Molybdenum-Catalyzed Ring-Closing Metathesis of Allenynes

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General. All manipulations were carried out in a nitrogen-filled gloved box and with standard Schlenk techniques under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck). NMR spectra were recorded on a Varian Gemini 2000 (¹H at 300.77 MHz and ¹³C NMR at 75.46 MHz) or a Varian Mercury 400 (¹H at 400.44 MHz). All NMR data were obtained in CDCl₃. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm. Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.00 ppm. High resolution mass spectra were recorded on a JEOL JMS-SX102A. IR spectra was recorded on a Shimadzu FTIR-8100 spectrometer.

Materials. 2,6-Diisopropylphenylimidoneophilidenemolybdenum(VI) bis(hexafluoro-*t*-butoxide) (Schrock catalyst, **1**) was purchased from Strem. Toluene was distilled from sodium–benzophenone ketyl before using for catalytic reactions. All other commercially available chemical resources were used without further purifications.

Typical Procedure for the Preparation of Tosylamine-bridged Allenynes^{1,2}

To a solution of pyridinium *p*-toluenesulfonate (PPTS) (1.78 g, 7.10 mmol, 5 mol %) in CH₂Cl₂ (60 mL) were added 2-methylbut-3-yn-2-ol (12.0 g, 143 mmol) and 3,4-dihydropyran (DHP) (50.0 g, 594 mmol). After being stirred at room temperature for 16 h, the volatile materials were removed under reduced pressure. The residue was taken up in ether, washed with water, dried over MgSO₄, and concentrated. Distillation under reduced pressure (35 °C/1.8 mmHg) gave pure 1,1-dimethylprop-2-ynyl tetrahydropyran-2-yl ether

(1) Cowie, J. S.; Landor, P. D.; Landor, S. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 3807.

(2) Wender, P. A.; Glorius, F.; Husfeld, C. O.; Langkopf, E.; Love, J. A. *J. Am. Chem. Soc.* **1999**, 121, 5348.

(22.0 g, 90%).

To a solution of 1,1-dimethylprop-2-ynyl tetrahydropyran-2-yl ether (4.00 g, 23.8 mmol) in THF (70.0 mL) at $-78\text{ }^{\circ}\text{C}$ was slowly added *n*-butyllithium (1.59 M hexane solution; 20 mL) over 30 min. HMPA (5.0 mL) was added to the mixture at $0\text{ }^{\circ}\text{C}$, and then paraformaldehyde (1.43 g, 47.6 mmol) was added. After being stirred at room temperature for 2h, the reaction was quenched by a phosphate buffer solution (pH 6.9), and the mixture was extracted with ether. The organic layer was washed with water, dried over MgSO_4 , and concentrated. Distillation under reduced pressure ($100\text{ }^{\circ}\text{C}/1.8\text{ mmHg}$) gave pure 4-methyl-4-(tetrahydropyran-2-yloxy)pent-2-yn-1-ol (3.40 g, 72%).

To an ether suspension (50 mL) of lithium aluminum hydride (1.57 g, 41.5 mmol) was added dropwise ether solution (15 mL) of 4-methyl-4-(tetrahydropyran-2-yloxy)pent-2-yn-1-ol (3.29 g, 16.6 mmol) over 30 min. After being stirred at room temperature for 3 h, the reaction was quenched by addition of a mixture of Celite[®] and sodium sulfate decahydrate ($v/v = 1/1$), and the mixture was filtrated. The solvent was removed under reduced pressure, and the residue was distilled under reduced pressure ($35\text{ }^{\circ}\text{C}/1.8\text{ mmHg}$) to give pure 4-methylpenta-2,3-dien-1-ol (1.03 g, 63%).

To a stirred solution of *N*-(prop-2-ynyl)tosylamine (584 mg, 2.79 mmol) in THF (7.0 mL) were added successively triphenylphosphine (1.39 g, 5.30 mmol), 4-methylpenta-2,3-dien-1-ol (903 mg, 9.20 mmol), and diisopropylcarbodiimide (DIAD) (903 mg, 4.46 mmol) at $0\text{ }^{\circ}\text{C}$. The reaction was warmed to room temperature over 30 min and was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane:AcOEt = 14:1) to give pure *N*-(4-methylpenta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (**3a**, 419 mg, 52%).

***N*-(4-Methylpenta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3a).** White solid; mp: 56-57 $^{\circ}\text{C}$; ^1H NMR δ 1.67 (d, $J = 3.0\text{ Hz}$, 6H), 1.99 (t, $J = 2.5\text{ Hz}$, 1H), 2.42 (s, 3H), 3.79 (d, $J = 6.9\text{ Hz}$, 2H), 4.16 (d, $J = 2.5\text{ Hz}$, 2H), 4.81-4.87 (m, 1H), 7.28 (d, $J = 8.1\text{ Hz}$, 2H), 7.73 (d, $J = 8.1\text{ Hz}$, 2H); ^{13}C NMR δ 20.3, 21.5, 35.5, 46.6, 73.3, 76.5, 83.6, 97.0, 127.6, 129.4, 136.1, 143.4, 203.8; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$ (M^+) 289.1136, found 289.1136.

Anal. Calcd for C₁₆H₁₉NO₂S: C, 66.40; H, 6.62; N, 4.84. Found: C, 66.26; H, 6.61; N, 4.80.

***N*-(4-Methylpenta-2,3-dienyl)-*N*-(prop-2-ynyl-3-*d*)tosylamine (3a-*d*).** White solid; mp: 52-53 °C; ¹H NMR δ 1.66 (d, *J* = 2.7 Hz, 6H), 2.42 (s, 3H), 3.79 (d, *J* = 7.2 Hz, 2H), 4.15 (s, 2H), 4.83-4.84 (m, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H); ¹³C NMR δ 20.3, 21.6, 35.5, 46.6, 73.6 (t, *J* = 17.7 Hz), 76.0, 83.6, 97.1, 127.7, 129.4, 136.1, 143.4, 203.9; HRMS (CI) calcd for C₁₆H₁₉DNO₂S (M⁺ + H) 291.1276, found 291.1273.

***N*-(4-Methylhexa-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3b).** Pale yellow solid; mp: 42-43 °C; ¹H NMR δ 0.97 (t, *J* = 7.4 Hz, 3H), 1.67 (d, *J* = 3.0 Hz, 3H), 1.92 (dq, *J* = 3.0, 7.4 Hz, 1H), 1.98 (t, *J* = 2.4 Hz, 1H), 2.41 (s, 3H), 3.77 (dd, *J* = 13.8, 6.9 Hz, 1H), 3.83 (dd, *J* = 13.8, 6.9 Hz, 1H), 4.13 (dd, *J* = 18.0, 2.4 Hz, 1H), 4.20 (dd, *J* = 18.0, 2.4 Hz, 1H), 4.90-4.97 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H); ¹³C NMR δ 12.0, 18.8, 21.5, 26.8, 35.5, 46.6, 73.4, 76.5, 85.6, 103.3, 127.6, 129.4, 136.1, 143.4, 202.9; HRMS (EI) calcd for C₁₇H₂₁NO₂S (M⁺) 303.1293, found 303.1293.

Dimethyl 8-methylnona-6,7-dien-1-yne-4,4-dicarboxylate (3c). Yellow oil; ¹H NMR δ 1.64 (d, *J* = 3.0 Hz, 6H), 1.98 (t, *J* = 2.7 Hz, 1H), 2.70 (d, *J* = 7.5 Hz, 2H), 2.85 (d, *J* = 2.7 Hz, 2H), 3.72 (s, 6H), 4.71-4.80 (m, 1H); ¹³C NMR δ 20.4, 22.5, 32.5, 52.7, 57.1, 71.2, 78.8, 82.1, 95.4, 170.1, 203.8; HRMS (EI) calcd for C₁₄H₁₈O₄ (M⁺) 250.1205, found 250.1212.

***N*-(3-Cyclohexylideneprop-2-enyl)-*N*-(prop-2-ynyl)tosylamine (3e).** White solid; mp: 79-80 °C; ^1H NMR δ 1.42-1.62 (m, 6H), 1.98 (t, J = 2.4 Hz, 1H), 2.06-2.10 (m, 4H), 2.42 (s, 3H), 3.80 (d, J = 6.9 Hz, 2H), 4.16 (d, J = 2.4 Hz, 2H), 4.81-4.86 (m, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 21.5, 25.8, 27.1, 31.2, 35.4, 46.7, 73.3, 76.4, 83.2, 104.1, 127.5, 129.3, 136.0, 143.3, 200.6; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_2\text{S}$ (M^+) 329.1449, found 329.1451.

***N*-(4-Isopropyl-5-methylhexa-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3f).** White solid; mp: 55-56 °C; ^1H NMR δ 0.99 (d, J = 7.1 Hz, 12H), 1.97 (t, J = 2.4 Hz, 1H), 2.15 (dsep, J = 2.4, 7.1 Hz, 2H), 2.42 (s, 3H), 3.81 (d, J = 6.9 Hz, 2H), 4.20 (d, J = 2.4 Hz, 2H), 5.10 (tt, J = 7.0, 2.1 Hz, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 21.5, 22.1, 22.4, 29.5, 35.6, 46.8, 73.7, 89.7, 120.1, 127.7, 129.4, 136.2, 143.4, 200.9; HRMS (CI) calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_2\text{S}$ ($\text{M}^+ + \text{H}$) 346.1841, found 346.1837.

***N*-(4-Methylpenta-2,3-dienyl)-*N*-(1-methylprop-2-ynyl)tosylamine (3g).** White solid; mp: 58-59 °C; ^1H NMR δ 1.49 (d, J = 7.0 Hz, 3H), 1.67 (d, J = 2.7 Hz, 6H), 2.12 (d, J = 2.2 Hz, 1H), 2.41 (s, 3H), 3.68 (dd, J = 15.6, 8.0 Hz, 1H), 3.90 (dd, J = 15.6, 5.3 Hz, 1H), 4.88 (dq, J = 7.0, 2.2 Hz, 1H), 5.03-5.11 (m, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 19.8, 20.2, 21.5, 22.6, 44.8, 45.9, 73.0, 81.5, 87.8, 97.0, 127.5, 129.4, 136.5, 143.2, 202.0; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}$ (M^+) 303.1293, found 303.1306.

***N*-(4-Phenylpenta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3h).** Pale yellow oil; ^1H NMR δ 1.99 (t, J = 2.6 Hz, 1H) 2.89 (d, J = 2.7 Hz, 3H), 2.41 (s, 3H), 3.90 (dd, J = 14.4, 7.2 Hz, 1H), 4.01 (dd, J = 14.4, 6.6 Hz, 1H), 4.16 (dd, J = 18.0, 2.6 Hz, 1H), 4.25 (dd, J = 15.9, 2.6 Hz, 1H), 5.33-5.40 (m, 1H), 7.19-7.39 (m, 7H), 7.74 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 17.0, 21.5, 36.0, 46.0, 73.8, 76.4, 88.1, 102.6, 125.8, 127.0, 127.6, 128.3, 129.5, 136.0, 136.1, 143.5, 205.8; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_2\text{S}$ (M^+) 351.1293, found 351.1297.

***N*-(4-Methylpenta-2,3-dienyl)-*N*-(but-3-ynyl)benzylamine (3i).** Yellow oil; ^1H NMR δ 1.65 (d, J = 2.7 Hz, 6H), 2.17 (t, J = 2.6 Hz, 1H), 3.09 (d, J = 6.9 Hz, 2H), 3.30 (d, J = 2.6 Hz, 2H), 3.63 (s, 2H), 4.12-4.98 (m, 1H), 7.19-7.33 (m, 5H); ^{13}C NMR δ 20.5, 41.3, 53.6, 56.7, 73.0, 78.7, 85.9, 95.3, 127.0, 128.2, 129.1, 138.5, 203.3; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{N}$ (M^+) 225.1517, found 225.1517.

Diethyl 8-methylnona-6,7-dien-1-yne-4,4-dicarboxylate (3j). Yellow oil; ^1H NMR δ 1.25 (t, J = 7.1 Hz, 6H), 1.65 (d, J = 3.0 Hz, 6H), 1.98 (t, J = 2.7 Hz, 1H), 2.71 (d, J = 7.8 Hz, 2H), 2.85 (d, J = 2.7 Hz, 2H), 4.12-4.25 (m, 4H), 4.72-4.81 (m, 1H); ^{13}C NMR δ 14.0, 20.4, 22.3, 32.3, 57.0, 61.5, 71.1, 78.9, 82.2, 95.2, 169.6, 203.9; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4$ (M^+) 278.1518, found 278.1516.

***N*-(Penta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3k).** White solid; mp: 45-46 °C; ¹H NMR δ 1.63 (dd, *J* = 7.1, 3.0 Hz, 3H), 2.00 (t, *J* = 2.7 Hz, 1H), 2.40 (s, 3H), 3.78 (ddd, *J* = 21.2, 7.2, 2.2 Hz, 1H), 3.86 (ddd, *J* = 21.2, 7.2, 2.2 Hz, 1H), 4.11 (dd, *J* = 18.3, 2.5 Hz, 1H), 4.18 (dd, *J* = 18.3, 2.5 Hz, 1H), 4.90-4.98 (m, 1H), 5.10-5.18 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H); ¹³C NMR δ 14.0, 21.5, 35.7, 46.2, 73.5, 76.4, 85.2, 87.4, 127.6, 129.4, 136.0, 143.5, 206.5; HRMS (EI) calcd for C₁₅H₁₇NO₂S (M⁺) 275.0980, found 275.0974.

***N*-(Buta-2,3-dienyl)-*N*-(prop-2-ynyl)tosylamine (3l).** White solid; mp: 55-56 °C; ¹H NMR δ 2.03 (t, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 3.88 (dt, *J* = 6.8, 2.5 Hz, 2H), 4.15 (d, *J* = 2.4 Hz, 2H), 4.78 (dt, *J* = 6.8, 2.5 Hz, 2H), 5.04 (quint, *J* = 6.8 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H); ¹³C NMR δ 21.5, 35.8, 45.6, 73.7, 76.4, 85.3, 127.6, 129.5, 136.0, 143.6, 209.7; HRMS (EI) calcd for C₁₄H₁₅NO₂S (M⁺) 261.0823, found 261.0825.

4-Methylpent-2,3-dienyl prop-2-ynyl ether (3m). Yellow oil; ¹H NMR δ 1.71 (d, *J* = 3.0 Hz, 6H), 2.41 (t, *J* = 2.5 Hz, 1H), 4.04 (d, *J* = 6.9 Hz, 2H), 4.17 (d, *J* = 2.5 Hz, 2H), 5.01-5.07 (m, 1H); ¹³C NMR δ 20.3, 56.3, 68.5, 74.1, 79.7, 85.4, 96.1, 203.4; HRMS (EI) calcd for C₉H₁₂O (M⁺) 136.0888, found 136.0886.

***N*-(4-Methylpent-2,3-dienyl)-*N*-(but-2-ynyl)tosylamine (3n).** White solid; mp: 42-43 °C; ¹H NMR δ 1.54 (t, *J* = 2.4 Hz, 3H), 1.66 (d, *J* = 2.7 Hz, 6H), 2.40 (s, 3H), 3.75 (d, *J* = 6.6

Hz, 2H), 4.07 (q, $J = 2.4$ Hz, 2H), 4.82-4.84 (m, 1H), 7.27 (d, $J = 8.3$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR δ 3.2, 20.4, 21.5, 36.1, 46.5, 71.6, 81.1, 83.9, 96.8, 127.7, 129.2, 136.2, 143.0, 203.6; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}$ (M^+) 303.1293, found 303.1290.

***N*-(4-Methylpent-2,3-dienyl)-*N*-(3-phenylprop-2-ynyl)tosylamine (3o).** White solid; mp: 58-59 °C; ^1H NMR δ 1.70 (d, $J = 2.7$ Hz, 6H), 2.36 (s, 3H), 3.88 (d, $J = 6.9$ Hz, 2H), 4.41 (s, 2H), 4.91-4.97 (m, 1H), 7.04 (d, $J = 8.1$ Hz, 2H), 7.23-7.33 (m, 5H), 7.71 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR δ 20.3, 21.4, 36.5, 46.8, 81.7, 83.7, 85.3, 97.0, 122.3, 127.7, 128.0, 128.2, 129.4, 131.4, 135.9, 143.3, 203.9; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_2\text{S}$ (M^+) 365.1449, found 365.1457.

***N*-(5-Methylhex-3,4-dienyl)-*N*-(prop-2-ynyl)tosylamine (3p).** Pale yellow oil; ^1H NMR δ 1.67 (d, $J = 3.0$ Hz, 6H), 2.02 (t, $J = 2.4$ Hz, 1H), 2.22 (dt, $J = 7.5, 7.5$ Hz, 2H), 2.42 (s, 2H), 3.25 (t, $J = 7.5$ Hz, 2H), 4.15 (d, $J = 2.4$ Hz, 2H), 4.85-4.94 (m, 1H), 7.29 (d, $J = 8.3$ Hz, 2H), 7.73 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR δ 20.6, 21.6, 27.8, 36.3, 46.0, 73.6, 76.6, 85.0, 95.9, 127.6, 129.4, 136.0, 143.4, 202.4; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}$ (M^+) 303.1293, found 303.1299.

***N*-(4-Methylpent-2,3-dienyl)-*N*-(but-3-ynyl)tosylamine (3q).** Pale yellow solid; mp: 62-63 °C; ^1H NMR δ 1.65 (d, $J = 2.7$ Hz, 6H), 1.96 (t, $J = 2.7$ Hz, 1H), 2.41 (s, 3H), 2.41-2.50 (m, 2H), 3.03-3.35 (m, 2H), 3.78 (d, $J = 7.2$ Hz, 2H), 4.71-4.80 (m, 1H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 19.0, 20.3, 21.5, 45.6, 48.3, 70.0, 80.9, 84.2, 97.1, 127.1, 129.7, 136.9, 143.2, 203.5; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}$ (M^+) 303.1293 found,

303.1296.

General Procedure for RCM of Allenynes. To a solution of Schrock complex (27.7 mg, 0.036 mmol) in dry toluene (4.0 mL) was added a solution of diethyl 8-methyl nona-2,3-diene-1-yne-4,4-dicarboxylate (**3j**, 67.1 mg, 0.241 mmol) in dry toluene (4.8 mL). After being stirred under argon atmosphere for 3 h at room temperature, the volatile material was removed under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane:AcOEt = 5:1) to give pure diethyl 3-(3-methylbuta-1,2-dienyl)cyclopent-3-ene-1,1-dicarboxylate (**4j**, 63.9 mg, 95%).

3-(3-Methylbuta-1,2-dienyl)-1-tosyl-3-pyrroline (4a). Pale yellow solid; mp: 114-115 °C; ^1H NMR δ 1.70 (d, J = 2.7 Hz, 6H), 2.42 (s, 3H), 4.05-4.07 (m, 2H), 4.13-4.16 (m, 2H), 5.42 (t, J = 1.8 Hz, 1H), 5.69 (t, J = 2.9 Hz, 1H), 7.32 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ 20.4, 21.5, 54.8, 55.5, 86.1, 98.6, 119.2, 127.4, 129.7, 134.3, 135.1, 143.3, 204.2; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$ (M^+) 289.1136, found 289.1138. Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$: C, 66.40; H, 6.62; N, 4.84. Found: C, 66.50; H, 6.64; N, 4.80.

3-(3-Methylbuta-1,2-dienyl-1-d)-1-tosyl-3-pyrroline (4a-d). Pale yellow solid; mp: 112-113 °C; ^1H NMR δ 1.71 (s, 6H), 2.43 (s, 3H), 4.04-4.07 (m, 2H), 4.14-4.17 (m, 2H), 5.42 (t, J = 1.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 20.4, 21.5, 54.8, 55.5, 86.1, 98.6, 119.1, 127.4, 129.7, 134.2, 135.1, 143.3, 204.1; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{18}\text{DNO}_2\text{S}$ (M^+) 290.1198, found 290.1199.

3-(3-Methylpenta-1,2-dienyl)-1-tosyl-3-pyrroline (4b). Yellow solid; mp: 88-89 °C; ^1H NMR δ 0.95 (t, J = 7.5 Hz, 3H), 1.71 (d, J = 2.7 Hz, 3H), 1.98 (dq, J = 3.3, 7.5 Hz, 2H),

2.42 (s, 3H), 4.03-4.06 (m, 2H), 4.13-4.17 (m, 2H), 5.42 (t, $J = 2.0$ Hz, 1H), 5.79 (q, $J = 3.0$ Hz, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 12.2, 19.0, 21.5, 26.9, 54.9, 55.5, 88.1, 104.9, 119.0, 127.4, 129.7, 134.1, 135.1, 143.4, 203.5; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}$ (M^+) 303.1293, found 303.1290.

Dimethyl 3-(3-Methylbuta-1,2-dienyl)cyclopent-3-ene-1,1-dicarboxylate (4c). Pale yellow solid; mp: 62-63 °C; ^1H NMR δ 1.72 (d, $J = 3.0$ Hz, 6H), 2.96-3.02 (m, 2H), 3.09 (q, $J = 2.0$ Hz, 2H), 3.74 (s, 6H), 5.42 (t, $J = 2.1$ Hz, 1H), 5.79 (t, $J = 2.9$ Hz, 1H); ^{13}C NMR δ 20.5, 41.0, 41.2, 52.8, 58.6, 88.4, 97.5, 122.6, 137.1, 172.6, 204.1; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4$ (M^+) 250.1205, found 250.1212.

Dimethyl 3-(3-Methylpenta-1,2-dienyl)cyclopent-3-ene-1,1-dicarboxylate (4d). ^1H NMR δ 0.99 (t, $J = 7.5$ Hz, 3H), 1.72 (d, $J = 2.7$ Hz, 3H), 1.99 (dq, $J = 3.3, 7.2$ Hz, 2H), 2.991-2.996 (m, 2H), 3.087-3.094 (m, 2H), 3.74 (s, 6H), 5.38-5.42 (m, 1H), 5.86-5.92 (m, 1H).

3-(2-Cyclohexylidenevinyl)-1-tosyl-3-pyrroline (4e). Yellow solid; mp: 101-102 °C; ^1H NMR δ 1.40-1.60 (m, 6H), 2.09-2.11 (m, 4H), 2.42 (s, 3H), 4.05-4.07 (m, 2H), 4.14-4.17 (m, 2H), 5.41 (t, $J = 1.8$ Hz, 1H), 5.70 (s, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.72 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR δ 21.5, 25.9, 27.3, 31.3, 54.8, 55.6, 85.9, 105.7, 118.9, 127.4, 129.7, 134.2, 135.1, 143.3, 200.9; HRMS (CI) calcd for $\text{C}_{19}\text{H}_{24}\text{NO}_2\text{S}$ ($\text{M}^+ + \text{H}$) 330.1528, found 330.1524.

3-(3-Isopropyl-4-methylpenta-1,2-dienyl)-1-tosyl-3-pyrroline (4f). Yellow solid; mp: 75-76 °C; ^1H NMR δ 0.98 (d, $J = 6.6$ Hz, 6H), 1.00 (d, $J = 6.6$ Hz, 6H), 2.19 (dsep, $J = 2.1, 6.6$

Hz, 2H), 2.42 (s, 3H), 4.01-4.04 (m, 2H), 4.15-4.18 (m, 2H), 5.41 (t, $J = 2.0$ Hz, 1H), 5.93 (s, 1H), 7.30 (d, $J = 8.3$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR δ 21.5, 22.2, 22.4, 29.9, 54.7, 55.7, 91.5, 118.8, 121.3, 127.4, 129.7, 134.0, 135.0, 143.4, 201.9; HRMS (CI) calcd for $\text{C}_{20}\text{H}_{28}\text{NO}_2\text{S}$ ($\text{M}^+ + \text{H}$) 346.1841, found 346.1840.

2-Methyl-3-(3-methylbuta-1,2-dienyl)-1-tosyl-3-pyrroline (4g). Yellow solid; mp: 89-90 °C; ^1H NMR δ 1.42 (d, $J = 6.3$ Hz, 3H), 1.72 (dd, $J = 8.3, 2.9$ Hz, 6H), 2.41 (s, 3H), 4.07 (dt, $J = 15.6, 2.1$ Hz, 1H), 4.18 (dq, $J = 15.6, 2.1$ Hz, 1H), 4.51 (t, $J = 6.3$ Hz, 1H), 5.35 (s, 1H), 5.63 (t, $J = 3.0$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.70 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR δ 20.0, 20.3, 21.5, 22.1, 54.4, 63.1, 85.9, 98.2, 118.9, 127.2, 129.6, 135.3, 139.8, 143.2, 204.2; HRMS (CI) calcd for $\text{C}_{17}\text{H}_{22}\text{NO}_2\text{S}$ ($\text{M}^+ + \text{H}$) 304.1371, found 304.1290.

3-(3-Phenylbuta-1,2-dienyl)-1-tosyl-3-pyrroline (4h). Yellow solid; mp: 144-145 °C; ^1H NMR δ 2.13 (d, $J = 2.7$ Hz, 3H), 2.43 (s, 3H), 4.08-4.11 (m, 2H), 4.18-4.22 (m, 2H), 5.58 (t, $J = 2.1$ Hz, 1H), 5.79 (d, $J = 2.7$ Hz, 1H), 7.22-7.34 (m, 7H), 7.70 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 17.3, 21.8, 54.9, 55.8, 90.3, 104.2, 121.0, 126.1, 127.5, 127.6, 128.6, 130.0, 134.3, 134.4, 136.0, 143.6, 207.6; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_2\text{S}$ (M^+) 351.1293, found 351.1295.

1-Benzyl-3-(3-methylbuta-1,2-dienyl)-3-pyrroline (4i). Yellow oil; ^1H NMR δ 1.68 (d, $J = 2.7$ Hz, 6H), 3.47-3.48 (m, 2H), 3.52-3.56 (m, 2H), 3.82 (s, 2H), 5.60 (t, $J = 1.8$ Hz, 1H), 5.81 (t, $J = 2.7$ Hz, 1H), 7.23-7.39 (m, 5H); ^{13}C NMR δ 20.5, 59.9, 60.5, 60.6, 87.1, 97.4, 122.5, 126.9, 128.3, 128.6, 137.1, 139.5, 204.0; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{19}\text{N}$ (M^+) 225.1517, found 225.1521.

Diethyl 3-(3-Methylbuta-1,2-dienyl)cyclopent-3-ene-1,1-dicarboxylate (4j). Yellow oil; ^1H NMR δ 1.24 (t, $J = 7.2$ Hz, 6H), 1.72 (d, $J = 2.7$ Hz, 6H), 2.97-2.98 (m, 2H), 3.06-3.07 (m, 2H), 4.19 (q, $J = 7.2$ Hz, 4H), 4.13 (t, $J = 8.1$ Hz, 1H), 5.41 ($J = 2.1$ Hz, 1H), 5.79 (t, $J = 2.7$ Hz, 1H); ^{13}C NMR δ 14.0, 20.6, 40.9, 41.1, 58.7, 61.5, 88.4, 97.5, 122.7, 137.0, 172.1, 204.1; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4$ (M^+) 278.1518, found 278.1517.

3-(Buta-1,2-dienyl)-1-tosyl-3-pyrroline (4k). Yellow solid; mp: 121-122 °C; ^1H NMR δ 1.69 (dd, $J = 7.1, 3.1$ Hz, 3H), 2.43 (s, 3H), 4.07-4.08 (m, 2H), 4.15-4.27 (m, 2H), 5.37 (quint, $J = 6.6$ Hz, 1H), 5.46 (d, $J = 1.2$ Hz, 1H), 5.80 (sext, $J = 3.2$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR δ 14.2, 21.5, 54.7, 55.5, 87.6, 89.1, 119.9, 127.4, 129.7, 134.1, 134.6, 143.4, 207.1; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2\text{S}$ (M^+) 275.0980, found 275.0981.

3-(3-Methyl-3-phenylbut-1-enyl)-1-tosyl-3-pyrroline (5). Yellow oil; ^1H NMR δ 1.40 (s, 6H), 2.42 (s, 3H), 4.17 (s, 4H), 5.51 (s, 1H), 5.68 (d, $J = 16.2$ Hz, 1H), 6.06 (d, $J = 16.2$ Hz, 1H), 7.28-7.33 (m, 7H), 7.73 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 21.5, 28.5, 40.7, 53.8, 55.0, 77.2, 119.8, 121.4, 126.0, 127.4, 128.2, 129.8, 134.2, 137.1, 143.3, 143.4, 147.9 [one sp^2 carbon signal is missing due to overlapping]; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_2\text{S}$ (M^+) 367.5054, found 367.1604.

Diels–Alder Reaction of Vinylallene **4c** and Maleic Anhydride³

To a stirred solution of vinylallene **4c** (23.5 mg, 0.093 mmol) in dry toluene (0.30 mL) at room temperature was added maleic anhydride (18.2 mg, 0.186 mmol). After 4 days, the solvent was removed, and the residue was purified by preparative thin-layer chromatography (hexane:AcOEt = 1:1) to give the Diels–Alder adduct **6** (22.5 mg, 70%).

(3) (a) Regás, D.; Afonso, M. M.; Rodríguez, M. L.; Palenzuela, J. A. *J. Org. Chem.* **2003**, 68, 7845. (b) Bentz, D.; Laschat, S. *Synthesis*, **2000**, 1766.

Dimethyl 4-isopropylidene-1,3-dioxo-1,3,3a,4,6,8,8a,8b-octahydroindeno[4,5-c]furan-7,7-dicarboxylate (6). White solid; 145-146 °C; ^1H NMR δ 1.81 (s, 3H), 1.99 (s, 3H), 2.69 (dd, $J = 11.0, 7.5$ Hz, 1H), 2.76 (m, 1H), 2.89 (dd, $J = 11.0, 10.5$ Hz, 1H), 3.05 (s, 2H), 3.62 (dd, $J = 9.2, 5.8$ Hz, 1H), 4.22 (d, $J = 5.8$ Hz, 1H), 6.32 (s, 1H); ^{13}C NMR δ 21.6, 21.9, 34.9, 37.3, 38.8, 44.2, 44.6, 52.93, 52.95, 59.7, 119.3, 119.8, 134.9, 141.4, 170.5, 170.9, 171.4, 171.9; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{O}_7$ (M^+) 348.1209, found 348.1208.