Supporting Information

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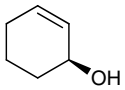
SI Text

1. General Methods. NMR spectra were acquired on a Varian AS 400 spectrometer, running at 400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal; app, apparent. ^{13}C NMR spectra were acquired on a broad band decoupled mode. In order to characterize ^{1}H NMR spectra of diastereomeric mixtures, the following notations are used. *denotes the minor diastereomer; $^+$denotes overlap of signals from both diastereomers, the number of protons given in the parentheses represent the sum of protons from both diastereomers. For ^{13}C NMR spectra of diastereomeric mixtures, no individual characterization is made. Mass spectra were recorded on a micromass LCT spectrometer using electrospray (ES^+) ionization techniques. Analytical thin layer chromatography (TLC) was performed using precoated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or $KMnO_4$ dip. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The enantiomeric excess (ee) of the products were determined by chiral stationary phase HPLC (Daicel Chiralpak AS/AD and Daicel Chiralcel OD/OJ/OB columns) or by GC using a chiral Agilent J&W Cyclosil-B column (length, 30 m; I.D., 0.250 mm; film, 0.25 μm.). Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (Silica gel 60, 230–400 mesh, Fluka) was used. Enones **1c**, **f**, **g** and catalysts **2a**, **b** were synthesized according to literature (1, 2).

2. Chiral Allylic Alcohols. ***General procedure for cyclic enones.*** An ordinary glass vial equipped with a magnetic stirring bar was charged with the enone **1** (0.25 mmol, 1.0 equivalent), the catalyst **2** (0.025 mmol, 0.1 equivalent) and dioxane (1.0 mL). After 30 min of stirring at rt, H_2O_2 (50 wt% in H_2O, 0.30 mmol, 1.2 equivalent) was added. The reaction was heated to 35–50 °C (see individual entries) and kept under vigorous stirring until complete conversion of the enone as monitored by TLC (usually 24–72 h). MeOH (5.0 mL), hydrazine monohydrate (1.25 mmol, 5.0 equivalent) and AcOH (0.63 mmol, 2.5 equivalent) were then added in the described sequence. After additionally 0.5–1 h of stirring at room temperature, the crude reaction mixture was diluted with $NaHCO_3$ (sat.), extracted with CH_2Cl_2 (3 × 10 mL), dried over $MgSO_4$ and most of the excess solvents (Note: volatile products!) were carefully removed in vacuo. The remaining volume (*ca.* 1–2 mL) was charged on silica gel and purified by FC (gradient: pentane to pentane/Et_2O 2:1).

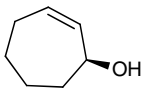
General procedure for acyclic enones. An ordinary glass vial equipped with a magnetic stirring bar was charged with the enone **1** (0.25 mmol, 1.0 equivalent), the catalyst **2** (0.025 mmol, 0.1 equivalent) and dioxane (1.0 mL). After 30 min of stirring at rt, H_2O_2 (50 wt% in H_2O, 0.30 mmol, 1.2 equivalent) was added. The reaction was heated to 50 °C and kept under vigorous stirring until complete conversion of the enone as monitored by TLC (usually 24–96 h). NaOH (0.5 mmol, 2.0 equivalent, 33 wt% in H_2O) was then added to facilitate the epoxide formation (monitored by TLC, usually within 10 min). Upon completion, the reaction mixture was cooled to room temperature and MeOH (5.0 mL), hydrazine monohydrate (1.25 mmol, 5.0 equivalent) and AcOH (1.25 mmol, 5.0 equivalent) were added in the described sequence. After additionally 0.5 h of stirring at room temperature, the crude reaction mixture was diluted with $NaHCO_3$ (sat.), extracted with CH_2Cl_2 (3 × 10 mL), dried over $MgSO_4$ and most of the excess solvents (Note: volatile products) were carefully removed in vacuo. The remaining volume (*ca.* 1–2 mL) was charged on silica gel and purified by FC (gradient: pentane to pentane/Et_2O 2:1).

4a (*S*)-Cyclohex-2-enol (Entry 1, Table 1).



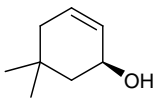
Following the general procedure (35 °C) **4a** was isolated by FC on silica gel in 50% yield as a colorless oil. All physical and spectroscopical data were in accordance with literature (3). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.83 (ddt, J = 1.3, 3.5, 10.1 Hz, 1H), 5.77-5.71 (m, 1H), 4.22-4.14 (m, 1H), 2.09-1.89 (m, 2H), 1.91-1.81 (m, 1H), 1.77-1.67 (m, 1H), 1.66-1.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.5, 129.8, 65.5, 32.0, 25.0, 18.9. m/z(EI): 98.0 (M^+). The ee was determined by GC; temperature ramp: 70–120 °C (10°C/ min), maintained for 10 min; τ_{major} = 9.0 min, τ_{minor} = 9.3 min (93% ee). $[\alpha]_D^{rt}$: −108.0 (c = 0.4, $CHCl_3$).

4b (*S*)-Cyclohept-2-enol (Entry 2, Table 1).



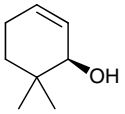
Following the general procedure (50 °C) **4b** was isolated by FC on silica gel in 45% yield as a colorless oil. All physical and spectroscopical data were in accordance with literature (4). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.75-5.68 (m, 2H), 4.38 (dm, J = 9.5 Hz, 1H), 2.24-2.09 (m, 1H), 2.06-1.95 (m, 1H), 1.95-1.70 (m, 3H), 1.69-1.49 (m, 3H), 1.42-1.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 130.1, 72.1, 36.7, 28.6, 26.8, 26.7. m/z(EI): 112.1 (M^+). The ee was determined by GC; temperature ramp: 70–120 °C (10 °C/ min), maintained for 15 min; τ_{major} = 15.2 min, τ_{minor} = 15.6 min (92% ee). $[\alpha]_D^{rt}$: −26.2 (c = 0.15, $CHCl_3$).

4c (*S*)-5,5-Dimethylcyclohex-2-enol (Entry 3, Table 1).



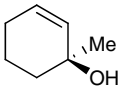
Following the general procedure (50 °C for 7d) **4c** was isolated by FC on silica gel in 58% yield as a colorless oil. All physical and spectroscopical data were in accordance with literature (5). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.74-5.66 (m, 2H), 4.33-4.19 (m, 1H), 1.94-1.68 (m, 3H), 1.40 (s, 1H), 1.30 (dd, J = 9.2, 12.4 Hz, 1H), 0.99 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.2, 128.2, 66.4, 45.4, 39.0, 31.3, 30.8, 26.1. m/z(EI): 126.1 (M^+). The ee was determined by GC; temperature ramp: 70–120 °C (1 °C/ min); τ_{major} = 35.9 min, τ_{minor} = 38.9 min (87% ee). $[\alpha]_D^{rt}$: −41.7 (c = 0.6, Et_2O).

4d (*R*)-6,6-Dimethylcyclohex-2-enol (Entry 4, Table 1).



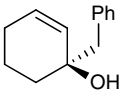
Following the general procedure (50 °C) **4d** was isolated by FC on silica gel in 47% yield as a colorless oil. All physical and spectroscopical data were in accordance with literature (4). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.75 (ddt, $J = 1.5$, 3.5, 10.0 Hz, 1H), 5.64 (ddd, $J = 2.1$, 5.2, 9.9 Hz, 1H), 3.74 (app s, 1H), 2.06-1.96 (m, 2H), 1.53-1.31 (m, 3H), 0.95 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.2, 129.2, 73.9, 33.5, 32.6, 26.2, 23.0, 21.6. m/z(EI): 126.1 (M^+). The ee was determined by GC; temperature ramp: 70–110 °C (1 °C/ min); $\tau_{major} = 33.2$ min, $\tau_{minor} = 33.7$ min (94% ee). $[\alpha]_D^{rt}$: −70.0 ($c = 0.2$, $CHCl_3$).

4e (*S*)-1-Methylcyclohex-2-enol (Entry 5, Table 1).



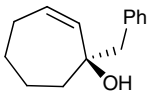
Following the general procedure (50 °C) **4e** was isolated by FC on silica gel in 40% yield as a colorless oil. All physical and spectroscopical data were in accordance with literature (6). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.74 (ddd, $J = 3.2$, 4.1, 10.0 Hz, 1H), 5.62 (dm, $J = 10.0$ Hz, 1H), 2.07-1.58 (m, 7H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 129.0, 67.9, 37.9, 29.3, 25.0, 19.5. m/z(EI): 112.0 (M^+). The ee was determined by GC; temperature ramp: 70–120 °C (10 °C/ min), then keep for 10 min; $\tau_{major} = 8.1$ min, $\tau_{minor} = 8.4$ min (94% ee). $[\alpha]_D^{rt}$: −70.0 ($c = 0.2$, Et_2O).

4f (*R*)-1-Benzylcyclohex-2-enol (Entry 6, Table 1).



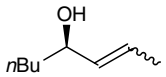
Following the general procedure (50 °C) **4f** was isolated by FC on silica gel in 40% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36-7.22 (m, 5H), 5.82 (ddd, $J = 3.2$, 4.3, 10.1 Hz, 1H), 5.60 (dt, $J = 2.1$, 10.1 Hz, 1H), 2.84 (s, 2H), 2.11-1.91 (m, 2H), 1.78-1.63 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 132.1, 130.7 (2C), 129.9, 128.1 (2C), 126.4, 69.6, 48.2, 35.7, 25.2, 19.0. Calculated for $[C_{13}H_{16}NaO]^+$: 211.1099; found: 211.1106. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/ min; $\tau_{major} = 6.7$ min, $\tau_{minor} = 7.4$ min (98% ee). $[\alpha]_D^{rt}$: −20.0 ($c = 0.3$, Et_2O).

4g (*R*)-1-Benzylcyclohept-2-enol (Entry 7, Table 1).



Following the general procedure (50 °C) **4g** was isolated by FC on silica gel in 45% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34-7.19 (m, 5H), 5.74 (ddd, $J = 5.6$, 6.5, 12.0 Hz, 1H), 5.51 (d, $J = 11.9$ Hz, 1H), 2.95 (d, $J = 13.3$ Hz, 1H), 2.84 (d, $J = 13.3$ Hz, 1H), 2.26-2.12 (m, 2H), 1.91-1.54 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.0, 130.8 (2C), 130.2, 128.1 (2C), 126.5, 75.8, 46.9, 38.7, 27.8, 27.4, 24.3. Calculated for $[C_{14}H_{18}NNaO_2S]^+$: 225.1250; found: 225.1258. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (98:2)]; flow rate 1.0 mL/ min; $\tau_{major} = 10.7$ min, $\tau_{minor} = 11.4$ min (99% ee). $[\alpha]_D^{rt}$: +92.0 ($c = 0.5$, Et_2O).

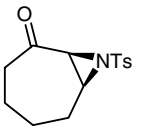
4h (*R*)-Oct-2-en-4-ol (Entry 9, Table 1).



Following the general procedure (50 °C) **4h** was isolated by FC on silica gel in 54% yield as a colorless oil (E/Z ratio 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.68-5.34 (m, 4H), 4.47-4.41 (m, 1H), 4.00 (app q, $J = 6.8$ Hz, 1H), 1.68 (ddd, $J = 0.6$, 1.6, 6.4 Hz, 3H), 1.66 (dd, $J = 1.7$, 7.0 Hz, 3H), 1.56-1.21 (m, 12H), 0.89 (t, $J = 7.0$ Hz, 3H), 0.88 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 133.6, 126.6, 126.1, 73.1, 67.3, 37.1, 37.0, 27.6, 27.5, 22.6, 22.6, 17.6, 14.0 (2C), 13.2. m/z(EI): 128.1 (M^+). The ee was determined by GC; temperature ramp: 70–110 °C (1 °C/ min); $\tau_{major} = 26.7$ min, $\tau_{minor} = 26.4$ min (96% ee); $\tau_{major} = 28.2$ min, $\tau_{minor} = 29.4$ min (96% ee). $[\alpha]_D^{rt}$: +14.2 ($c = 2.9$, $CHCl_3$).

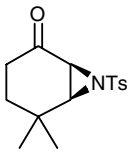
3. Chiral Allylic Amines. ***General procedure for the synthesis of aziridines.*** An ordinary glass vial equipped with a magnetic stirring bar was charged with TsONHTs **5** (0.38 mmol, 1.5 equivalent), the catalyst **2** (0.05 mmol, 0.2 equivalent), and $CHCl_3$ (1.0 mL). After 10 min of stirring at rt, enone **1** (0.25 mmol, 1.0 equivalent) and $NaHCO_3$ (0.5 mmol, 2 equivalent) were added sequentially. The reaction was kept under vigorous stirring (rt/40 °C) until complete conversion of the enone, as monitored by TLC (usually 24–48 h). H_2O was added to the reaction mixture, which was then extracted with CH_2Cl_2 (3 × 10 mL), dried over $MgSO_4$, concentrated in vacuo and purified by FC on silica gel (gradient: pentane to pentane/EtOAc 1:4).

6b (1*S*,7*S*)-8-tosyl-8-azabicyclo[5.1.0]octan-2-one.



Following the general procedure (40 °C) **6b** was isolated by FC in 93% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.81 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H), 3.25 (dd, $J = 1.6$, 7.9 Hz, 1H), 3.19 (dd, $J = 4.8$, 7.9 Hz, 1H), 2.56 (ddd, $J = 3.6$, 11.5, 13.6 Hz, 1H), 2.45 (s, 3H), 2.37-2.31 (m, 1H), 2.25-2.21 (m, 1H), 1.83-1.78 (m, 1H), 1.71-1.66 (m, 3H), 1.01-0.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 145.3, 134.3, 130.2 (2C), 128.2 (2C), 48.5, 41.9, 40.9, 27.3, 23.7, 23.6, 21.9. Calculated for $[C_{14}H_{17}NNaO_3S]^+$: 302.0827; found: 302.0828. $[\alpha]_D^{rt}$: +23.4 ($c = 2.13$, $CHCl_3$). The enantiomeric excess was determined after transformation into the corresponding allylic amine **7b**, following the general procedure described below for the Wharton transposition. Isolated yield of **7b** after purification by FC: 40% (98% *ee*).

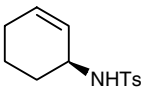
6d (1*S*,6*S*)-5,5-dimethyl-7-tosyl-7-azabicyclo[4.1.0]heptan-2-one.



Following the general procedure (rt) **6d** was isolated by FC in 89% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.81 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 3.19 (d, $J = 6.6$ Hz, 1H), 2.99 (dd, $J = 1.6$, 6.6 Hz, 1H), 2.44 (s, 3H), 2.28 (ddd, $J = 2.5$, 6.0, 19.1 Hz, 1H), 2.14 (ddd, $J = 6.7$, 12.4, 19.1 Hz, 1H), 1.79 (dt, $J = 6.0$, 13.1 Hz, 1H), 1.30-1.23 (m, 1H), 1.06 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 145.4, 134.4, 130.1 (2C), 128.4 (2C), 50.4, 44.7, 33.9, 30.3, 29.8, 27.9, 23.7, 21.9. Calculated for $[C_{15}H_{19}NNaO_3S]^+$: 316.0983; found: 316.0987. $[\alpha]_D^{rt}$: −15.6 ($c = 2.97$, $CHCl_3$). The enantiomeric excess was determined after transformation into the corresponding allylic amine **7d**, following the general procedure described below for the Wharton transposition. Isolated yield of **7d** after purification by FC: 56% (97% *ee*).

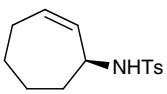
General procedure for the one-pot synthesis of allylic amines. An ordinary glass vial equipped with a magnetic stirring bar was charged with TsONHTs **5** (0.38 mmol, 1.5 equivalent), the catalyst **2** (0.05 mmol, 0.2 equivalent), and $CHCl_3$ (1.0 mL). After 10 min of stirring at rt, enone **1** (0.25 mmol, 1.0 equivalent) and $NaHCO_3$ (0.5 mmol, 2 equivalent) were added sequentially. The reaction was kept under vigorous stirring until complete conversion of the enone as monitored by TLC (usually 24–72 h). MeOH (5.0 mL), hydrazine (1.25 mmol, 5.0 equivalent) and AcOH (1.13 mmol, 4.5 equivalent) were then added in the described sequence. After additionally 1 h of stirring at 50 °C, the crude reaction mixture was cooled to rt, diluted with $NaHCO_3$ (sat.), extracted with CH_2Cl_2 (3 × 10 mL), dried over $MgSO_4$, concentrated in vacuo and purified by FC on silica gel (gradient: pentane to pentane/EtOAc 1:1).

7a (*S*)-*N*-(Cyclohex-2-enyl)-4-methylbenzenesulfonamide (Entry 1, Table 2).



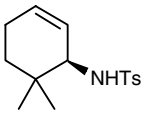
Following the general procedure **7a** was isolated by FC in 56% yield as a colorless oil. All physical and spectroscopical data were in accordance with literature (7). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.77 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 5.79-5.73 (m, 1H), 5.34 (dm, $J = 10.0$ Hz, 1H), 4.51 (d, $J = 8.0$ Hz, 1H), 3.85-3.77 (m, 1H), 2.43 (s, 3H), 1.97-1.50 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.3, 131.6, 129.7 (2C), 127.0, 127.0 (2C), 48.9, 30.3, 24.5, 21.5, 19.3. Calculated for $[C_{13}H_{17}NNaO_2S]^+$: 274.0877; found: 274.0878. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{major} = 17.3$ min, $\tau_{minor} = 18.7$ min (96% ee). $[\alpha]_D^{rt}$: −39.6 ($c = 1.24$, $CHCl_3$). For *ent*-**7a**: $[\alpha]_D^{rt}$: +48.9 ($c = 1.44$, $CHCl_3$, 95% ee).

7b (*S*)-*N*-(Cyclohept-2-enyl)-4-methylbenzenesulfonamide (Entry 3, Table 2).



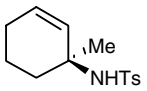
Following the general procedure **7b** was isolated by FC in 48% yield as a colorless oil. All physical and spectroscopical data were in accordance with literature. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.75 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 7.9$ Hz, 2H), 5.70 (dddd, $J = 2.1$, 5.4, 7.2, 11.6 Hz, 1H), 5.40 (dd, $J = 4.1$, 11.5 Hz, 1H), 4.64-4.56 (m, 1H), 4.02-3.91 (m, 1H), 2.42 (s, 3H), 2.17-1.95 (m, 2H), 1.90-1.70 (m, 2H), 1.68-1.48 (m, 3H), 1.43-1.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.0, 133.9, 132.7, 129.6 (2C), 127.0 (2C), 54.4, 34.6, 28.3, 26.9, 26.5, 21.5. Calculated for $[C_{14}H_{19}NNaO_2S]^+$: 288.1034; found: 288.1030. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{major} = 16.7$ min, $\tau_{minor} = 17.3$ min (98% ee). $[\alpha]_D^{rt}$: −8.0 ($c = 0.92$, $CHCl_3$).

7d (*R*)-*N*-(6,6-Dimethylcyclohex-2-enyl)-4-methylbenzenesulfonamide (Entry 4, Table 2).



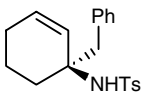
Following the general procedure **7d** was isolated by FC in 50% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.77 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 5.64-5.59 (m, 1H), 4.99 (ddd, $J = 2.3$, 5.0, 10.0 Hz, 1H), 4.31 (d, $J = 9.8$ Hz, 1H), 3.51-3.45 (m, 1H), 2.43 (s, 3H), 2.00-1.90 (m, 2H), 1.40 (t, $J = 6.0$ Hz, 2H), 0.90 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.4, 129.8, 129.6 (2C), 127.0 (2C), 127.0, 58.2, 34.1, 32.8, 27.0, 22.5, 21.6, 21.5. Calculated for $[C_{15}H_{21}NNaO_2S]^+$: 302.1190; found: 302.1191. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{major} = 12.8$ min, $\tau_{minor} = 13.9$ min (97% ee). $[\alpha]_D^{rt}$: −58.0 ($c = 0.97$, $CHCl_3$).

7e (*S*)-4-Methyl-*N*-(1-methylcyclohex-2-enyl)benzenesulfonamide (Entry 5, Table 2).



Following the general procedure **7e** was isolated by FC in 57% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.76 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 5.65 (dt, $J = 3.7$, 10.0 Hz, 1H), 5.49 (d, $J = 10.0$ Hz, 1H), 4.68 (s, 1H), 2.41 (s, 3H), 2.00-1.83 (m, 3H), 1.63-1.41 (m, 3H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 140.5, 131.5, 129.5, 129.3 (2C), 127.0 (2C), 55.2, 36.4, 27.8, 24.5, 21.5, 18.5. Calculated for $[C_{14}H_{19}NNaO_2S]^+$: 288.1034; found: 288.1034. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{major} = 12.6$ min, $\tau_{minor} = 14.0$ min (99% ee). $[\alpha]_D^{rt}$: −64.4 ($c = 1.19$, $CHCl_3$).

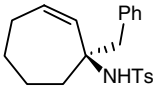
7f (*R*)-*N*-(1-Benzylcyclohex-2-enyl)-4-methylbenzenesulfonamide (Entry 6, Table 2).



Following the general procedure **7f** was isolated by FC in 61% yield as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, $J = 8.3$ Hz, 2H), 7.35-7.19 (m, 7H), 5.66-5.60 (m, 2H), 4.31

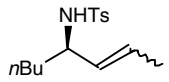
(s, 1H), 3.14 (d, $J = 13.3$ Hz, 1H), 2.83 (d, $J = 13.3$ Hz, 1H), 2.40 (s, 3H), 1.83-1.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.2, 136.1, 131.2, 131.1 (2C), 129.1 (2C), 128.8, 128.2 (2C), 127.3 (2C), 126.8, 57.4, 47.7, 34.1, 24.7, 21.5, 17.9. Calculated for $[C_{20}H_{23}NNaO_2S]^+$: 364.1347; found: 364.1350. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (95:5)]; flow rate 1.0 mL/min; $\tau_{major} = 19.1$ min, $\tau_{minor} = 20.5$ min (99% ee). M.p.: 117 °C. $[\alpha]_D^{rt}$: −22.1 ($c = 1.00$, $CHCl_3$). For *ent*-**7f**: $[\alpha]_D^{rt}$: +37.5 ($c = 1.41$, $CHCl_3$).

7g (*R*)-*N*-(1-Benzylcyclohept-2-enyl)-4-methylbenzenesulfonamide (Entry 8, Table 2).



Following the general procedure **7g** was isolated by FC in 42% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 (d, $J = 8.3$ Hz, 2H), 7.34-7.19 (m, 7H), 5.63 (ddd, $J = 5.5$, 6.3, 11.8 Hz, 1H), 5.52 (d, $J = 12.1$ Hz, 1H), 4.32 (s, 1H), 3.27 (d, $J = 13.3$ Hz, 1H), 2.85 (d, $J = 13.3$ Hz, 1H), 2.40 (s, 3H), 1.89-1.29 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.2, 136.3, 133.6, 133.5, 131.2 (2C), 129.1 (2C), 128.2 (2C), 127.3 (2C), 126.8, 63.2, 47.9, 37.0, 27.7, 26.8, 24.1, 21.5. Calculated for $[C_{21}H_{25}NNaO_2S]^+$: 378.1504; found: 378.1502. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{major} = 10.7$ min, $\tau_{minor} = 12.5$ min (94% ee). $[\alpha]_D^{rt}$: −3.1 ($c = 1.31$, $CHCl_3$).

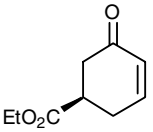
7h (*R*)-4-Methyl-*N*-(oct-2-en-4-yl)benzenesulfonamide (Entry 9, Table 2).



Following the general procedure **7h** was isolated by FC in 52% yield as a colorless oil (*E*/*Z* ratio 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.74-7.69 (m, 4H), 7.28-7.24 (m, 4H), 5.39-5.29 (m, 2H), 5.09-4.97 (m, 2H), 4.47-4.35 (m, 2H), 4.09-3.99 (m, 1H), 3.71-3.63 (m, 1H), 2.41 (s, 6H), 1.58-1.14 (m, 18H), 0.85-0.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 143.0, 138.3, 138.2, 130.6, 130.4, 129.3 (2C), 129.3 (2C), 127.4, 127.3 (2C), 127.2 (2C), 126.4, 56.1, 50.8, 36.0, 35.6, 27.5, 27.4, 22.3, 22.3, 21.5, 21.5, 17.5, 17.5, 13.9, 13.9. Calculated for $[C_{15}H_{23}NNaO_2S]^+$: 304.1347; found: 304.1347. The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{major} = 9.4$ min, $\tau_{minor} = 7.5$ min (97% ee); $\tau_{major} = 8.8$ min, $\tau_{minor} = 8.3$ min (93% ee). $[\alpha]_D^{rt}$: −32.6 ($c = 0.74$, $CHCl_3$).

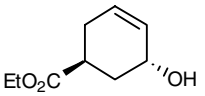
4. Diastereoselective Synthesis. ***General approach to cis and trans disubstituted allylic products.***

8 (*R*)-Ethyl 5-oxocyclohex-3-enecarboxylate.



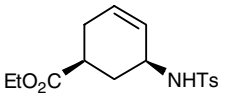
The titled compound was synthesized in analogy to a previous reported procedure in 85% yield as a pale yellow oil (8). All physical and spectroscopical data were in accordance with literature (9). The ee was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{major} = 10.4$ min, $\tau_{minor} = 13.9$ min (75% ee). $[\alpha]_D^{rt}$: +17.1 ($c = 0.18$, $CHCl_3$).

9a (1*S*,5*R*)-Ethyl 5-hydroxycyclohex-3-enecarboxylate.



Following the general procedure for synthesis of allylic alcohols and by employing **2b** as catalyst, compound **9a** was isolated by FC (Gradient: pentane to pentane/Et_2O 1:2) in 60% yield as a pale yellow oil (d.r. 94:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.90 (ddd, $J = 2.2$, 4.5, 10.0 Hz, 1H), 5.87-5.82 (m, 1H), 4.27 (app s, 1H), 4.15 (q, $J = 7.5$ Hz, 2H), 2.82-2.72 (m, 1H), 2.40-2.05 (m, 3H), 1.82 (ddd, $J = 4.2$, 12.3, 13.7 Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 129.6, 127.9, 63.3, 60.5, 34.6, 33.8, 27.7, 14.2. Calculated for $[C_9H_{14}NaO_3]^+$: 193.0835; found: 193.0841. The ee was determined by GC; Temperature ramp: 70–150 °C (1 °C/min); $\tau_{major} = 73.1$ min, $\tau_{minor} = 72.1$ min (92% ee). $[\alpha]_D^{rt}$: +47.7 ($c = 0.43$, $CHCl_3$).

9b (1*S*,5*S*)-Ethyl 5-(4-methylphenylsulfonamido)cyclohex-3-enecarboxylate.



Following the general procedure for synthesis of allylic amines and by employing **2a** as catalyst, compound **9b** was isolated by FC in 46% yield as a pale yellow oil (d.r. 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.77* (d, $J = 8.3$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.32-7.28+ (m, 4H), 5.85-5.79* (m, 1H), 5.76-5.69 (m, 1H), 5.43-5.40* (m, 1H), 5.37 (d, $J = 10.0$ Hz, 1H), 4.67 (d, $J = 8.9$ Hz, 1H), 4.45* (d, $J = 7.5$ Hz, 1H), 4.12$^+$ (q, $J = 7.1$ Hz, 4H), 4.00-3.90 (m, 1H), 3.90-3.86* (m, 1H), 2.65-2.52$^+$ (m, 2H), 2.43 (s, 3H), 2.41* (s, 3H), 2.24-2.13$^+$ (m, 6H), 1.61-1.50$^+$ (m, 2H), 1.24$^+$ (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 143.4, 138.3, 138.0, 130.3, 129.7, 128.6, 128.0, 127.0, 125.4, 60.7, 60.6, 49.5, 47.3, 38.2, 34.9, 32.6, 32.0, 27.0, 26.9, 21.5, 14.2, 14.1. Calculated for $[C_{16}H_{21}NNaO_4S]^+$: 346.1089; found: 346.1091. The ee of the major diastereomer was determined by HPLC using a Chiralpak AD column [hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; $\tau_{major} = 31.1$ min, $\tau_{minor} = 35.2$ min (95% ee). $[\alpha]_D^{rt}$: +4.6 ($c = 1.1$, $CHCl_3$).

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