Supporting Information

Ruthenium-Catalyzed Propargylic Substitution Reaction of Propargylic Alcohols with Thiols: A General Synthetic Route to Propargylic Sulfides

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General Method. ¹H NMR (400, 300, and 270 MHz) and ¹³C NMR (100, 75, and 67.8 MHz) spectra were recorded using CDCl₃ as solvent. Quantitative GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m x 0.25 mm CBP10 fused silica capillary column. GC-MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. Mass spectra were measured on a JEOL JMS600H mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use.

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Ruthenium-Catalyzed Propargylic Substitution Reaction of Propargylic Alcohols Bearing Internal Alkyne Group with Thiols. A typical experimental procedure for the reaction of 1,3-diphenyl-2-propyn-1-ol (**2a**) with *n*BuSH catalyzed by [Cp*RuCl(μ_2 -SMe) $_2$ RuCp*(OH $_2$)]OTf (**1e**) is described below. In a 20 mL flask was placed **1e** (12.2 mg, 0.015 mmol) under N $_2$. Anhydrous ClCH $_2$ CH $_2$ Cl (8 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (64.1 mg, 0.30 mmol) and *n*BuSH (135 mg, 1.50 mmol), the reaction flask was kept at 60 °C for 1 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO $_2$) with EtOAc-hexane (1/9) to give butyl 1,3-diphenyl-2-propynyl sulfide (**3aa**) as a pale yellow oil (78.0 mg, 0.278 mmol, 92% yield).

Butyl 1,3-diphenyl-2-propynyl sulfide (3aa): ^1H NMR δ 0.89 (t, 3H, J = 7.2 Hz), 1.40 (m, 2H), 1.61 (m, 2H), 2.62 (m, 1H), 2.77 (m, 1H), 4.98 (s, 1H), 7.27-7.37 (m, 6H), 7.46 (m, 2H), 7.56 (d, 2H, J = 7.2 Hz). ^{13}C NMR δ 13.6, 22.0, 31.1, 31.4, 39.3, 85.7, 87.4, 123.0, 127.6, 127.9, 128.2, 128.5, 131.7, 138.6. HRMS Calcd for C $_{19}$ H $_{20}$ S [M] 280.1286. Found 280.1281.

For comparison, reactions of **2a** with *n*BuSH in the presence of various mono- and diruthenium complexes were carried. Typical results are shown in Table S1. Cationic thiolate-bridged diruthenium complexes [Cp*RuCl(μ_2 -SR) $_2$ Cp*Ru(OH $_2$)]OTf (R = *i*Pr (**1d**) and Me (**1e**)) were effective in this reaction (see text). Unfortunately, conventional monoruthenium complexes such as [Cp*RuCl(PPh $_3$) $_2$], [CpRuCl(PPh $_3$) $_2$] (Cp = η^5 -C $_5$ H $_5$), [RuCl $_2$ (PPh $_3$) $_3$], [RuCl $_2$ (*p*-cymene)] $_2$, [(indenyl)RuCl(PPh $_3$) $_2$], [RuCl $_2$ (dppe) $_2$] (dppe = 1,2-bis(diphenylphosphino)ethane), and [Cp*RuCl(μ_2 -Cl) $_2$ RuCp*Cl] did not work at all as catalysts.

Table S1. Reaction of Propargylic Alcohol (**2a**) with ⁿBuSH.^a

catalyst (mol %)	additive (mol %)	yield of 3aa (%) ^b
[Cp*RuCl(μ-SMe) ₂ Cp*Ru(OH ₂)]OTf (1e) (5)	—	92
[Cp*RuCl(μ-S ⁱ Pr) ₂ Cp*Ru(OH ₂)]OTf (1d) (5)	—	92
[Cp*RuCl(μ-SMe) ₂ Cp*RuCl] (1a) (5)	NH ₄ BF ₄ (10)	trace
[Cp*RuCl(μ-S ⁱ Pr) ₂ Cp*RuCl] (1b) (5)	NH ₄ BF ₄ (10)	trace
[RuCl ₂ (PPh ₃) ₃] (5)	NH ₄ BF ₄ (10)	0
[RuCl ₂ (<i>p</i> -cymene) ₂] (5)	NH ₄ BF ₄ (10)	trace
[CpRuCl(PPh ₃) ₂] (5)	NH ₄ BF ₄ (10)	0
[(indenyl)RuCl(PPh ₃) ₂] (5)	NH ₄ BF ₄ (10)	trace
[Cp*RuCl ₂] ₂ (5)	NH ₄ BF ₄ (10)	0

^a All the reactions of PhCH(OH)C≡CPh (**2a**) (0.10 mmol) with ⁿBuSH (0.50 mmol) were carried out in the presence of a catalyst in ClCH₂CH₂Cl at 60 °C for 1 h.

^b Isolated yield.

Spectroscopic data and isolated yield of other products are as follows.

Cyclohexyl 1,3-diphenyl-2-propynyl sulfide (3ab): Yield 93%. A pale yellow oil. ¹H NMR δ 1.26-2.11 (m, 10H), 3.00 (m, 1H), 5.05 (s, 1H), 7.24-7.35 (m, 6H), 7.43-7.46 (m, 2H), 7.56 (d, 2H, *J* = 8.1 Hz). ¹³C NMR δ 25.8, 25.9, 26.0, 33.1, 33.6, 38.1, 44.3, 85.5, 87.7, 122.9, 127.5, 127.7, 128.0, 128.1, 128.4, 131.5, 138.5. Anal Calcd for C₂₁H₂₂S: C, 82.30; H, 7.24. Found: C, 82.07; H, 7.27.

3-Methylbutyl 1,3-diphenyl-2-propynyl sulfide (3ac): Yield 76%. A pale yellow oil. ¹H NMR δ 0.87 (d, 6H, *J* = 6.5 Hz), 1.51 (m, 2H), 1.67 (sept, 1H, *J* = 6.5 Hz), 2.63 (m, 1H), 2.79 (m, 1H), 4.98 (s, 1H), 7.26-7.37 (m, 6H), 7.46 (m, 2H), 7.56 (d, 2H, *J* =

7.5 Hz). ^{13}C NMR δ 22.3, 22.4, 27.5, 29.8, 38.0, 39.3, 85.7, 87.3, 122.9, 127.5, 127.7, 128.1, 128.4, 131.6, 138.4. HRMS Calcd for $\text{C}_{20}\text{H}_{22}\text{S}$ [M] 294.1442. Found 294.1435.

Phenyl 1,3-diphenyl-2-propynyl sulfide (3ad): Yield 70%. A pale yellow oil. ^1H NMR δ 5.21 (s, 1H), 7.26-7.29 (m, 6H), 7.38 (m, 2H), 7.46 (m, 7H). ^{13}C NMR δ 44.3, 86.8, 87.3, 122.7, 127.7, 127.9, 128.1, 128.1, 128.3, 128.3, 128.5, 131.5, 133.2, 134.3, 137.8. HRMS Calcd for $\text{C}_{21}\text{H}_{15}\text{S}$ [M-H] 299.0894. Found 299.0889.

2-Methoxycarbonylethyl 1,3-diphenyl-2-propynyl sulfide (3ae): Yield 92%. A pale yellow oil. ^1H NMR δ 2.65 (t, 2H, $J = 7.3$ Hz), 2.91 (dt, 1H, $J = 7.3$ and 14 Hz), 3.04 (dt, 1H, $J = 7.3$ and 14 Hz), 3.66 (s, 3H), 5.04 (s, 1H), 7.28-7.38 (m, 6H), 7.47 (m, 2H), 7.55 (d, 2H, $J = 6.8$ Hz). ^{13}C NMR δ 26.7, 34.4, 39.6, 51.7, 86.1, 86.8, 122.6, 127.7, 127.8, 128.1, 128.3, 128.5, 131.6, 137.9, 172.0. HRMS Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2\text{S}$ [M] 310.1028. Found 310.1021.

3-Chloropropyl 1,3-diphenyl-2-propynyl sulfide (3af): Yield 90%. A pale yellow oil. ^1H NMR δ 2.03 (quintet, 2H, $J = 6.5$ Hz), 2.76 (dt, 1H, $J = 6.5$ and 13 Hz), 2.90 (dt, 1H, $J = 6.5$ and 13 Hz), 3.59 (t, 2H, $J = 6.5$ Hz), 4.98 (s, 1H), 7.26-7.36 (m, 6H), 7.46 (m, 2H), 7.55 (d, 2H, $J = 6.8$ Hz). ^{13}C NMR δ 28.8, 31.9, 39.4, 43.5, 86.0, 86.9, 122.6, 127.7, 127.7, 128.1, 128.2, 128.4, 131.5, 138.0. HRMS Calcd for $\text{C}_{18}\text{H}_{27}\text{ClS}$ [M] 300.0740. Found 300.0741.

2-Hydroxyethyl 1,3-diphenyl-2-propynyl sulfide (3ag): Yield 52%. A pale yellow oil. ^1H NMR δ 2.01 (brs, 1H), 2.84 (dt, 1H, $J = 7.3$ and 14 Hz), 3.04 (dt, 1H, $J = 7.3$ and 14 Hz), 3.79 (t, 2H, $J = 6.0$ Hz), 5.05 (s, 1H), 7.25-7.40 (m, 6H), 7.49 (m, 2H), 7.57 (d, 2H, $J = 7.2$ Hz). ^{13}C NMR δ 35.1, 39.2, 60.8, 86.2, 87.0, 122.5, 127.8, 127.9, 128.2, 128.4, 128.6, 131.6, 138.0. HRMS Calcd for $\text{C}_{17}\text{H}_{16}\text{OS}$ [M] 268.0922. Found 268.0929.

Butyl 3-(1,1,5-triphenyl-1-penten-4-ynyl) sulfide (3ba): Yield 96%. A pale yellow oil. ^1H NMR δ 0.84 (t, 3H, $J = 7.0$ Hz), 1.26-1.48 (m, 4H), 2.57-2.66 (m, 2H), 4.52 (d, 1H, $J = 9.9$ Hz), 6.16 (d, 1H, $J = 9.9$ Hz), 7.19-7.45 (m, 15H). ^{13}C NMR δ 13.7, 22.0, 31.0, 31.6, 34.4, 84.2, 87.1, 122.9, 125.4, 127.5, 127.6, 128.0, 128.1, 128.3, 129.8, 131.6, 138.4, 141.2, 142.9. HRMS Calcd for $\text{C}_{27}\text{H}_{25}\text{S}$ [M-H] 381.1677. Found 381.1689.

Butyl 1-phenyl-2-heptynyl sulfide (3da): Yield 87%. A pale yellow oil. ^1H NMR δ 0.85-0.94 (m, 6H), 1.34-1.62 (m, 8H), 2.29 (dt, 2H, $J = 2.1$ and 7.0 Hz), 2.53 (dt, 1H, $J = 6.0$ and 14 Hz), 2.69 (dt, 1H, $J = 6.0$ and 14 Hz), 4.75 (t, 1H, $J = 2.1$ Hz), 7.23-7.33 (m, 3H), 7.47 (d, 2H, $J = 7.0$ Hz). ^{13}C NMR δ 13.6, 13.7, 18.7, 22.0, 22.1, 30.9, 31.1, 31.3, 39.0, 77.8, 86.2, 127.3, 127.6, 128.2, 139.1. Anal Calcd for $\text{C}_{17}\text{H}_{24}\text{S}$: C, 78.40; H, 9.29. Found: C, 78.23; H, 9.42.

3-Methylbutyl 1-phenyl-2-heptynyl sulfide (3db): Yield 90%. A pale yellow oil. ^1H NMR δ 0.87 (d, 3H, $J = 6.8$ Hz), 0.87 (d, 3H, $J = 6.8$ Hz), 0.91 (t, 3H, $J = 7.0$ Hz), 1.47 (m, 6H), 1.65 (sept, 1H, $J = 6.8$ Hz), 2.30 (dt, 2H, $J = 2.1$ and 6.5 Hz), 2.55 (m, 1H), 2.68 (m, 1H), 4.75 (s, 1H), 7.23-7.33 (m, 3H), 7.47 (d, 2H, $J = 7.0$ Hz). ^{13}C NMR δ 13.6, 18.7, 22.0, 22.2, 22.3, 27.6, 29.7, 30.9, 38.0, 39.1, 77.8, 86.3, 127.3, 127.6, 128.2, 139.1. Anal Calcd for $\text{C}_{18}\text{H}_{26}\text{S}$: C, 78.77; H, 9.55. Found: C, 78.50; H, 9.64.

Butyl 1-phenyl-2-nonyl sulfide (3ea): Yield 83%. A pale yellow oil. ^1H NMR δ 0.89 (t, 6H, $J = 7.0$ Hz), 1.30-1.56 (m, 12H), 2.29 (dt, 2H, $J = 2.1$ and 6.5 Hz), 2.54 (dt, 1H, $J = 7.3$ and 12 Hz), 2.71 (dt, 1H, $J = 7.3$ and 12 Hz), 4.75 (s, 1H), 7.24-7.34 (m, 3H), 7.48 (d, 2H, $J = 7.0$ Hz). ^{13}C NMR δ 13.7, 14.1, 19.0, 22.1, 22.6, 28.6, 28.8, 31.2, 31.4, 39.1, 77.6, 86.4, 127.3, 127.7, 128.2, 139.2. HRMS Calcd for $\text{C}_{19}\text{H}_{28}\text{S}$ [M] 288.1912. Found 288.1905.

Butyl 4,4-dimethyl-1-phenyl-2-pentynyl sulfide (3fa): Yield 86%. A pale yellow oil. ^1H NMR δ 0.89 (t, 3H, $J = 7.0$ Hz), 1.19 (s, 9H), 1.38 (m, 2H), 1.58 (m, 2H), 2.54 (dt, 1H, $J = 7.3$ and 12 Hz), 2.71 (dt, 1H, $J = 7.3$ and 12 Hz), 4.75 (s, 1H), 7.19-7.34 (m, 3H), 7.49 (d, 2H, $J = 7.0$ Hz). ^{13}C NMR δ 13.7, 22.1, 27.7, 31.1, 31.3, 31.3, 38.8, 76.3, 94.8, 127.2, 127.6, 128.2, 139.2. HRMS Calcd for $\text{C}_{17}\text{H}_{24}\text{S}$ [M] 260.1599. Found 260.1598.

3-Methylbutyl 4,4-dimethyl-1-phenyl-2-pentynyl sulfide (3fb): Yield 87%. A pale yellow oil. ^1H NMR δ 0.87 (d, 3H, $J = 6.8$ Hz), 0.88 (d, 3H, $J = 6.8$ Hz), 1.19 (s, 9H), 1.49 (m, 2H), 1.65 (sept, 1H, $J = 6.8$ Hz), 2.55 (m, 1H), 2.71 (m, 1H), 4.76 (s, 1H), 7.23-7.34 (m, 3H), 7.49 (d, 2H, $J = 7.0$ Hz). ^{13}C NMR δ 22.3, 22.4, 27.6, 27.7, 29.6, 31.1, 38.1, 38.8, 76.2, 94.8, 127.2, 127.6, 128.2, 139.2. HRMS Calcd for $\text{C}_{18}\text{H}_{26}\text{S}$ [M] 274.1755. Found 274.1756.

Butyl 1-(4-methylphenyl)-3-phenyl-2-propynyl sulfide (3ga): Yield 90%. A pale yellow oil. ^1H NMR δ 0.89 (t, 3H, $J = 7.2$ Hz), 1.34 (m, 2H), 1.44 (m, 2H), 2.32 (s, 3H), 2.54 (dt, 1H, $J = 7.3$ and 12 Hz), 2.71 (dt, 1H, $J = 7.3$ and 12 Hz), 4.95 (s, 1H), 7.13 (d, 2H, $J = 8.1$ Hz), 7.27-7.29 (m, 3H), 7.44 (d, 2H, $J = 8.1$ Hz), 7.48 (d, 2H, $J = 7.0$ Hz). ^{13}C NMR δ 13.7, 21.1, 22.1, 31.2, 31.5, 39.1, 85.4, 87.6, 122.9, 127.6, 128.0, 128.1, 129.1, 131.5, 135.4, 137.2. Anal Calcd for $\text{C}_{20}\text{H}_{22}\text{S}$: C, 81.58; H, 7.53. Found: C, 81.39; H, 7.51.

3-Methylbutyl 1-(4-methylphenyl)-3-phenyl-2-propynyl sulfide (3gb): Yield 92%. A pale yellow oil. ^1H NMR δ 0.88 (d, 3H, $J = 6.8$ Hz), 0.88 (d, 3H, $J = 6.8$ Hz), 1.51 (m, 2H), 1.65 (sept, 1H, $J = 6.8$ Hz), 2.32 (s, 3H), 2.63 (m, 1H), 2.79 (m, 1H), 4.96 (s, 1H), 7.13 (d, 2H, $J = 8.1$ Hz), 7.28 (m, 3H), 7.43 (m, 4H). ^{13}C NMR δ 21.2,

22.3, 22.4, 27.6, 29.9, 38.1, 39.0, 85.5, 87.5, 122.9, 127.6, 128.0, 128.1, 129.1, 131.5, 135.4, 137.2. HRMS Calcd for C₂₁H₂₄S [M] 308.1599. Found 308.1597.

Butyl 1-methyl-1,3-diphenyl-2-propynyl sulfide (3ha): Yield 84%. A pale yellow oil. ¹H NMR δ 0.81 (t, 3H, *J* = 7.2 Hz), 1.32 (m, 2H), 1.49 (m, 2H), 1.96 (s, 3H), 2.46 (dt, 1H, *J* = 7.2 and 12 Hz), 2.71 (dt, 1H, *J* = 7.2 and 12 Hz), 7.25-7.36 (m, 6H), 7.50 (m, 2H), 7.77 (d, 2H, *J* = 7.2 Hz). ¹³C NMR δ 13.6, 22.1, 30.7, 31.1, 31.4, 46.5, 85.5, 91.8, 123.2, 126.5, 127.2, 128.1, 128.2, 128.3, 131.6, 143.5. HRMS Calcd for C₂₀H₂₂S [M] 294.1442. Found 294.1442.

Ruthenium-Catalyzed Propargylic Substitution Reaction of Propargylic Alcohols Bearing Terminal Alkyne Group with Thiols. A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**4a**) with *n*BuSH catalyzed by [Cp*₂RuCl(μ₂-SMe)₂RuCp*(OH₂)]OTf (**1e**) is described below. In a 20 mL flask was placed **1e** (23.1 mg, 0.03 mmol) under N₂. Anhydrous ClCH₂CH₂Cl (15 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **4a** (79.3 mg, 0.60 mmol) and *n*BuSH (270 mg, 3.00 mmol), the reaction flask was kept at 60 °C for 1 h. The solvent was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO₂) with EtOAc-hexane (1/9) to give butyl 1-phenyl-2-propynyl sulfide (**5aa**) as a pale yellow oil (106 mg, 0.51 mmol, 86% yield).

Butyl 1-phenyl-2-propynyl sulfide (5aa): ¹H NMR δ 0.89 (t, 3H, *J* = 7.2 Hz), 1.38 (m, 2H), 1.58 (m, 2H), 2.58 (s, 1H), 2.58 (m, 1H), 2.76 (m, 1H), 4.73 (d, 1H, *J* = 1.8 Hz), 7.23-7.35 (m, 3H), 7.49 (d, 2H, *J* = 7.2 Hz). ¹³C NMR δ 13.6, 22.0, 30.9, 31.2,

38.3, 73.6, 81.9, 127.7, 127.7, 128.5, 137.8. HRMS Calcd for C₁₃H₁₇S [M+H]⁺ 205.1051. Found 205.1052.

For comparison, reactions of **4a** with ⁿBuSH in the presence of various mono- and diruthenium complexes were carried out. Typical results are shown in Table S2. In sharp contrast to the catalytic reaction of propargylic alcohols bearing *internal alkyne group* (vide infra), neutral thiolate-bridged diruthenium complexes [Cp^{*}RuCl(μ₂-SR)₂RuCp^{*}Cl] (R = Me (**1a**), ⁱPr (**1b**), ⁿPr (**1c**)) were also effective in the reaction of propargylic alcohols bearing *terminal alkyne group*. On the other hand, conventional monoruthenium complexes such as [RuCl₂(PPh₃)₃], [RuCl₂(*p*-cymene)]₂, [CpRuCl(PPh₃)₂] (Cp = η⁵-C₅H₅), [(indenyl)RuCl(PPh₃)₂] and [Cp^{*}RuCl(μ₂-Cl)₂RuCp^{*}Cl], did not work at all as catalysts.

Table S2. Reaction of ⁿPropargylic Alcohol (**4a**) with ⁿBuSH.^a

Reaction scheme showing the conversion of **4a** to **5aa** using ⁿBuSH, a catalyst, and an additive in ClCH₂CH₂Cl at 60 °C for 1 h.

catalyst (mol %)	additive (mol %)	GLC conv. (%)	GLC yield (%)
[Cp [*] RuCl(μ-SMe) ₂ Cp [*] Ru(OH ₂)]OTf (1e) (5)	–	100	>95
[Cp [*] RuCl(μ-SMe) ₂ Cp [*] RuCl] (1a) (5)	NH ₄ BF ₄ (10)	100	>95
[Cp [*] RuCl(μ-S ⁱ Pr) ₂ Cp [*] RuCl] (1b) (5)	NH ₄ BF ₄ (10)	100	>95
[Cp [*] RuCl(μ-S ⁿ Pr) ₂ Cp [*] RuCl] (1c) (5)	NH ₄ BF ₄ (10)	100	>95
[RuCl ₂ (PPh ₃) ₃] (5)	NH ₄ BF ₄ (10)	19	0
[RuCl ₂ (<i>p</i> -cymene)] ₂ (5)	NH ₄ BF ₄ (10)	11	0
[CpRuCl(PPh ₃) ₂] (5)	NH ₄ BF ₄ (10)	73	0
[(indenyl)RuCl(PPh ₃) ₂] (5)	NH ₄ BF ₄ (10)	10	0
[Cp [*] RuCl ₂] ₂ (5)	NH ₄ BF ₄ (10)	66	0

^a All the reactions of PhCH(OH)C≡CH (**4a**) (0.10 mmol) with ⁿBuSH (0.50 mmol) were carried out in the presence of a catalyst in ClCH₂CH₂Cl at 60 °C for 1 h.

Spectroscopic data and isolated yield of other products are as follows.

Octyl 1-phenyl-2-propynyl sulfide (5ab): Yield 87%. A pale yellow oil. ¹H NMR δ 0.87 (t, 3H, *J* = 7.2 Hz), 1.27 (m, 10H), 1.60 (m, 2H), 2.46-2.77 (m, 2H), 2.57 (d, 1H, *J* = 2.4 Hz), 4.73 (d, 1H, *J* = 2.4 Hz), 7.23-7.35 (m, 3H), 7.49 (d, 2H, *J* = 7.2 Hz). ¹³C

NMR δ 14.0, 22.6, 28.9, 28.9, 29.1, 31.6, 31.8, 38.4, 73.5, 81.8, 127.6, 127.7, 128.4, 137.8. Anal Calcd for $C_{17}H_{24}S$: C, 78.40; H, 9.29. Found: C, 78.20; H, 9.43.

3-Methylbutyl 1-phenyl-2-propynyl sulfide (5ac): Yield 88%. A pale yellow oil. 1H NMR δ 0.86 (d, 3H, $J = 6.5$ Hz), 0.87 (d, 3H, $J = 6.5$ Hz), 1.48 (m, 2H), 1.63 (sept, 1H, $J = 6.5$ Hz), 2.58 (d, 1H, $J = 2.7$ Hz), 2.48 (m, 1H), 2.73 (m, 1H), 4.74 (d, 1H, $J = 2.7$ Hz), 7.23-7.36 (m, 3H), 7.51 (d, 2H, $J = 6.7$ Hz). ^{13}C NMR δ 22.2, 22.4, 27.6, 29.7, 37.8, 38.4, 73.6, 81.9, 127.6, 127.7, 128.4, 137.7. HRMS Calcd for $C_{14}H_{19}S$ [M+H] 219.1207. Found 219.1207.

Cyclohexyl 1-phenyl-2-propynyl sulfide (5ad): Yield 82%. A pale yellow oil. 1H NMR δ 1.26-2.15 (m, 10H), 2.57 (d, 1H, $J = 2.4$ Hz), 2.93 (m, 1H), 4.81 (s, 1H, $J = 2.4$ Hz), 7.24-7.35 (m, 3H), 7.50 (d, 2H, $J = 7.2$ Hz). ^{13}C NMR δ 25.8, 32.8, 33.4, 37.0, 44.1, 73.4, 82.4, 127.7, 127.8, 128.5, 138.0. HRMS Calcd for $C_{15}H_{19}S$ [M+H] 231.1207. Found 231.1205.

Phenylmethyl 1-phenyl-2-propynyl sulfide (5ae): Yield 79%. A pale yellow oil. 1H NMR δ 2.63 (d, 1H, $J = 2.4$ Hz), 3.75 (d, 1H, $J = 13$ Hz), 3.96 (d, 1H, $J = 13$ Hz), 4.53 (d, 1H, $J = 2.4$ Hz), 7.23-7.32 (m, 8H), 7.42 (d, 2H, $J = 7.2$ Hz). ^{13}C NMR δ 36.4, 38.0, 74.1, 81.7, 127.0, 127.7, 127.8, 128.4, 128.4, 128.9, 137.0, 137.3. HRMS Calcd for $C_{16}H_{15}S$ [M+H] 239.0894. Found 239.0895.

3-Chloropropyl 1-phenyl-2-propynyl sulfide (5af): Yield 79%. A pale yellow oil. ^1H NMR δ 2.01 (quintet, 2H, $J = 6.5$ Hz), 2.61 (d, 1H, $J = 2.4$ Hz), 2.73 (m, 1H), 2.86 (m, 1H), 3.58 (t, 2H, $J = 6.5$ Hz), 4.75 (d, 1H, $J = 2.4$ Hz), 7.31-7.34 (m, 3H), 7.49 (d, 2H, $J = 7.2$ Hz). ^{13}C NMR δ 28.7, 31.7, 38.5, 43.4, 74.1, 81.5, 127.6, 127.8, 128.5, 137.3. HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{ClS}$ $[\text{M}+\text{H}]$ 225.0505. Found 225.0506.

Phenyl 1-phenyl-2-propynyl sulfide (5ag): Yield 24%. A pale yellow oil. ^1H NMR δ 2.57 (d, 1H, $J = 2.4$ Hz), 4.98 (d, 1H, $J = 2.4$ Hz), 7.27-7.42 (m, 10H). ^{13}C NMR δ 43.2, 74.6, 81.9, 127.8, 127.9, 128.2, 128.3, 128.6, 133.1, 133.7, 137.2. HRMS Calcd for $\text{C}_{16}\text{H}_{13}\text{S}$ $[\text{M}+\text{H}]$ 225.0738. Found 225.0736.

Butyl 1-(4-methylphenyl)-2-propynyl sulfide (5ba): Yield 83%. A pale yellow oil. ^1H NMR δ 0.90 (t, 3H, $J = 7.2$ Hz), 1.41 (m, 2H), 1.61 (m, 2H), 2.34 (s, 3H), 2.55 (d, 1H, $J = 2.4$ Hz), 2.59 (m, 1H), 2.81 (m, 1H), 4.84 (d, 1H, $J = 2.4$ Hz), 7.14-7.22 (d, 2H, $J = 6.0$ Hz), 7.65 (d, 2H, $J = 6.0$ Hz). ^{13}C NMR δ 13.6, 18.9, 22.0, 30.9, 31.4, 35.6, 73.0, 82.4, 126.1, 127.8, 127.9, 130.6, 135.4, 135.4. HRMS Calcd for $\text{C}_{14}\text{H}_{19}\text{S}$ $[\text{M}+\text{H}]$ 219.1207. Found 219.1204.

Butyl 1-(4-fluorophenyl)-2-propynyl sulfide (5ca): Yield 84%. A pale yellow oil. ^1H NMR δ 0.89 (t, 3H, $J = 7.2$ Hz), 1.40 (m, 2H), 1.59 (m, 2H), 2.56 (m, 1H), 2.60 (d, 1H, $J = 2.4$ Hz), 2.73 (m, 1H), 4.73 (d, 1H, $J = 2.4$ Hz), 7.01 (t, 2H, $J = 8.7$ Hz), 7.47 (m, 2H). ^{13}C NMR δ 13.6, 21.9, 30.9, 31.2, 37.6, 73.8, 81.7, 115.3 (d, $J = 22$ Hz), 129.4 (d, $J = 8$ Hz), 123.6 (d, $J = 3$ Hz), 165.1 (d, $J = 246$ Hz). HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{FS}$ $[\text{M}+\text{H}]$ 223.0957. Found 223.0955.

Butyl 1-(2-naphthyl)-2-propynyl sulfide (5da): Yield 94%. A pale yellow oil. ^1H NMR δ 0.86 (t, 3H, $J = 7.2$ Hz), 1.38 (m, 2H), 1.57 (m, 2H), 2.54 (m, 1H), 2.64 (d, 1H, $J = 2.4$ Hz), 2.73 (m, 1H), 4.89 (d, 1H, $J = 2.4$ Hz), 7.45 (m, 2H), 7.60 (dd, 1H, $J = 1.8$ and 8.4 Hz), 7.79 (m, 3H), 7.92 (s, 1H). ^{13}C NMR δ 13.6, 21.9, 30.8, 31.1, 38.6, 73.9, 81.8, 125.7, 126.1, 126.2, 126.4, 127.6, 127.9, 128.4, 132.8, 132.9, 135.1. HRMS Calcd for $\text{C}_{17}\text{H}_{19}\text{S}$ $[\text{M}+\text{H}]$ 255.1207. Found 255.1207.

Butyl 1-cyclohexyl-2-propynyl sulfide (5ea): Yield 62%. A pale yellow oil. ^1H NMR δ 0.92 (t, 3H, $J = 7.2$ Hz), 1.21-1.94 (m, 15H), 2.35 (d, 1H, $J = 2.4$ Hz), 2.70 (m, 2H), 3.38 (m, 1H). ^{13}C NMR δ 13.6, 22.1, 26.0, 26.1, 29.7, 31.2, 31.4, 40.9, 41.8, 72.3, 82.8. HRMS Calcd for $\text{C}_{13}\text{H}_{23}\text{S}$ $[\text{M}+\text{H}]$ 211.1520. Found 211.1521.

Butyl 3-(1,1-diphenyl-1-penten-4-ynyl) sulfide (5fa): Yield 47%. A pale yellow oil. ^1H NMR δ 0.84 (t, 3H, $J = 7.2$ Hz), 1.34 (m, 4H), 2.42 (d, 1H, $J = 2.4$ Hz), 2.57 (m, 2H), 4.28 (dd, 1H, $J = 2.4$ and 11 Hz), 6.06 (d, 1H, $J = 11$ Hz), 7.22-7.41 (m, 10H). ^{13}C

NMR δ 13.5, 21.9, 30.8, 31.4, 33.3, 72.0, 81.9, 125.0, 127.6, 127.7, 127.8, 128.2, 128.4, 129.7, 138.4, 141.2, 143.4. Anal Calcd for C₂₁H₂₂S: C, 82.30; H, 7.24. Found: C, 82.29; H, 7.27.

Butyl 1,1-diphenyl-2-propynyl sulfide (5ga): Yield 60%. A pale yellow oil. ¹H NMR δ 0.85 (t, 3H, *J* = 7.2 Hz), 1.37 (m, 2H), 1.52 (m, 2H), 2.61 (t, 1H, *J* = 7.2 Hz), 2.89 (s, 1H), 5.24 (s, 1H), 7.21-7.32 (m, 6H), 7.67 (d, 4H, *J* = 7.2 Hz). ¹³C NMR δ 13.7, 22.2, 30.2, 32.1, 54.7, 75.2, 85.4, 127.2, 127.7, 128.0, 141.8. Anal Calcd for C₁₉H₂₀S: C, 81.38; H, 7.19. Found: C, 81.56; H, 7.30.

Preparation of [Cp*₂RuCl(μ₂-SMe)₂RuCp*(OH₂)]OTf (1e). [Cp*₂RuCl(μ₂-SMe)₂RuCp*(OH₂)]OTf (**1e**) was prepared according to a similar method for **1d**.^{S1} In a 50 mL flask was placed **1a** (965 mg, 1.52 mmol) under N₂. Anhydrous tetrahydrofuran (THF) (20 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of AgOTf (398 mg, 1.52 mmol), the reaction flask was kept at room temperature for 20 h. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from CH₂Cl₂-*n*-hexane to give black crystals of **1e** (1.017 mg, 1.32 mmol, 87%). ¹H NMR δ 1.63 (s, 30H), 2.51 (s, 6H), 3.30 (brs, 2H). ¹³C NMR δ 1.1, 10.5, 96.5. Anal Calcd for C₂₃H₃₈ClF₃O₄Ru₂S₃: C, 35.91; H, 4.98. Found: C, 35.78; H, 4.11.

X-ray Crystallographic Studies of 1e. Black crystals of **1e** suitable for X-ray analysis were obtained by recrystallization from CH₂Cl₂-*n*-hexane. The single crystal was sealed in a Pyrex glass capillary under N₂ atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K α radiation. Details of crystal and data collection parameters are summarized in Table S3. The positions of non-hydrogen atoms were determined by heavy-

atom Patterson methods and subsequent Fourier syntheses. An ORTEP drawing of **1e** is shown in Figure S1.

Table S3. Crystallographic Data for **1e**.

formula	C ₂₃ H ₃₆ ClF ₃ O ₄ Ru ₂ S ₃
formula weigh	767.30
cryst size (mm ³)	0.10 x 0.10 x 0.10
cryst system	triclinic
space group	<i>P</i> -1(#2)
cryst color	black
<i>a</i> (Å)	8.7183(3)
<i>b</i> (Å)	12.1533(6)
<i>c</i> (Å)	15.4338(9)
α (°)	73.528(2)
β (°)	74.898(2)
γ (°)	78.929(1)
<i>V</i> (Å ³)	1501.7(1)
<i>Z</i>	2
<i>d</i> _{calc} (g cm ⁻³)	1.697
<i>F</i> (000)	772.00
μ _{calc} (cm ⁻¹)	13.49
no. of unique data	14275
no. of data used ($I > 3\sigma(I)$)	9837
no. of params refined	325
<i>R</i> ^a	0.039
<i>R</i> _w ^b	0.048
goodness of fit indicator	1.48
maximum residuals (e Å ⁻³)	1.34

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

Figure S1. Crystal structure of **1e**. The hydrogen atoms and OTf anion are omitted for clarity.

In contrast to the reaction of 2,4-diphenyl-3-buten-2-ol (**2h**) (Table 2, run 14) with *n*BuSH, the reaction of 1,1,3-triphenyl-2-propyn-1-ol with *n*BuSH at 60 °C for 16 h afforded not the corresponding propargylic product but 1,3,3-triphenyl-2-propen-1-one^{S2} in 80% yield as a sole product (Scheme S1). The spectroscopic data of the ketone are as follows.

Scheme S1

1,3,3-Triphenyl-2-propen-1-one: ¹H NMR δ 7.10 (s, 1H), 7.18-7.46 (m, 13H), 7.89 (d, 2H, *J* = 7.2 Hz). ¹³C NMR δ 123.9, 127.9, 128.2, 128.3, 128.4, 128.6, 129.2, 129.6, 132.5, 138.1, 138.8, 141.2, 154.5, 192.4.

References and Notes

- (S1) (a) Matsuzaka, H.; Takagi, Y.; Hidai, M. *Organometallics* **1994**, *13*, 13. (b) Takagi, Y.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Organometallics* **1997**, *16*, 4445.
- (S2) Katritzky, A. R.; Denisenko, S. N.; Oniciu, D. C.; Ghiviriga, I. *J. Org. Chem.* **1998**, *63*, 3450.