Supporting Materials

Novel Rhodium-Catalyzed Cycloisomerization of 1,6-Enynes with an Intramolecular Halogen Shift

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- A. General procedure:** All reactions and manipulations were conducted in an Ar-filled glovebox or using standard Schlenck techniques. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). ¹H and ¹³C were recorded on a Bruker AMX-300 spectrometers. Chemical shifts were reported in ppm down field from tetramethylsilane with the solvent resonance as the internal standard. MS spectra were recorded on the HP-5973N mass spectrometer. Element analyse was recorded on the CarloERBA1106 spectrometer.
- B. Materials:** 1,2-dichloroethane was distilled from P₂O₅ prior to use. The silver salt AgSbF₆ and RhCl₃ were purchased from Aldrich. [Rh(COD)Cl]₂,¹ [Rh(COD)₂]SbF₆,² Rh(CO)Cl(PPh₃)₂,³ [Rh(dppb)Cl]₂⁴ and RhCl(PPh₃)₃⁵ were prepared according to the reported literature procedures.
- C. General method for cycloisomerization of enyne with RhCl(PPh₃)₃:** Under Argon atmosphere, a 25ml Schlenk tube is charged with 0.2 mmol of enyne **1**, 10 mol% of RhCl(PPh₃)₃ and 3 mL of ClCH₂CH₂Cl (DCE). The mixture was stirred under reflux. The reaction was monitored by TLC. After the reaction was complete, the reaction mixture is directly subjected to column chromatography using PE-EtOAc (20:1-10:1) as eluent.

2a **R=CH₃, X=O**: Yield: 92%.

¹H NMR (300 MHz, CDCl₃) δ: 2.67 (d, *J* = 1.4Hz, 3H); 3.85-3.90 (m, 1H); 4.14 (dd, *J* = 2.3Hz, *J* = 9.0Hz, 1H); 4.39 (dd, *J* = 7.5Hz, *J* = 9.0Hz, 1H); 5.17-5.23 (m, 2H); 5.75-5.87 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 22.9; 44.7; 69.5; 117.0; 124.4; 134.3; 149.2; 167.6. IR (cm⁻¹): 1755; 1658. MS (*m/z*): 172 (M⁺, ³⁵Cl). Anal. Calcd for C₈H₉O₂Cl: C, 55.67; H, 5.26. Found: C, 55.90; H, 5.46.

2b **R=Ph, X=O**: Yield: 90%, m. p. 66-68 °C.

¹H NMR (300 MHz, CDCl₃) δ: 4.03-4.09 (m, 1H); 4.22 (dd, *J* = 2.1Hz, *J* = 9.0Hz, 1H); 4.50 (dd, *J* = 7.2Hz, *J* = 9.0Hz, 1H); 5.30-5.36 (m, 2H); 5.88-6.00 (m, 1H); 7.37-7.50 (m, 5H). ¹³C NMR (75MHz, CDCl₃) δ: 45.8; 69.3; 117.4; 125.3; 128.0; 128.9; 130.3; 134.0; 135.3; 147.9; 196.0. IR (cm⁻¹): 1757; 1642. MS (*m/z*): 234 (M⁺, ³⁵Cl). Anal. Calcd for C₁₃H₁₁O₂Cl: C, 66.53; H, 4.72. Found: C, 66.53; H, 4.90.

2c **R=C₄H₉, X=O**: Yield: 87%

¹H NMR (300 MHz, CDCl₃) δ: 0.86 (t, *J* = 7.2Hz, 3H); 1.26-1.34 (m, 2H); 1.52-1.55 (m, 2H); 2.97-3.20 (m 2H); 3.84-3.90 (m, 1H); 4.08 (dd, *J* = 2.4Hz, *J* = 9.0Hz, 1H); 4.32 (dd, *J* = 6.9Hz, *J* = 9.0Hz, 1H); 5.08-5.15 (m, 2H); 5.76-5.88 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ: 13.7; 21.8; 30.0; 34.5; 44.8; 67.5; 116.9; 124.2; 134.4; 154.5; 167.4. IR (cm⁻¹): 1757; 1652. MS (*m/z*): 214 (M⁺, ³⁵Cl). Anal. Calcd for C₁₁H₁₅O₂Cl: C, 61.54; H, 7.04. Found: C, 61.47; H, 7.21.

2d **R = CH₂OCH₃, X = O**: Yield: 72%.

¹H NMR (300 MHz, CDCl₃) δ: 3.39 (s, 3H); 3.91-3.96 (m, 1H); 4.22 (dd, *J* = 2.1Hz, *J* = 9.0Hz, 1H); 4.46 (dd, *J* = 7.5Hz, *J* = 9.0Hz, 1H); 4.70 (d, *J* = 13.2Hz, 1H); 4.82 (d, *J* = 13.2Hz, 1H); 5.21-5.28 (m, 2H); 5.84 (m, 1H). ¹³C NMR (75MHz, CDCl₃) δ: 44.7; 58.1; 69.0; 69.9; 117.6; 128.2; 133.5; 148.4; 166.8. IR (cm⁻¹): 1756; 1655. MS (*m/z*): 202 (M⁺, ³⁵Cl). Anal. Calcd for C₉H₁₀O₂Cl: C, 53.37; H, 5.43. Found: C, 53.59; H, 5.42.

2e R = CH₃, X = NBn: Yield: 89%.

¹H NMR (300 MHz, CDCl₃) δ: 2.71 (d, *J* = 1.2Hz, 3H); 2.98 (dd, *J* = 1.2Hz, *J* = 9.9Hz, 1H); 3.45 (dd, *J* = 8.1Hz, *J* = 9.9Hz, 1H); 3.63-3.66 (m, 1H); 4.42 (d, *J* = 15Hz, 1H); 4.58 (d, *J* = 15Hz, 1H); 5.05-5.11 (m, 1H); 5.64-5.76 (m, 1H); 7.22-7.36 (m, 5H). ¹³C NMR (75MHz, CDCl₃) δ: 22.2; 41.1; 46.9; 49.0; 115.7; 127.6; 128.1; 128.7; 128.1; 129.5; 136.0; 142.2; 165.7. IR (cm⁻¹): 1689; 1656. MS (*m/z*): 261 (M⁺, ³⁵Cl). Anal. Calcd for C₁₅H₁₅ONCl: C, 68.83; H, 6.16; N, 5.35. Found: C, 68.63; H, 6.26; N, 5.26.

2f R = Ph, X = NBn: Yield: 85%.

¹H NMR (300 MHz, CDCl₃) δ: 3.03 (dd, *J* = 1.8Hz, *J* = 10.2Hz, 1H); 3.51 (dd, *J* = 1.5Hz, *J* = 10.2Hz, 1H); 3.80-3.85 (m, 1H); 4.33 (d, *J* = 14.4Hz, 1H); 4.57 (d, *J* = 14.4Hz, 1H); 5.14-5.22 (m, 2H); 5.74-5.85 (m, 1H); 7.18-7.50 (m, 10H). ¹³C NMR (75MHz, CDCl₃) δ: 41.9; 47.0; 48.8; 116.1; 127.6; 127.7; 128.2; 128.7; 129.1; 129.4; 131.0; 135.5; 135.9; 136.5; 141.0; 164.0; IR (cm⁻¹): 1637; 1694. MS (*m/z*): 323 (M⁺, ³⁵Cl). HRMS Calcd for C₂₀H₁₈ONCl : 323.1077. Found: 323.1078.

2g R=CH₃, X=NTs: Yield: 83%. m. p. 94-96 °C.

¹H NMR (300 MHz, CDCl₃) δ: 2.44 (s, 3H); 2.57 (d, *J* = 1.2Hz, 3H); 3.69-3.74 (m, 1H); 3.78 (dd, *J* = 1.5Hz, *J* = 10.0Hz, 1H); 3.90 (dd, *J* = 7.8Hz, *J* = 10.0Hz, 1H); 5.08-5.16 (m, 2H); 5.67-5.79 (m, 1H); 7.34 (d, *J* = 8.4Hz, 2H); 7.92 (d, *J* = 8.4Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ: 21.7; 22.9; 40.9; 48.9; 116.7; 128.1; 129.7; 129.7; 134.5; 134.8; 145.3; 148.2; 163.7. IR (cm⁻¹): 1713; 1651. MS (*m/z*): 325 (M⁺, ³⁵Cl). Anal. Calcd for C₁₅H₁₆ONClS: C, 55.30; H, 4.95; N, 4.30. Found: C, 55.45; H, 5.10; N, 4.19.

1a': ¹H NMR (300 MHz, CDCl₃) δ: 2.01(s, 3H); 4.32-4.35 (m, 2H); 4.54-4.57 (m, 1H); 4.30 (dd, *J* = 1.0Hz, 10.2Hz, 1H); 5.43 (dd, *J* = 1.0Hz, 16.8Hz, 1H); 5.82-5.88 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ: 3.8; 58.0; 67.4; 71.7; 86.8; 119.6; 133.9; 152.9. IR (cm⁻¹):

2246; 1716; 1252; 1069. MS (m/z): 137 ($M^+ - ^{35}\text{Cl}$). HRMS: $\text{C}_8\text{H}_9\text{O}_2\text{Cl}-\text{Cl}$: 137.0590, Found: $[M^+ - \text{Cl}]$ 137.0587.

References:

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