Equilibrating C-S Bond Formation by C-H and S-S Bond Metathesis.
Rhodium-Catalyzed Alkylthiolation Reaction of 1-Alkynes with Disulfides

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¹H-NMR and ¹³C-NMR spectra were obtained on a Varian Mercury (400 MHz). Chemical shift values are given in ppm relative to internal Me₄Si. IR spectra were recorded on a JASCO FT/IR-410. MS spectra were taken with a JEOL JMS-DX303 or a JEOL JMS-AX500.

1-{2-(*t*-Butoxycarbonylamino)ethyl}-2-triethylsilylethyne **3.** In a two-necked flask equipped with a reflux condenser were placed tetrakis(triphenylphosphine)hydriderrhodium¹⁰ (2 mol%, 4.6 mg), 1,1'-bis(diphenylphosphino)ferrocene (dppf) (3 mol%, 3.3 mg), triethylsilylethyne **1** (0.2 mmol, 35.8 μ L) in acetone (2.0 mL) under an argon atmosphere, to which bis{2-(*t*-butoxycarbonylamino)ethyl} disulfide **2**¹¹ (0.6 mmol, 211 mg) was added. The solution was heated at reflux for 1 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel and recycling HPLC using Cadenza CD-C18 (MeOH) giving **3** (48.5 mg, 77%), 2-(*t*-butoxycarbonylamino)ethanethiol **4** (24.4 mg, 69%), and **5** (2.5 mg, 4%). **3**: Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 8.0 Hz), 0.98 (9H, t, *J* = 8.0 Hz), 1.45 (9H, s), 2.82 (2H, t, *J* = 5.6 Hz), 3.51 (2H, q, *J* = 5.6 Hz), 5.05 (1H, bs). ¹³C-NMR (100 MHz, CDCl₃) δ 4.5, 7.6, 28.4, 35.7, 39.4, 79.5, 93.9, 98.8, 155.5. IR (neat) 3349, 2956, 2875, 2092, 1703, 1507, 1251, 1172, 860, 737 cm⁻¹. MS (EI) *m/z* 315 (**M**⁺, 4%), 230 (**M**⁺-85, 100%). HRMS Calcd for C₁₅H₂₉NO₂SSi: 315.1688. Found: 315.1676. **5**: Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.68 (6H, q, *J* = 7.6 Hz), 0.96 (9H, t, *J* = 7.6 Hz), 1.44 (9H, s), 2.90 (2H, t, *J* = 6.4 Hz), 3.36 (2H, q, *J* = 6.4 Hz), 4.83 (1H, bs), 5.43 (1H, s), 5.50 (1H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 3.1, 7.4, 28.5, 30.1, 38.8, 79.4, 116.2, 142.0, 155.5. IR (neat) 3354, 2954, 2875, 1697, 1513, 1252, 1172, 1006, 735 cm⁻¹. MS (EI) *m/z* 317 (**M**⁺, 12%), 145 (**M**⁺-172, 100%). HRMS Calcd for C₁₅H₃₁NO₂SSi: 317.1844. Found: 317.1830.

1-Methylthio-2-triethylsilylethyne. Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 8.0 Hz), 0.99 (9H, t, *J* = 7.6 Hz), 2.41 (3H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 4.6, 7.6, 19.7, 96.8, 97.0. IR (neat) 2955, 2932, 2912, 2875, 2092 cm⁻¹. MS (EI) *m/z* 186 (**M**⁺, 25%), 157 (**M**⁺-29, 100%). HRMS Calcd for C₉H₁₈SSi: 186.0898. Found: 186.0907. **1-Methylthio-1-triethylsilylethene.** Obtained in 2% yield. ¹H-NMR (400 MHz, CDCl₃) δ 0.69 (6H, q, *J* = 8.0 Hz), 0.97 (9H, t, *J* = 8.0 Hz), 2.24 (3H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 3.2, 7.4, 13.6, 114.5, 144.5. IR (neat) 3064, 2954, 2912, 1738 cm⁻¹. MS (EI) *m/z* 188 (**M**⁺, 36%), 159 (72), 133 (100), 105 (67). HRMS. Calcd for

C₉H₂₀SSi: 188.1055. Found: 188.1055.

1-Butylthio-2-triethylsilylethyne. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 8.0 Hz), 0.93 (3H, t, *J* = 7.6 Hz), 0.99 (9H, t, *J* = 8.0 Hz), 1.45 (2H, sextet, *J* = 7.6 Hz), 1.74 (2H, quintet, *J* = 7.6 Hz), 2.73 (2H, t, *J* = 7.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.7, 7.6, 13.7, 21.5, 31.2, 35.5, 95.6, 97.8. IR (neat) 2956, 2934, 2913, 2874, 2090 cm⁻¹. MS (EI) *m/z* 228 (M⁺, 18%), 199 (100), 171 (49).

HRMS. Calcd for C₁₂H₂₆SSi: 228.1368. Found: 228.1368. **1-Butylthio-1-triethylsilylethene.** Obtained in 5% yield. ¹H-NMR (400 MHz, CDCl₃) δ 0.68 (6H, q, *J* = 8.0 Hz), 0.93 (3H, t, *J* = 7.2 Hz), 0.96 (9H, t, *J* = 8.0 Hz), 1.44 (2H, sextet, *J* = 7.2 Hz), 1.63 (2H, quintet, *J* = 7.2 Hz), 2.72 (2H, t, *J* = 7.2 Hz), 5.38 (1H, s), 5.39 (1H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 3.2, 7.4, 13.9, 22.5, 29.9, 30.0, 115.1, 143.8. IR (neat) 2955, 2912, 2874, 1551 cm⁻¹. MS (EI) *m/z* 230 (M⁺, 44%), 201 (67), 175 (98), 145 (100), 115 (98). HRMS. Calcd for C₁₂H₂₆SSi: 230.1524. Found: 230.1524.

1-(3-Methylbutylthio)-2-triethylsilylethyne. Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 8.0 Hz), 0.92 (6H, d, *J* = 6.8 Hz), 0.99 (9H, t, *J* = 8.0 Hz), 1.64 (2H, q, *J* = 7.2 Hz), 1.74 (1H, septet, *J* = 7.2 Hz), 2.73 (2H, t, *J* = 7.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.6, 7.6, 22.4, 27.0, 33.9, 38.1, 95.6, 98.0. IR (neat) 2956, 2874, 2097, 1466, 1017 cm⁻¹. MS (EI) *m/z* 242 (M⁺, 17%), 213 (M⁺-29, 100%). HRMS Calcd for C₁₃H₂₆SSi: 242.1524. Found: 242.1531.

1-Octylthio-2-triethylsilylethyne. Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 8.0 Hz), 0.88 (3H, t, *J* = 7.6 Hz), 0.99 (9H, t, *J* = 8.0 Hz), 1.24-1.32 (8H, m), 1.38-1.45 (2H, m), 1.75 (2H, quintet, *J* = 7.6 Hz), 2.71 (2H, t, *J* = 7.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.6, 7.6, 14.2, 22.8, 28.3, 29.1, 29.20, 29.23, 31.9, 35.8, 95.6, 97.9. IR (neat) 2928, 2855, 2091, 1458, 1017, 863, 725 cm⁻¹. MS (EI) *m/z* 284 (M⁺, 8%), 255 (M⁺-29, 100%). HRMS Calcd for C₁₆H₃₂SSi: 284.1994. Found: 284.1996. **1-Octylthio-1-triethylsilylethene.** Obtained in 3% yield. Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.68 (6H, q, *J* = 7.6 Hz), 0.88 (3H, t, *J* = 7.2 Hz), 0.96 (9H, t, *J* = 7.2 Hz), 1.25-1.35 (8H, m), 1.35-1.45 (2H, m), 1.63 (2H, quintet, *J* = 7.2 Hz), 2.71 (2H, t, *J* = 7.2 Hz), 5.38 (2H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 3.1, 7.4, 14.3, 22.8, 27.9, 29.28, 29.32, 29.4, 30.1, 31.9, 115.1, 143.8. IR (neat) 2926, 2873, 1458, 1247, 1171 cm⁻¹. MS (EI) *m/z* 286 (M⁺, 24%), 145 (M⁺-141, 100%). HRMS Calcd for C₁₆H₃₄SSi: 286.2150. Found: 286.2136.

1-(2-Methoxyethylthio)-2-triethylsilylethyne. Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 8.0 Hz), 0.99 (9H, t, *J* = 8.0 Hz), 2.89 (2H, t, *J* = 6.8 Hz), 3.39 (3H, s), 3.70 (2H, t, *J* = 6.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 4.6, 7.6, 34.9, 58.9, 70.2, 94.5, 98.3. IR (neat) 2955, 2874, 2091, 1457, 1119, 860, 727 cm⁻¹. MS (EI) *m/z* 230 (M⁺, 36%), 201 (M⁺-29, 100%). HRMS Calcd for C₁₁H₂₂OSSi: 230.1161. Found: 230.1161.

1-(2-Methoxycarbonylethylthio)-2-triethylsilylethyne. Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 8.0 Hz), 0.99 (9H, t, *J* = 8.0 Hz), 2.81 (2H, t, *J* = 7.2 Hz), 2.95 (2H, t, *J* = 7.2 Hz), 3.71 (3H, s). ¹³C-NMR (100 MHz, CDCl₃) δ 4.6, 7.6, 30.4, 33.8, 52.0, 94.0, 99.5, 171.6. IR (neat) 2955, 2091, 1743, 1245, 1017, 859, 737 cm⁻¹. MS (EI) *m/z* 258 (M⁺, 29%), 201 (M⁺-57, 100%). HRMS Calcd for C₁₂H₂₂O₂SSi: 258.1110. Found: 258.1103. **1-(2-Methoxycarbonylethylthio)-1-triethylsilylethene.** Obtained in 2% yield. Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ 0.67 (6H, q, *J* = 8.0 Hz), 0.95 (9H, t, *J* = 8.0 Hz), 2.66 (2H, t, *J* = 7.2 Hz), 3.02 (2H, t, *J* = 7.6 Hz), 3.70 (3H, s),

5.42 (1H, s), 5.43 (1H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 3.1, 7.4, 24.8, 32.8, 51.9, 115.8, 128.3, 176.9. IR (neat) 2953, 2875, 1742, 1437, 1241, 1007, 722 cm^{-1} . MS (EI) m/z 260 (M^+ , 17%), 231 (M^+ -29, 100%). HRMS Calcd for $\text{C}_{12}\text{H}_{24}\text{O}_2\text{SSi}$: 260.1266. Found: 260.1266.

1-Methylthio-2-triisopropylsilylethyne. $\text{RhH}(\text{PPh}_3)_4$ (4 mol%) and dppf (6 mol%) were used, which improved the yield of the product. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 2.41 (3H, s), 1.06 (21H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 11.5, 18.7, 19.9, 95.8, 97.4. IR (neat) 2943, 2892, 2866, 2091, 1462 cm^{-1} . MS (EI) m/z 228 (M^+ , 7%), 185 (M^+ -43, 100%). HRMS Calcd for $\text{C}_{12}\text{H}_{24}\text{SSi}$: 228.1368. Found: 228.1860.

1-Octylthio-2-triisopropylsilylethyne. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.88 (3H, t, J = 6.8 Hz), 1.07 (21H, s), 1.24-1.32 (8H, m), 1.38-1.43 (2H, m), 1.77 (2H, quintet, J = 7.2 Hz), 2.71 (2H, t, J = 7.2 Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 11.5, 14.2, 18.7, 22.8, 28.3, 29.19, 29.24, 31.9, 35.9, 95.9, 96.8. IR (neat) 2927, 2865, 2089, 1463, 995, 882 cm^{-1} . MS (EI) m/z 326 (M^+ , 12%), 283 (M^+ -43, 100%). HRMS Calcd for $\text{C}_{19}\text{H}_{38}\text{SSi}$: 326.2463. Found: 326.2446.

1-Octylthio-2-(2,6-dimethylphenyl)ethyne. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.88 (3H, t, J = 7.2 Hz), 1.24-1.34 (8H, m), 1.42-1.50 (2H, m), 1.83 (2H, quintet, J = 7.2 Hz), 2.40 (6H, s), 2.80 (2H, t, J = 7.2 Hz), 7.00 (2H, d, J = 7.2 Hz), 7.06 (1H, dd, J = 8.8, 6.4 Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 14.2, 21.2, 22.8, 28.4, 29.2, 29.3, 29.5, 31.9, 36.3, 87.4, 90.7, 123.3, 126.5, 127.1, 139.8. IR (neat) 2926, 2854, 2158, 1465, 768 cm^{-1} . MS (EI) m/z 274 (M^+ , 100%), 162 (M^+ -112, 73%). HRMS Calcd for $\text{C}_{18}\text{H}_{26}\text{S}$: 274.1755. Found: 274.1740. **1-Octylthio-1-(2,6-dimethylphenyl)ethene.** Obtained in 38% yield. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.88 (3H, t, J = 6.8 Hz), 1.24-1.32 (8H, m), 1.37-1.45 (2H, m), 1.67 (2H, quintet, J = 7.2 Hz), 2.33 (6H, s), 2.70 (2H, t, J = 7.2 Hz), 4.99 (1H, s), 5.14 (1H, s), 7.01 (2H, d, J = 7.2 Hz), 7.08 (1H, dd, J = 8.0, 6.4 Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 14.2, 19.7, 22.8, 28.2, 29.3, 31.7, 31.9, 107.7, 127.1, 127.4, 136.1, 139.2, 143.9. IR (neat) 2925, 2854, 1593, 1465, 1064, 849, 768 cm^{-1} . MS (EI) m/z 276 (M^+ , 27%), 163 (M^+ -113, 100%). HRMS Calcd for $\text{C}_{18}\text{H}_{28}\text{S}$: 276.1912. Found: 276.1901.

1-Methylthio-2-(2,4,6-trimethylphenyl)ethyne. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 2.26 (3H, s), 2.37 (6H, s), 2.49 (3H, s), 6.83 (2H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 20.2, 21.0, 21.4, 87.6, 89.8, 120.1, 127.4, 137.2, 139.9. IR (neat) 2924, 2854, 2732, 2158, 1609 cm^{-1} . MS (EI) m/z 190 (M^+ , 100%), 143 (M^+ -47, 91%). HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{S}$: 190.0816. Found: 190.0803. **1-Methylthio-1-(2,4,6-trimethylphenyl)ethene.** Obtained in 18% yield. ^1H -NMR (400 MHz, CDCl_3) δ 2.25 (3H, s), 2.27 (3H, s), 2.28 (6H, s), 5.00 (1H, s), 5.09 (1H, s), 6.85 (2H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 15.1, 19.6, 21.1, 107.4, 127.9, 136.0, 136.1, 137.0, 144.9. IR (neat) 3090, 2198, 2856, 1602 cm^{-1} . MS (EI) m/z 192 (M^+ , 67%), 177 (100). HRMS. Calcd for $\text{C}_{12}\text{H}_{16}\text{S}$: 192.0973. Found: 192.0999.

1-Methylthio-2-(1-adamantyl)ethyne. ^1H -NMR (400 MHz, CDCl_3) δ 1.67 (6H, t, J = 2.8 Hz), 1.85 (6H, d, J = 2.8 Hz), 1.92 – 1.98 (3H, br), 2.34 (3H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 19.8, 28.1, 30.9, 36.4, 42.9, 68.9, 100.9. IR (neat) 2906, 2849, 1450 cm^{-1} . MS (EI) m/z 206 (M^+ , 100%), 191 (82). HRMS. Calcd for $\text{C}_{13}\text{H}_{18}\text{S}$: 206.1129. Found: 206.1102. Mp. 67-69 $^{\circ}\text{C}$ (hexane). **1-Methylthio-1-(1-adamantyl)ethene.** Obtained in 12% yield. ^1H -NMR (400 MHz, CDCl_3) δ 1.68

(3H, d, J = 11.6 Hz), 1.73 (3H, d, J = 12.0 Hz), 1.83 (6H, d, J = 3.2 Hz), 1.99 – 2.06 (3H, br), 2.20 (3H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 14.8, 28.9, 36.9, 39.3, 42.2, 100.7, 158.0. IR (neat) 2900, 2847, 1588 cm^{-1} . MS (EI) m/z 208 (M^+ , 100%), 135 (38). HRMS. Calcd for $\text{C}_{13}\text{H}_{20}\text{S}$: 208.1286. Found: 208.1251. Mp. 62-64 $^{\circ}\text{C}$ (hexane).

1-Octylthio-2-(1-adamantyl)ethyne. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.88 (3H, t, J = 6.8 Hz), 1.24-1.33 (8H, m), 1.37-1.44 (2H, m), 1.67 (6H, bs), 1.71 (2H, quintet, J = 7.2 Hz), 1.86 (6H, bd, J = 3.2 Hz), 1.94 (3H, bs), 2.64 (2H, t, J = 7.2 Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 14.3, 22.8, 28.1, 28.3, 29.1, 29.2, 29.3, 31.0, 31.9, 35.7, 36.4, 43.0, 67.3, 102.1. IR (neat) 2925, 2851, 2657, 1451 cm^{-1} . MS (EI) m/z 304 (M^+ , 84%), 135 (M^+ -169, 100%). HRMS Calcd for $\text{C}_{20}\text{H}_{32}\text{S}$: 304.2225. Found: 304.2214. **1-Octylthio-1-(1-adamantyl)ethene.** Obtained in 7% yield. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.88 (3H, t, J = 7.2 Hz), 1.21-1.33 (8H, m), 1.35-1.45 (2H, m), 1.64 (2H, quintet, J = 7.6 Hz), 1.69 (6H, bd, J = 8.0 Hz), 1.82 (6H, d, J = 2.4 Hz), 2.01 (3H, bs), 2.65 (2H, t, J = 7.2 Hz), 4.64 (1H, s), 5.07 (1H, s). ^{13}C -NMR (100 MHz, CDCl_3) δ 14.3, 22.8, 28.2, 28.9, 29.29, 29.34, 29.4, 31.9, 36.9, 39.5, 42.1, 102.2, 156.9. IR (neat) 2924, 2850, 1590, 1451 cm^{-1} . MS (EI) m/z 306 (M^+ , 17%), 194 (M^+ -112, 100%). HRMS Calcd for $\text{C}_{20}\text{H}_{34}\text{S}$: 306.2381. Found: 306.2385.

1-Phenylthio-2-triethylsilylethyne. In a two-necked flask were placed tetrakis(triphenylphosphine)hydriderrhodium (2 mol%, 4.6 mg) and dppf (4 mol%, 3.3 mg) in acetone (1.5 mL) under an argon atmosphere, and the mixture was heated at reflux for 10 min. After cooled to room temperature, **1** (1.0 mmol, 179 μL) and diphenyl disulfide (0.2 mmol, 43.6 mg) were added, and the solution was stirred at the temperature for 12 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel and recycling HPLC using Cadenza CD-C18 (MeOH) giving the title compound (42.7 mg, 86%) and 1-phenylthio-1-triethylsilylethene (20 mg, 40%). Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.68 (6H, q, J = 8.0 Hz), 1.04 (9H, t, J = 8.0 Hz), 7.20 (1H, t, J = 7.6 Hz), 7.32 (2H, t, J = 7.6 Hz), 7.41 (2H, d, J = 8.0 Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 4.6, 7.6, 90.7, 104.1, 125.9, 126.3, 129.0, 132.4. IR (neat) 2955, 2874, 2094, 1478, 1018, 862 cm^{-1} . MS (EI) m/z 248 (M^+ , 36%), 219 (M^+ -29, 100%). HRMS Calcd for $\text{C}_{14}\text{H}_{20}\text{OSSi}$: 248.1055. Found: 248.1031. **1-Phenylthio-1-triethylsilylethene.** Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.72 (6H, q, J = 8.0 Hz), 1.00 (9H, t, J = 8.0 Hz), 5.20 (1H, s), 5.42 (1H, s), 7.30-7.37 (3H, m), 7.44 (2H, d, J = 7.2 Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 3.3, 7.4, 120.1, 128.1, 129.0, 131.9, 134.8, 145.0. IR (neat) 2953, 2874, 1477, 1238, 1006, 777 cm^{-1} . MS (EI) m/z 250 (M^+ , 48%), 195 (M^+ -55, 100%). HRMS Calcd for $\text{C}_{14}\text{H}_{22}\text{SSi}$: 250.1211. Found: 250.1172.

1-(*p*-Tolylthio)-2-triethylsilylethyne. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.66 (6H, q, J = 8.0 Hz), 1.03 (9H, t, J = 8.0 Hz), 2.32 (3H, s), 7.13 (2H, d, J = 8.0 Hz), 7.30 (2H, d, J = 8.8 Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 4.6, 7.6, 21.1, 91.4, 103.4, 126.2, 128.7, 129.8, 136.3. IR (neat) 2955, 2874, 2094, 1492, 1016, 862, 802 cm^{-1} . MS (EI) m/z 262 (M^+ , 60%), 233 (M^+ -29, 100%). HRMS Calcd for $\text{C}_{15}\text{H}_{22}\text{SSi}$: 262.1211. Found: 262.1181. **1-(*p*-Tolylthio)-1-triethylsilylethene.** Obtained in 28% yield. Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.71 (6H, q, J = 8.0 Hz), 1.00 (9H, t, J = 8.0 Hz), 2.36 (3H, s), 5.13 (1H, s), 5.37 (1H, s), 7.16 (2H, d, J = 8.0 Hz), 7.32 (2H, d, J = 8.0 Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 3.3, 7.4, 21.4, 119.0, 130.0, 131.5, 135.0, 138.3, 145.4. IR (neat) 2953, 2874, 1491, 1458, 1238, 1005 cm^{-1} . MS (EI) m/z 264 (M^+ , 75%), 209 (M^+ -55, 100%).

HRMS Calcd for $C_{15}H_{24}SSi$: 264.1368. Found: 264.1338.

1-(*p*-Chlorophenyl)thio-2-triethylsilylethyne. Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 0.67 (6H, q, J = 8.0 Hz), 1.03 (9H, t, J = 8.0 Hz), 7.29 (2H, d, J = 8.8 Hz), 7.34 (2H, d, J = 8.8 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 4.6, 7.6, 90.1, 104.8, 127.2, 129.2, 131.1, 132.3. IR (neat) 2955, 2874, 2095, 1475, 1089, 1011, 861 cm^{-1} . MS (EI) m/z 282 (M^+ , 41%), 253 (M^+ -29, 100%). HRMS Calcd for $C_{14}H_{19}SSiCl$: 282.0665. Found: 282.0661. **1-(*p*-Chlorophenyl)thio-1-triethylsilylethene.** Obtained in 19% yield. Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 0.71 (6H, q, J = 8.0 Hz), 0.99 (9H, t, J = 8.0 Hz), 5.21 (1H, s), 5.45 (1H, s), 7.31 (2H, d, J = 8.8 Hz), 7.36 (2H, d, J = 8.8 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 3.2, 7.4, 120.7, 129.3, 130.5, 132.2, 135.9, 138.1. IR (neat) 2954, 2875, 1474, 1093, 1014, 822 cm^{-1} . MS (EI) m/z 284 (M^+ , 52%), 229 (M^+ -55, 100%). HRMS Calcd for $C_{14}H_{21}SSiCl$: 284.0822. Found: 284.0809.

1-Phenylthio-2-(2,4,6-trimethylphenyl)ethyne. Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 2.29 (3H, s), 2.44 (6H, s), 6.88 (2H, s), 7.21 (1H, t, J = 7.6 Hz), 7.33 (2H, t, J = 7.2 Hz), 7.49 (2H, d, J = 7.2 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 21.2, 21.5, 81.7, 95.8, 119.7, 125.8, 126.2, 127.6, 129.0, 133.6, 138.1, 140.5. IR (neat) 2916, 2156, 1609, 1582, 1478, 1440, 1024 cm^{-1} . MS (EI) m/z 252 (M^+ , 100%), 219 (M^+ -33, 58%). HRMS Calcd for $C_{17}H_{16}S$: 252.0973. Found: 252.0945. **1-Phenylthio-1-(2,4,6-trimethylphenyl)ethene.** Obtained in 46% yield. Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 2.27 (3H, s), 2.37 (6H, s), 4.83 (1H, s), 4.95 (1H, s), 6.86 (2H, s), 7.37-7.39 (3H, m), 7.56-7.58 (2H, m). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 19.7, 21.2, 109.8, 128.0, 128.8, 129.2, 131.7, 135.5, 136.2, 137.3, 142.4, 145.6. IR (neat) 2918, 1604, 1475, 1439, 1158, 1065 cm^{-1} . MS (EI) m/z 254 (M^+ , 49%), 145 (M^+ -109, 100%). HRMS Calcd for $C_{17}H_{18}S$: 254.1129. Found: 254.1121.

1-Phenylthio-2-(1-methoxycyclohexyl)ethyne. $RhH(PPh_3)_4$ (2.5 mol%) and dppf (5 mol%) were used, and the mixture was heated at reflux for 2 h. Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 1.28-1.37 (1H, m), 1.51-1.61 (3H, m), 1.63-1.72 (4H, m), 1.96-2.03 (2H, m), 3.40 (3H, s), 7.21 (1H, t, J = 7.6 Hz), 7.33 (2H, t, J = 8.0 Hz), 7.40 (2H, d, J = 7.6 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 22.9, 25.5, 36.8, 51.0, 71.9, 75.0, 100.4, 125.8, 126.2, 129.1, 132.9. IR (neat) 2935, 2857, 2168, 1583, 1478, 1442, 1285, 1091, 925 cm^{-1} . MS (EI) m/z 246 (M^+ , 62%), 203 (M^+ -43, 100%). HRMS Calcd for $C_{15}H_{18}OS$: 246.1078. Found: 246.1054. **1-Phenylthio-1-(1-methoxycyclohexyl)ethene.** Obtained in 88% yield. Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 1.20-1.29 (1H, m), 1.52-1.67 (7H, m), 2.04-2.07 (2H, m), 4.62 (1H, s), 5.21 (1H, s), 7.31-7.37 (3H, m), 7.48 (2H, d, J = 7.6 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 21.9, 25.9, 34.2, 49.7, 78.6, 110.1, 128.1, 129.1, 133.0, 135.0, 153.5. IR (neat) 2935, 2856, 1602, 1439, 1147, 1074, 930, 871 cm^{-1} . MS (EI) m/z 248 (M^+ , 19%), 113 (M^+ -135, 100%). HRMS Calcd for $C_{15}H_{20}OS$: 248.1235. Found: 248.1217.

1-Phenylthio-2-{1-(*t*-butyldimethylsilyloxy)cyclohexyl}ethyne. $RhH(PPh_3)_4$ (2.5 mol%) and dppf (5 mol%) were used, and the mixture was heated at reflux for 2 h. Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 0.16 (6H, s), 0.89 (9H, s), 1.31-1.39 (1H, m), 1.41-1.49 (1H, m), 1.50-1.60 (2H, m), 1.64-1.74 (4H, m), 1.85-1.92 (2H, m), 7.20 (1H, t, J = 7.2 Hz), 7.32 (2H, t, J = 7.2 Hz), 7.41 (2H, d, J = 7.2 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ -2.7, 18.3, 22.9, 25.4, 26.0, 41.1, 70.2, 70.7, 103.8, 125.9, 126.2, 129.0. IR (neat) 2933, 2856, 2173, 1479, 1253, 1095, 1052, 837 cm^{-1} . MS (EI) m/z 346 (M^+ ,

0.3%), 289 (M^+ -57, 100%). HRMS Calcd for $C_{20}H_{30}OSSi$: 346.1787. Found: 346.1788. **1-Phenylthio-1-{1-(*t*-butyldimethylsilyloxy)cyclohexyl}ethene**. Obtained in 99% yield. Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 0.15 (6H, s), 0.94 (9H, s), 1.25-1.33 (1H, m), 1.47-1.55 (3H, m), 1.63-1.73 (2H, m), 1.79 (2H, td, J = 13.2, 3.6 Hz), 1.90-1.97 (2H, m), 4.55 (1H, s), 5.29 (1H, s), 7.31 (1H, t, J = 7.6 Hz), 7.34 (2H, t, J = 7.2 Hz), 7.47 (2H, dd, J = 7.6, 1.6 Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ -2.1, 18.9, 22.8, 26.0, 26.3, 38.4, 76.5, 108.9, 128.0, 129.1, 133.4, 134.8, 155.2. IR (neat) 2924, 1602, 1470, 1255, 1145, 1022, 836, 773 cm^{-1} . MS (EI) m/z M^+ , not detected. 333 (M^+ -15, 2%), 291 (M^+ -57, 100%). HRMS Calcd for $C_{20}H_{32}OSSi$: 348.1943, not detected. Calcd for $C_{20}H_{32}OSSi-C_4H_9$: 291.1239. Found: 291.1249.

Reaction of 1-Octanethiol and 2-{2-(*t*-Butoxycarbonylamino)ethylthio}-1-triisopropylsilylethyne **6.** In a two-necked flask equipped with a reflux condenser were placed tetrakis(triphenylphosphine)hydriderrhodium (4 mol%, 6.9 mg), dppf (6 mol%, 5.0 mg), **6** (0.15 mmol, 54 mg), and 1-octanethiol (0.15 mmol, 21.9 mg) in acetone (2.0 mL) under an argon atmosphere. The solution was heated at reflux for 1 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving triisopropylsilylacetylene **7** (4.9 mg, 18%), 1-octylthio-2-triisopropylsilylethyne **8** (13.4 mg, 27%), **4** (11.5 mg, 43%), dioctyl disulfide (4.6 mg, 0.016 mmol), octyl 2-(*t*-butoxycarbonylamino)ethyl disulfide (8.0 mg, 0.025 mmol), and bis{2-(*t*-butoxycarbonylamino)ethyl} disulfide (0.7 mg, 0.002 mmol) with recovered 1-octanethiol (7.3 mg, 30%) and **6** (22.1 mg, 41%).

Alkylthio Exchange Reaction of 1-Alkylthio-1-alkyne and Disulfide. In a two-necked flask equipped with a reflux condenser were placed tetrakis(triphenylphosphine)hydriderrhodium (2 mol%, 5.8 mg), dppf (4 mol%, 5.5 mg), 1-butylthio-2-triethylsilylethyne **9** (0.25 mmol, 57 mg), and bis(4-methoxybutylthio) disulfide (0.75 mmol, 178.5 mg) in acetone (0.5 mL) under an argon atmosphere. The solution was heated at reflux for 0.5 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 1-(4-methoxybutylthio)-2-triethylsilylethyne (51.6 mg, 80%), butyl 4-methoxybutyl disulfide (35.4 mg, 68%) as well as recovered **9** (7.4 mg, 13%) and disulfide (126.7 mg, 71%).

References

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