Supporting Information

Rhodium-Catalyzed Hydroalkynylation of Internal Alkynes with Silylacetylenes: An Alkynylrhodium(I) Intermediate Generated from [Rh(OH)(binap)]₂
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**General.** All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for $^1$H, 125 MHz for $^{13}$C, and 202 MHz for $^{31}$P). Chemical shifts are reported in δ ppm referenced to an internal SiMe₄ standard for $^1$H NMR, chloroform-$d$ (δ 77.16) for $^{13}$C NMR, and external P(OMe)₃ standard for $^{31}$P NMR: the following abbreviations are used; s: singlet, d: doublet, t: triplet, sext: sextet, m: multiplet, br: broad. GC-MS spectra were taken on Shimazu GCMS-QP5050A. Elemental analyses were performed at Center for Organic Elemental Microanalysis of Kyoto University.

**Materials.** 1,4-Dioxane was distilled over benzophenone-ketyl under N₂. Rhodium complexes, [Rh(OH)(cod)$_2$]$^1$ and [Rh(OH)((R)-binap)]$_2$,$^2$ were prepared according to the reported procedure. Compounds 1a, 1b, 1d, 1g–1i, 2m, 2n, and 2o were purchased and used as received. Compounds 1c [104620-64-6], 1e [1719-19-3], and 1f [1655-05-6] were prepared by the reported procedures and were characterized by $^1$H NMR.

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General procedures for rhodium-catalyzed addition of silylacetylenes to internal alkynes. To a solution of [Rh(OH)((R)-binap)]_2 (5) (7.4 mg, 0.010 mmol of Rh) in 1,4-dioxane (0.40 mL) in a screw cap test tube was added silylacetylene (0.30 mmol) and internal alkyne (0.20 mmol) successively, and the tube was capped tightly. Then, the mixture was allowed to stir at 40–60 °C (bath temp.) for an appropriate time (see Table 1). The reaction mixture was cooled to room temperature and was passed through a short silica gel column eluting with Et₂O. After evaporation of the solvent, the residue was purified by preparative TLC or flash column chromatography on silica gel with EtOAc-hexane as eluent. The results are summarized in Table 1 and equation 6. The reactions of (triphenylsilyl)acetylene (2m) (0.4 mmol) with internal alkynes 1g–1i (0.2 mmol) were performed in 1,4-dioxane (0.50 mL) at 80 °C for 3 h in the presence of [Rh(OH)(cod)]_2 (2.3 mg, 0.010 mmol of Rh) and 1,6-bis(diphenylphosphino)hexane (5.4 mg, 0.012 mmol). The stereochemistry of the major products was determined by NOE analysis.

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\text{Ph} \quad \text{SiPh}_3
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Compound 3am: Colorless oil. ^1H NMR (CDCl₃) δ 2.15 (s, 3H), 7.04 (s, 1H), 7.21–7.50 (m, 14H), 7.60–7.80 (m, 6H); ^13C NMR (CDCl₃) δ 19.2, 87.7, 113.7, 119.6, 127.6, 128.1, 128.5, 129.2, 130.0, 133.9, 135.7, 136.6, 138.2. Anal. Calcd for C₂₉H₂₄Si: C, 86.95; H 6.04. Found: C, 87.20; H, 6.13.

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\text{Ph} \quad \text{SiPh}_3
\]

Compound 3bm: White solid. ^1H NMR (CDCl₃) δ 1.26 (t, J = 7.4 Hz, 3H), 2.49 (qd, J = 7.4, 1.1 Hz, 2H), 7.03 (s, 1H), 7.21–7.50 (m, 14H), 7.65–7.75 (m, 6H); ^13C NMR (CDCl₃) δ 13.4, 24.9, 88.9, 112.3, 126.7, 127.6, 128.1, 128.5, 129.0, 130.0, 134.0, 135.7, 136.5, 137.5. Anal. Calcd for C₃₀H₂₆Si: C, 86.91; H 6.32. Found: C, 86.84; H, 6.33.

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\text{Ph} \quad \text{SiPh}_3
\]

Compound 3cm: Pale yellow oil. ^1H NMR (CDCl₃) δ 3.32 (s, 3H), 4.35 (s, 2H), 4.73 (s, 2H), 7.26 (s, 1H), 7.27–7.45 (m, 14H), 7.68–7.74 (m, 6H); ^13C NMR (CDCl₃) δ 55.6, 65.4, 89.7, 96.2, 111.2, 121.3, 128.1, 128.5, 128.6, 129.2, 130.0, 133.8, 135.4, 135.7, 141.8. Anal. Calcd for C₃₁H₂₉O₂Si: C, 80.83; H 6.13. Found: C, 81.07; H, 6.23.
**Compound 3dm:** Colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 2.01 (t, $J = 5.9$ Hz, 1H, $\text{O}H$), 4.41 (d, $J = 5.9$ Hz, 2H), 7.18 (s, 1H), 7.26–7.46 (m, 14H), 7.65–7.74 (m, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 61.0, 91.4, 109.9, 123.9, 127.9, 128.2, 128.6, 129.2, 130.2, 133.5, 135.4, 135.7, 140.1. Anal. Calcd for C$_{29}$H$_{24}$OSi: C, 83.61; H 5.81. Found: C, 83.91; H, 5.90.

**Compound 3em:** Colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 1.53 (s, 6H), 1.72 (s, 1H, $\text{O}H$), 7.18 (s, 1H), 7.22–7.45 (m, 14H), 7.65–7.70 (m, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 30.9, 74.1, 89.9, 110.9, 127.7, 128.2, 128.9, 130.1, 132.9, 133.7, 135.7, 136.8, 137.7. Anal. Calcd for C$_{31}$H$_{28}$OSi: C, 83.74; H 6.35. Found: C, 83.34; H, 6.46.

**Compound 3fm:** White solid. $^1$H NMR (CDCl$_3$) $\delta$ 1.55–1.70 (m, 4H), 2.05 (s, 3H), 2.10–2.20 (m, 4H), 5.75 (s, 1H), 6.40 (s, 1H), 7.34–7.42 (m, 9H), 7.65–7.70 (m, 6H); $^{13}$C NMR (CDCl$_3$) $\delta$ 19.3, 20.0, 22.9, 26.0, 28.8, 85.8, 115.0, 116.0, 128.0, 129.9, 131.2, 134.2, 135.3, 135.7, 141.4. GC/MS calcd for C$_{29}$H$_{28}$Si 404 (M$^+$), found 404 (14%), 221 (84), 183 (100).

**Compound 3en:** Colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 0.66 (q, $J = 7.9$ Hz, 6H), 1.04 (t, $J = 7.9$ Hz, 9H), 1.47 (s, 6H), 1.75 (s, 1H, $\text{O}H$), 7.03 (s, 1H), 7.20–7.35 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ 4.6, 7.7, 30.7, 73.9, 92.6, 107.5, 127.5, 128.2, 128.8, 133.3, 136.1, 137.1. Anal. Calcd for C$_{19}$H$_{26}$OSi: C, 75.94; H 9.39. Found: C, 75.71; H, 9.24.

**Compound 3eo:** Colorless oil. $^1$H NMR (CDCl$_3$) $\delta$ 1.12 (br s, 21H), 1.48 (s, 6H), 1.77 (s, 1H, $\text{O}H$), 7.02 (s, 1H), 7.23–7.35 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ 11.5, 18.8, 30.8, 74.1, 91.3, 108.2, 127.4, 128.1, 128.9, 133.4, 135.9, 137.1. Anal. Calcd for C$_{22}$H$_{34}$OSi: C, 77.13; H 10.00. Found: C, 76.74; H, 10.16.
Compound 3gm: Colorless oil. $^1$H NMR (CDCl$_3$) δ 0.92 (t, $J = 7.6$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H), 1.41 (sext, $J = 7.3$ Hz, 2H), 1.61 (sext, $J = 7.3$ Hz, 2H), 2.10 (dt, $J = 7.6, 7.3$ Hz, 2H), 2.19 (t, $J = 7.3$ Hz, 2H), 6.10 (t, $J = 7.6$ Hz, 1H), 7.34–7.42 (m, 9H), 7.63–7.69 (m, 6H); $^{13}$C NMR (CDCl$_3$) δ 13.9, 14.1, 21.8, 22.5, 30.6, 32.6, 85.4, 112.7, 123.2, 128.0, 129.9, 134.3, 135.7, 140.9. Anal. Calcd for C$_{28}$H$_{30}$Si: C, 85.22; H, 7.66. Found: C, 85.08; H, 7.69.

Compound 3hm: Colorless oil. $^1$H NMR (CDCl$_3$) δ 3.35 (s, 3H), 3.38 (s, 3H), 4.09 (s, 2H), 4.13 (d, $J = 6.4$ Hz, 2H), 6.37 (t, $J = 6.4$ Hz, 1H), 7.35–7.43 (m, 9H), 7.64–7.70 (m, 6H); $^{13}$C NMR (CDCl$_3$) δ 58.3, 58.5, 68.6, 70.1, 88.9, 109.6, 122.7, 128.1, 130.0, 133.7, 135.7, 140.1. Anal. Calcd for C$_{26}$H$_{26}$O$_2$Si: C, 78.35; H 6.58. Found: C, 78.25; H, 6.52.

Compound 3im: White solid. $^1$H NMR (CDCl$_3$) δ 2.37 (s, 3H), 3.72 (s, 3H), 6.24 (s, 1H), 7.35–7.46 (m, 9H), 7.61–7.66 (m, 6H); $^{13}$C NMR (CDCl$_3$) δ 19.8, 51.5, 94.3, 110.5, 125.7, 128.2, 130.3, 133.0, 135.7, 137.4, 166.4. Anal. Calcd for C$_{25}$H$_{22}$O$_2$Si: C, 78.50; H 5.80. Found: C, 78.69; H, 5.65.
Preparation of alkynylrhodium(I) complex 6.

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\frac{1}{2}[\text{Rh(OH)}(\text{R-binap})]_2 + \text{HSiPh}_3 \rightarrow \begin{array}{c}
\text{PPh}_3 \\
\text{toluene} \\
80 ^\circ C, 1 \text{ h}
\end{array}
\]

A mixture of \([\text{Rh(OH)}(\text{R-binap})]_2\) (5) (74.3 mg, 0.100 mmol of Rh), (triphenylsilyl)acetylene (42.7 mg, 0.150 mmol), and \(\text{PPh}_3\) (31.5 mg, 0.120 mmol) in toluene (1.0 mL) was heated at 80 °C for 1 h under argon with stirring. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting orange solid was washed with hexane (5 mL x 3) and dried under vacuum. Dissolution of the crude mixture in toluene (2 mL) and layering with hexane (4 mL) gave orange crystals of 6. The crystals were washed with hexane and dried under vacuum. The yield of 6 was 86% (109.0 mg, 0.086 mmol). Complex 6: Orange crystals. \(^{31}\text{P NMR (C}_6\text{D}_6)\) δ 32.6 (ddd, \(^2J_{\text{P-P,trans}} = 332\) Hz, \(^1J_{\text{Rh-P}} = 153\) Hz, \(^2J_{\text{P-P, cis}} = 43\) Hz), 35.5 (ddd, \(^2J_{\text{P-P,trans}} = 332\) Hz, \(^1J_{\text{Rh-P}} = 149\) Hz, \(^2J_{\text{P-P, cis}} = 31\) Hz), 37.8 (ddd, \(^1J_{\text{Rh-P}} = 132\) Hz, \(^2J_{\text{P-P, cis}} = 43\) Hz, \(^2J_{\text{P-P, cis}} = 31\) Hz). Anal. Calcd for \(\text{C}_{82}\text{H}_{62}\text{P}_3\text{RhSi}:\) C, 77.47; H, 4.92. Found: C, 77.18; H, 4.93.
Preparation of \(^{13}\)C-labeled alkynes 7-\(^{13}\)C. Alkynes 7-\(^{13}\)C(\(\alpha\)) and 7-\(^{13}\)C(\(\beta\)) were prepared by the following procedures using \(^{13}\)C-labeled methyl Grignard reagent.

\[\text{PhCl} \quad \text{PhOCl} \quad \text{MeNH(OMe)} \cdot \text{HCl} \quad \text{pyridine, 0 °C~rt, 1 h}\]  \[\text{PhCl} \quad \text{PhOCl} \quad \text{MeNH(OMe)} \cdot \text{HCl} \quad \text{pyridine, 0 °C~rt, 1 h}\]

**Compound s3:** To a mixture of \(s1\) (2.65 g, 10.0 mmol) and \(N,O\)-dimethylhydroxylamine hydrochloride (1.95 g, 20.0 mmol) in \(\text{CHCl}_3\) (20 mL) was added dropwise pyridine (1.58 g, 20.0 mmol) at 0 °C. After completion of the addition, the cooling bath was removed and the mixture was allowed to stir at room temperature for 2 h. The mixture was quenched with \(\text{H}_2\text{O}\) and extracted with \(\text{Et}_2\text{O}\). The combined organic layer was washed with brine, dried over \(\text{Na}_2\text{SO}_4\), filtered, and concentrated on a rotary evaporator. The crude \(s2\) was dissolved in \(\text{MeOH}\) (20 mL) and the solution was heated under reflux for 3 h. After concentration of the reaction mixture on a rotary evaporator, the residue was subjected to column chromatography on silica gel with \(\text{EtOAc-hexane (1/3)}\) as an eluent to give \(s3\) (1.67 g, 5.85 mmol, 59%).

**Compound s4:** To a solution of \(s3\) (2.00 g, 7.00 mmol) in THF (7 mL) was added dropwise \(\text{MeMgI (or} \quad \text{*MeMgI)}\) solution, which was prepared from \(\text{MeI}\) (1.00 g, 7.00 mmol) and \(\text{Mg}\) (204 mg, 8.40 mg atom) in \(\text{Et}_2\text{O}\) (3 mL), at 0 °C under \(\text{N}_2\), and then the mixture was allowed to stir at room temperature for 2 h. The mixture was quenched with \(\text{H}_2\text{O}\) and extracted with \(\text{Et}_2\text{O}\). The combined organic layer was washed with brine, dried over \(\text{Na}_2\text{SO}_4\), filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography.
on silica gel with EtOAc-hexane (1/15) as an eluent to give \textbf{s4} [7473-97-4] (1.20 g, 4.99 mmol, 71%). For preparation of \textbf{s4}, \textsuperscript{13}C, \textsuperscript{13}C-labeled MeI (90% \textsuperscript{13}C) was used.

\textbf{Compound s5}: To a solution of \textbf{s4} (1.20 g, 5.00 mmol) in THF (5 mL) at \textsuperscript{−}78 °C was added dropwise KHMDS (0.50 M in toluene, 12 mL, 6.0 mmol), and the mixture was allowed to stir at this temperature for 2 h. To the mixture was added \textsubscript{N}N-bis(trifluoromethylsulfonyl)-2-aminopyridine (2.10 g, 6.00 mmol), and the mixture was warmed to room temperature. After stirring for 12 h, the mixture was quenched with H\textsubscript{2}O and extracted with Et\textsubscript{2}O. The combined organic layer was washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (1/20) as an eluent to give \textbf{s5} (1.79 g, 4.16 mmol, 96%).

\textbf{Compound s5}: Colorless oil. \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \(\delta\) 3.08 (s, 3H), 5.43 (d, \(J = 3.9\) Hz, 1H), 5.55 (d, \(J = 3.9\) Hz, 1H), 7.32–7.41 (m, 6H), 7.42–7.48 (m, 4H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}) \(\delta\) 52.6, 85.5, 104.4, 118.7 (q, \(J_{C-F} = 319\) Hz), 128.3, 128.5, 129.1, 138.2, 156.5. Anal. Calcd for C\textsubscript{17}H\textsubscript{15}F\textsubscript{3}O\textsubscript{2}S: C, 54.83; H, 4.06. Found: C, 55.02; H, 4.15.

\begin{center}
\textbf{s5} \textsuperscript{13}C
\end{center}

\textbf{Compound s6}: To a solution of diisopropylamine (1.40 mL, 9.60 mmol) in THF (9 mL) at 0 °C was added dropwise n-BuLi (1.57 M in hexane, 6.11 mL, 9.60 mmol) and the mixture was allowed to stir for 20 min. Then, the mixture was cooled to \textsuperscript{−}78 °C and \textbf{s5} (1.79 g, 4.79 mmol) in THF (5 mL) was added. After stirring for 2 h, the mixture was quenched with H\textsubscript{2}O and extracted with Et\textsubscript{2}O. The combined organic layer was washed with brine, dried

\begin{center}
S-8
\end{center}
over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (1/20) as an eluent to give **s6 [13632-79-6]** (950 mg, 4.25 mmol, 89%).

**Compound s7:** To a solution of **s6** (950 mg, 4.25 mmol) in THF at –20 °C was slowly added n-BuLi (1.57 M in THF, 3.25 mL, 5.10 mmol) with stirring. After 2 h, chlorotriphenylsilane (1.53 g, 5.10 mmol) was added and the mixture was warmed to room temperature. After stirring for 3 h, the mixture was quenched with H₂O and extracted with Et₂O. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (1/10) as an eluent to give **s7** (2.00 g, 4.16 mmol, 98%).

**Compound s7:** White solid. ¹H NMR (CDCl₃) δ 3.42 (s, 3H), 7.22–7.26 (m, 2H), 7.27–7.33 (m, 4H), 7.27–7.33 (m, 4H), 7.36 (t, J = 7.6 Hz, 6H), 7.40–7.45 (m, 3H), 7.60 (d, J = 7.6 Hz, 4H), 7.66 (d, J = 7.6 Hz, 6H); ¹³C NMR (CDCl₃) δ 53.0, 81.7, 90.1, 109.6, 126.9, 127.8, 128.2, 128.3, 130.2, 133.4, 135.7, 143.0. Anal. Calcd for C₃₄H₂₈OSi: C, 84.96; H 5.87. Found: C, 84.73; H, 5.78.

**Compound s8 (7-¹³C(β)):** A solution of **s7** (2.00 g, 4.20 mmol) in AcOH/H₂O (5/1, 33 mL) was heated at 100 °C for 30 min. Solvents were removed by a rotary evaporator, and the residue was subjected to column chromatography on silica gel with EtOAc-hexane (1/10) as an eluent to give **s8** (1.48 g, 3.15 mmol, 76%).
Compound s8: White solid. $^1$H NMR (CDCl$_3$) $\delta$ 3.05 (s, 1H), 7.16–7.22 (m, 2H), 7.22–7.28 (m, 4H), 7.29–7.39 (m, 9H), 7.60–7.69 (m, 10H); $^{13}$C NMR (CDCl$_3$) $\delta$ 75.1, 87.5, 112.7, 126.2, 127.9, 128.1, 128.4, 130.2, 133.2, 135.7, 144.6. Anal. Calcd for C$_{33}$H$_{26}$OSi: C, 84.94; H 5.62. Found: C, 84.72; H, 5.55.

Compound s10: To a solution of s8 (1.47 g, 3.15 mmol) in THF (12 mL) was added TBAF (1.0 M in THF, 3.4 mL, 3.4 mmol) at 0 °C. After stirring for 3 h, the mixture was quenched with H$_2$O and extracted with Et$_2$O. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue was passed through a short column of silica gel with EtOAc-hexane (1/10) as an eluent to give s9 [3923-52-2]. To the crude s9 in THF (6 mL) was added NaH (60% oil dispersion, 4.65 mmol) and the mixture was stirred at room temperature for 30 min. $^3$BuMe$_2$SiCl (701 mg, 4.65 mmol) and Bu$_4$NI (111 mg, 0.30 mmol) were added, and after 3 h, the mixture was quenched with H$_2$O and extracted with Et$_2$O. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (1/10) as an eluent to give s10 (960 mg, 2.97 mmol, 94% based on s8 employed).

Compound s10: White solid. $^1$H NMR (CDCl$_3$) $\delta$ 0.12 (s, 6H), 1.08 (s, 9H), 2.98 (s, 1H), 7.32 (t, $J$ = 7.3 Hz, 2H), 7.39 (t, $J$ = 7.3 Hz, 4H), 7.68 (t, $J$ = 7.3 Hz, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ –3.1, 18.7, 26.2, 75.5, 77.3, 86.6, 126.3, 127.4, 128.1, 146.5. Anal. Calcd for C$_{21}$H$_{26}$OSi: C, 78.21; H 8.13. Found: C, 78.50; H, 8.27.
Compound s14: All reaction steps were monitored by TLC (silica gel). To a solution of s10 (968 mg, 3.00 mmol) in THF (5 mL) at –20 °C was added n-BuLi (1.57 M in THF, 2.30 mL, 3.61 mmol) and the mixture was allowed to stir for 30 min. The mixture was warmed to 0 °C and benzophenone (655 mg, 3.60 mmol) was added. After 30 min, the mixture was quenched with H₂O and extracted with Et₂O. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue was passed through a short column of silica gel with EtOAc-hexane (1/9) as an eluent. After evaporation of the solvent, the crude s11 was dissolved in THF (6 mL), and NaH (60% oil dispersion, 4.40 mmol) was added at 0 °C. After 30 min, MeI (625 mg, 4.40 mmol) was added at 0 °C. After 30 min, NaH (60% dispersion) was added to the mixture, and the mixture was warmed to 0 °C and benzophenone (655 mg, 3.60 mmol) was added. After 30 min, the mixture was quenched with H₂O and extracted with Et₂O. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. To the crude s12 in THF (6 mL) was added TBAF solution (1.0 M in THF, 3.0 mL, 3.0 mmol) at 0 °C, and after 1 h, the mixture was quenched with H₂O and extracted with Et₂O. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue was passed through a short column of silica gel with EtOAc-hexane (1/4) as an eluent. To the crude s13 in toluene (3 mL) was added powdered NaOH (120 mg, 3.00 mmol), and the mixture was heated at 110 °C for 3 h. The mixture was quenched with H₂O and extracted with Et₂O. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The residue was subjected to column chromatography on silica gel with hexane as an eluent to give s14 as colorless oil (552 mg, 2.49 mmol, 83% based on s10 employed).
Compound s16 (7-13C(α)): This compound was prepared by the same procedure as compound s8. Compounds s6, s7, and s8 were the same as s14, s15, and s16, respectively, when they do not contain a 13C-enriched carbon atom.

**Preparation of alkynylrhodium(I) complex 6-13C(α).**

A mixture of [Rh(OH)((R)-binap)]2 (5) (150 mg, 0.202 mmol of Rh), alkyne 7-13C(α) (142 mg, 0.304 mmol), and PPh3 (78.7 mg, 0.300 mmol) in degassed toluene (5.0 mL) was heated at 80 °C for 3 h under N2 with stirring. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting orange solid was washed with degassed hexane (2 mL x 2) and dried under vacuum. Dissolution of the crude mixture in toluene (2 mL) and layering with hexane (4 mL) gave orange crystals of 6-13C(α). The crystals were washed with hexane and dried under vacuum. The yield of 6-13C(α) was 76% (196 mg, 0.154 mmol). Complex 6-13C(α): 31P NMR (C6D6) δ 32.6 (dddd, 2J_P,P_cis = 332 Hz, 1J_Rh,P = 153 Hz, 2J_P,P_cis = 43 Hz, 2J_C,P_cis = 21 Hz), 35.5 (dddd, 2J_P,P_cis = 332 Hz, 1J_Rh,P = 149 Hz, 2J_P,P_cis = 31 Hz, 2J_C,P_cis = 22 Hz), 37.8 (dddd, 1J_Rh,P = 132 Hz, 2J_C,P_trans = 92 Hz 2J_P,P_cis = 43 Hz, 2J_P,P_cis = 31 Hz).

13C NMR (C6D6) δ 155.0 (dddd, 2J_P,C_trans = 92 Hz, 1J_Rh,C = 43 Hz, 2J_P,C_cis = 22 Hz, 2J_P,C_cis = 21 Hz, C(α)).

31P NMR (C6D6)
Preparation of alkylnylrhodium(I)-complex $^{13}$C(β).

The complex $^{6-13}$C(β) was prepared by the same procedure as the complex $^{6-13}$C(α) using alcohol $^{7-13}$C(β). Complex $^{6-13}$C(β): $^{31}$P NMR (C$_6$D$_6$) δ 32.6 (ddddd, $^2$J$_{P,C,trans}$ = 332 Hz, $^1$J$_{Rh,P}$ = 153 Hz, $^2$J$_{P,P,cis}$ = 43 Hz, $^3$J$_{C,P,cis}$ = 4 Hz), 35.5 (ddddd, $^2$J$_{P,P,trans}$ = 332 Hz, $^1$J$_{Rh,P}$ = 149 Hz, $^2$J$_{P,P,cis}$ = 31 Hz, $^3$J$_{C,P,cis}$ = 2 Hz), 37.8 (ddddd, $^2$J$_{Rh,P}$ = 132 Hz, $^3$J$_{P,P,cis}$ = 43 Hz, $^2$J$_{P,P,cis}$ = 31 Hz, $^3$J$_{C,P,trans}$ = 22 Hz). $^{13}$C NMR (C$_6$D$_6$) δ 117.7 (ddddd, $^3$J$_{P,C,trans}$ = 22 Hz, $^2$J$_{Rh,C}$ = 10 Hz, $^3$J$_{P,C,cis}$ = 4 Hz, $^3$J$_{P,C,cis}$ = 2 Hz, C(α)).

$^{31}$P NMR (C$_6$D$_6$)
Stoichiometric reaction of 1-phenyl-1-propyne (1a) with complex 6 in the presence of acetic acid in an NMR tube (eq 4). To a solution of complex 6 (25.4 mg, 0.020 mmol) in 1,4-dioxane (0.50 mL) in an NMR tube was added 1-phenyl-1-propyne (1a) (2.3 mg, 0.020 mmol) and acetic acid (1.2 mg, 0.020 mmol). Then, the mixture was heated at 80 °C (bath temp.). After 20 h, complete conversion of complex 6 was observed by $^{31}$P NMR. The mixture was passed through a short silica gel column eluting with Et$_2$O. The yield of the products (78% yield, $\text{3am/4am} = 90/10$) was determined by $^1$H NMR using 1,4-dimethoxybenzene as an internal standard.

Catalytic reaction of 1-phenyl-1-propyne (1a) with (triphenylsilyl)acetylene (2m) in the presence of alkynylrhodium-complex 6 (eq 5). To a solution of complex 6 (12.7 mg, 0.010 mmol) in 1,4-dioxane (0.40 mL) in a screw cap test tube was added (triphenylsilyl)acetylene (2m) (113.8 mg, 0.40 mmol) and 1-phenyl-1-propyne (1a) (23.2 mg, 0.20 mmol) successively, and the tube was capped tightly. Then, the mixture was allowed to stir at 80 °C (bath temp.) for 3 h. The reaction mixture was cooled to room temperature and was passed through a short silica gel column eluting with Et$_2$O. After evaporation of the solvent, the residue was purified by preparative TLC (silica gel, hexane/ethyl acetate = 25/1) gave the adducts (95% yield, $\text{3am/4am} = 91/9$).
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 125 MHz)