SUPPORTING INFORMATION

Synthesis of Pyrrolidines via Palladium(II)-Catalyzed Aerobic Oxidative Carboamination of Butyl Vinyl Ether and Styrenes with Allyl Tosylamides

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General considerations. All commercially available chemicals were used as received. ^1H and ^{13}C NMR spectra were recorded on Bruker or Varian 300 MHz spectrometers. The chemical shifts (δ) are given in parts per million relative to internal TMS (0.00 ppm for ^1H) or CDCl_3 (77.23 ppm for ^{13}C). Flash chromatography was performed on silica gel 60 (particle size 0.040-0.063mm, 230-400 mesh ASTM, purchased from Sorbent Technology).

General procedure for oxidative coupling of *N*-allyltosylamides with butyl vinyl ether. A typical procedure is given for the oxidative coupling of *N*-allyltosylamide with butyl vinyl ether. Into a custom vessel was weighed $\text{Pd}(\text{OAc})_2$ (0.0710 mmol, 15.9 mg), $\text{Cu}(\text{OAc})_2(\text{OH}_2)$ (0.0710 mmol, 14.2 mg), catechol (0.142 mmol, 15.6 mg), *N*-allyltosylamide (1.42 mmol, 300 mg) and 3 Å molecular sieves (312 mg, 44 mg/mL). The vessels were mounted into a custom 6-well parallel reactor mounted on a Large Capacity Mixer (Glas-Col) and the headspace was purged with molecular oxygen while gently vortexing for ca. 15 min. 7.10 mL anhydrous acetonitrile and butyl vinyl ether (1.49 mmol, 201 μL) were added sequentially via syringe. The reaction was vortexed under an oxygen atmosphere (1 atm) for 24 hours. Excess solvent was removed in vacuo, and the remaining black oil was loaded onto a silica gel column, which had been slurry-packed with 1:4 EtOAc:Hexanes (eluent) and 5% (by volume of slurry) triethylamine and washed with excess eluent to remove triethylamine prior to product loading. The product was isolated in a 76% yield.

General procedure for oxidative coupling of *N*-allyltosylamides with styrene substrates. A typical procedure is given for the oxidative coupling of *N*-crotyltosylamide with styrene. To a stir-bar-equipped 25 mL round-bottomed flask with a 14/20 ground glass joint was weighed $\text{Pd}(\text{OAc})_2$ (0.067 mmol, 14.9 mg), $\text{Cu}(\text{OC}(\text{O})\text{CF}_3)_2$ ($\text{Cu}(\text{TFA})_2$, 0.067 mmol, 19.3 mg), and *N*-crotyltosylamide (1.33 mmol, 300 mg). 3.56 mL of a 1:1 mixture of toluene and styrene was added via syringe, followed by methyl acrylate (0.67 mmol, 60 μL). The reaction was stirred in a fume hood open to the atmosphere at room temperature for 24 hours. The resultant black liquid was loaded directly onto a silica gel column which had been slurry-packed with toluene. The product was isolated by eluting with a gradient of ether in toluene, beginning with pure toluene and ending with 5% diethyl ether in toluene, to give a 97% yield.

Procedure for reduction of acetophenone side-product (methoxyacetophenone): purification of products arising from 2- and 4-vinylanisole. This procedure is conducted following the above procedure for product purification. The product/side product mixture was dissolved in ca. 150 mL diethyl ether. LiAlH_4 (2.66 mmol, 101 mg) was added to the stirred solution, and the reaction stirred for 15 minutes. Water (1 mL), 15% $\text{NaOH}_{(\text{aq})}$ (2 mL), and water (3 mL) were successively added, and the slurry was filtered over celite directly into a 250 mL separatory funnel. The organic layer was washed twice with water (ca. 100 mL) and once with brine (ca. 75 mL), dried over anhydrous MgSO_4 , and filtered. Volatile organic solvents were removed in vacuo to furnish pure product in 68% yield (2-(4-methoxyphenyl)-4-vinyl-1-tosylpyrrolidine) or 71% yield (2-(2-methoxyphenyl)-4-vinyl-1-tosylpyrrolidine).

Product characterization data.

2-*n*-butoxy-4-methylen-1-tosylpyrrolidine (S1). 76% yield (334 mg), clear light yellow oil. HRMS: m/z (ESI) calculated $[\text{MNa}]^+ = 332.1296$, measured 332.1299 ($\Delta = 0.9$ ppm). ^1H NMR (300 MHz, CDCl_3) δ 0.90 (t, $J = 7.6$ Hz, 3H), δ 1.34 (m, 2H), δ 1.52 (m, 2H), δ 2.29 (m, 1H), δ 2.41 (m, 4H), δ 3.47 (m, 1H), δ 3.69 (m, 1H), δ 3.92 (m, 2H), δ 4.94 (m, 2H), δ 5.30 (d, $J = 5.4$ Hz, 1H), δ 7.29 (m, 2H), δ 7.71 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 13.94, δ 19.36, δ 21.56, δ 31.51, δ 39.81, δ 50.76, δ 67.35, δ 90.11, δ 108.23, δ 127.36, δ 129.78, δ 136.22, δ 143.29, δ 143.65.

2-*n*-butoxy-4-vinyl-1-tosylpyrrolidine (S2). 87% yield (375 mg), clear light yellow oil, 1.4:1 mixture of diastereomers. HRMS: m/z (ESI) calculated $[\text{MNa}]^+ = 346.1453$, measured 346.1455 ($\Delta = 0.6$ ppm).

Diastereomer 1: ^1H NMR (300 MHz, CDCl_3) δ 0.9 (t, J = 7.1 Hz, 3H), δ 1.28-1.42 (m, 2H), δ 1.48-1.59 (m, 2H), δ 1.69 (ddd, J = 13.3, 6.4, 2.4 Hz, 1H), δ 2.05 (ddd, J = 14.8, 8.7, 6.1 Hz, 1H), δ 2.42 (s, 3H), δ 2.51 (m, 1H), δ 3.10 (dd, J = 11.3, 7.5 Hz, 1H), δ 3.42-3.51 (m, 1H), δ 3.59 (dd, J = 11.1, 7.7 Hz, 1H), δ 3.68-3.79 (m, 1H), δ 4.90 (m, 1H), δ 4.96 (m, 1H), δ 5.28 (dd, J = 6.0, 2.8 Hz, 1H), δ 5.78 (m, 1H), δ 7.30 (m, 2H), δ 7.73 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 13.97, δ 19.43, δ 21.59, δ 31.76, δ 39.33, δ 42.10, δ 52.27, δ 67.93, δ 91.08, δ 115.41, δ 127.34, δ 129.74, δ 137.43, δ 139.24, δ 143.54.

Diastereomer 2: ^1H NMR (300 MHz, CDCl_3) δ 0.92 (t, J = 7.3 Hz, 3H), δ 1.28-1.42 (m, 3H), δ 1.48-1.59 (m, 2H), δ 1.94 (dd, J = 12.4, 6.1 Hz, 1H), δ 2.42 (s, 3H), δ 2.87 (t, J = 9.9 Hz, 1H), δ 3.14 (m, 1H), δ 3.42-3.51 (m, 2H), δ 3.68-3.79 (m, 1H), δ 4.94 (m, 1H), δ 5.03 (dt, J = 15.8, 1.3 Hz, 1H), δ 5.18 (d, J = 4.9 Hz, 1H), δ 5.50 (ddd, J = 17.5, 10.1, 7.6 Hz, 1H), δ 7.30 (m, 2H), δ 7.73 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 13.97, δ 19.43, δ 21.59, δ 31.76, δ 39.33, δ 41.04, δ 52.09, δ 67.64, δ 90.43, δ 116.29, δ 127.52, δ 129.74, δ 135.85, δ 136.89, δ 143.59.

2-*n*-butoxy-4-isopropenyl-1-tosylpyrrolidine (S3). 80% yield (339 mg), clear light yellow oil, 1.3:1 mixture of diastereomers. HRMS: m/z (ESI) calculated $[\text{MNa}]^+ = 360.1609$, measured 360.1600 ($\Delta = 2.5$ ppm).

Diastereomer 1: ^1H NMR (300 MHz, CDCl_3) δ 0.92 (t, J = 7.2 Hz, 3H), δ 1.28-1.40 (m, 2H), δ 1.47-1.57 (m, 2H), δ 1.56 (m, 3H), δ 1.91 (dd, J = 12.3, 5.8 Hz, 1H), δ 2.18-2.27 (m, 1H), δ 2.43 (s, 3H), δ 2.93 (dd, J = 10.2, 9.2 Hz, 1H), δ 3.15 (m, 1H), δ 3.43-3.80 (m, 3H), δ 4.62 (m, 1H), δ 4.71 (m, 1H), δ 5.19 (d, J = 4.9 Hz, 1H), δ 7.29-7.33 (m, 2H), δ 7.72-7.77 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 13.96, δ 19.42, δ 20.56, δ 21.55, δ 31.71, δ 37.52, δ 43.33, δ 51.08, δ 67.62, δ 90.40, δ 111.17, δ 127.50, δ 129.69, δ 135.85, δ 143.55.

Diastereomer 2: ^1H NMR (300 MHz, CDCl_3) δ 0.90 (t, J = 7.2 Hz, 3H), δ 1.28-1.40 (m, 3H), δ 1.47-1.57 (m, 2H), δ 1.63 (m, 3H), δ 1.75 (m, 1H), δ 2.23-2.36 (m, 1H), δ 2.43 (s, 3H), δ 3.15 (dd, J = 11.3, 10.1 Hz, 1H), δ 3.43-3.80 (m, 3H), δ 4.65 (m, 1H), δ 4.72 (m, 1H), δ 5.32 (dd, J = 6.4, 3.9 Hz, 1H), δ 7.29-7.33 (m, 2H), δ 7.72-7.77 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 13.96, δ 19.39, δ 20.72, δ 21.55, δ 31.75, δ 37.87, δ 44.68, δ 50.87, δ 67.62, δ 91.12, δ 111.34, δ 127.24, δ 129.73, δ 137.30, δ 143.28.

2-phenyl-4-methylen-1-tosylpyrrolidine (S4). 50% yield (335 mg), light yellow solid. HRMS: m/z (ESI) calculated $[\text{MNa}]^+ = 336.1034$, measured 336.1041 ($\Delta = 2.1$ ppm). ^1H NMR (300 MHz, CDCl_3) δ 2.40 (s, 3H), δ 2.41-2.82 (m, 2H), δ 4.10 (m, 2H), δ 4.93 (m, 3H), δ 7.24 (m, 7H), δ 7.57 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.64, δ 29.86, δ 41.54, δ 52.67, δ 63.27, δ 108.32, δ 126.55, δ 127.56, δ 128.54, δ 129.68, δ 135.44, δ 142.20, δ 143.48, δ 143.55.

2-phenyl-4-vinyl-1-tosylpyrrolidine (S5). 97% yield (423 mg), yellow oil, 1.9:1 mixture of diastereomers. HRMS: m/z (ESI) calculated $[\text{MH}]^+ = 328.1371$, measured 328.1371 ($\Delta < 1$ ppm).

Diastereomer 1: ^1H NMR (300 MHz, CDCl_3) δ 1.67-1.81 (m, 1H), δ 1.91 (ddd, J = 12.4, 6.2, 2.1 Hz, 1H), δ 2.41 (s, 3H), δ 2.88 (m, 1H), δ 3.06 (t, J = 9.4 Hz, 1H), δ 3.75 (dd, J = 9.2, 7.1 Hz, 1H), δ 4.89 (dd, J = 8.4, 3.0 Hz, 1H), δ 4.92-5.03 (m, 2H), δ 5.51 (ddd, J = 17.2, 10.1, 7.1 Hz, 1H), δ 7.18-7.31 (m, 7H), δ 7.66-7.90 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.65, δ 40.66, δ 41.46, δ 53.72, δ 63.01, δ 116.45, δ 126.20, δ 127.20, δ 127.67, δ 128.45, δ 129.73, δ 134.94, δ 136.95, δ 143.04, δ 143.57.

Diastereomer 2: δ 1.67-1.81 (m, 1H), δ 2.35-2.44 (m, 2H), δ 2.40 (s, 3H), δ 3.27 (dd, J = 11.2, 10.0 Hz, 1H), δ 3.87 (m, 1H), δ 4.68 (dd, J = 9.5, 6.8 Hz, 1H), δ 4.92-5.03 (m, 2H), δ 5.61 (ddd, J = 17.3, 10.3, 6.8 Hz, 1H), δ 7.18-7.31 (m, 7H), δ 7.58-7.62 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.65, δ 42.68, δ 43.52, δ 54.59, δ 64.36, δ 116.54, δ 126.49, δ 127.34, δ 127.56, δ 128.50, δ 129.73, δ 135.67, δ 136.66, δ 142.73, δ 143.46.

2-isopropenyl-4-isopropenyl-1-tosylpyrrolidine (S6). 93% yield (398 mg), yellow oil, 1.6:1 mixture of diastereomers. HRMS: m/z (ESI) calculated $[\text{MNa}]^+ = 364.1347$, measured 364.1334 ($\Delta = 3.6$ ppm).

Diastereomer 1: ^1H NMR (300 MHz, CDCl_3) δ 1.59 (m, 3H), δ 1.71-1.94 (m, 2H), δ 2.42 (s, 3H), δ 2.84 (m, 1H), δ 3.09 (dd, J = 10.4, 9.2 Hz, 1H), δ 3.79 (dd, J = 8.9, 7.6 Hz, 1H), δ 4.60-4.76 (m, 2H), δ 4.93 (dd, J = 8.2, 1.7 Hz, 1H), δ 7.16-7.35 (m, 7H), δ 7.68-7.72 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.21, δ 21.67, δ 39.64, δ 42.84, δ 52.75, δ 63.01, δ 111.22, δ 126.23, δ 127.20, δ 127.69, δ 128.48, δ 129.76, δ 134.97, δ 143.04, δ 143.16, δ 143.59.

Diastereomer 2: ^1H NMR (300 MHz, CDCl_3) δ 1.65 (m, 3H), δ 1.71-1.94 (m, 1H), δ 2.29 (m, 1H), δ 2.35-2.43 (m, 1H), δ 2.41 (s, 3H), δ 3.35 (t, J = 11.0 Hz, 1H), δ 3.93 (ddd, J = 11.2, 7.3, 1.7 Hz, 1H), δ 4.60-4.76 (m, 3H), δ 7.16-7.35 (m, 7H), δ 7.59-7.63 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.38, δ 21.67, δ 42.27, δ 45.07, δ 53.75, δ 64.57, δ 111.28, δ 126.56, δ 127.40, δ 127.58, δ 128.54, δ 129.72, δ 135.79, δ 142.81, δ 143.16, δ 143.45.

2-(4-chlorophenyl)-4-vinyl-1-tosylpyrrolidine (S7). 94% yield (453 mg), yellow amorphous solid, 2.0:1 mixture of diastereomers. HRMS: m/z (ESI) calculated $[MNa]^+ = 384.0801$, measured 384.0791 ($\Delta = 2.6$ ppm).

Diastereomer 1: 1H NMR (300 MHz, $CDCl_3$) δ 1.77 (ddd, $J = 12.4, 10.8, 8.2$ Hz, 1H), δ 1.88 (ddd, $J = 12.4, 6.3, 2.5$, 1H), δ 2.43 (s, 3H), δ 2.85 (m, 1H), δ 3.04 (t, $J = 9.5$ Hz, 1H), δ 3.74 (dd, $J = 9.2, 8.4$ Hz, 1H), δ 4.84 (dd, $J = 8.1, 2.3$ Hz, 1H), δ 4.94-5.04 (m, 2H), δ 5.50 (ddd, $J = 17.3, 10.2, 7.2$ Hz, 1H), δ 7.14-7.32 (m, 6H), δ 7.65-7.69 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.58, 40.53, δ 41.31, δ 53.70, δ 62.34, δ 116.56, δ 127.56, δ 127.60, δ 128.50, δ 129.76, δ 132.84, δ 134.50, δ 136.58, δ 141.71, δ 143.75.

Diastereomer 2: 1H NMR (300 MHz, $CDCl_3$) δ 1.56-1.68 (m, 2H), δ 2.38 (m, 1H), δ 2.42 (s, 3H), δ 3.26 (dd, $J = 11.0, 9.9$ Hz, 1H), δ 3.86 (ddd, $J = 11.4, 7.2, 1.8$ Hz, 1H), δ 4.63 (ddd, $J = 9.6, 6.8$ Hz, 1H), δ 4.94-5.04 (m, 2H), δ 5.61 (ddd, $J = 17.2, 10.1, 6.7$ Hz, 1H), δ 7.14-7.32 (m, 6H), δ 7.58-7.62 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.58, δ 42.58, δ 43.31, δ 54.47, δ 63.69, δ 116.64, δ 127.49, δ 127.85, δ 128.55, δ 129.76, δ 132.90, δ 135.21, δ 136.38, δ 141.34, δ 143.67.

2-(4-methoxyphenyl)-4-vinyl-1-tosylpyrrolidine (S8). 95% yield (452 mg), clear tan oil, 1.9:1 mixture of diastereomers. HRMS: m/z (ESI) calculated $[MH]^+ = 358.1477$, measured 358.1474 ($\Delta < 1$ ppm).

Diastereomer 1: 1H NMR (300 MHz, $CDCl_3$) δ 1.64-1.78 (m, 1H), δ 1.89 (ddd, $J = 12.4, 6.2, 2.0$ Hz, 1H), δ 2.41 (s, 3H), δ 2.87 (m, 1H), δ 3.04 (t, $J = 9.2$ Hz, 1H), δ 3.76 (m, 1H), δ 3.78 (s, 3H), δ 4.84 (dd, $J = 8.0, 1.7$ Hz, 1H), δ 4.92-5.04 (m, 2H), δ 5.50 (ddd, $J = 17.3, 10.3, 7.4$ Hz, 1H), δ 6.76-6.86 (m, 2H), δ 7.13-7.30 (m, 4H), δ 7.65-7.69 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.56, δ 40.60, δ 41.40, δ 53.60, δ 55.31, δ 62.44, δ 113.74, δ 116.33, δ 127.25, δ 127.56, δ 129.66, δ 134.74, δ 135.08, δ 136.96, δ 143.47, δ 158.71.

Diastereomer 2: 1H NMR (300 MHz, $CDCl_3$) δ 1.64-1.78 (m, 1H), δ 2.31-2.45 (m, 2H), δ 2.40 (s, 3H), δ 3.26 (dd, $J = 10.9, 10.2$ Hz, 1H), δ 3.79 (s, 3H), δ 3.86 (m, 1H), δ 4.62 (dd, $J = 9.8, 7.1$ Hz, 1H), δ 4.92-5.04 (m, 2H), δ 5.62 (ddd, $J = 17.7, 10.1, 7.2$ Hz, 1H), δ 6.76-6.86 (m, 2H), δ 7.13-7.30 (m, 4H), δ 7.57-7.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.56, δ 42.43, δ 43.40, δ 54.39, δ 55.31, δ 62.44, δ 113.74, δ 116.33, δ 127.25, δ 127.56, δ 129.66, δ 134.60, δ 135.54, δ 136.68, δ 143.32, δ 158.83.

2-(2-methoxyphenyl)-4-vinyl-1-tosylpyrrolidine (S9). 87% yield (452 mg), clear tan oil, 2.4:1 mixture of diastereomers. HRMS: m/z (ESI) calculated $[MNa]^+ = 380.1296$, measured 380.1282 ($\Delta = 3.7$ ppm).

Diastereomer 1: 1H NMR (300 MHz, $CDCl_3$) δ 1.68-1.72 (m, 1H), δ 1.82-1.88 (m, 1H), δ 2.41 (s, 3H), δ 2.80 (m, 1H), δ 2.99 (t, $J = 9.9$ Hz, 1H), δ 3.75 (m, 1H), δ 3.78 (s, 3H), δ 4.89-5.04 (m, 2H), δ 5.16 (br. d, $J = 7.5$ Hz, 1H), δ 5.50 (ddd, $J = 17.5, 10.2, 7.2$ Hz, 1H), δ 6.81 (dd, $J = 8.2, 0.9$ Hz, 1H), δ 6.93 (td, $J = 7.4, 0.9$ Hz, 1H), δ 7.16-7.32 (m, 3H), δ 7.45-7.48 (m, 1H), δ 7.70-7.74 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.62, δ 39.90, δ 40.59, δ 53.72, δ 55.24, δ 58.82, δ 110.15, δ 116.21, δ 120.33, δ 127.32, δ 127.67, δ 129.70, δ 131.24, δ 134.76, δ 137.04, δ 143.43, δ 155.71.

Diastereomer 2: 1H NMR (300 MHz, $CDCl_3$) δ 1.68-1.72 (m, 1H), δ 2.29-2.49 (m, 2H), δ 2.34 (s, 3H), δ 3.27 (dd, $J = 10.6, 10.2$ Hz, 1H), δ 3.72 (s, 3H), δ 3.83 (m, 1H), δ 4.89-5.04 (m, 3H), δ 5.59 (ddd, $J = 17.8, 10.6, 7.1$ Hz, 1H), δ 6.76 (dd, $J = 8.2, 0.9$ Hz, 1H), δ 6.93 (td, $J = 7.4, 1.2$ Hz, 1H), δ 7.16-7.32 (m, 3H), δ 7.45-7.48 (m, 1H), δ 7.61-7.65 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.62, δ 40.97, δ 42.74, δ 54.27, δ 55.24, δ 59.77, δ 110.47, δ 116.21, δ 120.70, δ 127.56, δ 128.21, δ 129.58, δ 130.81, δ 135.63, δ 137.04, δ 143.21, δ 156.28.