Supporting Information for

A Straightforward Synthesis of (–)-Phaseolinic Acid

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General Methods. All the solvents were distilled from an appropriate drying agent and stored under nitrogen atmosphere. The crude products were purified by column chromatography on silica gel of 230-400 mesh (flash chromatography). Thin-layer chromatograms were performed on HF₂₅₄ silica gel plates (using CH₂Cl₂, hexane/EtOAc or CH₂Cl₂/hexane as the eluents, as indicated after the *R_f* values). NMR spectra were recorded in CDCl₃ at 200, 300 MHz or 400 MHz for ¹H, 50.3, 75.4 or 100.6 MHz for ¹³C. Chemical shifts are given in ppm with respect to internal TMS. Infrared spectra were measured on NaCl plates (neat) or in KBr; only the most significant absorptions, in cm⁻¹, are indicated. Optical rotations were measured at 20 ± 2 °C. (*S*)-Oct-1-yne-3-ol is commercially available. Enantioenriched compounds (*S*)-**8** and (*S*)-**9** could be obtained from enzymatic resolution of racemic oct-1-en-3-ol according to a literature procedure¹ or from (*S*)-oct-1-yne-3-ol by standard procedures.

(*S,S*)-Bis(1-pentylprop-2-ynyloxy)diphenylsilane (10), (*S*)-Oct-1-yn-3-ol [(*S*)-**4**] (0.5 g, 4.96 mmol) was dissolved in anhyd CH₂Cl₂ (10 mL) at 0 °C under N₂ atmosphere. Then, diphenyldichlorosilane (379 μL, 1.94 mmol) and 2,6-dimethylpyridine (847 μL, 7.27 mmol) were added via syringe. The mixture was stirred overnight at rt. The solution was partitioned with CH₂Cl₂ and brine, the organic layer was dried over anhyd MgSO₄. The crude residue was purified by flash chromatography (95:5 hexane/EtOAc) to give **10** (676 mg, 85%) as colorless oil; *R_f* = 0.65 (95:5 hexane/EtOAc); [α]_D -38.6 (*c* 1.1, CHCl₃); IR (film) 3311, 3072, 2110, 1594, 1084; ¹H NMR (CDCl₃, 400 MHz) δ 0.84-0.88 (t, *J* = 6.6, 6H), 1.22-1.28 (m, 8H), 1.43-1.45 (m, 4H), 1.70-1.78 (m, 4H), 2.37 (d, *J* = 2.1, 2H), 4.64 (td, *J* = 6.4, 2.1, 2H), 7.34-7.43 (m, 6H), 7.70-7.72 (m, 4H); ¹³C NMR (CDCl₃, 50.3 MHz) δ 14.0, 22.6, 24.5, 31.4, 38.1, 63.4, 72.5, 84.6, 127.5, 130.3, 132.4, 135.1; HRMS (FAB+) calcd for C₂₈H₃₇O₂Si [M+H]⁺ 433.2563, found 433.2542; Anal. Calcd for C₂₈H₃₆O₂Si: C, 77.73; H, 8.39. Found C, 77.41; H 8.49.

(*S,S*)-Bis(1-pentylprop-2-enyloxy)diphenylsilane (11). Quinoline (25 μL, 0.21 mmol) and Pd/CaCO₃ (5% Pd, 91 mg, 0.043 mmol) were added to a solution of silane **10** (575 mg, 1.33 mmol) in EtOAc (10 mL) under nitrogen. H₂ was bubbled through the mixture for a few minutes. Then, the mixture was kept under H₂ pressure (1 atm) and shaken vigorously for 4 hours. The mixture was filtered through a small pad of Celite®. Additional EtOAc was added to wash the pad. The solvent was evaporated in vacuo and

¹ Ohtani, T.; Nakatsukasa, H.; Kamezawa, M.; Tachibana, H.; Naoshima, Y. *J. Mol. Catal. Part B: Enzymatic* **1998**, *4*, 53–60.

the residue was purified by flash chromatography (98:2 hexane/EtOAc) to give **11** (528 mg, 91%) as colorless oil: R_f = 0.78 (95:5 hexane/EtOAc) or 0.7 (80:20 hexane/CH₂Cl₂); $[\alpha]_D^{25}$ +40.5 (c 1.32, CHCl₃); IR (film) 3072, 3052, 1646, 1592, 1038. ¹H NMR (CDCl₃, 400 MHz) δ 0.82-0.86 (t, J = 6.6, 6H), 1.21-1.28 (m, 12H), 1.44-1.54 (m, 4H), 4.30 (dt, J = 6.4, 6.4, 2H), 4.98 (dd, J = 10.2, 1.8, 2H), 5.07 (dd, J = 17.2, 1.8, 2H), 5.81 (ddd, J = 17.2, 10.2, 6.4, 2H), 7.33-7.40 (m, 6H), 7.64-7.66 (m, 4H); ¹³C NMR (CDCl₃, 50.3 MHz) δ 14.1, 22.6, 24.4, 31.8, 37.5, 74.3, 114.2, 127.4, 129.9, 133.8, 135.1, 140.6; HRMS (FAB+) calcd for C₂₈H₄₁O₂Si [M+H]⁺ 437.2876, found 437.2873; Anal. Calcd for C₂₈H₄₀O₂Si: C, 77.01; H, 9.23. Found C, 76.83; H 9.99.

(6S,7Z,9S)-Tetradec-7-en-6,9-diol [(S,S)-5]. Tetrabutylammonium fluoride (TBAF, 335 mg, 1.05 mmol) in THF (5 mL) was added to a solution of (S,S)-**12** (140 mg, 0.35 mmol) in THF (3 mL). After 4 h additional TBAF (65 mg, 0.2 mmol) was added and the solution was stirred overnight. The solvent was removed and CH₂Cl₂ was added. The solution was washed with phosphate buffer (pH = 7). The organic layer was dried over anhyd MgSO₄. The crude was purified by column chromatography on silica gel (90:10 hexane/EtOAc) gave (S,S)-**5** as a colorless oil (75 mg, 96%): R_f = 0.5 (65:35 hexane/EtOAc); $[\alpha]_D^{25}$ -2.6 (c 1.1, CHCl₃); IR (film) 3361, 2958, 2931, 1468; ¹H NMR (CDCl₃, 300 MHz) δ 0.89 (t, J = 6.6, 6H), 1.30-1.52 (m, 14H), 1.85 (bs, 2H), 4.44 (td, J = 6.0, 2.0, 2H), 5.48 (m, 2H); ¹³C NMR (CDCl₃, 100.6 MHz) δ 14.0, 22.6, 25.1, 31.7, 37.6, 68.3, 134.3; HRMS (EI) calcd for C₁₄H₂₈O₂ [M]⁺ 228.2089, found 228.2088; Anal. Calcd for C₁₄H₂₈O₂: C, 73.63; H, 12.36. Found C, 73.42; H 12.38.

(6S,7Z,9S)-6,9-Dipropanoiloxitetradec-7-ene [(S,S)-13]. Triethylamine (640 μ L, 4.60 mmol) was added to a solution of (S,S)-**5** (350 mg, 1.53 mmol) and DMAP (19 mg, 0.16 mmol) in CH₂Cl₂ (10 mL). The solution was cooled to 0 °C and propionic anhydride (592 μ L, 4.62 mmol) was added dropwise. The mixture was stirred at rt overnight. Then, the solution was diluted with CH₂Cl₂ (15 mL) and washed with 0.5 M HCl (5 mL), saturated aq. KHCO₃ (2 x 5 mL) and brine (5 mL). The organic layer was dried over anhyd MgSO₄. Removal of volatiles gave (S,S)-**13** (520 mg, 100%) as a colorless oil: R_f = 0.91 (9:1 hexane/EtOAc) or 0.71 (CH₂Cl₂); $[\alpha]_D^{25}$ +4.02 (c 1.2, CHCl₃); IR (film) 2958, 2863, 1736, 1185; ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, J = 7.0, 6H), 1.12 (t, J = 7.6, 6H), 1.29 (m, 12H), 1.51-1.65 (m, 4H), 2.29 (m, 4H), 5.40 (m, 2H), 5.62 (m, 2H); ¹³C NMR (CDCl₃, 100.6 MHz) δ 9.2, 14.0, 22.5, 24.6, 27.8, 31.6, 34.5, 70.5, 131.3, 173.5; HRMS (EI) calcd for C₂₀H₃₆O₄ [M]⁺ 340.2614, found 340.2626. Anal. Calcd for C₂₀H₃₆O₄: C, 70.55; H, 10.66. Found C, 70.25; H 10.78.

Ireland-Claisen rearrangement of (*S,S*)-13** in THF.** A toluene solution of KHMDS (0.5 M, 1.74 mL, 0.87 mmol) was added dropwise to a solution of (*S,S*)-**13** (100 mg, 0.29 mmol), TBDMSCl (177 mg, 1.17 mmol) and anhyd THF (3 mL) in a flask sealed with a septum, at $-78\text{ }^{\circ}\text{C}$ under argon. After the addition, the mixture was stirred 45 min and then was allowed warm to rt overnight. Then, most of the volatiles were removed under vacuum, anhyd toluene (3 mL) was added and the mixture was heated (130 $^{\circ}\text{C}$ bath temperature) for 12 h. The reaction mixture was partitioned by adding diethyl ether (8 mL) and brine (8 mL). The aqueous layer was washed with additional diethyl ether and the combined organic layers were dried (MgSO_4), and concentrated in vacuum. The residue was filtered through a pad of silica gel (65:35 hexane/EtOAc) and the crude mixture was treated with THF (2 mL) and aq. LiOH (6 M, 1 mL) at 70 $^{\circ}\text{C}$ for 14 h. Then, the solution was acidified with aq HCl (2 M, 6 mL), additional THF (3 mL) was added and the mixture was heated at 50 $^{\circ}\text{C}$ for 3 h. The mixture was partitioned by adding CH_2Cl_2 (10 mL), and the aqueous layer was washed with additional CH_2Cl_2 (10 mL). The organic layers were dried (MgSO_4). Evaporation of solvents and purification by flash chromatography on silica gel gave (9:1 hexane/EtOAc) yielded lactone (3*R*,4*S*,5*S*)-**7** (32 mg, 41%) and lactone (3*S*,4*S*,5*S*)-**7** (16 mg, 21%).

(3R,4S,5S)-3