

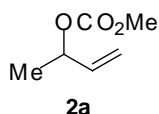
Representative Experimental Procedures and Characterization Data

(1R)-1-(Phenylprop-2-enyl)-(1S)-1-[(phenylmethoxy)methyl]prop-2-enyl-[(4-methylphenyl)sulfonyl]amine (9). Trimethyl phosphite (25 μ L, 0.42 mmol) was added directly to a red solution of Wilkinson's catalyst (0.046 g, 0.1 mmol, 10 mol%) in anhydrous THF (2.0 mL) at 30 °C, under an atmosphere of argon. The catalyst was allowed to form over *ca.* 30 minutes resulting in a light yellow homogeneous solution. The allylamine **1** (0.332 g, 1.0 mmol) was weighed into a flame dried, 10 mL, 1 neck round bottom flask, and dissolved in anhydrous THF (2 mL). The allylamine **1** was then placed under an atmosphere of argon and warmed to 30 °C. Lithium hexamethyldisilylazide (1.0 mL, 1.00 mmol, 1.0M solution in THF) was then added dropwise to the 30 °C solution of **1**, and the anion allowed to form over *ca.* 30 minutes. The anion solution was then transferred, *via* Teflon[®] cannula, to the rhodium catalyst and rinsed with anhydrous THF (2 x 0.5 mL). The optically active allylic carbonate (**R**)-**2b** (0.097 g, 0.51 mmol; $\geq 99\%$ *e.e.* by chiral HPLC analysis) was then added dropwise, *via* tared 250 μ L syringe to the preformed rhodium catalyst. The reaction was stirred at 30 °C for *ca.* 6 hours (t.l.c. control; 1:4 ethyl acetate/hexane), and then partitioned sequentially between diethyl ether and aqueous solutions of saturated NaHCO₃ and NaCl. The combined organic extracts were then dried (Na₂SO₄), filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash column chromatography (eluting with a 5-15% ethyl acetate/hexane gradient) furnished the *allylamines* **9/10** (0.195 g, 87%) as a clear oil: $[\alpha]_D^{18} = 3.7$ (*c* = 1.0, CHCl₃); HPLC analysis (Zorbax[®] Rx-Sil column) 2°:1° = 31:1, *ds* $\geq 99:1$; IR (CHCl₃) 3066 (m), 3031 (s), 2926 (m), 2866 (m), 1599 (w), 1496 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 7:1 mixture of rotamers) δ 7.69 (dt, *J* = 8.3, 1.9 Hz, 0.25H), 7.58 (dt, *J* = 8.3, 1.9 Hz, 1.75H), 7.33-7.18 (m, 10.25H), 7.13 (d, *J* = 8.1 Hz, 1.75H), 6.25 (ddd, *J* = 17.2, 10.4, 7.7 Hz, 0.88H), 5.90 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1H), 5.91-5.82 (m, 0.12H), 5.70 (d, *J* = 6.8 Hz, 0.12H), 5.36 (d, *J* = 7.7 Hz, 0.88H), 5.26 (dt, *J* = 10.4, 1.2 Hz, 0.12H), 5.20 (dt, *J* = 10.4, 1.1 Hz, 0.88H), 5.11 (dt, *J* = 17.1, 1.3 Hz, 1H), 4.97 (dt, *J* = 10.5, 1.2 Hz, 1H), 4.68 (dt, *J* = 17.4, 1.2 Hz, 1H), 4.44 (A of AB, *J*_{AB} = 11.9 Hz, 1H), 4.40 (B of AB, *J*_{AB} = 11.9 Hz, 1H), 4.08-4.06 (m, 1H), 3.87 (A of ABX, *J*_{AB} = 9.7 Hz, *J*_{AX} = 6.1 Hz, 1H), 3.72 (B of ABX, *J*_{AB} = 9.6 Hz, *J*_{BX} = 7.2 Hz, 1H), 2.40 (s, 0.38H), 2.34 (s, 2.62H); ¹³C NMR (100 MHz, CDCl₃) δ 142.79 (e), 138.82 (e), 138.56 (e), 137.95 (e), 135.66 (o), 135.57 (o), 129.13 (o), 128.86 (o), 128.46 (o), 128.25 (o), 128.00 (o), 127.69 (o), 127.55 (o), 127.45 (o), 118.60

(e), 118.11 (e), 72.97 (e), 71.69 (e), 63.54 (o), 60.30 (o), 21.45 (o); HRMS (FAB, M⁺+H) calcd for C₂₇H₃₀NO₃S 448.1946, found 448.1931.

(2*S*,5*R*)-1-(4-Methylphenylsulfonyl)-5-phenyl-2-[(phenylmethoxy)methyl]-3-pyrroline (3).

The diene **9** (0.223 g, 0.50 mmol) was weighed into a flame dried, 10 mL, 1 neck round bottom flask, and dissolved in anhydrous benzene (5 mL). The reaction flask was then equipped with a reflux condenser and placed under an atmosphere of nitrogen. RuCl₂(CHC₆H₅)(PCy₃)₂ (21 mg, 5.1 mol%), was then added in one portion and the reaction mixture heated at reflux for *ca.* 24 hours (t.l.c. control; 3:7 ethyl acetate/hexane). The reaction mixture was concentrated *in vacuo* to afford a crude oil. Purification by flash chromatography (eluting with a 20-25% ethyl acetate/hexane gradient) furnished the 2,5-disubstituted pyrroline **3** (18 mg, 86%) as a straw colored semi-solid: [α]_D¹⁸ = 4.9 (c = 1.0, CHCl₃); IR (CHCl₃) 3030 (m), 2925 (w), 2866 (w), 1599 (m), 1495 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dt, *J* = 8.3, 1.8 Hz, 2H), 7.36-7.18 (m, 12H), 5.84 (dt, *J* = 6.2, 2.1 Hz, 1H), 5.63 (dt, *J* = 6.2, 2.0 Hz, 1H), 5.44 (q, *J* = 2.1 Hz, 1H), 4.69-4.65 (m, 1H), 4.53 (A of AB, *J*_{AB} = 11.8 Hz, 1H), 4.50 (B of AB, *J*_{AB} = 11.8 Hz, 1H), 3.93 (dd, *J* = 9.2, 4.0 Hz, 1H), 3.62 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.50 (e), 140.60 (e), 137.99 (e), 134.88 (e), 130.06 (o), 129.57 (o), 128.36 (o), 128.34 (o), 128.18 (o), 127.78 (o), 127.71 (o), 127.67 (o), 127.62 (o), 127.45 (o), 73.81 (e), 73.55 (e), 70.91 (o), 66.95 (o), 21.50 (o); HRMS (FAB, M⁺+H) calcd for C₂₅H₂₆NO₂S 420.1633, found 420.1620.

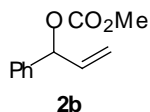


¹H NMR (400 MHz, CDCl₃) δ 5.86-5.77 (m, 1H), 5.25 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.18-5.12 (m, 2H), 3.73 (s, 3H), 1.33 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 155.05 (e), 137.01 (o), 116.43 (e), 75.12 (o), 54.49 (o), 19.92 (o).

IR (CHCl₃) 3091 (m), 3029 (s), 2989 (s), 2958 (s), 2937 (m), 1747 (s), 1648 (m) cm⁻¹.

HRMS (EI, M⁺) calcd for C₆H₁₀O₃ 130.0630, found 130.0619.

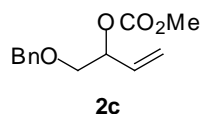


^1H NMR (400 MHz, CDCl_3) δ 7.38-7.27 (m, 5H), 6.08-5.98 (m, 2H), 5.38-5.24 (m, 2H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.97 (e), 138.22 (e), 135.72 (o), 128.57 (o), 128.38 (o), 127.02 (o), 117.43 (e), 80.15 (o), 54.76 (o).

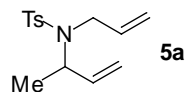
IR (CHCl_3) 3091 (m), 3068 (m), 3033 (s), 3017 (s), 3013 (s), 2958 (m), 1756 (s), 1646 (m) cm^{-1} .

HRMS (EI, M^+) calcd for $\text{C}_{11}\text{H}_{12}\text{O}_3$ 192.0786, found 192.0796.



^1H NMR (400 MHz, CDCl_3) δ 7.36-7.25 (m, 5H), 5.83 (ddd, $J = 17.1, 10.7, 6.4$ Hz, 1H), 5.38 (d, $J = 17.3$ Hz, 1H), 5.30 (dt, $J = 11.1, 6.2$ Hz, 1H), 5.27 (d, $J = 10.6$ Hz, 1H), 4.56 (s, 2H), 3.77 (s, 3H), 3.62-3.54 (m, 2H).

IR (CHCl_3) 3088 (w), 3064 (m), 3030 (m), 2956 (m), 2861 (m), 1748 (s), 1648 (m) cm^{-1} .



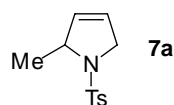
HPLC analysis (Zorbax[®] Rx-Sil column) 2 $^\circ$:1 $^\circ = \geq 99$:1.

^1H NMR (400 MHz, CDCl_3) δ 7.69 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 5.79 (dddd, $J = 16.8, 10.2, 6.4, 5.9$ Hz, 1H), 5.62 (ddd, $J = 17.4, 10.6, 4.8$ Hz, 1H), 5.15 (dq, $J = 17.1, 1.5$ Hz, 1H), 5.08-5.04 (m, 2H), 5.02 (ddd, $J = 7.0, 1.9, 1.1$ Hz, 1H), 4.56-4.49 (m, 1H), 3.81 (ddt, $J = 16.4, J = 5.8, J = 1.6$ Hz, 1H), 3.64 (ddt, $J = 16.4, J = 6.4, J = 1.4$ Hz, 1H), 2.39 (s, 3H), 1.19 (d, $J = 6.9$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.99 (e), 138.17 (e), 137.79 (o), 136.16 (o), 129.52 (o), 127.13 (o), 116.92(e), 116.73 (e), 54.88 (o), 46.34 (e), 21.46 (o), 17.72 (o).

IR (CHCl_3) 3082 (m), 3028 (s), 2986 (m), 2928 (m), 1641(w), 1599 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}$) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2\text{NaS}$ 288.1034, found 288.1048.

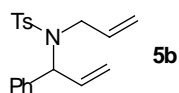


^1H NMR (400 MHz, CDCl_3) δ 7.70 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.28 (d, $J = 7.9$ Hz, 2H), 5.55 (dq, $J = 6.4, 1.7$ Hz, 1H), 5.52 (dq, $J = 6.4, 2.0$ Hz, 1H), 4.51-4.44 (m, 1H), 4.15 (ddt, $J = 14.7, 5.4, 1.8$ Hz, 1H), 4.05 (dq, $J = 14.7, 2.1$ Hz, 1H), 2.39 (s, 3H), 1.39 (d, $J = 6.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.30 (e), 134.81 (e), 131.48 (o), 129.66 (o), 127.39 (o), 123.78 (o), 63.07 (o), 55.30 (e), 22.82 (o), 21.50 (o).

IR (CHCl_3) 3017 (s), 2964 (m), 2929 (m), 2876 (m), 1595 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}$) calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2\text{NaS}$ 260.0721, found 260.0719.



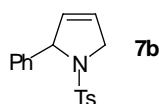
HPLC analysis (Zorbax[®] Rx-Sil column) 2^o:1^o = 32:1.

^1H NMR (400 MHz, CDCl_3) δ 7.69 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.29-7.21 (m, 7H), 6.02 (ddd, $J = 17.1, 10.3, 6.9$ Hz, 1H), 5.64 (d, $J = 7.0$ Hz, 1H), 5.45 (ddt, $J = 16.8, 10.3, 6.4$ Hz, 1H), 5.26 (dt, $J = 10.4, 1.2$ Hz, 1H), 5.12 (dt, $J = 17.1, 1.3$ Hz, 1H), 4.92-4.85 (m, 2H), 3.80 (ddt, $J = 16.3, 6.1, 1.4$ Hz, 1H), 3.70 (ddt, $J = 16.3, 6.6, 1.2$ Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.03 (e), 138.03 (e), 135.02 (o), 134.46 (o), 129.35 (o), 128.36 (o), 128.27 (o), 127.73 (o), 127.49 (o), 119.15 (e), 117.19 (e), 114.55 (e), 63.38 (o), 47.82 (e), 21.50 (o).

IR (CHCl_3) 3086 (m), 3029 (s), 3011 (m), 2926 (m), 1641 (s), 1599 (s) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}$) calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_2\text{NaS}$ 350.1191, found 350.1203.

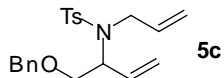


^1H NMR (400 MHz, CDCl_3) δ 7.49 (dt, $J = 8.3, 1.8$ Hz, 2H), 7.29-7.21 (m, 5H), 7.17 (d, $J = 8.2$ Hz, 2H), 5.77 (dq, $J = 6.1, 2.0$ Hz, 1H), 5.64 (dq, $J = 6.3, 2.2$ Hz, 1H), 5.52-5.49 (m, 1H), 4.33 (dq, $J = 14.5, 2.3$ Hz, 1H), 4.24 (ddt, $J = 14.5, 5.6, 2.1$ Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.10 (e), 140.42 (e), 135.48 (e), 130.59 (o), 129.42 (o), 128.43 (o), 127.78 (o), 127.25 (o), 127.21 (o), 124.47 (o), 70.21 (o), 55.37 (e), 21.47 (o).

IR (CHCl_3) 3027 (s), 2920 (w), 2867 (w), 1599 (m), 1494 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}$) calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_2\text{NaS}$ 322.0878, found 322.0862.



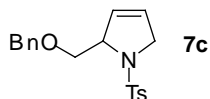
HPLC analysis (Zorbax[®] Rx-Sil column) 2°:1° = ≥99:1.

¹H NMR (400 MHz, CDCl₃) δ 7.71-7.65 (m, 2H), 7.33-7.20 (m, 5H), 7.16 (d, *J* = 8.2 Hz, 2H), 5.77-5.64 (m, 2H), 5.19-5.09 (m, 2H), 5.09 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.01 (dq, *J* = 10.2, 1.3 Hz, 1H), 4.66-4.61 (m, 1H), 4.44 (A of AB, *J*_{AB} = 11.8 Hz, 1H), 4.39 (B of AB, *J*_{BA} = 11.8 Hz, 1H), 3.93-3.77 (m, 1H), 3.77-3.70 (m, 1H), 3.63-3.55 (m, 2H), 2.64-2.36 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 142.92 (e), 138.04 (e), 135.79 (e), 133.85 (o), 129.67 (o), 129.32 (o), 128.32 (o), 127.70 (o), 127.64 (o), 127.44 (o), 118.84 (e), 117.07 (e), 72.90 (e), 70.41 (e), 59.21 (o), 47.53 (e), 21.51 (o).

IR (CHCl₃) 3029 (s), 3010 (m), 2925 (m), 2864 (m), 1642 (w), 1599 (m), 1496 (m) cm⁻¹.

HRMS (FAB, M⁺+H) calcd for C₂₁H₂₆NO₃S 372.1633, found 372.1628.

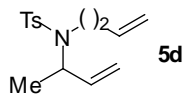


¹H NMR (400 MHz, CDCl₃) δ 7.68 (dt, *J* = 8.3, 1.7 Hz, 2H), 7.35-7.24 (m, 7H), 5.74 (dq, *J* = 6.4, 2.1 Hz, 1H), 5.66-6.64 (m, 1H), 4.55 (s, 2H), 4.53-4.49 (m, 1H), 4.15 (ddt, *J* = 14.8, 5.2, 2.1 Hz, 1H), 4.07 (dq, *J* = 14.8 Hz, 2.3 Hz, 1H), 3.89 (dd, *J* = 9.3, 3.8 Hz, 1H), 3.54 (dd, *J* = 9.3, 7.6 Hz, 1H), 2.39 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.56 (e), 138.13 (e), 134.20 (e), 129.73 (o), 128.51 (o), 128.37 (o), 127.63 (o), 127.45 (o), 125.57 (o), 73.65 (e), 73.57 (e), 66.43 (o), 55.80 (e), 21.53 (o).

IR (CHCl₃) 3030 (s), 2957 (s), 2926 (s), 2869 (s), 1599 (m) cm⁻¹.

HRMS (FAB, M⁺+H) calcd for C₁₉H₂₂NO₂S 344.1320, found 344.1344.



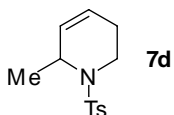
HPLC analysis (Zorbax[®] Rx-Sil column) 2°:1° = 23:1.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 5.71 (ddt, *J* = 17.2, 10.3, 6.9 Hz, 1H), 5.61 (ddd, *J* = 17.4, 10.7, 4.7 Hz, 1H), 5.09-4.98 (m, 4H), 4.52-4.45 (m, 1H), 3.14-2.98 (m, 2H), 2.47-2.24 (m, 2H), 2.40 (s, 3H), 1.17 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.01 (e), 138.03 (o), 135.02 (o), 129.58 (o), 127.09 (o), 116.68 (e), 116.57 (e), 54.50 (o), 43.35 (e), 35.96 (e), 21.48 (o), 17.30 (o).

IR (CHCl_3) 3067 (m), 3030 (s), 3012 (s), 2927 (m), 2864 (m), 1641 (m), 1599 (m) cm^{-1} .

HRMS (EI, $\text{M}^+\text{+H}$) calcd for $\text{C}_{15}\text{H}_{22}\text{NO}_2\text{S}$ 280.1371, found 280.1381.

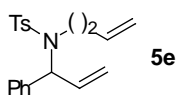


^1H NMR (400 MHz, CDCl_3) δ 7.68 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.23 (d, $J = 8.3$ Hz, 2H), 5.64-5.60 (m, 1H), 5.58-5.53 (m, 1H), 4.40-4.38 (m, 1H), 3.82-3.77 (m, 1H), 3.10 (ddd, $J = 14.1, 11.5, 4.3$ Hz, 1H), 2.38 (s, 3H), 1.94-1.85 (m, 1H), 1.81-1.74 (m, 1H), 1.21 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.91 (e), 138.50 (e), 129.54 (o), 129.46 (o), 126.84 (o), 124.35 (o), 49.50 (o), 37.75 (e), 23.68 (e), 21.50 (o), 20.37 (o).

IR (CHCl_3) 3086 (m), 3065 (m), 3029 (s), 3010 (m), 2925 (w), 1643 (w), 1599 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}^+$) calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2\text{NaS}$ 274.0878, found 274.0875.



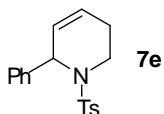
HPLC analysis (Zorbax[®] Rx-Sil column) 2^o:1^o = 44:1.

^1H NMR (400 MHz, CDCl_3) δ 7.70 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.31-7.24 (m, 7H), 5.93 (ddd, $J = 17.1, 10.6, 6.5$ Hz, 1H), 5.64 (d, $J = 6.4$ Hz, 1H), 5.46 (ddt, $J = 17.2, 10.3, 6.9$ Hz, 1H), 5.23 (dt, $J = 10.4, 1.3$ Hz, 1H), 5.02 (dt, $J = 17.2, 1.3$ Hz, 1H), 4.86 (ddt, $J = 10.3, 2.0, 1.0$ Hz, 1H), 4.79 (dq, $J = 17.1, 1.6$ Hz, 1H), 3.17 (A of ABXY, $J_{AB} = 14.8$ Hz, $J_{AX} = 11.0$ Hz, $J_{AY} = 5.5$ Hz, 1H), 3.06 (B of ABXY, $J_{AB} = 14.8$ Hz, $J_{BX} = 11.0$ Hz, $J_{BY} = 5.2$ Hz, 1H), 2.40 (s, 3H), 2.24-2.13 (m, 1H), 1.76-1.66 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 143.04 (e), 138.66 (e), 137.80 (e), 134.80 (o), 134.06 (o), 129.40 (o), 128.43 (o), 128.29 (o), 127.85 (o), 127.38 (o), 119.14 (e), 116.56 (e), 63.06 (o), 44.85 (e), 34.83 (e), 21.49 (o).

IR (CHCl_3) 3085 (m), 3060 (m), 3029 (s), 3015 (s), 2933 (w), 1641 (m), 1599 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}^+$) for $\text{C}_{20}\text{H}_{23}\text{NO}_2\text{NaS}$ 364.1347, found 364.1360.

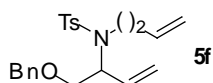


$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.41-7.38 (m, 2H), 7.32-7.24 (m, 3H), 7.19 (d, $J = 8.1$ Hz, 2H), 5.84-5.82 (m, 2H), 5.50 (bs, 1H), 3.74 (ddq, $J = 14.4, 6.2, 0.8$ Hz, 1H), 3.05 (ddd, $J = 14.4, 11.7, 4.6$ Hz, 1H), 2.38 (s, 3H), 2.05-1.92 (m, 1H), 1.87-1.80 (m, 1H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.96 (e), 139.64 (e), 138.17 (e), 129.38 (o), 128.31 (o), 128.17 (o), 127.66 (o), 126.98 (o), 126.29 (o), 126.03 (o), 55.88 (o), 38.20 (e), 23.23 (e), 21.44 (o).

IR (CHCl_3) 3030 (s), 3016 (w), 2930 (m), 1599 (m), 1494 (m), 1452 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+ + \text{Na}^+$) calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_2\text{NaS}$ 336.1034, found 336.1032.



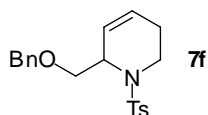
HPLC analysis (Zorbax[®] Rx-Sil column) $2^\circ:1^\circ = 35:1$.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.34-7.16 (m, 7H), 5.70-5.60 (m, 2H), 5.18-5.14 (m, 1H), 5.13-5.08 (m, 1H), 5.00-4.97 (m, 1H), 4.95-4.94 (m, 1H), 4.59 (qt, $J = 6.4, 1.5$ Hz, 1H), 4.47 (A of AB, $J_{AB} = 11.8$ Hz, 1H), 4.41 (B of AB, $J_{AB} = 11.8$ Hz, 1H), 3.60 (d, $J = 6.5$ Hz, 2H), 3.23 (A of ABXY, $J_{AB} = 14.8, J_{AX} = 10.5, J_{AY} = 5.6$ Hz, 1H), 3.09 (B of ABXY, $J_{AB} = 14.9, J_{BX} = 10.5, J_{BY} = 5.6$ Hz, 1H), 2.42-2.23 (m, 2H), 2.37 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.91 (e), 137.89 (e), 137.66 (e), 134.93 (o), 133.88 (o), 129.35 (o), 128.32 (o), 127.67 (o), 127.66 (o), 127.30 (o), 118.67 (e), 116.67 (e), 73.02 (e), 70.69 (e), 58.99 (o), 44.57 (e), 35.25 (e), 21.47 (o).

IR (CHCl_3) 3011 (s), 2926 (m), 2864 (m), 1641 (m), 1599 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+ + \text{H}$) calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_3\text{S}$ 386.1790, found 386.1811.



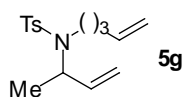
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.35-7.24 (m, 5H), 7.19 (d, $J = 8.0$ Hz, 2H), 5.80-5.73 (m, 1H), 5.72-5.66 (m, 1H), 4.53 (A of AB, $J_{AB} = 12.1$ Hz, 1H), 4.50-4.48 (m, 1H), 4.47 (B of AB, $J_{AB} = 12.1$ Hz, 1H), 3.82 (dd, $J = 14.2, 5.4$ Hz, 1H), 3.61 (A of ABX, $J_{AB} = 9.7$ Hz,

$J_{AX} = 5.5$ Hz, 1H), 3.54 (B of ABX, $J_{AB} = 9.7$ Hz, $J_{BX} = 5.8$ Hz, 1H), 3.20 (ddd, $J = 14.3, 11.5, 4.5$ Hz, 1H), 2.37 (s, 3H), 1.92-1.81 (m, 1H), 1.80-1.73 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.98 (e), 138.32 (e), 138.05 (e), 129.49 (o), 128.32 (o), 127.53 (o), 127.52 (o), 126.93 (o), 126.67 (o), 125.14 (o), 73.13 (e), 72.38 (e), 52.77 (o), 39.50 (e), 23.22 (e), 21.47 (o).

IR (CHCl_3) 3029 (s), 3016 (s), 2928 (m), 2862 (m), 1653 (w), 1599 (m), 1496 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}$) calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_3\text{NaS}$ 380.1296, found 380.1301.



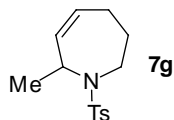
HPLC analysis (Zorbax[®] Rx-Sil column) 2°:1° = $\geq 99:1$.

^1H NMR (400 MHz, CDCl_3) δ 7.69 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.26 (d, $J = 8.3$ Hz, 2H), 5.75 (ddt, $J = 17.1, 10.3, 6.6$ Hz, 1H), 5.61 (ddd, $J = 17.3, 10.7, 4.7$ Hz, 1H), 5.08-4.93 (m, 4H), 4.51-4.44 (m, 1H), 3.10-2.93 (m, 2H), 2.40 (s, 3H), 2.04-1.97 (m, 2H), 1.85-1.56 (m, 2H), 1.17 (d, $J = 6.9$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.92 (e), 138.13 (o), 138.09 (e), 137.66 (o), 129.55 (o), 127.07 (o), 116.49 (e), 115.06 (e), 54.51 (o), 43.50 (e), 31.10 (e), 30.47 (e), 21.47 (o), 17.36 (o).

IR (CHCl_3) 3083 (m), 3028 (s), 2980 (s), 2941 (m), 1640 (m), 1599 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}$) calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_2\text{NaS}$ 316.1347, found 316.1363.

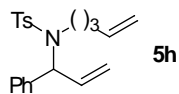


^1H NMR (400 MHz, CDCl_3) δ 7.68 (dt, $J = 8.3, 1.9$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 5.61 (A of ABXYZ, $J_{AB} = 11.5, J_{AX} = 7.0, J_{AY} = 4.5, J_{AZ} = 1.5$ Hz, 1H), 5.41 (B of ABXYZ, $J_{AB} = 11.3, J_{BX} = 5.0, J_{BY} = 2.0, J_{BZ} = 0.6$ Hz, 1H), 4.79-4.72 (m, 1H), 3.82-3.74 (m, 1H), 3.17 (dt, $J = 14.1, 6.0$ Hz, 1H), 2.39 (s, 3H), 2.23-2.12 (m, 1H), 2.03-1.95 (m, 1H), 1.88-1.76 (m, 1H), 1.75-1.61 (m, 1H), 1.08 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.76 (e), 138.35 (e), 132.22 (o), 129.48 (o), 129.45 (o), 126.88 (o), 53.09 (o), 42.59 (e), 27.74 (e), 24.81 (e), 21.46 (o), 18.42 (o).

IR (CHCl_3) 3085 (m), 3068 (m), 3029 (s), 3010 (m), 2985 (m), 2926 (m), 2864 (m), 1643 (w), 1599 (m) cm^{-1} .

HRMS (FAB, M^+Na) calcd for $C_{14}H_{19}NO_2NaS$ 288.1034, found 288.1036.



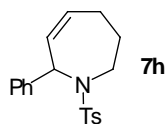
HPLC analysis (Zorbax[®] Rx-Sil column) $2^\circ:I^\circ = 89:1$.

1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, $J = 8.3, 1.8$ Hz, 2H), 7.30-7.20 (m, 7H), 5.94 (ddd, $J = 17.1, 10.5, 6.7$ Hz, 1H), 5.62 (d, $J = 6.6$ Hz, 1H), 5.58-5.48 (m, 1H), 5.23 (dt, $J = 10.4, 1.2$ Hz, 1H), 5.04 (dt, $J = 17.2, 1.3$ Hz, 1H), 4.86 (t, $J = 1.3$ Hz, 1H), 4.84-4.81 (m, 1H), 3.13-2.99 (m, 2H), 2.40 (s, 3H), 1.80-1.73 (m, 2H), 1.61-1.49 (m, 1H), 1.19-1.08 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.94 (e), 138.75 (e), 137.83 (e), 137.44 (o), 134.14 (o), 129.35 (o), 128.35 (o), 128.23 (o), 127.74 (o), 127.36 (o), 119.19 (e), 114.92 (e), 63.10 (o), 44.94 (e), 30.97 (e), 29.20 (e), 21.46 (o).

IR ($CHCl_3$) 3030 (s), 2981 (m), 2928 (m), 2871 (w), 1641 (m), 1600 (m) cm^{-1} .

HRMS (FAB, M^+Na) calcd for $C_{21}H_{25}NO_2NaS$ 378.1504, found 378.1518.

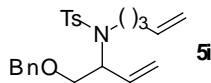


1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, $J = 8.3$ Hz, 2H), 7.30-7.23 (m, 7H), 5.97 (d, $J = 5.9$ Hz, 1H), 5.90-5.87 (m, 1H), 5.82-5.78 (m, 1H), 3.64-3.56 (m, 1H), 2.94 (dt, $J = 14.0, 5.0$ Hz, 1H), 2.41 (s, 3H), 2.07-1.99 (m, 1H), 1.89-1.80 (m, 1H), 1.56-1.46 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.85 (e), 138.44 (e), 138.19 (e), 132.88 (o), 129.32 (o), 128.77 (o), 128.33 (o), 128.00 (o), 127.41 (o), 127.15 (o), 59.02 (o), 44.10 (e), 26.33 (e), 26.31 (e), 21.46 (o).

IR ($CHCl_3$) 3013 (s), 2933 (s), 2884 (m), 1810 (w), 1654 (w), 1599 (s) cm^{-1} .

HRMS (FAB, M^+H) calcd for $C_{19}H_{22}NO_2S$ 328.1371, found 328.1391.



HPLC analysis (Zorbax[®] Rx-Sil column) $2^\circ:I^\circ = 84:1$.

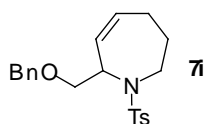
1H NMR (400 MHz, $CDCl_3$, 5:1 mixture of rotamers) δ 7.68 (d, $J = 8.3$ Hz, 1.67H), 7.65 (d, $J = 8.3$ Hz, 0.33H), 7.35-7.21 (m, 5H), 7.17 (d, $J = 7.9$ Hz, 2H), 5.87-5.75 (m, 0.33H), 5.74-5.61 (m,

1.67H), 5.15 (dt, $J = 10.7, 1.3$ Hz, 1H), 5.11 (dt, $J = 17.4, 1.4$ Hz, 1H), 5.00-4.91 (m, 2H), 4.60-4.55 (m, 1H), 4.46 (A of AB, $J_{AB} = 11.8$ Hz, 1H), 4.40 (B of AB, $J_{AB} = 11.9$ Hz, 1H), 3.59 (d, $J = 6.5$ Hz, 2H), 3.19-3.10 (m, 1H), 3.07-2.95 (m, 1H), 2.39 (s, 3H), 1.97-1.92 (m, 2H), 1.77-1.56 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.82 (e), 137.87 (e), 137.64 (e), 137.54 (o), 133.99 (o), 129.29 (o), 128.26 (o), 127.64 (o), 127.60 (o), 127.24 (o), 118.61 (e), 115.02 (e), 72.95 (e), 70.60 (e), 58.95 (o), 44.62 (e), 30.95 (e), 29.74 (e), 21.42 (o).

IR (CHCl_3) 3066 (m), 3029 (s), 3017 (s), 2927 (s), 2865 (s), 1641 (m), 1599 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}$) for $\text{C}_{23}\text{H}_{29}\text{NO}_3\text{NaS}$ 422.1766, found 422.1778.

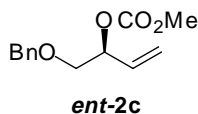


^1H NMR (400 MHz, CDCl_3) δ 7.71 (dt, $J = 8.3, 1.8$ Hz, 2H), 7.34-7.26 (m, 3H), 7.22-7.17 (m, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 5.80-5.74 (m, 1H), 5.55-5.50 (m, 1H), 4.97-4.92 (m, 1H), 4.43 (A of AB, $J_{AB} = 12.0$ Hz, 1H), 4.34 (B of AB, $J_{AB} = 12.0$ Hz, 1H), 3.77-3.69 (m, 1H), 3.52 (A of ABX, $J_{AB} = 10.3$ Hz, $J_{AX} = 8.0$ Hz, 1H), 3.45 (B of ABX, $J_{AB} = 10.3$ Hz, $J_{BX} = 5.4$ Hz, 1H), 3.18 (dt, $J = 14.4, 6.1$ Hz, 1H), 2.35 (s, 3H), 2.26-2.14 (m, 1H), 2.05-1.96 (m, 1H), 1.86-1.77 (m, 1H), 1.69-1.58 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 142.61 (e), 138.36 (e), 137.85 (e), 132.08 (o), 129.21 (o), 128.32 (o), 127.95 (o), 127.67 (o), 127.62 (o), 127.28 (o), 72.81 (e), 69.71 (e), 57.04 (o), 43.41 (e), 27.67 (e), 24.96 (e), 21.47 (o).

IR (CHCl_3) 2928 (s), 2362 (m), 2253 (s), 1670 (m), 1600 (w), 1558 (w) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+H}$) calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_3\text{S}$ 372.1633, found 372.1622.



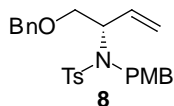
$[\alpha]_D^{19} = 4.7$ ($c = 1.0$, CHCl_3); Chiral HPLC analysis (Daicel[®] OD column) *e.e.* = $\geq 99\%$.

^1H NMR (400 MHz, CDCl_3) δ 7.36-7.25 (m, 5H), 5.83 (ddd, $J = 17.1, 10.7, 6.4$ Hz, 1H), 5.38 (d, $J = 17.3$ Hz, 1H), 5.30 (dt, $J = 11.1, 6.2$ Hz, 1H), 5.27 (d, $J = 10.6$ Hz, 1H), 4.56 (s, 2H), 3.77 (s, 3H), 3.62-3.54 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 155.16 (e), 137.78 (e), 132.66 (o), 128.37 (o), 127.69 (o), 127.61 (o), 118.73 (e), 76.68 (e), 73.22 (e), 71.11 (e), 54.75 (o).

IR (CHCl₃) 3088 (w), 3064 (m), 3030 (m), 2956 (m), 2861 (m), 1748 (s), 1648 (m) cm⁻¹.

HRMS (CI, M⁺) calcd for C₁₃H₂₀NO₄ 254.1392, found 254.1395.



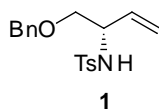
$[\alpha]_D^{18} = 3.6$ ($c = 1.01$, CHCl₃); HPLC analysis (Zorbax[®] Rx-Sil column) 2°:1° = 70:1.

¹H NMR (400 MHz, CDCl₃, 5.7:1 mixture of rotamers) δ 7.70 (dt, $J = 8.4, 1.7$ Hz, 0.3H), 7.68 (dt, $J = 8.3, 1.8$ Hz, 1.7H), 7.34-7.13 (m, 9 H), 6.84 (dt, $J = 8.7, J = 2.1$ Hz, 0.3H), 6.75 (d, $J = 8.7$ Hz, 1.7H), 5.53 (ddd, $J = 17.2, 10.6, 6.5$ Hz, 1H), 5.11 (dt, $J = 10.6, 1.2$ Hz, 1H), 4.99 (dt, 17.4, 1.3 Hz, 1H), 4.58-4.53 (q, $J = 6.8$ Hz, 1H), 4.42 (A of AB, $J_{AB} = 15.5$ Hz, 1H), 4.27 (s, 1H), 4.17 (B of AB, $J_{AB} = 15.5$ Hz, 1H), 3.78 (s, 0.45H), 3.76 (s, 2.55H), 3.47 (A of ABX, $J_{AB} = 9.9$ Hz, $J_{AX} = 7.0$ Hz, 1H), 3.31 (B of ABX, $J_{AB} = 9.9$ Hz, $J_{BX} = 6.8$ Hz, 1H), 2.44 (s, 0.45H), 2.38 (s, 2.55H).

¹³C NMR (100 MHz, CDCl₃) δ 158.94 (e), 142.93 (e), 137.97 (e), 137.79 (e), 133.77 (o), 129.61 (e), 129.59 (o), 129.37 (o), 128.23 (o), 127.63 (o), 127.54 (o), 127.51 (o), 127.29 (o), 119.21 (e), 113.95 (o), 113.61 (o), 72.77 (e), 70.57 (e), 59.39 (o), 55.22 (o), 48.09 (e), 21.50 (o).

IR (CHCl₃) 3031 (m), 3011 (m), 2935 (w), 2865 (m), 1612 (m), 1513 (s) cm⁻¹.

HRMS (FAB, M⁺+Na) calcd for C₂₆H₂₉NO₄NaS 474.1715, found 474.1707.



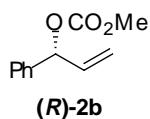
$[\alpha]_D^{18} = 5.9$ ($c = 1.01$, CHCl₃); Chiral HPLC analysis (Daicel[®] OD column) *e.e.* = $\geq 99\%$.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.35-7.20 (m, 7H), 5.68 (ddd, $J = 17.1, 10.5, 6.5$ Hz, 1H), 5.15 (dt, $J = 17.2, 1.2$ Hz, 1H), 5.08 (dt, $J = 10.4, 1.1$ Hz, 1H), 5.00 (d, $J = 6.6$ Hz, 1H), 4.39 (s, 2H), 3.93-3.87 (m, 1H), 3.40 (A of ABX, $J_{AB} = 9.5$ Hz, $J_{AX} = 5.4$ Hz, 1H), 3.36 (B of ABX, $J_{AB} = 9.5$ Hz, $J_{BX} = 4.7$ Hz, 1H), 2.39 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.25 (e), 137.56 (e), 137.37 (e), 135.11 (o), 129.49 (o), 128.42 (o), 127.85 (o), 127.64 (o), 127.21 (o), 117.45 (e), 73.13 (e), 71.73 (e), 55.71 (o), 21.50 (o).

IR (CHCl₃) 3382 (bm), 3030 (m), 2866 (m), 1599 (w), 1496 (m), cm⁻¹.

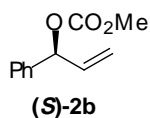
HRMS (FAB, M⁺+H) calcd for C₁₈H₂₂NO₂S 316.1371, found 316.1351.



$[\alpha]_D^{18} = -42.1$ ($c = 1.01$, CHCl_3); Chiral HPLC analysis (Daicel[®] OD column) *e.e.* = $\geq 99\%$.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38-7.27 (m, 5H), 6.08-5.98 (m, 2H), 5.38-5.24 (m, 2H), 3.76 (s, 3H).

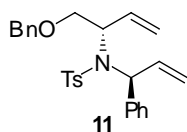
IR (CHCl_3) 3091 (m), 3068 (m), 3033 (s), 3017 (s), 3013 (s), 2958 (m), 1756 (s), 1646 (m) cm^{-1} .



$[\alpha]_D^{19} = 47.8$ ($c = 1.02$, CHCl_3); Chiral HPLC analysis (Daicel[®] OD column) *e.e.* = $\geq 99\%$.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38-7.27 (m, 5H), 6.08-5.98 (m, 2H), 5.38-5.24 (m, 2H), 3.76 (s, 3H).

IR (CHCl_3) 3091 (m), 3068 (m), 3033 (s), 3017 (s), 3013 (s), 2958 (m), 1756 (s), 1646 (m) cm^{-1} .



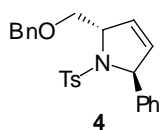
$[\alpha]_D^{18} = 3.7$ ($c = 1.0$, CHCl_3); HPLC analysis (Zorbax[®] Rx-Sil column) $2^\circ:1^\circ = 42:1$, $ds \geq 22:1$.

$^1\text{H NMR}$ (400 MHz, CDCl_3 , 10:1 mixture of rotamers) δ 7.73-7.70 (m, 0.18H), 7.67 (dt, $J = 8.3$, 1.9 Hz, 1.82H), 7.45-7.39 (m, 2H), 7.36-7.21 (m, 6H), 7.18-7.14 (m, 2H), 7.12-7.06 (m, 2H), 6.15 (ddd, $J = 17.4$, 10.3, 7.1 Hz, 1H), 6.06 (ddd, $J = 17.4$, 10.5, 6.8 Hz, 0.91H), 5.86 (ddd, $J = 17.2$, 10.4, 6.8 Hz, 0.09H), 5.71 (d, $J = 6.9$ Hz, 0.09H), 5.42 (d, $J = 7.1$ Hz, 0.91H), 5.22 (dt, $J = 10.6$, 1.3 Hz, 1H), 5.20 (dt, $J = 10.4$, 1.3 Hz, 1H), 5.20 (dt, $J = 17.3$, 1.3 Hz, 1H), 5.02 (dt, $J = 17.2$, 1.3 Hz, 1H), 4.18 (A of AB, $J_{AB} = 12.0$ Hz, 1H), 4.14 (B of AB, $J_{AB} = 12.0$ Hz, 1H), 4.09-4.04 (m, 1H), 3.79 (dd, $J = 9.7$, 8.3 Hz, 1H), 3.30 (dd, $J = 9.6$, 4.7 Hz, 1H), 2.41 (s, 0.27H), 2.37 (s, 2.73H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.86 (e), 139.00 (e), 138.65 (e), 137.92 (e), 135.74 (o), 134.66 (o), 129.12 (o), 128.38 (o), 128.28 (o), 128.19 (o), 127.76 (o), 127.70 (o), 127.48 (o), 127.42 (o), 119.16 (e), 118.80 (e), 72.74 (e), 72.11 (e), 64.03 (o), 59.74 (o), 21.47 (o).

IR (CHCl_3) 3028 (m), 3012 (m), 2926 (w), 2865 (m), 1599 (m), 1496 (m) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+Na}$) calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_3\text{NaS}$ 470.1766, found 470.1788.



$[\alpha]_D^{18} = 3.7$ ($c = 1.01$, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38-7.27 (m, 5H), 7.19-7.15 (m, 1H), 7.09-7.05 (m, 2H), 6.98-6.95 (m, 4H), 6.94-6.88 (m, 2H), 6.04 (dt, $J = 6.3, 1.9$ Hz, 1H), 5.68 (dt, $J = 6.4, 1.9$ Hz, 1H), 5.60 (dt, $J = 5.3, 1.9$ Hz, 1H), 4.73-4.68 (m, 1H), 4.60 (A of AB, $J_{AB} = 12.1$ Hz, 1H), 4.57 (B of AB, $J_{AB} = 12.0$ Hz, 1H), 4.24 (dd, $J = 9.2, 3.6$ Hz, 1H), 3.75 (dd, $J = 9.2, 7.6$ Hz, 1H), 2.28 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.05 (e), 138.26 (e), 137.70 (e), 137.30 (e), 130.34 (o), 128.99 (o), 128.73 (o), 128.38 (o), 128.35 (o), 127.99 (o), 127.90 (o), 127.65 (o), 127.60 (o), 126.49 (o), 73.50 (e), 73.06 (e), 71.56 (o), 66.23 (o), 21.33 (o).

IR (CHCl_3) 3030 (m), 2925 (m), 2866 (m), 1599 (w), 1495 (w) cm^{-1} .

HRMS (FAB, $\text{M}^+\text{+H}$) calcd for $\text{C}_{25}\text{H}_{26}\text{NO}_3\text{S}$ 420.1633, found 420.1605.