SUPPORTING INFORMATION FOR

Attempts to Improve the Overall Stereoselectivity of Ireland-Claisen Rearrangement

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CONTENTS:

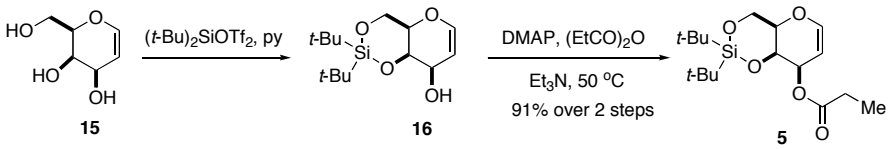
General Experimental Practices

Tetrahydrofuran, dimethylformamide, and toluene were dried according to the procedure described by Grubbs.[1] All solvents were determined to contain less than 50 ppm H_2O by Karl Fischer coulometric moisture analysis. Reagents are commercial grade and were used as supplied. Reactions involving air or moisture sensitive reagents or intermediates were performed under an inert atmosphere of nitrogen or argon in glassware that was flame dried. LHMDS was purchased from Sigma-Aldrich (225770-100mL), and it was used within two months when the bottle was opened (Good quality is significant important for silyl ketene acetal formation). Analytical thin layer chromatography (TLC) was performed with E. Merck precoated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. TLC plates were visualized by staining with AMCAN (ammonium molybdate/cerium ammonium nitrate), potassium permagnate, or *p*-anisaldehyde. Flash chromatography separations were performed on E. Merck kieselgel 60 (230-400) mesh silica gel. ^{1}H NMR spectra were recorded on a Varian Inova 600 or Varian Inova 500. Chemical shifts were reported in parts per million (ppm). The residual solvent peak was used as an internal reference. Coupling constants (*J*) are reported in Hz and the splitting abbreviations used are: s, singlet; d, doublet; t, triplet; app t, apparent triplet; q, quartet; m, multiplet; comp, complex multiplet; br, broad. ^{13}C NMR spectra were recorded at 125 MHz. Fast atom bombardment (FAB) mass spectra were obtained with 3-nitrobenzyl alcohol or glycerol as the matrix. Sodium iodide was added when indicated. Chemical ionization (CI) mass spectra were obtained with ammonia as the reagent gas. Electrospray ionization experiments were performed on Micromass Inc., Platform II Atmospheric Pressure Ionization Mass Spectrometer.

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

Experimental Details for the Synthesis Outlined in Scheme 5 and Scheme 6

(a) Preparation of Propionate 5:



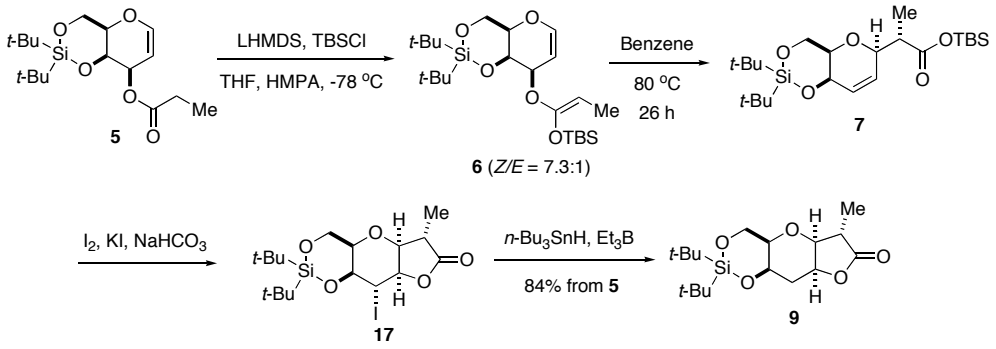
(4a*R*,8*R*,8a*R*)-2,2-Di-*tert*-butyl-4,4a,8,8a-tetrahydropyrano[3,2-*d*][1,3,2]dioxasilin-8-yl propionate (5). A solution of $(t\text{-Bu})_2SiOTf_2$ (26.7 mL, 73.2 mmol) in CH_2Cl_2 (133 mL) was added dropwise to a solution of D-galactal **15** (10.0 g, 68.4 mmol, from Carbosynth Limited in UK) in DMF (342 mL) at -45 °C over 40 min. After stirring at -45 °C for 1 h, freshly distilled pyridine (20.3 mL, 205 mmol) was added. The reaction was allowed to warm to 0 °C and stirred at 0 °C for 1 h. The mixture was quenched by addition of saturated $NaHCO_3$ (50 mL) and diluted with hexanes/EtOAc (5:1, 2.5 L). The organic layer was washed with brine (1 x 500 mL, 4 x 200 mL), dried ($MgSO_4$) and concentrated to give crude allylic alcohol **16** whose ^1H and ^{13}C NMR spectral data were consistent with those reported.[2]

A solution of crude alcohol **16**, propionic anhydride (21.9 mL, 171 mmol), and DMAP (835 mg, 6.8 mmol) in Et_3N (456 mL) was stirred at 50 °C for 13 h. The mixture was concentrated and then diluted with hexanes/EtOAc (10:1, 0.8 L). The organic layer was washed with water (4 x 100 mL) and brine (100 mL), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (40:1 to 10:1) to afford 21.2 g (91% over 2 steps from **15**) of propionate **5** as a white solid; mp 86 °C; $[\alpha]^{25}_D$ +117 (*c* 1.00, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$; see the spectrum on page S18) δ 6.41 (dd, *J* = 6.6, 1.8 Hz, 1 H), 5.26-5.23 (m, 1 H), 4.80 (d, *J* = 4.8 Hz, 1 H), 4.64 (dd, *J* = 6.6, 1.8 Hz, 1 H), 4.26 (dd, *J* = 13.0, 1.8 Hz, 1 H), 4.22 (dd, *J* = 13.0, 1.8 Hz, 1 H), 3.87 (br, 1 H), 2.37 (dq, *J* = 7.6, 1.8 Hz, 2 H),

[2] Abdel-Rahman, A. A.-H.; Winterfeld, G. A.; Takhi, M.; Schmidt, R. R. *Eur. J. Org. Chem.* **2002**, 713.

1.16 (t, J = 7.6 Hz, 3 H), 1.00 (s, 9 H), 0.99 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S19) δ 174.6, 145.9, 98.8, 73.3, 67.6, 67.5, 65.2, 28.0. 27.8, 27.2, 23.5, 21.1, 9.6; mass spectrum (ESI) m/z 365.1742 [$C_{17}H_{30}O_5SiNa$ (M+Na) requires 365.1760].

(b) Ireland-Claisen Rearrangement for One Day, and The Yield was Determined at Lactone Stage:



Iodolactone 17. A solution of LHMDS (91.5 mL of a 1.0 M solution in THF, 91.5 mmol) was added dropwise to a solution of TBSCl (15.9 g, 106 mmol) in THF (240 mL) and HMPA (fresh distilled, 120 mL) at -78 °C. Once addition was complete, the reaction mixture was stirred at -78 °C for 10 min, warmed to 0 °C and stirred at 0 °C for 10 min, and then cooled to -78 °C. A solution of propionate **5** (12.0 g, 35 mmol) in THF (60 mL) was added dropwise over 40 min. The mixture was stirred at -78 °C for 1 h, warmed to 0 °C over 30 min, and stirred at 0 °C for 20 min. The mixture was poured onto cold hexanes (-15 °C, 3 L). The organic layer was washed with water (5 x 600 mL) and brine (2 x 600 mL), dried (Na_2SO_4), and concentrated to afford silyl ketene acetal **6** (Z/E = 7.3:1, ^{1}H NMR, C_6D_6; see the spectrum on page S20).

A solution of silyl ketene acetal **6** in benzene (500 mL) was stirred at 80 °C for 26 h under nitrogen and then concentrated under reduce pressure. The residue was dried under vacuum for 18 h at room temperature to give crude carboxylate **7** together with propionate **5** and silyl ketene acetal *E*-**6** in a ca. 12% combined yield. Without purification, carboxylate **7** was submitted to iodolactonization condition.

Saturated sodium bicarbonate solution (350 mL) was added to a solution of carboxylate **7** in THF (700 mL), and the mixture was stirred at room temperature for 2 h. Potassium iodide (23.2 g, 140 mmol), iodine (35.4 g, 140 mmol), and sodium bicarbonate (11.8 g, 140 mmol) were added. The mixture was stirred for 69 h, quenched with saturated $Na_2S_2O_3$ (200 mL), and diluted with hexanes/EtOAc (1:1, 2 L). The organic layer was washed with brine (3 x 500 mL), dried (Na_2SO_4) and concentrated to give crude iodolactone **17**, which was subjected to the following reduction condition (*n*-Bu_3SnH, Et_3B) without purification. The crude iodolactone **17** can be purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (15:1 to 10:1) to afford a white solid; mp 143 °C; $[\alpha]^{25}_D$ -18.2 (*c* 0.61, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S22) δ 4.73 (s, 1 H), 4.68-4.64 (m, 1 H), 4.53-4.51 (m, 1 H), 4.32 (d, *J* = 2.4 Hz, 1 H), 4.24 (dd, *J* = 12.9, 2.4 Hz, 1 H), 4.21 (dd, *J* = 12.9, 1.2 Hz, 1 H), 3.99 (t, *J* = 3.0 Hz, 1 H), 2.75 (q, *J* = 8.2 Hz, 1 H), 1.26 (d, *J* = 8.2 Hz, 3 H), 1.01 (s, 9 H), 0.96 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S23) δ 177.7, 77.6, 76.7, 71.9, 69.3, 67.8, 44.2, 27.5, 27.0, 25.5, 23.3, 20.3, 12.4; mass spectrum (ESI) *m/z* 469.0884 [$C_{17}H_{30}IO_5Si$ (M+H) requires 469.0907].

Lactone 9. Triethylborane (1.75 mL, 1.0 M solution in hexanes, 1.75 mmol) was added to a solution of crude iodolactone **17** and *n*-Bu_3SnH (14 mL, 52.5 mmol) in toluene (233 mL) under nitrogen. The mixture was stirred for 1.5 h and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (4:1 to 1:1) to afford 10.1 g (84% from propionate **5**) of lactone **9** as a white solid; mp 102 °C; $[\alpha]^{25}_D$ -40.5 (*c* 0.95, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S24) δ 4.42-4.39 (m, 1 H), 4.31-4.29 (m, 1 H), 4.24 (dd, *J* = 12.3, 2.4 Hz, 1 H), 4.16 (dd, *J* = 12.3, 1.5 Hz, 1 H), 3.96 (d, *J* = 3.0 Hz, 1 H), 3.31-3.28 (m, 1 H), 2.73 (q, *J* = 7.9 Hz, 1 H), 2.58 (d, *J* = 15.9 Hz, 1 H), 1.94 (ddd, *J* = 15.9, 5.2, 4.2 Hz, 1 H), 1.27 (d, *J* = 7.9 Hz, 3 H), 1.02 (s, 9 H), 0.97 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S25) δ 178.7, 79.8, 73.8, 72.4, 67.6, 65.7, 44.1, 32.2, 27.5, 27.0, 23.2, 20.1, 12.6; mass spectrum (ESI) *m/z* 343.1933 [$C_{17}H_{31}O_5Si$ (M+H) requires 343.1941].

(c) Ireland-Claisen Rearrangement for Three Days:

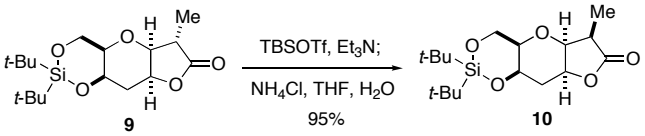
Iodolactone 17. A solution of LHMDS (38.0 mL of a 1.0 M solution in THF, 38.0 mmol) was added dropwise to a solution of TBSCl (6.60 g, 43.8 mmol) in THF (100 mL) and HMPA (fresh distilled, 50 mL) at -78 °C. Once addition was complete, the reaction mixture was stirred at -78 °C for 10 min, warmed to 0 °C and stirred at 0 °C for 10 min, and then cooled to -78 °C. A solution of propionate **5** (5.0 g, 14.6 mmol) in THF (25 mL) was added dropwise over 40 min. The mixture was stirred at -78 °C for 1 h, warmed to 0 °C over 30 min, and stirred at 0 °C for 30 min. The mixture was poured onto cold hexanes (-15 ºC, 1.5 L). The organic layer was washed with water (5 x 300 mL) and brine (2 x 300 mL), dried (Na_2SO_4), and concentrated to afford silyl ketene acetal **6** (*Z*/*E* = 6.5:1, ^{1}H NMR, C_6D_6).

A solution of silyl ketene acetal **6** in benzene (210 mL) was stirred at 80 °C for 72 h under nitrogen and then concentrated under reduce pressure. The residue was dried under vacuum for 14 h at room temperature to give crude carboxylate **7** together with 2% propionate **5** (All silyl ketene acetals were consumed; For ^{1}H NMR, see the spectrum on page S21). Without purification, carboxylate **7** was submitted to iodolactonization condition.

Saturated sodium bicarbonate solution (73 mL) was added to a solution of carboxylate **7** in THF (146 mL), and the mixture was stirred at room temperature for 2 h. Potassium iodide (9.70 g, 58.4 mmol), iodine (14.8 g, 58.4 mmol), and sodium bicarbonate (4.90 g, 58.4 mmol) were added. The mixture was stirred for 72 h, quenched with saturated $Na_2S_2O_3$ (90 mL), and diluted with hexanes/EtOAc (1:1, 1 L). The organic layer was washed with brine (3 x 200 mL), dried (Na_2SO_4) and concentrated to give crude iodolactone **17**, which was subjected to the following reduction condition (*n*-Bu_3SnH, Et_3B) without purification.

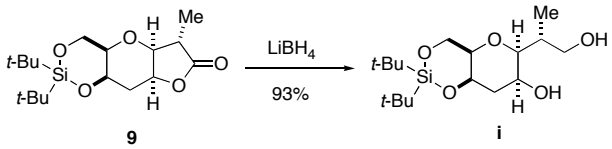
Lactone 9. Triethylborane (0.73 mL, 1.0 M solution in hexanes, 0.73 mmol) was added to a solution of crude iodolactone **17** and *n*-Bu_3SnH (5.87 mL, 21.9 mmol) in toluene (97 mL) under nitrogen. The mixture was stirred for 1.5 h and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (4:1 to 1:1) to afford 4.72 g (94% from propionate **5**) of lactone **9** as a white solid.

(d) Epimerization of Lactone 9:



Epimer 10. TBSOTf (805 μL, 3.50 mmol) was added dropwise to a solution of lactone **9** (100 mg, 0.29 mmol) and Et_3N (813 μL, 5.84 mmol) in CH_2Cl_2 (4.1 mL) at 0 °C. The mixture was stirred at room temperature for 2 h, diluted with EtOAc (30 mL), washed with $NaHCO_3$ (3 x 5 mL), dried (Na_2SO_4) and concentrated. The residue was dissolved in THF/H_2O/NH_4Cl(sat, aq) (10:1:1, 6 mL). The mixture was stirred at 50 °C for 14 h, and then diluted with EtOAc (30 mL). The organic layer was washed with brine (2 x 4 mL), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (4:1 to 1:1) to afford 95 mg (95%) of lactone **10** as a white solid; mp 146 °C; $[\alpha]^{25}_D$ -24.1 (*c* 0.75, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S26) δ 4.30 (ddd, *J* = 4.8, 2.4, 1.8 Hz, 1 H), 4.27 (dd, *J* = 12.3, 2.7 Hz, 1 H), 4.23-4.21 (m, 1 H), 4.19 (dd, *J* = 12.3, 1.8 Hz, 1 H), 4.13 (dd, *J* = 4.2, 2.7 Hz, 1 H), 3.30-3.28 (m, 1 H), 2.70 (dq, *J* = 7.2, 4.8 Hz, 1 H), 2.57 (dt, *J* = 15.6, 1.8 Hz, 1 H), 1.94 (ddd, *J* = 15.6, 4.8, 4.2 Hz, 1 H), 1.28 (d, *J* = 7.2 Hz, 3 H), 1.01 (s, 9 H), 0.96 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S27) δ 177.9, 76.4, 74.1, 72.7, 67.7, 65.7, 42.2, 32.6, 27.7, 27.1, 23.3, 20.2, 7.8; mass spectrum (ESI) *m/z* 343.1945 [$C_{17}H_{31}O_5Si$ (M+H) requires 343.1941].

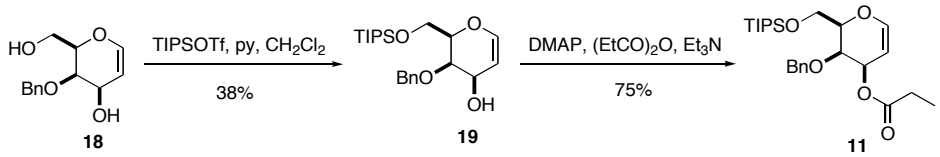
(e) Reduction of Lactone 9 to Diol i:



(4a*R*,6*S*,7*S*,8a*R*)-2,2-di-*tert*-butyl-hexahydro-6-((*R*)-1-hydroxypropan-2-yl)pyrano[3,2-*d*][1,3,2]dioxasilin-7-ol (i). Lithium borohydride (1.40 g, 64.3 mmol) was added slowly to a solution of lactone **9** (2.20 g, 6.42 mmol) in THF (64 mL) at 0 °C. After stirring for 2 h, methanol (0.64 mL) was added. The mixture was stirred at 0 °C for 12 h and then room temperature for another 12 h. The reaction was quenched at 0 °C by carefully addition of EtOAc (20 mL), followed by saturated sodium bicarbonate (40 mL). The mixture was stirred at 0 °C until all bubbles disappeared. Hexanes (60 mL) was added, and organic layer was separated. The aqueous layer was extracted with hexanes/Et_2O (1:1, 4 x 80 mL). All organic layers were combined, dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (4:1 to 1:1) to afford 2.08 g (93%) of diol **i** as a white solid; mp 143 °C; $[\alpha]^{25}_D$ +2.9 (*c* 0.48, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S28) δ 4.43 (t, *J* = 3.0 Hz, 1 H), 4.26 (dd, *J* = 12.6, 3.0 Hz, 1 H), 4.20 (d, *J* = 12.6 Hz, 1 H), 4.07 (d, *J* = 10.2 Hz, 1 H), 3.85-3.81 (m, 1 H), 3.76 (ddd, *J* = 11.4, 5.1, 2.7 Hz, 1 H), 3.50 (dt, *J* = 11.4, 6.3 Hz, 1 H), 3.38-3.36 (m, 1 H), 3.22 (d, *J* = 7.2 Hz, 1 H), 3.00 (dd, *J* = 6.3, 5.1 Hz, 1 H), 2.32 (dt, *J* = 14.7, 3.0 Hz, 1 H), 2.09 (dq, *J* = 6.8, 2.7 Hz, 1 H), 1.77 (dt, *J* = 14.7, 3.0 Hz, 1 H), 1.06 (d, *J* = 6.8 Hz, 3 H), 1.04 (s, 9 H), 1.03 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S29) δ 84.0, 76.9, 69.3, 68.6, 64.4, 63.5, 37.9, 36.6, 27.7, 27.1, 23.1, 20.2, 13.9; mass spectrum (ESI) *m/z* 369.2072 [$C_{17}H_{34}O_5SiNa$ (M+Na) requires 369.2073]. (For X-ray analysis, see the attached cif file.)

Experimental Details for the Synthesis Outlined in Scheme 7

(a) Synthesis of Propionate 11:



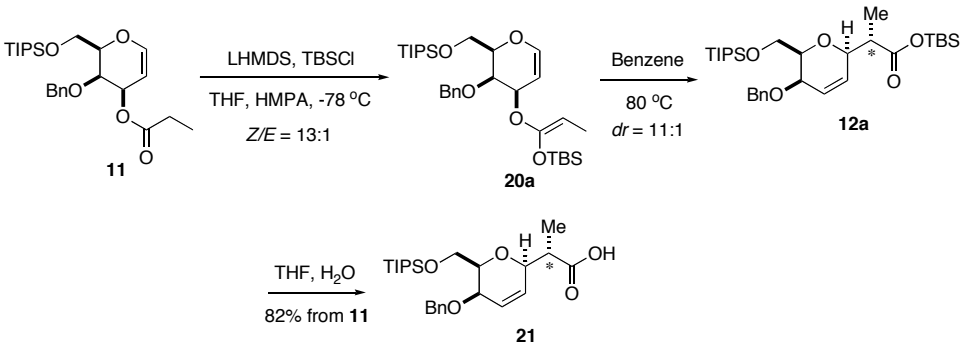
Alcohol 19. TIPSOTf (0.84 mL, 3.14 mmol) was added to a solution of diol **18**[3] (730 mg, 3.14 mmol) and pyridine (0.76 mL, 9.42 mmol) in CH_2Cl_2 (16 mL) at -50 ºC. The reaction was slowly warm up to 0 ºC over 90 min, and then stirred at 0 ºC for 1 h. A solution of EtOAc (30 mL) and hexanes (30 mL) was added. The organic layer was washed with H_2O (15 mL), $NaHCO_3$ (15 mL) and brine (15 mL), dried (Na_2SO_4), and concentrated. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (40:1 to 10:1) to afford 463 mg (38%) of alcohol **19** as a colorless oil; $[\alpha]^{25}_D$ -7.8 (*c* 0.49, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S30) δ 7.37-7.27 (comp, 5 H), 6.30 (dd, *J* = 6.0, 1.2 Hz, 1 H), 4.81 (d, *J* = 11.7 Hz, 1 H), 4.74 (d, *J* = 11.7 Hz, 1 H), 4.69 (ddd, *J* = 6.0, 2.7, 1.2 Hz, 1 H), 4.35-4.31 (m, 1 H), 4.02-3.98 (comp, 2 H), 3.96 (dd, *J* = 10.2, 5.4 Hz, 1 H), 3.89 (dd, *J* = 10.2, 7.2 Hz, 1 H), 2.44 (d, *J* = 10.2 Hz, 1 H), 1.16-1.03 (comp, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S31) δ 144.2, 138.0, 128.6, 128.0, 127.9, 103.2, 76.7, 74.5, 72.6, 63.0, 61.3, 18.0, 11.9; mass spectrum (ESI) *m/z* 415.2264 [$C_{22}H_{36}O_4SiNa$ (M+Na) requires 415.2281].

Propionate 11. A solution of alcohol **19** (463 mg, 1.18 mmol), propionic anhydride (0.38 mL, 2.95 mmol), DMAP (58 mg, 0.47 mmol) in Et_3N (11.8 mL) was stirred at 50 ºC for 12 h. The mixture was concentrated and diluted with EtOAc (50 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (40:1 to 30:1) to afford 395 mg (75%) of propionate **11** as a colorless oil; $[\alpha]^{25}_D$ -25.1 (*c* 0.62, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S32) δ 7.34-7.23 (comp, 5 H), 6.39 (dd, *J* = 6.0, 1.8 Hz, 1 H), 5.49 (ddd, *J* = 6.0, 3.0, 1.2 Hz, 1 H), 4.74 (d, *J* = 11.7 Hz, 1 H), 4.71 (ddd, *J* = 6.0, 3.0, 0.9 Hz, 1 H), 4.59 (d, *J* = 11.7 Hz, 1 H), 4.10 (t, *J* = 6.0 Hz, 1 H), 4.08-4.05 (m, 1 H), 3.94 (dd, *J* = 10.8, 4.8 Hz, 1 H), 3.87 (dd, *J* = 10.8, 6.0 Hz, 1 H), 2.35-2.22 (m, 2 H), 1.11 (t, *J* = 7.8 Hz, 3 H), 1.09-1.02 (comp, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S33) δ

[3] Aicher, T. D.; Buszek, K. R.; Fang, F. G.; Forsyth, C. J.; Jung, S. H.; Kishi, Y.; Scola, P. M. *Tetrahedron Lett*. **1992**, *33*, 1549.

174.1, 145.5, 138.1, 128.3, 127.8, 127.7, 98.7, 77.4, 73.7, 70.7, 65.5, 61.0, 27.7, 17.9, 11.9, 9.0; mass spectrum (ESI) *m/z* 471.2565 [$C_{25}H_{40}O_5SiNa$ (M+Na) requires 471.2543].

(b) Ireland-Claisen Rearrangement of TBS Silyl Ketene Acetal 20a and Characterization at Acid 21:



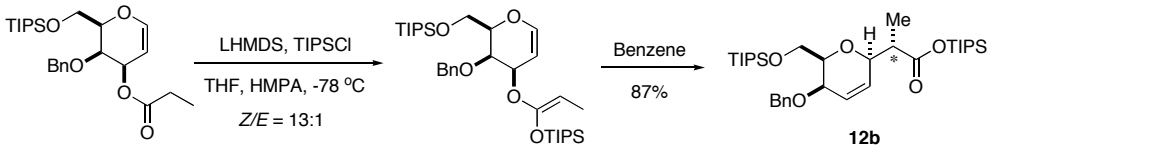
Acid 21. A solution of LHMDS (0.10 mL of a 1.0 M solution in THF, 0.10 mmol) was added dropwise to a solution of TBSCl (17 mg, 113 μmol) in THF (0.66 mL) and HMPA (fresh distilled, 0.33 mL) at -78 °C. Once addition was complete, the reaction mixture was stirred at -78 °C for 5 min, warmed to 0 °C and stirred at 0 °C for 5 min, and then cooled to -78 °C. A solution of propionate **11** (17 mg, 38 μmol) in THF (0.2 mL) was added dropwise over 2 min. The mixture was stirred at -78 °C for 45 min, warmed to 0 °C, and stirred at 0 °C for 15 min. The mixture was poured onto hexanes (15 mL). The organic layer was washed with water (4 x 2 mL) and brine (2 mL), dried (Na_2SO_4), and concentrated to afford silyl ketene acetal **20a** (*Z*/*E* = 13:1, ^{1}H NMR, C_6D_6; see the spectrum on page S34).

A solution of silyl ketene acetal **20a** in benzene (1 mL) was stirred at 80 °C for 16 h under nitrogen and then concentrated under reduce pressure. The residue was dried under vacuum for 2 h at room temperature to give crude carboxylate **12a** (*dr* = 11:1, ^{1}H NMR, C_6D_6; see the spectrum on page S35), in which TBS group tended to fall off during flash chromatography on silica gel.

For compound characterization, TBS group was removed to give acid **21**. H_2O (0.5 mL) was added to a solution of crude carboxylate **12a** in THF (5 mL) at room temperature, and the reaction was stirred for 14 h. The mixture was concentrated under

reduced pressure. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (4:1 to 1:1) to afford 14 mg (82%) of **21** as a colorless oil; $[\alpha]^{25}_{D}$ -77.5 (*c* 0.67, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S36) δ 7.32-7.23 (comp, 5 H), 6.14 (ddd, *J* = 10.5, 5.4, 1.8 Hz, 1 H), 5.92 (d, *J* = 10.5 Hz, 1 H), 4.66 (d, *J* = 12.0 Hz, 1 H), 4.53 (d, *J* = 12.0 Hz, 1 H), 4.38 (app d, *J* = 2.4 Hz, 1 H), 3.94 (dd, *J* = 10.2, 6.3 Hz, 1 H), 3.88 (dd, *J* = 10.2, 5.4 Hz, 1 H), 3.87-3.83 (m, 1 H), 3.69 (t, *J* = 6.0 Hz, 1 H), 2.82-2.75 (m, 1 H), 1.25 (d, *J* = 7.2 Hz, 3 H), 1.16-0.97 (comp, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S37) δ 175.1, 138.5, 130.4, 128.3, 127.7, 127.6, 127.1, 79.2, 76.2, 70.7, 67.3, 62.5, 43.4, 18.0, 12.2, 12.0, 11.9; mass spectrum (ESI) *m/z* 471.2550 [$C_{25}H_{40}O_5SiNa$ (M+Na) requires 471.2543].

(c) General Procedure of Ireland-Claisen Rearrangement of TIPS Silyl Ketene Acetal 20b:



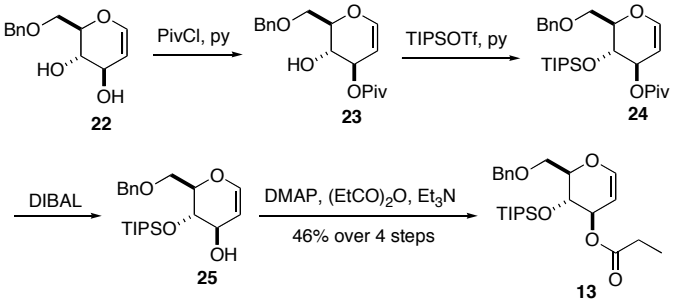
(1) 80 °C, 1 days: *dr* = 14 : 1, no SKA left
(2) 40 °C, 1 day: SKA: P = 45% (*Z/E* = 8:1): 55% (*dr* = 30:1)
40 °C, 2 day: SKA: P = 20% (*Z/E* = 5:1): 80% (*dr* = 23:1)
40 °C, 4 day: SKA: P = 4% (*Z/E* = 2:1): 96% (*dr* = 19:1)

A solution of LHMDS (0.10 mL of a 1.0 M solution in THF, 0.10 mmol) was added dropwise to a solution of TIPSCl (24 μL, 113 μmol) in THF (0.66 mL) and HMPA (fresh distilled, 0.33 mL) at -78 °C. Once addition was complete, the reaction mixture was stirred at -78 °C for 5 min, warmed to 0 °C and stirred at 0 °C for 5 min, and then cooled to -78 °C. A solution of propionate **11** (17 mg, 38 μmol) in THF (0.2 mL) was added dropwise over 2 min. The mixture was stirred at -78 °C for 45 min, warmed to 0 °C, and stirred at 0 °C for 25 min. The mixture was poured onto hexanes (15 mL). The organic layer was washed with water (5 x 3 mL) and brine (3 mL), dried (Na_2SO_4), and concentrated to afford silyl ketene acetal **20b** (*Z/E* = 13:1, ^{1}H NMR, C_6D_6; see the spectrum on page S38).

A solution of silyl ketene acetal **20b** in C_6D_6 (2 mL) was stirred at 40 °C for 4 days under nitrogen and then concentrated under the reduced pressure. The *dr* of crude carboxylate **12b** was 19:1 (^{1}H NMR, C_6D_6; see the spectrum on page S39), and 4% of silyl ketene acetal **20b** (*Z*/*E* = 2:1, ^{1}H NMR) remained in the mixture. Carboxylate **12b** can be purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (40:1 to 10:1) to afford 20 mg (87% from **11**) of carboxylate **12b** as a colorless oil; $[\alpha]^{25}_{D}$ -78.6 (*c* 1.10, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S40) δ 7.34-7.22 (comp, 5 H), 6.00 (ddd, *J* = 10.2, 5.4, 2.4 Hz, 1 H), 5.89 (dd, *J* = 10.2, 1.2 Hz, 1 H), 4.65 (d, *J* = 12.0 Hz, 1 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 4.44-4.40 (m, 1 H), 3.98 (dd, *J* = 9.6, 8.4 Hz, 1 H), 3.86 (app dt, *J* = 2.4, 2.4 Hz, 1 H), 3.76 (dd, *J* = 9.6, 5.4 Hz, 1 H), 3.62-3.57 (m, 1 H), 2.58 (dq, *J* = 6.8, 1.2 Hz, 1 H), 1.32-1.26 (comp, 3 H), 1.21 (d, *J* = 6.8 Hz, 3 H), 1.10-1.01 (comp, 39 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S41) δ 174.0, 139.3, 133.1, 128.2, 127.6, 127.3, 125.9, 78.4, 76.1, 70.9, 67.6, 62.1, 45.5, 18.0, 18.0, 17.8, 12.0, 11.9; mass spectrum (ESI) *m*/*z* 627.3888 [$C_{34}H_{60}O_5Si_2Na$ (M+Na) requires 627.3877].

Experimental details for the synthesis outlined in Scheme 8

(a) Synthesis of Propionate 13:



Glucal 23. PivCl (0.52 mL, 3.38 mmol) was added to a solution of diol **22**[4] (400 mg, 1.69 mmol), DMAP (4.1 mg, 0.34 mmol) and pyridine (1.10 mL, 13.5 mmol) in DCM (11.3 mL), and the reaction was stirred at room temperature for 15 h. The mixture

[4] Bussolo, V. D.; Caselli, M.; Pineschi, M.; Crotti, P. *Org. Lett.* **2003**, *5*, 2173.

was diluted with EtOAc (50 mL). The organic layer was washed with saturated sodium carbonate (2 x 10 mL), water (10 mL) and brine (10 mL), dried (Na_2SO_4), and concentrated. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (10:1 to 7:1) to afford 343 mg (63%) of glucal **23** as a colorless oil; $[\alpha]^{25}_D$ +1.5 (*c* 0.64, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$; see the spectrum on page S42) δ 7.36-7.25 (comp, 5 H), 6.45 (dd, *J* = 6.2, 1.5 Hz, 1 H), 5.20 (dt, *J* = 6.0, 2.0 Hz, 1 H), 4.66 (dd, *J* = 6.2, 2.5 Hz, 1 H), 4.62 (d, *J* = 7.2 Hz, 1 H), 4.58 (d, *J* = 7.2 Hz, 1 H), 4.00-3.95 (m, 1 H), 3.92 (ddd, *J* = 9.0, 6.0, 3.0 Hz, 1 H), 3.82-3.77 (comp, 2 H), 3.34 (d, *J* = 3.0 Hz, 1 H), 1.19 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S43) δ 180.0, 146.1, 137.7, 128.4, 127.7, 127.7, 98.9, 77.3, 73.6, 73.0, 68.7, 68.1, 38.8, 27.0; mass spectrum (ESI) *m/z* 343.1530 [$C_{18}H_{24}O_5Na$ (M+Na) requires 343.1521].

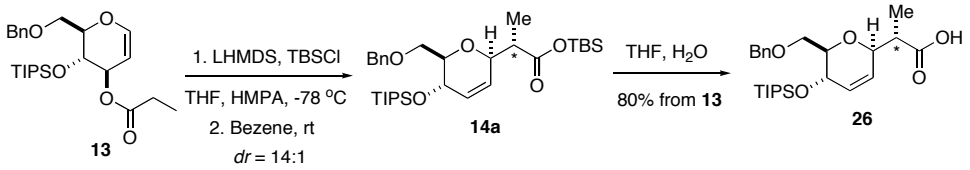
Glucal 24. TIPSOTf (0.56 mL, 2.14 mmol) was added to a solution of glucal **23** (343 mg, 1.07 mmol) and pyridine (1.04 mL, 12.8 mmol) in DCM (10.7 mL), and the reaction was stirred at room temperature for 6 h. The mixture was diluted with hexanes/EtOAc (4:1, 40 mL). The organic layer was washed with saturated sodium carbonate (2 x 10 mL), water (10 mL) and brine (10 mL), dried (Na_2SO_4), and concentrated. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (40:1 to 10:1) to afford 510 mg (100%) of glucal **24** as a colorless oil; $[\alpha]^{25}_D$ -52.9 (*c* 0.64, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S44) δ 7.34-7.24 (comp, 5 H), 6.44 (d, *J* = 5.7 Hz, 1 H), 4.97 (app t, *J* = 3.9 Hz, 1 H), 4.77 (ddd, *J* = 5.7, 4.8, 1.2 Hz, 1 H), 4.59 (d, *J* = 6.0 Hz, 1 H), 4.53 (d, *J* = 6.0 Hz, 1 H), 4.27-4.23 (m, 1 H), 4.07 (dt, *J* = 4.2, 1.2 Hz, 1 H), 3.74 (dd, *J* = 10.2, 7.5 Hz, 1 H), 3.59 (dd, *J* = 10.2, 3.9 Hz, 1 H), 1.12 (s, 9 H), 1.08-1.00 (comp, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S45) δ 177.6, 145.5, 137.9, 128.4, 127.7, 127.7, 97.2, 78.0, 73.4, 68.6, 68.0, 67.5, 38.7, 27.1, 26.5, 18.0, 12.5; mass spectrum (ESI) *m/z* 499.2862 [$C_{27}H_{44}O_5SiNa$ (M+Na) requires 499.2856].

Alcohol 25. A solution of DIBAL (3.75 mL of a 1.0 M solution in hexanes, 3.75 mmol) was added dropwise to a solution of glucal **24** (510 mg, 1.07 mmol) in CH_2Cl_2 (11 mL) at -78 ºC over 4 min. Once the addition was complete, the reaction was stirred at -78 ºC for 40 min and then quenched with saturated sodium potassium tartrate solution (4 mL). The mixture was stirred at room temperature for 2 h and then diluted with

hexanes/EtOAc (1:1, 30 mL). The organic layer was washed with brine (5 x 3 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (15:1 to 7:1) to afford 352 mg (84%) of **25** as a colorless oil; $[\alpha]^{25}_D$ +13.2 (*c* 0.64, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S46) δ 7.34-7.25 (comp, 5 H), 6.41 (dd, *J* = 6.0, 1.2 Hz, 1 H), 4.74 (ddd, *J* = 6.0, 3.6, 0.6 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 4.54 (d, *J* = 12.0 Hz, 1 H), 4.06-4.01 (comp, 2 H), 3.93 (dd, *J* = 6.0, 4.8 Hz, 1 H), 3.78 (dd, *J* = 10.2, 3.0 Hz, 1 H), 3.73 (dd, *J* = 10.2, 5.4 Hz, 1 H), 2.12 (d, *J* = 1.2 Hz, 1 H), 1.13-1.00 (comp, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S47) δ 144.4, 137.6, 128.4, 127.8, 127.7, 101.8, 78.0, 73.6, 71.9, 69.5, 68.1, 18.1, 12.6; mass spectrum (ESI) *m/z* 415.2268 [$C_{22}H_{36}O_4SiNa$ (M+Na) requires 415.2281].

Propionate 13. A solution of alcohol **25** (352 mg, 0.90 mmol), propionic anhydride (0.29 mL, 2.24 mmol), DMAP (11 mg, 0.09 mmol) in Et_3N (9 mL) was stirred at 50 ºC for 2 h. The mixture was concentrated and then diluted with hexanes/EtOAc (3:1, 30 mL). The organic layer was washed with saturated sodium bicarbonate solution (10 mL), water (2 x 10 mL) and brine (10 mL), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (80:1 to 40:1) to afford 350 mg (87%) of propionate **13** as a colorless oil; $[\alpha]^{25}_D$ -45.7 (*c* 0.64, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S48) δ 7.34-7.24 (comp, 5 H), 6.42 (dd, *J* = 6.3, 0.6 Hz, 1 H), 5.08 (dt, *J* = 3.6, 1.2 Hz, 1 H), 4.76 (dd, *J* = 6.3, 3.6 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 4.52 (d, *J* = 12.0 Hz, 1 H), 4.16-4.10 (comp, 2 H), 3.74 (dd, *J* = 10.5, 6.0 Hz, 1 H), 3.70 (dd, *J* = 10.5, 3.6 Hz, 1 H), 2.31-2.20 (m, 2 H), 1.08 (t, *J* = 7.8 Hz, 3 H), 1.07-0.98 (comp, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S49) δ 173.7, 145.5, 137.8, 128.3, 127.6, 127.6, 98.0, 78.0, 73.4, 70.9, 68.2, 67.5, 27.7, 18.0, 17.9, 12.6, 8.9; mass spectrum (ESI) *m/z* 471.2553 [$C_{25}H_{40}O_5SiNa$ (M+Na) requires 471.2543].

(b) Ireland-Claisen Rearrangement of TBS Silyl Ketene Acetal and Characterization at Acid 26:



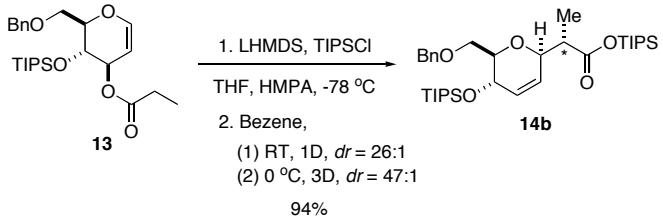
Acid 26. A solution of LHMDS (87 μL of a 1.0 M solution in THF, 87 μmol) was added dropwise to a solution of TBSCl (15 mg, 0.10 mmol) in THF (0.66 mL) and HMPA (fresh distilled, 0.33 mL) at -78 °C. Once addition was complete, the reaction mixture was stirred at -78 °C for 10 min, warmed to 0 °C and stirred at 0 °C for 5 min, and then cooled to -78 °C. A solution of propionate **13** (15 mg, 33 μmol) in THF (0.2 mL) was added dropwise over 2 min. The mixture was stirred at -78 °C for 40 min, warmed to 0 °C, and stirred at 0 °C for 15 min. The mixture was poured onto hexanes (15 mL). The organic layer was washed with water (5 x 3 mL) and brine (3 mL), dried (Na_2SO_4), and concentrated (The *Z*/*E* ratio was not reliably estimated since the Ireland-Claisen rearrangement occurred at RT).

The residue in benzene (2 mL) was stirred at room temperature for 24 h under nitrogen and then concentrated under reduce pressure. The residue was dried under vacuum for 2 h at room temperature to give crude carboxylate **14a** (*dr* = 14:1, ^{1}H NMR, C_6D_6; see the spectrum on page S50), in which TBS group tended to fall off during flash chromatography on silica gel.

For compound characterization, TBS group was removed to give acid **26**. H_2O (0.5 mL) was added to a solution of crude carboxylate **14a** in THF (5 mL) at room temperature, and the reaction was stirred for 24 h. The mixture was concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with hexanes/EtOAc (5:1 to 1:1) to afford 12 mg (80%) of **26** as a colorless oil; $[\alpha]^{25}_D$ +95.1 (*c* 0.67, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S51) δ 7.35-7.22 (comp, 5 H), 5.91 (d, *J* = 10.5 Hz, 1 H), 5.67 (d, *J* = 10.5 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 4.53 (d, *J* = 12.0 Hz, 1 H), 4.46-4.40 (comp, 2 H), 3.75 (dd, *J* = 10.3, 1.8 Hz, 1 H), 3.69 (dd, *J* = 10.3, 5.1 Hz, 1 H), 3.58-3.52 (m, 1 H), 2.73 (dq, *J* = 6.6, 2.4 Hz, 1 H), 1.19 (d, *J* = 6.6 Hz, 3 H), 1.04-0.98 (comp, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S52) δ 175.0, 138.1, 132.6, 128.4, 127.6, 127.6, 125.4, 79.3, 75.2, 73.3,

69.0, 63.9, 43.6, 18.1, 18.0, 12.6, 11.6; mass spectrum (ESI) *m/z* 471.2533 [$C_{25}H_{40}O_5SiNa$ (M+Na) requires 471.2543].

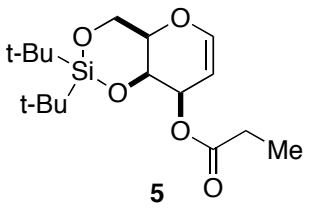
(c) General Procedure of Ireland-Claisen Rearrangement of TIPS Silyl Ketene Acetal:



Carboxylate 14b. A solution of LHMDS (580 μL of a 1.0 M solution in THF, 0.58 mmol) was added dropwise to a solution of TIPSCl (143 μg, 0.67 mmol) in THF (4.4 mL) and HMPA (fresh distilled, 2.2 mL) at -78 °C. Once addition was complete, the reaction mixture was stirred at -78 °C for 5 min, warmed to 0 °C and stirred at 0 °C for 5 min, and cooled to -78 °C. A solution of propionate **13** (100 mg, 0.22 mmol) in THF (1.3 mL) was added dropwise over 10 min. The mixture was stirred at -78 °C for 45 min, warmed to 0 °C over 30 min, and stirred at 0 °C for 25 min. The mixture was poured onto hexanes (80 mL, -10 °C). The organic layer was washed with cold water (5 x 20 mL, 0 °C) and brine (30 mL, 0 °C) (The *Z*/*E* ratio was not reliably estimated since the Ireland-Claisen rearrangement occurred slowly at 0 °C).

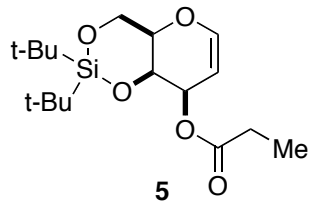
The mixture was stored at 0 °C for 3 days, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was dried under vacuum for 2 h at room temperature to give crude carboxylate **14b** (*dr* = 43:1, ^{1}H NMR, C_6D_6; see the spectrum on page S53), which was purified by flash chromatography on silica gel, eluting with hexanes/EtOAc (40:1 to 10:1) to afford 123 mg (91% from **13**) of carboxylate **14b** as a colorless oil; $[\alpha]^{25}_D$ +63.2 (*c* 1.01, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$; see the spectrum on page S54) δ 7.33-7.22 (comp, 5 H), 5.82 (dt, *J* = 10.5, 2.4 Hz, 1 H), 5.69 (dt, *J* = 10.5, 1.8 Hz, 1 H), 4.59 (d, *J* = 12.0 Hz, 1 H), 4.55 (d, *J* = 12.0 Hz, 1 H), 4.77-4.44 (m, 1 H), 4.35-4.31 (m, 1 H), 3.71 (dd, *J* = 11.1, 1.8 Hz, 1 H), 3.65 (dd, *J* = 11.1, 5.4 Hz, 1 H), 3.46 (dq, *J* = 5.4, 1.8 Hz, 1 H), 2.57 (dq, *J* = 7.2, 1.2 Hz, 1 H), 1.31-1.25 (comp, 3 H), 1.19 (d, *J* = 7.2 Hz, 3

H), 1.08-0.98 (comp, 39 H); ^{13}C NMR (125 MHz, $CDCl_3$; see the spectrum on page S55) δ 173.9, 138.7, 131.2, 128.7, 128.2, 127.6, 127.3, 79.8, 75.7, 73.4, 69.8, 64.5, 45.9, 18.1, 18.1, 17.9, 17.8, 12.7, 12.1, 11.9; mass spectrum (ESI) *m/z* 627.3891 [$C_{34}H_{60}O_5Si_2Na$ (M+Na) requires 627.3877].



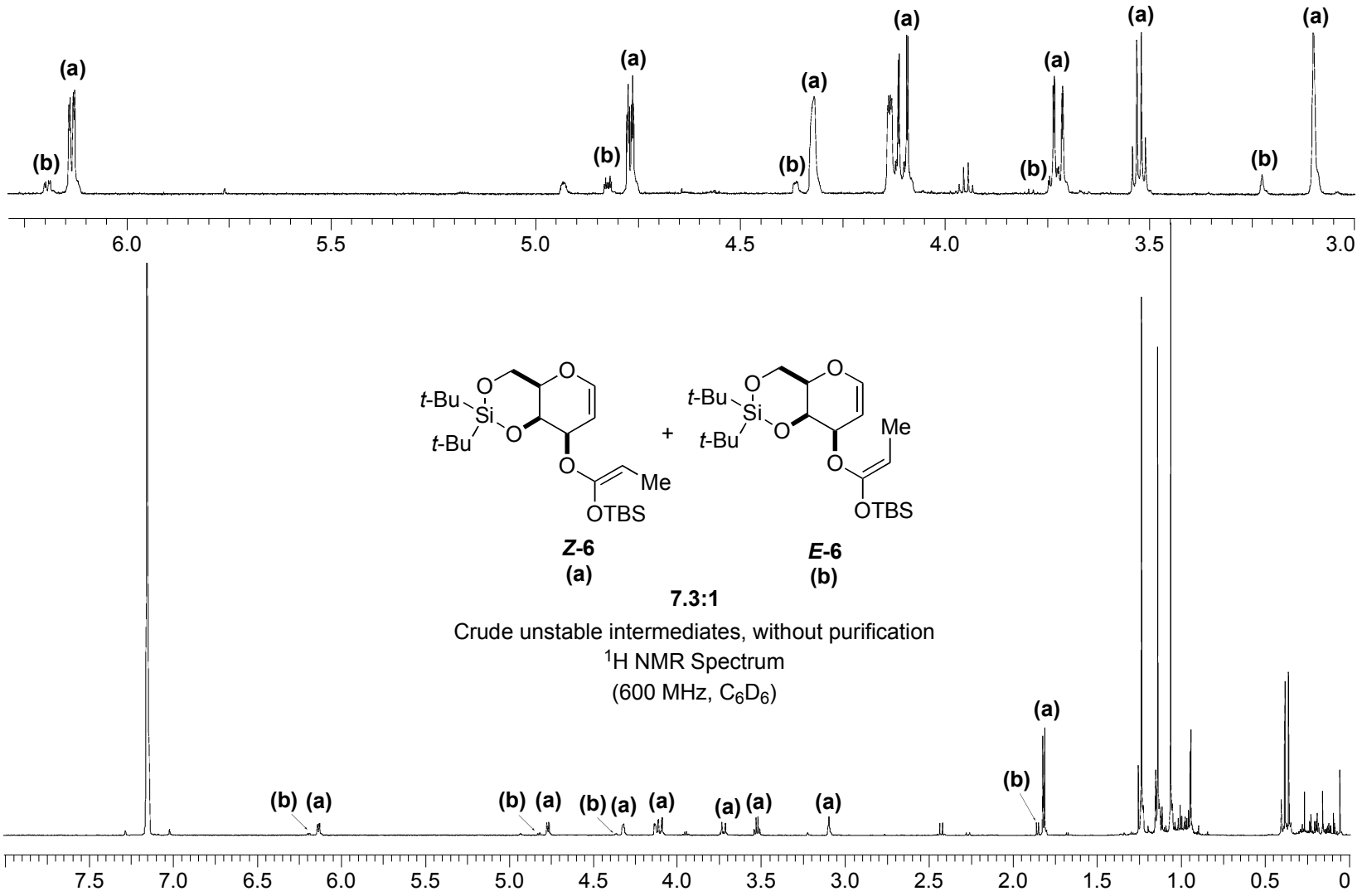
5

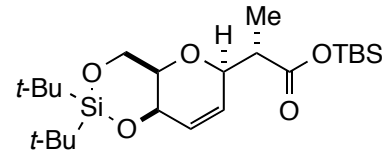
^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



5

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)


(a)
(b)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
t-Bu
Si
O
t-Bu
Me
OTBS
+
Z-6
(a)
E-6
(b)
7.3:1
Crude unstable intermediates, without purification
1H NMR Spectrum
(600 MHz, C6D6)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

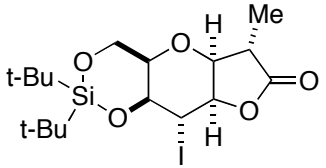


7

Crude material, without purification

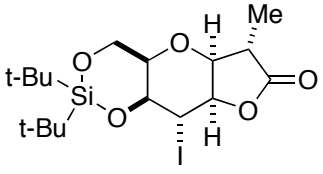
^{1}H NMR Spectrum

(600 MHz, C_6D_6)



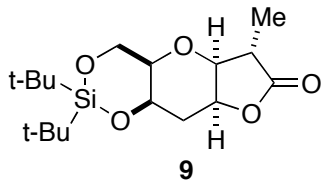
17

^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



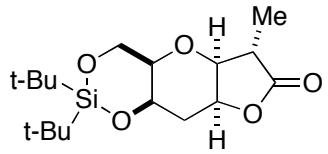
17

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



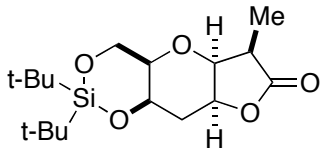
9

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



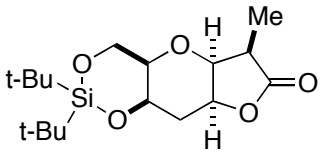
9

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



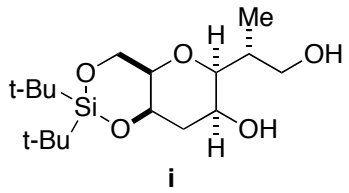
10

^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



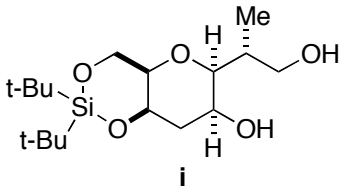
10

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



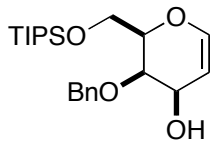
i

^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



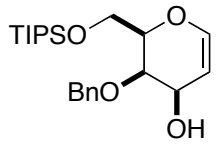
i

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



19

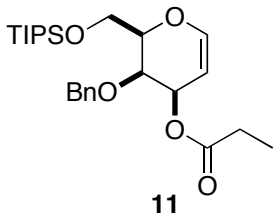
^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



19

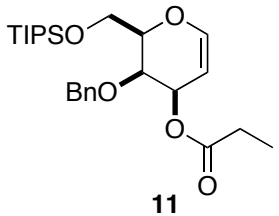
^{13}C NMR Spectrum

(125 MHz, $CDCl_3$)



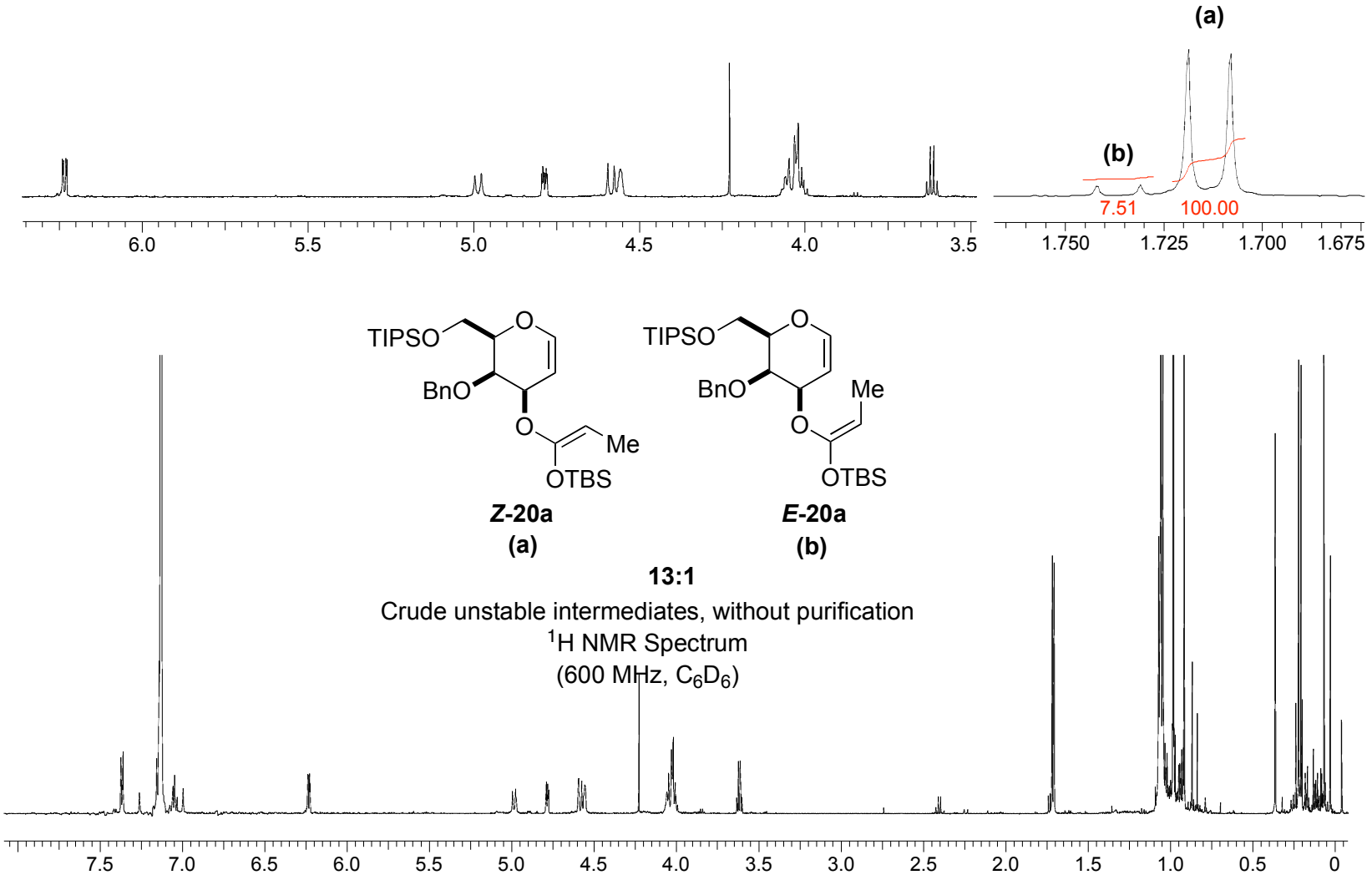
11

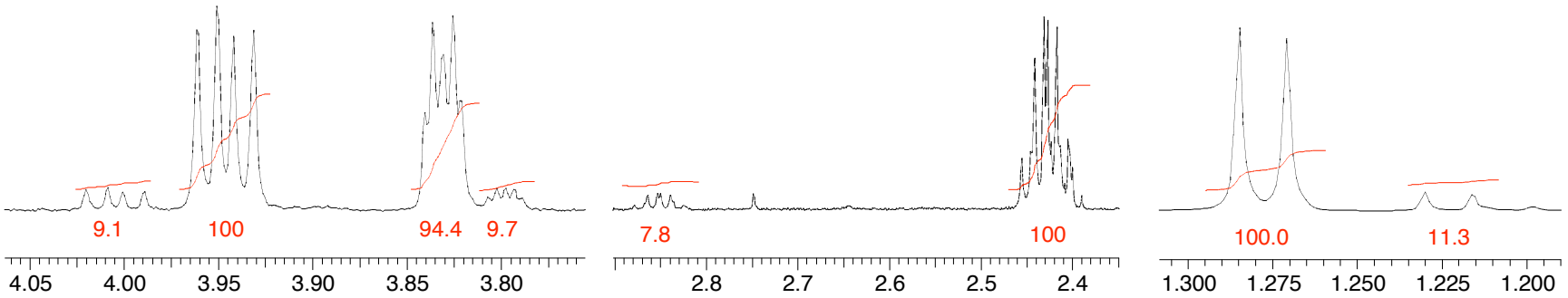
^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)

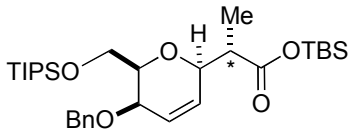


11

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)

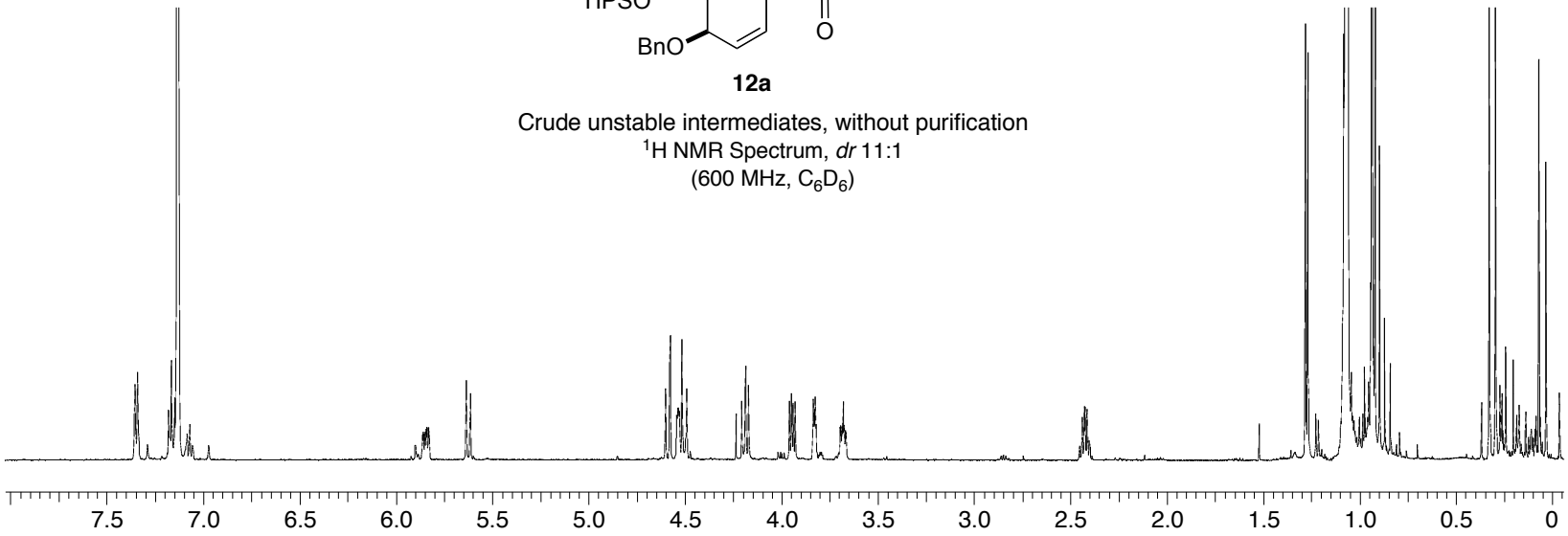

(a)
(b)
7.51
100.00
TIPSO
BnO
O
Me
OTBS
Z-20a
(a)
E-20a
(b)
13:1
Crude unstable intermediates, without purification
1H NMR Spectrum
(600 MHz, C6D6)

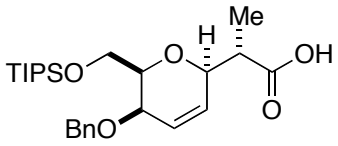




12a

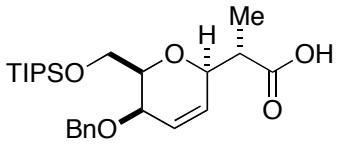
Crude unstable intermediates, without purification
^{1}H NMR Spectrum, *dr* 11:1
(600 MHz, C_6D_6)





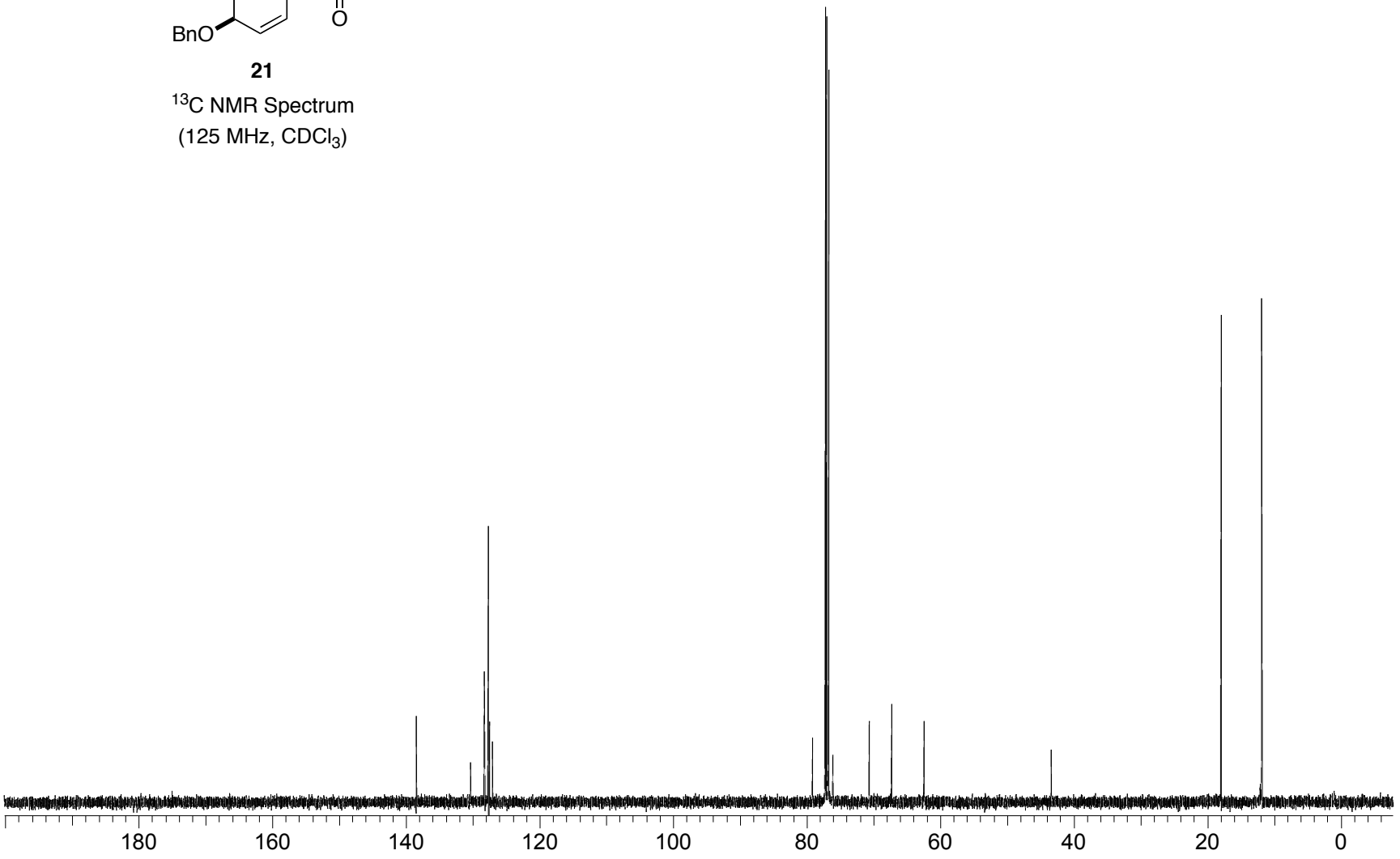
21

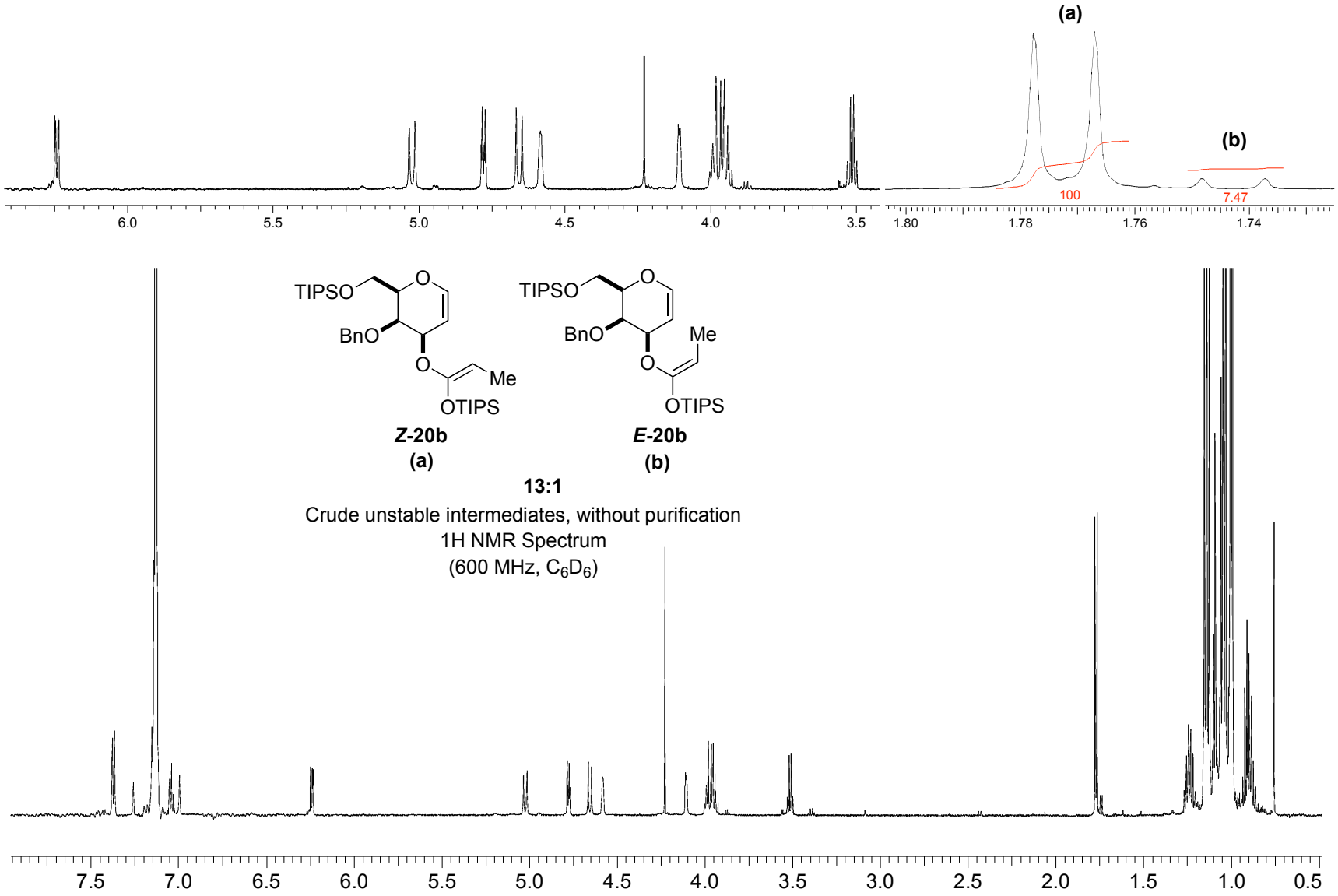
^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)

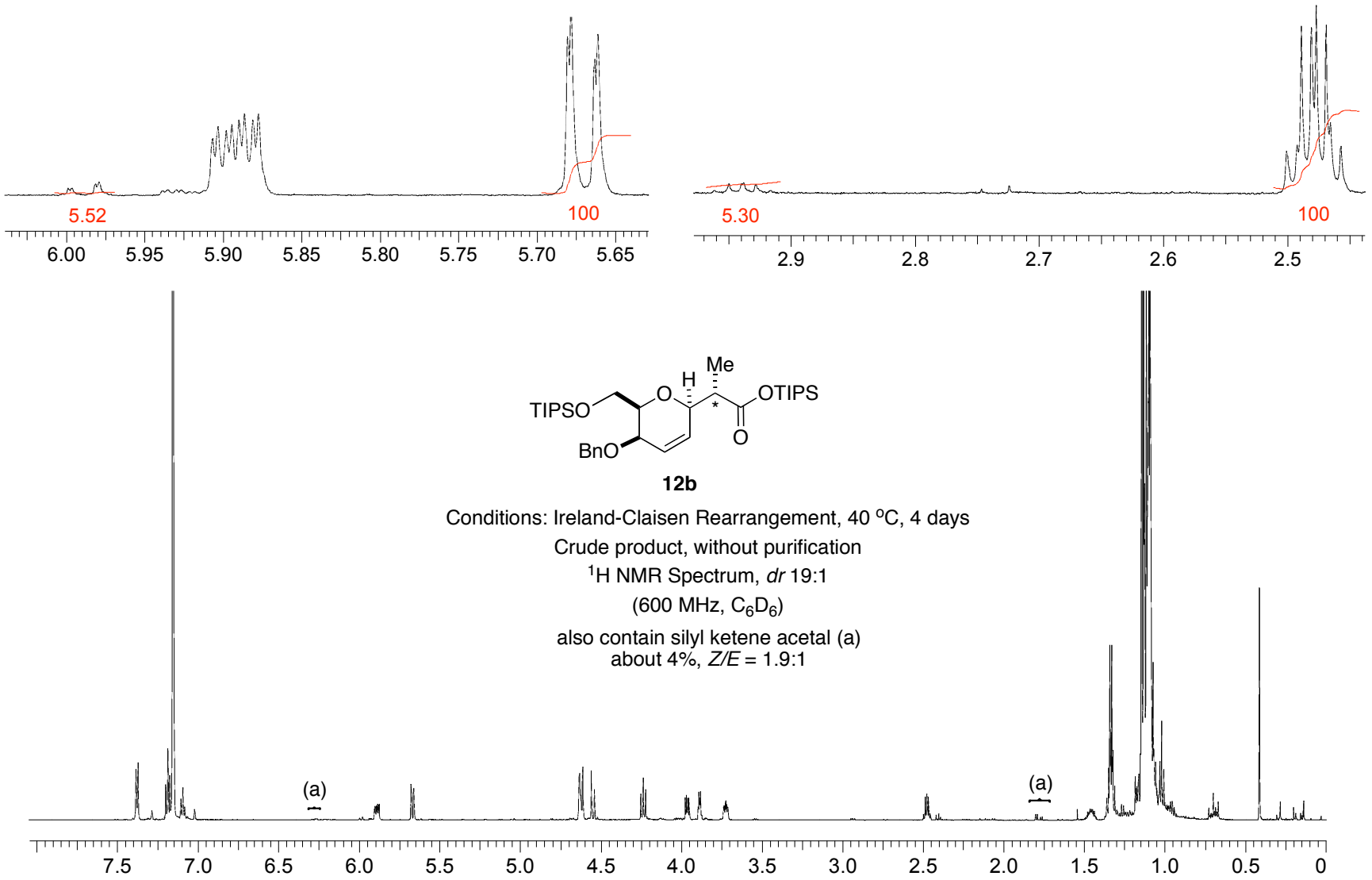


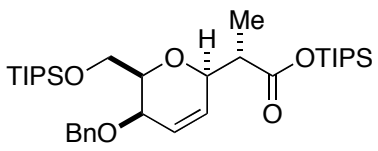
21

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



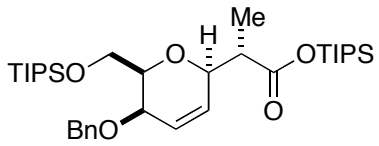

(a)
(b)
100
7.47
TIPSO
BnO
O
Me
OTIPS
Z-20b
(a)
E-20b
(b)
13:1
Crude unstable intermediates, without purification
1H NMR Spectrum
(600 MHz, C6D6)


5.52
100
6.00
5.95
5.90
5.85
5.80
5.75
5.70
5.65
5.30
100
2.9
2.8
2.7
2.6
2.5
Me
H
O
TIPSO
OTIPS
*
O
BnO
12b
Conditions: Ireland-Claisen Rearrangement, 40 °C, 4 days
Crude product, without purification
1H NMR Spectrum, dr 19:1
(600 MHz, C6D6)
also contain silyl ketene acetal (a)
about 4%, Z/E = 1.9:1
(a)
(a)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0



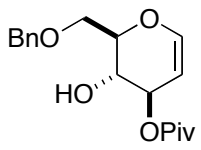
12b

^{1}H NMR spectrum
(600 MHz, $CDCl_3$)



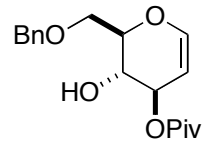
12b

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



23

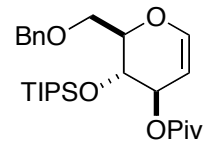
^{1}H NMR Spectrum
(500 MHz, $CDCl_3$)



23

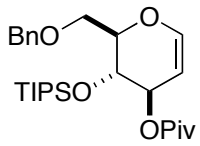
^{13}C NMR Spectrum

(125 MHz, $CDCl_3$)



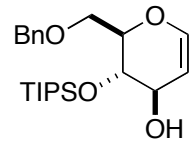
24

^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



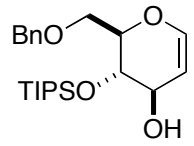
24

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



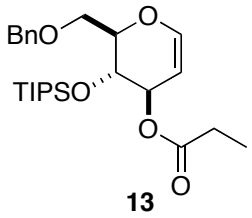
25

^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



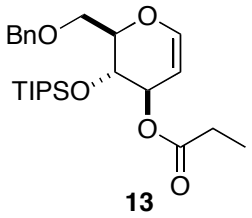
25

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



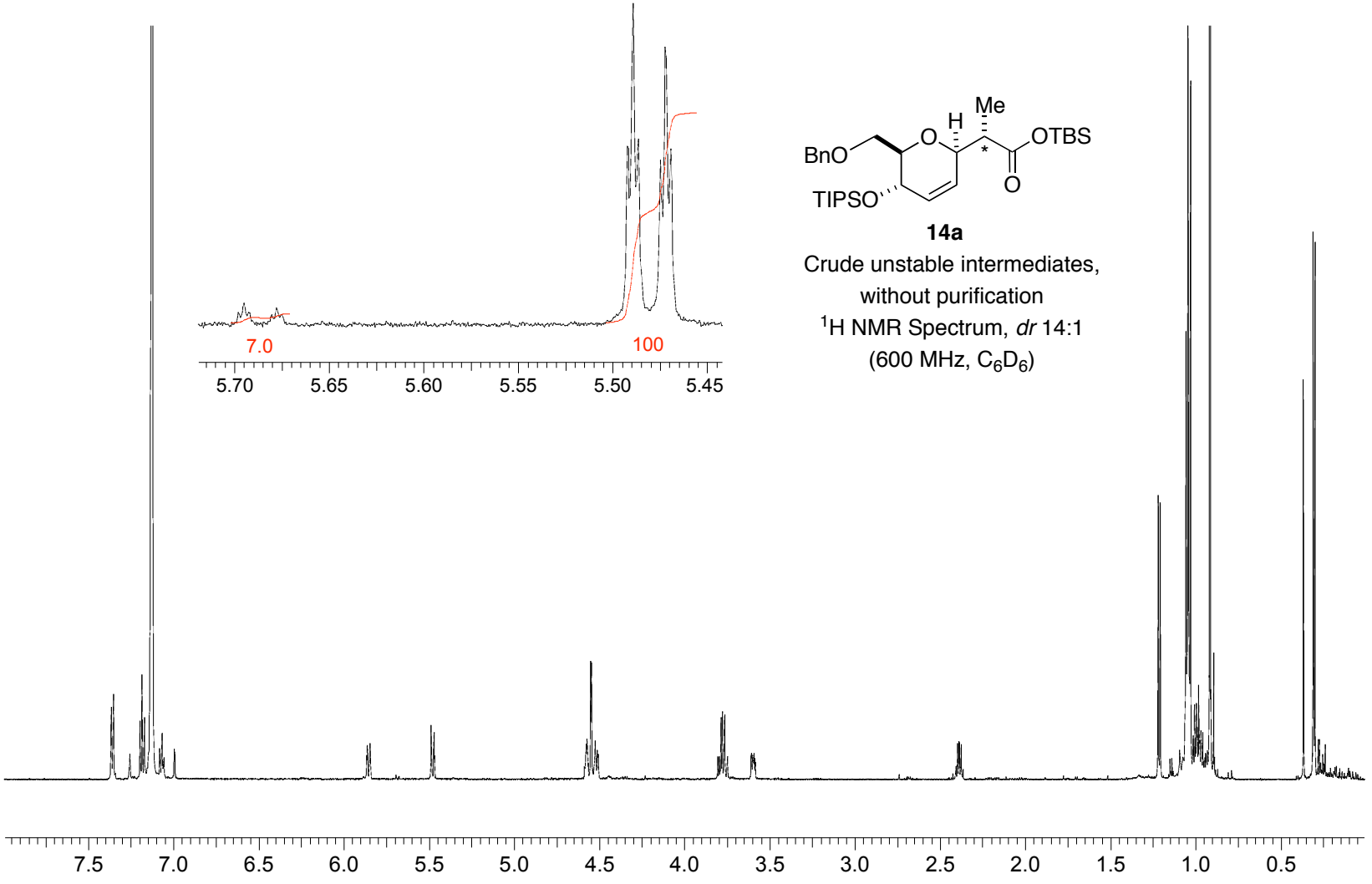
13

^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



13

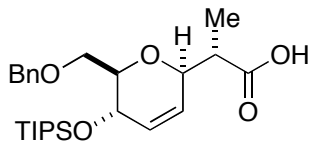
^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)



14a

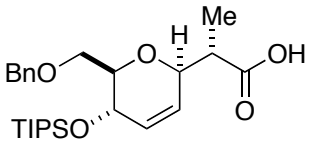
Crude unstable intermediates, without purification

^{1}H NMR Spectrum, *dr* 14:1 (600 MHz, C_6D_6)



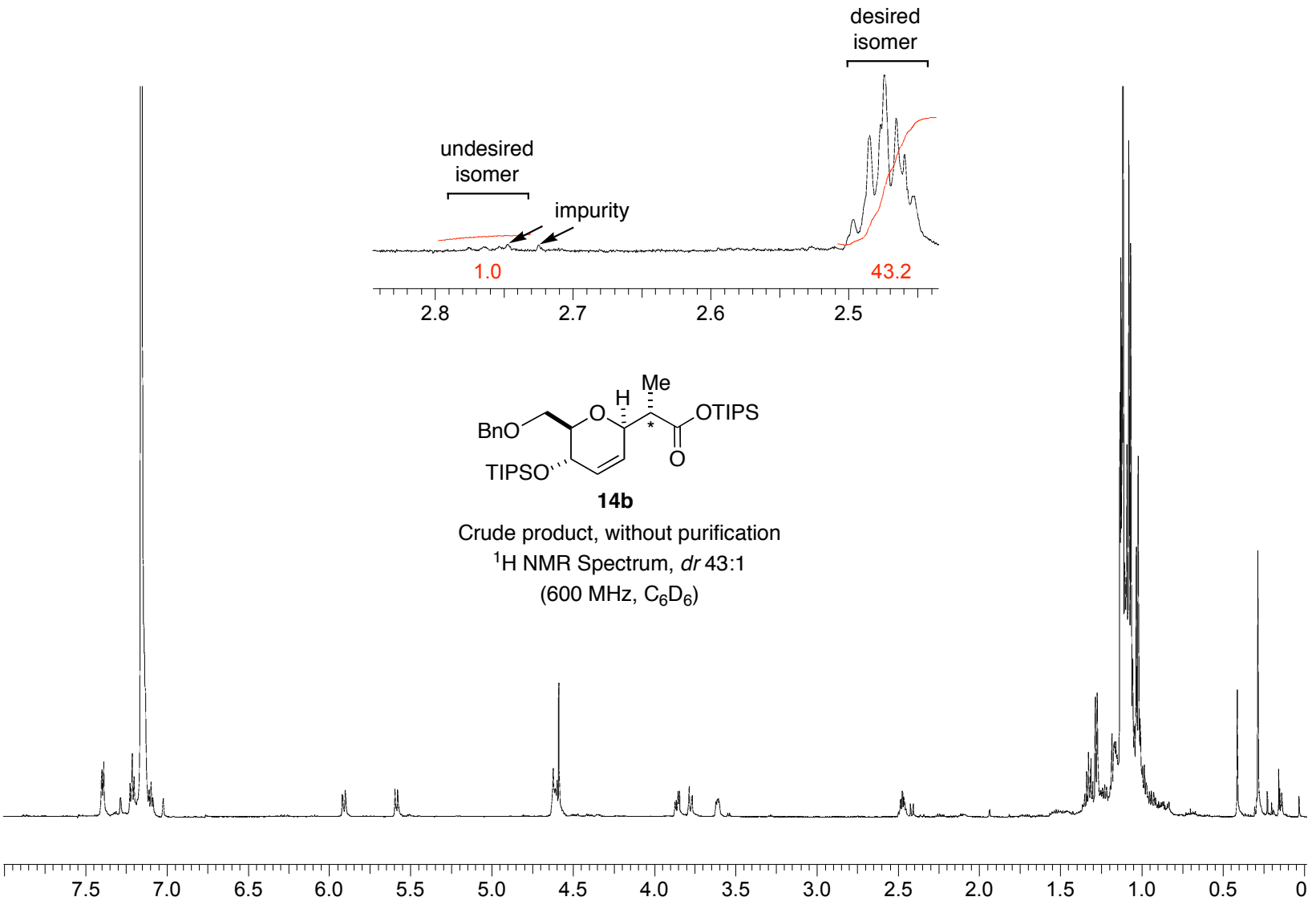
26

^{1}H NMR Spectrum
(600 MHz, $CDCl_3$)



26

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)

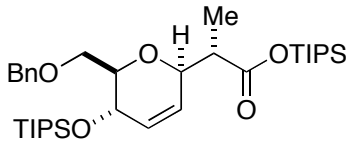


14b

Crude product, without purification

^{1}H NMR Spectrum, *dr* 43:1

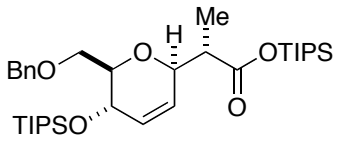
(600 MHz, C_6D_6)



14b

^{1}H NMR Spectrum

(600 MHz, $CDCl_3$)



14b

^{13}C NMR Spectrum
(125 MHz, $CDCl_3$)