Supporting Information

Ruthenium-Catalyzed Propargylation of Aromatic Compounds with Propargylic Alcohols

Yoshiaki Nishibayashi,[†] Masato Yoshikawa,[†] Youichi Inada,[†] Masanobu Hidai,^{*††} and Sakae Uemura^{*†}

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

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.

[†] Kyoto University

^{††} Tokyo University of Science

Ruthenium-Catalyzed Propargylation of Aromatic Compounds with Propargylic Alcohols. A typical experimental procedure for the reaction of 2-methylfuran with 1-phenyl-2-propyn-1-ol (**2a**) catalyzed by [Cp*RuCl(μ_2 -SMe) $_2$ RuCp*Cl] (**1a**) is described below. In a 20 mL flask were placed **1a** (19 mg, 0.03 mmol) and NH₄BF₄ (6 mg, 0.06 mmol) under N₂. Anhydrous ClCH₂CH₂Cl (15 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (79 mg, 0.60 mmol) and 2-methylfuran (492 mg, 6.00 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 2-methyl-5-(1-phenyl-2-propynyl)furan (**3a**) as a pale yellow oil (100 mg, 0.51 mmol, 85% yield).

3a: ¹H NMR δ 2.23 (s, 3H), 2.41 (d, 1H, J = 3.0 Hz), 5.00 (s, 1H), 5.88 (s, 1H), 6.06 (d, 1H, J = 3.0 Hz), 7.25-7.43 (m, 5H). ¹³C NMR δ 13.6, 37.0, 71.8, 82.3, 106.2, 107.4, 127.3, 127.7, 128.6, 138.5, 151.3, 152.0. Anal Calcd for C₁₄H₁₂O: C, 85.68; H, 6.16. Found: C, 85.41; H, 5.88.

For comparison, reactions of 2-methylfuran with **2a** in the presence of various mono- and di-ruthenium complexes were carried out. Typical results are shown in Table S1. Similar thiolate-bridged diruthenium(III, III) complexes [Cp*RuCl(μ_2 -SR) $_2$ RuCp*Cl] (R = *n*Pr, *i*Pr) and [Cp*RuCl(μ_2 -S^{*i*}Pr) $_2$ RuCp*(OH₂)]OTf were effective in this reaction. In addition, the allenylidene complex [Cp*RuCl(μ_2 -SMe) $_2$ RuCp*(C=C=CHPh)]BF₄ (**4a**) was also effective in this catalytic reaction. On the other hand, conventional monoruthenium complexes such as [Cp*RuCl(PPh₃) $_2$], [CpRuCl(PPh₃) $_2$] (Cp = η^5 -C₅H₅), [RuCl₂(PPh₃) $_3$], [RuCl₂(*p*-cymene)] $_2$, [(indenyl)RuCl(PPh₃) $_2$], [RuCl₂(dppe) $_2$] (dppe = 1,2-bis(diphenylphosphino)ethane), and [Cp*RuCl(μ_2 -Cl) $_2$ RuCp*Cl] which were known to react with propargylic alcohols to produce the corresponding allenylidene complexes, did not work at all as catalysts.

Table S1. Propargylation of 2-Methylfuran with Propargylic Alcohol (**2a**).^a

catalyst (mol %)	additive (mol %)	GLC conv. (%)	GLC yield (%)
[Cp*RuCl(SMe)] ₂ (1a) (5)	NH ₄ BF ₄ (10)	100	>95 (85) ^b
[Cp*RuCl(S ⁿ Pr)] ₂ (1b) (5)	NH ₄ BF ₄ (10)	100	87
[Cp*RuCl(S ⁱ Pr)] ₂ (1c) (5)	NH ₄ BF ₄ (10)	100	78
[Cp*RuCl(S ⁱ Pr) ₂ Ru(OH ₂)Cp*]OTf (1d) (5)	NH ₄ BF ₄ (10)	100	>95
[Cp*RuCl(SMe) ₂ Ru(=C=C=CHPh)Cp*]BF ₄ (6) (5)	–	100	>95
[Cp*RuCl(PPh ₃) ₂] (5)	NH ₄ BF ₄ (10)	36	0
[RuCl ₂ (PPh ₃) ₃] (5)	NH ₄ BF ₄ (10)	18	0
[RuCl ₂ (<i>p</i> -cymene)] ₂ (5)	NH ₄ BF ₄ (10)	40	0
[(indenyl)RuCl(PPh ₃) ₂] (5)	NH ₄ BF ₄ (10)	44	0

^a All the reactions of 2-methylfuran (1.00 mmol) with PhCH(OH)C≡CH (**2a**) (0.10 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.

3b: Yield 83%. A pale yellow oil. ¹H NMR δ 2.22 (s, 3H), 2.33 (s, 3H), 2.39 (s, 1H), 4.96 (s, 1H), 5.86 (s, 1H), 6.06 (s, 1H), 7.13 (d, 2H, *J* = 7.5 Hz), 7.29 (d, 2H, *J* = 7.5 Hz). ¹³C NMR δ 13.6, 21.0, 36.7, 71.6, 82.5, 106.2, 107.3, 127.6, 129.3, 135.6, 137.0, 151.5, 151.9. Anal Calcd for C₁₅H₁₄O: C, 85.68; H, 6.71. Found: C, 85.44; H, 6.59.

3c: Yield 70%. A pale yellow oil. ^1H NMR δ 2.23 (s, 3H), 2.42 (d, 1H, $J = 2.4$ Hz), 4.98 (s, 1H), 5.88 (s, 1H), 6.06 (d, 1H, $J = 2.4$ Hz), 7.01 (t, 2H, $J = 8.8$ Hz), 7.38 (dd, 2H, $J = 8.8$ and 5.4 Hz). ^{13}C NMR δ 13.6, 36.3, 72.0, 82.0, 106.2, 107.5, 115.3 (d, $J = 22$ Hz), 129.3 (d, $J = 9$ Hz), 134.2 (d, $J = 4$ Hz), 151.0, 152.1, 162.0 (d, $J = 246$ Hz). Anal Calcd for $\text{C}_{14}\text{H}_{11}\text{FO}$: C, 78.49; H, 5.18. Found: C, 78.30; H, 5.07.

3d: Yield 77%. A pale yellow oil. ^1H NMR δ 2.21 (s, 3H), 2.26 (s, 3H), 2.29 (d, 1H, $J = 2.7$ Hz), 2.35 (s, 6H), 5.43 (s, 1H), 5.86 (s, 1H), 6.03 (s, 1H), 6.85 (s, 2H). ^{13}C NMR δ 13.6, 20.4, 20.8, 31.7, 70.6, 81.7, 106.0, 107.3, 129.9, 131.5, 136.8, 136.9, 150.3, 151.5. Anal Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: C, 85.67; H, 7.61. Found: C, 85.45; H, 7.28.

3e: Yield 84%. A pale yellow oil. ^1H NMR δ 2.24 (s, 3H), 2.45 (d, 1H, $J = 3.0$ Hz), 5.71 (s, 1H), 5.88 (s, 1H), 6.04 (d, 1H, $J = 3.0$ Hz), 7.50 (m, 3H), 7.62 (d, 1H, $J = 7.0$ Hz), 7.80 (d, 1H, $J = 8.0$ Hz), 7.87 (d, 1H, $J = 7.0$ Hz), 8.12 (d, 1H, $J = 8.0$ Hz). ^{13}C NMR δ 13.6, 37.2, 72.1, 82.2, 106.2, 107.6, 125.9, 125.9, 126.2, 126.4, 127.6, 127.9, 128.4, 132.7, 133.4, 135.8, 151.2, 152.1. Anal Calcd for $\text{C}_{18}\text{H}_{14}\text{O}$: C, 87.78; H, 5.73. Found: C, 87.53; H, 5.64.

3f: Yield 75%. A pale yellow oil. ^1H NMR δ 1.17 (t, 3H, $J = 7.5$ Hz), 2.40 (d, 1H, $J = 2.5$ Hz), 2.58 (q, 2H, $J = 7.5$ Hz), 5.00 (d, 1H, $J = 2.5$ Hz), 5.88 (d, 1H, $J = 3.0$ Hz),

6.07 (d, 1H, $J = 3.0$ Hz), 7.23-7.42 (m, 5H). ^{13}C NMR δ 12.0, 21.3, 37.0, 71.7, 82.2, 104.5, 107.2, 127.3, 127.7, 128.6, 138.5, 151.1, 157.7. Anal Calcd for $\text{C}_{15}\text{H}_{14}\text{O}$: C, 85.68; H, 6.71. Found: C, 85.43; H, 6.69.

3g: Yield 51%. A pale yellow oil. ^1H NMR δ 2.40 (d, 1H, $J = 1.2$ Hz), 3.75 (s, 3H), 4.93 (s, 1H), 5.04 (d, 1H, $J = 3.0$ Hz), 6.07 (d, 1H, $J = 3.0$ Hz), 7.25-7.42 (m, 5H). ^{13}C NMR δ 36.9, 57.6, 71.9, 79.8, 81.9, 107.6, 127.3, 127.7, 128.6, 138.2, 142.8, 161.3. Anal Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$: C, 79.22; H, 5.70. Found: C, 78.99; H, 5.51.

3h: Yield 59%. A yellow oil. ^1H NMR δ 2.23 (s, 3H), 2.30 (d, 1H, $J = 2.4$ Hz), 4.47 (dd, 1H, $J = 9.9$ and 2.4 Hz), 5.88 (d, 1H, $J = 3.0$ Hz), 6.09 (d, 1H, $J = 3.0$ Hz), 6.15 (d, 1H, $J = 9.9$ Hz), 7.25-7.40 (m, 10H). ^{13}C NMR δ 13.6, 31.7, 70.6, 82.4, 106.2, 106.6, 124.9, 127.6, 128.1, 128.4, 129.8, 138.7, 150.5, 151.9. Anal Calcd for $\text{C}_{22}\text{H}_{18}\text{O}$: C, 88.56; H, 6.08. Found: C, 88.40; H, 5.85.

3i: Yield 61%. A pale yellow oil. ^1H NMR δ 1.10-1.90 (m, 10H), 2.18 (d, 1H, $J = 2.7$ Hz), 2.27 (s, 3H), 3.55 (m, 1H), 5.48 (dd, 1H, $J = 11$ and 2.7 Hz), 5.88 (d, 1H, $J = 3.0$ Hz), 6.06 (d, 1H, $J = 3.0$ Hz). ^{13}C NMR δ 13.6, 26.1, 26.2, 27.5, 29.2, 31.0, 70.9, 82.4, 105.9, 107.0, 150.9, 151.1. Anal Calcd for $\text{C}_{14}\text{H}_{18}\text{O}$: C, 83.12; H, 8.97. Found: C, 83.05; H, 8.83.

3j: Yield 68%. A pale yellow oil. ^1H NMR δ 2.42 (d, 1H, $J = 3.0$ Hz), 5.04 (d, 1H, $J = 3.0$ Hz), 6.21 (d, 1H, $J = 3.0$ Hz), 6.30 (m, 1H), 7.25-7.43 (m, 6H). ^{13}C NMR δ 37.0, 72.0, 81.9, 106.7, 110.3, 127.5, 127.7, 128.6, 138.2, 142.3, 153.1. Anal Calcd for $\text{C}_{13}\text{H}_{10}\text{O}$: C, 85.69; H, 5.53. Found: C, 85.56; H, 5.35.

3k: Yield 67%. A brown oil. ^1H NMR δ 2.45 (d, 1H, $J = 2.4$ Hz), 5.06 (d, 1H, $J = 2.4$ Hz), 6.00 (s, 1H), 6.13 (q, 1H, $J = 2.8$ Hz), 6.68 (q, 1H, $J = 2.3$ Hz), 7.21-7.39 (m, 5H), 8.11 (s, 1H). ^{13}C NMR δ 36.3, 72.2, 83.1, 106.5, 108.6, 117.4, 127.3, 127.6, 128.7, 129.9, 139.5. IR (neat, cm^{-1}) 2118 ($\text{C}\equiv\text{C}$), 3289 ($\equiv\text{C}-\text{H}$), 3430 ($\text{N}-\text{H}$). Anal Calcd for $\text{C}_{13}\text{H}_{11}\text{N}$: C, 86.15; H, 6.12; N, 7.73. Found: C, 85.88; H, 5.93; N, 7.50.

3l: Yield 94%. A yellow oil. ^1H NMR δ 2.43 (d, 1H, $J = 2.4$ Hz), 3.43 (s, 3H), 5.06 (d, 1H, $J = 2.4$ Hz), 6.02 (s, 1H), 6.07 (s, 1H), 6.55 (s, 1H), 7.22-7.44 (m, 5H). ^{13}C NMR δ 34.2, 35.4, 72.2, 83.0, 106.7, 108.5, 122.9, 127.1, 127.7, 128.6, 130.4, 139.0. Anal Calcd for $\text{C}_{14}\text{H}_{13}\text{N}$: C, 86.12; H, 6.72; N, 7.17. Found: C, 85.85; H, 6.55; N, 6.99.

3m: Yield 86%. A pale yellow oil. ^1H NMR δ 2.40 (s, 3H), 2.48 (s, 1H), 5.13 (s, 1H), 6.55 (s, 1H), 6.74 (s, 1H), 7.25-7.54 (m, 5H). ^{13}C NMR δ 15.3, 38.7, 72.3, 83.9, 124.6,

124.9, 128.6, 128.8, 130.9, 139.5, 140.6, 142.3. Anal Calcd for C₁₄H₁₂S: C, 79.20; H, 5.70. Found: C, 79.11; H, 5.64.

3n: Yield 52%. White crystals. ¹H NMR δ 2.41 (d, 1H, *J* = 2.6 Hz), 5.23 (s, 1H), 7.02-7.52 (m, 10H), 7.87 (br, 1H). ¹³C NMR δ 34.6, 71.3, 84.8, 111.2, 116.2, 119.4, 119.6, 122.2, 122.6, 125.8, 126.9, 127.8, 128.5, 136.6, 140.6. Anal. Calcd for C₁₇H₁₃N: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.12; H, 5.51; N, 5.95.

6a: Yield 50%. White crystals. ¹H NMR δ 2.44 (d, 1H, *J* = 2.7 Hz), 2.89 (s, 6H), 4.93 (s, 1H), 6.67 (d, 2H, *J* = 8.6 Hz), 7.19-7.38 (m, 7H). ¹³C NMR δ 40.6, 41.9, 72.2, 85.3, 112.8, 126.7, 127.7, 128.4, 128.5, 129.1, 141.7, 149.5. Anal. Calcd for C₁₇H₁₇N: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.47; H, 7.19; N, 5.82.

6b: Yield 58%. A brown solid. ¹H NMR δ 2.49 (d, 1H, *J* = 2.6 Hz), 2.91 (s, 6H), 4.96 (s, 1H), 6.67 (d, 2H, *J* = 8.8 Hz), 7.19 (d, 2H, *J* = 8.8 Hz), 7.47-7.56 (m, 4H). ¹³C NMR δ 40.7, 41.9, 73.0, 84.3, 112.6, 125.3, 125.4, 127.8, 127.9, 128.3, 128.9, 145.7, 149.6. Anal. Calcd for C₁₈H₁₆NF₃: C, 71.28; H, 5.32; N, 4.62. Found: C, 71.55; H, 5.28; N, 4.42.

6c: Yield 53%. A yellow oil. ^1H NMR δ 2.45 (s, 1H), 2.90 (s, 6H), 4.88 (s, 1H), 6.6 (d, 2H, $J = 8.4$ Hz), 7.16-7.2 (m, 6H). ^{13}C NMR δ 40.5, 41.3, 72.6, 84.8, 112.7, 128.3, 128.6, 129.1, 132.5, 140.4, 149.7. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{NCl}$: C, 75.69; H, 5.98; N, 5.19. Found: C, 75.91; H, 5.93; N, 4.89.

6d: Yield 23%. Yellow crystals. ^1H NMR δ 2.30 (s, 3H), 2.43 (d, 1H, $J = 2.6$ Hz), 2.89 (s, 6H), 4.89 (s, 1H), 6.66 (d, 2H, $J = 6.6$ Hz), 7.07-7.26 (m, 6H). ^{13}C NMR δ 21.1, 40.7, 41.6, 72.1, 85.5, 112.6, 127.5, 128.2, 129.1, 129.1, 136.1, 138.8, 149.4. Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{N}$: C, 86.70; H, 7.68; N, 5.62. Found: C, 86.43; H, 7.58; N, 5.44.

6f: Yield 30%. Yellow crystals. ^1H NMR δ 2.52 (s, 1H), 2.88 (s, 6H), 5.09 (s, 1H), 6.66 (d, 2H, $J = 8.8$ Hz), 7.25 (d, 2H, $J = 8.8$ Hz), 7.41-7.88 (m, 7H). ^{13}C NMR δ 40.6, 42.1, 72.7, 85.1, 112.6, 125.6, 125.8, 125.9, 126.1, 127.5, 127.8, 128.2, 128.4, 128.6, 132.3, 133.3, 139.0, 149.5. HRMS Calcd for $\text{C}_{21}\text{H}_{19}\text{N}$ [M] 285.1517. Found 285.1516.

6g: Yield 23%. A reddish brown oil. ^1H NMR δ 1.13 (t, 6H, $J = 7.0$ Hz), 2.45 (s, 1H), 3.31 (q, 4H, $J = 7.0$ Hz), 4.91 (s, 1H), 6.61 (d, 2H, $J = 7.9$ Hz), 7.16-7.40 (m, 7H). ^{13}C NMR δ 12.5, 41.9, 44.3, 72.1, 85.4, 111.7, 126.6, 127.7, 128.5, 129.2, 141.8, 146.7. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{N}$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.62; H, 8.24; N, 5.14.

6h: Yield 49%. A pale brown oil. ^1H NMR δ 2.46 (d, 1H, $J = 2.6$ Hz), 3.26 (s, 3H), 4.95 (s, 1H), 6.91-7.40 (m, 14H). ^{13}C NMR δ 40.2, 42.2, 72.5, 84.9, 120.1, 120.7, 121.4, 126.9, 127.7, 128.5, 128.6, 129.1, 133.6, 141.3, 147.8, 148.8. Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{N}$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.75; H, 6.56; N, 4.59.

6i: Yield 63%. A red solid, 57.0-57.8 $^{\circ}\text{C}$. ^1H NMR δ 2.46 (d, 1H, $J = 2.0$ Hz), 4.95 (d, 1H, $J = 2.0$ Hz), 5.64 (brs, 1H), 6.87 (t, 2H, $J = 7.6$ Hz), 7.00 (m, 4H), 7.02-7.26 (m, 5H), 7.30 (m, 2H), 7.38 (d, 1H, $J = 7.6$ Hz). ^{13}C NMR δ 42.1, 72.6, 84.9, 117.7, 117.8, 120.9, 126.9, 127.7, 128.6, 128.6, 129.3, 133.5, 141.3, 141.9, 142.9. IR (neat, cm^{-1}) 2114 ($\text{C}\equiv\text{C}$), 3289 ($\equiv\text{C}-\text{H}$), 3399 ($\text{N}-\text{H}$). Anal. Calcd for $\text{C}_{21}\text{H}_{17}\text{N}$: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.79; H, 6.10; N, 5.27.

6j and 6k: Yield 60% (a mixture of **6j** and **6k** was obtained in a ratio of 1 to 5). A yellow oil. **6k**; ^1H NMR δ 2.35 (d, 1H, $J = 3.0$ Hz), 4.94 (d, 1H, $J = 3.0$ Hz), 6.24 (t, 1H, $J = 3.0$ Hz), 6.30 (m, 1H), 6.73 (t, 1H, $J = 3.0$ Hz), 7.11-7.38 (m, 10H). ^{13}C NMR δ 35.3, 71.6, 84.0, 108.1, 108.9, 120.1, 122.8, 126.7, 127.4, 128.2, 128.9, 132.1, 139.5, 139.9. **6j**; ^1H NMR δ 2.41 (d, 1H, $J = 3.0$ Hz), 6.22 (m, 1H), 7.00 (m, 2H). Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{N}$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.88; H, 5.84; N, 5.37.

6l: Yield 48%. A green oil. ^1H NMR δ 2.44 (d, 1H, $J = 2.6$ Hz), 2.69 (s, 3H), 2.86 (t, 2H, $J = 8.1$ Hz), 3.23 (t, 2H, $J = 8.1$ Hz), 4.89 (s, 1H), 6.38 (d, 1H, $J = 7.7$ Hz), 7.04-7.39 (m, 7H). ^{13}C NMR δ 28.6, 36.2, 42.3, 56.2, 72.2, 85.4, 106.8, 123.7, 126.6, 126.7, 127.6, 128.4, 130.4, 130.9, 141.8, 152.4. Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{N}$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.31; H, 6.98; N, 5.65.

6m: Yield 52%. A pale yellow oil. ^1H NMR δ 1.85 (s, 3H), 2.04 (s, 1H), 3.79 (s, 3H), 3.85 (s, 3H), 5.90 (s, 1H), 6.36 (s, 1H), 7.24-7.39 (m, 6H), 7.55 (brs, 1H). ^{13}C NMR δ 24.2, 30.2, 55.4, 56.0, 72.7, 83.1, 95.4, 100.6, 111.3, 126.4, 126.8, 128.5, 137.6, 138.5, 156.9, 159.8, 167.8. Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.55; H, 6.27; N, 4.46.

6n: Yield 38%. A pale yellow oil. ^1H NMR δ 2.26 (dd, 1H, $J = 1.3$ and 2.6 Hz), 3.73 (s, 6H), 3.78 (s, 3H), 5.69 (s, 1H), 6.13 (s, 2H), 7.15 (d, 1H, $J = 7.3$ Hz), 7.23 (t, 2H, $J = 7.3$ Hz), 7.43 (d, 2H, $J = 7.3$ Hz). ^{13}C NMR δ 30.5, 55.3, 55.9, 68.9, 84.8, 91.5, 110.8, 125.8, 127.1, 127.7, 140.9, 158.5, 160.4. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$: C, 76.57; H, 6.43. Found: C, 76.48; H, 6.44.

6o: Yield 87%. A blue solid. ^1H NMR δ 2.45 (s, 1H), 5.66 (s, 1H), 7.03-8.33 (m, 12H). ^{13}C NMR δ 35.8, 71.7, 85.2, 116.9, 122.4, 123.0, 126.7, 127.5, 128.5, 133.5, 134.5, 137.1, 137.6, 141.3. Anal. Calcd for $\text{C}_{19}\text{H}_{14}$: C, 94.18; H, 5.82. Found: C, 94.31; H, 5.74.

6p: Yield 81%. A blue oil. ^1H NMR δ 2.48 (d, 1H, $J = 2.6$ Hz), 5.64 (d, 1H, $J = 2.6$ Hz), 7.11-7.35 (m, 7H), 7.59 (t, 1H, $J = 9.7$ Hz), 7.86 (d, 1H, $J = 3.9$ Hz), 8.31 (dd, 2H, $J = 5.3$ and 9.7 Hz). ^{13}C NMR δ 35.2, 72.1, 84.7, 117.0, 122.6, 123.3, 127.7, 128.6, 128.9, 132.5, 133.4, 134.5, 137.0, 137.2, 137.8, 140.0, 141.4. Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{Cl}$: C, 82.46; H, 4.73. Found: C, 82.20; H, 4.72.

Spectroscopic data and isolated yield of the following six products (**3o-3t**), which are not included in Tables 1 and 2 (in the text), are described below.

3o: Yield 95%. A pale yellow oil. ^1H NMR δ 0.90-1.25 (m, 5H), 1.58-1.74 (m, 5H), 2.18 (d, 1H, $J = 2.7$ Hz), 3.47 (dd, 1H, $J = 2.7$ and 7.0 Hz), 3.60 (s, 3H), 6.04 (m, 2H), 6.52 (t, 1H, $J = 2.4$ Hz). ^{13}C NMR δ 26.1, 26.2, 30.0, 31.5, 34.1, 36.2, 42.0, 70.7, 83.8, 106.6, 107.5, 122.0, 130.5. Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{N}$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.45; H, 9.34; N, 6.83.

3p: Yield 92%. A pale yellow oil. ^1H NMR δ 2.33 (s, 3H), 2.41 (d, 1H, $J = 3.0$ Hz), 3.43 (s, 3H), 5.02 (d, 1H, $J = 3.0$ Hz), 6.05 (m, 2H), 6.55 (t, 1H, $J = 2.4$ Hz), 7.12 (d, 2H, $J = 8.1$ Hz), 7.23 (d, 2H, $J = 8.1$ Hz). ^{13}C NMR δ 21.0, 34.1, 35.1, 71.9, 83.2, 106.6, 108.4, 122.8, 127.4, 129.2, 130.6, 136.0, 136.7. Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{N}$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.85; H, 7.19; N, 6.61.

3q: Yield 92%. A yellow oil. ^1H NMR δ 2.45 (d, 1H, $J = 2.0$ Hz), 3.44 (s, 3H), 5.04 (s, 1H), 5.98 (d, 1H, $J = 2.0$ Hz), 6.06 (t, 1H, $J = 3.0$ Hz), 6.57 (s, 1H), 7.01 (dd, 2H, $J = 8.7$ and 8.7 Hz), 7.32 (dd, 2H, $J = 8.7$ and 8.7 Hz). ^{13}C NMR δ 34.1, 34.7, 72.4, 82.8, 100.5, 106.7, 108.5, 115.3 (d, $J = 21$ Hz), 123.1, 129.1 (d, $J = 8$ Hz), 130.2, 134.7 (d, $J = 3$ Hz), 163.5 (d, $J = 265$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}$: C, 78.85; H, 5.67; N, 6.57. Found: C, 78.74; H, 5.55; N, 6.42.

3r: Yield 90%. A yellow oil. ^1H NMR δ 2.49 (d, 1H, $J = 3.0$ Hz), 3.45 (s, 3H), 5.22 (d, 1H, $J = 3.0$ Hz), 6.08 (m, 2H), 6.58 (t, 1H, $J = 2.4$ Hz), 7.42 (m, 3H), 7.83 (m, 4H). ^{13}C NMR δ 34.2, 35.6, 72.6, 82.9, 106.7, 108.7, 123.1, 125.9, 125.9, 126.1, 126.2, 127.6, 127.9, 128.4, 130.3, 132.6, 133.3, 136.4. Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{N}$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.01; H, 5.99; N, 5.68.

3s: Yield 91%. A yellow oil. ^1H NMR δ 1.87 (s, 3H), 2.14 (s, 3H), 2.40 (d, 1H, $J = 3.0$ Hz), 4.96 (d, 1H, $J = 3.0$ Hz), 5.94 (s, 1H), 7.23-7.43 (m, 5H). ^{13}C NMR δ 9.81, 11.3, 37.0, 71.7, 82.4, 109.9, 114.6, 127.3, 127.8, 128.6, 138.5, 147.2, 150.0. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}$: C, 85.68; H, 6.71. Found: C, 85.52; H, 6.47.

3t: Yield 79%. A pale yellow oil. ^1H NMR δ 2.24 (s, 3H), 2.45 (d, 1H, $J = 2.4$ Hz), 5.70 (d, 1H, $J = 2.0$ Hz), 5.87 (d, 1H, $J = 2.4$ Hz), 6.03 (d, 1H, $J = 3.6$ Hz), 7.44-7.53 (m, 3H), 7.62 (d, 1H, $J = 6.8$ Hz), 7.80 (d, 1H, $J = 8.4$ Hz), 7.86 (d, 1H, $J = 8.0$ Hz), 8.12 (d, 1H, $J = 8.4$ Hz). ^{13}C NMR δ 13.6, 34.2, 72.0, 82.4, 106.3, 108.2, 123.5, 125.5, 125.7, 126.0, 126.2, 128.4, 128.8, 130.9, 134.0, 150.8, 151.9. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{O}$: C, 87.78; H, 5.73. Found: C, 87.60; H, 5.64.

Unfortunately, no effective propargylation proceeded when the following aromatic compounds were used (vide infra).

Interestingly, the reaction of indoline with **2a** gave *N*-(1-phenyl-2-propenyl)indole selectively in 74% yield (Scheme S1). A pale yellow oil. ^1H NMR δ 5.01 (d, 1H, $J = 16.9$ Hz), 5.36 (d, 1H, $J = 10.3$ Hz), 6.09 (d, 1H, $J = 5.7$ Hz), 6.30-6.39 (m, 1H), 6.52 (d, 1H, $J = 3.3$ Hz), 7.07-7.29 (m, 9H), 7.62 (d, 1H, $J = 7.7$ Hz). ^{13}C NMR δ 61.9, 101.5, 110.1, 118.5, 119.6, 120.9, 121.5, 126.2, 127.5, 127.9, 128.7, 128.8, 136.0, 139.0.

Scheme S1

Preparation of [Cp*RuCl(μ_2 -SMe) $_2$ RuCp*(=C=C=CHPh)]BF $_4$ (4a**).** A typical experimental procedure for the preparation of [Cp*RuCl(μ_2 -SMe) $_2$ RuCp*(=C=C=CHPh)]BF $_4$ (**4a**) is described below. In a 200 mL flask were placed **1a** (510 mg, 0.80 mmol), NH $_4$ BF $_4$ (109 mg, 1.04 mmol), and MgSO $_4$ (1 g) under N $_2$. Anhydrous tetrahydrofuran (THF) (100 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (219 mg, 1.66 mmol), the reaction flask was kept at room temperature for 30 min. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from CH $_2$ Cl $_2$ –diethyl ether to give black crystals of **4a** (378 mg, 0.467 mmol, 58%).

Yield 58%. Black crystals. ^1H NMR δ 1.66 (s, 15H), 1.85 (s, 15H), 2.73 (s, 6H), 7.39 (t, 2H, $J = 7.5$ Hz), 7.66 (t, 1H, $J = 7.5$ Hz), 7.72 (d, 2H, $J = 7.5$ Hz) 8.89 (s, 1 H). ^{13}C NMR δ 10.4, 10.6, 20.1, 99.4, 105.6, 130.2, 132.4, 134.0, 142.6, 151.2, 198.0, 319.7. IR (KBr, cm^{-1}) 1945 (C=C=C). Anal Calcd for C $_{31}$ H $_{42}$ BClF $_4$ Ru $_2$ S $_2$: C, 46.36; H, 5.27. Found: C, 46.00; H, 5.15.

Reaction of **2a with pyrrole- d_5 in the presence of **1a** and NH $_4$ BF $_4$.** In a 20 mL flask were placed **1a** (0.03 mmol) and NH $_4$ BF $_4$ (0.06 mmol) under N $_2$. Anhydrous ClCH $_2$ CH $_2$ Cl (18 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **1a** (0.60 mmol) and pyrrole- d_5 (3.00 mmol), the reaction flask was kept at 60 $^\circ\text{C}$ 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 (3/7) to give 2-(1-phenyl-2-propynyl)pyrrole (**3l'**) as a brown oil (83 mg, 0.46 mmol, 77% yield). ^1H NMR (CDCl $_3$) δ 2.45 (d, 0.20H, $J = 2.4$ Hz), 5.06 (d, 1H, $J = 2.4$ Hz), 7.21-7.39 (m, 5H), 8.11 (s, 1H). IR (neat, cm^{-1}) 2585 ($\equiv\text{C}-D$), 3428 ($N-H$). This result indicates the 80% deuterium content at the C–3 position.

X-ray Crystallographic Studies of 6n. Colorless crystals of **6n** 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 S2. The positions of non-hydrogen atoms were determined by direct methods (SIR97) and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of **6n** is shown in Figure S1.

Table S2. Crystallographic Data for **6n**.

formula	C ₁₈ H ₁₈ O ₃
formula weigh	282.34
cryst size (mm ³)	1.20 x 0.60 x 0.50
cryst system	triclinic
space group	<i>P</i> -1(#2)
cryst color	colorless
<i>a</i> (Å)	8.573(3)
<i>b</i> (Å)	8.613(3)
<i>c</i> (Å)	21.722(7)
α (°)	87.52(1)
β (°)	92.459(9)
γ (°)	98.35(2)
<i>V</i> (Å ³)	1584.4(8)
<i>Z</i>	4
<i>d</i> _{calc} (g cm ⁻³)	1.184
<i>F</i> (000)	600.00
μ _{calc} (cm ⁻¹)	0.80
no. of unique data	4942
no. of data used (<i>I</i> > 3 σ (<i>I</i>))	2771
no. of params refined	414
<i>R</i> ^a	0.108
<i>R</i> _w ^b	0.085
goodness of fit indicator	5.42
maximum residuals (e Å ⁻³)	0.23

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

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