Supplementary Material

Preparation of Garner's Aldehyde, the Weinreb amide precursors, 1-7, and 25-27.

***N*-(*tert*-Butoxycarbonyl)-L-serine, 7**[1]

To a solution of *L*-serine (2.00g, 19.03 mmol) in 30 mL H_20 and 10 mL dioxane at 0ºC, NaOH (1.60g, 39.96 mmol in 5 mL H_2O) was added. Di-*tert*-butyl dicarbonate (4.98g, 22.84 mmol) was added and the resulting mixture was allowed to warm to room temperature overnight. The aqueous layer was then washed twice with diethyl ether to remove any unreacted di-*tert*-butyl dicarbonate, acidified with concentrated H_2SO_4, and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated to yield a thick oil, **7**, which was used without further purification.

***L*-Serine methyl ester**

L-serine (64 g, 0.60 mol) was dissolved in 600 mL methanol under nitrogen. Thionyl chloride (44.0 mL, 0.60 mol) was added slowly at room temperature. The reaction mixture was refluxed for 8 h. Methanol (500 mL) was distilled into aqueous KOH solution and 100 mL of toluene was added and 150 mL of solvent was distilled into aqueous KOH solution. The remaining solution was concentrated in *vacuo* to afford *L*-serine methyl ester[2] as a white solid (90.0 g, 0.57 mol, 95%): IR (KBr): 3416 (s), and 1745 (s) cm^{-1}; ^1H NMR (D_2O): δ 4.38 (brs, 1H), 4.21-4.08 (dd, 2H), and 3.95 (s, 3H) ppm; ^{13}C NMR (D_2O): δ 168.9, 59.2, 54.7, and 53.7 ppm.

***N*-Boc-*L*-serine, methyl ester**

L-serine methyl ester hydrochloride (30.5 g, 0.196 mol) was dissolved in 500 mL of CH_2Cl_2. Triethylamine (57 mL, 0.392 mol) and di-*tert*-butyl dicarbonate (51 g, 0.235 mol) were added, and the reaction mixture was stirred at room temperature for 24 h under nitrogen. The solution was washed with water (300 mL), saturated sodium bicarbonate (300 mL) and brine (300 mL). The organic layer was dried ($MgSO_4$) and concentrated in *vacuo* to afford N-Boc-*L*-serine methyl ester[2] as pale yellow oil (40.7 g, 0.186 mol, 95%). The crude product was used without further purification. IR (neat): 3430 (s), 2979 (s), and 1710 (s) cm^{-1}; ^1H NMR: δ 5.40 (brs, 1H), 4.32 (brs, 1H), 3.91-3.81(m, 2H), 3.72 (s, 3H), and 1.40 (s, 9H) ppm; MS (m/*z*): 57(100), 133, and 189.

***N*-Boc 2,2-Dimethyloxazolidine-3,4*S*-dicarboxylic acid methyl ester**

N-Boc-*L*-Serine methyl ester (30.0 g, 0.135 mol) was dissolved in benzene (500 mL). 2,2-Dimethoxypropane (DMP, 29 mL, 0.277 mol) and TsOH•H_2O (0.40 g, 2.2 mmol) were added to the solution, which was refluxed for 12 h under nitrogen. Benzene (300 mL) was removed by distillation, and fresh DMP (9 mL) and benzene (150 mL) were added and the solution was refluxed for 3 h. Benzene (200 mL) was slowly removed by distillation, the solution cooled and diethyl ether (300 mL) was added. Washing with saturated $NaHCO_3$ solution (2x100 mL) and brine (100 mL) was followed by drying over $MgSO_4$, and concentration in *vacuo*. The crude product was purified by vacuum distillation to afford *N*-Boc 2,2-Dimethyloxazolidine-3,4*S*-dicarboxylic acid methyl ester[2] as a pale yellow oil (33.2 g, 0.128 mol, 95%). IR (neat): 2980 (s), 1707 (s), and 1386 (s) cm^{-1}; ^1H NMR: δ 4.50-4.37 (dd, 1H), 4.17-4.11 (dd, 1H), 4.06-4.02 (dd, 1H), 3.76 (s, 3H), and 1.67-1.42 ppm (m, 15H) ppm; ^{13}C NMR: δ 80.5, 66.5, 59.5, 52.7, 28.5, 25.4, 25.2, and 24.6 ppm; MS (m/*z*): 57 (100), 144, and 244.

_N_-Boc (4_S_)-4-Formyl-2,2-dimethyloxazolidine, 1

_N_-Boc 2,2-Dimethyloxazolidine-3,4_S_-dicarboxylic acid methyl ester (6g, 23.2 mmol) was dissolved in toluene (45 mL) at room temperature, and the solution was cooled to –78°C. Diisobutylaluminum hydride (DIBAL, 1M in toluene, 35 mL, 34.8 mmol) cooled to –78°C was added to the solution via cannula over a period of 30 minutes, then stirred for 3.5 h at –78°C. Methanol (9 mL) cooled at –78°C was slowly added via cannula to the reaction mixture. The reaction mixture poured onto silica gel (50g) suspended in ethyl acetate, and stirred for 10 minutes. The suspension was vacuum-filtered through a short pack of silica gel, and washed several times with ethyl acetate. Concentration in *vacuo* and purification using vacuum distillation gave _N_-Boc (4_S_)-4-formyl-2,2-dimethyloxazolidine[2,3] as a colorless oil (4.3g, 18.8 mmol, 81%). IR (neat): 2980 (s) and 1703(s) cm^{-1}; ^1H NMR: δ 9.6-9.5 (d, 1H), 4.3-3.9 (m, 3H), and 1.6-1.4 (m, 15H) ppm; ^{13}C NMR: δ 202, 154, 98, 84, 68, 67, 31, 29, and 27 ppm; MS (m/_z_):57 (100), 100, 156, and 214.

[2-(*tert*)-Butyl-diphenyl-silanyloxy)-1-(methoxy-methyl-carbamoyl)-ethyl]-carbamic acid *tert*-butyl ester, 2.

A catalytic amount of DMAP (0.05 g) was added to a solution of [2-hydroxy-1-(methoxy-methyl-carbamoyl)-ethyl]-carbamic acid *tert*-butyl ester (0.93 g, 3.75 mmol) and imidazole (0.76 g, 11.10 mmol) in dry DMF (4.2 mL). After 30 min *tert*-butyldiphenylsilyl chloride (TBDPSCl, 1.14 mL, 4.39 mmol) was added, and the reaction mixture was stirred overnight. The reaction mixture was diluted with saturated aqueous NH_4Cl, and the solution was extracted with CH_2Cl_2. The organic extract was washed with H_2O, brine, dried over $MgSO_4$ and concentrated. The DMF was removed via Kugelrohr and further purified by flash column chromatography on silica gel (CH_2Cl_2/EtOAc 100:0 to 80:20 to 0:100) to provide the compound as a viscous oil, **2**[4] (1.70g, 3.49 mmol, 93%): ^1H NMR (400 MHz, $CDCl_3$): δ 7.68-7.65 (m, 4H), 7.43-7.39 (m, 6H), 5.48-5.46 (d, _J_ = 8.5 Hz, 1H), 4.86 (bs, 1H), 3.90-3.89 (s, 2H), 3.67 (s, 3H), 3.21 (s, 3H), 1.46-1.40 (s, 9H), and 1.06-1.00 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 155.4, 135.6, 133.1, 129.8, 127.7, 79.5, 64.1, 61.4, 52.5, 32.1, 28.4, 26.7, 19.2, 14.2, and 1.1 ppm.

12-Methyl-1-tridecanol, 3

Magnesium turnings (1.52 g, 62.72 mmol) were suspended in dry THF (25 mL) and 2-bromopropane (4.93 mL, 52.54 mmol) was added with vigorous stirring at room temperature. After refluxing started, dry THF (25 mL) was added. The reaction mixture was stirred until it cooled completely and turned grey. 11-Bromo-1-undecanol (2.00 g, 7.96 mmol) was dissolved in dry THF (7 mL), and in a separate flask LiCl (0.71 g, 16.72 mmol) and $CuCl_2$ (1.09 g, 8.12 mmol) were dissolved in dry THF (13 mL). The Grignard solution was cooled to –78°C, and the solution containing the alcohol was added via cannula, followed by the solution containing the $LiCuCl_4$ salt. The reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched with saturated aqueous ammonium chloride. Water and diethyl ether were added, and the layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was further purified by flash column chromatography on silica gel (80:20 petroleum ether:EtOAc) to give 12-methyl-1-tridecanol (**3**,[5] 1.60 g, 7.48 mmol, 94%). ^1H NMR (400 MHz, $CDCl_3$): δ 3.68-3.65 (t, _J_ = 6.7 Hz, 2H), 1.61-1.49 (m, 3H), 1.34-1.04, (m, 19H), and 0.90-0.74 ppm (d, _J_ = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 63.1, 39.1, 32.8, 29.9, 29.7, 29.6, 29.4, 28.0, 27.4, 25.7, and 22.7 ppm. MS (EI) *m/z* 196 (M –H_2O): 168, 140, 111, 97, 83, 69, 56.

14-Methyl-1-pentadecanol, 4

Magnesium turnings (1.52 g, 62.72 mmol) were suspended in dry THF (25 mL) and 1-bromo-3-methylbutane (6.57 mL, 52.54 mmol) was added with vigorous stirring at room temperature. After refluxing started, dry THF (25 mL) was added. The reaction mixture was stirred until it cooled completely and turned grey in color. 11-Bromo-1-undecanol (2.00 g, 7.96 mmol) was dissolved in dry THF (7 mL), and in a separate flask LiCl (0.71 g, 16.72 mmol) and $CuCl_2$ (1.09 g, 8.12 mmol) were dissolved in dry THF (13 mL). The Grignard solution was cooled to –78°C, and the solution containing alcohol was added via cannula, followed by the solution containing the $LiCuCl_4$ salt. The reaction mixture allowed to warm to room temperature overnight, and quenched with saturated aqueous

ammonium chloride. Water and diethyl ether were added, and the layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$, brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was further purified by flash column chromatography on silica gel (80:20 petroleum ether: EtOAc) to give 14-methyl-1-pentadecanol **4**[6] (1.84 g, 7.56 mmol, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.69- 3.63 (t, *J* = 6.6 Hz, 2H), 1.60-1.46 (m, 3H), 1.37-1.07, (m, 23H), and 0.89-0.87 ppm (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.1, 39.1, 32.8, 29.9, 29.7, 29.6, 29.4, 28.0, 27.4, 25.7, and 22.6 ppm; MS (EI) *m/z* 224 (M –H_2O): 196, 168, 140, 125, 111, 97, 83, 69, 57.

12-Methyl-1-bromotridecane, 5

Triphenylphosphine (3.16 g, 12.04 mmol) was added to a stirred solution of 12-methyl-1-tridecanol (**3**, 1.79 g, 8.35 mmol) in 20 mL of dry CH_2Cl_2. The reaction was cooled in an ice bath and *N*-bromosuccinimide (2.04 g, 11.46 mmol) was added in portions. The resulting mixture was allowed to warm to room temperature over a period of 2 h. The solvent was evaporated, the residue filtered, and washed several times with hexane. The filtrate was concentrated *in vacuo* and purified by flash column chromatography (hexane) on silica gel to yield a clear oil, **5**[7] (1.89 g, 6.76 mmol, 81%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45-3.40 (t, *J* = 6.8 Hz, 2H), 1.92-1.83 (p, *J* = 6.8 Hz, 2H), 1.60-1.42 (m, 3H), 1.28 (m, 14H), 1.18-1.14 (m, 2.07), and 0.89-0.87 ppm (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.3, 34.2, 33.1, 30.2, 27.6, and 22.9 ppm; MS (EI) *m/z* 276, 263, 235, 191, 177, 137, 135, 111, 97, 85, 69, 57.

14-Methyl-1-bromopentadecane, 6

Triphenylphosphine (2.87 g, 10.93 mmol) was added to a stirred solution of 14-methyl-1-pentadecanol (**4**, 1.84 g, 7.59 mmol) in 40 mL of dry CH_2Cl_2. The reaction was cooled in an ice bath and *N*-bromosuccinimide (1.85 g, 10.40 mmol) was added in portions. The resulting mixture was allowed to warm to room temperature overnight, the solvents were evaporated and the residue was filtered and washed several times with hexane. The filtrate was concentrated *in vacuo*, and purified by flash column chromatography (100% petroleum ether) on silica gel to yield a clear oil, **6**[8] (1.99 g, , 6.53 mmol, 86%): IR (neat): 2920, 2860, 2300, 2290, 1400, 1050 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.44-3.41 (t, *J* = 7.2 Hz, 2H), 1.92-1.85 (p, *J* = 7.0 Hz, 2H), 1.60-1.19 (m, 23), 0.91-0.88 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.1, 33.8, 32.9, 30.0, 29.8, 29.7, 29.6, 29.5, 29.1, 28.8, 28.2, 28.0, 27.5, 22.7 ; MS (EI) *m/z* 291, 261, 191, 151, 137, 135, 111, 97, 85, 71, 57, 53.

1-Pentadecanal, 25

A stirred suspension of pyridinium chlorochromate (PCC, 4.2 g, 19.5 mmol) in CH_2Cl_2 (26 mL) was treated with 1-pentadecanol (3 g, 13 mmol) in one portion. The reaction mixture was stirred for 4 h and diethyl ether (30 mL) was added. The mixture was stirred vigorously and the supernatant passed through a 2 inch pad of silica gel. The eluant was concentrated in *vacuo* and purified by silica gel chromatography (5% ether/hexane) to give 1-pentadecanal **25**[9] as a colorless oil (2.65 g, 17.55 mmol, 90%). IR (neat): 2924 (s), 2854 (m), and 1727 (m) cm^{-1}; ^{1}H NMR: δ 9.76-9.75 (t, 1H), 2.42-2.41 (td, 2H), 1.56 (m, 2H), 1.3-1.26 (m, 12H), and 0.9-0.86 ppm (t, 3H); ^{13}C NMR: δ 206, 47, 35, 33-25, and 17 ppm; MS (m/*z*): 57 (100), 82, 96, 152, 180, and 182 ppm.

Ethyl heptadec-2*E*-enoate, 26

Triethyl phosphonoacetate (2.6 mL, 13 mmol) was added, dropwise, to a suspension of NaH (0.38 g, 15.8 mmol) in anhydrous THF (16 mL), at 0°C. After stirring for 30 minutes at 0°C, 1-pentadecanal (**25**, 2.9 g, 13 mmol) was added in one portion, and the temperature was allowed to rise to room temperature. The reaction mixture was poured into brine (10 mL) and diethyl ether (20 mL). The organic layer was separated, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (5% diethyl ether in hexane) to give ethyl heptadec-2*E*-enoate **26**[10] as a colorless oil (3.68 g, 12.4 mmol, 95%, >98% *trans*). IR (neat): 2925 (s), and 1720 (s) cm^{-1}; ^{1}H NMR: δ 6.70-6.93 (dt, 1H), 5.83-5.79 (d, 1H), 4.21-4.15 (q, 2H), 2.21-2.16 (q, 2H), 1.46-1.26 (m, 38H), and 0.88-0.84 ppm (t, 6H); ^{13}C NMR: δ 170, 152, 124, 63, 35-31, 25.6, 17, and 17 ppm.

Heptadec-2*E*-enoic acid, 27

Aqueous LiOH (1N, 0.8 mL, 0.8 mmol) was added to a stirred solution of ethyl heptadec-2*E*-enoate **26** (0.2 g, 0.67 mmol) in THF (1.3 mL) and MeOH (0.7 mL), at room temperature. The reaction mixture was stirred overnight and then concentrated under reduced pressure. The residue was poured into EtOAc, acidified with dilute aqueous HCl (5%) to pH 3, and extracted with EtOAc. The organic phase was washed with water and brine, dried with $MgSO_4$, and concentrated in *vacuo*. The residue was precipitated from hexane to give heptadec-2*E*-enoic acid **27**[11] as a white solid (0.15 g, 0.563 mmol, 84%) and used without further purification. IR (KBr): 3411 (m), 2922 (s), 2850 (m), 1691 (m), and 1654 (m) cm^{-1}; ^1H NMR: δ 7.12-7.05 (dt, 1H), 5.84-5.77 (d, 1H), 2.25-2.2 (q, 2H), 1.48-1.26 (m, 41H), and 0.89-0.84 ppm (t, 6H); ^{13}C NMR: δ 175, 155, 37-26, and 17 ppm.

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