Ruthenium-Catalyzed *S*-Propargylation of Thiols Enables the Rapid Synthesis of Propargylic Sulfides

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Supporting Information

Experimental details and characterization of all new compounds

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General. GLC analyses were carried out on a gas chromatograph equipped with a glass column (3 mm i.d. x 3 m) packed with Silicone OV-17 (2 % on Chromosorb W(AW-DMCS), 60-80 mesh). The ^1H -NMR spectra were recorded at 300 MHz, and the ^{13}C -NMR spectra were recorded at 75 MHz. Samples were analyzed in CDCl_3 , and the chemical shift values are expressed relative to Me_4Si as an internal standard. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Materials. The reagents used in this study were dried and purified before use by standard procedures. Propargylic Carbonates (**1a-d**) were prepared from the corresponding alcohols and methyl chloroformate according to the reported procedure.¹ $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $[\text{RuCl}_2(\text{CO})_3]_2$, and $\text{Ru}_3(\text{CO})_{12}$ were obtained commercially, and used without further purification. $\text{CpRuCl}(\text{cod})$,² $\text{Cp}^*\text{RuCl}(\text{cod})$,³ $\text{CpRuCl}(\text{CO})_2$,⁴ $\text{RuCl}_2(\text{PPh}_3)_3$,⁵ $\text{RuH}_2(\text{PPh}_3)_4$,⁶ $\text{Ru}(\eta^6\text{-cot})(\text{dmfm})_2$,⁷ $\text{Pd}(\text{PPh}_3)_4$,⁸ $\text{RhCl}(\text{PPh}_3)_3$,⁹ and $\text{CpRuCl}(\text{PPh}_3)_2$ ¹⁰ were prepared as described in the literature.

Propargylation of Aromatic Thiols (2a-e) with Propargylic Carbonates (1a-c, e). A mixture of propargylic carbonate (**1**, 1.0 mmol), aromatic thiol (**2**, 1.5 mmol), $\text{CpRuCl}(\text{cod})$ (0.10 mmol), and *N*-methylpiperidine (3.0 mL) was placed in a two-necked 20-mL Pyrex flask equipped with a magnetic stirring bar under a flow of argon. The reaction was carried out at 100 °C for 0.5 h – 8 h with stirring. After the reaction mixture was cooled, the products were isolated by Kugelrohr distillation except for **3i**. **3i** was isolated by column chromatography (Florisil® (60-100 mesh), eluent: pentane/ethyl acetate (100/1 in v/v)).

Propargylation of 2a with Trimethylsilyl-Substituted Propargyl Carbonate (1d). A mixture of trimethylsilyl-substituted propargyl carbonate (**1d**, 1.0 mmol), benzenethiol (**2a**, 1.5 mmol), $\text{CpRuCl}(\text{cod})$ (0.10 mmol), and *N*-methylpiperidine (3.0 mL) was placed in a heavy-walled sealed glass tube equipped with a magnetic stirring bar under a flow of argon. The reaction was carried out at 100 °C for 2 days with stirring. After the reaction mixture was cooled, the products were isolated by Kugelrohr distillation.

Propargylation of Aliphatic Thiols (4a-c) with Propargylic Carbonate (1a). A mixture of propargylic carbonate (**1a**, 1.0 mmol), aliphatic thiol (**4**, 1.2 mmol),

CpRuCl(PPh₃)₂ (0.030 mmol), and *N*-methylpiperidine (3.0 mL) was placed in a two-necked 20-mL Pyrex flask equipped with a magnetic stirring bar under a flow of argon. The reaction was carried out at 100 °C for 8 h with stirring. After the reaction mixture was cooled, the products were isolated by column chromatography (Florisil® (60-100 mesh), eluent: pentane/ethyl acetate (50/1 in v/v)).

All of the products are characterized below.

Phenyl 3-phenylprop-2-ynyl sulfide (3a). Yellow liquid. bp 110-120 °C (2.0 mmHg, Kugelrohr); IR (neat) 1439, 2188, 3057 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 3.84 (s, 2H), 7.23-7.52 (m, 10H); ¹³C NMR (CDCl₃, 75 MHz): δ 23.8, 83.7, 85.2, 122.9, 127.0, 128.17, 128.20, 128.9, 130.6, 131.7, 135.2; MS (EI) m/z 224 (M⁺). Anal. Calcd for C₁₅H₁₂S: C 80.31, H 5.66. Found: C 80.22, H 5.39.

Pent-2-ynyl phenyl sulfide (3b). Yellow liquid. bp 100-120 °C (2.0 mmHg, Kugelrohr); IR (neat) 1439, 2233, 3058 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 1.08 (t, 3H, *J*=7.52 Hz), 2.17 (qt, 2H, *J*=7.52, 2.39 Hz), 3.61 (t, 2H, *J*=2.39 Hz), 7.19-7.45 (m, 5H); ¹³C NMR (CDCl₃, 75 MHz): δ 12.5, 13.8, 23.1, 74.8, 85.2, 126.5, 128.8, 129.8, 135.7; MS (EI) m/z 176 (M⁺). Anal. Calcd for C₁₁H₁₂S: C 74.95, H 6.86. Found: C 75.18, H 6.94.

But-2-ynyl phenyl sulfide (3c). Colorless liquid. bp 80-90 °C (3.0 mmHg, Kugelrohr); IR (neat) 1439, 2233, 3058 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 1.80 (t, 3H, *J*=2.57 Hz), 3.60 (q, 2H, *J*=2.57 Hz), 7.21-7.43 (m, 5H); ¹³C NMR (CDCl₃, 75 MHz): δ 3.6, 23.0, 74.6, 79.5, 126.5, 128.8, 129.5, 135.8; MS (EI) m/z 162 (M⁺). Anal. Calcd for C₁₀H₁₀S: C 74.02, H 6.21. Found: C 74.28, H 6.24.

But-2-ynyl 4-fluorophenyl sulfide (3d). Yellow liquid. bp 70-80 °C (10.0 mmHg, Kugelrohr); IR (neat) 1488, 2232, 2917 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 1.80 (t, 3H, *J*=2.55 Hz), 3.53 (q, 2H, *J*=2.55 Hz), 7.44 (dd, 2H, *J*=5.23, 8.72 Hz), 7.02 (t, 2H, *J*=8.72 Hz); ¹³C NMR (CDCl₃, 75 MHz): δ 3.6, 24.3, 74.6, 79.8, 115.9 (d, *J*=21.8 Hz), 130.4 (d, *J*=3.1 Hz), 133.0 (d, *J*=8.1 Hz), 162.2 (d, *J*=246.6 Hz); MS (EI) m/z 180 (M⁺). Anal. Calcd for C₁₀H₉FS: C 66.64, H 5.03, F 10.54. Found: C 66.79, H 5.24, F 10.70.

But-2-ynyl 4-chlorophenyl sulfide (3e). Yellow liquid. bp 90-100 °C (10.0 mmHg, Kugelrohr); IR (neat) 1476, 2233, 2916 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 1.80 (t,

3H, $J=2.57$ Hz), 3.57 (q, 2H, $J=2.57$ Hz), 7.27 (d, 2H, $J=8.53$ Hz), 7.35 (d, 2H, $J=8.53$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 3.6, 23.2, 74.3, 79.8, 129.0, 131.0, 132.6, 134.2; MS (EI) m/z 198 (M^++2), 196 (M^+). Anal. Calcd for $\text{C}_{10}\text{H}_9\text{ClS}$: C 61.06, H 4.61, S 16.30. Found: C 60.88, H 4.73, S 16.42.

But-2-ynyl 4-methoxyphenyl sulfide (3f). Yellow liquid. bp 80-90 °C (15.0 mmHg, Kugelrohr); IR (neat) 1494, 2231, 2938 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.80 (t, 3H, $J=2.57$ Hz), 3.48 (q, 2H, $J=2.57$ Hz), 3.80 (s, 3H), 6.86(d, 2H, $J=8.90$ Hz), 7.44 (d, 2H, $J=8.90$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 3.6, 25.1, 55.3, 75.0, 79.5, 114.5, 125.7, 133.9, 159.4; MS (EI) m/z 192 (M^+). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{SO}$: C 68.71, H 6.29, S 16.68. Found: C 68.66, H 6.32, S 16.85.

But-2-ynyl 4-methylphenyl sulfide (3g). Colorless liquid. bp 70 °C (7.0 mmHg, Kugelrohr); IR (neat) 1493, 2232, 2917 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.80 (t, 3H, $J=2.57$ Hz), 2.33 (s, 3H), 3.55 (q, 2H, $J=2.57$ Hz), 7.12 (d, 2H, $J=7.99$ Hz), 7.34 (d, 2H, $J=7.99$ Hz); ^{13}C NMR (CDCl_3 , 75 MHz): δ 3.7, 21.0, 23.7, 74.8, 79.4, 129.6, 130.6, 131.9, 136.8; MS (EI) m/z 176 (M^+). Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{S}$: C 74.95, H 6.86. Found: C 74.81, H 6.88. Exact mass calcd for $\text{C}_{11}\text{H}_{12}\text{S}$: 176.0660. Found: 176.0658.

Phenyl 3-trimethylsilylprop-2-ynyl sulfide (3h). Colorless liquid. bp 80-90 °C (18.0 mmHg, Kugelrohr); IR (neat) 1251, 1438, 2176, 3061 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 0.13 (s, 9H), 3.62 (s, 2H), 7.25-7.48 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 0.00, 24.3, 88.9, 101.7, 127.3, 129.0, 131.1, 135.2; MS (EI) m/z 220 (M^+). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{SSi}$: C 65.39, H 7.32. Found: C 65.37, H 7.39.

Octyl 3-phenylprop-2-ynyl sulfide (5a). Yellow liquid. bp 110-120 °C (5.0 mmHg, Kugelrohr); IR (neat) 1442, 2358, 2925 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 0.87 (t, 3H, $J=6.79$ Hz), 1.10-1.60 (m, 10H), 1.66 (quintet, 2H, $J=7.16$ Hz), 2.73 (t, 2H, $J=7.34$ Hz), 3.48 (s, 2H), 7.24-7.41 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 14.1, 20.2, 22.6, 28.8, 29.1, 29.2 (two overlapping signals), 31.7, 31.8, 82.8, 85.6, 123.1, 128.0, 128.2, 131.7; MS (EI) m/z 260 (M^+). Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{S}$: C 78.40, H 9.29. Found: C 78.54, H 9.56.

Pentyl 3-phenylprop-2-ynyl sulfide (5b). Colorless liquid. bp 70-80 °C (5.0 mmHg, Kugelrohr); IR (neat) 1442, 2254, 2927 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 0.90 (t,

3H, $J=6.84$ Hz), 1.30-1.45 (m, 4H), 1.67 (quintet, 2H, $J=7.32$ Hz), 2.73 (t, 2H, $J=7.32$ Hz), 3.49 (s, 2H), 7.20-7.41 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 14.0, 20.3, 22.3, 28.8, 31.1, 31.8, 82.8, 85.6, 123.1, 128.0, 128.1, 131.6; MS (EI) m/z 218 (M^+). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{S}$: C 77.01, H 8.31. Found: C 76.97, H 8.47. Exact mass calcd for $\text{C}_{14}\text{H}_{18}\text{S}$: 218.1129. Found: 218.1124.

Cyclohexyl 3-phenylprop-2-ynyl sulfide (5c). Yellow liquid. bp 100-110 °C (3.0 mmHg, Kugelrohr); IR (neat) 1447, 2334, 2928 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 1.25-2.07 (m, 10H), 2.92-3.00 (m, 1H), 3.51 (s, 2H), 7.25-7.43 (m, 5H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 18.6, 25.8, 26.0, 33.1, 43.3, 82.6, 86.0, 123.2, 128.0, 128.2, 131.6; MS (EI) m/z 230 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{S}$: C 78.21, H 7.88. Found: C 77.92, H 8.01.

(Z)-1,2-Bis(phenylthio)-1,3-diphenylprop-1-ene (6a). Colorless liquid. Column chromatography on SiO_2 (Merck Silica gel 60 #107734, eluent: pentane/acetone = 100/1 v/v%). IR (neat) 1476, 1581, 1947, 3058 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 3.56 (s, 2H), 6.87-6.89 (m, 2H), 7.08-7.35 (m, 18H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 39.5, 126.1, 127.1, 127.2, 127.4, 127.8, 128.0, 128.4, 128.5, 128.8, 129.7, 131.8, 132.7, 133.4, 133.7, 133.9, 135.2, 138.3, 138.9. Exact mass calcd for $\text{C}_{27}\text{H}_{22}\text{S}_2$ (FAB): 410.1163. Found: 410.1173.

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