** as an oil (31.5 mg, 0.138 mmol, 68% yield). R_F 0.23 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.08 (d, *J* = 8.0 Hz, 1H), 7.34-7.21 (comp.m, 5H), 6.4 (d, *J* = 15.7 Hz, 1H), 6.07-5.95 (comp.m, 2H), 2.38 (d, *J* = 7.4 Hz, 2H), 2.22 (s, 3H), 1.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 169.2, 137.3, 132.9, 128.6, 127.3, 126.2, 126.1, 125.8, 44.3, 41.7, 26.7, 14.1; IR (neat) 3026, 2969, 1669 cm^{-1}. HRMS (EI) m/z calcd for $[C_{16}H_{20}O+H]^+$ 229.1592, found 229.1588.



Aldehyde 35. The general procedure outlined above was followed (using 47.8 mg, 0.121 mmol of the corresponding hydrazone **34**) to provide aldehyde **35** (19.7 mg, 0.075 mmol, 62% yield) as a yellow oil. Flash chromatographic purification (9:1 hexanes:ethyl acetate eluent). R_F 0.24 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (d, *J* = 7.7 Hz, 1H), 7.41-7.22 (comp.m, 10H), 7.02 (dd, *J* = 7.2, 15.7 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.19-6.05 (comp.m, 2H), 3.74 (dt, *J* = 7.4, 7.4 Hz, 1H), 2.78 (dd, *J* = 7.4, 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 160.0, 140.9, 137.2, 132.6, 132.4, 129.0, 128.6, 127.9, 127.4, 127.4, 126.7, 126.2, 49.2, 28.5; IR (neat) 3082, 3059, 3027, 2924, 1689 cm^{-1}. HRMS (EI) m/z calcd for $[C_{19}H_{18}O]^+$ 262.1358, found 262.1359.

Structural Elucidations and Correlations to Confirm Relative Stereochemistry:

Scheme 2.

Enolether 6a. Enolether **6a** was assigned the (*Z*) stereochemistry based on the coupling constants of the vinyl hydrogens.

Enolether 6b. Enolether **6b** was assigned the (*Z*) stereochemistry based on the shown NOE interactions between the vinyl methyl and the vinyl hydrogen.

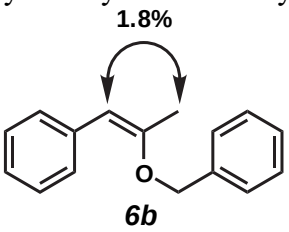
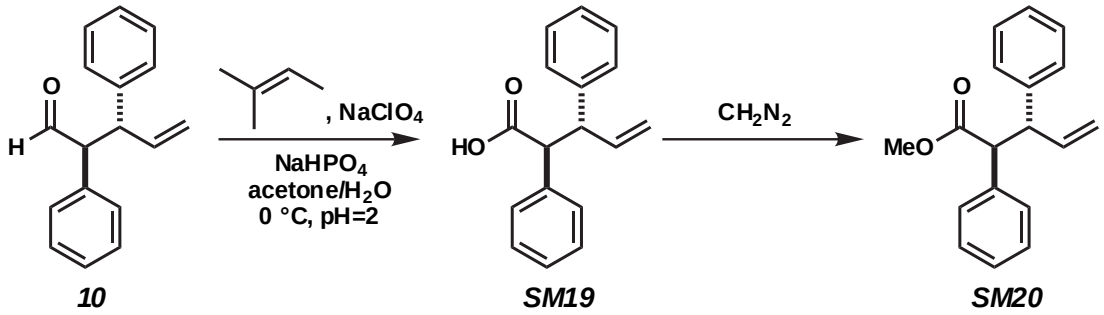


Table 1.

Aldehyde 8. Aldehyde **8** was assigned the shown stereochemistry based on analogy with aldehyde **10**.

Aldehyde 10. Chemical correlation by conversion to known ester **SM20**.

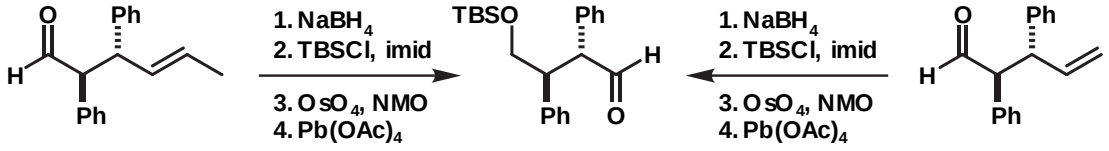


Ester SM20. To a flask (100 mL) containing aldehyde **10** (98.4 mg, 0.416 mmol) and equipped with a magnetic stirbar was added acetone (20 mL) and $NaHPO_4$ buffer (10 mL saturated H_2O solution) adjusted to pH 2 by addition of HCl (concd). This mixture was cooled to 0 °C, and 2-methyl-2-butene (650 µl, 6.13 mmol) was added. Immediately, a solution of $NaClO_4$ (93.6 mg, 0.827 mmol) in H_2O (10 mL) was added in one portion. TLC analysis (R_F 0.29, 3:1 hexanes:ethyl acetate eluent, CAM stain) showed complete

conversion to the acid within 1 min. A 1:1 mixture of $CHCl_3$:H_2O (40 mL) was added, the layers were separated, and the aqueous phase was extracted three times with $CHCl_3$ (4 mL). The combined organic portions were dried over Na_2SO_4, and the solvent was removed under reduced pressure to leave an amorphous white solid. This solid was purified by flash column chromatography (9:1 hexanes:ethyl acetate with 1% AcOH eluent) to yield the acid **SM19** (99.8 mg, 0.340 mmol, 95% yield) as a white solid. Acid **SM19** (12.1 mg, 0.048 mmol) was then dissolved in Et_2O at 0 °C in a scratch-free flask (50 mL) equipped with a new, teflon-coated magnetic stirbar, and treated carefully with a solution of CH_2N_2 in Et_2O (0.2 *M*, 5 mL). Complete conversion was seen by TLC (3:1 hexanes:ethyl acetate eluent, *p*-anisaldehyde staining), and AcOH was added dropwise until the yellow color in the reaction mixture was quenched. The solvent was then removed under reduced pressure to yield pure ester **SM20** (12.8 mg, 0.048 mmol, 100% yield) as a colorless oil. The spectral data for **SM20** exactly matched that reported in the literaure.[6] R_F 0.64 (3:1 hexanes:ethyl acetate eluent).

Aldehyde 12. The stereochemistry of aldehyde **12** was assigned based on analogy with aldehyde **10**.

Aldehyde 14. Chemical correlation to aldehyde **10** by conversion of both to aldehyde **SM21**.



14 ***SM21*** ***10***

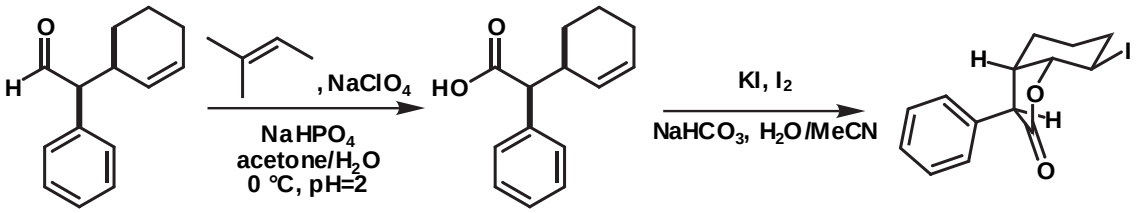
Aldehyde SM21. A flask (15 mL), equipped with a magnetic stirbar, was charged with diasteroeomerically pure aldehyde **14** (23.7 mg, 0.094 mmol) and a 1:1 mixture of CH_2Cl_2 and MeOH (2 mL). To this solution was added $NaBH_4$ (5.6 mg, 0.147 mmol) in one

(6) Corey, E. J.; Lee, D.-H. *J. Am. Chem. Soc.* 1991, **113**, 4026

portion. TLC analysis (R_F 0.26, 3:1 hexanes:ethyl acetate eluent) showed immediate completion. CH_2Cl_2 (2 mL) and H_2O (4 mL) were then added, the layers were separated, and the aqueous phase was extracted three times with CH_2Cl_2 (2 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude alcohol product (23.5 mg, 0.093 mmol) was then dissolved in THF in a flask (15 mL), which was subsequently charged with imidazole (24.3 mg, 0.357 mmol) and *tert*-butyl-dimethylsilyl chloride (48.8 mg, 0.324 mmol). This solution was heated to reflux for 6.5 hr, then cooled when TLC analysis (R_F 0.56, 15:1 hexanes:ethyl acetate eluent) showed completion. After addition of H_2O (5 mL) and Et_2O (3 mL), the layers were separated, and the aqueous phase was extracted with Et_2O (3 x 3 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed under reduced pressure. This crude product was subjected to flash chromatographic purification (50:1 hexanes:ethyl acetate eluent) to furnish the silyl ether as a clear oil. This oil (33.4 mg, 0.091 mmol) was transferred to a vial (20 mL) equipped with magnetic stirbar and diluted with THF (1.5 mL) and H_2O (0.5 mL). NMO (35.0 mg, 0.299 mmol) was added, followed by OsO_4 (5 mg, 0.020 mmol). The solution was stirred at room temperature for 7 hr, when complete conversion was observed by TLC analysis (R_F 0.66, 1:1 hexanes:ethyl acetate eluent). The reaction mixture was quenched by addition of saturated aq $Na_2S_2O_4$ (4 mL) and Et_2O (2 mL). The layers were separated and the aqueous phase was extracted with Et_2O (5 x 2 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed under reduced pressure. This crude product was subjected to flash chromatographic purification (5:1 hexanes:ethyl acetate eluent) to furnish the diol as a clear oil. This diol (17.0 mg, 0.0440 mmol), dissolved in CH_2Cl_2 (1 mL), was added in a dropwise fashion to a stirred, 0 °C solution of $Pb(OAc)_4$ (37.3 mg, 0.084 mmol) in CH_2Cl_2 (1 mL). TLC analysis showed immediate conversion to the aldehyde (R_F 0.41, 9:1 hexanes:ethyl acetate eluent). Heptane (2 mL) was added and the hetergeneous mixture was filtered through celite, which was washed three times with

heptane (1 mL). The resulting clear solution was concentrated to an oil under reduced pressure, and then diluted with ethyl acetate (3 mL). This solution was filtered through a small plug of silica, which was washed five times with ethyl acetate (1 mL). The solvent was removed under reduced pressure to produce the crude product. This product was purified by flash column chromatography (15:1 hexanes:ethyl acetate eluent) to furnish pure adehyde **SM21** as a clear oil (10.2 mg, 0.029 mmol, 31% overall yield). R_F 0.41 (9:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (d, *J* = 2.8 Hz, 1H), 7.42-7.24 (comp.m, 10H), 4.16 (dd, *J* = 2.2, 9.3 Hz, 1H), 3.66-3.49 (comp.m, 3H), 0.84 (s, 9H), -0.17 (s, 3H), -0.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.1, 140.7, 134.8, 129.9, 129.0, 129.0, 128.4, 127.8, 64.4, 60.7, 49.3, 26.1, 18.5, -5.5, -5.5; IR (neat) 3063, 3030, 2954, 1727 cm^{-1}. HRMS (EI) m/z calcd for $[C_{22}H_{30}O_2Si+H]^+$ 355.2093, found 355.2095. The identical procedure commencing with aldehyde **10** (19.0 mg, 0.080 mmol) also furnished aldehyde **SM21** (11.9 mg, 0.34 mmol, 43% overall yield), demonstrating identical relative stereochemistries between aldehyde **10** and aldehyde **14**.

Aldehyde 16. Chemical conversion to crystaline iodolactone **SM23**.

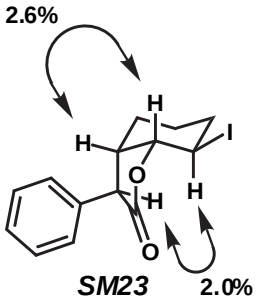


16 ***SM22*** ***SM23***

Lactone SM23. To a flask (50 mL) containing aldehyde **16** (74.2 mg, 0.426 mmol) and equipped with a magnetic stirbar was added acetone (8 mL) and $NaHPO_4$ buffer (4 mL saturated H_2O solution) adjusted to pH 2 by addition of HCl (concd). This mixture was cooled to 0 °C, and 2-methyl-2-butene (500 µl, 4.72 mmol) was added. Immediately, a solution of $NaClO_4$ (85.6 mg, 0.757 mmol) in H_2O (4 mL) was added in one portion. TLC analysis (R_F 0.35, 3:1 hexanes:ethyl acetate eluent, CAM stain) showed complete conversion to the acid within 1 min. A 1:1 mixture of $CHCl_3$:H_2O (16

mL) was added, the layers were separated, and the aqueous phase was extracted three times with $CHCl_3$ (8 mL). The combined organic portions were dried over Na_2SO_4, and the solvent was removed under reduced pressure to leave an amorphous white solid. This solid was purified by flash column chromatography (9:1 hexanes:ethyl acetate with 1% AcOH) to yield the acid **SM22** in quantitative yield. A flask (25 mL) containing acid **SM22** (76.0 mg, 0.351 mmol, 5:1 diastereomeric ratio) was equipped with a magnetic stirbar and charged with MeCN (4 mL), and the mixture was cooled to 0 °C. A solution of $NaHCO_3$ (41.7 mg, 0.497 mmol) in H_2O (4 mL total volume) was then added and the mixture stirred for 5 min. KI (76.6 mg, 0.461 mmol) and I_2 (118.0 mg, 0.464 mmol) were then added simultaneously. The reaction was allowed to warm to room temperature over 45 min, and then stirred for 2 h. The addition of 10% $Na_2S_2O_3$ (aq) (4 mL) quenched the reaction, and the addition of brine (10 mL) and EtOAc (20 mL) followed. The resulting layers were separated and the aqueous phase was extracted three times with EtOAc (5 mL). The organic layers were dried over Na_2SO_4, and then the solvent was removed under reduced pressure. The crude white solid was purified by flash column chromatography (15:1 → 9:1 hexanes:ethyl acetate gradient eluent) to furnish **SM23** (85.2 mg, 0.249 mmol, 71% yield) as a white solid. Crystals suitable for X-ray diffraction were grown from an EtOAc/heptane mixture. mp 158.0-159.1 (dec); R_F 0.53 (3:1 hexanes:ethyl acetate eluent); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.20 (comp.m, 5H), 4.82 (dd, *J* = 6.6, 7.7 Hz, 1H), 4.25 (ddd, *J* = 3.9, 7.7, 9.9 Hz, 1H), 3.68 (d, *J* = 9.9 Hz, 1H), 2.83 (ddd, *J* = 5.5, 10.4, 10.4 Hz, 1H), 2.35-2.26 (m, 1H), 2.06-1.94 (m, 1H), 1.80-1.56 (comp.m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 134.8, 129.1, 128.3, 128.0, 83.3, 49.7, 43.8, 35.0, 27.7, 24.8, 22.2; IR (neat) 3030, 2935, 2860, 1776 cm^{-1}. HRMS (EI) m/z calcd for $[C_{14}H_{15}IO_2+H]^+$ 343.0195, found 343.0189. The minor diastereomer was also isolated (18.7 mg, 0.053 mmol, 15% yield).

NOE values were determined for this product between the lactone hydrogen and the hydrogen geminal to the iodide, as well as between the bridgehead hydrogens as shown below.



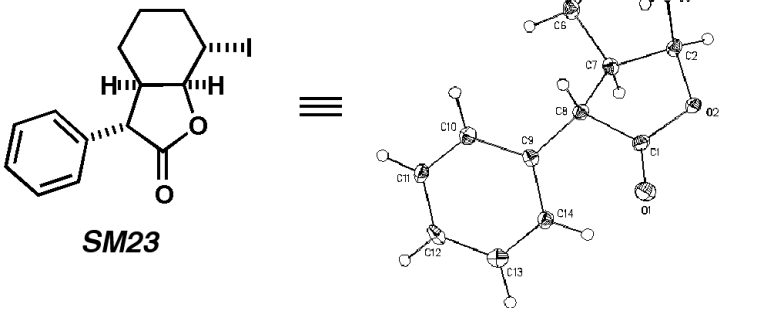


Table 1. Crystal data and structure refinement for SM23 (CCDC 186889). **Note:** The crystallographic data has been deposited in the Cambridge Database (CCDC). The deposition number is 186889.

Empirical formula	$C_{14}H_{15}IO_2$
Formula weight	342.16
Crystallization Solvent	Heptane/Chloroform
Crystal Habit	Lozenge
Crystal size	0.12 x 0.12 x 0.10 mm^3
Crystal color	Colorless

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 MoKa
Data Collection Temperature	98(2) K
q range for 13809 reflections used in lattice determination	2.56 to 28.45°
Unit cell dimensions	a = 8.7729(6) b = 8.8307(6)

	c = 15.9057(11)
Volume	1232.23(15) ^{3}
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.844 Mg/m^3
F(000)	672
Data collection program	Bruker SMART v5.054
q range for data collection	2.56 to 28.30°
Completeness to q = 28.30°	97.1%
Index ranges	-11 † h † 11, -11 † k † 11, -20 † l † 21
Data collection scan type	w scans at 7 f settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	18248
Independent reflections	2922 [R_{int}= 0.0576]
Absorption coefficient	2.586 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.7820 and 0.7467

Structure solution and Refinement

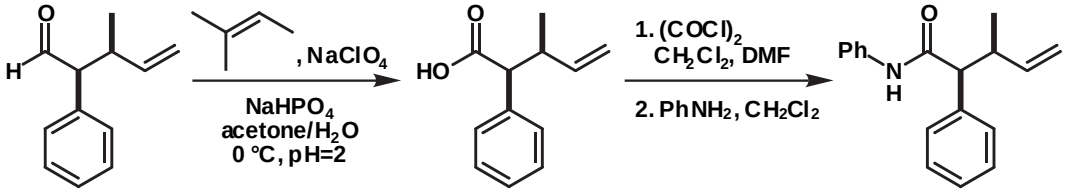
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	2922 / 0 / 214
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.358
Final R indices [I>2s(I), 2781 reflections]	R1 = 0.0194, *w*R2 = 0.0381
R indices (all data)	R1 = 0.0214, *w*R2 = 0.0385
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/s^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	-0.017(17)
Largest diff. peak and hole	0.801 and -0.495 e. $^{-3}$

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 $F^2 > 2s(F^2)$ 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.

Aldehyde 20. Chemical correlation by conversion to known amide **SM25**.



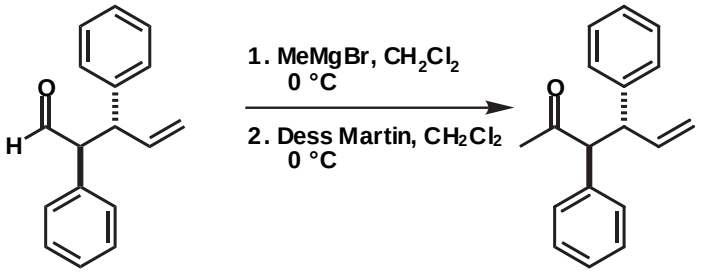
20 *SM24* *SM25*

Amide SM25. To a flask (50 mL) containing aldehyde **20** (56.0 mg, 0.321 mmol) and equipped with a magnetic stirbar was added acetone (8 mL) and $NaHPO_4$ buffer (4 mL saturated H_2O solution) adjusted to pH 2 by addition of HCl (concd). This mixture was cooled to 0 °C, and 2-methyl-2-butene (500 µl, 4.72 mmol) was added. Immediately, a solution of $NaClO_4$ (73.3 mg, 0.757 mmol) in H_2O (4 mL) was added in one portion. TLC analysis (R_F 0.34, 3:1 hexanes:ethyl acetate eluent, CAM stain) showed complete conversion to the acid within 1 min. A 1:1 mixture of $CHCl_3$:H_2O (16 mL) was added, the layers were separated, and the aqueous phase was extracted three times with $CHCl_3$ (8 mL). The combined organic portions were dried over Na_2SO_4, and the solvent was removed under reduced pressure to leave an amorphous white solid. This solid was purified by flash column chromatography (9:1 hexanes:ethyl acetate with 1% AcOH) to yield the acid **SM24** in quantitative yield.

Acid **SM24** (61.1 mg, 0.321 mmol) was dissolved in CH_2Cl_2 (2 mL) in a flask (15 mL) equipped with magnetic stirbar and cooled to 0 °C. Oxalyl chloride (100 µL) was added via syringe, as was a catalytic amount of DMF (3 µl). Once gas generation ceased,

the temperature was allowed to rise to 23 °C, and the reaction was stirred for 2 h until TLC analysis showed completion (treatment of a sample with MeOH produced the corresponding methyl ester; R_F 0.71, 3:1 hexanes ethyl acetate eluent). The reaction solvent was removed under reduced pressure, and then benzene was added and removed under reduced pressure twice to displace any excess oxalyl chloride. This acid chloride was then dissolved in CH_2Cl_2 (2 mL) and added to a 0 °C solution of aniline (1 mL) in CH_2Cl_2 (2 mL). TLC analysis showed immediate completion of the reaction. The mixture was diluted with Et_2O (8 mL) and washed with 5% HCl (aq, 4 mL), $NaHCO_3$ (saturated aq, 4 mL), and water (4 mL). The Et_2O phase was then dried over Na_2SO_4, the solvent was removed under reduced pressure, and the product was subjected to flash chromatographic purification (15:1→ 9:1 hexanes:ethyl acetate gradient eluent) to furnish amide **SM25** as a yellow oil (67.2 mg, 0.253 mmol, 79% yield for two steps). The spectral data for **SM25** exactly matched that reported in the literaure.[7] R_F 0.60 (9:1 hexanes:ethyl acetate eluent).

Ketone 24. Chemical correlation by independent synthesis from aldehyde **10**.



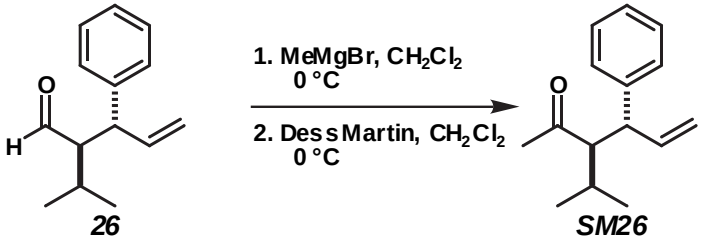
10 ***24***

Ketone 24. A flame-dried flask (15 mL) equipped with a magnetic stirbar was charged with aldehyde **26** (52.0 mg, 0.220 mmol) and Et_2O (2 mL). When this solution had been cooled to 0 °C, a solution of MeMgBr (3.0 *M* in THF, 100 µl, 0.300 mmol) was added *via* syringe. TLC analysis showed immediate reaction, and H_2O (4 mL) was added in order to quench the reaction mixture. Et_2O (3 mL) was then added and the layers were

(7) Ban, E. M.; Gil, S.; Mestres, R.; Parra, M. *Tetrahedron* **1998**, *54*, 15305.

separated. The H_2O layer was washed three times with Et_2O (3 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was then removed under reduced pressure to afford the secondary alcohol (R_F 0.23, 3:1 hexanes:ethyl acetate eluent). The secondary alcohol was then dissolved in CH_2Cl_2 (1.5 mL) and Dess Martin periodinane (143.9 mg, 0.339 mmol) was added to the resulting solution. Ketone **24** was immediately formed, so the reaction was quenched by the addition of a 1:1 solution of saturated $NaHCO_3$ (aq) and saturated $Na_2S_2O_3$ (aq) (2 mL). This mixture was extracted three times with CH_2Cl_2 (3 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The ketone was then purified by flash column chromatography (15:1 hexanes:ethyl acetate) to yield pure ketone **24** (47.6 mg, 0.190 mmol, 86% yield for two steps) with spectroscopic data identical to that observed for Bamford-Stevens/Claisen derived ketone. R_F 0.34 (3:1 hexanes:ethyl acetate eluent);

Aldehyde 26. Chemical correlation by conversion to a known ketone **SM26**.



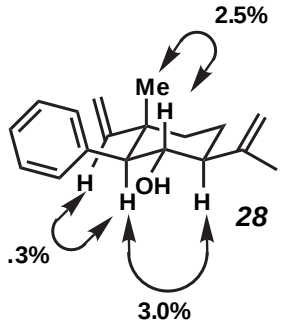
26 *SM26*

Ketone SM26. A flame-dried flask (15 mL) equipped with a magnetic stirbar was charged with aldehyde **26** (27.0 mg, 0.133 mmol) and Et_2O (1.5 mL). When this solution had been cooled to 0 °C, a solution of MeMgBr (3.0 *M* in THF, 60 µl, 0.180 mmol) was added *via* syringe. TLC analysis showed immediate reaction, and H_2O (4 mL) was added in order to quench the crude reaction mixture. Et_2O (3 mL) was then added and the layers were separated. The H_2O layer was washed three times with Et_2O (3 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was then removed under reduced pressure to afford the secondary alcohol (R_F 0.23, 9:1 hexanes:ethyl acetate eluent). The secondary alcohol was then dissolved in CH_2Cl_2 (1.5 mL) and Dess Martin

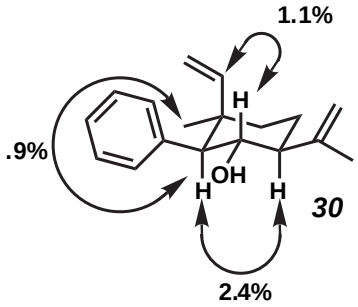
periodinane (143.9 mg, 0.339 mmol) was added to the resulting solution. Ketone **SM26** was immediately formed, and the reaction was quenched by the addition of a 1:1 solution of saturated aq $NaHCO_3$ and saturated aq $Na_2S_2O_3$ (2 mL). This mixture was extracted three times with CH_2Cl_2 (3 mL), the combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The ketone was then purified by flash column chromatography (15:1 hexanes:ethyl acetate) to yield pure compound **SM26** (19.5 mg, 0.090 mmol, 68% yield for two steps) as a colorless foam. The spectral data for this compound correspond to those reported previously for the *anti* product.[8] R_F 0.44 (2:1 hexanes:ethyl acetate eluent).

Table 2.

Alcohol 28. The stereochemistry was assigned based on the shown NOE interactions between the axial substituents.



Alcohol 30. The stereochemistry was assigned based on the shown NOE interactions between the axial substituents.



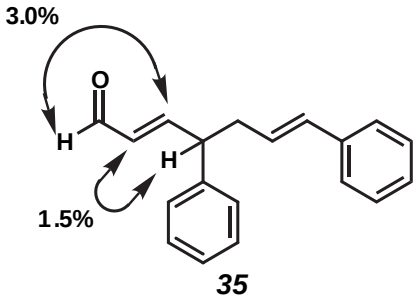
(8) Daub, G. W.; Sanchez, M. G.; Cromer, R. A.; Gibson, L. L. *J. Org. Chem.* 1982, **47**, 745

Alcohol 31. The stereochemistry was assigned by analogy to 20.

Alcohol 32. The stereochemistry was assigned by analogy to 28.

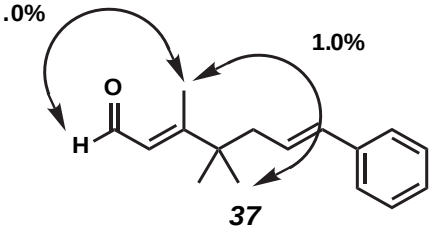
Alcohol 33. The stereochemistry was assigned by analogy to 30.

Aldehyde 35. The stereochemistry was assigned as the (*E*) stereochemistry based on the shown NOE interactions between the vinyl hydrogens and their respective *cis*-allylic hydrogens.



35

Aldehyde 37. The stereochemistry was assigned as the (*E*) stereochemistry based on the shown NOE interactions between the respective *cis*-allylic groups.



37