Supporting Information

Ruthenium-Catalyzed Reactions of 1-Cyclopropyl-2-propyn-1-ols with Anilines and Water via Allenylidene Intermediates: Selective Preparation of Tri- and Tetrasubstituted Conjugated Enynes

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General Method. ^1H NMR (270 MHz) and ^{13}C NMR (67.8 MHz) spectra were measured on a JEOL Excalibur 270 spectrometer using CDCl_3 as solvent. 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. IR spectra were recorded on a JASCO FT/IR 4100 Fourier transform infrared spectrophotometer. Elemental analyses were performed at Microanalytical Center of The University of Tokyo. GC-MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvent were dried by the usual methods and distilled before use.

Thiolate-bridged diruthenium complexes (**2**) were prepared according to our previous procedure.^{S1,S2} 1-Cyclopropyl-2-phenyl-2-propyn-1-ol (**1a**) was a known compound.^{S3} Other propargylic alcohols were prepared by the reactions of the corresponding ketones with ethynylmagnesium bromide.

Preparation of Propargylic Alcohols. A typical experimental procedure for the preparation of **1b** from the corresponding ketones is described below. To a solution of ethynylmagnesium bromide (0.5 M THF solution; 16 mL, 32 mmol) at 0 °C was added dropwise a solution of cyclopropyl 4-methylphenyl ketone (2.40 g, 15 mmol) in diethyl ether (50 mL). The resulting mixture was stirred at room temperature for 6 h. The mixture was treated with saturated NH₄Cl aq. (50 mL). The organic layer was extracted with diethyl ether (10 mL x 3) and the combined organic layer was dried over anhydrous MgSO₄ and concentrated in vacuo. The crude material was purified by column chromatography (SiO₂, eluent: hexane/diethyl ether 5/1) to give **1b** (1.80 g, 9.6 mmol, 64% yield) as a colorless oil.

1b. ¹H NMR δ 0.54-0.78 (m, 4 H), 1.36 (m, 1H), 2.35 (s, 3H), 2.43 (s, 1H), 2.57 (s, 1H), 7.18 (d, 2H, *J* = 8.0 Hz), 7.56 (d, 2H, *J* = 8.0 Hz). ¹³C NMR δ 2.2, 3.1, 21.0, 23.3, 73.9, 74.1, 84.0, 125.2, 128.9, 137.5, 141.3. HRMS Calcd for C₁₃H₁₄O [M]: 186.1045. Found: 186.1041.

Spectroscopic data and isolated yield of other propargylic alcohols (**1**) are as follows.

1c. A colorless oil. 64% isolated yield. ¹H NMR δ 0.55-0.76 (m, 4 H), 1.39 (m, 1H), 2.40 (s, 1H), 2.58 (s, 1H), 3.82 (s, 3H), 6.90 (d, 2H, *J* = 8.5 Hz), 7.60 (d, 2H, *J* = 8.5 Hz). ¹³C NMR δ 2.2, 2.9, 23.2, 55.2, 73.8, 84.0, 113.4, 126.6, 136.4, 159.0. HRMS Calcd for C₁₃H₁₄O₂ [M]: 202.0994. Found: 202.1008.

1d. A pale yellow oil. 83% isolated yield. ^1H NMR δ 0.56-0.79 (m, 4 H), 1.36 (m, 1H), 2.45 (s, 1H), 2.59 (s, 1H), 7.02 (dd, 2H, J = 8.1 and 8.0 Hz), 7.58 (dd, 2H, J = 8.0 and 2.4 Hz). ^{13}C NMR δ 2.2, 3.2, 23.5, 73.8, 74.3, 83.6, 114.9 (d, J = 23 Hz), 127.1 (d, J = 8 Hz), 140.0, 162.3 (d, J = 245 Hz). HRMS Calcd for $\text{C}_{12}\text{H}_{11}\text{O}$ [M]: 190.0794. Found: 190.0787.

1e. A colorless oil. 77% isolated yield. ^1H NMR δ 0.56-0.81 (m, 4 H), 1.32 (m, 1H), 2.49 (s, 1H), 2.59 (s, 1H), 7.33 (d, 2H, J = 8.1 Hz), 7.60 (d, 2H, J = 8.1 Hz). ^{13}C NMR δ 2.2, 3.2, 23.5, 73.8, 74.4, 83.3, 126.8, 128.3, 133.6, 142.8. HRMS Calcd for $\text{C}_{12}\text{H}_{11}\text{ClO}$ [M]: 206.0498. Found: 206.0481.

1f. A pale yellow oil. 70% isolated yield. ^1H NMR δ 0.61-0.86 (m, 4 H), 1.52 (m, 1H), 2.61 (brs, 2H), 6.97 (m, 1H), 7.25 (m, 2H). ^{13}C NMR δ 2.6, 3.1, 23.4, 71.7, 73.7, 83.2, 124.2, 125.1, 126.4, 148.9. HRMS Calcd for $\text{C}_{10}\text{H}_{10}\text{OS}$ [M]: 178.0452. Found: 178.0419.

1g. A colorless oil. 54% isolated yield. ^1H NMR δ 0.38 (m, 2 H), 0.93 (brs, 3H), 1.06 (brs, 2H), 2.28 (s, 1H), 2.55 (s, 1H), 7.24-7.34 (m, 3H), 7.62-7.64 (m, 2H). ^{13}C NMR δ 10.3, 11.5, 19.8, 24.8, 73.2, 75.5, 85.6, 126.0, 127.6, 127.9, 142.8. HRMS Calcd for $\text{C}_{13}\text{H}_{14}\text{O}$ [M]: 186.1045. Found: 186.1055.

1h. A white solid, 83.0-84.5 °C. 55% isolated yield. ^1H NMR δ 0.84 (brs, 2 H), 1.38-1.58 (m, 2H), 2.50 (s, 1H), 2.64 (s, 1H), 7.05-7.35 (m, 10H). ^{13}C NMR δ 9.8, 10.8, 35.8, 74.1, 75.8, 85.4, 126.3, 126.8, 127.1, 127.4, 127.6, 132.4, 140.7, 142.4. HRMS Calcd for $\text{C}_{18}\text{H}_{16}\text{O}$ [M]: 248.1201. Found: 248.1189.

Ruthenium-Catalyzed Reactions of 1-Cyclopropyl-2-propyn-1-ols (1**) with Nucleophiles in the Presence of a Catalytic Amount of Cationic Thiolate-bridged Diruthenium Complex (**2a**).** A typical experimental procedure for the reaction of **1a** with aniline catalyzed by **2a** is described below. In a 20 mL flask was placed **2a** (5.7 mg, 0.0075 mmol) under N₂. Anhydrous and degassed 1,2-dichloroethane (ClCH₂CH₂Cl) (2.5 mL) was added, and then the mixture was magnetically stirred at room temperature. After addition of aniline (233 mg, 2.5 mmol) and **1a** (43 mg, 0.25 mmol), the flask was kept at 60 °C for 1 h. The reaction mixture was concentrated under reduced pressure, and then the residue was purified by column chromatography (SiO₂, eluent: hexane/diethyl ether 19/1) to give **3a** (55 mg, 0.22 mmol, 89% yield) as an orange oil.

¹H NMR δ 2.86 (dt, 2H, *J* = 7.0 and 6.8 Hz), 3.34 (t, 2H, *J* = 6.8 Hz), 3.37 (s, 1H), 3.75 (brs, 1H), 6.54 (t, 1H, *J* = 7.0 Hz), 6.65 (m, 2H), 6.72 (t, 1H, *J* = 7.6 Hz), 7.19 (t, 2H, *J* = 7.6 Hz), 7.26–7.35 (m, 3H), 7.61 (d, 2H, *J* = 7.1 Hz). ¹³C NMR δ 31.3, 43.1, 80.6, 83.7, 112.8, 117.4, 124.7, 125.9, 127.9, 128.4, 129.2, 136.4, 137.2, 148.1. IR (neat, cm⁻¹) 2096 (C≡C), 3286 (≡C–H), 3410 (*N*-H). Anal Calcd for C₁₈H₁₇N: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.39; H, 7.15; N, 5.56.

When the reaction of **1a** with aniline-*d*₇ was carried out under the same reaction conditions, the corresponding product (**3a'**) was obtained in 93% yield as a brown oil. ¹H NMR δ 2.85 (dt, 2H, *J* = 7.0 and 6.8 Hz), 3.33 (t, 2H, *J* = 6.8 Hz), 3.36 (s, 0.18H), 3.74 (brs, 1H), 6.53 (t, 1H, *J* = 7.0 Hz), 7.25–7.35 (m, 3H), 7.61 (d, 2H, *J* = 7.1 Hz). IR (neat, cm⁻¹) 2096 (C≡C), 2576 (≡C–D), 3410 (*N*-H). This result indicates that 82% deuterium content at the terminal alkyne moiety of **3a'**.

For comparison, reactions of **1a** with aniline in the presence of other thiolate-bridged diruthenium complexes were carried out. Typical results are shown in Table S1. The reaction in the presence of **2a** (3 mol%) proceeded smoothly even at room temperature, **3a** being obtained in 77% yield (Table S1, run 2). Unfortunately, only the use of the **2a** (1 mol%) dramatically decreased the yield of **3a** (Table S1, run 3). The reaction also proceeded smoothly when neutral diruthenium complex such as **2b** was used as a catalyst together with NH_4BF_4 (Table S1, runs 4 and 5). The diruthenium complex with the sterically demanding group exhibited a slightly lower catalytic activity (Table S1, run 6). Lower yields of **3a** were obtained in the presence of dicationic and cationic diruthenium complexes such as **2d** and **2e** (Table S1, runs 7 and 8).

Table S1. Ruthenium-Catalyzed 1a with Aniline in the Presence of Thiolate-bridged Diruthenium Complexes (2).^a

run	catalyst (mol%)	time (h)	yield of 3a ^b (%)
1	$[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{Ru}(\text{OH}_2)\text{Cp}^*]\text{OTf}$ (2a) (3)	1	89
2	$[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{Ru}(\text{OH}_2)\text{Cp}^*]\text{OTf}$ (2a) (3) ^c	2	77
3	$[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{Ru}(\text{OH}_2)\text{Cp}^*]\text{OTf}$ (2a) (1)	18	46
4	$[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2]$ (2b) (5)	24	trace
5	$[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2]$ (2b) (5) ^d	1	32
6	$[\text{Cp}^*\text{RuCl}(\mu_2\text{-S}^i\text{Pr})_2\text{Ru}(\text{OH}_2)\text{Cp}^*]\text{OTf}$ (2c) (3)	1	76
7	$[\text{Cp}^*\text{Ru}(\mu_2\text{-SMe})_2\text{Ru}(\text{OH}_2)\text{Cp}^*](\text{OTf})_2$ (2d) (5)	48	66
8	$[\text{Cp}^*\text{RuCl}(\mu_2\text{-SMe})_2\text{Ru}(\text{OH}_2)\text{Cp}^*]\text{NTf}_2$ (2e) (5)	1	79

^a All the reactions of **1a** (0.25 mmol) with aniline (2.50 mmol) were carried out in the presence of catalyst in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (2.5 mL) at 60 °C. ^b Isolated yield. ^c At room temperature. ^d In the presence of NH_4BF_4 (10 mol%).

Spectroscopic data and isolated yield of other products (**3**) are as follows.

3b. A brown oil. 83% isolated yield. ^1H NMR δ 2.36 (s, 3H), 2.84 (dt, 2H, $J = 7.3$ and 6.8 Hz), 3.33 (t, 2H, $J = 6.8$ Hz), 3.35 (s, 1H), 3.75 (brs, 1H), 6.49 (t, 1H, $J = 7.3$ Hz), 6.65 (d, 2H, $J = 7.6$ Hz), 6.71 (t, 1H, $J = 7.6$ Hz), 7.14-7.23 (m, 4H), 7.50 (d, 2H, $J = 8.0$ Hz). ^{13}C NMR δ 21.1, 31.3, 43.2, 80.8, 83.5, 112.8, 117.4, 124.6, 125.8, 129.1, 129.2, 134.5, 135.4, 137.7, 148.2. Anal Calcd for $\text{C}_{19}\text{H}_{19}\text{N}$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.05; H, 7.33; N, 5.25.

3c. A brown solid, 67.8-69.4 °C. 65% isolated yield. ^1H NMR δ 2.23 (s, 3H), 2.82 (dt, 2H, $J = 7.3$ and 6.8 Hz), 3.29 (t, 2H, $J = 6.8$ Hz), 3.34 (s, 1H), 3.75 (brs, 1H), 6.52 (t, 1H, $J = 7.3$ Hz), 6.56 (d, 2H, $J = 8.2$ Hz), 6.98 (d, 2H, $J = 8.2$ Hz), 7.26-7.36 (m, 3H), 7.58 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR δ 20.4, 31.4, 43.5, 80.7, 83.6, 113.0, 124.6, 125.9, 126.6, 127.8, 128.4, 129.7, 136.6, 137.3, 145.9. Anal Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.09; H, 7.11; N, 4.83.

3d. A brown oil. 80% isolated yield. ^1H NMR δ 2.82 (dt, 2H, $J = 7.3$ and 7.0 Hz), 3.31 (t, 2H, $J = 7.3$ Hz), 3.35 (s, 1H), 3.71 (brs, 1H), 6.45 (t, 1H, $J = 7.0$ Hz), 6.63 (d, 2H, $J = 7.6$ Hz), 6.70 (t, 1H, $J = 7.3$ Hz), 7.01 (dd, 2H, $J = 8.8$ and 8.8 Hz), 7.20 (dd, 2H, $J = 7.6$ and 7.3 Hz), 7.55

(dd, 2H, $J = 8.8$ and 5.1 Hz). ^{13}C NMR δ 31.4, 41.1, 80.5, 83.8, 112.8, 115.2 (d, $J = 22$ Hz), 117.5, 123.7, 127.6 (d, $J = 8$ Hz), 129.2, 133.4 (d, $J = 4$ Hz), 136.2 (d, $J = 2$ Hz), 148.1, 162.5 (d, $J = 247$ Hz). Anal Calcd for $\text{C}_{18}\text{H}_{16}\text{NF}$: C, 81.48; H, 6.08; N, 5.28. Found: C, 81.64; H, 6.32; N, 5.14.

3e. A pale yellow solid, 47.0-48.0 °C. 83% isolated yield. ^1H NMR δ 2.84 (dt, 2H, $J = 7.0$ and 6.8 Hz), 3.33 (t, 2H, $J = 6.8$ Hz), 3.37 (s, 1H), 3.73 (brs, 1H), 6.52 (t, 1H, $J = 7.0$ Hz), 6.65 (d, 2H, $J = 8.6$ Hz), 6.72 (t, 1H, $J = 7.3$ Hz), 7.19 (dt, 2H, $J = 8.6$ and 7.3 Hz), 7.31 (d, 2H, $J = 8.6$ Hz), 7.53 (d, 2H, $J = 8.6$ Hz). ^{13}C NMR δ 31.4, 43.0, 80.2, 84.0, 112.8, 117.5, 123.7, 127.2, 128.5, 129.2, 133.7, 135.7, 136.9, 148.1. Anal Calcd for $\text{C}_{18}\text{H}_{16}\text{NCl}$: C, 76.72; H, 5.72; N, 4.97. Found: C, 76.74; H, 5.97; N, 4.81.

3f. A pale brown solid, 48.0-50.0 °C. 45% isolated yield. ^1H NMR δ 2.81 (dt, 2H, $J = 7.3$ and 6.8 Hz), 3.32 (t, 2H, $J = 6.8$ Hz), 3.32 (s, 1H), 6.42 (t, 1H, $J = 7.3$ Hz), 6.72 (d, 2H, $J = 7.6$ Hz), 6.76 (t, 1H, $J = 7.3$ Hz), 6.98 (t, 1H, $J = 3.8$ Hz), 7.18-7.26 (m, 4H). ^{13}C NMR δ 30.8, 43.4, 79.4, 82.9, 113.3, 118.0, 119.1, 124.5, 125.1, 127.3, 129.3, 134.4, 142.1, 147.4. Anal Calcd for $\text{C}_{16}\text{H}_{15}\text{NS}$: C, 75.85; H, 5.97; N, 5.53. Found: C, 75.64; H, 6.22; N, 5.30.

3g. A brown solid, 55.0-56.5 °C. 75% isolated yield. ^1H NMR δ 2.83 (dt, 2H, J = 6.8 and 7.4 Hz), 3.24 (t, 2H, J = 6.8 Hz), 3.27 (s, 1H), 3.82 (s, 3H), 6.34 (t, 2H, J = 7.4 Hz), 6.56 (d, 1H, J = 7.3 Hz), 6.63 (t, 1H, J = 7.3 Hz), 6.80 (d, 2H, J = 8.9 Hz), 7.10 (dt, 2H, J = 7.6 and 7.3 Hz), 7.46 (d, 2H, J = 8.9 Hz). ^{13}C NMR δ 31.3, 43.2, 55.3, 80.9, 83.4, 112.8, 113.8, 117.3, 124.1, 127.1, 129.2, 129.9, 134.4, 148.2, 159.4. Anal Calcd for $\text{C}_{19}\text{H}_{19}\text{N}$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.07; H, 7.61; N, 5.11.

3h. A reddish brown oil. 75% isolated yield. ^1H NMR δ 2.24 (s, 6H), 2.83 (dt, 2H, J = 7.0 and 7.4 Hz), 3.31 (t, 2H, J = 7.0 Hz), 3.37 (s, 1H), 6.29 (s, 2H), 6.38 (s, 1H), 6.54 (t, 1H, J = 7.4 Hz), 7.24-7.38 (m, 3H), 7.60 (d, 2H, J = 7.3 Hz). ^{13}C NMR δ 21.5, 31.4, 43.2, 80.6, 83.6, 110.8, 119.4, 124.6, 125.9, 127.8, 128.4, 136.6, 137.2, 138.8, 148.2. Anal Calcd for $\text{C}_{20}\text{H}_{21}\text{N}$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.00; H, 7.80; N, 4.84.

3i. A brown oil. 80% isolated yield. ^1H NMR δ 2.84 (dt, 2H, J = 7.2 and 6.8 Hz), 3.29 (t, 2H, J = 6.8 Hz), 3.35 (s, 1H), 6.52 (t, 2H, J = 7.2 Hz), 6.62-6.63 (m, 2H), 6.90 (t, 2H, J = 8.5 Hz), 7.28-7.37 (m 3H), 7.60 (d, 2H, J = 7.0 Hz). ^{13}C NMR δ 31.2, 43.9, 80.6, 83.7, 113.8 (d, J = 7 Hz), 115.6 (d, J = 22 Hz), 124.9, 125.9, 127.9, 128.4, 136.2, 137.2, 144.3, 155.9 (d, J = 235 Hz). Anal Calcd for $\text{C}_{18}\text{H}_{16}\text{NF}$: C, 81.48; H, 6.08; N, 5.28. Found: C, 81.70; H, 6.31; N, 5.11.

3j. A pale yellow solid, 44.9-45.5 °C. 78% isolated yield. ^1H NMR δ 2.84 (dt, 2H, J = 7.0 and 6.8 Hz), 3.33 (t, 2H, J = 6.8 Hz), 3.37 (s, 1H), 3.73 (brs, 1H), 6.52 (t, 1H, J = 7.0 Hz), 6.56 (d, 2H, J = 9.0 Hz), 7.13 (d, 2H, J = 9.0 Hz), 7.29-7.40 (m, 3H), 7.61 (d, 2H, J = 6.8 Hz). ^{13}C NMR δ 31.1, 43.2, 80.6, 83.7, 113.8, 121.9, 124.9, 125.9, 127.9, 128.4, 129.0, 136.0, 137.1, 146.7. Anal Calcd for $\text{C}_{18}\text{H}_{16}\text{NCl}$: C, 76.72; H, 5.72; N, 4.97. Found: C, 76.63; H, 5.98; N, 4.82.

3k. A reddish brown oil. 78% isolated yield. ^1H NMR δ 2.84 (dt, 2H, J = 7.6 and 6.8 Hz), 3.35 (t, 2H, J = 6.8 Hz), 3.35 (s, 1H), 3.83 (s, 3H), 6.49 (t, 2H, J = 7.6 Hz), 6.56 (d, 2H, J = 8.9 Hz), 7.27-7.36 (m, 3H), 7.58 (d, 2H, J = 6.8 Hz), 7.85 (d, 2H, J = 8.9 Hz). ^{13}C NMR δ 31.0, 42.5, 51.5, 80.5, 83.9, 111.5, 118.3, 125.2, 125.9, 128.0, 128.4, 131.5, 135.6, 137.0, 151.8, 167.3. Anal Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.39; H, 6.36; N, 4.47.

3l. A reddish brown oil. 71% isolated yield. ^1H NMR δ 2.88 (dt, 2H, J = 7.0 and 6.8 Hz), 3.35 (s, 1H), 3.40 (t, 2H, J = 6.8 Hz), 3.84 (s, 3H), 6.53 (t, 1H, J = 7.0 Hz), 6.60 (t, 1H, J = 7.1 Hz), 6.77 (d, 1H, J = 8.0 Hz), 7.27-7.36 (m, 4H), 7.60 (d, 2H, J = 7.2 Hz), 7.91 (d, 1H, J = 7.9 Hz). ^{13}C NMR δ 31.1, 42.2, 51.4, 80.5, 83.7, 110.2, 111.4, 114.8, 124.8, 126.0, 127.8, 128.3, 131.7, 134.5, 135.9, 137.4, 150.8, 169.0. Anal Calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.38; H, 6.23; N, 4.48.

3m. A brown oil. 82% isolated yield. ^1H NMR δ 2.84 (dt, 2H, $J = 6.8$ and 7.6 Hz), 3.35 (t, 2H, $J = 6.8$ Hz), 3.35 (s, 1H), 6.49 (t, 1H, $J = 7.6$ Hz), 6.61 (d, 2H, $J = 8.1$ Hz), 7.24-7.40 (m, 5H), 7.58 (d, 2H, $J = 6.8$ Hz). ^{13}C NMR δ 31.0, 42.7, 80.5, 83.8, 111.9, 118.8 (q, $J = 33$ Hz), 125.2, 125.0 (q, $J = 270$ Hz), 125.9, 126.6 (q, $J = 4$ Hz), 128.0, 128.4, 135.7, 137.1, 150.5. HRMS Calcd for $\text{C}_{19}\text{H}_{16}\text{NF}_3$ [M]: 315.1235. Found: 315.1226.

3n. A yellow oil. 82% isolated yield. ^1H NMR δ 2.80 (dt, 2H, $J = 7.6$ and 7.3 Hz), 2.99 (s, 3H), 3.35 (s, 1H), 3.53 (d, 2H, $J = 7.3$ Hz), 6.50 (t, 1H, $J = 7.6$ Hz), 6.72 (t, 1H, $J = 7.4$ Hz), 6.80 (d, 2H, $J = 8.6$ Hz), 7.23-7.55 (m, 5H), 7.57 (d, 2H, $J = 8.1$ Hz). ^{13}C NMR δ 28.8, 38.2, 51.7, 80.6, 83.4, 112.4, 116.3, 124.3, 125.9, 127.7, 128.4, 129.2, 136.4, 137.5, 149.0. Anal Calcd for $\text{C}_{19}\text{H}_{19}\text{N}$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.27; H, 7.58; N, 5.14.

3o. A pale yellow solid, 84.4-86.2 °C. 52% isolated yield. ^1H NMR δ 2.90 (dt, 2H, $J = 7.6$ and 7.5 Hz), 3.31 (s, 1H), 3.90 (t, 2H, $J = 7.5$ Hz), 6.48 (t, 1H, $J = 7.6$ Hz), 6.96 (t, 2H, $J = 7.3$ Hz), 7.07 (d, 4H, $J = 7.8$ Hz), 7.25-7.36 (m, 7H), 7.54 (d, 2H, $J = 8.1$ Hz). ^{13}C NMR δ 29.6, 51.1, 80.6, 83.5, 121.0, 121.3, 124.4, 125.9, 127.7, 128.3, 129.3, 136.2, 137.4, 147.7. Anal Calcd for $\text{C}_{24}\text{H}_{21}\text{N}$: C, 89.12; H, 6.54; N, 4.33. Found: C, 88.91; H, 6.81; N, 4.20.

3p. A dark brown oil. 87% isolated yield. ^1H NMR δ 1.81 (s, 1H), 2.79 (dt, 2H, J = 7.0 and 6.5 Hz), 3.36 (s, 1H), 3.80 (t, 2H, J = 6.5 Hz), 6.54 (t, 1H, J = 7.0 Hz), 7.25-7.36 (m, 3H), 7.61 (d, 2H, J = 6.8 Hz). ^{13}C NMR δ 34.6, 61.8, 80.6, 83.5, 124.8, 125.9, 127.8, 128.3, 135.6, 137.3. Anal Calcd for $\text{C}_{12}\text{H}_{12}\text{O}$: C, 83.69; H, 7.02. Found: C, 83.49; H, 7.22.

3q. A pale yellow solid, 45.4-46.9 °C. 77% isolated yield. ^1H NMR δ 2.35 (s, 3H), 2.79 (dt, 2H, J = 7.3 and 6.5 Hz), 3.34 (s, 1H), 3.82 (t, 2H, J = 6.5 Hz), 6.50 (t, 1H, J = 7.3 Hz), 7.15 (d, 2H, J = 8.3 Hz), 7.50 (d, 2H, J = 8.3 Hz). ^{13}C NMR δ 21.1, 34.7, 62.0, 80.8, 83.3, 124.8, 125.8, 129.1, 134.5, 134.6, 137.7. Anal Calcd for $\text{C}_{13}\text{H}_{14}\text{O}$: C, 83.83; H, 7.58. Found: C, 83.70; H, 7.74.

3r. A pale yellow solid, 42.8-44.0 °C. 70% isolated yield. ^1H NMR δ 2.79 (dt, 2H, J = 6.8 and 6.5 Hz), 3.36 (s, 1H), 3.83 (t, 2H, J = 6.5 Hz), 6.48 (t, 1H, J = 6.8 Hz), 7.02 (dd, 2H, J = 8.4 and 8.0 Hz), 7.58 (dd, 2H, J = 8.0 and 5.7 Hz). ^{13}C NMR δ 34.6, 61.9, 80.5, 83.7, 115.2 (d, J = 21 Hz), 123.9, 127.6 (d, J = 8 Hz), 133.5, 135.3, 162.5 (d, J = 247 Hz). Anal Calcd for $\text{C}_{12}\text{H}_{11}\text{FO}$: C, 75.77; H, 5.83. Found: C, 75.93; H, 6.11.

3s. A yellow oil. 85% isolated yield. ^1H NMR δ 1.77 (s, 3H), 2.80 (t, 2H, $J = 7.0$ Hz), 3.13 (s, 1H), 3.32 (t, 2H, $J = 7.0$ Hz), 3.78 (brs, 1H), 6.60 (d, 2H, $J = 7.8$ Hz), 6.64 (t, 1H, $J = 7.3$ Hz), 7.10-7.31 (m, 7H). ^{13}C NMR δ 19.5, 37.3, 42.1, 80.7, 84.0, 112.7, 120.3, 127.1, 128.2, 129.0, 129.2, 138.6, 145.5, 148.3. Anal Calcd for $\text{C}_{19}\text{H}_{19}\text{N}$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.13; H, 7.55; N, 5.30.

3t. A brown oil. 84% isolated yield ($E/Z = 98/2$). *E*-isomer: ^1H NMR δ 1.83 (s, 3H), 2.25 (s, 3H), 2.85 (t, 2H, $J = 7.0$ Hz), 3.19 (s, 1H), 3.36 (t, 2H, $J = 7.0$ Hz), 3.70 (brs, 1H), 6.60 (d, 2H, $J = 8.3$ Hz), 6.99 (d, 2H, $J = 8.3$ Hz), 7.02-7.37 (m, 5H); *Z*-isomer: ^1H NMR δ 6.37 (d, 2H, $J = 8.3$ Hz), 6.92 (d, 2H, $J = 8.3$ Hz). *E*-isomer: ^{13}C NMR δ 19.5, 20.4, 37.4, 42.5, 80.7, 84.0, 112.9, 120.2, 126.4, 127.1, 128.2, 129.0, 129.7, 138.6, 145.7, 146.0. Anal Calcd for $\text{C}_{20}\text{H}_{21}\text{N}$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.01; H, 7.83; N, 4.91.

3u. A brown oil. 83% isolated yield ($E/Z = 98/2$). *E*-isomer: ^1H NMR δ 1.83 (s, 3H), 2.85 (t, 2H, $J = 7.0$ Hz), 3.18 (s, 1H), 3.34 (t, 2H, $J = 7.0$ Hz), 3.73 (brs, 1H), 6.58 (dd, 2H, $J = 8.9$ and 4.3 Hz), 6.90 (dd, 2H, $J = 8.9$ and 8.7 Hz), 7.25-7.38 (m, 5H); *Z*-isomer: ^1H NMR δ 6.30 (dd, 2H, $J = 8.9$ and 4.3 Hz). *E*-isomer: ^{13}C NMR δ 19.5, 37.3, 42.7, 80.7, 84.0, 113.5 (d, $J = 7$ Hz), 115.6 (d, $J = 22$ Hz), 120.4, 127.2, 128.2, 129.0, 138.5, 144.6 (d, $J = 2$ Hz), 145.4, 155.7 (d, $J = 234$ Hz). Anal Calcd for $\text{C}_{19}\text{H}_{18}\text{FN}$: C, 81.69; H, 6.49; N, 5.01. Found: C, 81.74; H, 6.67; N, 4.83.

3v. A brown oil. 82% isolated yield (*E/Z* = 98/2). *E*-isomer: ^1H NMR δ 1.83 (s, 3H), 2.85 (t, 2H, *J* = 7.0 Hz), 3.19 (s, 1H), 3.35 (t, 2H, *J* = 7.0 Hz), 3.88 (brs, 1H), 6.58 (d, 2H, *J* = 6.5 Hz), 7.13 (d, 2H, *J* = 6.5 Hz), 7.27-7.38 (m, 5H); *Z*-isomer: ^1H NMR δ 6.32 (d, 2H, *J* = 6.5 Hz), 7.03 (d, 2H, *J* = 6.5 Hz). *E*-isomer: ^{13}C NMR δ 19.5, 37.1, 42.2, 80.8, 83.9, 113.7, 120.4, 121.7, 127.2, 128.2, 128.95, 128.98, 138.5, 145.2, 146.8. Anal Calcd for $\text{C}_{19}\text{H}_{18}\text{ClN}$: C, 77.15; H, 6.13; N, 4.74. Found: C, 77.21; H, 6.36; N, 4.61.

3w. A white solid, 90.1-91.1 °C. 80% isolated yield. ^1H NMR δ 3.22 (s, 4H), 3.33 (s, 1H), 3.77 (brs, 1H), 6.54 (d, 2H, *J* = 8.1 Hz), 6.66 (t, 1H, *J* = 7.3 Hz), 7.02-7.16 (m, 12H). ^{13}C NMR δ 37.8, 42.1, 82.2, 84.1, 112.7, 117.1, 121.4, 126.9, 127.3, 127.7, 128.2, 129.0, 129.1, 129.6, 138.0, 139.8, 148.1, 148.7. Anal Calcd for $\text{C}_{24}\text{H}_{21}\text{N}$: C, 89.12; H, 6.54; N, 4.33. Found: C, 89.15; H, 6.54; N, 4.33.

As described in the manuscript, the reactions of **1a** with other nucleophiles (vide infra) under the same reaction conditions did not gave the corresponding enynes (**3**).

NuH: PhCH₂NH₂ *n*BuNH₂ MeCONH₂ PhSO₂NH₂

EtOH PhOH *n*BuSH

Interestingly, the reaction of **1a** with diphenylphosphine oxide under the same reaction conditions gave only the corresponding propargylic phosphine oxide (**5a**) in 79% isolated yield. The molecular structure of **5a** was confirmed by X-ray analysis. This result indicates that the phosphorus-carbon bond formation reaction occurred only at the propargylic position, in sharp contrast to the nitrogen-carbon bond formation reaction (*vide supra*).

5a. A white solid, 85.3-85.7 °C. 79% isolated yield. ¹H NMR δ 0.26-0.44 (m, 4H), 2.03-2.15 (m, 1H), 2.60 (d, 1H, *J* = 5.7 Hz), 7.17-7.27 (m, 5H), 7.32-7.51 (m, 4H), 7.65-7.78 (m, 4H), 80.8-8.16 (m, 2H). ³¹P NMR δ 32.4 (s). Anal Calcd for C₂₄H₂₁OP: C, 80.88; H, 5.94. Found: C, 80.64; H, 6.19.

Preparation of 4a. In a 100 mL flask were placed **2a** (510 mg, 0.195 mmol) and anhydrous MgSO₄ (50 mg) under N₂. Anhydrous THF (50 mL) was added, and then the mixture was magnetically stirred at room temperature. After addition of **1a** (219 mg, 0.290 mmol), the reaction flask was kept at room temperature for 20 min. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from CH₂Cl₂-diether ether to give black crystals of **4a** (161 mg, 0.177 mmol, 91%). ¹H NMR δ 1.36-1.42 (m, 2H), 1.54-1.58 (m, 2H), 1.61 (s, 15H), 1.78 (s, 15H), 2.66 (s, 6H), 2.88-2.93 (m, 1H), 7.38 (t, 2H, *J* = 7.6 Hz), 7.60 (t, 1H, *J* = 7.6 Hz), 7.82 (d, 2H, *J* = 7.6 Hz). IR (KBr, cm⁻¹) 1956 (C=C=C). Anal Calcd for C₃₅H₄₆ClF₃O₃Ru₂S₃: C, 46.42; H, 5.12. Found: C, 46.37; H, 5.25.

The mechanistic study on the relative reactivity in the reactions of propargylic alcohols

(1) with anilines in the presence of 2a. The relative reactivity of substituted anilines ($X\text{-C}_6\text{H}_4\text{NH}_2$, $X = p\text{-Me, H, } p\text{-Cl}$) for the reactions with propargylic alcohol (**1a**) in the presence of **2a** was determined (Scheme S1). The relative rates were determined by the conversion of **1a** when conversions were low (<10%). The rate data correlate well with the Hammett linear free energy relationship with use of σ vales. Better correlation ($\rho = +1.67$) was obtained with a σ^+ . Thus, the reaction with *p*-chloroaniline, whose conjugated acid has a high acidity, proceeded more smoothly because the proton transfer should take place rapidly in the second step of Scheme 2.

Scheme S1

X-ray crystallography. Crystallographic data are summarized in Table S2. The crystals were immersed in immersion oil (Sigma-Aldrich, Cat. Code: I0890) on a nylon loop and mounted on a Rigaku RAXIS RAPID imaging plate system. Data were collected at -100°C under a cold nitrogen stream using graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Empirical absorption corrections were applied. Structures were solved by Patterson method^{S4} for **4a** or the direct methods^{S5} for the others **3c**, and **5a**·0.5H₂O, and refined on F^2 by full-matrix least-squares using Crystal Structure software package.^{S6} The asymmetric unit of **5a**·0.5H₂O contained two independent molecules of **5a** and one water solvate. Anisotropic thermal parameters were introduced for all non-hydrogen atoms except for the water oxygen atom O(3) in **5a**·0.5H₂O which was isotropically refined. Hydrogen atoms of **4a** were generated at calculated positions ($d_{C-H} = 0.97$ Å) and were treated as riding atoms with isotropic thermal factors. Hydrogen atoms of water molecule in **5a**·0.5H₂O were not located. All other hydrogen atoms were located by difference-Fourier map and refined isotropically. The selected bond lengths and angles are given in Tables S3-S5. Crystallographic data are also given in CIF files.

Table S2. Summary of Crystallographic Data.

	4a	3c	5a·0.5H₂O
formula	C ₃₅ H ₄₆ ClF ₃ O ₃ Ru ₂ S ₃	C ₁₉ H ₁₉ NO	C ₂₄ H ₂₂ O _{1.5} P
Mw	905.51	277.37	365.41
crystal size, mm	0.40x 0.20x 0.05	0.50x 0.40x 0.20	0.50 x 0.50 x 0.30
crystal color, habit	black plate	colorless plate	colorless prism
crystal system	<i>monoclinic</i>	<i>monoclinic</i>	<i>triclinic</i>
space group	<i>P2₁/n</i> (#14)	<i>P2₁/n</i> (#14)	<i>P1</i> - (#2)
<i>a</i> /Å	13.1648(4)	11.4362(7)	10.2129(10)
<i>b</i> /Å	17.9501(7)	8.1087(5)	12.7886(12)
<i>c</i> /Å	16.4012(7)	17.7590(19)	16.5713(14)
α /deg	90	90	100.309(6)
β /deg	106.7197(19)	108.488(2)	100.6786(1)
γ /deg	90	90	105.315(2)
<i>V</i> /Å ³	3711.9(2)	1561.8(2)	1991.2(3)
<i>Z</i>	4	4	4
<i>d</i> _{calcd} /g cm ⁻³	1.620	1.179	1.219
μ (Mo-K α)/mm ⁻¹	1.103	0.0723	0.150
reflections collected	33343	12556	16806
unique reflections	8475 (<i>R</i> _{int} = 0.078)	3547 (<i>R</i> _{int} = 0.078)	8833 (<i>R</i> _{int} = 0.050)
refined parameters	470	266	641
GOF on <i>F</i> ²	0.96	1.02	1.01
<i>R</i> 1 ^a (<i>F</i> ² > 2 σ)	0.041	0.057	0.065
<i>wR</i> 2 ^b (all data)	0.076	0.119	0.174

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, \quad ^b wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

Table S3. Selected Interatomic Distances (Å) and Bond Angles (deg) for **4a**.

Distances			
Ru(1)-Ru(2)	2.7691(4)	Ru(1)-S(1)	2.2974(10)
Ru(1)-S(2)	2.3067(10)	Ru(2)-S(1)	2.3023(11)
Ru(2)-S(2)	2.3079(10)	Ru(2)-Cl(1)	2.4079(11)
Ru(1)-C(1)	1.920(4)	C(1)-C(2)	1.242(6)
C(2)-C(3)	1.377(6)	C(3)-C(4)	1.460(4)
C(4)-C(5)	1.492(5)	C(5)-C(6)	1.462(6)
C(6)-C(4)	1.511(6)		
Angles			
S(1)-Ru(1)-S(2)	106.14(4)	S(1)-Ru(1)-C(1)	93.66(11)
S(2)-Ru(1)-C(1)	92.30(12)	S(1)-Ru(2)-S(2)	106.14(4)
Cl(1)-Ru(2)-S(1)	91.45(3)	Cl(1)-Ru(2)-S(2)	90.79(3)
Ru(1)-C(1)-C(2)	170.3(3)	C(1)-C(2)-C(3)	176.2(4)
C(2)-C(3)-C(4)	119.6(3)	C(2)-C(3)-C(7)	120.3(3)
C(4)-C(3)-C(7)	120.0(3)	C(3)-C(4)-C(5)	120.7(3)
C(3)-C(4)-C(6)	116.2(3)	C(5)-C(4)-C(6)	58.3(3)
C(4)-C(5)-C(6)	61.5(3)	C(4)-C(6)-C(5)	60.2(2)

Table S4. Selected Interatomic Distances (Å) and Bond Angles (deg) for **3c**.

Distances			
N(1)-C(1)	1.428(2)	N(1)-C(14)	1.3689(19)
C(1)-C(2)	1.522(2)	C(2)-C(3)	1.479(2)
C(3)-C(4)	1.335(2)	C(4)-C(5)	1.430(2)
C(4)-C(7)	1.471(2)	C(5)-C(6)	1.163(2)

Angles			
C(1)-N(1)-C(14)	124.29(15)	N(1)-C(1)-C(2)	113.81(16)
C(1)-C(2)-C(3)	112.16(16)	C(2)-C(3)-C(4)	125.95(15)
C(3)-C(4)-C(5)	119.19(15)	C(3)-C(4)-C(7)	123.58(13)
C(5)-C(4)-C(7)	117.23(15)	C(4)-C(5)-C(6)	179.4(2)

Table S5. Selected Interatomic Distances (Å) and Bond Angles (deg) for **5a**-0.5H₂O

molecule A		molecule B	
Distances			
P(1)-O(1)	1.4893(18)	P(2)-O(2)	1.487(2)
P(1)-C(1)	1.878(2)	P(2)-C(25)	1.882(3)
C(1)-C(2)	1.469(3)	C(25)-C(26)	1.471(4)
C(1)-C(4)	1.530(4)	C(25)-C(28)	1.551(4)
C(1)-C(10)	1.540(4)	C(25)-C(34)	1.532(3)
C(2)-C(3)	1.183(3)	C(26)-C(27)	1.180(4)
C(10)-C(11)	1.510(5)	C(34)-C(35)	1.505(5)
C(10)-C(12)	1.489(5)	C(34)-C(36)	1.495(4)
C(11)-C(12)	1.489(6)	C(35)-C(36)	1.492(6)
Angles			
C(1)-P(1)-O(1)	109.91(12)	C(25)-P(2)-O(2)	108.93(12)
C(13)-P(1)-O(1)	112.14(12)	C(37)-P(2)-O(2)	111.06(12)
C(19)-P(1)-O(1)	110.56(11)	C(43)-P(2)-O(2)	111.20(12)
P(1)-C(1)-C(2)	107.8(2)	P(2)-C(25)-C(26)	110.4(2)
C(4)-C(1)-C(2)	112.0(2)	C(28)-C(25)-C(26)	109.9(2)
C(10)-C(1)-C(2)	110.1(2)	C(34)-C(25)-C(26)	111.1(2)
C(1)-C(2)-C(3)	177.0(3)	C(25)-C(26)-C(27)	178.9(3)
C(1)-C(10)-C(11)	119.2(2)	C(25)-C(34)-C(35)	121.0(2)
C(1)-C(10)-C(12)	122.4(3)	C(25)-C(34)-C(36)	122.3(2)
C(12)-C(10)-C(11)	59.5(2)	C(36)-C(34)-C(35)	59.6(2)
C(10)-C(11)-C(12)	59.6(2)	C(34)-C(35)-C(36)	59.9(2)
C(10)-C(12)-C(11)	60.9(2)	C(34)-C(36)-C(35)	60.5(2)

Theoretical Calculations. All the density functional theory calculations were performed by Gaussian 03 program package.^{S7}

Table S6. Relative energies ΔE and relative free energies ΔG at 298.15K

Model	ΔE (kcal/mol)	ΔG (kcal/mol)
I + NH ₃	0.0	0.0
TS1 ^a	+2.4	+15.5
II	−27.6	−9.8
TS2 ^b	−23.9	−8.6
III	−25.2	−9.1

^a The transition state of the reaction of **I** with NH₃.

^b The transition state of the reaction of **II**.

Table S7. Total energies E and Gibbs free energies G at 298.15K

Model	E (Hartree)	G (Hartree)
I	−921.756279	−921.469083
NH ₃	−56.548280	−56.532505
TS1	−978.300703	−977.976890
II	−978.348514	−978.017169
TS2	−978.342662	−978.015229
III	−978.344686	−978.016047

I

TS1

317i cm⁻¹

II

TS2

613i cm⁻¹

III

Figure S1. Optimized structures. Bond lengths are given in Å.

Table S8. The Cartesian coordinates of atoms in **I** (Å)

Atom	x	y	z
Ru	-0.942021	0.544054	0.000000
Ru	0.455924	-1.913318	0.000000
Cl	2.875034	-1.497655	0.000000
S	0.207655	-0.459289	1.912073
S	0.207655	-0.459289	-1.912073
C	1.776212	0.473312	2.412771
H	2.407584	0.640870	1.544077
H	2.289649	-0.164734	3.135378
H	1.453403	1.405026	2.883640
C	1.776212	0.473312	-2.412771
H	2.407584	0.640870	-1.544077
H	2.289649	-0.164734	-3.135378
H	1.453403	1.405026	-2.883640
C	-3.169074	-0.402568	0.000000
C	-2.994793	0.426677	1.161786
C	-2.994793	0.426677	-1.161786
C	-2.724713	1.775483	0.724598
C	-2.724713	1.775483	-0.724598
H	-3.424757	-1.451756	0.000000
H	-3.062884	0.103330	2.191532
H	-3.062884	0.103330	-2.191532
H	-2.599273	2.636765	1.364814
H	-2.599273	2.636765	-1.364814
C	0.984348	-4.177983	0.000000
C	0.195801	-3.885232	1.167138
C	0.195801	-3.885232	-1.167138
C	-1.103042	-3.418919	0.721531
C	-1.103042	-3.418919	-0.721531
H	2.015279	-4.501913	0.000000
H	0.511049	-4.013960	2.192809
H	0.511049	-4.013960	-2.192809
H	-1.932513	-3.163113	1.365497
H	-1.932513	-3.163113	-1.365497
C	0.272733	2.023930	0.000000
C	1.031249	3.042287	0.000000
C	1.943919	4.056934	0.000000

H	3.003361	3.779889	0.000000
C	1.666843	5.483577	0.000000
H	2.537215	6.129880	0.000000
C	0.394383	6.035500	0.746338
H	0.545097	6.969689	1.277474
H	-0.196945	5.291109	1.269764
C	0.394383	6.035500	-0.746338
H	0.545097	6.969689	-1.277474
H	-0.196945	5.291109	-1.269764

Table S9. The Cartesian coordinates of atoms in NH_3 (Å)

Atom	x	y	z
N	0.000000	0.000000	0.051702
H	0.000000	0.994007	-0.120639
H	0.860835	-0.497003	-0.120639
H	-0.860835	-0.497003	-0.120639

Table S10. The Cartesian coordinates of atoms in **TS1** (Å)

Atom	x	y	z
Ru	-0.250708	0.957322	-0.192787
Ru	2.162741	-0.446294	0.161459
Cl	1.742101	-2.869707	0.210407
S	0.948149	-0.262974	-1.926581
S	0.480015	-0.115242	1.869137
C	0.094926	-1.853569	-2.491718
H	-0.086642	-2.501495	-1.637661
H	0.783567	-2.330945	-3.192716
H	-0.828940	-1.560550	-2.995344
C	-0.500843	-1.670637	2.311201
H	-0.596819	-2.314633	1.441360
H	0.065824	-2.176347	3.096045
H	-1.470301	-1.334926	2.687672

C	0.649445	3.212095	-0.149704
C	0.001613	2.965856	-1.408154
C	-0.332463	3.055983	0.888464
C	-1.389131	2.670632	-1.158192
C	-1.596974	2.728027	0.276304
H	1.683153	3.492394	-0.010267
H	0.470140	2.998500	-2.382248
H	-0.158364	3.168077	1.949888
H	-2.145442	2.493016	-1.909088
H	-2.537555	2.599462	0.791617
C	4.414333	-0.959387	0.453424
C	4.258639	-0.223735	-0.772301
C	3.980153	-0.127139	1.542994
C	3.735955	1.088613	-0.440640
C	3.565301	1.148892	0.990738
H	4.736562	-1.987587	0.534716
H	4.506945	-0.580489	-1.761617
H	3.983834	-0.399427	2.588743
H	3.553073	1.887226	-1.145161
H	3.231007	2.001618	1.564167
C	-1.732811	-0.303657	-0.344216
C	-2.704021	-1.089984	-0.472257
C	-3.631850	-2.115328	-0.651702
H	-3.232979	-3.133511	-0.688440
C	-5.019768	-1.997883	-0.806126
H	-5.600489	-2.895340	-0.992394
C	-5.754213	-0.658109	-0.861323
H	-5.113742	0.183953	-1.118525
H	-6.672382	-0.683996	-1.446445
C	-5.884246	-0.952171	0.582605
H	-5.091545	-0.669959	1.264074
H	-6.663666	-1.611209	0.944395
N	-7.183405	0.754620	1.586128
H	-7.242505	0.586190	2.589678
H	-6.713195	1.632663	1.372730
H	-8.095753	0.695256	1.136151

Table S11. The Cartesian coordinates of atoms in **II** (Å)

Atom	x	y	z
Ru	0.219232	1.159689	0.097686
Ru	-1.914014	-0.663778	-0.070322
Cl	-1.259448	-3.000901	0.339870
S	-0.810384	0.010804	1.977772
S	-0.132985	-0.446518	-1.715085
C	0.274558	-1.333737	2.746000
H	0.690051	-1.974188	1.972874
H	-0.377692	-1.911044	3.404661
H	1.051335	-0.821812	3.318711
C	1.035784	-1.937615	-1.690876
H	1.637663	-1.924422	-0.782557
H	0.411658	-2.832337	-1.693734
H	1.639107	-1.887159	-2.604578
C	-1.098283	3.133863	-0.366376
C	-0.502004	3.231967	0.938835
C	-0.039089	3.027327	-1.331067
C	0.930631	3.198865	0.789238
C	1.219001	3.070967	-0.628908
H	-2.154586	3.170535	-0.586908
H	-1.032876	3.320580	1.876697
H	-0.163536	2.939449	-2.401878
H	1.656936	3.299259	1.582603
H	2.200861	3.091895	-1.079031
C	-4.069969	-1.515009	-0.321205
C	-4.070849	-0.544584	0.740289
C	-3.683898	-0.859437	-1.541584
C	-3.694863	0.734078	0.172245
C	-3.454292	0.538992	-1.239887
H	-4.257444	-2.572913	-0.206727
H	-4.326870	-0.734423	1.772782
H	-3.599916	-1.326131	-2.512618
H	-3.657440	1.669936	0.710765
H	-3.199207	1.301458	-1.961814

C	1.955656	0.333300	0.600586
C	3.084682	-0.098158	0.926222
C	4.261649	-0.549998	1.621128
H	4.181266	-0.504600	2.708976
C	5.450331	-0.998770	1.131479
H	6.207550	-1.256191	1.871501
C	5.934571	-1.196888	-0.296722
H	6.638133	-0.388459	-0.564553
H	6.544787	-2.111110	-0.314776
C	4.900110	-1.368187	-1.419641
H	4.144640	-2.112840	-1.155593
H	5.393283	-1.669625	-2.349124
N	4.141943	-0.068785	-1.706263
H	3.515865	-0.169707	-2.514093
H	4.793740	0.706279	-1.876565
H	3.541673	0.143880	-0.834515

Table S12. The Cartesian coordinates of atoms in **TS2** (Å)

Atom	x	y	z
Ru	0.116864	1.227261	-0.008212
Ru	-1.891976	-0.750835	-0.001674
Cl	-0.933536	-3.002415	0.229151
S	-0.652809	-0.026697	1.942747
S	-0.373933	-0.319073	-1.833119
C	0.605982	-1.293123	2.569102
H	1.100123	-1.784100	1.735830
H	0.041336	-2.022507	3.152868
H	1.308355	-0.747798	3.204556
C	0.927371	-1.672823	-2.056208
H	1.417857	-1.887272	-1.110251
H	0.399230	-2.560749	-2.406867
H	1.619858	-1.306382	-2.820415
C	-1.365815	3.123763	-0.287642
C	-0.631561	3.255765	0.941614
C	-0.416452	3.088445	-1.367307
C	0.774789	3.317068	0.627966

C	0.908533	3.212232	-0.812616
H	-2.440966	3.097943	-0.386274
H	-1.055434	3.311311	1.934936
H	-0.651441	2.994840	-2.418832
H	1.579002	3.467547	1.333540
H	1.830731	3.272894	-1.372178
C	-3.966407	-1.806978	-0.042663
C	-3.946714	-0.867879	1.046141
C	-3.785958	-1.083850	-1.273356
C	-3.764347	0.456955	0.487524
C	-3.665154	0.323472	-0.947596
H	-4.037592	-2.880906	0.052858
H	-4.066272	-1.108833	2.092841
H	-3.766266	-1.514965	-2.264080
H	-3.757389	1.378640	1.051574
H	-3.567958	1.126802	-1.663982
C	1.895097	0.528049	0.255117
C	3.120540	0.158857	0.379936
C	4.100973	-0.018795	1.456172
H	3.786282	0.342816	2.435291
C	5.349578	-0.551291	1.374305
H	5.926142	-0.553201	2.300180
C	6.108351	-1.149368	0.200368
H	6.872841	-0.427648	-0.137845
H	6.681429	-2.008283	0.576920
C	5.309628	-1.649843	-1.014982
H	4.537730	-2.360947	-0.700276
H	5.984278	-2.160827	-1.712675
N	4.605921	-0.516896	-1.716623
H	4.118460	-0.824169	-2.562693
H	5.246489	0.248560	-1.947496
H	3.704054	-0.087830	-0.781086

Table S13. The Cartesian coordinates of atoms in **III** (Å)

Atom	x	y	z
Ru	0.096683	1.234552	-0.061321

Ru	-1.892773	-0.768095	0.034248
Cl	-0.878928	-2.995452	0.222642
S	-0.595437	-0.023620	1.925909
S	-0.482758	-0.300453	-1.870677
C	0.703995	-1.269329	2.510495
H	1.189476	-1.742267	1.662082
H	0.167090	-2.015211	3.099525
H	1.409469	-0.714988	3.134293
C	0.872306	-1.587925	-2.169293
H	1.209786	-2.005193	-1.223821
H	0.421410	-2.369293	-2.784570
H	1.670337	-1.075968	-2.713158
C	-1.422121	3.121044	-0.220040
C	-0.560829	3.284383	0.920566
C	-0.593681	3.069046	-1.393351
C	0.803011	3.352429	0.453672
C	0.783917	3.213085	-0.988110
H	-2.501433	3.087645	-0.199690
H	-0.876850	3.363867	1.951785
H	-0.937329	2.951445	-2.412117
H	1.676754	3.525499	1.065343
H	1.640572	3.263848	-1.644789
C	-3.942119	-1.869327	0.038167
C	-3.884647	-0.975359	1.165060
C	-3.844290	-1.090825	-1.166564
C	-3.763148	0.375961	0.654107
C	-3.735704	0.304154	-0.788126
H	-3.986235	-2.947686	0.091186
H	-3.948357	-1.262251	2.205035
H	-3.863456	-1.479922	-2.174686
H	-3.742915	1.273641	1.255565
H	-3.694526	1.138284	-1.473976
C	1.856147	0.555207	0.097002
C	3.112443	0.189164	0.174202
C	4.032810	0.299936	1.320254
H	3.644093	0.815513	2.198016
C	5.314693	-0.148626	1.378297
H	5.844058	0.069770	2.307613
C	6.167636	-0.895835	0.364700

H	6.885752	-1.501443	0.934314
H	6.788187	-0.166591	-0.185985
C	5.488683	-1.842751	-0.647910
H	4.746924	-2.468115	-0.136563
H	6.259658	-2.513357	-1.056919
N	4.789096	-1.103639	-1.741291
H	5.398363	-0.428260	-2.207598
H	4.371561	-1.730386	-2.431385
H	3.590191	-0.265933	-0.766685

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^1H and ^{13}C NMR spectra of **1b-h**, and **3m** are shown in the following pages.