

## Supporting Material

**General.** Unless otherwise stated, all reactions were carried out under strictly anhydrous, air-free conditions. Formation of all ligand-metal complexes was done in a glove box under N<sub>2</sub>. All solvents were dried and distilled by standard procedures. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired on a Varian Unity 400 MHz Spectrometer. The <sup>1</sup>H (400 MHz) and <sup>13</sup>C chemical shifts (101 MHz) are given in parts per million (δ) with respect to internal TMS standards or residual solvent peaks. The <sup>13</sup>C NMR spectra were acquired with proton decoupling, and <sup>19</sup>F nondecoupling. FTIR spectra were recorded on a Bruker IFS-55 spectrometer and optical rotations were recorded on a Perkin Elmer 120 polarimeter at room temperature. Enantiomeric ratios were obtained using a Chiracel@ OD chiral HPLC column. All racemic standards were obtained prior to the catalyzed reaction products. The title α-imino ester **1a** was made from ethyl glyoxylate<sup>1</sup> and *N*-toluenesulfonylisocyanate (Aldrich) by Weinreb's procedure.<sup>2</sup> The silylimine **1b** was made by a modification of the reported procedure.<sup>3</sup> The enol silanes **2a-h** were made by standard protocols.<sup>4</sup> All other starting materials were purchased from Aldrich Chemical Company, except for (R)-Tol-BINAP which was purchased from Strem. Reported optical rotations are corrected to enantiomeric purity.

**Preparation of Ethyl-*N*-*tert*-butyldimethylsilyl imino ester (1a).** To a solution of ethyl glycine hydrochloride (2.8 g, 20 mmol) in THF (10 mL) was added triethylamine (4.5 g, 44 mmol) and 4-*N,N*-dimethylaminopyridine (25 mg, 0.2 mmol). The reaction mixture was cooled to 0 °C and a solution of *tert*-butyldimethylchlorosilane (3.0 g, 20 mmol) in THF (10 mL) was added over a 5 min period. The reaction was stirred for 12 h, diluted with diethyl ether (50 mL), and filtered. The filtrate was concentrated *in vacuo* and the crude residue was distilled under high vacuum yielding 3.7 g (85%) of *N-tert*-butyldimethylsilylglycine. To a stirred solution of this product in THF (30 mL) at 0 °C was added *tert*-butyl hypochlorite over 5 min. The reaction was stirred at 0 °C for 2 h and filtered through a coarse fritted funnel. The filtrate was concentrated *in vacuo*, weighed (4.0 g, 16.2 mmol) and dissolved in 30 mL of diethyl ether. The mixture was cooled to 0°C and a solution of freshly distilled DBU (2.0g, 16.2 mmol) in Et<sub>2</sub>O (5 mL) was added over a 5 min period. The reaction was stirred for 1 hour at 0°C and filtered. The filtrate was concentrated and the residue, >98% **1a** by <sup>1</sup>H NMR, was used without further purification.<sup>3</sup>

**General alkylation procedure using Ag(I), Cu(I), and Ni(II) complexes.** The metal BINAP complexes were formed by dissolving (R)-BINAP (25 mg, 0.04 mmol) or (R)-Tol-BINAP (with Cu(I)) and metal (Ag(I),

Ni(II)) perchlorate or hexafluoroantimonate (0.035 mmol) in THF (1-2 mL) and stirring at room temperature for 30 min. The  $\alpha$ -imino ester **1b** (100 mg, 0.40 mmol) was then added to the metal complex solution. The mixture was then placed under nitrogen in a  $-80^{\circ}\text{C}$  MeOH cryogenic bath (FTS Systems). A solution of the enol silane **2a** (83 mg, 0.43 mmol) in THF (0.5 mL) was added to the reaction mixture dropwise over 2 h. The reaction was stirred overnight at  $-80^{\circ}\text{C}$  to ensure complete reaction and was then quenched dropwise with MeOH (5 mL). Upon warming the quenched reaction to room temperature, it was diluted with water (10 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (2 x 10 mL). The combined organic layers were washed with saturated  $\text{NaHCO}_3$  (5 mL) and brine (5 mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. The crude residue (175 mg) was subject to column chromatography (20% EtOAc/hexanes) on a small silica gel plug yielding 138 mg of **4a** (95% yield). Recrystallization from ether/hexane afforded product in  $>99\%$  ee.

**General alkylation procedure for Pd(II) complexes.** The metal ligand complex was made by mixing (*R*-BINAP-PdCl<sub>2</sub> (Aldrich, 31 mg, 0.04 mmol) and AgClO<sub>4</sub> (15 mg, 0.076 mmol) in acetonitrile. The fluffy white precipitate (AgCl) was filtered off and the resulting acetonitrile solution was concentrated *in vacuo* leaving the (*R*)-BINAP-Pd(ClO<sub>4</sub>)<sub>2</sub> as a yellow crystalline solid. The solid was dissolved in  $\text{CH}_2\text{Cl}_2$  and used in an analogous manner to the aforementioned procedure.

**(*S*)-Ethyl-3-Benzoyl-2-(tosylamino)propanoate (4a).**<sup>5</sup> White crystalline solid mp =  $90\text{--}92^{\circ}\text{C}$ ;  $[\alpha]_{\text{D}} = +73.2^{\circ}$  ( $c = 1$ ,  $\text{CHCl}_3$ ); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.86 (d, 2H), 7.76 (d, 2H), 7.58 (t, 1H), 7.42 (t, 2H), 7.22 (d, 2H), 5.79 (d, 1H), 4.22 (m, 1H), 4.03 (q, 2H), 3.60 (m, 2H), 2.39 (s, 3H), 1.08 (t, 3H) ppm; <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  196.9, 170.3, 143.6, 137.0, 135.9, 133.8, 129.7, 128.7, 128.1, 127.2, 62.1, 51.9, 42.1, 21.6, 13.8 ppm; IR ( $\text{CH}_2\text{Cl}_2$ ): 3354, 1741, 1682; HPLC (10% EtOH/Hexane, 1.4 mL/min) (*R*) = 12.44, (*S*) = 14.09 min. Anal. Calcd for  $\text{C}_{19}\text{H}_{21}\text{NO}_5\text{S}$ : C, 60.78; H, 5.64; N, 3.73. Found C, 60.53; H, 5.61; N, 3.69.

**Absolute Configuration of 4a.** (*S*)-Ethyl-3-Benzoyl-2-(tosylamino)propanoate (**4a**) was made independently by Wessig et al. from (*S*)-aspartic acid.<sup>5</sup> This material possessed an almost identical optical rotation to our synthetic material ( $[\alpha]_{\text{D}} = +74.1^{\circ}$  ( $c = 1.0$ ,  $\text{CHCl}_3$ )). The absolute configuration of the other products was then based on analogy to this case (sign of optical rotation, HPLC elution times were consistent with stereoregularity).

**(*S*)-Ethyl-3-(4-Methoxybenzoyl)-2-(tosylamino)propanoate (4b).** White crystalline solid mp =  $98\text{--}100^{\circ}\text{C}$ ;  $[\alpha]_{\text{D}} = +58.0^{\circ}$  ( $c = 0.147$ ,  $\text{CHCl}_3$ ); <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.82 (d, 2H), 7.75 (d, 2H), 7.24 (d, 2H), 6.88 (d,

2H), 5.82 (d, 1H), 4.23 (m, 1H), 4.02 (q, 2H), 3.82 (s, 3H), 3.56 (m, 2H), 2.38 (s, 3H), 1.06 (t, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  195.2, 170.3, 163.8, 143.3, 137.0, 130.3, 129.4, 128.8, 127.0, 113.7, 61.8, 55.4, 51.8, 41.6, 21.3, 13.7 ppm; IR ( $\text{CH}_2\text{Cl}_2$ ): 3354, 1741, 1674; HPLC (10% EtOH/Hexane, 1.4 mL/min) (*R*) = 18.63, (*S*) = 20.76 min. Anal. Calcd for  $\text{C}_{20}\text{H}_{23}\text{NO}_6\text{S}$ : C, 59.24; H, 5.72; N, 3.46. Found C, 59.00; H, 5.70; N, 3.50.

**(S)-Ethyl-3-pivaloyl-2-(tosylamino)propanoate (4c).** Colorless oil;  $[\alpha]_{\text{D}} = +60.4^\circ$  ( $c = 0.12$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.71 (d, 2H), 7.28 (d, 2H), 5.60 (d, 1H), 4.00 (m, 3H), 3.10 (m, 2H), 2.41 (s, 3H), 1.07 (s, 9H), 1.05 (t, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  213.4, 170.3, 143.5, 136.8, 129.5, 127.1, 61.9, 51.7, 43.7, 40.5, 26.0, 21.4, 13.8 ppm; IR ( $\text{CH}_2\text{Cl}_2$ ): 3359, 1739, 1705; HPLC (5% iPrOH/Hexanes, 1.0 mL/min) (*R*) = 19.01, (*S*) = 20.91 min. Anal. Calcd for  $\text{C}_{17}\text{H}_{25}\text{NO}_5\text{S}$ : C, 57.44; H, 7.09; N, 3.94. Found C, 57.31; H, 7.02; N, 3.99.

**(S)-Ethyl-3-(4-dimethylaminobenzoyl)-2-(tosylamino)propanoate (4d).** White crystalline solid mp = 121-124 °C;  $[\alpha]_{\text{D}} = +70.4^\circ$  ( $c = 0.117$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.70 (m, 4H), 7.20 (d, 2H), 6.58 (d, 2H), 5.85 (d, 1H), 4.21 (m, 1H), 3.97 (q, 2H), 3.43 (dq, 2H), 3.00 (s, 6H), 2.36 (s, 3H), 1.04 (t, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  194.4, 170.7, 153.6, 143.3, 137.2, 130.3, 129.4, 127.1, 123.6, 110.5, 61.7, 52.1, 41.1, 39.9, 21.4, 13.8 ppm; IR ( $\text{CDCl}_3$ ): 3376, 1736, 1657; HPLC (10% EtOH/Hexane, 1.4 mL/min) (*R*) = 29.75, (*S*) = 31.96 min. Anal. Calcd for  $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_5\text{S}$ : C, 60.26; H, 6.27; N, 6.70. Found C, 60.18; H, 6.27; N, 6.61.

**(S)-Ethyl-3-(4-fluorobenzoyl)-2-(tosylamino)propanoate (4e).** White crystalline solid mp = 100-102 °C;  $[\alpha]_{\text{D}} = +17.9^\circ$  ( $c = 0.021$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.84 (m, 2H), 7.72 (d, 2H), 7.22 (d, 2H), 7.09 (t, 2H), 5.78 (bs, 1H), 4.22 (m, 1H), 4.00 (q, 2H), 3.58 (m, 2H), 2.39 (s, 3H), 1.08 (t, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  195.2, 170.2, 166.0 (d,  $J_{\text{C-F}} = 255.8$ ), 143.5, 136.8, 132.2, 130.8 (d,  $J_{\text{C-F}} = 9.2$  Hz), 129.5, 127.1, 115.8 (d,  $J_{\text{C-F}} = 22.0$  Hz), 62.0, 51.8, 41.9, 21.4, 13.7 ppm; IR ( $\text{CDCl}_3$ ): 3380, 1737, 1688; HPLC (10% EtOH/Hexane, 1.4 mL/min) (*R*) = 13.15, (*S*) = 16.44 min. Anal. Calcd for  $\text{C}_{19}\text{H}_{20}\text{FNO}_5\text{S}$ : C, 58.00; H, 5.13; N, 3.56. Found C, 57.86; H, 5.23; N, 3.55.

**(S)-Ethyl-3-(4-chlorobenzoyl)-2-(tosylamino)propanoate (4f).** White crystalline solid mp = 106-108 °C;  $[\alpha]_{\text{D}} = +32.9^\circ$  ( $c = 0.059$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.78 (d, 2H), 7.73 (d, 2H), 7.41 (d, 2H), 7.23 (d, 2H), 5.76 (d, 1H), 4.23 (m, 1H), 4.02 (q, 2H), 3.58 (m, 2H), 2.40 (s, 3H), 1.08 (t, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  195.6, 170.1, 143.6, 140.2, 136.8, 134.1, 129.6, 129.4, 129.0, 127.1, 62.1, 51.7, 41.9, 21.4, 13.8 ppm; IR ( $\text{CDCl}_3$ ): 3376, 1738, 1685; HPLC (10% EtOH/Hexane, 1.4 mL/min) (*R*) = 13.02, (*S*) = 17.07 min. Anal. Calcd for  $\text{C}_{19}\text{H}_{20}\text{ClNO}_5\text{S}$ : C, 55.74; H, 4.93; N, 3.42. Found C, 55.58; H, 4.88; N, 3.45.

**(S)-Ethyl-2-(tosylamino)-3-(4-trifluoromethylbenzoyl)propanoate (4g).** White crystalline solid mp = 114-117 °C;  $[\alpha]_D = +41.0^\circ$  ( $c = 0.087$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.98 (d, 2H), 7.75 (m, 4H), 7.25 (d, 2H), 5.75 (d, 1H), 4.24 (m, 1H), 4.07 (q, 2H), 3.62 (d, 2H), 2.40 (s, 3H), 1.10 (t, 3H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  196.0, 170.0, 143.7, 138.3, 136.8, 135.1 (q,  $J_{\text{C-F}} = 30.5$  Hz), 129.7, 128.4, 127.2, 125.8 (q,  $J_{\text{C-F}} = 3.6$  Hz), 120.4 (q,  $J_{\text{C-F}} = 281.4$  Hz), 62.2, 51.7, 42.3, 21.4, 13.8 ppm; IR ( $\text{CH}_2\text{Cl}_2$ ): 3354, 1741, 1694; HPLC (10% EtOH/Hexane, 1.4 mL/min) (*R*) = 13.30, (*S*) = 18.42 min. Anal. Calcd for  $\text{C}_{20}\text{H}_{20}\text{F}_3\text{NO}_5\text{S}$ : C, 54.16; H, 4.55; N, 3.16. Found C, 53.90; H, 4.66; N, 3.07.

**(S)-Ethyl-3-( $\beta$ -naphthoyl)-2-(tosylamino)propanoate (4h).** White crystalline solid mp = 100-104 °C;  $[\alpha]_D = +42.5^\circ$  ( $c = 0.066$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.31 (s, 1H), 7.80 (m, 6H), 7.53 (m, 2H), 7.21 (d, 2H), 5.82 (d, 1H), 4.34 (m, 1H), 4.08 (q, 2H), 3.80 (m, 2H), 2.38 (s, 3H), 1.10 (t, 3H) ppm;  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  196.7, 170.3, 143.4, 136.9, 135.7, 133.1, 132.2, 130.1, 129.5, 128.8, 128.4, 127.7, 127.1, 126.9, 123.3, 62.0, 51.9, 41.9, 21.3, 13.7 ppm; IR ( $\text{CH}_2\text{Cl}_2$ ): 3354, 1741, 1684; HPLC (10% EtOH/Hexane, 1.4 mL/min) (*R*) = 11.39, (*S*) = 12.70 min. Anal. Calcd for  $\text{C}_{23}\text{H}_{23}\text{NO}_5\text{S}$ : C, 64.92; H, 5.45; N, 3.29. Found C, 64.75; H, 5.42; N, 3.33.

**Deprotection of  $\gamma$ -oxo- $\alpha$ -tosylamino ester 4a.**<sup>6</sup> The  $\gamma$ -oxo amino ester (*R*)-**4a** (100 mg, 0.27 mmol) was refluxed with phenol (200 mg, 2.1 mmol) in 33% HBr/AcOH (2 mL) for 12 h. Water (2 mL) was added to the mixture which was then heated to 50 °C for 1 h. The reaction mixture was then concentrated *in vacuo* to about 0.5 mL. The product was isolated by ion exchange [Amberlite IR-120 (Plus) resin] and was characterized as L-3-(benzoyl)alanine (40 mg, 75%).<sup>7</sup> The optical rotation ( $[\alpha]_D = +43.9^\circ$  ( $c = 0.10$ , 6N HCl) indicated no detectable racemization.

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