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Formal Gold- and Rhodium-Catalyzed Regiodivergent C−H Alkynylation of 2-Pyridones

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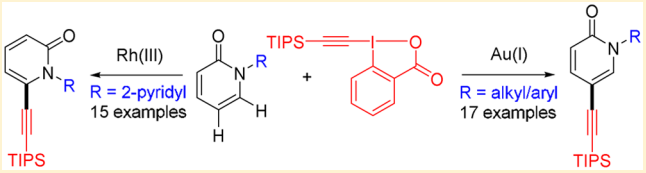
Supporting Information

ABSTRACT: Formal regiodivergent C−H alkynylation of 2-pyridones bearing different *N*-substituents has been realized under Au(I) and Rh(III) catalysis using a hypervalent iodine alkyne reagent. When catalyzed by Au(I), the alkynylation occurred at the most electron-rich 5-position via an electrophilic alkynylation pathway. The selectivity was switched to the 6-position under assistance of an *N*-chelation group when a Rh(III) catalyst was employed. A rhodacylic complex has been isolated as a key intermediate.



Transition-metal-catalyzed C−H activation is a rapidly evolving area that has attracted increasing attention over the past decades.[1] The C−H activation strategy has allowed both facile construction and derivatization of a large number of heterocycles that are known to exhibit biological activities.[2] Despite the great progress, the selective activation of a specific C−H bond remains a challenge, and ideally, different selectivities are controllable under different catalytic conditions, where this switch of selectivity may be correlated to different reaction mechanisms.

On the other hand, the 2-pyridone scaffold is a key structural motif widely found in a variety of natural and bioactive compounds.[3] While a number of synthetic methods have been reported for the facile construction of the 2-pyridone rings using different transition metals,[4] selective C−H functionalization of 2-pyridone rings can be challenging. In 2009, Nakao and Hiyama reported the selective functionalization of 2-pyridones at the 6-position with the assistance of a Lewis acid additive.[5] Later, Gallagher achieved oxidative C−H olefination of a specific 2-pyridone at the 3-position.[6] In 2012, we have reported both oxidative olefination and arylation at the 3- and 5-positions, and the selectivity can vary with the substituent in the 2-pyridone ring (substrate control).[7] In 2014, the Miura group achieved the arylation of 2-pyridones at the 3-position via a radical pathway.[8] In addition, Miura also realized the copper-catalyzed arylation of 2-pyridones at the 6-position,[9] in which the coupling proceeded via a chelation-assisted C−H activation mechanism. Despite the progress, it remains distinctly challenging to selectively control and switch the site selectivity of 2-pyridones due to the electronic and steric similarity of C−H bonds in this substrate.

Different selectivities of C−H functionalization of indoles (C-2 and C-3) and other heterocycles have been extensively studied and offered important inspirations.[10] Driven by the need to achieve diversified and switchable selectivity of diverse heterocycles, we aimed to explore the C−H alkynylation of 2-pyridones. Waser et al. demonstrated that electron-rich heterocycles reacted at the most electron-rich site with hypervalent iodine alkynes and the reaction occurred via an electrophilic alkynylation mechanism.[11] We reasoned that the intrinsic electronic effect of the 2-pyridone rings may also allow the alkynylation to occur with distinct site selectivity. On the other hand, we and others have demonstrated that this alkynylating reagent can undergo facile coupling with both electron-rich and electron-poor arenes via a Rh(III)- and Ir(III)-catalyzed C−H activation mechanism.[12] The combination of these two distinct mechanisms should allow the controllable switch of the site selectivity. We now report the Au(I)- and Rh(III)-catalyzed C−H alkynylation of 2-pyridones at the 5- and 6-positions, respectively.

We initiated our C−H alkynylation studies with the optimization of the reaction conditions for the coupling of *N*-methyl 2-pyridone (**1a**) with 1-(triisopropylsilyl)ethynyl-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX, **2a**), and the results are given in Table 1. Au(I) catalysts were our first choice because Waser et al. demonstrated that Au(I) species displayed high activity in the alkynylation of a variety of electron-rich heteroarens.[11] However, using AuCl as the catalyst in the absence of any additive gave essentially no conversion (50 °C). The desired product **3a** was observed when $Zn(OTf)_2$ was introduced as an additive (entry 2).[11,12e] This product was fully characterized, and the alkynylation occurred exclusively at the most electron-rich 5-position. The observed site selectivity agrees with previous reports.[6,7,13] The yield was slightly improved when the Zn(II) additive was replaced by a stoichiometric amount of TFA,[11c] which likely activated both the catalyst and the alkynylating reagent, and the optimal amount of TFA was found to be 1.5 equiv (entries 3−5). Screening of solvents revealed 1,4-dioxane as the optimal one. The reaction was strongly temperature-dependent. Thus, increasing the temperature to 80 °C produced **3a** in 92% isolated yield (entry 7). In contrast to the high efficiency of

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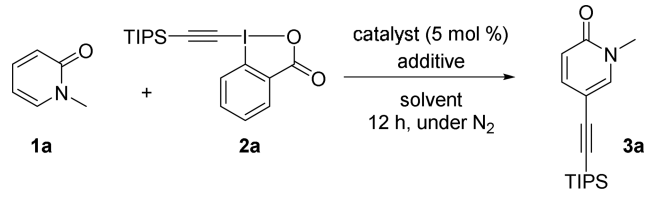
Table 1. Optimization Studies[a]



entry	catalyst (mol %)	additive (equiv)	solvent	temp (°C)	yield (%)[b]
1[d]	AuCl (5)	none	MeCN	50	0
2[d]	AuCl (5)	$Zn(OTf)_2$ (0.2)	MeCN	50	25
3	AuCl (5)	TFA (1)	MeCN	50	34
4	AuCl (5)	TFA (3)	MeCN	50	35
5	AuCl (5)	TFA (1.5)	MeCN	50	46
6	AuCl (5)	TFA (1.5)	dioxane	50	58
7	AuCl (5)	TFA (1.5)	dioxane	80	92
8	$AuCl_3$ (5)	TFA (1.5)	MeCN	50	<5
9	$Au(PPh_3)Cl$ (5)	TFA (1.5)	MeCN	50	40
10	$Pd(OAc)_2$ (5)	TFA (1.5)	MeCN	50	<5
11[c,d]	$Pd(OAc)_2$ (5)	AgOAc (2)	dioxane	80	30

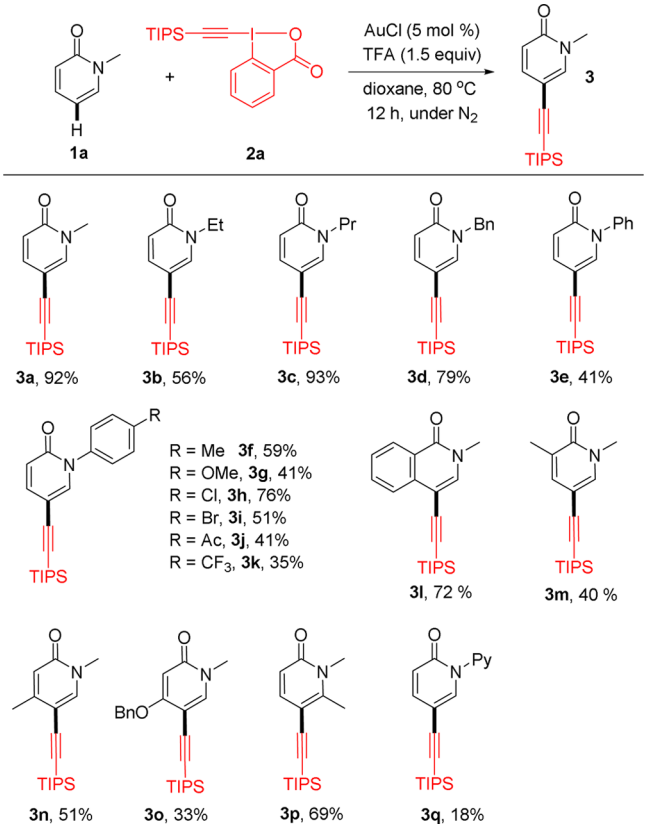
[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), AuCl (5 mol %), TFA (0.3 mmol), 1,4-dioxane (2.0 mL), 80 °C, 12 h, sealed tube under nitrogen. [b]Isolated yield after column chromatography. [c](Bromoethynyl)triisopropylsilane was used instead of **2a**. [d]Without TFA.

AuCl, other Au(I) and Au(III) catalysts only gave inferior results (entries 8, 9). Although palladium catalysts are among the first reported catalysts that can catalyze the alkynylative coupling between electron-rich heteroarenes and bromoalkynes,[14] using $Pd(OAc)_2$ as a catalyst only gave poor conversions (entries 10, 11).

Having determined the optimal conditions, we next examined the scope and limitations of this coupling system (Scheme 1). Extension of the *N*-alkyl group has been successful, and a series of products were isolated in good to high yields (**3a**–**3d**). *N*-Aryl substituted 2-pyridones also underwent smooth coupling, albeit in lower yields. The reduced yields might be attributed to the lower nucleophilicity of substrates. However, we did not observe the electronic effect of the *N*-aryl substituent on the reaction yields. Various substituents on the pyridine ring are also tolerated. The coupling of an isoquinolone afforded the desired product (**3l**) in 72% yield. Introduction of different substituents into the 3-, 4-, and 6-positions is well-tolerated, and the isolation of **3n** and **3p** in good yields indicates tolerance of steric hindrance. In contrast, the coupling between *N*-(2-pyridyl)pyridone and TIPS-EBX proceeded with low efficiency (**3q**).

We next turned to alkynylation of 2-pyridones assisted by an *N*-directing group. We reasoned that, in this case, the reaction may proceed via a chelation-assisted C–H activation pathway,[9] leading to C(6)-alkynylation. Indeed, by following the Rh(III)-catalyzed C–H alkynylation conditions that we have reported,[12e] the coupling of *N*-(2-pyridyl)pyridone with TIPS-EBX proceeded smoothly at 80 °C, and the coupled product **5aa** was isolated in 95% yield (Scheme 2). ^1H NMR analyses of the product confirmed the C(6)-selectivity, indicating a switch of the reaction mechanism. The scope of this coupling was next explored. Both electron-donating and electron-withdrawing groups at 3-, 4-, and 5-positions are tolerated. However, the substrate with a 5-methyl group failed to give the desired product. In line with the Au-catalyzed system, the 2-isoquinolone substrate also reacted with high efficiency (**5la**). Variation of the substituents at different positions of the pyridine ring revealed that the reaction was marginally affected, indicating that the electronic effects of the directing group had limited influence (**5ha**–**5ka**). The directing group is not limited to a pyridine ring, and the alkynyation of

Scheme 1. Au(I)-Catalyzed C5-Alkynylation of 2-Pyridone[a,b]



[a]Reaction conditions: 2-pyridone (0.20 mmol), TIPS-EBX (0.24 mmol), AuCl (5 mol %), TFA (0.3 mmol), dioxane (2.0 mL), 80 °C, 12 h, sealed tube under nitrogen. [b]Isolated yield after column chromatography.

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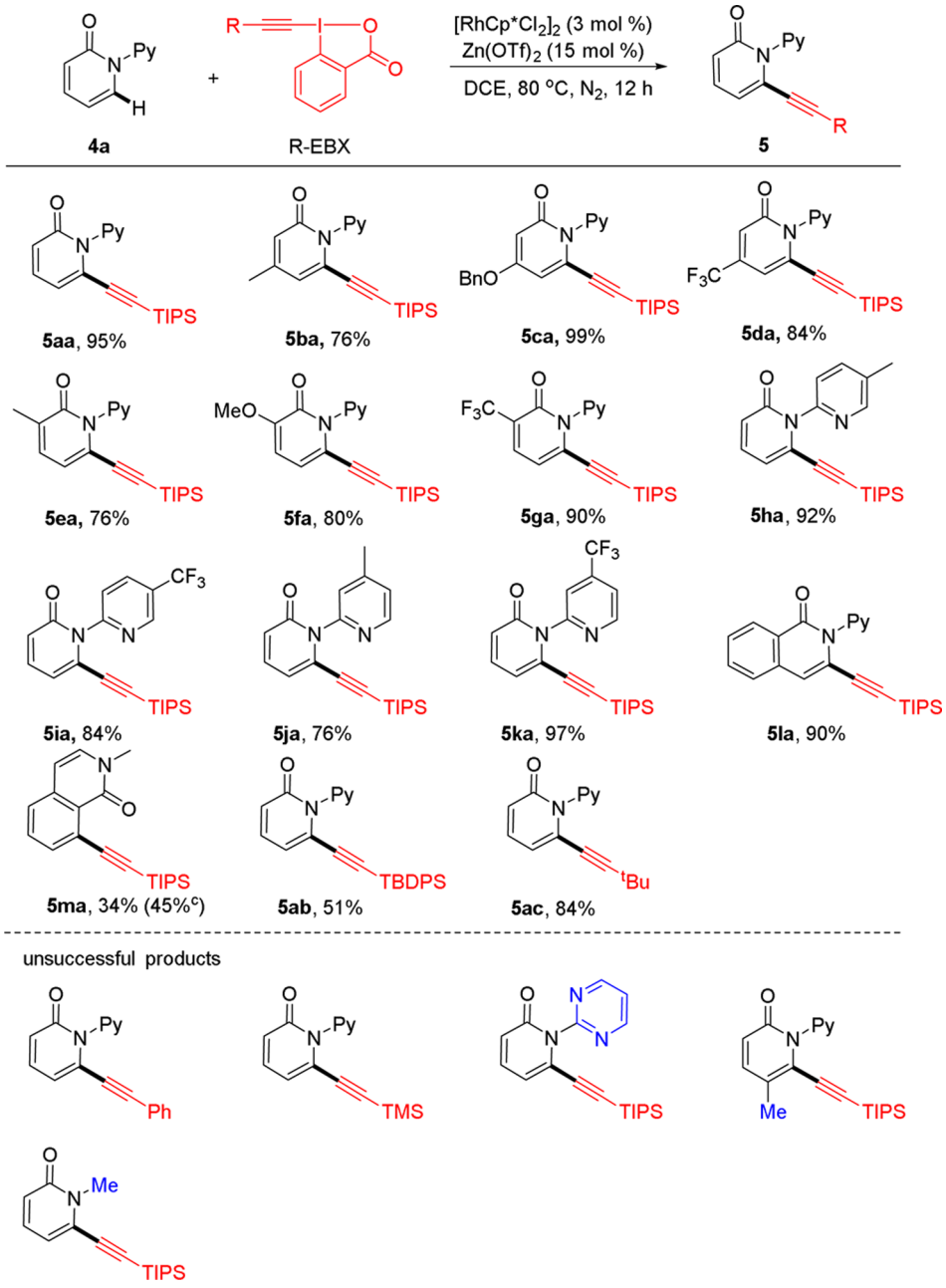
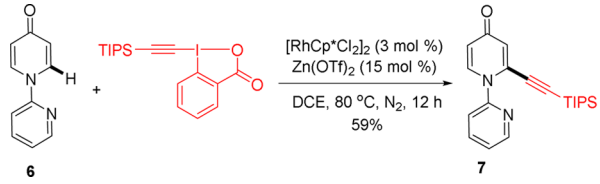
Scheme 2. Rh(III)-Catalyzed Alkynylation of 2-Pyridones under Chelation Assistance[a,b]



[a]Reaction conditions: 2-pyridone (0.20 mmol), TIPS-EBX (0.24 mmol), $[RhCp^*Cl_2]_2$ (3 mol %), $Zn(OTf)_2$ (15 mol %), DCE (2.0 mL), 80 °C, 12 h, pressure tube under nitrogen. [b]Isolated yield after column chromatography. [c]$[RhCp^*(MeCN)_3](SbF_6)_2$ (8 mol %), DCM (2.0 mL), 80 °C, 12 h.

N-methylisoquinolone occurred at the *peri* position in moderate yield (**5ma**). The choice of a directing group is essential, and the 2-pyrimidyl ring failed to function as a directing group. The reaction also failed when *N*-methyl 2-pyridone was applied, indicating that the rhodium- and the gold-catalyzed reaction conditions are not switchable. The alkynylating reagent could be extended to TBDPS-EBX and ^{t}Bu-EBX, although TMS- and Ph-EBX both failed to give the desired products, likely due to lack of steric protection.[12e]

In addition to 2-pyridones, we also examined the alkynylation of a structurally related 4-pyridone substrate (**6**).[10b] Under the same Rh(III)-catalyzed conditions, the coupling of *N*-(2-pyridyl)-4-pyridone with TIPS-EBX afforded product **7** in 59% yield (eq 1), where essentially no dialkynylation was detected.



(1)

Mechanistic studies have been performed (Scheme 3). To probe the Au(I)-catalyzed catalytic mechanism, H/D exchange was performed first (Scheme 3a). H/D exchange of **1a** has been attempted under Au(I) catalysis using CD_3COOD as the deuterium source. However, essentially no exchange has been

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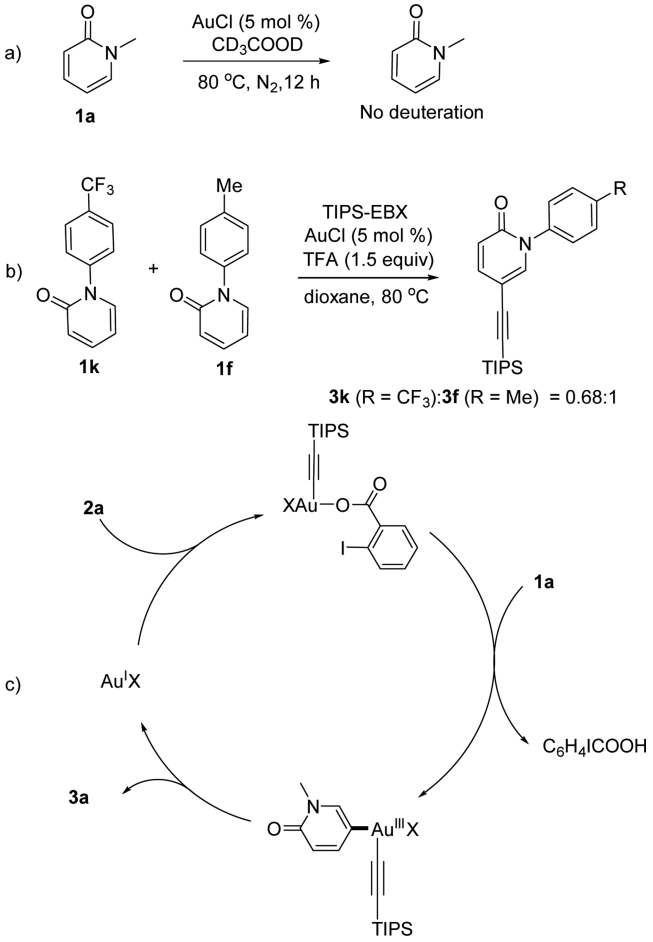
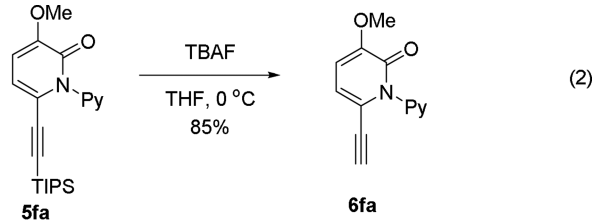
Scheme 3. Mechanistic Consideration of Au-Catalyzed Alkynylation



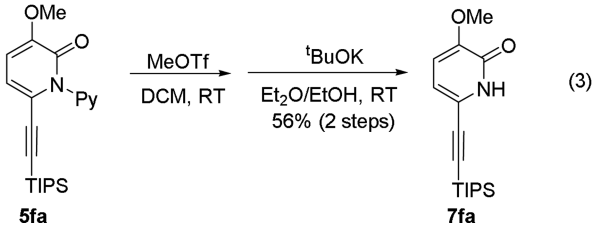
detected. Then, the competition between **1k** and **1f** differing in electronic effect of the *N*-aryl group under the Au(I)-catalyzed conditions afforded **3ka** and **3fa** in a 0.68:1 ratio (Scheme 3b), indicating that an electron-donating group tends to favor the reaction. In a proposed mechanism of Au-catalyzed C−H alkynylation of 2-pyridone **1a**, it is likely that **1a** does not directly undergo auration. It may nucleophilically attack a Au(III) alkynyl intermediate generated from oxidative addition of a Au(I) species (oxidative addition−electrophilic auration mechanism, Scheme 3c).[11b] Alternatively, it might act as a nucleophile to attack the activated alkyne (π-activation mechanism).[11b]

In contrast, the Rh(III)-catalyzed H/D exchange of **4f** in the presence of CD_3COOD was observed at the 6-position (D 50%), indicating the relevancy of C−H activation (Scheme 4a). To further explore the C−H activation process, **4a** was allowed to react with a stoichiometric amount of $[RhCp^*Cl_2]_2$ in the presence of NaOAc (Scheme 4b). Although the reaction failed to go to completion, rhodacyle **8** was isolated in 40% yield after column chromatography and was fully characterized. In particular, the Rh-*C* resonates characteristically at δ = 184 as a doublet in the ^{13}C NMR spectrum. Complex **8** proved to be an active intermediate because, when catalyzed by **8** (6 mol %), the coupling of **4f** with TIPS-EBX afforded the product **5fa** in 82% yield (Scheme 4c). Next, several substrate competition reactions were carried out. In the competition between **4f** and **4g** under the Rh(III) conditions (Scheme 4d), the more electron-rich substrate **4f** also reacted at a higher rate. In a competition reaction between **4a** and a typical a 2-arylpyridine (**9**, Scheme 4e), the 2-pyridone **4a** reacted at a slightly higher rate, indicative of the comparable reactivity of these two substrates. On the basis of the preliminary results and literature precedents,[11,12] a plausible mechanism of the Rh(III)-catalyzed C−H alkynylation reaction is given in Scheme 4f. Cyclometalation of 2-pyridone **4a** gives a rhodacycle **A**. Subsequent oxidative addition of the C−I bond in the R-EBX reagent affords a Rh(V) alkynyl benzoate intermediate **B**, which undergoes C−C reductive elimination to release the alkynylated product together with a Rh(III) benzoate intermediate **C**. Protonolysis of **C** released the 2-iodobenzoate byproduct and regenerated the Rh(III) catalyst.

Derivatization of the coupled product has been performed to demonstrate the synthetic usefulness of this method. Treatment of **5fa** with TBAF led to facile desilylation, and the product **6fa** was isolated in 85% yield (eq 2). Treatment of **5fa** with MeOTf, followed by base treatment of the methylated intermediate, afforded the deprotected NH 2-pyridone **7fa** in 56% overall yield (eq 3). Thus, the *N*-pyridyl ring represents a removable directing group.



(2)



(3)

In summary, we have realized formal regiodivergent C−H alkynylation of different 2-pyridones under Au(I) and Rh(III) catalysis. Under the Au(I) conditions, the alkynylation occurred at the most electron-rich 5-position via an electrophilic alkynylation pathway, while the selectivity was switched to the 6-position in the presence of a Rh(III) catalyst under assistance of an *N*-chelation group. A rhodacyclic intermediate has been isolated, and this coupling occurs via a C−H activation mechanism. The switch of the regioselectivity results from different mechanisms in a combination of different substrates and metal catalysts. Future studies are directed to regiodivergent functionalization of other heteroarenes via Rh(III)-catalyzed C−H activation.

EXPERIMENTAL SECTION

General Information. All chemicals were obtained from commercial sources and were used as received unless otherwise noted. 2-Pyridones[15] and hypervalent iodine alkynes[16] were prepared by following literature reports. All reactions were carried out using Schlenk techniques or in a nitrogen-filled glovebox. NMR spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^1H and ^{13}C NMR spectroscopy. HRMS data were obtained via ESI mode with a TOF mass analyzer. Column

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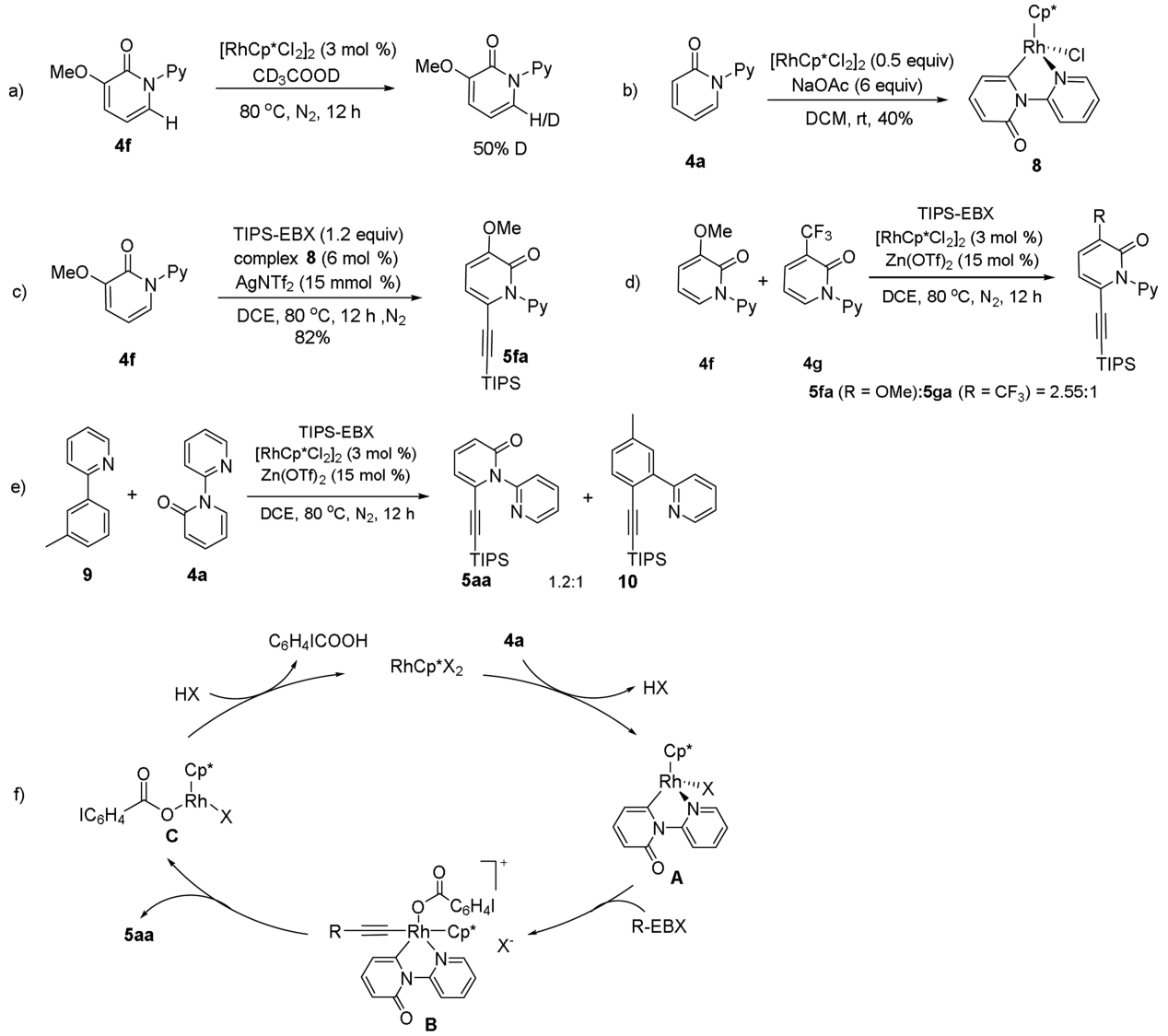
Scheme 4. Mechanistic Consideration of Rh(III)-Catalyzed Alkynylation



chromatography was performed on silica gel (300−400 mesh) using ethyl acetate (EA)/petroleum ether (PE) or MeOH/CH_2Cl_2.

General Procedure for Synthesis of 3. 1-Methylpyridin-2(1*H*)-one (0.20 mmol), alkynes (0.24 mmol), AuCl (5 mol %), TFA (0.3 mmol), and 1,4-dioxane (2 mL) were charged into a reaction tube. The reaction mixture was stirred at 80 °C for 12 h. After the mixture cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford product **3**.

1-Methyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (***3a***). Brown solid (53 mg, 92%, 0.18 mmol); mp 99−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.4 Hz, 1H), 7.42 (dd, J = 9.4, 2.4 Hz, 1H), 6.57 (d, J = 9.4 Hz, 1H), 3.60 (s, 3H), 1.16 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 142.2, 142.1, 120.2, 102.8, 102.0, 91.3, 37.7, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{28}NOSi^+$: 290.1935, found 290.1937.

1-Ethyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (***3b***). Yellow solid (34 mg, 56%, 0.11 mmol); mp 98−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 2.2 Hz, 1H), 7.40 (dd, J = 9.4, 2.3 Hz, 1H), 6.56 (d, J = 9.4 Hz, 1H), 4.04 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H), 1.17 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 141.9, 140.9, 120.6, 102.9, 102.2, 91.1, 45.2, 18.6, 14.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{30}NOSi^+$: 304.2091, found 304.2092.

1-Propyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (***3c***). Yellow solid (59 mg, 93%, 0.19 mmol); mp 101−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 2.2 Hz, 1H), 7.40 (dd, J = 9.4, 2.4 Hz, 1H), 6.56 (d, J = 9.4 Hz, 1H), 3.94 (t, J = 7.4 Hz, 2H), 1.86 (m, 2H), 1.17 (apparent s, 21H), 1.03 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 141.9, 141.3, 120.6, 102.6, 102.3, 91.1, 51.6, 22.5, 18.6, 11.2, 11.0. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{32}NOSi^+$: 318.2248, found 318.2250.

1-Benzyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (***3d***). Yellow solid (58 mg, 79%, 0.16 mmol); mp 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 2.3 Hz, 1H), 7.39−7.28 (m, 6H), 6.57 (d, J = 9.4 Hz, 1H), 5.12 (s, 2H), 1.09 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 142.3, 141.1, 135.8, 129.0, 128.2, 128.1, 120.9, 103.3, 102.1, 91.6, 52.4, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{23}H_{32}NOSi^+$: 366.2248, found 366.2250.

1-Phenyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (***3e***). Yellow solid (29 mg, 41%, 0.082 mmol); mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 2.4 Hz, 1H), 7.52−7.48 (m, 2H), 7.46−7.41 (m, 2H), 7.39−7.36 (m, 2H), 6.60 (d, J = 9.5 Hz, 1H), 1.10 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 142.7, 141.8, 140.3, 129.5, 128.9, 126.6, 121.4, 103.2, 101.8, 91.9, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{30}NOSi^+$: 352.2091, found 352.2096.

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1-(p-Tolyl)-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3f**). Yellow solid (43 mg, 59%, 0.12 mmol); mp 100−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 2.3 Hz, 1H), 7.41 (dd, J = 9.4, 2.5 Hz, 1H), 7.30−7.23 (m, 4H), 6.59 (d, J = 9.4 Hz, 1H), 2.40 (s, 3H), 1.10 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 142.4, 142.0, 138.9, 137.8, 130.1, 126.3, 121.4, 102.8, 102.0, 91.6, 21.2, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{23}H_{32}NOSi^+$: 366.2248, found 366.2248.

1-(4-Methoxyphenyl)-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3g**). Yellow solid (31 mg, 41%, 0.082 mmol); mp 98−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 2.4 Hz, 1H), 7.42 (dd, J = 9.5, 2.5 Hz, 1H), 7.28 (dt, J = 8.8 Hz, 2.0 Hz, 2H), 6.99 (dt, J = 8.8 Hz, 2.0 Hz, 2H), 6.59 (d, J = 9.5 Hz, 1H), 3.84 (s, 3H), 1.10 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 142.5, 142.1, 133.1, 127.6, 121.3, 114.6, 102.9, 102.0, 91.7, 55.6, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{23}H_{32}NO_2Si^+$: 382.2197, found 382.2197.

1-(4-Chlorophenyl)-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3h**). Yellow solid (59 mg, 76%, 0.15 mmol); mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.4 Hz, 1H), 7.54 (dt, J = 8.6, 1.8 Hz, 2H), 7.49 (dd, J = 9.5, 2.4 Hz, 1H), 7.40 (dt, J = 8.6, 1.8 Hz, 2H), 6.66 (d, J = 9.5 Hz, 1H), 1.17 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 142.7, 141.2, 138.6, 134.8, 129.6, 127.9, 121.5, 103.3, 101.6, 92.1, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{29}ClNOSi^+$: 386.1701, found 386.1702.

1-(4-Bromophenyl)-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3i**). Yellow solid (44 mg, 51%, 0.10 mmol); mp 129−130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.62 (s, 1H), 7.52 (s, 1H), 7.43 (d, J = 9.5 Hz, 1H), 7.27 (d, J = 7.3 Hz, 2H), 6.60 (d, J = 9.5 Hz, 1H), 1.10 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 142.8, 141.2, 139.2, 132.7, 128.3, 122.9, 121.5, 103.4, 101.6, 92.2, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{29}BrNOSi^+$: 430.1196, found 430.1198.

1-(4-Acetylphenyl)-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3j**). Yellow solid (32 mg, 41%, 0.082 mmol); mp 103−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dt, J = 8.6, 1.8 Hz, 2H), 7.61 (d, J = 2.4 Hz 1H), 7.57 (dt, J = 8.6, 1.8 Hz, 2H), 7.50 (dd, J = 9.5, 2.4 Hz, 1H), 6.67 (d, J = 9.5 Hz, 1H), 2.70 (s, 3H), 1.16 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 160.7, 143.9, 142.8, 140.8, 137.0, 129.5, 126.8, 121.6, 103.5, 101.5, 92.3, 26.7, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{24}H_{32}NO_2Si^+$: 394.2197, found 394.2199.

1-(4-(Trifluoromethyl)phenyl)-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3k**). Yellow solid (29 mg, 35%, 0.070 mmol); mp 65−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.76 (s, 1H), 7.55−7.53 (m, 3H), 7.45 (dd, J = 9.5, 2.4 Hz, 1H), 6.62 (d, J = 9.5 Hz, 1H), 1.10 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 143.1, 142.9, 140.8, 131.0 (q, J = 32.9 Hz), 127.2, 126.7 (q, J = 3.8 Hz), 123.6 (q, J = 270.8 Hz), 121.7, 103.6, 101.4, 92.4, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{23}H_{29}F_3NOSi^+$: 420.1965, found 420.1970.

2-Methyl-4-((triisopropylsilyl)ethynyl)isoquinolin-1(2H)-one (**3l**). Yellow solid (49 mg, 72%, 0.14 mmol); mp 113−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, J = 8.0, 0.6 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.82−7.75 (td, J = 1.8, 0.3 Hz, 1H), 7.62−7.55 (td, J = 2.0, 0.3 Hz,1H), 7.50 (s, 1H), 3.68 (s, 3H), 1.23 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 137.3, 136.2, 132.6, 127.7, 127.4, 125.2, 125.0, 101.5, 100.8, 94.4, 37.2, 18.7, 11.3. HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{30}NOSi^+$: 340.2091, found 340.2093.

1,3-Dimethyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3m**). Yellow solid (24 mg, 40%, 0.08 mmol); mp 67−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.30 (s, 1H), 3.60 (s, 3H), 2.20 (s, 3H), 1.17 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 139.6, 139.1, 129.4, 102.6, 102.2, 90.6, 37.8, 18.6, 16.9, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{30}NOSi^+$: 304.2091, found 304.2093.

1,4-Dimethyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3n**). Yellow solid (31 mg, 51%, 0.10 mmol); mp 104−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 6.45 (s, 1H), 3.57 (s, 3H), 2.32 (s, 3H), 1.17 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 151.9, 141.5, 118.8, 104.5, 100.9, 94.2, 37.2, 20.6, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{30}NOSi^+$: 304.2091, found 304.2091.

4-(Benzyloxy)-1-methyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3o**). Yellow solid (26 mg, 33%, 0.066 mmol); mp 121−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.50−7.48 (m, 2H), 7.44−7.38 (m, 3H), 6.03 (s, 1H), 5.08 (s, 2H), 3.55 (s, 3H), 1.12 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 142.3, 135.0, 128.5, 128.2, 127.5, 98.4, 98.1, 97.5, 94.7, 70.3, 36.9, 18.5, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{24}H_{34}NO_2Si^+$: 396.2353, found 396.2354.

1,6-Dimethyl-5-((triisopropylsilyl)ethynyl)pyridin-2(1H)-one (**3p**). Yellow solid (42 mg, 69%, 0.14 mmol); mp 64−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 9.4 Hz, 1H), 6.48 (d, J = 9.4 Hz, 1H), 3.61 (s, 3H), 2.65 (s, 3H), 1.17 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 150.5, 141.6, 117.0, 103.4, 102.5, 93.5, 31.8, 19.3, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{30}NOSi^+$: 304.2091, found 304.2092.

5-((Triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**3q**). Waxy yellow solid (13 mg, 18%, 0.036 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 4.7 Hz, 1H), 8.09 (d, J = 2.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.87−7.82 (m, 1H), 7.42 (dd, J = 9.5, 2.4 Hz, 1H), 7.37−7.32 (m, 1H), 6.60 (d, J = 9.5 Hz, 1H), 1.10 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 151.3, 149.1, 142.9, 140.0, 137.9, 123.5, 121.7, 121.5, 103.6, 102.0, 91.7, 18.6, 11.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{29}N_2OSi^+$: 353.2044, found 353.2045.

General Procedure for Synthesis of 5. 2*H*-[1,2′-Bipyridin]-2-one (0.2 mmol), alkynes (0.24 mmol), $[RhCp^*Cl_2]_2$ (3 mol %), $Zn(OTf)_2$ (15 mol %), and DCE (2 mL) were charged into a pressure tube. The reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the desired product **5**.

6-((Triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5aa**). White solid (67 mg, 95%, 0.19 mmol); mp 65−67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 3.8 Hz, 1H), 7.92 (td, J = 7.7, 1.9 Hz, 1H), 7.46−7.38 (m, 3H), 6.73 (dd, J = 9.3, 1.0 Hz, 1H), 6.61 (dd, J = 6.9, 1.1 Hz, 1H), 0.96 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 152.1, 149.7, 139.3, 138.3, 130.7, 124.1, 123.5, 122.7, 112.5, 101.9, 98.3, 18.3, 10.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{29}N_2OSi^+$: 353.2044, found 353.2046.

4-Methyl-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ba**). Yellow solid (56 mg, 76%, 0.15 mmol); mp 104−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 3.9 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.36−7.34 (m, 2H), 6.48 (s, 1H), 6.43 (s, 1H), 2.21 (s, 3H), 0.90 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 152.2, 151.0, 149.7, 138.3, 129.5, 124.0, 123.7, 121.0, 115.2, 101.1, 98.4, 21.2, 18.4, 10.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{31}N_2OSi^+$: 367.2200, found 367.2201.

4-(Benzyloxy)-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ca**). Yellow solid (91 mg, 99%, 0.20 mmol); mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 4.1 Hz, 1H), 7.84 (td, J = 7.8, 1.6 Hz, 1H), 7.40−7.34 (m, 7H), 6.38 (d, J = 2.5 Hz, 1H), 6.09 (d, J = 2.4 Hz, 1H), 5.04 (s, 2H), 0.89 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 164.0, 152.0, 149.7, 138.3, 135.1, 130.5, 128.8, 128.5, 127.7, 124.1, 123.9, 107.9, 101.6, 99.8, 98.0, 70.4, 18.4, 10.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{28}H_{35}N_2O_2Si^+$: 459.2462, found 459.2465.

4-(Trifluoromethyl)-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5da**). Yellow solid (71 mg, 84%, 0.17 mmol); mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.8, 1.1 Hz, 1H), 7.90 (td, J = 7.8, 1.9 Hz, 1H), 7.43−7.38 (m, 2H), 6.94 (s, 1H), 6.65 (d, J = 1.7 Hz, 1H), 0.90 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 151.4, 150.0, 141.4 (q, J = 33.9 Hz), 138.7, 132.5, 124.6,123.3, 121.8 (q, J = 272.7 Hz), 119.8 (q, J = 4.4 Hz), 107.3 (q, J = 2.8 Hz), 104.6, 97.3, 18.4, 10.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{28}F_3N_2OSi^+$: 421.1918, found 421.1919.

3-Methyl-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ea**). Yellow solid (56 mg, 76%, 0.15 mmol); mp 93−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68(dt, J = 4.8, 0.8 Hz, 1H), 7.89 (td, J = 7.7, 1.8 Hz, 1H), 7.44−7.40 (m, 2H), 7.26 (d, J = 7.0 Hz, 1H), 6.55 (d, J = 7.0 Hz, 1H), 2.22 (s, 3H), 0.94 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 152.5, 149.6, 138.2, 136.4, 132.3, 128.0, 123.9,

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123.5, 112.4, 100.5, 98.6, 18.3, 17.2, 10.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{31}N_2OSi^+$: 367.2200, found 367.2198.

*3-Methoxy-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5fa**).* Yellow solid (61 mg, 80%, 0.16 mmol); mp 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (ddd, J = 4.8, 1.8, 0.8 Hz, 1H), 7.88 (td, J = 7.8, 1.9 Hz, 1H), 7.42−7.38 (m, 2H), 6.65 (d, J = 7.8 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 3.88 (s, 3H), 0.93 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 151.9, 151.4, 149.6, 138.3, 124.1, 123.5, 121.9, 112.3, 112.0, 99.1, 98.6, 56.1, 18.4, 10.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{31}N_2O_2Si^+$: 383.2149, found 383.2150.

*3-(Trifluoromethyl)-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ga**).* Yellow solid (76 mg, 90%, 0.18 mmol); mp 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, J = 4.7, 0.7 Hz, 1H), 7.88 (td, J = 7.8, 1.8 Hz, 1H), 7.75 (d, J = 7.4 Hz, 1H), 7.42−7.39 (m, 2H), 6.59 (d, J = 7.4 Hz, 1H), 0.90 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 151.2, 149.9, 138.8 (q, J = 5.0 Hz), 138.6, 134.7, 124.6, 123.5, 122.4 (q, J = 270.2 Hz), 121.8 (q, J = 31.1 Hz), 110.3, 105.8, 97.4, 18.3, 10.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{28}F_3N_2OSi^+$: 421.1918, found 421.1920.

*5′-Methyl-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ha**).* Yellow solid (67 mg, 92%, 0.18 mmol); mp 80−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.65 (dd, J = 8.0, 2.0 Hz, 1H), 7.33 (dd, J = 9.3, 6.9 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 6.54 (d, J = 6.9 Hz, 1H), 2.38 (s, 3H), 0.90 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 150.1, 149.8, 139.4, 138.9, 134.2, 131.0, 122.8, 122.7, 112.5, 101.7, 98.4, 18.3, 10.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{31}N_2OSi^+$: 367.2200, found 367.2201.

*5′-(Trifluoromethyl)-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ia**).* Yellow solid (71 mg, 84%, 0.17 mmol); mp 100−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 1.4 Hz, 1H), 8.12 (dd, J = 8.3, 2.2 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.38 (dd, J = 9.4, 6.9 Hz, 1H), 6.69 (dd, J = 9.4, 0.9 Hz, 1H), 6.59 (dd, J = 6.9, 1.0 Hz, 1H), 0.89 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 155.0, 147.0 (q, J = 4.0 Hz), 139.8, 135.8 (q, J = 3.4 Hz), 130.2, 127.2 (q, J = 33.0 Hz), 123.9, 123.1 (q, J = 271.0 Hz), 122.8, 112.9, 102.9, 100.0, 97.9, 18.3, 10.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{28}F_3N_2OSi^+$: 421.1918, found 421.1920.

*4′-Methyl-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ja**).* Yellow solid (56 mg, 76%, 0.15 mmol); mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 5.0 Hz, 1H), 7.38 (dd, J = 9.3, 6.9 Hz, 1H), 7.25 (s, 1H), 7.23 (d, J = 5.0 Hz, 1H), 6.72 (dd, J = 9.3, 1.0 Hz, 1H), 6.58 (dd, J = 6.9, 1.0 Hz, 1H), 2.45 (s, 3H), 0.95 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 152.2, 150.1, 149.4, 139.3, 130.8, 125.2, 124.0, 122.7, 112.3, 101.6, 98.3, 20.9, 18.3, 10.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{31}N_2OSi^+$: 367.2200, found 367.2199.

*4′-(Trifluoromethyl)-6-((triisopropylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ka**).* Yellow solid (82 mg, 97%, 0.19 mmol); mp 109−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J = 5.1 Hz, 1H), 7.71 (s, 1H), 7.66 (d, J = 5.1 Hz, 1H), 7.43 (dd, J = 9.4, 6.9 Hz, 1H), 6.74 (dd, J = 9.4, 1.0 Hz, 1H), 6.64 (dd, J = 6.9, 1.0 Hz, 1H), 0.94 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 153.2, 150.8, 141.6 (q, J = 34.6 Hz), 139.7, 130.3, 122.8, 122.2 (q, J = 271.8 Hz), 120.0 (q, J = 3.2 Hz), 119.9 (q, J = 3.7 Hz), 112.8, 102.8, 97.9, 18.2, 10.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{28}F_3N_2OSi^+$: 421.1918, found 421.1917.

*2-(Pyridin-2-yl)-3-((triisopropylsilyl)ethynyl)isoquinolin-1(2H)-one (**5la**).* Yellow solid (72 mg, 90%, 0.18 mmol); mp 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.8 Hz, 1H), 8.40 (d, J = 7.9 Hz, 1H), 7.87 (td, J = 7.7, 1.4 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 7.53−7.48 (m, 2H), 7.45 (d, J = 7.9 Hz, 1H), 7.37 (dd, J = 7.4, 4.9 Hz, 1H), 6.94 (s, 1H), 0.92 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 152.5, 149.7, 138.3, 136.4, 133.0, 128.2, 127.9, 126.5, 126.1, 124.8, 124.1, 124.0, 113.5, 99.6, 99.3, 18.5, 11.0. HRMS: m/z: $[M + H]^+$ calculated for $C_{25}H_{31}N_2OSi^+$: 403.2200, found 403.2201.

*2-Methyl-8-((triisopropylsilyl)ethynyl)isoquinolin-1(2H)-one (**5ma**).* White solid (30 mg, 45%, 0.09 mmol); mp 88−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 7.04 (d, J = 7.3 Hz, 1H), 6.35 (d, J = 7.3 Hz, 1H), 3.56 (s, 3H), 1.20 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 138.4, 135.1, 133.1, 130.7, 126.1, 126.05, 123.9, 107.1, 105.3, 97.6, 37.3, 18.8, 11.6. HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{30}NOSi^+$: 340.2091, found 340.2095.

*6-((tert-Butyldiphenylsilyl)ethynyl)-2H-[1,2′-bipyridin]-2-one (**5ab**).* Yellow solid (44 mg, 51%, 0.10 mmol); mp 161−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59−8.58 (m, 1H), 7.80 (td, J = 7.7, 1.9 Hz, 1H), 7.51 (dd, J = 8.0, 1.3 Hz, 4H), 7.44 (d, J = 7.9 Hz, 1H), 7.41−7.36 (m, 3H), 7.34−7.25 (m, 5H), 6.72 (dd, J = 9.4, 1.0 Hz, 1H), 6.67 (dd, J = 6.9, 1.0 Hz, 1H), 0.90 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 152.0, 149.9, 139.4, 138.5, 135.4, 131.9, 130.4, 129.8, 127.8, 124.3, 123.6, 123.4, 113.2, 100.3, 100.1, 26.9, 18.6. HRMS: m/z: $[M + H]^+$ calculated for $C_{28}H_{27}N_2OSi^+$: 435.1887, found 435.1885.

*6-(3,3-Dimethylbut-1-yn-1-yl)-2H-[1,2′-bipyridin]-2-one (**5ac**).* Yellow solid (42 mg, 84%, 0.17 mmol); mp 141−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.6 Hz, 1H), 7.89 (t, J = 7.7 Hz, 1H), 7.42−7.32 (m, 3H), 6.64 (d, J = 9.3 Hz, 1H), 6.42 (d, J = 6.9 Hz, 1H), 0.95 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 152.6, 149.5, 139.7, 138.3, 131.5, 124.0, 123.6, 121.6, 110.8, 108.0, 72.8, 29.9, 27.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{16}H_{17}N_2O^+$: 253.1335, found 253.1336.

*2-((Triisopropylsilyl)ethynyl)-4H-[1,2′-bipyridin]-4-one (**7**).* Yellow waxy solid (42 mg, 59%, 0.12 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, J = 4.8, 1.0 Hz, 1H), 7.90 (td, J = 7.9, 1.8 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.46 (dd, J = 7.4, 4.9 Hz, 1H), 6.78 (d, J = 2.7 Hz, 1H), 6.52 (dd, J = 7.9, 2.7 Hz, 1H), 1.01 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.8, 152.7, 149.4, 139.9, 138.2, 132.1, 124.2, 124.0, 121.0, 118.3, 103.5, 97.7, 18.3, 10.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{29}N_2OSi^+$: 353.2044, found 353.2046.

Synthesis and Characterization of Rhodium(III) Complex 8. 2*H*-[1,2′-Bipyridin]-2-one (**4a**, 0.21 mmol), $[RhCp^*Cl_2]_2$ (0.1 mmol), and NaOAc (0.6 mmol) were stirred overnight in CH_2Cl_2 (6 mL) at room temperature. The solvent was then removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and filtered to remove NaOAc. Column chromatography was performed on silica gel using ethyl acetate (EA)/petroleum ether (PE) = 4:1 to afford complex **8** in 40% yield (36 mg, 0.080 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, J = 8.7 Hz, 1H), 8.59 (dd, J = 5.5, 1.2 Hz, 1H), 7.89−7.84 (m, 1H), 7.28 (dd, J = 6.2, 5.3 Hz, 1H), 7.16 (dd, J = 8.9, 6.9 Hz, 1H), 6.67 (dd, J = 6.8, 0.8 Hz, 1H), 6.18 (dd, J = 8.9, 0.9 Hz, 1H), 1.64 (s, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0 (d, J_{Rh-C} = 37.0 Hz), 166.2, 158.4, 150.1, 139.7, 139.1, 122.4, 118.8, 115.3, 114.3, 97.6 (d, J_{Rh-C} = 6.3 Hz), 9.1. HRMS: $[M - Cl]^+$ calculated for $C_{20}H_{22}N_2ORh^+$: 409.0787, found 409.0785.

Synthesis and Characterization of 6fa. Compound **6fa** was obtained as a brown solid (39 mg, 85%, 0.17 mmol) by following a reported procedure.[12e] mp: 101−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 3.8 Hz, 1H), 7.89 (td, J = 7.7, 1.7 Hz, 1H), 7.44−7.37 (m, 2H), 6.60 (dd, J = 17.6, 7.7 Hz, 2H), 3.87 (s, 3H), 2.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 151.8, 151.6, 149.5, 138.4, 124.3, 123.6, 120.7, 112.8, 111.7, 83.9, 76.2, 56.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{11}N_2O_2^+$: 227.0815, found 227.0813.

Synthesis and Characterization of 7fa. Compound **7fa** was obtained as a brown solid by following a reported procedure.[9] mp: 139−141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, J = 7.7 Hz, 1H), 6.31 (d, J = 7.6 Hz, 1H), 3.76 (s, 3H), 1.04 (apparent s, 21H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 151.4, 119.4, 113.1, 111.5, 98.8, 96.2, 55.9, 18.6, 11.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{28}NO_2Si^+$: 306.1884, found 306.1883.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02410.

Experimental procedures and copies of NMR spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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