Supporting information for:

Rhodium-catalyzed Alkyne Hydrothiolation with Aromatic and Aliphatic Thiols.

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General Procedures. Manipulation of organometallic compounds was performed using standard Schlenk techniques under an atmosphere of dry nitrogen or in a nitrogen-filled Vacuum Atmospheres drybox ($O_2 < 2$ ppm). NMR spectra were recorded on Bruker Avance 300 or Bruker Avance 400 spectrometers. 1H , ^{13}C and ^{19}F NMR spectra are reported in parts per million and were referenced to residual solvent. Coupling constant values were extracted assuming first-order coupling. The multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, td = triplet of doublets. ³All spectra were obtained at 25°C. Elemental analyses were performed using a Carlo Erba Elemental Analyzer EA 1108. GC spectra were recorded on a Varian CP-3800 or an HP 5890 Series II gas chromatograph. Mass spectra were recorded on a Kratos MS-50 mass spectrometer.

Materials and Methods. Pentane, hexane, CH_2Cl_2 , benzene, 1,2-dichloroethane, diethyl ether, THF and toluene were dried by passage through solvent purification columns.¹ $CDCl_3$ was purified by vacuum transfer from P_2O_5 and was degassed prior to use. C_6D_6 was purified by vacuum transfer from Na/benzophenone. All organic reagents were obtained from commercial sources and used as received. Rhodium complex **I** was purchased from Strem Chemicals and was used without further purification. Rhodium complex **II**,² was prepared by a modification of the published procedure (described below).

Synthesis of complex II:

A solution of $\text{RhCl}(\text{PPh}_3)_3$ (1.00 g, 1.08 mmol) in THF (15 mL) were combined in the glove box in a 20 mL vial equipped with a screw cap and a magnetic stir bar. KTp^* (potassium hydrotris{3,5-dimethylpyrazolyl}borate) (0.364 g, 1.08 mmol) was added to the solution. The mixture was stirred for 2 h at room temperature (for optimal yield, reaction time should not be increased). The volatiles were removed under reduced pressure at room temperature, then the residue was dissolved in toluene-1,2-dichloroethane (1:1 ratio, 10 mL) and was filtered through Celite. The resulting red solution was evaporated to dryness to give 0.92 g of $\text{Tp}^*\text{Rh}(\text{PPh}_3)_2$ (92% yield). Crystals were obtained by recrystallization of the product from toluene-hexane. ^1H and ^{13}C NMR data are consistent with literature data.²

General experimental procedure for hydrothiolation:

$\text{Tp}^*\text{Rh}(\text{PPh}_3)_2$ (280 mg, 0.30 mmol, 3 mol %), toluene (2 mL), 1,2-dichloroethane (2 mL), thiol (11 mmol) and alkyne (10 mmol) were combined in the glove box in a 20 mL vial equipped with a magnetic stir bar and a screw cap. The vial was removed from the glove box and monitored by GC. After the reaction was completed, the resulting mixture was filtered through silica gel, washed by toluene, concentrated under vacuum. Flash chromatography (SiO_2 , petroleum ether or a mixture of petroleum ether:diethyl ether as eluent) provided the product.

Notes: The reactions proceed very slowly in the absence of the catalyst, indicating that background reactions are minimal. The addition of a non-nucleophilic base (2,2-lutidine) does not impede or improve the reaction.

Analytical data for hydrothiolation products:

¹H NMR (C₆D₆, 400 MHz): δ 7.49 (m, 2H), 7.12-6.90 (m, 8H), 5.27 (s, 1H), 5.05 (s, 1H), 3.57 (s, 2H). ¹³C{¹H} NMR (C₆D₆, 400 MHz): δ 145.63, 139.94, 137.43, 129.66, 129.15, 128.65, 128.63, 127.55, 127.26, 111.83, 37.21. HRMS (EI) m/z calcd for C₁₅H₁₄S: 226.0816; found: 226.0813. Anal. calcd for C₁₅H₁₄S: C, 79.60; H, 6.23; S, 14.17; found: C, 80.00; H, 6.49.

¹H NMR (CDCl₃, 400 MHz): δ 7.60 (m, 2H), 7.37 (m, 3H), 5.50 (d, 1H, *J* = 3.4 Hz), 5.22 (d, 1H, *J* = 3.2 Hz), 2.71 (m, 2H), 1.70 (m, 2H), 1.05 (m, 3H). ¹³C{¹H} NMR (CDCl₃, 400 MHz): δ 145.13, 139.73, 128.20, 128.17, 126.99, 110.18, 34.00, 21.80, 13.42. HRMS

(EI) m/z calcd for $C_{11}H_{14}S$: 178.0816; found: 178.0812. Anal. calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.91; S, 17.98; found: C, 73.69; H, 7.88.

1H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.10 (m, 5H), 5.46 (s, 1H), 5.23 (s, 1H), 3.34 (m, 1H), 2.05-1.30 (m, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ 400 MHz): δ 145.67, 139.98, 128.24, 127.17, 127.04, 111.64, 43.85, 33.05, 24.83. HRMS (EI) m/z calcd for $C_{13}H_{16}S$: 204.0973; found: 204.0965. Anal. calcd for $C_{13}H_{16}S$: C, 76.41; H, 7.89; S, 15.69; found: C, 76.15, H, 7.72.

^1H NMR (C_6D_6 , 400 MHz): δ 7.58 (m, 2H), 7.26-7.04 (m, 5H), 6.81 (m, 2H), 5.41 (s, 1H), 5.18 (s, 1H), 3.76 (s, 2H), 3.34 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 160.43, 145.18, 137.60, 132.30, 129.17, 128.78, 128.62, 127.23, 114.11, 110.49, 54.77, 37.30. HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{OS}$: 256.0922; found: 256.09178. Anal. calcd for $\text{C}_{16}\text{H}_{16}\text{OS}$: C, 74.96; H, 6.29; O, 6.24; S, 12.51; found: C, 74.89; H, 6.14.

^1H NMR (C_6D_6 , 400 MHz): δ 7.40-7.14 (m, 7H), 6.81 (d, 2H, $J = 8.84\text{ Hz}$), 6.51 (d, 1H, $J = 15.6\text{ Hz}$), 6.50 (d, 1H, $J = 15.6\text{ Hz}$), 3.96 (s, 2H), 3.77 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 158.87, 137.44, 129.84, 128.82, 128.61, 128.48, 127.24, 126.84, 121.50, 114.03, 55.28, 37.64. HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{OS}$: 256.0922; found: 256.09178. Anal. calcd for $\text{C}_{16}\text{H}_{16}\text{OS}$: C, 74.96; H, 6.29; O, 6.24; S, 12.51; found: C, 74.95; H, 6.43.

^1H NMR (C_6D_6 , 400 MHz): δ 7.82 (m, 1H), 7.49 (m, 1H), 7.07 (m, 2H), 6.85-6.50 (m, 5H), 5.32 (s, 1H), 5.18 (s, 1H), 3.84 (t, 2H, $J = 7.0\text{ Hz}$), 3.25 (s, 3H), 2.81 (t, 2H, $J = 7.0\text{ Hz}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 160.51, 158.99, 144.34, 131.25, 129.70, 128.89, 121.11, 114.88, 114.16, 113.97, 66.30, 54.77, 31.07. HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2\text{S}$: 286.1028; found: 286.1028. Anal. calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2\text{S}$: C, 71.30; H, 6.34; O, 11.17; S, 11.20; found: C, 71.65; H, 6.47.

^1H NMR (C_6D_6 , 400 MHz): δ 7.25-6.95 (m, 5H), 6.35 (td, 1H, $J_1 = 4.1$ Hz, $J_2 = 1.6$ Hz), 5.19 (s, 1H), 4.93 (s, 1H), 3.68 (s, 2H), 2.09 (m, 2H), 1.90 (m, 2H), 1.50-1.25 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 146.2, 137.8, 135.5, 129.2, 128.6, 127.7, 127.2, 108.4, 37.2, 27.2, 25.9, 23.1, 22.3. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{18}\text{S}$: 230.1129; found: 230.1129. Anal. calcd for $\text{C}_{15}\text{H}_{18}\text{S}$: C, 78.21; H, 7.88; S, 13.92; found: C, 78.60, H, 7.89.

^1H NMR (C_6D_6 , 400 MHz): δ 7.25-6.90 (m, 5H), 5.06 (s, 1H), 4.62 (s, 1H), 3.64 (s, 2H), 1.150 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 156.8, 137.2, 129.3, 128.6, 127.3, 103.4, 37.9, 37.3, 30.1. HRMS (type) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{S}$: 206.1129; found: 206.1127. Anal. calcd for $\text{C}_{13}\text{H}_{18}\text{S}$: C, 75.67; H, 8.79; S, 15.54; found: C, 75.30; H, 8.40.

Note: **A** was separable from **B/C** with use of silver nitrate-impregnated silica gel. **B** and **C** were not separable and analytical data are reported as a 4:1 mixture of these isomers. **B** is formed by isomerization of **A**.

^1H NMR (C_6D_6 , 400 MHz): δ 7.22–6.95 (m, 5H), 4.95 (s, 1H), 4.69 (s, 1H), 3.67 (s, 2H), 2.16 (t, 2H, $J = 7.6$ Hz), 1.50 (m, 2H), 1.25–1.05 (m, 6H), 0.821 (t, 3H, $J = 7.0$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 147.02, 137.61, 129.51, 129.03, 127.64, 106.35, 38.26, 36.84, 32.34, 29.53, 29.39, 23.35, 14.69. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{S}$: 234.1442; found: 234.1440. Anal. calcd for $\text{C}_{15}\text{H}_{22}\text{S}$: C, 76.86; H, 9.46; S, 13.68; found: C, 76.46; H, 9.20.

4:1 mixture of **B** and **C**. ^1H NMR (C_6D_6 , 400 MHz): δ 7.20–6.95 (m, 5H: 5H **B** and 5H **C**), 5.82 (d, 0.19 H:1H **C**, $J = 15.0$ Hz), 5.61 (m, 0.19H: 1H **C**), 5.41 (td, 0.78 H: 1H **B**, $J_1 = 7.15$ Hz, $J_2 = 1.2$ Hz), 3.60 (s, 1.6 H: 2H **B**), 3.56 (s, 0.42 H: 2H **C**), 2.19 (m, 1.6 H: 2H **B**), 1.89 (s, 2.8H: 3H **B**), 1.25–1.02 (m, 6.5H: 6H **B** and 10H **C**), 0.82 (m, 3H: 3H **B**

and 3H C). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 139.55, 138.77, 133.38, 132.46, 129.86, 129.51, 129.34, 129.01, 128.93, 127.54, 127.38, 123.35, 38.04, 36.15, 33.84, 32.38, 32.18, 30.25, 29.95, 29.77, 29.38, 24.56, 23.35, 23.31, 14.69, 14.67. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{S}$ (mixture of **B** and **C**, same elemental composition): 234.1442; found: 234.1440. Anal. calcd for $\text{C}_{15}\text{H}_{22}\text{S}$: C, 76.86; H, 9.46; S, 13.68; found: C, 76.62; H, 9.14 (mixture of **B** and **C**, same elemental composition).

^1H NMR (CDCl_3 , 400 MHz): δ 7.90-6.95 (m, 10H), 6.88 (s, 1H), 3.30-3.06 (m, 1H), 2.15-1.40 (m, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): δ 141.97, 132.25, 131.50, 129.54, 128.46, 128.38, 128.12, 127.90, 127.59, 126.98, 44.77, 33.34, 24.76. HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{S}$: 280.1286; found: 280.1282. Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{S}$: C, 81.38; H, 7.19; S, 11.43; found: C, 81.78; H, 7.37.

Note: **D** and **E** were not separable and analytical data are reported as a 3.5:1 mixture of these isomers.

3.5:1 mixture of **D** and **E**. ^1H NMR (CD_3OD , 300 MHz): δ 7.28-7.07 (m, 10H: 10H **D** and 10H **E**), 6.31 (s, 0.78H: 1H **D**), 5.86 (q, 0.22H: 1H **E**, $J = 7.1$ Hz), 3.96 (s, 1.58H: 2H **D**), 3.50 (s, 0.43H: 2H **E**), 1.99 (s, 2.3H: 3H **D**), 1.51 (d, 0.66H: 3H **E**, $J = 7.0$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3OD , 300 MHz): δ 138.94, 138.77, 135.46, 134.97, 134.71, 130.84, 130.11, 130.00, 129.71, 129.66, 129.37, 128.81, 128.20, 127.40, 126.17, 123.01, 37.40, 20.03. HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{16}\text{S}$: 240.0973; found: 240.0971.

^1H NMR (C_6D_6 , 400 MHz): δ 7.68 (m, 2H), 7.42 (m, 2H), 7.15-6.88 (m, 6H), 5.38 (s, 1H), 5.37 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 145.12, 139.18, 134.39, 132.22, 129.27, 128.83, 128.68, 127.51, 127.42, 115.94. HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{S}$: 212.0660; found: 212.0662. Anal. calcd for $\text{C}_{14}\text{H}_{12}\text{S}$: C, 79.20; H, 5.70; S, 15.10; found: C: 78.88; H: 5.69.

^1H NMR (C_6D_6 , 400 MHz): δ 7.60-6.80 (m, 10H), 6.69 (d, 1H, $J = 15.4$ Hz), 6.60 (d, 1H, $J = 15.5$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 136.84, 135.88, 132.18, 130.25, 130.02, 129.37, 128.84, 127.70, 126.34, 123.72. HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{12}\text{S}$: 212.0660; found: 212.0662. Anal. calcd for $\text{C}_{14}\text{H}_{12}\text{S}$: C, 79.20; H, 5.70; S, 15.10; found: C, 79.18; H, 5.74.

^1H NMR (CDCl_3 , 400 MHz): δ 7.54 (d, 2H, $J = 8.9\text{ Hz}$), 7.35 (m, 2H), 7.30-7.14 (m, 3H), 6.82 (dd, 2H, $J_1 = 6.8\text{ Hz}$, $J_2 = 2.1\text{ Hz}$), 5.59 (s, 1H), 5.24 (s, 1H), 3.77 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): δ 159.79, 143.65, 134.08, 131.62, 131.15, 128.98, 128.39, 127.09, 114.72, 113.60, 55.22. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{OS}$: 242.0765; found: 242.0771. Anal. calcd for $\text{C}_{15}\text{H}_{14}\text{OS}$: C, 74.34; H, 5.82; O, 6.60; S, 13.23; found: C, 74.15; H, 5.85.

^1H NMR (CDCl_3 , 400 MHz): δ 7.40-7.17 (m, 7H), 6.85 (d, 2H, $J = 8.8\text{ Hz}$), 6.71 (dd, 2H, $J_1 = 20.3\text{ Hz}$, $J_2 = 15.4\text{ Hz}$), 3.80 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): δ 159.36, 135.92, 132.72, 129.37, 129.24, 129.07, 127.36, 126.58, 120.05, 114.12, 55.32. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{OS}$: 242.0765; found: 242.0771. Anal. calcd for $\text{C}_{15}\text{H}_{14}\text{OS}$: C, 74.34; H, 5.82; O, 6.60; S, 13.23; found: C, 74.74; H, 6.01.

^1H NMR (CDCl_3 , 300 MHz): δ 7.55-7.15 (m, 6H), 6.82-6.72 (m, 2H), 5.60 (d, 1H, $J = 1.7$ Hz), 5.57 (s, 1H). $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 300 MHz): δ -33.16, (m, 1F), -34.08 (t, 1F, $J_1 = 9.3\text{Hz}$, $J_2 = 10.2\text{Hz}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): δ 162.50, 160.00, 137.12, 133.03, 132.14, 131.53, 129.08, 127.68, 123.05, 120.20, 111.02, 104.17. HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{F}_2\text{S}$: 248.0471; found: 248.0469. Anal. calcd for $\text{C}_{14}\text{H}_{10}\text{F}_2\text{S}$: C, 67.72; H, 4.06; F, 15.30; S, 12.91; found: C, 68.00; H, 4.36.

^1H NMR (CDCl_3 , 400 MHz): δ 7.50-7.36 (m, 3H), 7.08 (d, 1H, $J = 16.4$ Hz), 6.93-6.76 (m, 5H), 6.41 (d, 1H, $J = 16.4$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 300 MHz): δ -28.80, (m), -30.17 (m), -32.05 (m), -35.61 (m). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 400 MHz): δ 162.83, 160.43, 134.16, 133.52, 128.13, 120.56, 111.73, 109.83, 108.22, 104.36, 93.32, 84.43. HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{F}_2\text{S}$: 248.0471; found: 248.0469.

^1H NMR (C_6D_6 , 400 MHz): δ 7.80-6.70 (m, 9H), 5.47 (s, 1H), 5.23 (s, 1H), 1.91 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 133.13, 132.93, 131.55, 130.21, 132.02, 128.94, 128.57, 128.56, 127.52, 114.24, 41.37. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{S}$: 226.0816; found: 226.0815. Anal. calcd for $\text{C}_{15}\text{H}_{14}\text{S}$: C, 79.60; H, 6.23; S, 14.17; found: C, 79.74; H, 6.38.

^1H NMR (C_6D_6 , 400 MHz): δ 7.29 (m, 2H), 7.02 (m, 5H), 6.85 (d, 2H, $J = 7.9$ Hz), 6.80 (d, 1H, $J = 15.5$ Hz), 6.63 (d, 1H, $J = 15.5$ Hz), 2.00 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 131.92, 131.03, 130.88, 130.22, 128.81, 128.12, 127.89, 127.47, 126.26, 124.91, 20.89. HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{S}$: 226.0816; found: 226.0815. Anal. calcd for $\text{C}_{15}\text{H}_{14}\text{S}$: C, 79.60; H, 6.23; S, 14.17; found: C, 79.87; H, 6.35.

^1H NMR (C_6D_6 , 400 MHz): δ 7.53 (m, 2H), 7.05-6.85 (m, 7H), 5.46 (s, 1H), 5.25 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 114.20, 138.70, 133.60, 133.20, 132.36, 128.86, 128.62, 127.45, 121.53, 117.09. HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{BrS}$: 289.9765, 291.9744; found: 289.9767, 291.9749. Anal. calcd for $\text{C}_{14}\text{H}_{11}\text{BrS}$: C, 57.74; H, 3.81; Br, 27.44; S, 11.01; found: C, 58.10; H, 3.65.

^1H NMR (C_6D_6 , 400 MHz): δ 7.12-6.96 (m, 7H), 6.91-6.84 (m, 2H), 6.63, (d, 1H, J = 15.6 Hz), 6.56 (d, 1H, J = 15.6 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 400 MHz): δ 136.64, 135.12, 133.22, 132.41, 131.24, 128.87, 127.88, 126.42, 122.60, 120.95. HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{BrS}$: 289.9765, 291.9744; found: 289.9767, 291.9749. Anal. calcd for $\text{C}_{14}\text{H}_{11}\text{BrS}$: C, 57.74; H, 3.81; Br, 27.44; S, 11.01; found: C: 58.14; H: 3.70.

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