A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition

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Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201802806
Angew. Chem. 10.1002/ange.201802806

Link to VoR: http://dx.doi.org/10.1002/anie.201802806
http://dx.doi.org/10.1002/ange.201802806

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10.1002/anie.201802806

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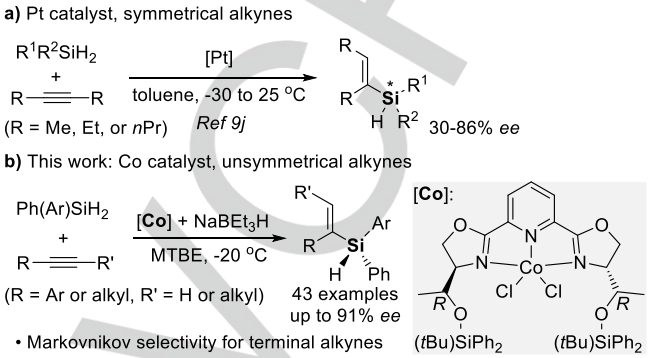
Asymmetric Synthesis of Silicon-Stereogenic Vinylhydrosilanes via Cobalt-Catalyzed Regio- and Enantioselective Alkyne Hydrosilylation with Dihydrosilanes

Huanan Wen, Xiaolong Wan and Zheng Huang*

Abstract: *The strategic carbon-to-silicon substitution at a stereogenic center can produce chiral silanes with significantly improved properties relative to their carbon-congeners. We report here an unprecedented cobalt-catalyzed asymmetric hydrosilylation of unsymmetrical alkynes with dihydrosilane, furnishing Si-stereogenic vinylhydrosilanes with high regio- and enantioselectivity. The absolute configurations of the products were determined by chiroptical methods in combination with DFT calculations. The synthetic versatility of vinylhydrosilanes as chiral building blocks were further demonstrated by asymmetric Si–H insertion and catalytic hydroboration reactions.*

Optically pure organosilanes containing a Si-stereocenter are not naturally occurring, but have attracted increasing attention in medicinal chemistry[1] and material sciences[2] because sila-substitution (i.e., C/Si switch of the stereocenter) can cause significant difference regarding their biological and physicochemical properties.[3] Additionally, they are vital intermediates for stereoselective transformations in organic synthesis.[4] While methods for the synthesis of relevant α-carbon-stereogenic chiral silanes have been well known,[5] the asymmetric synthesis of Si-stereogenic compounds is much more challenging. Due to the low stability of the sp^2-hybridized Si species,[6] addition reactions to Si-containing double bonds are not viable to construct Si-stereocenters. The traditional methods for synthesis of such compounds require stoichiometric amounts of chiral reagents.[4a-c,7] To this end, the development of catalytic approaches using readily accessible reagent(s) is desired.

Two catalytic strategies involving the desymmetrization of prochiral tetraorganosilanes and dihydrosilanes have been reported for the synthesis of Si-stereogenic silanes. In the context of tetraorganosilanes,[8] Shintani and other colleagues have made a series of contributions, including asymmetric Si–C bond activation of silacyclobutanes.[8a,8b] The desymmetrization of dihydrosilanes is of particular interest because the resulting chiral monohydrosilanes can find various synthetic applications, such as diastereoselective dehydrogenative Si–O coupling with racemic alcohols[7c] and synthesis of optically active Si-containing polymers through intermolecular alkene hydrosilylation.[2a] Among a few known approaches for the desymmetrization of dihydrosilanes,[9] the asymmetric hydrosilylation of alkynes with dihydrosilanes is an attractive protocol considering that the products contain two functionalities, vinyl and Si–H, toward further transformations. In 2012, Tomooka reported a Pt-catalyzed



Scheme 1. Asymmetric alkyne hydrosilylation with dihydrosilane.

hydrosilylation of internal alkynes to form vinylsilanes with up to 86% *ee*.[9j] The substrates disclosed therein were symmetrical internal alkyl alkynes, and thus the issue of regioselectivity did not arise (Scheme 1a).[9j]

Base-metal-catalyzed hydrosilylation of multiple C–C bonds have garnered much attention over the past decade, not only because of the earth abundance and environmentally benign nature of the metals, but also because they may be complementary to, or even supplant the traditional precious-metal catalysis in terms of selectivity.[10,11] In 2016, Lu's group and our group independently reported a Co-catalyzed Markovnikov-selective hydrosilylation of terminal alkynes with Ph_2SiH_2 by employing iminopyridine-oxazoline (IPO)[11g] and pyridine-bis(oxazoline) (PyBox)[11f] ligands, respectively. Later, Lu described (IPO)Co-catalyzed asymmetric synthesis of α-carbon-stereogenic silanes via sequential Markovnikov hydrosilylation/hydrogenation of terminal alkynes[5d] or Markovnikov hydrosilylation of terminal alkenes.[5c] Herein, we describe a new cobalt catalyst of PyBox for regio- and enantioselective hydrosilylation of terminal and internal alkynes with diaryl dihydrosilane ($Ph(Ar)SiH_2$, Ar ≠ Ph), yielding a novel class of Si-stereogenic vinylhydrosilanes (Scheme 1b).

We commenced the study by examining Co catalysts of chiral PyBox ligands for asymmetric hydrosilylation of phenylacetylene **1a** with a prochiral dihydrosilane $Ph(Ar)SiH_2$ (Ar = 2,6-$(Me)_2C_6H_3$) **2** (Table 1). The Co catalysts were generated in situ from $Co(acac)_2$ and PyBox, and NaO*t*Bu was selected as the catalyst activator.[12] In the presence of $Co(acac)_2$ (2.0 mol%) and a *i*Bu-substituted PyBox **L1** (4.0 mol%), the reaction of **1a** with **2** (1 equiv) in THF at 25 °C after 12 h formed the branched vinylhydrosilane **3a** in high yield and high regioselectivity (97% yield, *b*:*l* = 98:2), but with low enantioselectivity (22% *ee*) (entry 1). The run using a *i*Pr-substituted ligand **L2** led to similar regio- and enantioselectivity (entry 2). The enantioselectivity (51% *ee*) was substantially enhanced by using **L3** with a *s*Bu substituent, but at the expense of reduced yield (58% yield, entry 3). The use of a *t*Bu-substituted PyBox **L4** gave a poor yield (<10%, entry 4). To our satisfaction, two PyBox ligands with a hydroxyethyl group protected by *tert*-butyldiphenylsilyl **L5** and *tert*-butyldimethylsilyl **L6**, respectively, offered significantly improved results in terms of

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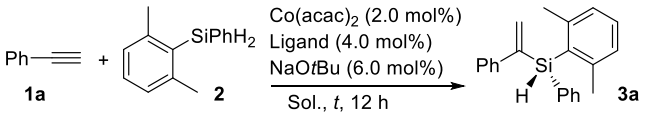
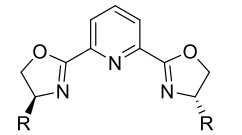
Table 1. Cobalt catalysts for regio- and enantioselective hydrosilylation of phenylacetylene with $PhArSiH_2$.[a]

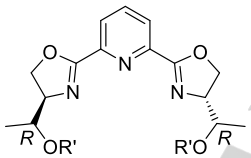


1a **2** **3a**

Entry	Ligand	Sol.	*t* (°C)	Yield [%][b]	*b*:*l* [b]	*ee* [c]
1	**L1**	THF	25	97	98:2	22
2	**L2**	THF	25	82	97:3	32
3	**L3**	THF	25	58	96:4	51
4	**L4**	THF	25	<10	--	--
5	**L5**	THF	25	81	>99:1	82
6	**L6**	THF	25	88	98:2	78
7	**L5**	DME	25	98	99:1	82
8	**L5**	MTBE	25	97	99:1	84
9	**L5**	MTBE	0	63	>99:1	89
10	**L5**	MTBE	-20	30	>99:1	91
11[d]	**L5**	MTBE	-20	66	>99:1	91
12[d,e]	**L5**	MTBE	-20	95	>99:1	91
13[d,e,f]	**L5•CoCl$_2$**	MTBE	-20	97	>99:1	91



L1: R = *i*Bu **L2**: R = *i*Pr
L3: R = *s*Bu **L4**: R = *t*Bu



L5: R' = Si*t*BuPh$_2$ **L6**: R' = Si*t*BuMe$_2$

[a] Conditions: **1a** (0.3 mmol), **2** (0.3 mmol), and solvent (3 mL). [b] Yields and *b*:*l* ratios were determined by GC with mesitylene as an internal standard. [c] Determined by chiral HPLC. [d] With 2.0 equiv **2**. [e] 24 h. [f] With **L5·CoCl$_2$** (2.0 mol%) and $NaBEt_3H$ (6.0 mol%).

yield and selectivity (entries 5 and 6). In particular, the run with **L5** furnished the highest regio- (*b*:*l* = >99:1) and enantioselectivity (82%) among all PyBox ligands investigated in this work, along with a useful yield (81%). Further optimization using **L5** as the ligand revealed that MTBE was the optimal solvent (entry 8). Moreover, decreasing the reaction temperatures led to further enhanced *ee* and even higher regioselectivity, but moderate-to-low yields (entries 9-10). Performing the reaction with two equiv of $Ph(Ar)SiH_2$ **2** and prolonged reaction time (24 h) did afford a high yield (95%) of **3a** with >99:1 *b*:*l* ratio and 91% *ee* (entry 12). The activator NaO*t*Bu was found to react with $Ph(Ar)SiH_2$ **2** to form Ph(Ar)SiH(O*t*Bu) (**S1**). Although in low yield (<5%), the polarity of **S1** is rather similar to that of **3a**, making the product purification difficult. To address this issue, we used an isolated, **L5**-ligated complex **L5·CoCl$_2$** (2.0 mol %) as the precatalyst and $NaBEt_3H$ as the activator. Under such conditions, the reaction gave **3a** in excellent yield (97%) with high regio- (>99:1) and enantioselectivity (91% *ee*) (entry 13).

The absolute configuration of **3a** was determined by the chiroptical method.[13] In addition, the ECD spectra for **3a** were calculated by TD-DFT to assign its absolute configuration.[14] The simulated spectrum is in good agreement with the experimental data, leading to the assignment of a *R* configuration to **3a** (see Supporting Information).

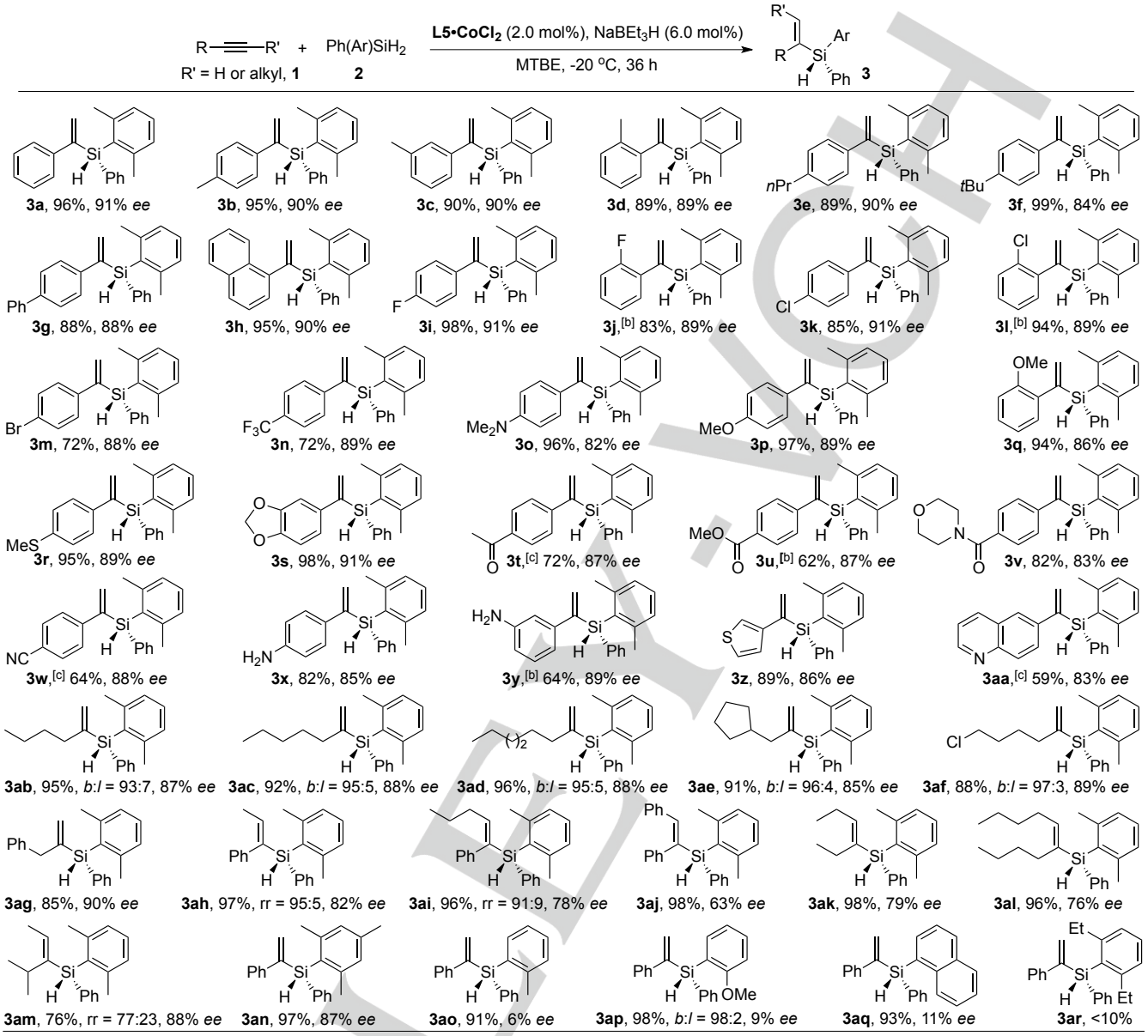
To explore the scope of the Co-catalyzed asymmetric hydrosilylation, **L5·CoCl$_2$** was applied to the reactions of various terminal and internal alkynes with **2** as the silane source. The results are summarized in Table 2. Unless otherwise noted, the regioselective ratios for all the reactions of terminal aryl alkynes were greater than 99:1, in favor of the Markovnikov products. Terminal aryl alkynes bearing both electron-donating and -withdrawing groups on the aryl rings gave the corresponding products in excellent isolated yields with high enantiopurities. Me (*para*, *meta*, *ortho*), F (*para*, *ortho*), and Cl (*para*, *ortho*) substituents at different positions of the aryl rings were tolerated, yielding the branched vinylsilanes (**3b-d, 3i-l**) with 89-91% *ee*. Other alkyl- and Ph-substituted aryl alkynes furnished the desired products (**3e-g**) in high yields and selectivities. The hydrosilylation of α-ethynylnaphthalene provided **3h** in 95% yield with 90% *ee*. In addition to F and Cl, the Br-substituted alkyne (**3m**) was a suitable substrate. Moreover, the substrates containing amine (**3o**), ether (**3p**, **3q**), thioether (**3r**), and acetal (**3s**) functionalities furnished the products with 82-91% *ee*. Noteworthily, a range of reactive functional groups, such as ketone (**3t**), ester (**3u**), amide (**3v**), and cyano (**3w**), were compatible with the hydrosilylation conditions (83-88% *ee*). The unprotected primary anilines (**3x**, **3y**) were also tolerated as demonstrated by the isolation of **3x** and **3y** in satisfactory yields and selectivities. Furthermore, the *S*- and *N*-containing heteroaromatic alkynes (**3z**, **3aa**) reacted in useful yields with good *ee*.

Importantly, the reactions are not limited to the terminal aryl alkynes. The challenging terminal alkyl alkynes underwent hydrosilylations smoothly, albeit with slightly reduced regioselectivity. The reactions of linear 1-hexyne (**3ab**), 1-heptyne (**3ac**) and 1-octyne (**3ad**), and branched alkyne (**3ae**) delivered high yields of chiral vinylsilanes with high regio- (93:7–95:5) and enantioselectivities (85-88% *ee*). The chloride functionality in the alkyl chain was tolerated, as shown by the isolation of **3af** with high yield and selectivity. The reaction of benzyl alkyne gave the desired product **3ag** in 85% yield with 99:1 *b*:*l* ratio and 90% *ee*.

The Co-catalyzed hydrosilylation of arylalkyl-disubstituted internal alkynes furnished the products (**3ah**, **3ai**) in high yields with high regioselectivity (91:9–95:5), favoring the products with the Si group added to the C-atom attached to the aryl group. The enantioselectivities (78-82% *ee*) are slightly lower than that obtained for the terminal alkynes (versus **3a** and **3ab**). The reactions of symmetrical diaryl (**3aj,** 63% *ee*) and dialkyl (**3ak, 3al,** 76-79% *ee*) internal alkynes occurred with moderate-to-good enantioselectivities. Notably, the unsymmetrical dialkyl alkyne, 4-methyl-2-pentyne, gave the product **3am** with a 77:23 rr ratio and 88% *ee*, in favor the product with Si group addition to the sterically more demanding C-atom.

Preliminary investigations of the scope of diaryl dihydrosilanes revealed that the *ortho*-substituents in the aryl ring have a large impact on the enantioselectivity. The incorporation of an additional Me group at the *para* position has a negligible effect on the selectivity (**3an**, 87% *ee*), as expected. However, the substitution of

Table 2. Cobalt-catalyzed asymmetric hydrosilylation of various terminal and internal alkynes with $PhArSiH_2$.[a]



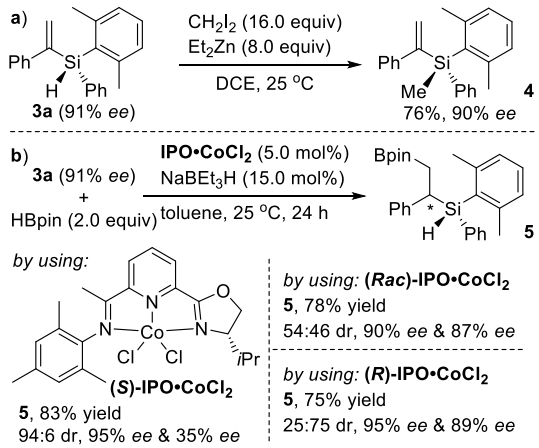
[a] Conditions: on 0.3 mmol scale in MTBE (3 mL) for 36 h. Isolated yields and *ee* values determined by HPLC or SFC on a chiral stationary phase. Unless otherwise noted, *b:l* >99:1. [b] With 5.0 mol% **L5·CoCl$_2$**. [c] With 10.0 mol% **L5·CoCl$_2$** for 70 h.

one *ortho*-Me for H-atom led to a sharp decline in the enantiocontrol (**3ao**, 6% *ee*). Similarly, the mono *ortho*-MeO substituted silane led to low enantioselectivity (**3ap**, 9% *ee*), while the run with 1-naphthalenyl substituted silane gave **3aq** with 11% *ee*. The silane with Et substituents is too sterically bulky to undergo the hydrosilylation (**3ar**, <10%).

The hydrosilylation process proved to be scalable. Using 1 mol% of **L5·CoCl$_2$**, the reaction of phenylacetylene **1a** (6.0 mmol) with 2 equiv of dihydrosilane **2** at −20 °C yielded 1.8 g of **3a** (94% isolated yield) with 91% *ee*.

The silicon-stereogenic vinylhydrosilanes could undergo various transformations through the derivatization of the vinyl and Si–H moieties (Scheme 2). For example, treatment of **3a** with excess CH_2I_2 and $ZnEt_2$ in DCE at 25 °C resulted in a Si–H insertion reaction, giving the Me-substituted tetraorganosilane **4** in high yield with a retention of the configuration on Si-stereocenter (76% yield, 90% *ee*) (Scheme 2a, the *R* configuration of **4** was again determined by the combination of chiroptical methods and TD-DFT calculations, see Supporting Information for details). Next, we explored the possibility for the formation of chiral 1,2-borosilane via Co-catalyzed asymmetric anti-Markovnikov hydroboration of the Si-stereogenic vinylsilane.[11g] Using (*S*)-

$IPO{\cdot}CoCl_2$ as the precatalyst and $NaBEt_3H$ as the activator, the reaction of **3a** with HBpin (2 equiv) at 25 °C gave 83% 1,2-borysilane **5** with excellent diastereoselectivity (94:6) and enantioselectivity (95% *ee*). The asymmetric induction of the chiral Si-stereogenic center on the hydroboration reaction is minimal, as demonstrated by the low diastereoselectivity (54:46) obtained in the reaction using a racemic $IPO{\cdot}CoCl_2$ catalyst. The chirality of (*R*)-$IPO{\cdot}CoCl_2$ appeared to be less matched with the chiral silane **3a** than its *S* isomer, furnishing **5** with 25:75 dr (Scheme 2b).



Scheme 2. Derivatizations of chiral vinylhydrosilane.

In conclusion, we have described an efficient and selective cobalt complex of PyBox for asymmetric formation of synthetic valuable silicon-stereogenic vinylhydrosilane via alkyne hydrosilylation with a prochiral dihydrosilane. The method shows high Markovnikov selectivity in the reactions of terminal alkynes.To our knowledge, this is the first example of alkyne hydrosilylations combining both high regioselectivity and enantioselectivity. Moreover, the results achieved here represent the highest level of enantiocontrol for alkyne hydrosilylation.

Acknowledgements

We gratefully acknowledge the financial support from National Key R&D Program of the MOST of China (2016YFA0202900, 2015CB856600), NSFC (21422209, 21432011, 21732006), CAS (XDB20000000, QYZDB-SSW-SLH016), and STCSM (17JC1401200).

Conflict of interest

The author declare no conflict of interest.

Keywords: asymmetric catalysis • cobalt • hydrosilylation • Si-stereogenic • vinylsilanes

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10.1002/anie.201802806

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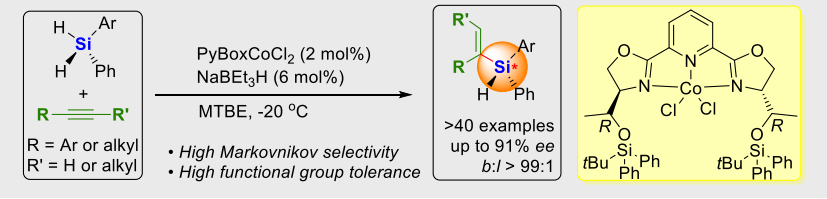

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Asymmetric Synthesis of Silicon-Stereogenic Vinylhydrosilanes via Cobalt-Catalyzed Regio- and Enantioselective Alkyne Hydrosilylation with Dihydrosilanes

A chiral cobalt catalyst of PyBox effects regio- and enantioselective hydrosilylation of unsymmetrical alkynes with a prochiral dihydrosilane, yielding optically pure vinylhydrosilanes with a silicon-stereogenic center.