Asymmetric Alkylation of *tert*-Butyl Glycinate Schiff Base with Chiral Quaternary Ammonium Salt under Micellar Conditions

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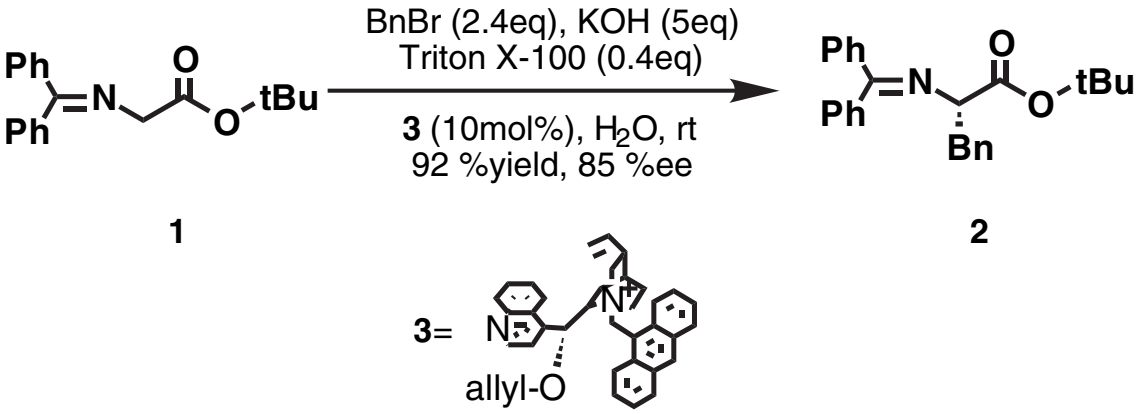
Supporting information



Representative Procedure for Catalytic Enantioselective Alkylation of *tert*-Butyl Glycinate-Benzophenone Schiff Base 1 under Phase Transfer Conditions in Water (Benzylation): To a mixture of **1** (50 mg, 0.17 mmol), *O*(9)-Allyl-*N*-9-anthracenylmethylcinchonidium bromide **3** (1 mol%, 1.0 mg) and Triton X-100 (0.4 eq, 45 mg) in aqueous 1N KOH solution (0.85 ml) was added benzyl bromide (2.4 eq, 0.048 ml) at room temperature. The reaction mixture was stirred vigorously at the same temperature for 24 hr. The mixture was then extracted with ethyl acetate three times. The organic extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (ether/hexane = 1:10) gave the alkylation product **2** (R = CH_2Ph) (60.3 mg, 92% yield) as a colorless oil. The enantiomeric excess was determined by chiral HPLC analysis [DAICEL CHIRALCEL OD, hexane:isopropanol = 99:5, flow rate = 0.5 ml/min, retention time; *R*-**2** (minor): 15 min and *S*-**2** (major) : 27 min].

2 (R = benzyl): *Anal.* Calcd. for $C_{26}H_{27}NO_2$: C, 81.01; H, 7.06; N, 3.63. Found: C, 81.12; H, 7.14; N, 3.59. $[\alpha]^{D}_{22}$ −185 (*c* = 0.91, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.37-7.24 (m, 6H), 7.20-7.13 (m.3H), 7.05 (d, *J* = 6.7 Hz, 2H), 6.60 (d, *J* = 4.6 Hz, 2H), 4.11 (dd, *J* = 4.0, 9.2 Hz, 1H), 3.23 (dd, *J* = 4.3, 13.4 Hz, 1H), 3.16 (dd, *J* = 9.5, 13.1 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.8, 170.3, 139.5, 138.3, 136.3, 130.1, 129.8, 128.7, 128.2, 128.05, 128.02, 127.9, 127.6, 126.1, 81.1, 67.9, 39.6, 28.0; IR ($CHCl_3$) 3019, 2360, 1727, 1212 cm^{-1}; MS (FAB^+) 386 (MH, 100), 330, 284.

2 (R = 4-fluorobenzyl): *Anal*. Calcd. for $C_{26}H_{26}FNO_2$: C, 77.39; H, 6.49; N, 3.47. Found: C, 77.44; H, 6.78; N, 3.35. $[\alpha]^{D}_{23}$ −185.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (br d, *J* = 7.0 Hz, 2H), 7.39-7.29 (m, 6H), 7.03-7.00 (m, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 5.2 Hz, 2H), 4.08 (dd, *J* = 4.3, 9.1 Hz, 1H), 3.19 (dd, *J* = 4.3, 13.4 Hz, 1H), 3.13 (dd, *J* = 9.0, 13.6 Hz, 1H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.7, 170.4, 139.4, 136.3, 131.3, 131.2, 130.2, 128.7,

128.3, 128.1, 128.0, 127.6, 114.9, 114.7, 81.2, 67.8, 38.7, 28.0; IR ($CHCl_3$) 2980, 1727, 1215 cm^{-1}; MS (FAB^+) 404 (MH), 348, 302, 154 (100).

2 (R = propargyl): $[\alpha]^D_{21}$ −75.6 (*c* = 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (br d, *J* = 7.3, 2H), 7.46-7.32 (m, 6H), 7.27-7.25 (m, 2H), 4.17 (dd, *J* = 5.1, 8.2 Hz, 1H), 2.84-2.73 (m, 2H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR($CDCl_3$, 126 MHz) δ 171.4, 169.5, 139.6, 136.2, 130.3, 128.9, 128.6, 128.3, 128.2, 128.0, 81.6, 81.2, 70.0, 64.7, 28.0, 23.3; IR ($CHCl_3$) 3308, 1728, 1154 cm^{-1}; MS (FAB^+) 334 (MH), 278, 154 (100). HRMS (FAB^+) Calcd. for $C_{22}H_{24}NO_2$: 334.1807. Found: 334.1805.

2 (R = allyl): *Anal*. Calcd. for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.78; H, 7.77; N, 3.89. $[\alpha]^D_{21}$ −80.4 (*c* = 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.65-7.63 (br d, *J* = 7.1 Hz, 2H), 7.44-7.16 (m, 8H), 5.76-5.68 (m, 1H), 5.07 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.01 (dt, *J* = 10.1, 0.9 Hz, 1H), 4.07 (dd, 7.6, 5.2 Hz, 1H), 2.69-2.58 (m, 2H), 1.44 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.9, 170.1, 139.7, 136.6, 134.7, 130.1, 128.8, 128.5, 128.4, 127.94, 127.92, 117.2, 81.0, 65.8, 38.1, 28.0; IR ($CHCl_3$) 3063, 3010, 2981, 2929, 1727, 1624, 1577, 1446, 1369, 1315, 1283 cm^{-1}; MS (FAB^+) 336 (MH), 280 (100), 234.

2 (R = CH_2-2-naphthyl): *Anal*. Calcd. for $C_{30}H_{29}NO_2$: C, 82.73; H, 6.71; N, 3.22. Found: C, 82.66; H, 6.54; N, 3.23. $[\alpha]^D_{18}$ −141.7 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.76-7.7.74 (m, 1H), 7.67-7.64 (m, 2H), 7.55 (br d, *J* = 8.5 Hz, 2H), 7.50 (s, 1H), 7.40-7.25 (m, 6H), 7.20-7.14 (m, 3H), 6.53 (br s, 2H), 4.24 (dd, *J* = 4.1, 9.3 Hz, 1H), 3.41 (dd, *J* = 4.1, 13.6 Hz, 1H), 3.32 (dd, *J* = 9.5, 13.5 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR($CDCl_3$, 126 MHz) δ 170.8, 170.4, 139.5, 136.2, 135.9, 133.4, 132.0, 130.0, 128.7, 128.3, 128.22, 128.15, 127.94, 127.87, 127.6, 127.5, 127.4, 125.7, 125.2, 81.1, 67.8, 39.7, 28.0; IR ($CHCl_3$) 3059, 3015, 3008, 2982, 2931, 1725, 1151 cm^{-1}; MS (FAB^+) 436 (MH, 100), 380, 334.

2 (R = 4-(trifluoromethyl)benzyl): *Anal*. Calcd. for $C_{27}H_{26}F_3NO_2$: C, 71.51; H, 5.78; N, 3.09. Found: C, 71.25; H, 5.93; N, 2.98. $[\alpha]^D_{18}$ −135.2 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 1.2, 8.5 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.40-7.26 (m, 6H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.62 (br d, *J* = 5.5 Hz, 2H), 4.13 (dd, *J* = 4.3, 9.2 Hz, 1H), 3.27 (dd, *J* = 4.3, 13.4 Hz, 1H), 3.21 (dd, *J* = 9.2, 13.4 Hz, 1H), 1.45 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.6, 170.4, 142.7, 139.3, 136.1, 130.3, 130.1, 128.7, 128.4, 128.1, 128.0, 127.5, 125.0, 124.9, 81.5, 67.5, 39.3, 28.0; IR ($CHCl_3$) 3009, 2981, 2932, 1727, 1165 cm^{-1}; MS (FAB^+) 454 (MH), 398 (100), 352.

2 (R = cinnamyl): *Anal*. Calcd. for $C_{28}H_{29}NO_2$: C, 81.72; H, 7.10; N, 3.40. Found: C, 81.52; H, 7.19; N, 3.11. $[\alpha]^D_{13}$ −33.1 (*c* = 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.52-7.35 (m, 10H), 7.31-7.23 (m, 3H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.20 (m, 1H), 4.20 (dd, *J* = 5.2, 7.6 Hz, 1H), 2.93 (dd, *J* = 6.7, 13.1 Hz, 1H), 2.87 (dd, *J* = 6.7, 14.5 Hz, 1H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 170.8, 170.2, 139.6, 137.4, 136.6, 132.4, 130.2, 128.8, 128.5, 128.41, 128.35, 128.0, 127.9, 127.0, 126.5, 126.0, 81.1, 66.1, 37.3, 28.1; IR ($CHCl_3$) 3020, 3012, 2980, 1255, 1622, 1152 cm^{-1}; MS (FAB^+) 412 (MH, 100), 356, 310.