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Rhodium-catalyzed asymmetric synthesis of silicon-stereogenic silicon-bridged arylpyridinones†

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A rhodium-catalyzed regio- and enantioselective synthesis of silicon-stereogenic silicon-bridged arylpyridinones has been developed through [2 + 2 + 2] cycloaddition of silicon-containing prochiral triynes with isocyanates. High yields and enantioselectivities have been achieved by employing an axially chiral monophosphine ligand, and this process could be applied to catalytic asymmetric synthesis of silicon-stereogenic chiral polymers for the first time. The reaction mechanism of the present catalysis has also been experimentally investigated to establish a reasonable catalytic cycle, advancing the mechanistic understanding of the rhodium-catalyzed pyridinone synthesis by [2 + 2 + 2] cycloaddition reactions.

Introduction

Asymmetric catalysis represents one of the most efficient approaches for the preparation of enantioenriched chiral compounds, and extensive research has been made in developing various catalytic asymmetric reactions during the past decades.[1] While most of them are directed toward the synthesis of carbon-stereogenic compounds, only limited structures are accessible for enantioenriched silicon-stereogenic compounds through asymmetric catalysis.[2,3] Because organosilanes are widely utilized in various fields of research, broadening the scope of accessible silicon-stereogenic enantioenriched organosilanes would be highly desirable. Among the known catalytic enantioselective methods for the creation of silicon stereocenters, most typical approach is the desymmetrization of prochiral dihydrodiorganosilanes by way of enantioposition-selective hydrosilylation or other Si–H bond functionalization reactions.[4] In contrast, the use of other types of prochiral organosilanes as substrates has been much less explored and such examples started to appear only very recently,[5] many of which are intramolecular processes.

As one of the rare examples of intermolecular reactions, we recently reported a rhodium-catalyzed asymmetric synthesis of silicon-stereogenic dibenzosiloles (silicon-bridged biaryls) by enantioselective [2 + 2 + 2] cycloaddition of prochiral triynes with internal alkynes.[5h,6] By taking advantage of the convergent nature of this intermolecular approach, we decided to further explore the enantioselective synthesis of a new family of silicon-stereogenic silicon-bridged π-conjugated compounds based on this strategy. Specifically, in this article, we describe the development of a catalytic regio- and enantioselective synthesis of silicon-stereogenic silicon-bridged arylpyridinones, dihydrobenzosilolopyridinones, by rhodium-catalyzed [2 + 2 + 2] cycloaddition of prochiral silicon-containing triynes with isocyanates, including the investigation of its mechanistic aspects.[7,8]

Results and discussion

Reaction development

As a starting point, we employed prochiral triyne **1a** as a model substrate for the cationic rhodium-catalyzed [2 + 2 + 2] cycloaddition with phenyl isocyanate (**2a**) in the presence of (*R*)-binap[9] as the ligand at 25 °C (Table 1, entry 1). Although potentially two regioisomers **3aa** and **3aa′** could be obtained depending on the orientation of isocyanate **2a**, the reaction selectively provided only **3aa** in 93% yield, albeit with low enantiomeric excess (14% ee). The change of ligand to (*R*)-H_8-binap[10] gave similarly low enantioselectivity (13% ee; entry 2), whereas the use of (*R*)-segphos[11] improved the enantioselectivity to 76% ee (entry 3). But, the ee was not further improved by using (*R*)-dm-segphos (68% ee; entry 4). In comparison to these axially chiral bisphosphine ligands, axially chiral monophosphine ligand (*R*)-MeO-mop[12] gave **3aa** with higher enantioselectivity (80% ee; entry 5), and the use of (*R*)-**L** having a methyl group at the 3′-position[13] further improved the enantioselectivity of **3aa** to 89% ee in 85% yield (entry 6). It is worth noting that only **3aa** was obtained without forming its

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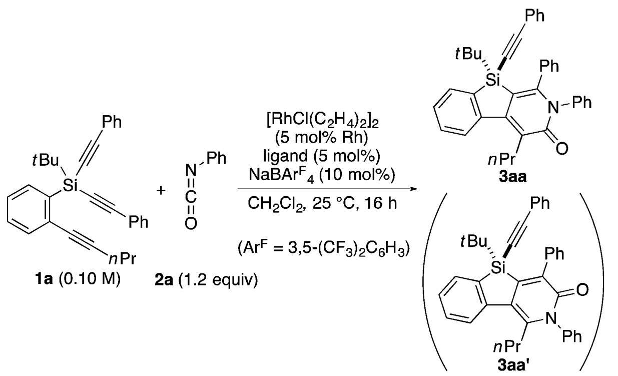
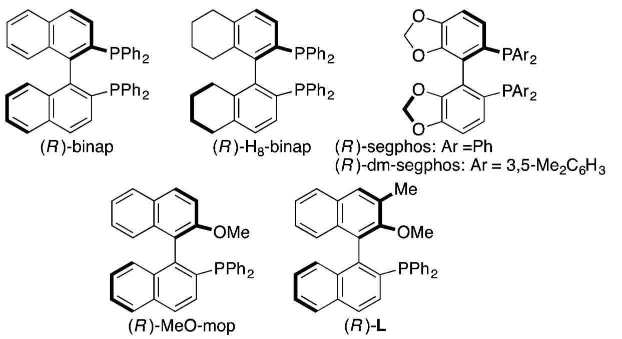
† Electronic supplementary information (ESI) available: Detailed experimental procedures. CCDC 1428796. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc03767k

Table 1 Rhodium-catalyzed asymmetric [2 + 2 + 2] cycloaddition of **1a** with **2a**: ligand effect



Entry	Ligand	Yield[a] (%)	ee[b] (%)
1	(*R*)-binap	93	14
2	(*R*)-H_8-binap	89	13
3	(*R*)-segphos	86	76
4	(*R*)-dm-segphos	93	68
5	(*R*)-MeO-mop	86	83
6	(*R*)-**L**	85	89



[a] Isolated yield. [b] Determined by chiral HPLC on a Chiralpak IA column with hexane/2-propanol = 95/5.

regioisomer **3aa′** for all of these reactions, and the structure of **3aa** including the absolute configuration was firmly established by X-ray crystallographic analysis with Cu-Kα radiation as shown in Fig. 1 after recrystallization of the product obtained in entry 6.[14]

Under the conditions described in Table 1, entry 6, various silicon-stereogenic dihydrobenzosilolopyridinones (silicon-bridged arylpyridinones) **3** can be synthesized with high yields and enantioselectivities as summarized in Table 2. Thus, 1-pentynyl group of **1a** (entry 1) can be replaced by other alkynyl groups such as 1-propynyl (**1b**), 4-methyl-1-pentynyl (**1c**), and unsubstituted ethynyl (**1d**) groups to give compounds **3ba**–**3da** in 76–85% yield with 88–91% ee (entries 2–4). Replacement of *tert*-butyl group on the silicon atom by less bulky cyclohexyl group (**1e**) also provides the corresponding product **3ea** with relatively high ee of 86% (entry 5), but the reaction of alkoxy-substituted substrate **1f** gives almost racemic product **3fa** under the present reaction conditions (entry 6). Triynes having two of

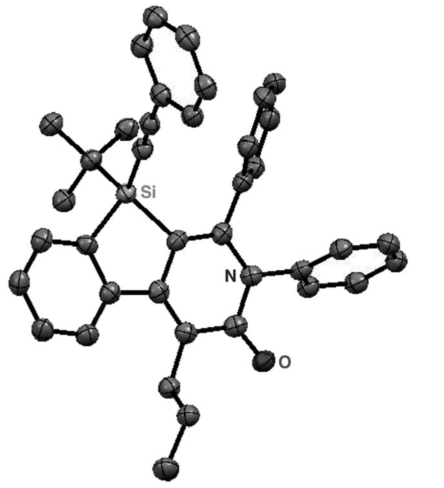
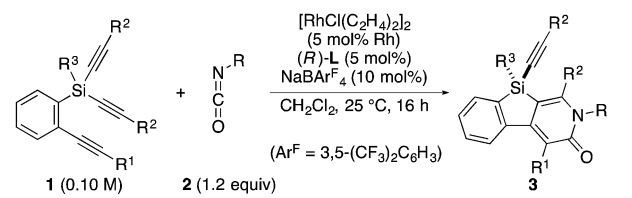
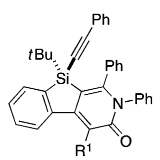
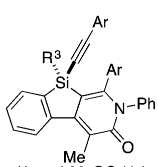
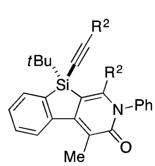
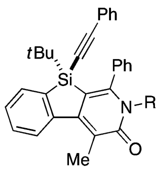


Fig. 1 X-Ray crystal structure of (*R*)-**3aa** (Flack parameter = 0.04(4)). Hydrogen atoms are omitted for clarity.

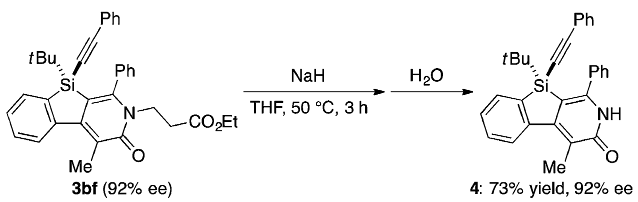
Table 2 Scope of rhodium-catalyzed asymmetric synthesis of silicon-bridged arylpyridinones **3**



Entry	Product		Yield[a] (%)	ee[b] (%)
1		**3aa** (R^1 = *n*Pr)	85	89
2		**3ba** (R^1 = Me)	84	91
3[c]		**3ca** (R^1 = *i*Bu)	76	88
4		**3da** (R^1 = H)	85	91
5	 (Ar = 4-MeOC$_6$H$_4$)	**3ea** (R^3 = Cy)	83	86
6		**3fa** (R^3 = O*t*Bu)	78	2
7		**3ga** (R^2 = 4-MeOC$_6$H$_4$)	94	91
8		**3ha** (R^2 = 4-FC$_6$H$_4$)	90	91
9		**3ia** (R^2 = *n*Pr)	83	54
10[d]		**3bb** (R = 4-MeOC$_6$H$_4$)	88[e]	91
11		**3bc** (R = 4-BrC$_6$H$_4$)	93	91
12		**3bd** (R = 4-IC$_6$H$_4$)	82	92
13		**3be** (R = CH$_2$Ph)	83	92
14		**3bf** (R = (CH$_2$)$_2$CO$_2$Et)	86	92

[a] Isolated yield. [b] Determined by chiral HPLC. [c] The reaction was conducted at 35 °C for 37 h. [d] The reaction was conducted with 1.1 equiv. of **2b**. [e] Containing *ca.* 3% of inseparable impurity.

the same substituted phenylethynyl groups on the silicon atom (**1g** and **1h**) are also suitable substrates for the reaction with isocyanate **2a** to give **3ga** and **3ha** with high enantiomeric excesses (91% ee; entries 7 and 8), but the use of an alkylethynyl-substituted variant (**1i**) results in the formation of product **3ia** with lower enantioselectivity (54% ee; entry 9). With regard to the isocyanate, not only aryl isocyanates (**2b**–**2d**) but also alkyl isocyanates (**2e** and **2f**) possessing functional groups such as halides and esters can be efficiently employed in the present catalysis to give **3bb**–**3bf** in uniformly high yields (82–93% yield) with 91–92% ee (entries 10–14). It is worth mentioning again that all of these reactions proceed with complete regioselectivity irrespective of the substrate combination. In addition to these *N*-arylated or *N*-alkylated products **3**, *N*-H compound **4** can also be accessed by treatment of ethoxycarbonylethyl-substituted compound **3bf** (92% ee) with NaH followed by protonation *via* a retro-Michael addition reaction (73% yield, 92% ee; eqn (1)).[15]



(1)

Synthesis of a silicon-stereogenic chiral polymer

The complete regioselectivity in the present [2 + 2 + 2] cycloaddition led us to investigate the preparation of enantioenriched chiral polymers based on the silicon-stereogenic center of silicon-bridged arylpyridinones. For example, the asymmetric [2 + 2 + 2] cycloaddition reaction of trimethylsilylethynyl-substituted compound **1j** with 4-iodophenyl isocyanate (**2d**) under Rh/(*R*)-**L** catalysis gave product **3jd** in 84% yield with 89% ee (eqn (2)). Subsequent removal of the trimethylsilyl group followed by recrystallization led to bifunctional monomer **5** with 99% ee in a good overall yield. The Sonogashira coupling polymerization of **5** in the presence of 3 mol% of methyl 4-iodobenzoate as an initiator successfully afforded **poly-5** in 93% yield with control of the number average molecular weight (M_n = 19 000 g mol^{-1}, *i.e.*, degree of polymerization = 35; eqn (3)).[16] As far as we are aware, this represents the first example of the synthesis of silicon-stereogenic chiral polymers based on the catalytic asymmetric construction of the silicon stereocenter.[17] The UV-vis and fluorescence spectra of **poly-5** are shown in Fig. 2: the UV-vis absorption and emission band maxima are at 352 nm and 440 nm, respectively, both of which are significantly red-shifted compared to the reported silicon-stereogenic chiral conjugated polymer.[17a] We also examined the CD spectrum of **poly-5** and found that it showed negative Cotton effects at 287 nm ($\Delta\varepsilon = -10.7$ unit-M^{-1} cm^{-1}) and 237 nm ($\Delta\varepsilon = -22.4$ unit-M^{-1} cm^{-1}) (Fig. 3).

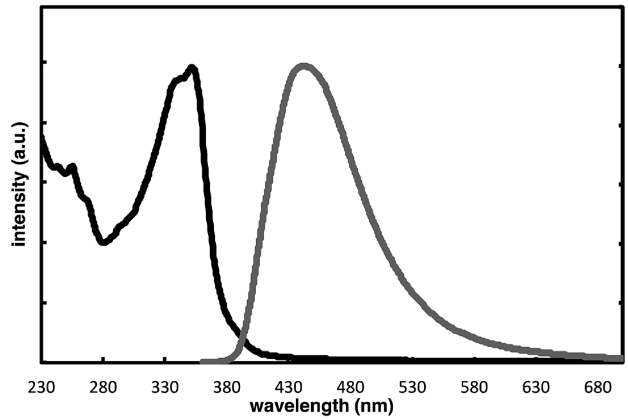


Fig. 2 Normalized UV-vis (black line; at 1.7 × 10^{-5} unit-M) and fluorescence spectra (gray line ($\Phi_F = 0.04$); at 1.7 × 10^{-5} unit-M; excited at 350 nm) of **poly-5** in CH_2Cl_2 at 25 °C.

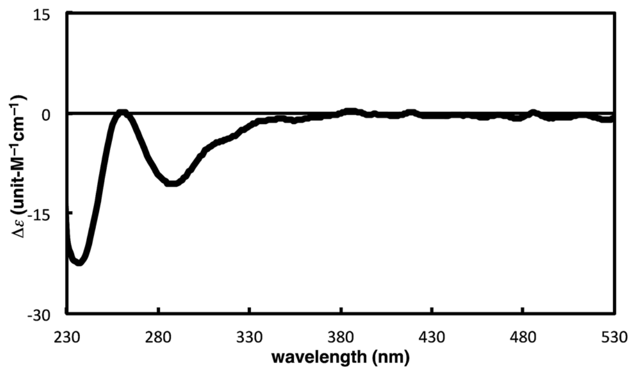
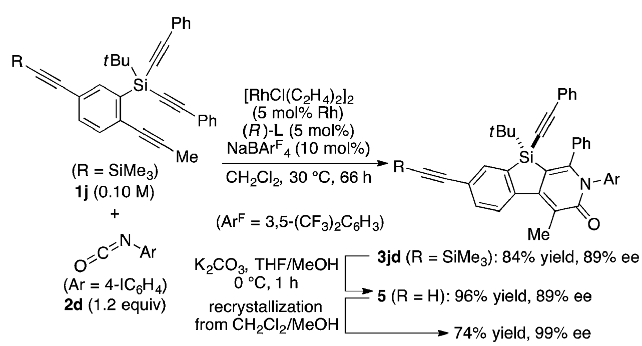
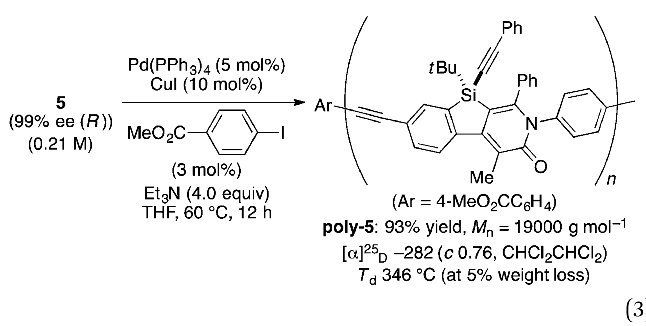


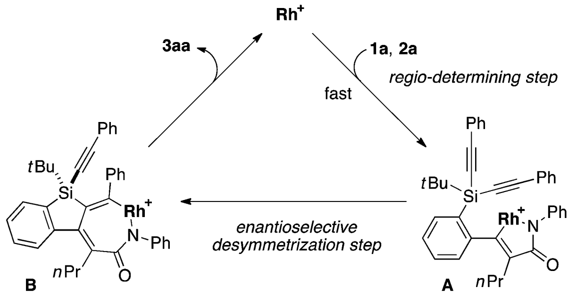
Fig. 3 CD spectrum of **poly-5** (at 1.7 × 10^{-5} unit-M) in CH_2Cl_2 at 25 °C.



(2)



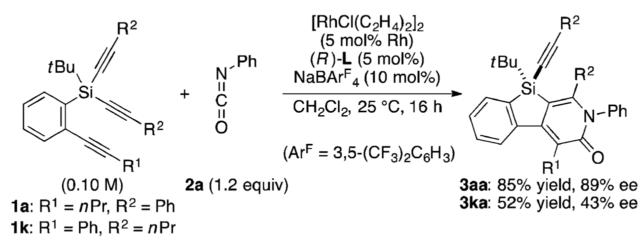
(3)



Scheme 1 Proposed catalytic cycle for the rhodium-catalyzed asymmetric [2 + 2 + 2] cycloaddition of **1a** with **2a** to give **3aa** (**Rh** = Rh((*R*)-**L**)).

Mechanistic considerations

To gain some insight into the origin of regioselective formation of compounds **3** in the present catalysis, we conducted control experiments using triynes **1a** and **1k**, which possess opposite substitution patterns on arylalkynes (R^1) and silylalkynes (R^2) with each other, in the reaction of isocyanate **2a** under Rh/(*R*)-**L** catalysis (eqn (4)). As was also described in Table 2, entry 1, the reaction of **1a** with **2a** selectively gave **3aa** as the sole regioisomer in 85% yield with 89% ee. The use of **1k** in place of **1a** under otherwise the same conditions turned out to give product **3ka** as the sole regioisomer as well, although the yield and ee became somewhat lower (52% yield, 43% ee). These results indicate that the proximal substituents of the alkynes that engage in the C–C or C–N bond-formation with an isocyanate do not influence the regioselectivity of this process. Instead, the regioselectivity is probably controlled by the reactivity difference between arylalkyne and silylalkyne of triyne **1**. Based on these results, a proposed catalytic cycle for the reaction of **1a** with **2a** is illustrated in Scheme 1. Thus, initial oxidative cyclization of alkyne on the benzene ring of **1a** and C=N of **2a** with cationic rhodium(I) species gives five-membered rhodacycle **A** having a Rh–N bond to set the regiochemistry in the product formation.[7d,18] Subsequent intramolecular insertion of one of the alkynes on silicon into the Rh–C bond of **A** takes place to give seven-membered rhodacycle **B**. The enantioselectivity of the silicon stereocenter is presumably determined at this insertion step. Rhodacycle **B** then undergoes reductive elimination to provide compound **3aa** along with regeneration of cationic rhodium(I) species.



(4)

We also carried out a series of kinetic experiments to gain more detailed understanding for the reaction of triyne **1a** with isocyanate **2a** in the presence of $[RhCl(C_2H_4)_2]_2$/(*R*)-**L**/$NaBAr^F{}_4$ as the catalyst in CH_2Cl_2 at 28 °C. As shown in Fig. 4, the reaction rate shows first-order dependency on the concentration of rhodium catalyst. In contrast, the initial concentrations of triyne **1a** and isocyanate **2a** have no influence on the initial rate of the production of **3aa** (Fig. 5 and 6), indicating that the reaction is zero-order in both [**1a**] and [**2a**]. These experimental results are consistent with the proposed catalytic cycle in Scheme 1, and the oxidative cyclization step to form intermediate **A** takes place rapidly (zero-order in both [**1a**] and [**2a**]). The turnover-limiting step is one of the subsequent intramolecular processes, either the insertion step to form intermediate **B** or the reductive elimination step from **B** (first-order in [**Rh**]).

Attempted kinetic resolution of triyne (±)-**1l** gave further information for the mechanism of the present catalysis. As

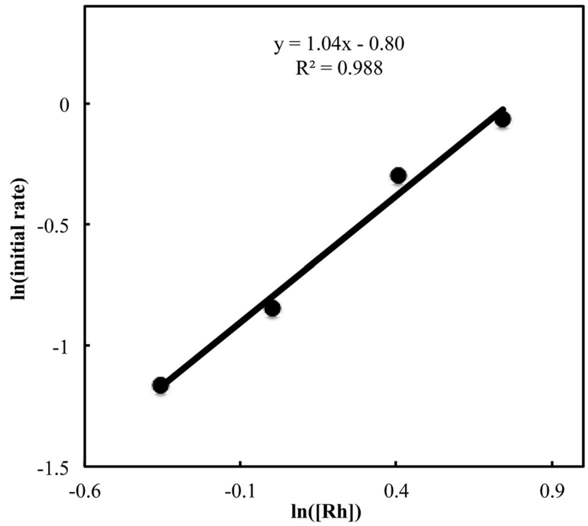


Fig. 4 Ln plot of the initial rate (mM min^{-1}) *vs.* concentration of Rh catalyst (mM) ([**Rh**]$_0$ = 0.7–2.1 mM, [**1a**]$_0$ = 50 mM, [**2a**]$_0$ = 50 mM).

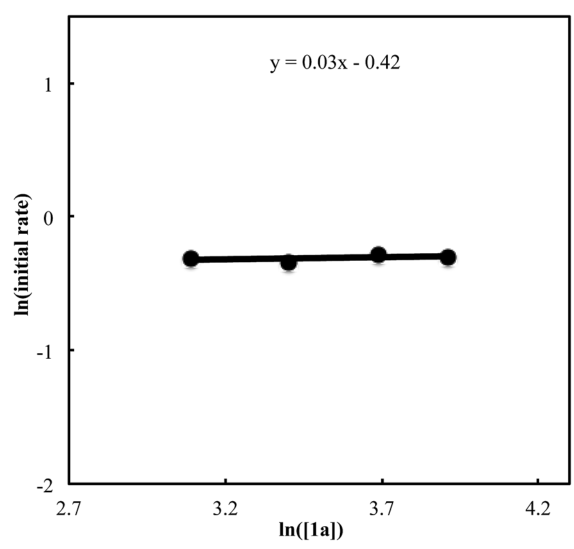


Fig. 5 Ln plot of the initial rate (mM min^{-1}) *vs.* concentration of triyne **1a** (mM) ([**Rh**]$_0$ = 1.5 mM, [**1a**]$_0$ = 22–50 mM, [**2a**]$_0$ = 50 mM).

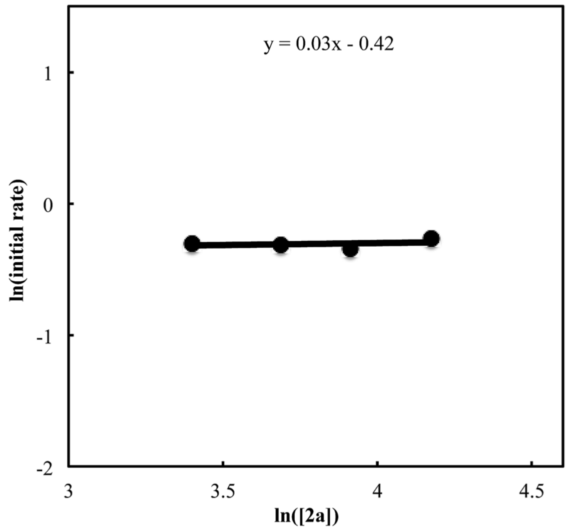
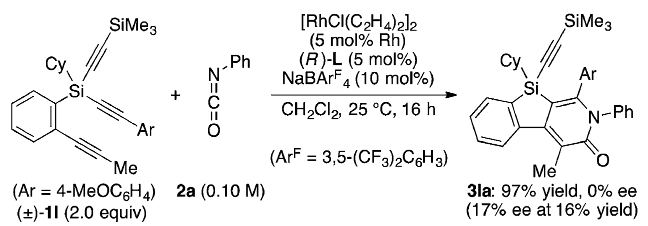


Fig. 6 Ln plot of the initial rate (mM min^{-1}) *vs.* concentration of isocyanate **2a** (mM) ($[Rh]_0$ = 1.5 mM, $[\mathbf{1a}]_0$ = 30 mM, $[\mathbf{2a}]_0$ = 30–65 mM).

shown in eqn (5), the reaction of (±)-**1l** (2.0 equiv.) with phenyl isocyanate **2a** in the presence of Rh/(*R*)-**L** selectively gave product **3la** in 97% yield based on **2a** (49% yield based on (±)-**1l**) by incorporating the 4-methoxyphenylethynyl group on silicon into the pyridinone framework with trimethylsilylethynyl group intact, and **3la** thus obtained was found to be completely racemic. In contrast, enantiopure (*S*)-(−)-**1l**, the matched enantiomer, reacted with **2a** at least 4.2 times faster than its opposite enantiomer (*R*)-(+)-**1l** under the catalysis of Rh/(*R*)-**L** (eqn (6) and (7)). These results indicate that the initial oxidative cyclization step in Scheme 1 occurs irreversibly and non-stereoselectively, and the subsequent enantio-discriminating insertion step is most likely the turnover-limiting step.



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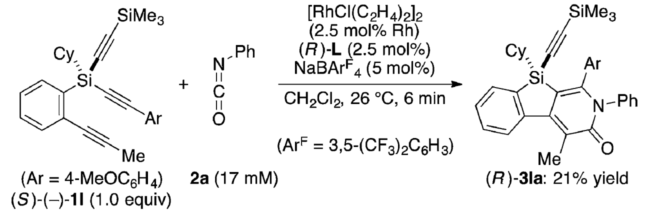

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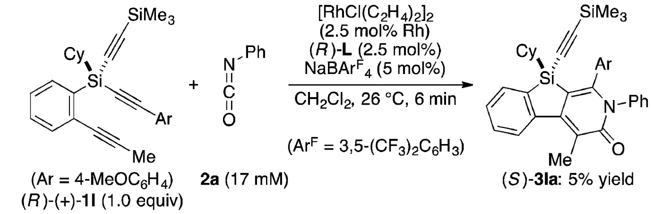

(7)

Conclusions

In summary, we have developed a rhodium-catalyzed regio- and enantioselective synthesis of silicon-stereogenic silicon-bridged arylpyridinones through [2 + 2 + 2] cycloaddition of silicon-containing prochiral triynes with isocyanates. High yields and enantioselectivities have been achieved by employing axially chiral monophosphine (*R*)-**L** as the ligand, and this process could be applied to the synthesis of silicon-stereogenic chiral polymers by way of a catalytic asymmetric construction of the silicon stereocenter for the first time. We have also investigated the mechanistic aspects of the present catalysis to establish a reasonable catalytic cycle based on a series of control experiments and kinetic studies, which represents a rare example of the experimental mechanistic study for the rhodium-catalyzed synthesis of pyridinones *via* [2 + 2 + 2] cycloaddition reactions.

Acknowledgements

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