Supporting Information

Preparation of 3. To an ice-cold solution of *N*-benzyl-3,4-isopropylidenedioxy-2,5-pyrrolidinedione (6.53 g, 25.0 mmol) in anhydrous THF (25.0 mL) was added a solution of 1M borane-THF (87.5 mL, 87.5 mmol). The resulting mixture was allowed to warm to room temperature and further stirred for 2.5 hours. The reaction was carefully quenched with methanol (25.0 mL) and concentrated to dryness. The residual crystalline material was then slurred in ethyl acetate/hexane (1:1, 20 mL), cooled to 0^{o}C, and filtered to give the borane-amine complex **5a** (5.01 g, 83%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.40-7.36 (m, 3H), 4.99 (m, 2H), 4.19 (s, 2H), 3.30 (dd, J = 5.5, 12.5 Hz, 2H), 3.25 (d, J = 12.5 Hz, 2H), 1.47 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5, 131.8, 129.2, 128.3, 113.6, 79.8, 65.2, 63.5, 26.5, 24.2.

Preparation of 4. A solution of borane-amine **3** (1.24 g, 5.00 mmol) in methanol (12.5 mL) was stirred at room temperature for 170 hours. The resulting solution was concentrated in vacuum and the residue was purified by flash chromatography using ether/pentane (1:1) to yield the free amine **4** (1.15 g, 99%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 5H), 4.64 (m, 2H), 3.61 (s, 3H), 3.03 (d, J = 11.5 Hz, 2H), 2.14 (m, 2H), 1.57 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 128.7, 128.5, 127.1, 111.4, 79.8, 59.9, 59.5, 26.7, 25.3.

Preparation of 1. To a suspension of 10% palladium on carbon (600 mg, 50% wet) in methanol (15 mL) was added a solution of borane-amine **3** (3.0 g, 12.0 mmol) in methanol (15 mL). The reaction vessel was immediately sealed and the mixture was stirred at room temperature for 12 hours. The crude reaction mixture was filtered through cotton and carefully concentrated under slight vacuum (200 mmHg). The residu was then purified by flash chromatography using methnol/dichloromethane (1:1) to yeild the secondary free-amine **1** (1.63 g, 94%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (s, 2H), 3.08 (d, J = 13.5 Hz, 2H), 2.48 (d, J = 13.5 Hz, 2H), 2.10 (s, 1H), 1.43 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 110.1, 81.8, 54.2, 26.5, 24.6.

Preparation of 5a. To an ice-cold solution of *t*-butyl *L*-prolinate (5.0 g, 29.0 mmol) in anhydrous THF (15.0 mL) was added a solution of 1M borane-THF (32.0 mL, 32.0 mmol). The resulting mixture was allowed to warm to room temperature and further stirred for 45 minutes. The reaction was carefully quenched with methanol (20.0 mL) and concentrated to dryness. The residual crystalline material was then slurried in ethyl acetate/hexane (1:9, 25 mL), cooled to 0^{o}C, and filtered to give the borane-amine complex **5a** (4.46 g, 83%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (brs, 1H), 3.61 (m, 1H), 3.33 (m, 1H), 2.87 (m, 1H), 2.30 (m, 1H), 2.01 (m, 1H), 1.95-1.05 (m, 6H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 83.8, 67.4, 55.1, 30.2, 28.1, 25.0.

Preparation of 5b. A mixture of pyrrolidine (83.0 mL, 990 mmol) and 2-(2-bromoethoxy) tetrahydro-2-*H*-pyran (15 mL, 99.0 mmol) was stirred at room temperature for 24 hours. The reaction mixture was then poured into a saturated aqueous sodium bicarbonate solution (100 mL) and extracted with ethyl acetate. The organic phase was washed with brine, dried ($MgSO_4$), filtered and concentrated. Flash chromatography of the residual material using methanol/dichloromethane (1:19) provided the alkylated pyrrolidine (18.2 g, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (m, 1H), 3.89-3.81 (m, 2H), 3.55-3.45 (m, 2H), 2.68 (t, J = 6.5 Hz, 2H), 2.56-2.52 (m, 4H), 1.83-1.45 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) 99.29, 66.83, 62.57, 55.89, 54.92, 30.86, 25.64, 23.64, 19.81. To an ice-cold solution of the foregoing pyrrolidine (13.3 g, 66.9 mmol) in anhydrous THF (65.0 mL) was added a solution of 1M borane-THF (74.0 mL, 74.0 mmol). The resulting solution was allowed to warm to room temperature and further stirred for 15 minutes. The reaction was carefully quenched with methanol (70.0 mL) and concentrated to dryness. The residual material was then purified by flash chromatography using ethyl acetate/hexane (3:7) to provide the borane-amine complex **5**b (13.2 g, 94%) as a colorless

oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (brs, 1H), 4.09 (m, 1H), 3.95-3.80 (m, 2H), 3.48 (t, J = 4.0 Hz, 1H), 3.19 (m, 2H), 2.96 (t, J = 6.0 Hz, 2H), 2.82 (m, 2H), 2.12 (m, 2H), 1.95-1.05 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 99.5, 63.9, 62.8, 62.5, 62.2, 30.8, 25.5, 22.9, 19.8.

Preparation of 5c. To an ice-cold solution of (*S*)-5-*t*-butyldimethylsilyloxymethylpyrrolidine[1] (4.00 g, 18.6 mmol) in anhydrous THF (20.0 mL) was added a solution of 1M borane-THF (28.0 mL, 28.0 mmol). The resulting mixture was allowed to warm to room temperature and further stirred for 30 minutes. The reaction was carefully quenched with methanol (35.0 mL) and concentrated to dryness. The residual material was then purified by flash chromatography using ethyl acetate/hexane (1:4) to provide the borane-amine complex **5c** (2.63 g, 62%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (brs, 1H), 4.00 (dd, J = 3.0, 11.0 Hz, 1H), 3.53 (dd, J = 2.0, 11.0 Hz, 1H), 3.26 (m, 1H), 2.98 (m, 1H), 2.81 (m, 1H), 2.0-1.0 (m, 7H), 0.83 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 66.8, 60.6, 55.6, 27.5, 26.0, 24.12, 18.4, -5.3.

Preparation of 5d. To an ice-cold solution of *N*-benzyl-(*S*)-5-*t*-butyldimethylsilyloxymethyl-2-pyrrolidi-none[2] (7.55 g, 23.7 mmol) in anhydrous THF (25.0 mL) was added a solution of 1M borane-THF (52.0 mL, 52.0 mmol). The resulting mixture was allowed to warm to room temperature and further stirred for 2.5 hours. The reaction was carefully quenched with methanol (50.0 mL) and concentrated to dryness. The residual material was then purified by flash chromatography using ethyl acetate/hexane (1:19) to provide the borane-amine complex **5d** (6.42 g, 85%) as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.35-7.32 (m, 3H), 4.42 (d, J = 13.5 Hz, 1H), 4.35 (dd, J = 8.0, 11.0 Hz, 1H), 4.13 (d, J = 13.5 Hz, 1H), 3.74 (dd, J = 4.5, 11.0 Hz, 1H), 3.09 (m, 1H), 3.01 (t, J = 8.5 Hz, 1H), 2.74 (q, J = 10.0 Hz, 1H), 2.09 (m, 1H), 1.80-1.20 (m, 6H), 0.93 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 131.7, 128.8, 128.3, 65.6, 64.1, 63.5, 60.0, 26.2, 25.9, 19.8, 18.5, -5.2.

Preparation of 5e. To an ice-cold solution of (*S*)-1-benzyl-2-pyrrolidinemethanol (6.5 mL, 36.7 mmol) in anhydrousTHF (20 mL) and DMF (20.0 mL) was added sodium hydride (1.61 g, 40.4 mmol, 60% dispersion in oil) and the resulting mixture was stirred at room temperature for 45 minutes. The reaction mixture was then cooled to 0^{o}C and chloromethyl methyl ether (3.07 mL, 40.4 mmol) was slowly added. After 8 hours of stirring at room temperature, the reaction mixture was cooled to 0^{o}C and quenched with a saturated aqueous ammonium chloride solution and extracted with ethyl acetate. The organic phase was washed with brine, dried ($MgSO_4$), filtered and concentrated. Flash chromatography of the residual material using ethyl acetate/hexane (1:4) provided the protected pyrrolidine (6.30 g, 73%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.22 (m, 5H), 4.63 (s, 2H), 4.10 (d, J = 13.0 Hz, 1H), 3.60 (dd, J = 5.0, 10.0 Hz, 1H), 3.50-3.38 (m, 2H), 3.36 (s, 3H), 2.95 (brt, J = 7.5 Hz, 1H), 2.75 (m, 1H), 2.22 (m, 1H), 1.95 (m, 1H), 1.76-1.65 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.31, 128.43, 127.15, 96.95, 71.02, 63.25, 59.70, 55.47, 54.77, 28.70, 22.89. To an ice-cold solution of the foregoing pyrrolidine (5.88 g, 25.0 mmol) in anhydrous THF (15.0 mL) was added a solution of 1M borane-THF (27.5 mL, 27.5 mmol). The resulting solution was allowed to warm to room temperature and further stirred for 3 hours. The reaction was carefully quenched with methanol (20.0 mL) and concentrated to dryness. The residual material was then purified by flash chromatography using ethyl acetate/hexane (1:4) to provide the borane-amine complex **5e** (5.56 g, 90%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 5H), 4.69 (dd, J = 6.0, 16.5 Hz, 2H), 4.36 (d, J = 13.5 Hz, 1H), 4.24 (dd, J = 7.5, 10.0 Hz, 1H), 4.13 (d, J = 13.5 Hz, 1H), 3.69 (dd, J = 5.0, 10.0 Hz, 1H), 3.43 (s, 3H), 3.15-3.00 (m, 2H), 2.78 (q, J = 10.0 Hz, 1H), 2.15-1.05 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.52, 131.34, 129.02, 128.46, 96.99, 67.91, 64.02, 63.61, 59.91, 55.84, 26.36, 19.96.

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