Supporting Information

Rh(I)-Catalyzed Cyclization of 1-Arylprop-2-yn-1-ol Derivatives Utilizing Rhodium 1,4-Migration

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General. All operations were performed under an argon atmosphere. ^1H and ^{13}C -NMR spectra were recorded on a Bruker DRX-500 (500 MHz for ^1H and 125 MHz for ^{13}C) or a JEOL AL-400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer in CDCl_3 (99.8% atom enriched, Acros Co., Ltd.). Chemical shifts are expressed in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual CHCl_3 (δ_{H} 7.26) for ^1H spectra and CDCl_3 (δ_{C} 77.0) for ^{13}C spectra. IR spectra were recorded on FT/IR-460 plus (JASCO Co., Ltd.). Silica Gel 60N or Silica Gel 60 (Kanto Chemical Co., Inc.) was used for silica-gel flash column chromatography. Merck Kieselgel 60 F₂₅₄ (0.25 mm thickness, coated on glass 20×20 cm²) plate was used for thin layer chromatography (TLC), and Wakogel B-5F coated on glass in a thickness of 0.9 mm was used for preparative TLC. LC-918 (Japan Analytical Industry Co. Ltd.) was used for further purifications. THF was freshly distilled from benzophenone ketyl, and all other solvents were distilled according to the usual procedures and stored over molecular sieves.

a) Preparation of 1-arylprop-2-yn-1-ol derivatives

A typical procedure for the preparation of propargyl alcohols (**1a–1k**) is described for the reaction using benzaldehyde as substrate:

A 1.55 M THF solution (2.0 mL, 3.1 mmol) of BuLi was added to a THF (10 mL) solution of trimethylsilylacetylene (0.5 mL, 3.5 mmol) at 0 °C. After the mixture was stirred for 1 h, benzaldehyde (0.26 mL, 2.6 mmol) was added. The reaction mixture was maintained at 0 °C for 1 h, and then was quenched with phosphate buffer (pH 7). Organic layer was extracted with ether twice, and the combined ether extract was washed with brine. After the organic layer was dried over MgSO₄, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (10% ethyl acetate in hexanes) to give propargyl alcohol **1a** (540 mg, quant.).

1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ol (**1a**)

IR (neat) 3366, 2959, 2173, 1494, 1454, 1251, 1040 cm⁻¹

^1H -NMR (400 MHz) δ = 0.21 (s, 9H), 2.18 (d, J = 6.0 Hz, 1H), 5.46 (d, J = 6.0 Hz, 1H), 7.34–7.41 (m, 3H), 7.42–7.56 (m, 2H).

^{13}C -NMR (100 MHz) δ = -0.09, 65.0, 91.6, 104.8, 126.7, 128.3, 128.5, 140.2.

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{OSi}$: C, 70.53; H, 7.89 Found: C, 70.28; H, 7.84

1-(4-methoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1b)

IR (neat) 3399, 2837, 2172, 1611, 1511, 1251, 1037 cm^{-1}

^1H -NMR (400 MHz) δ = 0.21 (s, 9H), 2.11 (d, J = 6.0 Hz, 1H), 3.82 (s, 3H), 5.40 (d, J = 6.0 Hz, 1H), 6.90–6.92 (m, 2H), 7.46–7.48 (m, 2H).

^{13}C -NMR (100 MHz) δ = -0.07, 55.3, 64.6, 91.3, 105.1, 113.9, 128.1, 132.6, 159.6.

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Si}$: C, 66.62; H, 7.74 Found: C, 66.33; H, 7.74

1-(4-fluorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1c)

IR (neat) 3348, 2961, 2174, 1605, 1508, 1414, 1252, 1038 cm^{-1}

^1H -NMR (400 MHz) δ = 0.21 (s, 9H), 2.17 (d, J = 6.0 Hz, 1H), 5.44 (d, J = 6.0 Hz, 1H), 7.03–7.09 (m, 2H), 7.50–7.54 (m, 2H).

^{13}C -NMR (100 MHz) δ = -0.10, 64.3, 91.9, 104.6, 115.4 (d, J = 21.5 Hz), 128.5 (d, J = 8.3 Hz), 136.1, 162.6 (d, J = 245 Hz).

Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{FOSi}$: C, 64.83; H, 6.80 Found: C, 64.55; H, 6.75

1,3-diphenylprop-2-yn-1-ol (1d)

The spectral data was consistent with those of the literature.¹

1-(benzo[*d*][1,3]dioxol-6-yl)-3-(trimethylsilyl)prop-2-yn-1-ol (1e)

IR (neat) 3399, 2959, 2173, 1488, 1443, 1250, 1039 cm^{-1}

^1H -NMR (400 MHz) δ = 0.21 (s, 9H), 2.12 (d, J = 6.0 Hz, 1H), 5.36 (d, J = 6.0 Hz, 1H), 5.97 (s, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.99–7.02 (m, 1H), 7.04–7.05 (m, 1H).

^{13}C -NMR (100 MHz) δ = -0.09, 64.8, 91.5, 101.2, 104.8, 107.4, 108.1, 120.4, 134.3, 147.6.

Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Si}$: C, 62.87; H, 6.49 Found: C, 62.67; H, 6.68

1-(3-naphthyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1f)

IR (neat) 3349, 2959, 2167, 1508, 1250, 1024 cm^{-1}

^1H -NMR (400 MHz) δ = 0.22 (s, 9H), 2.25 (d, J = 6.4 Hz, 1H), 5.62 (d, J = 6.4 Hz, 1H), 7.49–7.51 (m, 2H), 7.66 (dd, J = 8.4, 1.6 Hz, 1H), 7.84–7.88 (m, 3H), 7.99 (s, 1H).

^{13}C -NMR (100 MHz) δ = -0.07, 65.2, 91.9, 104.9, 124.6, 125.5, 126.2, 126.2, 127.6, 128.1, 128.4, 133.1, 133.2, 137.6.

Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{OSi}$: C, 75.54; H, 7.13 Found: C, 75.54; H, 7.34

1-(3-pyridyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1g)

IR (neat) 3139, 2961, 2165, 1594, 1580, 1251, 1058 cm^{-1}

^1H -NMR (400 MHz) δ = 0.21 (s, 9H), 2.41 (d, J = 6.0 Hz, 1H), 5.51 (d, J = 6.0 Hz, 1H), 7.31–7.34 (m, 1H), 7.86–7.89 (m, 1H), 8.56–8.59 (m, 1H), 8.78–8.79 (m, 1H).

^{13}C -NMR (100 MHz) δ = -0.17, 62.6, 92.3, 104.0, 123.4, 134.5, 136.2, 148.1, 149.1.

Anal. Calcd for C₁₁H₁₅NOSi: C, 64.34; H, 7.36; N, 6.82 Found: C, 64.06; H, 7.10; N, 6.69

1-[1-(*p*-tolylsulfonyl)pyrrol-2-yl]-3-(trimethylsilyl)prop-2-yn-1-ol (1h**)**

IR (neat) 3519, 2960, 2180, 1598, 1360, 1171 cm⁻¹

¹H-NMR (400 MHz) δ = 0.19 (s, 9H), 2.41 (s, 3H), 3.10 (d, J = 5.6 Hz, 1H), 5.78 (d, J = 5.6 Hz, 1H), 6.24 (t, J = 3.4 Hz, 1H), 6.61–6.62 (m, 1H), 7.25–7.26 (m, 1H), 7.28–7.31 (m, 2H), 7.72–7.74 (m, 2H).

¹³C-NMR (100 MHz) δ = -0.18, 21.7, 57.4, 90.7, 102.5, 111.6, 115.5, 124.2, 126.8, 130.0, 134.3, 135.9, 145.2.

Anal. Calcd for C₁₇H₂₁NO₃SSi: C, 58.76; H, 6.09 Found: C, 58.80; H, 6.18

1-(2-thienyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1i**)**

IR (neat) 3367, 2959, 2174, 1251, 1031 cm⁻¹

¹H-NMR (400 MHz) δ = 0.22 (s, 9H), 2.33 (d, J = 7.2 Hz, 1H), 5.64 (dd, J = 7.2, 0.8 Hz), 6.98 (dd, J = 5.2, 3.6 Hz, 1H), 7.18 (dt, J = 3.6, 1.2 Hz, 1H), 7.31 (dd, J = 5.2, 1.2 Hz).

¹³C-NMR (100 MHz) δ = -0.18, 60.6, 91.2, 104.0, 125.7, 126.1, 126.7, 144.2.

Anal. Calcd for C₁₀H₁₄OSSi: C, 57.09; H, 6.71; S, 15.24 Found: C, 56.83; H, 6.93; S, 14.96

1-(3-thienyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1j**)**

IR (neat) 3349, 2959, 2173, 1251, 1041 cm⁻¹

¹H-NMR (400 MHz) δ = 0.22 (s, 9H), 2.26 (d, J = 6.2 Hz, 1H), 5.48 (d, J = 6.2 Hz, 1H), 7.20 (dd, J = 5.0, 1.2 Hz, 1H), 7.32 (dd, J = 5.0, 2.8 Hz, 1H), 7.40–7.41 (m, 1H).

¹³C-NMR (100 MHz) δ = -0.11, 60.9, 90.7, 104.7, 122.7, 126.3, 126.4, 141.6.

Anal. Calcd for C₁₀H₁₄OSSi: C, 57.09; H, 6.71; S, 15.24 Found: C, 57.04; H, 6.77; S, 15.13

1-(2-furyl)-3-(trimethylsilyl)prop-2-yn-1-ol (1k**)**

IR (neat) 3366, 2960, 2176, 1595, 1503, 1252, 1042 cm⁻¹

¹H-NMR (400 MHz) δ = 0.20 (s, 9H), 2.14 (d, J = 6.6 Hz, 1H), 5.38 (d, J = 6.6 Hz, 1H), 6.50–6.51 (m, 1H), 7.40 (t, J = 1.8 Hz, 1H), 7.52 (m, 1H).

¹³C-NMR (100 MHz) δ = -0.13, 57.7, 90.0, 104.3, 109.1, 126.1, 140.2, 143.5.

Anal. Calcd for C₁₀H₁₄O₂Si: C, 61.81; H, 7.26 Found: C, 61.53; H, 7.22

b) Rhodium(I)-catalyzed cyclization of propargyl alcohols (1a–1k**)**

A typical procedure for the cyclization of propargyl alcohols (**1a–1k**) is described for the reaction using **1a** as substrate:

To a toluene (6.6 mL, 0.05 M) solution of propargyl alcohol **1a** (68.0 mg, 0.33 mmol) was added [Rh(cod)₂](BF₄) (13.5 mg, 0.033 mmol, 10 mol%) and P(4-tolyl)₃ (40.1 mg, 0.13 mmol, 40 mol%). The reaction mixture was stirred for 3.5 h at 90 °C, and then the solvent was removed under reduced pressure to give crude product, which was purified by PTLC (20% ethyl acetate in hexane) to afford indanone **2a** (54.1 mg, 80%).

3-(trimethylsilyl)indan-1-one (**2a**)

IR (neat) 2954, 1709, 1603, 1251 cm⁻¹

¹H-NMR (400 MHz) δ = 0.01 (s, 9H), 2.56 (dd, *J* = 19.4, 1.8 Hz, 1H), 2.76 (dd, *J* = 8.2, 1.8 Hz, 1H), 2.87 (dd, *J* = 19.4, 8.2 Hz, 1H), 7.26–7.30 (m, 1H), 7.35–7.37 (m, 1H), 7.51–7.55 (m, 1H), 7.72–7.74 (m, 1H).

¹³C-NMR (100 MHz) -3.0, 28.8, 39.6, 123.9, 125.6, 125.8, 134.3, 136.0, 158.6, 207.0.

Anal. Calcd for C₁₂H₁₆OSi: C, 70.53; H, 7.89 Found: C, 70.26; H, 7.97

5-methoxy-3-(trimethylsilyl)indan-1-one (**2b**)

IR (neat) 2959, 1691, 1600, 1583, 1244 cm⁻¹

¹H-NMR (400 MHz) δ = 0.02 (s, 9H), 2.52 (dd, *J* = 19.2, 2.0 Hz, 1H), 2.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 2.85 (dd, *J* = 19.2, 8.2 Hz, 1H), 3.89 (s, 3H), 6.77 (s, 1H), 6.80–6.83 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H).

¹³C-NMR (100 MHz) δ = -3.0, 28.8, 39.7, 55.5, 109.0, 113.5, 125.6, 129.5, 161.4, 164.9, 205.1.

Anal. Calcd for C₁₃H₁₈O₂Si: C, 66.62; H, 7.74 Found: C, 66.61; H, 7.61

5-fluoro-3-(trimethylsilyl)indan-1-one (2c)

IR (neat) 2955, 1710, 1613, 1586, 1253 cm^{-1}

^1H -NMR (400 MHz) δ = -0.08 (s, 9H), 2.47 (dd, J = 19.4, 2.2 Hz, 1H), 2.64 (dd, J = 8.4, 2.2 Hz, 1H), 2.78 (dd, J = 19.4, 8.4 Hz, 1H), 6.84–6.91 (m, 2H), 7.62 (dd, J = 8.2, 5.4 Hz, 1H).

^{13}C -NMR (100 MHz) δ = -3.1, 29.0, 112.0 (d, J = 22.3 Hz), 114.1 (d, J = 24.0 Hz), 126.1 (d, J = 10.7 Hz), 161.5 (d, J = 9.9 Hz), 166.9 (d, J = 253.2), 204.9.

Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{FOSi}$: C, 64.83; H, 6.80 Found: C, 64.55; H, 7.02

3-phenylindan-1-one (2d)

The spectral data was consistent with those of the literature.²

5,7-dioxo-2,3,6,7-tetrahydro-3-(trimethylsilyl)s-indacen-1(5H)-one (2e)

IR (neat) 2953, 1692, 1609, 1470, 1250 cm^{-1}

^1H -NMR (400 MHz) δ = 0.01 (s, 9H), 2.51 (dd, J = 19.6, 2.0 Hz, 1H), 2.61 (dd, J = 8.0, 2.0 Hz, 1H), 2.84 (dd, J = 19.6, 8.0 Hz, 1H), 6.03–6.04 (m, 2H), 6.71 (s, 1H), 7.07 (s, 1H).

^{13}C -NMR (100 MHz) δ = -3.0, 28.7, 40.1, 102.0, 102.5, 104.8, 130.5, 147.1, 154.0, 156.3, 204.8.

Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Si}$: C, 62.87; H, 6.49 Found: C, 62.97; H, 6.49

1,3-dioxo-1,2,7,8-tetrahydro-8-(trimethylsilyl)as-indacen-6(3H)-one (3e)

IR (neat) 2954, 1697, 1630, 1464, 1268 cm^{-1}

^1H -NMR (400 MHz) δ = 0.04 (s, 9H), 2.57 (dd, J = 19.2, 1.6 Hz, 1H), 2.75 (dd, J = 8.8, 1.6 Hz, 1H), 2.86 (dd, J = 19.2, 8.8 Hz, 1H), 6.00–6.19 (m, 2H), 6.80 (d, J = 8.2 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H).

^{13}C -NMR (100 MHz) δ = -2.67, 25.1, 40.2, 101.5, 107.4, 119.4, 132.1, 138.2, 142.9, 152.3, 204.5.

Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Si}$: C, 62.87; H, 6.49 Found: C, 62.81, H, 6.44

2,3-dihydro-3-(trimethylsilyl)cyclopenta[*b*]naphthalen-1-one (2f)

IR (neat) 2956, 1703, 1626, 1248 cm⁻¹

¹H-NMR (400 MHz) δ = 0.04 (s, 9H), 2.63–2.73 (m, 1H), 2.93–3.02 (m, 2H), 7.44–7.48 (m, 1H), 7.55–7.59 (m, 1H), 7.74 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.30 (s, 1H).

¹³C-NMR (100 MHz) δ = -3.1, 28.0, 40.1, 123.2, 124.6, 125.5, 127.5, 128.5, 130.3, 131.5, 134.2, 137.1, 151.1, 207.4.

Anal. Calcd for C₁₆H₁₈OSi: C, 75.54; H, 7.13 Found: C, 75.83; H, 7.41

1,2-dihydro-1-(trimethylsilyl)cyclopenta[*a*]naphthalen-3-one (3f)

IR (neat) 2954, 1700, 1252 cm⁻¹

¹H-NMR (400 MHz) δ = -0.03 (s, 9H), 2.83 (dd, J = 18.8, 0.8 Hz, 1H), 3.04 (dd, J = 18.8, 7.6 Hz, 1H), 3.35 (dd, J = 7.6, 0.8 Hz, 1H), 7.55–7.59 (m, 1H), 7.63–7.67 (m, 1H), 7.70–7.75 (m, 2H), 7.92 (d, J = 8.4 Hz, 1H), 8.00–8.03 (m, 1H).

¹³C-NMR (100 MHz) δ = -2.0, 28.3, 41.6, 119.7, 125.7, 125.9, 126.9, 128.8, 128.9, 129.8, 133.2, 136.7, 160.3, 206.2.

Anal. Calcd for C₁₆H₁₈OSi: C, 75.54; H, 7.13 Found: C, 75.66; H, 7.14

6,7-dihydro-7-(trimethylsilyl)cyclopenta[*b*]pyridin-5-one (2g)

IR (neat) 2925, 1715, 1577, 1420 cm⁻¹

¹H-NMR (400 MHz) δ = 0.05 (s, 9H), 2.60–2.67 (m, 1H), 2.89–2.97 (m, 2H), 7.21 (dd, J = 7.8, 4.8 Hz, 1H), 7.95 (dd, J = 7.8, 1.6 Hz, 1H), 8.74 (dd, J = 4.8, 1.6 Hz, 1H).

¹³C-NMR (100 MHz) δ = -2.85, 31.8, 39.1, 120.9, 128.9, 131.7, 155.3, 177.9, 205.3.

Anal. Calcd for C₁₁H₁₅NOSi: C, 63.34; H, 7.36; N, 6.82 Found: C, 63.63; H, 7.48; N, 6.88

4,5-dihydro-4-(trimethylsilyl)-1-(4-tolylsulfonyl)cyclopenta[*b*]pyrrol-6(1H)-one (2h)

IR (neat) 2955, 2254, 1695, 1596, 1252 cm^{-1}

^1H -NMR (400 MHz) δ = -0.01 (s, 9H), 2.35 (dd, J = 6.8, 1.6 Hz, 1H), 2.39 (s, 3H), 2.63 (dd, J = 18.8, 1.6 Hz, 1H), 2.98 (dd, J = 18.8, 6.8 Hz, 1H), 6.13 (d, J = 3.2 Hz, 1H), 7.28 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 3.2 Hz, 1H), 8.00 (d, J = 8.6 Hz, 2H).

^{13}C -NMR (100 MHz) δ = -3.37, 21.7, 23.9, 44.3, 108.4, 128.0, 129.7, 132.1, 133.8, 134.9, 145.4, 163.2, 188.5.

Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{SSi}$: C, 58.76; H, 6.09; N, 4.03 Found: C, 58.54; H, 6.09; N, 3.79

4,5-dihydro-4-(trimethylsilyl)cyclopenta[b]thiophen-6-one (2i)

IR (neat) 2953, 1689, 1418, 1251 cm^{-1}

^1H -NMR (400 MHz) δ = 0.04, (s, 9H), 2.68 (dd, J = 7.0, 1.8 Hz, 1H), 2.79 (dd, J = 19.0, 1.8 Hz, 1H), 3.16 (dd, J = 19.0, 7.0 Hz, 1H), 6.94 (d, J = 4.8 Hz, 1H), 7.87 (d, J = 4.8 Hz, 1H).

^{13}C -NMR (100 MHz) δ = -3.1, 28.1, 44.2, 123.2, 138.5, 140.5, 172.5, 197.4.

Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{OSSi}$: C, 57.09; H, 6.71; S, 15.24 Found: C, 57.29; H, 6.97; S, 15.36

4,5-dihydrocyclopenta[b]thiophen-6-one (4i)

IR (neat) 2926, 1684, 1513, 1462, 1435 cm^{-1}

^1H -NMR (500 MHz) δ = 2.98–3.00 (m, 2H), 3.02–3.04 (m, 2H), 7.04 (d, J = 4.8 Hz, 1H), 7.89 (d, J = 4.8 Hz, 1H).

^{13}C -NMR (125 MHz) δ = 23.9, 41.2, 123.9, 140.5, 168.9, 197.2.

Anal. Calcd for $\text{C}_7\text{H}_6\text{OS}$: C, 60.84; H, 4.38; S, 23.24 Found: C, 60.76; H, 4.65; S, 23.01

5,6-dihydrocyclopenta[b]thiophen-4-one (4j)

IR (neat) 2928, 1686, 1424, 1303, 1276 cm^{-1}

^1H -NMR (400 MHz) δ = 2.98–3.01 (m, 2H), 3.18–3.20 (m, 2H), 7.14 (d, J = 5.2 Hz, 1H), 7.31 (d, J = 5.2 Hz, 1H).

^{13}C -NMR (100 MHz) δ = 24.4, 41.8, 119.4, 130.8, 145.9, 170.5, 198.0.

Anal. Calcd for $\text{C}_7\text{H}_6\text{OS}$: C, 60.84; H, 4.38; S, 23.20 Found: C, 60.84; H, 4.61; S, 23.21

5,6-dihydrocyclopenta[b]furan-4-one (4k)

IR (neat) 2925, 1975, 1709, 1684, 1600 cm^{-1}

^1H -NMR (500 MHz) δ =2.90–3.02 (m, 4H), 6.52(d, J = 2.0 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1H).

^{13}C -NMR (125 MHz) δ = 22.2, 42.1, 105.3, 128.1, 149.6, 183.0, 195.4.

Anal. Calcd for $\text{C}_7\text{H}_6\text{O}_2$: C, 68.85; H, 4.95 Found: C, 69.13; H, 5.22

References

- (1) Pilcher, A. S.; DeShong, P. *J. Org. Chem.* **1996**, *61*, 6901.
- (2) Smonou, I.; Orfanopoulos, M. *Synth. Commun.* **1990**, *20*, 1387.