Supporting Information
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**Supporting Information for:**

[3+2] Cycloaddition of Aziridines and Alkenes Catalyzed by a Cationic Manganese Porphyrin

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**Instrumentation and Chemicals**

All manipulations of oxygen- and moisture-sensitive materials were conducted in a dry box or with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (\(^1\text{H}, 500 \text{ MHz}; \ ^{13}\text{C}, 125.7 \text{ MHz}\) spectrometer using tetramethylsilane (\(^1\text{H}\)) as an internal standard. \(^1\text{H} \) NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration, and identification. High-resolution mass spectra were obtained with a Thermo Fisher SCIENTIFIC EXACTIVE spectrometer. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns (toluene as an eluent). Infrared spectra (IR) spectra were determined on a SHIMADZU IR Affinity-1 spectrometer. TLC analyses were performed by means of Merck Kieselgel 60 F\(_{254}\) (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO\(_4\) solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50 mm). Unless otherwise noted, commercially available reagents were used without purification. 1,2-Dichloroethane was purchased from SIGMA-ALDRICH JAPANE K. K. stored over slices of sodium.
Experimental Procedure

General procedure. The reaction was performed in a 15 mL sealed tube equipped with a Teflon-coated magnetic stirrer bar. An aziridine (0.2 mmol), alkene (0.3 mmol) and \([\text{Mn(TPP)}]\text{SbF}_6\) (0.02 mmol) in 0.8 ml of 1,2-dichloroethane was heated at 100 °C for 12 hours under argon atmosphere. The resulting reaction mixture was cooled to ambient temperature and filtered through a silica gel pad, concentrated in vacuo. The residue was purified by flash silica gel column chromatography (20 g, 2×15 cm, hexane/ethyl acetate = 5:1) to give the corresponding product as an inseparable mixture of two diastereomers.

Preparation of \([\text{Mn(TPP)}]\text{SbF}_6\).

Mn(TPP)Cl (0.33 mmol, 232 mg) and AgSbF₆ (0.3 mmol, 103 mg) was dissolved in dry CH₂Cl₂ (10mL) and stirred for 5 h in dry box. The reaction mixture was filtered and concentrated to dryness. The complex was used without further purification. Other manganese porphyrin complex were also prepared by this procedure.
Characterization Data for Products

2-Phenyl-4-(p-tolyl)-1-tosylpyrrolidine (3aa).

5 : 4 (ratio of two diastereomers). Colorless oil. TLC: $R_f = 0.40$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.74–7.73 (m, 1.8H), 7.65–7.64 (m, 2H), 7.42–7.24 (m, 13.3H), 7.11–7.02 (m, 5.8H), 6.93–6.92 (m, 1.8H), 5.06 (d, $J = 8.0$ Hz, 0.9H), 4.81 (dd, $J = 6.5$, 10 Hz, 1H), 4.17–4.14 (m, 1H), 4.02 (dd, $J = 7.5$, 9.0 Hz, 0.9 Hz), 3.52–3.41 (m, 1.9H), 3.28 (dd, $J = 9.5$, 10.5 Hz, 0.9H), 2.97–2.89 (m, 1H), 2.69–2.65 (m, 1H), 2.46 (s, 2.7H), 2.44 (s, 3H), 2.32 (s, 3H), 2.30 (s, 2.7H), 2.18–2.14 (m, 0.9H), 2.11–2.00 (m, 1.9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 143.4, 143.2, 142.9, 142.6, 136.7, 136.6, 136.5, 135.9, 135.8, 134.8, 129.6, 129.5, 129.3, 129.2, 128.4, 128.3, 127.6, 127.4, 127.2, 127.1, 126.8, 126.8, 126.4, 126.1, 64.5, 63.0, 55.9, 55.1, 44.4, 43.3, 42.1, 41.0, 21.5, 21.4, 20.9, 20.9. IR (neat): 3028, 2954, 2923, 2870, 1599, 1494, 1348, 1338, 1182, 1027, 814, 662 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{24}$H$_{26}$NO$_2$S [M+H]$^+$ 392.1679, found 392.1663.

2,4-Diphenyl-1-tosylpyrrolidine (3ba).

5 : 4 (ratio of two diastereomers). Colorless oil. TLC: $R_f = 0.43$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.74–7.72 (m, 1.6H), 7.65–7.63 (m, 2H), 7.41–7.20 (m, 18H), 7.14–7.12 (m, 2H), 7.04–7.02 (m 1.6H), 5.06 (d, $J = 7.0$ Hz, 0.8H), 4.84 (dd, $J = 7.0$, 10 Hz, 1H), 3.54–3.44 (m, 1.8H), 3.31 (dd, $J = 10$, 10.5 Hz, 0.8H), 3.00–2.93 (m, 1H), 2.71–2.66 (m, 1H), 2.46 (s, 2.4H), 2.43 (s, 3H), 2.20–2.16 (m, 0.8H), 2.13–2.02 (m, 1.8H). $^{13}$C NMR (CDCl$_3$): $\delta$ 143.5, 143.3, 142.9, 142.5, 139.5, 139.1, 135.8, 134.9, 129.6, 129.5, 128.6, 128.4, 128.4, 127.6, 127.5, 127.3, 127.3, 127.1, 127.0, 127.0, 126.9, 126.4, 126.1, 125.5, 65.3, 55.9, 55.0, 44.4, 43.6, 42.1, 41.4, 21.5, 21.5. IR (neat): 3030, 2962, 2919, 1600, 1493, 1454, 1347, 1330, 1162, 1157, 1093, 1075, 1004, 811, 756, 703, 667 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{23}$H$_{24}$NO$_2$S [M+H]$^+$ 378.1522, found 378.1509.

4-(4-Chlorophenyl)-2-phenyl-1-tosylpyrrolidine (3ca).

10 : 9 (ratio of two diastereomers). Colorless oil. TLC: $R_f = 0.37$ (hexane/ethyl acetate = 3:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.72–7.70 (m, 1.6H), 7.64–7.62 (m, 2H), 7.39–7.20 (m, 16.2H), 7.07–7.05 (m, 2H), 6.96–6.95 (m, 1.6H), 5.06 (d, $J = 7.0$ Hz, 0.8H), 4.82 (dd, $J = 7.0$, 10 Hz, 1H), 4.14 (dd, $J = 7.5$, 9.5 Hz, 1H), 4.01 (dd, $J = 7.5$, 9.5 Hz, 0.8H), 3.49-3.40 (m, 1.8H), 3.28 (dd, $J = 9.5$, 10 Hz, 0.8H), 2.99–2.92 (m, 1H), 2.69–2.65 (m, 1H), 2.45 (s, 2.4H), 2.43 (s, 3H), 2.18–2.14 (m, 0.8H), 2.10–1.94 (m, 1.8H). $^{13}$C NMR (CDCl$_3$): $\delta$ 143.5, 143.4,
4-(4-Methoxyphenyl)-2-phenyl-1-tosylpyrrolidine (3da).

1 : 1 (ratio of two diastereomers). Colorless oil. TLC: \( R_f = 0.27 \) (hexane/ethyl acetate = 5:1). \( ^1 \)H NMR (CDCl\(_3\)): \( \delta \) 7.74–7.72 (m, 2H), 7.66–7.64 (m, 2H), 7.42–7.24 (m, 14H), 7.06–7.03 (m, 2H), 6.96–6.94 (m, 2H), 6.84–6.78 (m, 4H), 5.05 (d, \( J = 8.0 \) Hz, 1H), 4.80 (dd, \( J = 7.0 \), 10 Hz, 1H), 4.15–4.11 (m, 1H), 4.02–3.99 (m, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.50–3.38 (m, 2H), 3.24 (dd, \( J = 9.5 \), 10.5 Hz, 1H), 2.89 (sept, \( J = 6.5 \) Hz, 1H), 2.67–2.64 (m, 1H), 2.46 (s, 3H), 2.44 (s, 3H), 2.16–2.12 (m, 1H), 2.08–1.97 (m, 2H). \( ^{13} \)C NMR (CDCl\(_3\)): \( \delta \) 158.5, 158.4, 143.5, 143.3, 142.9, 142.5, 135.5, 134.5, 131.3, 130.9, 129.6, 129.5, 128.4, 128.3, 127.9, 127.9, 127.5, 127.4, 127.2, 127.1, 126.3, 126.0, 113.9, 113.9, 64.4, 62.9, 56.0, 55.2, 55.2, 44.5, 42.8, 42.1, 40.6, 21.5, 21.5. IR (neat): 3031, 2934, 1612, 1516, 1346, 1249, 1162, 1095, 1031, 816, 663 cm\(^{-1}\). HRMS (ESI\(^+\)) Calcd. for C\(_{23}\)H\(_{23}\)ClNO\(_2\)S [M+H]\(^+\) 412.1133, found 412.1117.

4-(4-(tert-Butyl)phenyl)-2-phenyl-1-tosylpyrrolidine (3ea).

10 : 7 (ratio of two diastereomers). White powder. TLC: \( R_f = 0.43 \) (hexane/ethyl acetate = 5:1). \( ^1 \)H NMR (CDCl\(_3\)): \( \delta \) 7.76–7.74 (m, 1.7H), 7.67–7.64 (m, 2H), 7.42–7.24 (m, 16.7H), 7.08–7.06 (m, 2H), 6.99–6.97 (m, 1.7H), 5.06 (d, \( J = 8.0 \) Hz, 0.85H), 4.83 (dd, \( J = 7.0 \), 10 Hz, 1H), 4.19–4.15 (m, 1H), 4.05–4.01 (m, 0.85H), 3.46–3.43 (m, 1.85H), 3.30 (dd, \( J = 9.5 \), 10.5 Hz, 0.85H), 2.99–2.90 (m, 1H), 2.72–2.68 (m, 1H), 2.47 (s, 2.55H), 2.44 (s, 3H), 2.19–2.15 (m, 0.85H), 2.12–2.02 (m, 1.85H), 1.31 (s, 9H), 1.30 (s, 7.65H). \( ^{13} \)C NMR (CDCl\(_3\)): \( \delta \) 150.1, 150.0, 143.4, 143.3, 142.9, 142.6, 136.5, 136.0, 135.8, 134.9, 129.7, 129.6, 129.5, 128.4, 128.3, 127.6, 127.4, 127.2, 127.1, 126.7, 126.6, 126.4, 126.1, 125.5, 125.5, 64.5, 63.1, 55.8, 55.1, 44.3, 43.2, 42.1, 41.0, 34.3, 31.3, 21.5, 21.4 cm\(^{-1}\). IR (KBr): 3028, 2964, 2864, 1451, 1353, 1162, 1106, 1022, 700, 669 cm\(^{-1}\). HRMS (ESI\(^+\)) Calcd. for C\(_{27}\)H\(_{32}\)NO\(_2\)S [M+H]\(^+\) 434.2148, found 434.2135.
2-Phenyl-1-tosyl-4-(4-((triisopropylsilyl)oxy)phenyl)pyrrolidine (3fa).

1 : 1 (ratio of two diastereomers). Yellow oil. TLC: $R_f = 0.29$ (hexane/ethyl acetate = 10:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.74–7.72 (m, 1.9H), 7.66–7.64 (m, 2H), 7.41–7.25 (m, 13.7H), 6.97–6.95 (m, 2H), 6.87–6.85 (m, 1.9H), 6.80–6.74 (m, 3.9H), 5.03 (d, $J = 8.0$ Hz, 0.95H), 4.78 (dd, $J = 7.0$, 10 Hz, 1H), 4.10 (dd, $J = 7.0$, 11.5 Hz, 1H), 4.00 (dd, $J = 7.5$, 9.0 Hz, 0.95H), 3.50–3.37 (m, 1.95H), 3.23 (dd, $J = 9.5$, 10.5 Hz, 0.95H), 2.92–2.82 (m, 1H), 2.68–2.61 (m, 1H), 2.46 (s, 2.85H), 2.44 (s, 3H), 2.15–2.11 (m, 0.95H), 2.07–1.96 (m, 1.95H), 1.27–1.19 (m, 5.85H), 1.09–1.07 (m, 35.1H). $^{13}$C NMR (CDCl$_3$): $\delta$ 155.0, 154.9, 143.4, 143.3, 142.9, 142.6, 135.5, 134.5, 131.6, 131.2, 129.6, 129.6, 128.4, 128.3, 127.8, 127.5, 127.4, 127.2, 127.0, 126.3, 126.0, 119.9, 119.8, 64.4, 62.9, 56.0, 55.2, 44.5, 42.9, 42.1, 40.6, 21.5, 21.5, 17.8, 12.5. IR (neat): 3031, 2944, 2867, 1349, 1265, 1164, 1097, 1026, 912, 883, 737, 698 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{32}$H$_{44}$NO$_3$SSi [M+H]$^+$ 550.2806, found 550.2790.

4-(Naphthalen-1-yl)-2-phenyl-1-tosylpyrrolidine (3ga).

10 : 9 (ratio of two diastereomers). Yellow oil. TLC: $R_f = 0.30$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.90–7.83 (m, 2.8H), 7.80–7.77 (m, 2H), 7.76–7.72 (m, 1.9H), 7.70–7.68 (m, 2.8H), 7.51–7.26 (m, 20H), 7.18–7.16 (m, 0.9H), 5.11 (m, 0.9H), 4.99 (dd, $J = 7.0$, 10 Hz, 1H), 4.30–4.19 (m, 2.8H), 3.64–3.52 (m, 2H), 3.45 (t, $J = 9.0$ Hz, 0.9H), 2.78–2.73 (m, 1H), 2.49 (s, 3H), 2.45 (s, 2.7H), 2.41–2.27 (m, 2.9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 143.6, 143.4, 142.8, 142.6, 135.5, 135.2, 134.5, 134.4, 133.8, 133.7, 131.8, 131.7, 129.7, 129.6, 129.0, 128.9, 128.5, 128.5, 127.7, 127.6, 127.6, 127.5, 127.3, 127.2, 126.3, 126.3, 126.1, 126.1, 125.7, 125.7, 125.4, 125.3, 122.9, 122.7, 122.5, 122.2, 64.2, 62.7, 55.6, 54.6, 43.0, 41.1, 39.3, 37.3, 21.6, 21.5. IR (neat): 3062, 2949, 2867, 1349, 1265, 1164, 1097, 1026, 912, 883, 737, 698 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{27}$H$_{26}$NO$_2$S [M+H]$^+$ 428.1679, found 428.1667.

2-(4-Chlorophenyl)-4-(p-tolyl)-1-tosylpyrrolidine (3ab).

5 : 4 (ratio of two diastereomers). White powder. TLC: $R_f = 0.39$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.73–7.71 (m, 1.7H), 7.66–7.64 (m, 2H), 7.36–7.26 (m, 11.1H), 7.11–7.09 (m, 2H), 7.08–7.06 (m, 1.7H), 7.02–7.00 (m, 2H), 6.92–6.90 (m, 1.7H), 4.99 (d, $J = 7.5$ Hz, 0.85H), 4.76 (dd, $J = 7.0$, 10 Hz, 1H), 4.15–4.11 (m, 1H), 4.00 (dd, $J = 7.5$, 9.0 Hz, 0.85H), 3.49 (t, $J = 11.5$ Hz, 1H), 3.44–3.37 (m,
0.85H), 3.25 (dd, J = 9.5, 10.5 Hz, 0.85H), 2.95–2.87 (m, 1H), 2.67–2.61 (m, 1H), 2.46 (s, 2.55H), 2.45 (s, 3H), 2.31 (s, 3H), 2.30 (s, 2.55H), 2.13–2.03 (m, 1.7H), 2.01–1.93 (m, 1H).

13C NMR (CDCl3): δ 143.6, 143.5, 141.5, 141.1, 136.8, 136.8, 136.2, 135.7, 135.5, 134.5, 133.0, 132.9, 129.7, 129.6, 129.3, 129.3, 128.5, 128.5, 127.8, 127.6, 127.5, 127.4, 126.8, 126.7, 63.9, 62.4, 55.9, 55.1, 44.3, 43.2, 42.0, 414.0, 21.5, 21.4, 20.9, 20.9. IR (KBr): 3024, 2922, 1597, 1489, 1345, 1088, 1012, 813, 669 545 cm⁻¹. HRMS (ESI⁺) Calcd. for C24H24ClNO2S [M+H]+ 426.1289, found 426.1274.

2-(4-Bromophenyl)-4-(p-tolyl)-1-tosylpyrrolidine (3ac).

5 : 4 (ratio of two diastereomers). White powder. TLC: Rf = 0.34 (hexane/ethyl acetate = 5:1). 1H NMR (CDCl3): δ 7.74–7.72 (m, 1.7H), 7.67–7.64 (m, 2H), 7.49–7.47 (m, 1.7H), 7.44–7.42 (m, 2H), 7.34–7.24 (m, 7.4H), 7.11–7.06 (m, 3.7H), 7.02–7.00 (m, 2H), 6.92–6.90 (m, 1.7H), 4.97 (d, J = 8.0 Hz, 0.85H), 4.73 (dd, J = 6.5, 10 Hz, 1H), 4.14–4.10 (m, 1H), 4.01 (dd, J = 7.0, 9.5 Hz, 0.85H), 3.50 (t, J = 11.5 Hz, 1H), 3.41–3.36 (m, 0.85H), 3.23 (dd, J = 9.5, 10.5 Hz, 0.85H), 2.93–2.85 (m, 1H), 2.66–2.61 (m, 1H), 2.47 (s, 2.55H), 2.45 (s, 3H), 2.32 (s, 3H), 2.30 (s, 2.55H), 2.12–1.93 (m, 2.7H). 13C NMR (CDCl3): δ 143.7, 143.6, 142.0, 141.6, 142.0, 136.8, 136.8, 136.0, 135.6, 135.1, 134.1, 131.5, 131.4, 129.7, 129.6, 129.3, 129.3, 128.1, 127.8, 127.5, 126.8, 126.7, 121.0, 120.9, 63.9, 62.4, 55.9, 55.1, 44.3, 43.1, 41.9, 40.9, 21.5, 21.5, 20.9, 20.9. IR (KBr): 3025, 2922, 1517, 1486, 1345, 1161, 1093, 1009, 813, 668, 545 cm⁻¹. HRMS (ESI⁺) Calcd. for C24H24BrNO2S [M+H]+ 470.0784, found 470.0769.

4-(p-Tolyl)-1-tosyl-2-(3-(trimethylsilyl)phenyl)pyrrolidine (3ad).

5 : 4 (ratio of two diastereomers). Colorless oil. TLC: Rf = 0.39 (hexane/ethyl acetate = 5:1). 1H NMR (CDCl3): δ 7.75–7.73 (m, 1.6H), 7.64–7.62 (m, 2H), 7.47–7.25 (m, 10.8H), 7.13–7.04 (m, 5.6H), 6.96–6.94 (m, 1.6H), 4.23–4.19 (m, 1H), 4.03 (dd, J = 7.5, 9.0 Hz, 0.8H), 3.52–3.42 (m, 1.8H), 3.33 (dd, J = 9.5, 10.5 Hz, 0.8H), 3.04–2.96 (m, 1H), 2.75–2.68 (m, 1H), 2.46 (s, 2.4H), 2.43 (s, 3H), 2.33 (s, 3H), 2.32 (s, 2.4H), 2.20–2.02 (m, 2.6H), 0.30 (s, 7.2H), 0.28 (s, 9H). 13C NMR (CDCl3): δ 143.4, 143.2, 141.9, 141.5, 140.4, 136.7, 136.6, 136.4, 136.0, 135.8, 134.8, 132.3, 132.1, 131.1, 130.7, 129.6, 129.5, 129.3, 129.2, 127.8, 127.7, 127.5, 127.3, 126.9, 126.8, 126.8, 126.7, 64.5, 63.1, 55.9, 55.1, 44.4, 43.3, 42.2, 41.0, 21.5, 21.5, 20.9, 20.9, –1.13, –1.14. IR (neat): 3025, 2954, 1598, 1346, 1248, 1162, 1118, 839, 753 cm⁻¹. HRMS (ESI⁺) Calcd. for C27H34NO2SSi [M+H]+ 464.2074, found 464.2060.
2-Methyl-2-phenyl-4-(p-tolyl)-1-tosylpyrrolidine (3ae).

10 : 7 (ratio of two diastereomers). Colorless oil. TLC: $R_f = 0.46$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.73–7.71 (m, 2H), 7.55–7.53 (m, 2H), 7.39–7.21 (m, 10.5H), 7.13–7.05 (m, 6.25H), 6.99–6.97 (m, 2H), 4.19–4.13 (m, 1.75H), 3.64–3.44 (m, 0.75H), 3.42 (dd, $J = 9.0$, 11.5 Hz, 0.75H), 3.35–3.25 (m, 2H), 2.47–2.42 (m, 4H), 2.40–2.36 (m, 3.75H), 2.31 (s, 2.25H), 2.28 (s, 3H), 2.15 (t, $J = 7.0$ Hz, 1H), 2.07 (s, 2.25H), 1.94 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 146.9, 145.5, 142.8, 142.4, 138.3, 137.7, 136.8, 136.6, 136.4, 136.3, 129.4, 129.3, 129.2, 128.2, 128.0, 127.2, 127.0, 126.9, 126.8, 126.8, 126.7, 126.3, 125.5, 70.8, 69.5, 56.3, 55.6, 53.2, 52.1, 41.4, 39.2, 27.1, 26.3, 21.5, 21.4, 21.0, 20.9. IR (neat): 3026, 2976, 2923, 1599, 1516, 1494, 1446, 1344, 1155, 1105, 1004, 911, 814 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{25}$H$_{28}$NO$_2$S [M+H]$^+$ 406.1835, found 406.1821.

2-(4-Methoxyphenyl)-2-methyl-4-(p-tolyl)-1-tosylpyrrolidine (3af).

10 : 7 (ratio of two diastereomers). Colorless oil. TLC: $R_f = 0.42$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.76–7.73 (m, 2H), 7.50-7.47 (m, 2H), 7.33-7.25 (m, 5H), 7.15-7.13 (m, 4H), 7.11-7.10 (m, 2H), 7.03-7.01 (m, 2H), 6.95-6.92 (m, 2H), 6.78-6.75 (m, 1.4H), 4.23-4.14 (m, 1.7H), 3.84 (s, 3H), 3.83 (s, 2.1H), 3.66-3.59 (m, 0.7H), 3.45 (dd, $J = 9.0$, 9.5 Hz, 0.7H), 3.38-3.30 (m, 2H), 2.50-2.44 (m, 3.7H), 2.41-2.23 (m, 3.8H), 2.34 (s, 2.1H), 2.32 (s, 3H), 2.19-2.14 (m, 1H), 2.08 (s, 2.1H), 1.95 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 158.3, 158.2, 142.7, 142.3, 139.1, 138.3, 137.8, 137.2, 136.7, 136.6, 136.5, 136.4, 129.4, 129.3, 129.2, 129.0, 127.5, 127.1, 126.9, 126.8, 126.6, 113.4, 113.2, 70.4, 69.0, 56.3, 55.6, 55.2, 52.9, 52.1, 41.2, 39.2, 27.2, 26.6, 21.4, 21.4, 20.9, 20.9. IR (neat): 2969, 2926, 2360, 1599, 1506, 1339, 1181, 1153, 1034, 908, 739, 662 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{26}$H$_{30}$NO$_3$S [M+H]$^+$ Calcd. for [M+H]$^+$ 436.1941, found 436.1926.

2-Methyl-2-(naphthalen-2-yl)-4-(p-tolyl)-1-tosylpyrrolidine (3ag).

5 : 4 (ratio of two diastereomers). White powder. TLC: $R_f = 0.47$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 8.07 (m, 1H), 7.94–7.92 (m, 1H), 7.89–7.86 (m, 2H), 7.83–7.75 (m, 4.4H), 7.68–7.62 (m, 1.8H), 7.55–7.49 (m, 3.6H), 7.42–7.40 (m, 0.8), 7.32–7.28 (m, 3.6H), 7.17 (s, 3.2H), 7.11–7.09 (m, 2H), 7.04–6.99 (m, 3.6H), 4.31(dd, $J = 8.5$, 8.5 Hz, 0.8H), 4.26 (dd, $J = 8.0$ Hz, 1H), 3.76–3.68 (m, 0.8H), 3.57 (dd, $J = 9.5$, 11 Hz, 0.8H), 3.49–3.45 (m, 1H), 3.41–3.34 (m,
1H), 2.61–2.51 (m, 1.8H), 2.36 (s, 2.4H), 2.35 (s, 2.4H), 2.32 (s, 3H), 2.28–2.23 (m, 3.4H), 2.09 (s, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 144.1, 142.8, 142.5, 142.4, 138.2, 137.6, 136.8, 136.6, 136.4, 136.3, 133.0, 132.8, 132.3, 132.2, 129.4, 129.3, 129.2, 128.9, 128.3, 128.2, 128.0, 127.7, 127.3, 127.2, 127.2, 126.9, 126.8, 126.8, 126.0, 125.9, 125.9, 125.8, 124.9, 124.8, 124.5, 123.8, 70.9, 69.5, 56.5, 55.7, 52.9, 52.0, 41.4, 39.3, 27.1, 26.4, 21.4, 21.3, 21.0, 20.9. IR (KBr): 2974, 2922, 1599, 1517, 1339, 1157, 1089, 1004, 814, 750, 674, 590 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{29}$H$_{30}$NO$_2$S [M+H]$^+$ 456.1992, found 456.1975.

2-Cyclopropyl-2-phenyl-4-(p-tolyl)-1-tosylpyrrolidine (3ah). $1 : 1$ (ratio of two diastereomers). White powder. TLC: $R_f = 0.42$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.81–7.76 (m, 4H), 7.59–7.57 (m, 2H), 7.44–7.36 (m, 4H), 7.32–7.24 (m, 6H), 7.16–7.08 (m, 8H), 7.01–6.99 (m, 2H), 4.25 (dd, $J = 6.5$, 7.5 Hz, 1H), 4.13 (t, $J = 8.0$ Hz, 1H), 3.53–3.32 (m, 4H), 2.45 (s, 3H), 2.41 (s, 3H), 2.33–2.29 (m, 7H), 2.21–2.15 (m, 1H), 2.06–2.03 (m, 2H), 1.90–1.84 (m, 1H), 1.64–1.58 (m, 2H), 0.95–0.85 (m, 2H), 0.72–0.62 (m, 3H), 0.54–0.48 (m, 1H), 0.28–0.20 (m, 2H). $^{13}$C NMR (CDCl$_3$): $\delta$ 148.3, 146.6, 142.6, 142.3, 138.9, 137.9, 136.8, 136.7, 136.6, 136.4, 129.3, 129.2, 129.1, 129.0, 128.0, 127.9, 127.3, 127.1, 127.0, 126.9, 126.8, 126.7, 126.0, 74.7, 73.3, 56.2, 55.9, 45.0, 43.0, 42.1, 38.5, 21.4, 21.4, 20.9, 20.9, 17.9, 17.6, 5.7, 5.3, 2.7, 1.9. IR (KBr): 3022, 2920, 1519, 1490, 1444, 1336, 1163, 1151, 1099, 814, 759, 684, 579 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{27}$H$_{30}$NO$_2$S [M+H]$^+$ 432.1992, found 432.1978.

4'-(p-Tolyl)-1'-tosyl-3,4-dihydro-2H-spiro[naphthalene-1,2'-pyrrolidine] (3ai). $5 : 4$ (ratio of two diastereomers). White powder. TLC: $R_f = 0.40$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.73–7.71 (m, 0.8H), 7.57–7.54 (m, 0.4H), 7.47–7.45 (m, 2H), 7.30–7.28 (m, 0.8H), 7.22–7.19 (m, 2.8H), 7.14–6.99 (m, 10H), 4.19 (dd, $J = 7.5$, 7.5 Hz, 0.4H), 4.13 (dd, $J = 8.0$, 8.5 Hz, 1H), 3.68–3.55 (m, 1.4H), 3.44–3.40 (m, 1.4H), 3.03–2.81 (m, 3.2H), 2.76–2.72 (m, 1H), 2.66–2.63 (m, 1H), 2.50–2.46 (m, 0.4H), 2.44 (s, 1.2H), 2.42 (s, 3H), 2.33 (s, 3H), 2.32 (s, 1.2H), 2.29–2.23 (m, 1H), 2.20–2.13 (m, 1.4H), 2.09–2.03 (m, 1.4H), 1.90–1.85 (m, 0.8H), 1.80–1.70 (m, 1H). $^{13}$C NMR (CDCl$_3$): $\delta$ 142.8, 142.7, 142.5, 141.2, 138.4, 138.0, 137.9, 136.7, 136.7, 136.6, 136.4, 135.2, 129.3, 129.3, 129.2, 129.1, 128.6, 127.6, 127.5, 127.3, 127.3, 127.1, 127.0, 126.7, 126.4, 126.0, 125.8, 70.9, 70.4, 56.0, 55.1, 52.4, 51.8, 41.3, 39.7, 36.5, 36.3, 29.7, 28.7, 22.8, 21.4, 21.4, 21.0, 20.9, 20.9. IR (KBr): 2928, 2867, 1516, 1488, 1448, 1334, 1154, 1103, 1093, 1029, 814, 759, 680 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{27}$H$_{30}$NO$_2$S [M+H]$^+$ 432.1992, found 432.1978.

White powder. TLC: $R_f = 0.52$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.75–7.73 (m, 2H), 7.28–7.26 (m, 2H), 7.12–7.07 (m, 4H), 3.85–3.82 (m, 1H), 3.38–3.30 (m, 1H), 3.13 (dd, $J = 9.0, 11$ Hz, 1H), 2.62–2.56 (m, 1H), 2.49–2.44 (m, 1H), 2.42–2.38 (m, 4H), 2.32 (s, 3H), 1.98–1.93 (m, 1H), 1.86–1.57 (m, 7H), 1.51–1.44 (m, 1H), 1.42–1.24 (m, 2H). $^{13}$C NMR (CDCl$_3$): $\delta$ 142.5, 138.9, 137.0, 136.6, 129.3, 129.2, 127.1, 126.9, 73.5, 55.1, 46.2, 40.8, 40.3, 39.7, 27.9, 27.7, 23.8, 22.8, 21.4, 20.9 cm$^{-1}$. IR (KBr): 2923, 2857, 1518, 1454, 1341, 1337, 1162, 1094, 1002, 811, 681 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{24}$H$_{32}$NO$_2$S [M+H]$^+$ 398.2148, found 398.2136.

3-Phenyl-1-tosyl-1-azaspiro[4.6]undecane (3bj).

White powder. TLC: $R_f = 0.55$ (hexane/ethyl acetate = 5:1). $^1$H NMR (CDCl$_3$): $\delta$ 7.75–7.72 (m, 2H), 7.31–7.26 (m, 4H), 7.24–7.18 (m, 3H), 3.88–3.84 (m, 1H), 3.38 (sept, $J = 6.0$ Hz, 1H), 3.16 (dd, $J = 9.0, 11$ Hz, 1H), 2.62–2.56 (m, 1H), 2.50–2.41 (m, 5H), 1.98–1.94 (m, 1H), 1.85–1.56 (m, 7H), 1.51–1.44 (m, 1H), 1.42–1.24 (m, 2H). $^{13}$C NMR (CDCl$_3$): $\delta$ 142.5, 140.1, 138.9, 129.4, 128.6, 127.1, 127.1, 127.0, 73.5, 54.9, 46.1, 40.8, 40.7, 39.7, 27.9, 27.7, 23.8, 22.8, 21.4. IR (KBr): 2929, 2859, 1455, 1335, 1161, 1149, 1096, 1003, 813, 700, 660, 589 cm$^{-1}$. HRMS (ESI$^+$) Calcd. for C$_{23}$H$_{30}$NO$_2$S [M+H]$^+$ 384.1992, found 384.1979.
$^1$H NMR and $^{13}$C NMR Spectra of Products

3aa
3ac

Ts

N

Br