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Communication

Rh(I)-Catalyzed Carbene Migration/Carbonylation/Cyclization: Straightforward Construction of Fully Substituted Aryne Precursors

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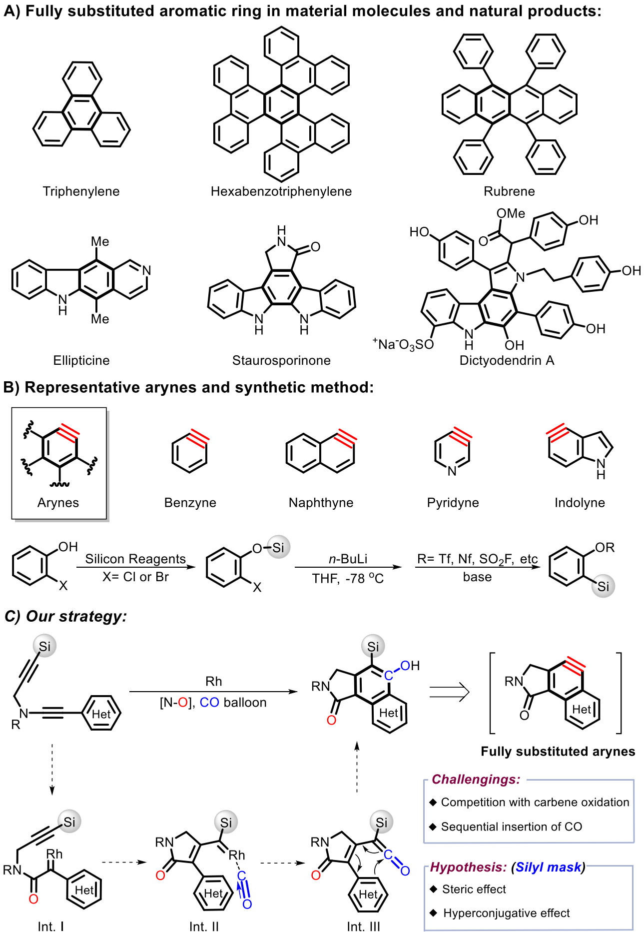
ABSTRACT: The Rh(I)-catalyzed cascade formation of carbenoid followed by a carbonylative cyclization of silyl diynes has been established to achieve diverse *ortho* silyl-substituted phenolics, enabling access to fully substituted aryne precursors via a one-step fluorosulfurylation. The silyl mask on the termini of alkynes is demonstrated not only to suppress the undesired oxidation but also to control the selectivity of CO insertion. Straightforward access to fully substituted arynes was comprehensively established and applied for the efficient construction of polycyclic aromatic molecules.

Scheme 1. Strategy for Fully Substituted Arynes Synthesis



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Arynes have long been recognized as powerful building blocks for the construction of functional arenes due to their excellent reactivity.[1] Since Robert's pioneer work on the validation of the triple-bonded nature of benzyne in 1953, a wide variety of arynes, such as naphthynes, pyridynes, and indolynes have been reported and applied for the synthesis of functional material molecules and natural products.[2] Triphenylenes, hexabenzotriphenylenes, and rubrenes, bearing a fully substituted aromatic ring skeleton, were efficiently constructed from benzyne, 9,10-phenanthryne, and naphthyne, respectively.[3] Meanwhile, arynes were efficiently employed for the synthesis of polycyclic natural products. Ellipticine was obtained through a cycloaddition reaction of pyridyne, and the fully substituted aromatic system of dictyodendrin A was constructed from a cascade reaction of benzyne (Scheme 1A).[4]

Regarding aryne generation, early methods relied on the dehydrohalogenation of aryl halides under basic conditions.[5] Subsequently, Kobayashi and co-workers developed a facile method for the generation of arynes via the fluoride-induced 1,2-elimination of 2-(trimethylsilyl)aryl triflates,[6] which were accessed from *ortho*-halogenated phenols followed by the introduction of a silyl substituent and leaving group (Scheme 1B).[7] Recently, an innovative strategy for polycyclic aryne syntheses was developed by Hoye's group through a hexadehydro-Diels−Alder (HDDA) process of triynes.[8]

On the basis of our research in the transition-metal-catalyzed carbonylative cyclization reaction of aryne,[9] we envisioned that fully substituted aryne precursors could be afforded from yne-ynamides via a cascade process of carbene migration, CO insertion, and 6π electrocyclization (Scheme 1C). Nevertheless, the competition of oxidation between two types of carbene and the sequential insertion of CO challenges the straightforward concept.[10,11] Because of the steric effect and the hyperconjugative effect of a silicon substituent,[12] a silyl mask is designed for the yne-ynamide to suppress undesired oxidation and the selectivity of CO insertion, facilitating aryne precursors simultaneously. Herein, we disclose a cascade strategy involving the carbonylative cyclization of silyl diynes via Rh(I)-catalyzed carbene migration and CO insertion

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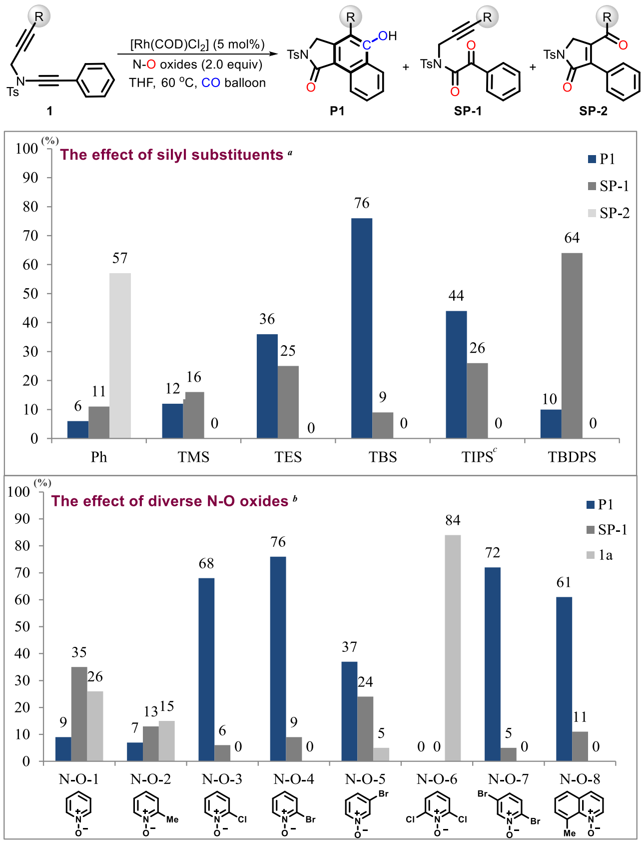
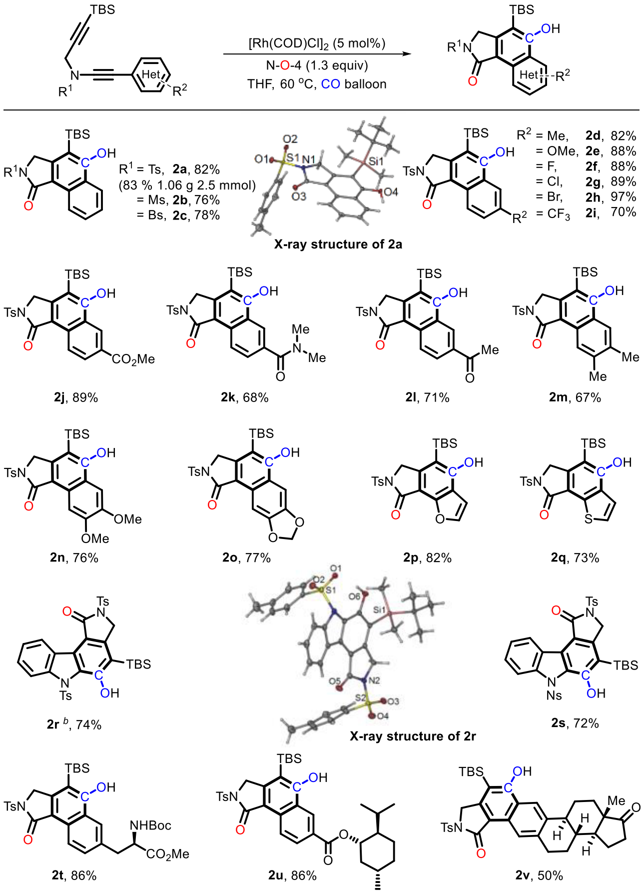
Table 1. Effects of Silyl Substituents and N-O Oxides[d]



[a]Reaction conditions: substrates **1** (0.1 mmol), $[Rh(COD)Cl]_2$ (5 mol %), 2-bromopyridine-*N*-oxide (0.2 mmol), tetrahydrofuran (2.0 mL), CO balloon, 60 °C. [b]Reaction conditions: **1a** (0.1 mmol), $[Rh(COD)Cl]_2$ (5 mol %), N-O oxides (0.2 mmol), tetrahydrofuran (2.0 mL), CO balloon, 60 °C. [c]10% of a 1,3-silyl migration product was detected. [d]^{1}H NMR yields are based on substrates **1** with 1,1,1,2-tetrachloroethane as the internal standard. TMS: trimethylsilyl; TES: triethylsilyl; TBS: t-butyldimethylsilyl; TIPS: triisopropylsilyl; TBDPS: t-butyldiphenylsilyl.

Table 2. Substrate Scope[a]



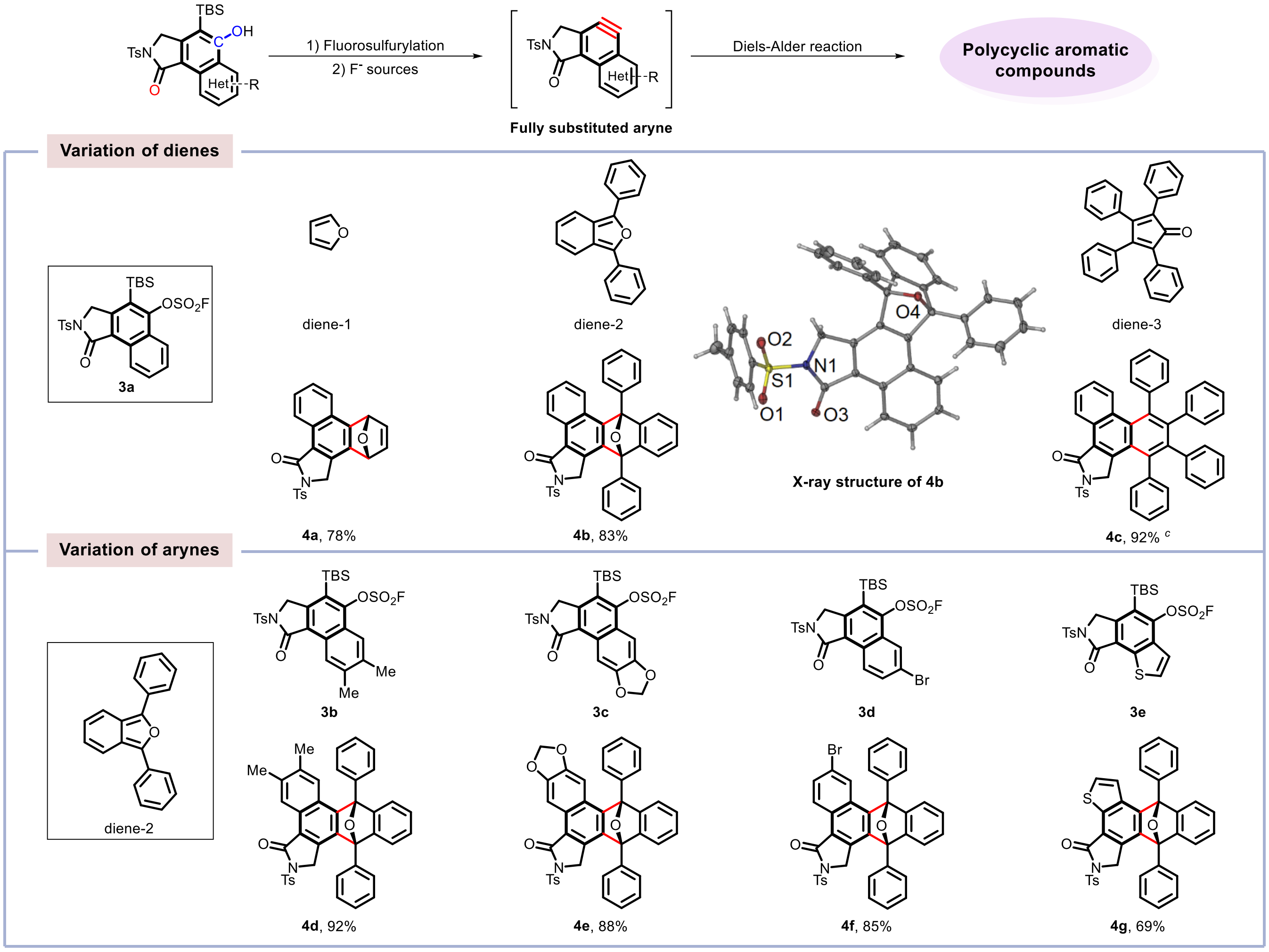
[a]Reaction conditions: substrates (0.1 mmol), $Rh(COD)Cl_2$ (5 mol %), N−O-4 compounds (0.13 mmol), tetrahydrofuran (2.0 mL), CO balloon, 60 °C, isolated yields. [b]Tetrahydrofuran/dichloroethane = 1:1, 80 °C.

assisted via a silyl mask effect to construct fully substituted aryne precursors, which are further applied for conjugated polycyclic aromatic molecule construction.

To realize the assumption, yne-tethered ynamide **1** and N-oxides were conducted in the presence of $[Rh(COD)Cl]_2$ catalyst under CO atmosphere.[13] First, the effect of substituents on a terminal alkyne was investigated. As shown in Table 1, when R is Ph, the desired cyclization product **P1** was obtained in only 6% yield, together with overoxidative diketone byproducts **SP-1** (11% yield) and **SP-2** (57% yield). Considering that the adjustable silyl groups will provide a steric hindrance to suppress the attack from N-oxide to rhodium carbenoid **Int II**, silyl-terminated diynes were examined as substrates. The trimethylsilyl (TMS) group successfully inhibited the oxidized byproduct **SP-2**, affording the cyclization product **P1** in 12% yield. Altering from TMS to TES group, the yield of **P1** increased to 36%. To our delight, the TBS-terminated diyne was the best choice and furnished **P1** in 76% yield. However, further increasing the steric effect of silyl substituents (TIPS and TBDPS) is inclined to result in the oxidized byproduct **SP-1** (26% and 64%, respectively). These results demonstrated that the transfer rate of Rh(I) carbene was substantially influenced by the size of the silicon substituent.

Furthermore, diverse N-O oxides were tested for the O-transfer step. When pyridine-*N*-oxide (N−O-1) was applied as a nucleophile, the desired product **P1** was obtained in only 9% yield combined with 35% of diketone byproduct **SP-1** and 26% of starting material, in which pyridine formed after a transformation deactivated the rhodium catalyst. Diverse 2-substituted N-O oxides were screened; considering that the steric hindrance effect on the 2-position of pyridine-*N*-oxide may inhibit the attack on the metal carbene center **Int I**,[14] 2-methyl substituted N-O oxide (N−O-2) was less effective for this reaction, while the σ-withdrawing group 2-chloro and bromo-substituted N-O oxide (N−O-3 and N−O-4) increased the yields of **P1** to 68% and 76%, respectively. Notably, 2-bromopyridine-*N*-oxide achieved a higher efficiency than the 3-substituted isomer (N−O-5). These results suggest that both steric and electronic effects on the 2-position of pyridine-*N*-oxide played an important role in preventing the oxidized byproduct **SP-1**. A larger steric hindrance, such as that of 2,6-dichloropyridine-*N*-oxide (N−O-6), resulted in a rather low reaction efficiency with 84% of the starting material recovered. Delightedly, the yield of **P1** could be further improved to 82% by decreasing the equivalent of N−O-4 (for more details see the Supporting Information).

Table 3. Generation of Arynes for the Construction of Polycyclic Aromatic Molecules[a,b,d]

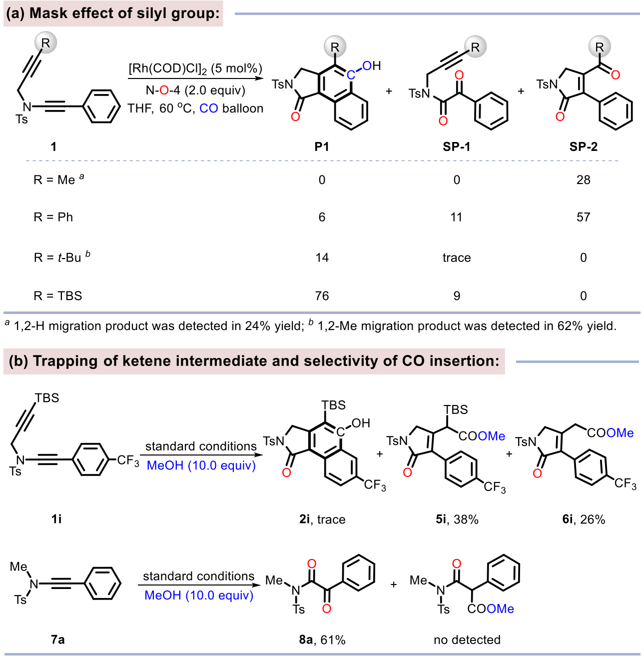


[a]Fluorosulfurylation conditions: phenolics (0.4 mmol), fluorosulfuryl imidazolium salt (1.2 equiv), Et$_3$N (1.5 equiv), MeCN (2.0 mL), rt. [b]Diels–Alder conditions: diene (0.05 mmol), **3a** (3.0 equiv), CsF (3.0 equiv), MeCN (1.0 mL), rt. [c]KF instead of CsF, and the reaction was conducted at 100 °C. [d]Isolated yields.

With the optimized conditions in hand, the scope of the Rh(I)-catalyzed carbene migratory carbonylative cyclization process was explored. All yne-ynamide substrates could be readily prepared via a Cu-catalyzed amidation of alkynyl bromides.[15] As shown in Table 2, the reaction of yne-ynamides with different N-sulfonyl groups was first investigated, leading to the desired phenolics in 76−83% yields (**2a**−**2c**). Meanwhile, a gram-scale operation was performed, successfully affording **2a** in 83% yield (1.06 g, 2.5 mmol). Next, substrates with both electron-donating and electron-withdrawing substituents on aromatic rings were subjected to this transformation, delivering the corresponding products in excellent yields (**2d**−**2i**). Various functional groups such as ester (**2j**), amide (**2k**), and acetyl (**2l**) were well-tolerated to produce the corresponding phenolics in 68−89% yields. In addition, yne-ynamides bearing 3,4-disubstituted aromatic rings afforded the desired **2m**−**2o** in 67−77% yields under standard conditions, and the 1,3-silyl migration byproduct was detected in these cases in 10−31% yields.[16] Furthermore, this reaction could be extended to heterocycle-substituted diynes, remarkably leading to the corresponding products **2p** and **2q** in 82% and 73% yields. The structure of pyrrolocarbazole lactam, which frequently existed in carbazole alkaloids serving as a potent PARP-1 inhibitor,[17] was successfully assembled via this method (**2r** and **2s**). In particular, naturally occurring motifs such as amino acids, menthol, and estrone are compatible with this system affording the corresponding phenolic derivatives in moderate to good yields (**2t**−**2v**). The structures of **2a** and **2r** were further confirmed by X-ray diffraction.[18]

Polycyclic aromatic molecules (PAMs) have attracted considerable attention due to their unique optoelectronic properties in materials science.[19] Among the various synthetic methods of producing PAMs, arynes as a powerful tool played an indispensable role. In particular, a cycloaddition reaction of arynes allowed the incorporation of benzene rings through multiple bond formation in one step, thus providing a significant increase in the structural complexity.[20] After the library of *ortho* TBS-substituted phenolics was established, diverse fully substituted aryne precursors were readily available through one-step fluorosulfurylation[21] and then employed to generate arynes for the construction of polycyclic aromatic molecules. As shown in Table 3, the cycloaddition reaction of aryne precursor **3a** with various dienes including furan, 1,3-diphenylisobenzofuran, and tetracyclone were conducted smoothly by adding F$^-$ sources in acetonitrile, leading to the corresponding polycyclic aromatic products in 78−92% yields

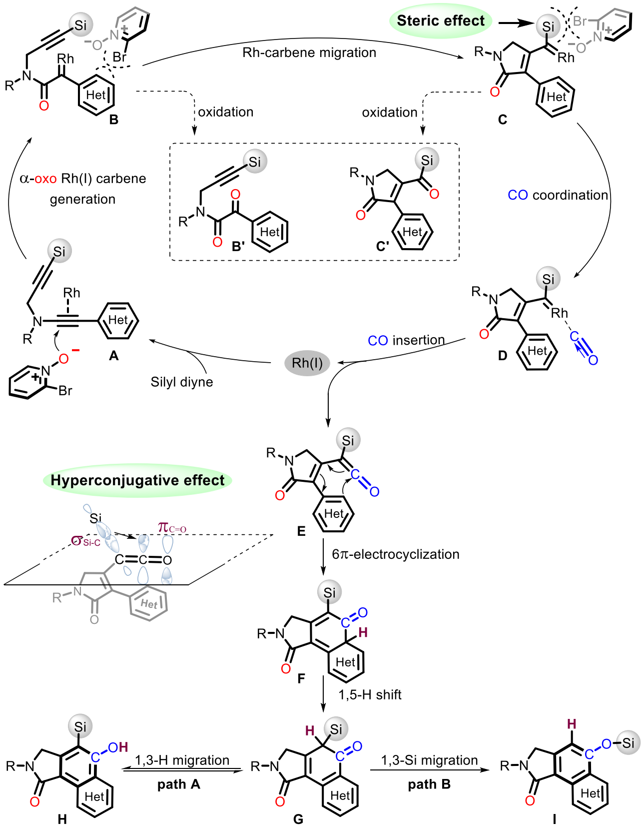
Scheme 2. Control Experiments



	P1	SP-1	SP-2
R = Me [a]	0	0	28
R = Ph	6	11	57
R = *t*-Bu [b]	14	trace	0
R = TBS	76	9	0

[a] 1,2-H migration product was detected in 24% yield; [b] 1,2-Me migration product was detected in 62% yield.

Scheme 3. Possible Mechanism



(**4a**−**4c**). The structure of **4b** was further confirmed through X-ray analysis.[18] Additionally, diverse fully substituted aryne precursors were subjected to the cycloaddition reaction with 1,3-diphenylisobenzofuran. Both electron-rich and electron-deficient functional groups on the aromatic rings were well-tolerated and furnished the corresponding products in 85−92% yields (**4d**−**4f**), in which a *para*-bromide-substituted molecule enabled the further possibility of derivation via cross-coupling. Meanwhile, the thiophene-substituted aryne could be well-generated in this way obtaining the cycloaddition product in 69% yield (**4g**). To our delight, these polycyclic aromatic molecules exhibited a strong fluorescence in solution, displaying the potential application in organic photoelectric materials.[22]

To gain further insight into the carbonylative cyclization process, a mechanistic study was conducted. First, besides the TBS substituent, other substituents were also accommodated on the alkyne termini. For example, substrates bearing methyl and phenyl groups led to the oxidized byproduct **SP-2** in 28% and 57% yields, respectively. An increase of steric hindrance (R = *t*Bu) could prevent the byproduct **SP-2**, but it was unfavorable for CO insertion. These experiments demonstrated that not only steric hindrance but also an electronic effect of a silicon substituent on alkyne termini played a crucial role in the cascade process (Scheme 2a). Next, in order to trap the possible ketene intermediate during the transformation, *para* CF_3-substituted substrate **1i** was subjected to the standard conditions in the presence of 10 equiv of methanol;[23] the envisaged methyl ester **5i** was obtained in 38% yield together with the desilylated counterpart **6i** (26%) and a trace amount of desired product **2i**, further confirming our hypothesis. Additionally, the treatment of ynamide **7a** under standard conditions only led to diketone product **8a** in 61% yield, which demonstrated Rh carbenoid in the first step is not suitable for CO insertion (Scheme 2b).

According to the observations above, a plausible mechanism is proposed (Scheme 3). First, a catalytic Rh(I) species was preferentially bounded to an electron-richer triple bond, followed by the attack from N-oxide to furnish α-oxo Rh(I) carbenoid **B**.[10c] Fortunately, the oxidized byproduct **B′** was fully inhibited by both a steric and electronic effect between substrate and pyridine N-oxide. Next, the migration of rhodium carbene **B** from a benzyl position to an α-position of a silyl group afforded intermediate **C**.[24,25] Then, the silyl vinylketene **E** was generated from intermediate **D** via CO coordination and insertion followed by the dissociation and regeneration of Rh.[26] The mask effect of silyl provided a steric hindrance to exclude the attack from 2-bromopyridine *N*-oxide to rhodium carbene again, successfully preventing the second oxidation risk from **C** to diketone **C′**. Meanwhile, a hyperconjugative $\sigma-\pi$ donation from Si−C bond to in-plane carbonyl π-orbital[27] perfectly stabilized the ketene intermediate for the process of CO insertion. Subsequently, a 6π-electrocyclization of **E** afforded the intermediate **F** followed by a 1,5-H shift to obtain cyclohexadienone **G**.[16c] The following aromatization possesses two possible pathways: the desired product **H** was afforded via a 1,3-H migration in dynamics dominant (path A), while the byproduct **I** was generated via a 1,3-Si migration at a higher temperature determined by thermodynamic stability (path B).[16,28]

In summary, we have developed a Rh(I)-catalyzed carbene migration/carbonylation/cyclization cascade reaction for the facile construction of fully substituted arynes, which display a great potential for organic photoelectric material synthesis. The steric and hyperconjugative effect of the silyl substituent on the alkyne is crucial in this cascade process to control the selective CO insertion by preventing the oxidation of the carbenoid intermediate. Further studies on construction of diverse arynes with structurally high complexity for an organic light-emitting diode (OLED) via this strategy are ongoing in our lab.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c13012.

Experimental procedures; NMR spectral, X-ray, and analytical data for all new compounds (PDF)
Crystallographic data (CIF)
Crystallographic data (CIF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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