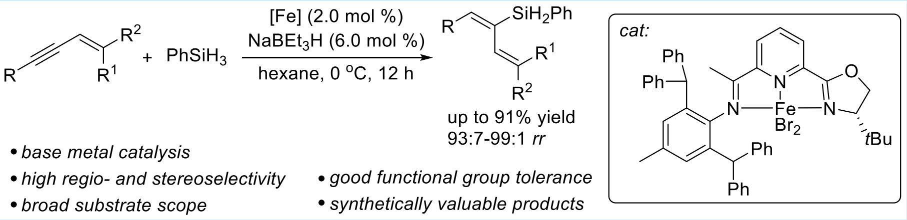
OL Organic Letters

pubs.acs.org/OrgLett Letter

Iron-Catalyzed Regio- and Stereoselective Hydrosilylation of 1,3-Enynes To Access 1,3-Dienylsilanes

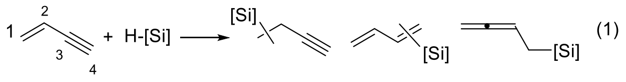
Zhihao Guo, Huanan Wen, Guixia Liu,* and Zheng Huang*

Cite This: *Org. Lett.* 2021, 23, 2375–2379 Read Online



ABSTRACT: A regio- and stereoselective hydrosilylation of 1,3-enynes with primary and secondary silanes to access 1,3-dienylsilanes is accomplished by employing an iron precatalyst bearing iminopyridine-oxazoline (IPO) ligand. The hydrosilylation proceeds via *syn*-addition of a Si—H bond to the alkyne group of 1,3-enynes, incorporating the silyl group at the site proximal to the alkene. The reaction features mild conditions, broad substrate scope, and good functional group tolerance. The synthetic utility was demonstrated by gram-scale reactions and further transformations.

Organosilanes are versatile reagents with low toxicity and reasonable stability, which can participate in various synthetic transformations.[1] Among them, stereodefined 1,3-dienylsilanes are particularly useful to introduce a synthetically valuable 1,3-diene moiety into organic skeletons.[2] Compared with other known methods,[3] hydrosilylation of readily accessible 1,3-enynes offers a straightforward and atom-economical route to 1,3-dienylsilanes. However, such transformation encounters considerable difficulties to control regio- and stereoselectivity due to the existence of several competing pathways including 1,2-, 1,4-, or 3,4-hydrosilylation, as well as other side reactions (eq 1).[4]



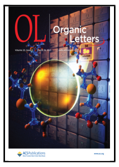
(1)

In the past decades, several selective hydrosilylations of 1,3-enynes to access 1,3-dienylsilanes have been achieved based on precious transition metals,[5−9] such as Pt, Rh, Pd, and Ru. Early studies focused on the hydrosilylation of silicon-substituted butenynes, and the selectivity was influenced by the substitution pattern around the alkyne group.[5] The application of Pt catalyzed cis- and/or Ru catalyzed trans-hydrosilylation of 1,3-enynes in total synthesis has been demonstrated by the group of Fürstner[6] and López[7] independently, but the reaction scope was not well illustrated. The first general regio- and stereoselective hydrosilyation of 1,3-enynes for the synthesis of 1,3-dienylsilanes was reported by Moberg and co-workers using Pd as the catalyst;[8] however, enynes containing terminal olefins are unreactive. In contrast with the successes achieved by precious metals, the development of earth abundant and sustainable catalysts for this transformation has received little attention.[10]

Iron is the most earth-abundant transition metal with minimal environment and toxicity impact. Impressive advantages have been gained for iron catalysis in recent years.[11] In particular, extensive work has been reported for iron-catalyzed hydrosilylation of alkenes and alkynes, some of which exhibited superior efficiency and selectivity compared to that of the noble metal catalysts.[12] In this context, iron becomes a promising candidate for selective hydrosilylation of more complicated substrates, such as 1,3-enynes. During the preparation of this manuscript, the group of Zhu reported a regiodivergent alkyne hydrosilylation, in which some 1,3-enynes were included as the substrates to afford 1,3-dienylsilanes with *syn*-hydrosilylation at the alkyne group selectively.[10b]

Our group has been interested in the development of base metal catalysis and has discovered several highly efficient Fe and Co catalyzed hydrosilylation reactions of alkenes, alkynes, 1,3-dienes, and allenes.[13] We report herein the discovery of an iron-catalyzed selective hydrosilylation of 1,3-enynes, affording 1,3-dienylsilanes in good yields with broad substrate scope.

Received: February 25, 2021
Published: March 10, 2021

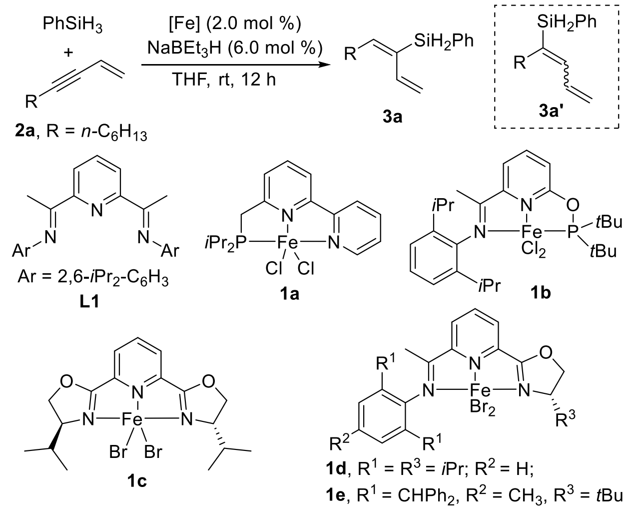


https://dx.doi.org/10.1021/acs.orglett.1c00670
Org. Lett. 2021, 23, 2375−2379

The hydrosilylation proceeds selectively via *syn*-addition of Si−H bond to the alkyne group incorporating the silyl group at the site proximal to the alkene.

In an initial investigation, we employed **2a** as the substrate and attempted the hydrosilylation in the presence of an iron precatalyst with $NaBEt_3H$ as the activator in THF at rt. We focused on the evaluation of tridentate iron complexes, which have proven to be efficient precatalysts for alkene or alkyne hydrosilylation.[14] High conversions but low selectivities were observed for iron complexes supported by pyridinediimine (**L1**), phosphine-bipyridine (**1a**), and phosphinite-iminopyridine (**1b**) ligands (Table 1, entries 1−3). In these cases, **2a** was consumed in varying degrees. However, vinyl silanes **3a** and **3a′** originated from hydrosilylation of the alkyne group of enyne were barely detected, and the poor chemoselectivity made the identification of the products difficult. The use of iron complex **1c** bearing a pyridinebisoxazoline ligand led to the formation of **3a** and its regioisomer **3a′** in yields of 15% and 16%, respectively (entry 4). With one oxazoline arm replaced by an imine, the iminopyridine-oxazoline (IPO) ligated iron complex **1d** enhanced the selectivity significantly, affording **3a** in 57% yield with a minor amount (5%) of the regioisomer **3a′** (entry 5). The structure of **3a** confirmed by NMR analysis indicates hydrosilylaton of 1,3-enynes proceeds selectively via *syn*-addition of a Si−H bond to the alkyne group incorporating the silyl group at the site proximal to the alkene. The high regioselectivity achieved by **1d** inspired us to do further structural modification on the IPO ligand. To our delight, the sterically more hindered (IPO)Fe complex **1e** bearing a *tert*-Bu group on the oxazoline arm and diphenyl methyl groups at the *ortho* positions of the *N*-aryl group showed excellent activity and regioselectivity, affording the 1,2-hydrosilylation product **3a** in satisfying yield (77%) with the ratio **3a**:**3a′** being more than 38:1 (entry 6). The influence of solvent, base, and temperature was investigated. Solvent screening revealed the use of nonpolar solvent (hexane) improved both the yield of **3a** (87%) and the regioselectivity (**3a′**: 1%, entry 7). Excellent yield (94%) and selectivity were obtained with NaO^tBu as the base (entry 8). The reaction proceeded smoothly even at 0 °C furnishing **3a** in 96% yield with excellent regioselectivity (**3a′**: 2%, entry 9).

Table 1. Identification of Iron Catalyst for Selective Monohydrosilylation of 1,3-Enyne 2a[a]



entry	cat.	activator	conv (%)[b]	yield (%)[b] 3a	yield (%)[b] 3a′
1	$FeBr_2$/**L1**	$NaBEt_3H$	82	<1	<1
2	**1a**	$NaBEt_3H$	100	4	3
3	**1b**	$NaBEt_3H$	63	<1	<1
4	**1c**	$NaBEt_3H$	85	15	16
5	**1d**	$NaBEt_3H$	98	57	5
6	**1e**	$NaBEt_3H$	100	77	2
7[c]	**1e**	$NaBEt_3H$	100	87	1
8[c]	**1e**	NaO^tBu	100	94	1
9[c,d]	**1e**	NaO^tBu	100	96	2

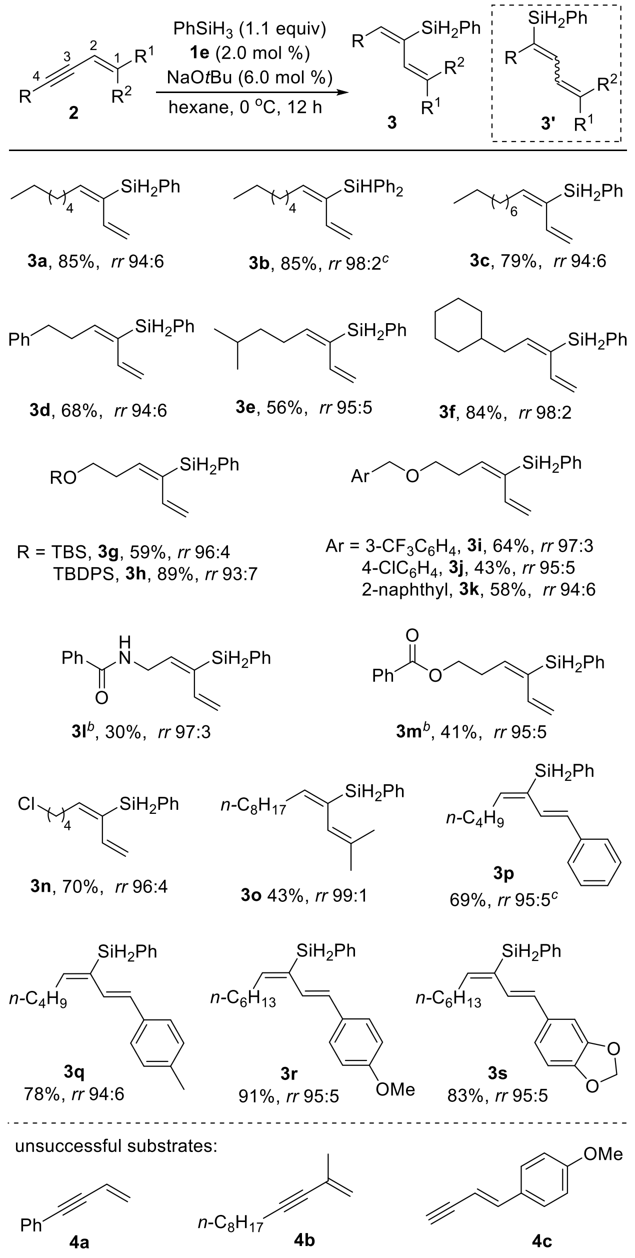
[a] Conditions: **2a** (0.3 mmol), $PhSiH_3$ (0.33 mmol), cat. (2 mol %), and $NaBEt_3H$ (6 mol %) in THF (2 mL) at room temperature for 12 h. [b] Determined by GC using mesitylene as the internal standard. [c] Hexane as the solvent. [d] 0 °C.

With optimal reaction conditions established, the scope and limitations of this iron catalyzed selective hydrosilylation were explored using 1,3-enynes with various substitution patterns (Scheme 1). Linear 1,3-enynes (**3a**−**3c**) bearing a terminal double bond and an internal triple bond were selectively hydrosilylated at alkyne positions, affording 1,3-dienylsilanes in good yields and excellent regioselectivity. In addition to primary hydrosilane, the use of secondary hydrosilane[15] also produced the corresponding product (**3b**) in comparable yield (85%) and regioselectivity (**3b**/**3b′** = 98:2). The selective hydrosilylation could be applicable to enynes with a branched alkyl substitution, as demonstrated by the formation of **3e** and **3f** in moderate yields and excellent regioselectivities. The reaction of enynes containing silyl and benzyl protected hydroxyl groups proceeded smoothly to furnish the desired products (**3g**−**3k**) selectively. Enynes with heteroatoms at the progargylic and homopropargylic position (**3l** and **3m**) were readily transformed to the desired products with excellent regioselectivities, but the yields were relatively low. These results also demonstrated that the reducible functionalities such as amide and ester could be tolerated under the hydrosilylaltion conditions. The synthetically useful $C(sp^3)$−Cl bond was also tolerated, giving chloro-substituted 1,3-dienylsilane **3n** in good yield (70%) with excellent regioselectivity (96:4). In contrast, poor selectivity was observed for 4-phenyl 1-buten-3-yne **4a**, leading to the formation of complicated mixtures.

The reaction is not only suitable for enynes with terminal alkenes but also feasible for 1,3-enynes bearing 1-monosubstitution and 1,1-disubstitution around the double bond. Selective hydrosilylation was achieved for 1,1-dimethyl 1-buten-3-yne to furnish **3o** in 43% yield with 99:1 (**3o**:**3o′**) regioselectivity. Besides aliphatic substitutions, aromatic substituitions were successfully employed at the 1-position of enynes, affording aryl 1,3-dienylsilanes (**3p**−**3s**) in good yields with excellent regioselectivities. However, the introduction of substitutions at the 2-position of enynes (such as **4b**) resulted in low conversion, probably as a result of the large steric hindrance around the alkyne group. In addition, the catalytic system is not compatible with enynes bearing termianl alkynes, as demonstrated by the low conversion of substrate **4c**.

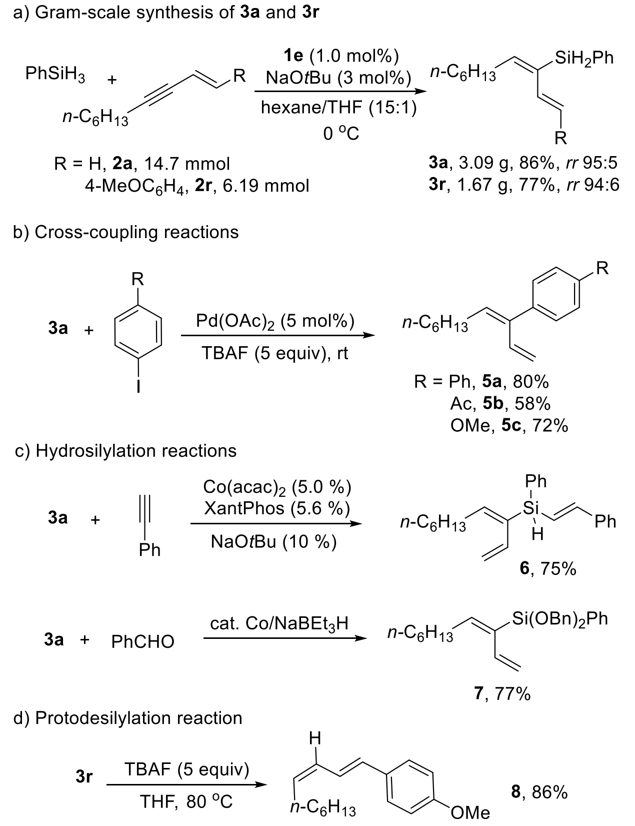
To further showcase the synthetic potential of this method, the selective hydrosilylation of 1,3-enyes was carried out on gram scale. With reduced catalyst loading (1.0 mol %), the gram scale synthesis of **3a** and **3r** was realized in high yields with excellent regioselectivities (Scheme 2a). The utility of 1,3-dienylsilanes was demonstrated by further derivatization.

Scheme 1. Selective Hydrosilylation of 1,3-Enynes to 1,3-Dienylsilanes[a]



[a]Conditions: **2** (0.3 mmol), $PhSiH_3$ (0.33 mmol), **1e** (2 mol %) and NaO^tBu (6 mol %) in hexane (2 mL) at 0 °C for 12 h. Isolated yields. The *rr* value represents the ratio of **3**:**3′**, which was determined by ^1H NMR of isolated product. [b]THF was used as solvent. [c]*rr* was determined by GC because the isomer cannot be identified in the ^1H NMR spectra.

Scheme 2. Gram-scale Synthesis and Elaboration of 1,3-Dienylsilanes



Hiyama—Denmark cross-coupling reactions of **3a** with aryl iodides proceeded smoothly under Pd catalysis. Aryl iodides bearing both electron-donating and -withdrawing groups were compatible, delivering the corresponding aryl-substituted dienes in moderate to good yields (**5a**−**5c**, 58−80%) in a stereospecific manner (Scheme 2b). The presence of Si−H bonds rendered the secondary silane **3a** suitable for further hydrosilylation (Scheme 2c). Treatment of **3a** with phenylacetylene with a cobalt catalyst of XantPhos led to regioselective anti-Markovnikov 1,2-hydrosilylation of the terminal alkyne, affording 1,3-dienyl vinylsilane **6** in 75% yield with (*E*)-stereoselectivity. Moreover, the Co-catalyzed dual hydrosilylation of benzaldehyde was performed to provide the corresponding bis(oxo)silane **7** in 77% yield. In addition, the dienylsilane product **3r** was ready to undergo protodesilylation upon treatment with TBAF to give *E*,*Z*-configured diene **8** in 86% yield (Scheme 2d).

In summary, we have developed an iron-catalyzed regio- and stereoselective hydrosilylation of 1,3-enynes to access 1,3-dienylsilanes with tridentate iminopyridine-oxazoline as the ligand. This catalytic system is applicable to 4-alkyl, 1,4-disubstituted, and 1,1,4-trisubstituted 1,3-enynes with good functional group tolerance. The protocol provides a straightforward and atom-economical route to synthetically valuable 1,3-dienylsilanes containing two Si−H bonds, which are ready for further transformations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00670.

General information, experimental procedures, characterization of products, and full analytical data with spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Guixia Liu − *State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of*

Sciences, Shanghai 200032, China; orcid.org/0000-0001-7565-2183; Email: guixia@sioc.ac.cn

Zheng Huang − *Chang-Kung Chuang Institute, East China Normal University, Shanghai 200062, China; State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China; School of Chemistry and Material Sciences, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China;* orcid.org/0000-0001-7524-098X; Email: huangzh@sioc.ac.cn

Authors

Zhihao Guo − *Chang-Kung Chuang Institute, East China Normal University, Shanghai 200062, China; State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

Huanan Wen − *State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c00670

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (Nos. 22072178, 21825109, 21821002, 21732006), the National Basic Research Program of China (No. 2016YFA0202900), the Strategic Priority Research Program of Chinese Academy of Sciences (No. XDB20000000), the Chinese Academy of Sciences Key Research Program of Frontier Sciences (No. QYZDB-SSW-SLH016), and the K. C. Wong Education Foundation is gratefully acknowledged.

■ REFERENCES

(1) (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. Silafunctional compounds in organic synthesis. Part 20. Hydrogen peroxide oxidation of the silicon-carbon bond in organoalkoxysilanes. *Organometallics* **1983**, *2*, 1694−1696. (b) Fleming, I.; Henning, R.; Plaut, H. The phenyldimethylsilyl group as a masked form of the hydroxy group. *J. Chem. Soc., Chem. Commun.* **1984**, 29−31. (c) Hiyama, T. How I came across the silicon-based cross-coupling reaction. *J. Organomet. Chem.* **2002**, *653*, 58−61. (d) Denmark, S. E.; Regens, C. S. Palladium-Catalyzed Cross-Coupling Reactions of Organosilanols and Their Salts: Practical Alternatives to Boron- and Tin-Based Methods. *Acc. Chem. Res.* **2008**, *41*, 1486−1499. (e) Nakao, Y.; Hiyama, T. Silicon-based cross-coupling reaction: an environmentally benign version. *Chem. Soc. Rev.* **2011**, *40*, 4893−4901.

(2) (a) Fleming, I.; Barbero, A.; Walter, D. Stereochemical Control in Organic Synthesis Using Silicon-Containing Compounds. *Chem. Rev.* **1997**, *97*, 2063−2192. (b) Welker, M. E. Recent advances in syntheses and reaction chemistry of boron and silicon substituted 1,3-dienes. *Tetrahedron* **2008**, *64*, 11529−11539. (c) Zhao, F.; Zhang, S.; Xi, Z. Silyl-substituted 1,3-butadienes for Diels−Alder reaction, ene reaction and allylation reaction. *Chem. Commun.* **2011**, *47*, 4348−4357.

(3) (a) Cai, M.; Hao, W.; Zhao, H.; Song, C. Novel stereoselective synthesis of 1,3-dienylsilanes via hydromagnesiation reaction of alkynylsilanes. *J. Organomet. Chem.* **2003**, *679*, 14−16. (b) Olsson, V. J.; Szabó, K. J. Synthesis of Allylsilanes and Dienylsilanes by a One-Pot Catalytic C−H Borylation−Suzuki−Miyaura Coupling Sequence. *Org. Lett.* **2008**, *10*, 3129−3131. (c) Takeda, T.; Mori, A.; Fujii, T.; Tsubouchi, A. Diversity oriented synthesis of conjugate dienes and alkenylcyclopropanes utilizing silyl group-substituted titanium carbene complexes as bimetallic synthetic reagents. *Tetrahedron* **2014**, *70*, 5776−5786. (d) Szudkowska-Frątczak, J.; Marciniec, B.; Hreczycho, G.; Kubicki, M.; Pawluć, P. Ruthenium-Catalyzed Silylation of 1,3-Butadienes with Vinylsilanes. *Org. Lett.* **2015**, *17*, 2366−2369. (e) Rivas, A.; Pequerul, R.; Barracco, V.; Domínguez, M.; López, S.; Jiménez, R.; Parés, X.; Alvarez, R.; Farrés, J.; de Lera, A. R. Synthesis of C11-to-C14 methyl-shifted all-trans-retinal analogues and their activities on human aldo-keto reductases. *Org. Biomol. Chem.* **2020**, *18*, 4788−4801.

(4) (a) Maruyama, Y.; Yoshiuchi, K.; Ozawa, F.; Wakatsuki, Y. Regio- and stereoselective hydrosilylation of 1,4-bis(trimethylsilyl)-3-buten-1-ynes. *Chem. Lett.* **1997**, *26*, 623−624. (b) Maruyama, Y.; Yoshiuchi, K.; Ozawa, F. Hydrosilylation of 1,4-bis(trimethylsilyl)-1-buten-3-ynes using late transition metal hydrides as catalyst precursors. *J. Organomet. Chem.* **2000**, *609*, 130−136. (c) Han, J. W.; Tokunaga, N.; Hayashi, T. Palladium-catalyzed asymmetric hydrosilylation of 4-substituted 1-buten-3-ynes. Catalytic asymmetric synthesis of axially chiral allenylsilanes. *J. Am. Chem. Soc.* **2001**, *123*, 12915−12916. (d) Luken, C.; Moberg, C. Silaborations of 1,3-enynes - Substrate controlled allene/1,3-diene selectively. *Org. Lett.* **2008**, *10*, 2505−2508. (e) Sang, H. L.; Yu, S.; Ge, S. Copper-catalyzed asymmetric hydroboration of 1,3-enynes with pinacolborane to access chiral allenylboronates. *Org. Chem. Front.* **2018**, *5*, 1284−1287. (f) Wang, B.; Li, Y.; Pang, J. H.; Watanabe, K.; Takita, R.; Chiba, S. Hydromagnesiation of 1,3-Enynes by Magnesium Hydride for Synthesis of Tri- and Tetra-substituted Allenes. *Angew. Chem., Int. Ed.* **2021**, *60*, 217−221.

(5) (a) Kusumoto, T.; Hiyama, T. Hydrosilylation of 1,4-bis(trimethylsilyl)-1,3-butadiyne. *Chem. Lett.* **1985**, *14*, 1405−1408. (b) Kusumoto, T.; Ando, K.; Hiyama, T. Hydrosilylation of 1,4-bis(trimethylsilyl)butadiyne and silyl-substituted butenynes. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1280−1290.

(6) (a) Micoine, K.; Fürstner, A. Concise Total Synthesis of the Potent Translation and Cell Migration Inhibitor Lactimidomycin. *J. Am. Chem. Soc.* **2010**, *132*, 14064−14066. (b) Gallenkamp, D.; Fürstner, A. Stereoselective Synthesis of E,Z-Configured 1,3-Dienes by Ring-Closing Metathesis. Application to the Total Synthesis of Lactimidomycin. *J. Am. Chem. Soc.* **2011**, *133*, 9232−9235.

(7) (a) Bergueiro, J.; Montenegro, J.; Cambeiro, F.; Saa, C.; López, S. Cross-Coupling Reactions of Organosilicon Compounds in the Stereocontrolled Synthesis of Retinoids. *Chem. - Eur. J.* **2012**, *18*, 4401−4410. (b) Bergueiro, J.; Montenegro, J.; Saa, C.; López, S. Synthesis of 11-cis-Retinoids by Hydrosilylation-Protodesilylation of an 11,12-Didehydro Precursor: Easy Access to 11- and 12-Mono- and 11,12-Dideuteroretinoids. *Chem. - Eur. J.* **2012**, *18*, 14100−14107.

(8) Zhou, H.; Moberg, C. Regio- and Stereoselective Hydrosilylation of 1,3-Enynes Catalyzed by Palladium. *Org. Lett.* **2013**, *15*, 1444−1447.

(9) (a) Trost, B. M.; Ball, Z. T.; Jöge, T. Regioselective Hydrosilylation of Propargylic Alcohols: An Aldol Surrogate. *Angew. Chem., Int. Ed.* **2003**, *42*, 3415−3418. (b) Trost, B. M.; Ball, Z. T. Alkyne Hydrosilylation Catalyzed by a Cationic Ruthenium Complex: Efficient and General Trans Addition. *J. Am. Chem. Soc.* **2005**, *127*, 17644−17655. (c) Choudhury, P. P.; Junker, C. S.; Pidaparthi, R. R.; Welker, M. E. Syntheses of 2-silicon-substituted 1,3-dienes. *J. Organomet. Chem.* **2014**, *754*, 88−93.

(10) (a) Wu, G.; Chakraborty, U.; Jacobi von Wangelin, A. Regiocontrol in the cobalt-catalyzed hydrosilylation of alkynes. *Chem. Commun.* **2018**, *54*, 12322. (b) Hu, M.-Y.; He, P.; Qiao, T.-Z.; Sun, W.; Li, W.-T.; Lian, J.; Li, J.-H.; Zhu, S.-F. Iron-Catalyzed

Regiodivergent Alkyne Hydrosilylation. *J. Am. Chem. Soc.* **2020**, *142*, 16894−16902.

(11) (a) Iron Catalysis II; Bauer, E. B., Ed.; *Topics in Organometallic Chemistry*; Springer: 2015; Vol. *50*. (b) Fürstner, A. Iron Catalysis in Organic Synthesis: A Critical Assessment of What It Takes To Make This Base Metal a Multitasking Champion. *ACS Cent. Sci.* **2016**, *2*, 778−789. (c) Shang, R.; Ilies, L.; Nakamura, E. Iron-Catalyzed C−H Bond Activation. *Chem. Rev.* **2017**, *117*, 9086−9139. (d) Wei, D.; Darcel, C. Iron Catalysis in Reduction and Hydrometalation Reactions. *Chem. Rev.* **2019**, *119*, 2550−2610. (e) Casnati, A.; Lanzi, M.; Cera, G. Recent Advances in Asymmetric Iron Catalysis. *Molecules* **2020**, *25*, 3889−3917.

(12) (a) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P. Iron-Catalyzed Hydrofunctionalisation of Alkenes and Alkynes. *ChemCatChem* **2015**, *7*, 190−222. (b) Chen, J.; Lu, Z. Asymmetric hydrofunctionalization of minimally functionalized alkenes via earth abundant transition metal catalysis. *Org. Chem. Front.* **2018**, *5*, 260−272. (c) Obligacion, J. V.; Chirik, P. J. Earth-abundant transition metal catalysts for alkene hydrosilylation and hydroboration. *Nat. Rev. Chem.* **2018**, *2*, 15−34. (d) Du, X.; Huang, Z. Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. *ACS Catal.* **2017**, *7*, 1227−1243. (e) de Almeida, L. D.; Wang, H.; Junge, K.; Cui, X.; Beller, M. Recent Advances in Catalytic Hydrosilylations: Developments beyond Traditional Platinum Catalysts. *Angew. Chem., Int. Ed.* **2021**, *60*, 550−565.

(13) (a) Peng, D.; Zhang, Y.; Du, X.; Zhang, L.; Leng, X.; Walter, M. D.; Huang, Z. Phosphinite-Iminopyridine Iron Catalysts for Chemoselective Alkene Hydrosilylation. *J. Am. Chem. Soc.* **2013**, *135*, 19154−19166. (b) Zuo, Z.; Zhang, L.; Leng, X.; Huang, Z. Iron-catalyzed asymmetric hydrosilylation of ketones. *Chem. Commun.* **2015**, *51*, 5073−5076. (c) Du, X.; Zhang, Y.; Peng, D.; Huang, Z. Base-Metal-Catalyzed Regiodivergent Alkene Hydrosilylations. *Angew. Chem., Int. Ed.* **2016**, *55*, 6671−6675. (d) Yang, Z.; Peng, D.; Du, X.; Huang, Z.; Ma, S. Identifying a cobalt catalyst for highly selective hydrosilylation of allenes. *Org. Chem. Front.* **2017**, *4*, 1829−1832. (e) Wen, H.; Wan, X.; Huang, Z. Asymmetric Synthesis of Silicon-Stereogenic Vinylhydrosilanes by Cobalt-Catalyzed Regio- and Enantioselective Alkyne Hydrosilylation with Dihydrosilanes. *Angew. Chem., Int. Ed.* **2018**, *57*, 6319−6323. (f) Wen, H.; Wang, K.; Zhang, Y.; Liu, G.; Huang, Z. Cobalt-Catalyzed Regio- and Enantioselective Markovnikov 1,2-Hydrosilylation of Conjugated Dienes. *ACS Catal.* **2019**, *9*, 1612−1618.

(14) Wen, H.; Liu, G.; Huang, Z. Recent advances in tridentate iron and cobalt complexes for alkene and alkyne hydrofunctionalizations. *Coord. Chem. Rev.* **2019**, *386*, 138−153.

(15) The use of tertiary silanes, such as Et_3SiH and $(EtO)_3SiH$, did not produce the desired product due to low reactivity.