Supporting Information

General Methods. Conventional organic solvents were purchased from Fisher. All chemicals were purchased from Aldrich Chemical Co and used without further purification, unless stated otherwise. Bromo-substituted polystyrene (1.97 mmol/g, 50-100 mesh, produced by co-polymerization of styrene, divinylbenzene (1%), and 4-bromostyrene) was obtained from NovaBiochem (San Diego). Tetrahydrofuran (THF) was distilled under N_2 from sodium/benzophenone ketyl and methylene chloride from calcium hydride. Flash chromatography was performed with Merck silica gel (230-400 mesh). TLC plates (silica gel 60-F254) were purchased from VWR Scientific. All ^{1}H NMR spectra were recorded on a Varian Gemini 300 MHz instrument (75 MHz for ^{13}C NMR spectra). Chemical shifts (δ) are reported downfield from tetramethylsilane (Me_4Si) in parts per million (ppm). Compounds were visualized with a ninhydrin spray reagent or a UV/vis lamp. Mass spectra (EI and FAB) were recorded on a VG Instrument VG70-250SE high-resolution mass spectrometer. Electrospray mass spectra (ES) were performed on a Micromass Quattro II instrument. Elemental analyses were obtained from Oneida Research Services Inc. (Whitesboro, NY). Melting points were obtained with a Fisher-Johns melting point apparatus and are uncorrected

Preparation of 2-(4-bromophenyl)-1,3-dioxolane. A mixture of 4-bromobenzaldehyde (9.5 g, 51.4 mmol) and ethylene glycol (6.4 g, 113 mmol) and *p*-toluenesulfonic acid (120 mg) in benzene (200 mL) was refluxed in a Dean Stark apparatus for 4 h. The reaction mixture was cooled to room temperature, and the solution was extracted with cold water/ethyl acetate. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated to give a colorless oil (11.4, 95%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.01-4.14 (4 H), 5.78 (s, 1 H), 7.37 (d, J = 8.34 Hz, 2 H), 7.53 (d, J = 8.34 Hz, 2 H); HRMS (EI) calcd for $C_9H_9BrO_2$ 227.9786, 229.9766, found 227.9771, 229.9754

Preparation of 2-(4-allyldimethylsilylphenyl)-1,3-dioxolane (3). To a solution of 2-(4-bromophenyl)-1,3-dioxolane (6.0 g, 26.2 mmol) in dried THF (200 mL) at -78 ^{o}C was added *t*-butyllithium (15.4 mL, 1.7 M solution in pentane, 26.2 mmol) over a period of 5 min. After 30 min of further stirring at -78 ^{o}C, allylchlorodimethylsilane (3.7 g, 27.5 mmol) in THF (20 mL) was added dropwise over a period of 10 min. The reaction mixture was stirred for 1 h and warmed to room temperature. THF was removed under reduced pressure, and the residue was extracted with cold water/ethyl acetate. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated to give a colorless oil (5.4 g, 91%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 6 H), 1.78 (d, J = 7.95 Hz, 2 H), 4.02-4.18 (4 H), 4.85 (s, 1 H), 4.90 (m, 1 H), 5.78 (m, 1 H), 5.85 (s, 1 H), 7.50 (d, J = 7.95 Hz, 2 H), 7.58 (d, J = 7.95 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) -3.4 (2C), 23.7, 65.4 (2C), 103.7, 113.6, 125.8 (2C), 133.8 (2C), 134.6, 138.8, 139.9; HRMS calcd for $C_{14}H_{20}O_2Si$ 248.1233, found 248.1230

Preparation of 4-allyldimethylsilylbenzaldehyde (4). A solution of 3 (12 g, 52.5 mmol) and *p*-toluenesulfonic acid (100 mg) in acetone (300 mL) was heated under reflux for 3 h. The reaction mixture was concentrated under reduced pressure, and acetone (300 mL) was added to the residue. After being refluxed for 3 h, the solution was concentrated, and the crude oil was purified by silica gel chromatography (1:20 ethyl acetate/hexanes) to afford a colorless oil (9.2 g, 86%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.32 (s, 6 H), 1.78 (d, J = 8.10 Hz, 2 H), 4.84 (s, 1 H), 4.89 (m, 1 H), 5.76 (m, 1 H), 7.67 (d, J = 8.10 Hz, 2 H), 7.85 (d, J = 8.10 Hz, 2 H), 10.05 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) -3.4 (2C), 23.5, 114.2, 128.8 (2C) 133.7, 134.4, (2C), 136.9, 147.6, 192.8; HRMS calcd for C!24ub $12H_{16}$OSi 204.0971, found 204.0972

Preparation of 4 from 1,4-dibromobenzene (5). (a) Preparation of 1-allyldimethylsilyl-4-bromobenzene. To a solution of 1,4-dibromobenzene (5, 28.3 g, 120 mmol) in dried THF (300 mL) at -78 ^{o}C was added *n*-butyllithium (40.0 mL, 2.5 M solution in hexanes, 100 mmol) over a period of 20 min. After 30 min of further stirring at -78 ^{o}C, allylchlorodimethylsilane (13.5 g, 100 mmol) in THF (50 mL) was added dropwise over a period of 20 min, and the reaction mixture was warmed to room temperature. After stirring for 1 h at room temperature the reaction mixture was concentrated, and the residue was extracted with ether and brine. The organic layer was dried (Na_2SO_4) and distilled under reduced pressure to provide a colorless liquid (21.9 g, 82%); bp 72 ^{o}C/0.1 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 6 H), 1.77 (d, J = 8.07 Hz, 2 H), 4.87 (m, 1 H), 4.92 (m, 1 H), 5.78 (ddt, J = 17.55, 9.51, and 8.07 Hz, 1 H), 7.41 (d, J = 8.28 Hz, 2 H), 7.52 (d, J = 8.28 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) -3.5 (2 C), 23.6, 113.8, 123.9, 130.9 (2 C), 134.2, 135.3 (2 C), 137.5; HRMS calcd for $C_{11}H_{15}BrSi$ 254.0127 and 254.0107, found 254.0128 and 256.0109.

(b) Preparation of 4. To a solution of 1-allyldimethylsilyl-4-bromobenzene (1.3 g, 5 mmol) in dry THF (70 mL) at -78 ^{o}C was added *t*-butyllithium (3.0 mL, 1.7 M solution in pentane, 5.1 mmol) over a period of 10 min. After 30 min stirring at -78 ^{o}C, anhydrous DMF (750 μL, 10 mmol) was added dropwise. The reaction mixture was stirred further for 1 h and warmed to room temperature. Saturated NH_4Cl (2 mL) was added to the solution, and the reaction mixture was concentrated. The residue was extracted with ethyl acetate (20 mL) and brine (5 mL), and the organic layer was dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (1:15 ethyl acetate/hexanes) to afford a colorless oil (860 mg, 82%).

Preparation of (*R*)-(-)-*N*-[(4-allyldimethylsilylphenyl)methylene]-*tert*-butanesulfinamide (6). To a solution of (*R*)-(-)-*tert*-butanesulfinamide (3.7 g, 30 mmol) and 4 (6.2 g, 30 mmol) in dry THF (15 mL) was added titanium(IV) propoxide (17 mL, 60 mmol). The mixture was refluxed for 1 h under a N_2 atmosphere. The reaction mixture was cooled immediately upon completion, and poured into brine (30 mL) with rapid stirring. The resulting white suspension was filtered through a pad of Celite, which was then washed with ethyl acetate (100 mL). The filtrate was transferred to a separatory funnel where the organic layer was washed with brine (20 mL), dried (Na_2SO_4), and concentrated. The crude oil was purified by column chromatography (1:5 ethyl acetat!e/hexanes) to afford a colorless oil (6.3 g, 68%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.30 (s, 6 H), 1.26 (s, 9 H), 1.76 (d, J = 7.92 Hz, 2 H), 4.83 (s, 1 H), 4.88 (d, J = 4.41 Hz, 1 H), 5.74 (ddt, J = 15.84, 9.27, 8.28 Hz, 1 H), 7.62 (d, J = 7.92 Hz, 2 H), 7.82 (d, J = 7.92 Hz, 2 H), 8.59 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) -3.5 (2C), 22.6 (3C), 23.4, 57.8, 113.9, 128.4 (2C), 134.0, 134.2 (2C), 134.4, 144.6, 162.8; HRMS (M+1) calcd for $C_{16}H_{26}NOSSi$ 308.1505, found 308.1415

Preparation of (*Rs,S*)-(-)-methyl *N*-(*tert*-butanesulfinyl)-3-amino-3-(4-allyldimethylsilyl)phenylpropanoate (7). To a solution of methyl acetate (1.5 mL, 18.5 mmol) in dried THF (25 mL) at -78 ^{o}C was added lithium diisopropylamide (2 M solution, 9.8 mL, 19.6 mmol), and the solution was stirred for 15 min. Chlorotitanium triisopropoxide (10.1 mL, 39.3 mmol) in THF (20 mL) was added dropwise at -78 ^{o}C to form a pale orange colored titanium enolate. After being stirred for 30 min a solution of 6 (3.8 mg, 12.3 mmol) in THF (10 mL) was added over a period of 20 min, and the reaction mixture was stirred for 3 h. Saturated NH_4Cl (20 mL) was added slowly at -78 ^{o}C, and the mixture was warmed to room temperature. Dilution of the mixture with water (10 mL)/EtOAc (100 mL) resulted in a white suspension which was filtered through a pad of Celite. The organic layer was concentrated, and the residue was extracted with EtOAc (40 mL)/brine (20 mL). Drying (Na_2SO_4) and concentration of the organic layer followed by column chromatography (1:1 ethyl acetate/hexanes) afforded a colorless oil (3.7 g, 79%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 6 H), 1.21 (s, 9 H), 1.73 (d, J = 7.98 Hz, 2 H), 2.87 (d, J = 5.64 Hz, 2 H), 3.64 (s, 3 H), 4.74 (bs, *N*H, 1 H), 4.80 (s, 1 H), 4.85 (m, 1 H), 5.74 (m, 1 H), 7.30 (d, J = 7.41 Hz, 2 H), 7.47 (d, J = 7.41 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) -3.4 (2C), 22.7 (3C), 23.7, 41.9, 52.0, 55.6, 55.8, 113.5, 126.5 (2C), 134.0 (2C), 134.5, 138.4, 141.4, 171.7; HRMS calcd for $C_{19}H_{31}NO_3SSi$ 381.1795, found 381.1782

Determination of enantiopurity of (*Rs,S*)-(-)-methyl *N*-(*tert*-butanesulfinyl)-3-amino-3-(4-allyldimethylsilyl)phenylpropanoate (8) by MPTA amide derivatization. To a solution of 7 (152 mg, 0.4 mmol) in MeOH (1 mL) was added 4 *N* HCl/dioxane (0.5 mL). After 5 min stirring, the solvent and HCl were removed under reduced pressure. To the crude amine solution in $CHCl_3$ (10 mL) was added pyridine (200 μL) followed by (*R*)-(-)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid chloride (75 mg, 0.3 mmol). The reaction solution was stirred for 2 h at room temperature. The solvent and excess pyridine were removed, and the crude oil was diluted with EtOAc (25 mL), washed (0.5 N HCl and brine) then dried. The organic layer was concentrated to obtain the MPTA amide derivative as a colorless oil (8, 124 mg, 83% based on MTPACl); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 6 H), 1.75 (d, J = 8.07 Hz, 2 H), 2.84 (dd, J = 9.90, 5.71 Hz, 1 H), 2.92 (dd, J = 8.70, 6.75 Hz, 1 H), 3.40 (s, 3 H), 3.80 (s, 3 H), 4.84 (s, 1 H), 4.88 (m, 1 H), 5.46 (m, 1 H), 5.77 (ddt, J = 16.53, 10.81, 8.10 Hz, 1 H), 7.30 (d, J = 7.80 Hz, 2 H), 7.39-7.43 (3 H), 7.50 (d, J = 7.80 Hz, 2 H), 7.54-7.58 (2 H), 7.76 (bd, J = 8.73 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) -3.3 (2C), 23.8, 28.1, 37.0, 39.8, 49.9, 52.1, 55.2, 113.7, 125.8 (2C), 128.0, 128.8(2C), 129.7(2C), 132.7, 134.4 (2C), 134.7, 138.6, 140,8, 143.1, 156.3, 166.0, 171.4; ^{19}F NMR ($CDCl_3$) δ -69.15 (with $CFCl_3$ as an internal reference) Analysis of the ^{1}H NMR and ^{19}F NMR spectral integrations showed less than 1% of the minor diastereomer. HRMS calcd for $C_{25}H_{30}NO_4F_3Si$ 493.1897, found 493.1904.

Hydroboration and Suzuki coupling of (*Rs,S*)-(-)-methyl *N*-(*tert*-butanesulfinyl)-3-amino-3-(4-allyldimethylsilyl)phenylpropanoate (7) to the bromopolystyrene resin. To a solution of 7 (763 mg, 2 mmol) in dried THF (8 mL) under a N_2 atmosphere was added 9-BBN (4 mL, 0.5 M solution in THF, 2 mmol) dropwise at 0 ^{o}C. The mixture was allowed to gradually warm to room temperature and then was stirred for 5 h. $Pd(PPh_3)_4$ (70 mg), 4-bromopolystyrene (1.0 g, 1.94 mmol/g), 2 *N* aqueous Na_2CO_3 (2 mL, 4 mmol), and DMF (10 mL) were added. The reaction flask and reflux condenser were wrapped with aluminium foil, and the mixture was refluxed for 24 h. $Pd(PPh_3)_4$ (70 mg) was added to the reaction mixture, which was refluxed again for 24 h. The resin was filtered and washed with THF (once), 1:1 THF/water (twice), water (twice), methanol (twice), CH_2Cl_2 (twice), then dried under reduced pressure. To demonstrate that the compound had coupled to the resin, an aliquot of the resin (200 mg) was treated with a solution of thioanisole (100 μL) and 50% TFA/CH_2Cl_2 (7 mL) for 5 min followed by washing with CH_2Cl_2 (8 mL × 4). The resin was treated with a solution of Br_2 (150 μL) in CH_2Cl_2 (8 mL) for 20 min. The cleavage solution was filtered and the resin was rinsed with CH_2Cl_2 (3 mL). Concentration of the combined filtrates gave (3*R*)-methyl-3-amino-3-(4-bromophenyl)-butyrate (10, 16.5 mg, loading level was determined to be 0.32 mequiv/g); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.04 (dd, J = 16.20, 6.30 Hz, 1 H), 3.35 (dd, J = 16.20, 6.30 Hz, 1 H), 3.58 (s, 3 H), 4.82 (m, 1 H), 7.43-7.48 (4 H). HRMS calcd for $C_{10}H_{12}BrNO_2$ 257.0051 and 259.0031, found 257.0053 and 259.0034.

Reaction of the resin bound β-amino acid (9) to give tripeptides 12. An aliquot of the resin prepared above (800 mg, 0.32 mequiv/g, 0.26 mmol) was treated with a solution of thioanisole (200 μL) and 50% TFA/CH_2Cl_2 (18 mL) for 5 min. The

resin was washed with CH_2Cl_2 (18 mL × 4), DMF (18 mL × 4), and treated with Fmoc-*L*-Ala-OH (3.5 equiv.), EDC (3.5 equiv.), HOBT•H_2O (3.5 equiv.), and triethylamine (3.5 equiv.) in DMF (18 mL) for 16 h at room temperature. After successive washing with DMF, MeOH, CH_2Cl_2, and DMF, the resin was stirred in 20% piperidine/DMF (18 mL) for 30 min, then washed with DMF, MeOH, CH_2Cl_2, and DMF. Coupling of the *N*-terminal amino acid was performed with benzoic acid (3.5 equiv.), EDC (3.5 equiv.), HOBT•H_2O (3.5 equiv.), and triethylamine (3.5 equiv.) in DMF (18 mL) for 16 h at room temperature. The resin was washed with DMF, MeOH, CH_2Cl_2, THF, and heated to reflux with LiOH (5 equiv.) in THF/ H_2O (8:1, 20 mL) for 2.5 h. After washing with THF, H_2O, MeOH, CH_2Cl_2, and DMF, the resin was treated with NH_2-Gly-OEt•HCl (3.5 equiv.), EDC (3.5 equiv.), HOBT•H_2O (3.5 equiv.), and triethylamine (3.5 equiv.) in DMF (18 mL) for 16 h at room temperature. The resin was rinsed with DMF, 1:1 DMF/water, MeOH, and CH_2Cl_2 and dried under reduced pressure. An aliquot of the resin (200 mg) was treated with CH_2Cl_2/TFA (1:1, 14 mL) for 24 h at room temperature. The cleavage solution was separated, and the resin was rinsed with CH_2Cl_2 (3 mL) and MeOH (5 mL). Concentration of the combined filtrates gave a white solid (12a, 24 mg, 88%; purity was determined to be higher than 95% based on the ^{1}H NMR spectrum); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (t, J = 7.16 Hz, 2 H), 1.42 (d, J = 6.62 Hz, 3 H), 2.76 (m, J = 2 H), 3.74 (m, 1 H), 4.01 (m, 1 H), 4.02 (q, J = 7.16 Hz, 2 H), 4.74 (m, 1 H), 5.49 (m, 1 H), 7.20-7.76 (10 H), 7.77 (d, J = 7.20 Hz, 2 H), 8.34 (d, J = 7.51 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.1, 18.0, 41.6, 42.5, 50.1, 50.8, 61.9, 126.9 (2C), 127.5 (2C), 127.9, 128.7 (2C), 128.9 (2C), 132.2, 133.3, 140.4, 168.2, 170.5, 171.6, 173.0; HRMS (ES, M+1) calcd for $C_{23}H_{27}N_3O_5$ 426.2030, found 426.2024. Anal. calcd for $C_{23}H_{27}N_3O_5$: C, 64.93; H, 6.40; N, 9.88, found C, 64.74; H, 6.57; N, 9.76.

The same procedure as described above was performed except that the cleavage of the final product was carried out with Br_2 (100 μL) in CH_2Cl_2 (8 mL) for 20 min. The cleavage solution was separated, and the resin was rinsed with CH_2Cl_2 (3 mL) and MeOH (5 mL). Concentration of the combined filtrates gave a white solid (12b, 30 mg, 94%; purity was determined to be higher than 95% based on the ^{1}H NMR spectrum); ^{1}H NMR (300 MHz, CD_3OD) δ 1.20 (t, J = 7.08 Hz, 3 H), 1.42 (d, J = 7.11 Hz, 3 H), 2.77 (dd, J = 6.63, 2.37 Hz, 2 H), 3.82 (s, 2 H), 4.10 (q, J = 7.08 Hz, 2 H), 4.56 (q, J = 7.15 Hz, 1 H), 5.30 (t, J = 6.89 Hz, 1 H), 7.26 (d, J = 8.46 Hz, 2 H), 7.43-7.56 (5 H), 7.87 (d, J = 6.87 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) 14.4, 18.3, 41.9, 42.4, 51.6, 51.9, 62.0, 122.3, 128.4 (2C), 128.6 (2C), 129.2 (2C), 131.1, 132.3 (2C), 133.6, 138.8, 169.1, 170.2, 172.6, 174.5; HRMS (ES, M+1) calcd for $C_{23}H_{27}BrN_3O_5$ 504.1135 and 506.1115, found 504,1153 and 506.1112. Anal. calcd for $C_{23}H_{26}BrN_3O_5$: C, 54.77; H, 5.20; N, 8.33, found C, 54.62; H, 5.14; N, 8.37.

The same procedure as described above was performed except that the cleavage of the final product was carried out with ICl (150 mg) in CH_2Cl_2 (8 mL) for 20 min. The cleavage solution was separated, and the resin was rinsed with CH_2Cl_2 (3 mL) and MeOH (5 mL). Concentration of the combined filtrates gave a white powder (12c, 30 mg, 95%; purity was determined to be higher than 95% based on the ^{1}H NMR spectrum); mp 181-185 ^{o}C; ^{1}H NMR (300 MHz, CD_3OD) δ 1.19 (t, J = 7.14 Hz, 3 H), 1.41 (d, J = 7.05 Hz, 3 H), 2.77 (dd, J = 6.72, 2.32 Hz, 2 H), 3.82 (s, 2 H), 4.09 (q, J = 7.14 Hz, 2 H), 4.55 (q, J = 7.17 Hz, 1 H), 5.29 (t, J = 6.72 Hz, 1 H), 7.12 (d, J = 8.13 Hz, 2 H), 7.44-7.57 (3 H), 7.65 (d, J = 8.28 Hz, 2 H), 7.87 (d, J = 6.99 Hz, 2 H); ^{13}C NMR (75 MHz, DMSO-d_6) 14.7, 18.5, 41.3, 41.9, 49.7, 50.0, 61.1, 128.2 (2C), 128.8 (2C), 129.5 (2C), 131.9, 134.9, 137.5 (2C), 138.1, 143.2, 166.9, 170.3, 170.4, 172.1; HRMS (EI) calcd for $C_{23}H_{26}IN_3O_5$ 551.0919, found 551.0920. Anal. calcd for $C_{23}H_{26}IN_3O_5$: C, 50.10; H, 4.75; N, 7.62, found C, 50.29; H, 4.92; N, 7.50.