

Electrochemical Hydrosilylation of Alkynes

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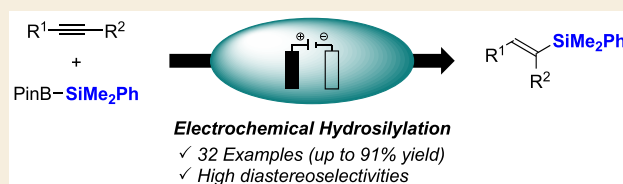
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ABSTRACT: Herein, the electrochemical hydrosilylation of alkynes is reported. In the presence of the Suginome reagent (PhMe₂Si–Bpin), a large panel of terminal alkynes and internal alkynes was successfully converted into the hydrosilylated product in good to excellent yields and good selectivity in favor of the linear product. Preliminary mechanistic study supported the involvement of a silyl radical, which reacted on the alkyne.

KEYWORDS: *Electrochemistry, hydrosilylation, alkynes, silyl radical, Suginome reagent*



Silicon-containing molecules are key compounds in organic synthesis and have found widespread applications in

Scheme 1. State of the Art and Present Work

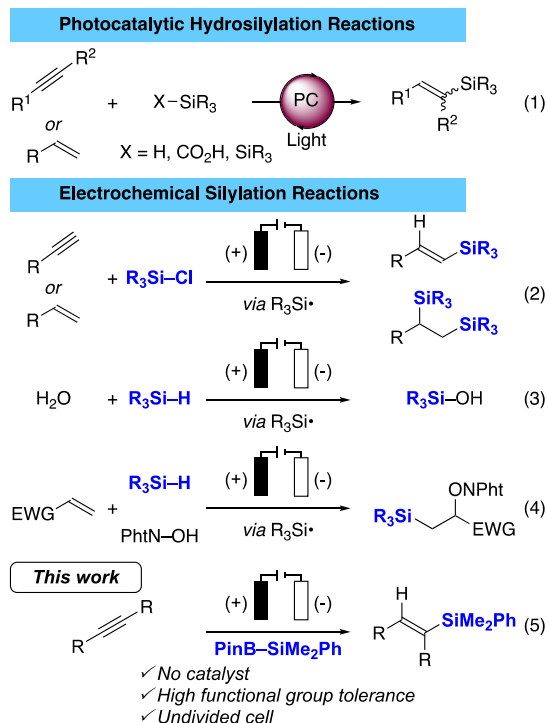


Table 1. Optimization of the Reaction^a

entry	variation from standard conditions	yield (%) ^b	l:b ^c
1	none	73	93:7
2	CH ₃ CN 100%	0	
3	THF instead of CH ₃ CN	42	86:14
4	CH ₃ CN:MeOH (4:1) instead of (9:1)	37	91:9
5	Ni foam electrodes instead of SST	<5	
6	Pt electrodes instead of SST	0	ND ^d
7	<i>n</i> Bu ₄ NOAc instead of <i>n</i> Bu ₄ NBF ₄	25	ND
8	<i>n</i>Bu₄NCl instead of <i>n</i>Bu₄NBF₄	87	90:10
9	no current	NR ^e	ND

^aReaction conditions: phenyl acetylene (0.4 mmol), Suginome reagent (1.5 equiv), *n*Bu₄NBF₄ [0.1 M] in CH₃CN:CH₃OH (9:1, 4 mL), rt, stainless steel electrodes (cathode and anode), 10 mA, 2 F·mol⁻¹, 5 mA·cm⁻², undivided cell, under air. ^bDetermined by ¹H NMR using CH₃NO₂ as an internal standard. ^cLinear:branched ratio determined on the crude reaction mixture using ¹H NMR. ^dND: Not determined. ^eNR: No reaction.

one.⁶ The synthetic arsenal for the hydrosilylation of alkenes and alkynes mainly relies on the use of expensive transition metal complexes (e.g., Speier and Karstedt catalysts), although outstanding progress in the development of earth abundant

materials and life sciences^{1–3} as well as in drug discovery programs.^{4,5} In addition, organosilicon species are strategic building blocks with applications in various important transformations (e.g., Hiyama–Denmark cross-coupling, Brook rearrangement, Hosomi–Sakurai allylation...). Among the available reaction manifolds to forge organosilicon species, the hydrosilylation reaction is probably the most important

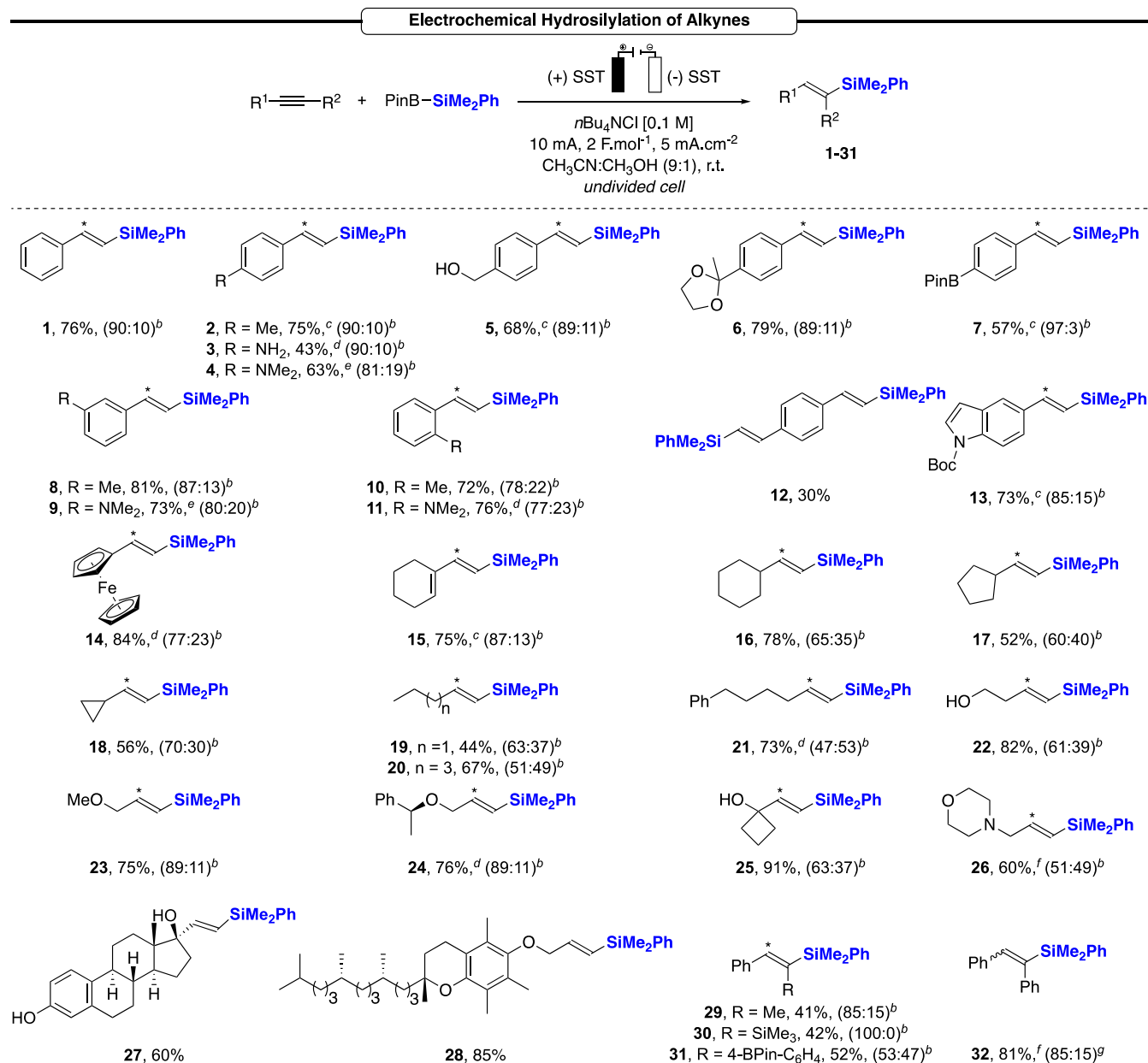
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Scheme 2. Electrochemical Hydrosilylation of Alkynes with the Suginome Reagent^a

^aReaction conditions: alkyne (0.4 mmol), Suginome reagent (1.5 equiv), *n*Bu₄NCl [0.1 M] in CH₃CN:CH₃OH (9:1, 4 mL), rt, stainless steel electrodes (cathode and anode), 10 mA, 2 F·mol⁻¹, 5 mA·cm⁻², undivided cell, under air. ^bDetermined by ¹H NMR on the crude reaction mixture, the major isomer was represented. ^c2.5 F·mol⁻¹. ^d3 F·mol⁻¹. ^e4 F·mol⁻¹. ^f3.5 F·mol⁻¹. ^gE:Z ratio determined for the crude reaction mixture.

metal catalyzed hydrosilylation reactions were recently outlined.⁷ Very recently, under the auspices of photocatalysis, an impetus to design new hydrosilylation reactions, through the generation of silyl radical, was witnessed and significant contributions were reported (Scheme 1, eq 1).^{8–17}

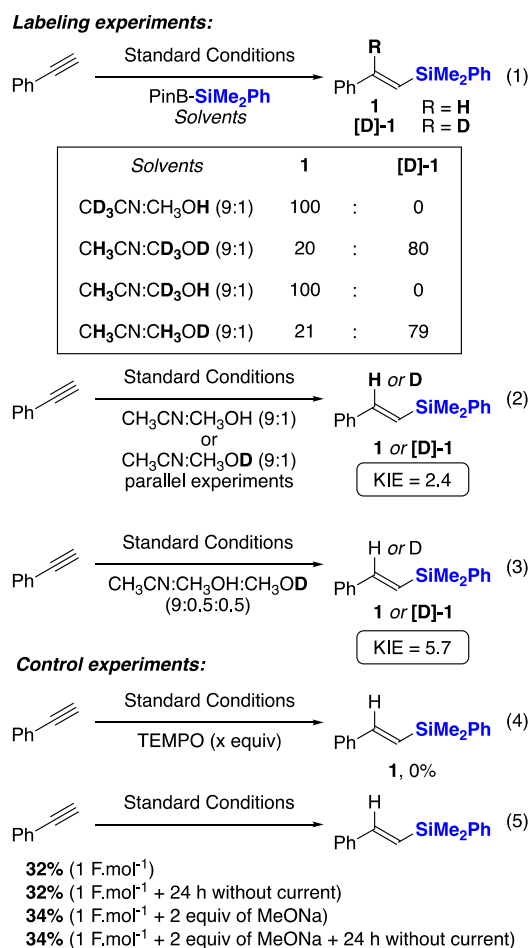
Moreover, organic electrochemistry has known a resurgence of interest and allowed the design of challenging transformations in a sustainable manner.^{18–24} Therefore, electrochemistry appeared as a method of choice for the efficient generation of silyl radicals. In 2020, Lin and co-workers developed the vicinal disilylation of alkenes, alkynes, and allenes as well as the hydrosilylation of alkenes and alkynes using chlorosilanes, under electroreductive conditions, as source of silyl radicals (Scheme 1, eq 2).²⁵ Subsequently, Zhang and co-workers reported the electrochemical conversion

of silanes into silanols according to an electro-oxidation process (Scheme 1, eq 3).²⁶ Then, He and co-workers described the electrochemical silyl-oxygenation of electron-deficient terminal alkenes.²⁷ This methodology is based on the in situ formation of a silyl radical from a silane with an electrogenerated *N*-oxyl radical from the corresponding *N*-hydroxy species (Scheme 1, eq 4).

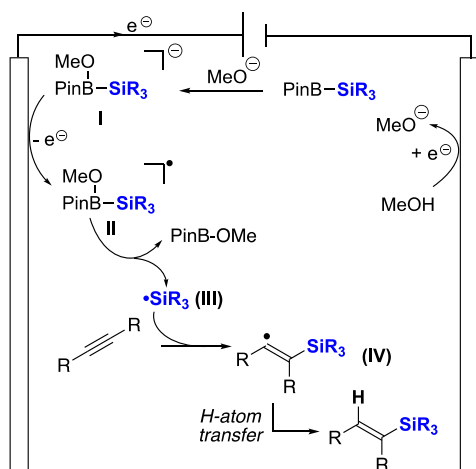
In light of the conspicuous absence of electrochemical hydrosilylation of alkynes, we conjectured that an original approach using the Suginome reagent (PhMe₂Si–Bpin) would enable the formation of a silyl radical.

Indeed, we recently demonstrated the possible oxidation of this reagent in the presence of a photocatalyst to generate the corresponding silyl radical and promote the hydrosilylation of alkynes and alkenes under continuous flow conditions.²⁸

Scheme 3. Control Experiments



Scheme 4. Plausible Mechanism for the Electrochemical Hydrosilylation Reaction with the Suginome Reagent



Hence, we intend to harness this possible oxidation in a catalyst free process using electrochemical conditions to develop the hydrosilylation of alkynes (Scheme 1, eq 5). Based on the above blueprints, we started our investigations by studying the hydrosilylation of phenyl acetylene.

After investigations, we discovered that the reaction in an undivided cell using stainless steel electrodes at both the anode and the cathode, a constant current of 10 mA, a total charge of 2 F mol⁻¹ in a 0.1 M solution of *n*Bu₄NBF₄ in a 9:1 mixture of

CH₃CN/CH₃OH gave the desired product **1** in 73% yield as a 93:7 mixture of linear and branched products and a complete *E*-selectivity for the linear product (Table 1, entry 1). In the course of the optimization, we found that the presence of CH₃OH was crucial for the formation of **1**, and CH₃CN was the best cosolvent (entry 3) and an optimum ratio of 9:1 was beneficial (entry 4). Moreover, the use of other electrodes at both the cathode or the anode was detrimental for the reaction (entries 5 and 6). Finally, a survey of the electrolytes demonstrated that switching from *n*Bu₄NBF₄ to *n*Bu₄NCl, gave the hydrosilylated product **1** in 87% as 90:10 mixture of the linear and branched isomers, while *n*Bu₄NOAc was less efficient (entries 7 and 8). Finally a control experiment revealed that the reaction did not proceed in the absence of current (entry 9).

With these optimized conditions in hand, we examined the scope and the limitations of this electrochemical hydrosilylation reaction (Scheme 2). First, the substitution of the aromatic ring on the phenyl acetylene scaffold was studied. The presence of electron-donating (NH₂ and NMe₂) or methyl group at the *para*-position was well tolerated and the products were isolated in good to excellent yields with a good selectivity in favor of the linear product (2–4). Then, other substituents, like alcohol (5), acetal (6), or boronic acid ester (7), were introduced, giving the hydrosilylated products in similar yields and selectivities. Note that in the case of the boronic ester (7), the product was contaminated with the product resulting from the desilylation reaction (ca. 19%). The substitution pattern was also evaluated, and the substitution at neither the *meta* nor the *ortho* position hampers the reaction efficiency (8–11). Pleasingly, the functionalization of a bis-alkyne was performed, although the yield of the reaction remained modest (30%). The reaction was also tolerant to indole and ferrocene substituents as shown with the compounds **13** and **14**. Then, an enyne was tested and the reaction was selective to the alkyne residue, giving **15** in a good 75% and a 87:13 ratio in favor of the linear product. Alkyl-substituted alkynes were then evaluated, and the products **16–21** were obtained in good to excellent yield and poor to moderate selectivities toward the formation of the linear product (up to 70:30). The reaction was tolerant to the unprotected alcohol as well as the ether motif, giving the product in good yield, albeit with a moderate linear:branched selectivity (22–24). Interestingly, the presence of a tertiary alcohol or a morpholine moiety did not hamper the efficiency of the reaction, as demonstrated with compounds **25** and **26**. Then, the reaction was tested on complex molecules (i.e., ethynyl estradiol and α -tocopherol derivatives) and the products **27** and **28** were isolated in good 60% and 85% yields, respectively, demonstrating the efficiency of the reaction on complex structures. Finally, the reaction was evaluated with internal alkynes, and the corresponding vinyl silanes **29–32** were isolated in moderate to excellent yield and good to excellent selectivity (85:15 to 100:0).

To get a better understanding of the reaction, we carried out several control experiments.²⁹ First, labeling experiments using a mixture of deuterated and nondeuterated solvents were conducted to ascertain the origin of H atom incorporated into the final product (Scheme 3, eq 1). These results suggested that the H-atom, added to the alkene, results from the cleavage of the O–H bond of the methanol, despite a higher bond dissociation energy (BDE) compared to CH₃CN.³⁰ Note that similar levels of deuterium incorporation were obtained when

the labeling experiments were performed with the aliphatic substituted alkyne **23**.²⁹ Then, the kinetic isotopic effect was measured. In parallel reactions, KIE = 2.4 was measured, while the reaction carried out in a CH₃CN:CH₃OH:CH₃OD mixture (9:0.5:0.5) gave KIE = 5.4 (Scheme 3, eqs 2 and 3). These results support that the H abstraction after the addition of the silyl residue to the alkyne could be the rate determining step. Then, a control experiment demonstrated that the reaction is suppressed in the presence of TEMPO. Then, we precluded that the reaction might result from the presence of metallic salts released from the electrodes. Indeed, when the reaction was stopped after 64 min (1 F·mol⁻¹) and allowed to stir for an additional period of 24 h, no increase of the reaction yield was witnessed (Scheme 1, eq 5). Finally, we demonstrated that the addition of MeONa (2 equiv) to the reaction mixture did not enhance the rate of the reaction (Scheme 3, eq 5). Moreover, additional stirring of the reaction mixture for 24 h in the presence of immersed electrodes and 2 equiv of MeONa did not increase the reaction yield. This result suggests that no side reaction involving the methoxide anion and the Suginome reagent occurred in our electrochemical process. In addition, this result highlights the requirement of electricity to promote the reaction. With these observations in hand, we suggested the following mechanism (Scheme 4).

First, the methoxide anion, generated by the reduction of the methanol at the cathode, reacted with the Suginome reagent to form a borate species **I**. A subsequent anodic oxidation of the borate **I**²⁸ could generate the radical species **II**, which decomposes into PinB-OMe and the silyl radical **III**. Then, a fast addition³¹ of this radical to the alkyne led to the highly reactive vinyl radical **IV**. A final H abstraction resulted in the formation of the hydrosilylated product. With regard to this final H-abstraction and taking into account the labeling experiments and the previous studies from our group,^{32–34} we suggested that the H atom comes from the O–H bond of the methanol. However, taking into account the high bond dissociation energy of this bond,³⁰ a possible coordination of the latter to a boron species (i.e., a Lewis acid center) might decrease the bond dissociation energy of the O–H bond and therefore allow the H abstraction by the radical **IV**.

In conclusion, we report herein a practical procedure for the hydrosilylation of alkynes under electrochemical conditions. The reaction proceeded smoothly and was applied to the functionalization of a large panel of terminal and disubstituted alkynes in good to excellent yields and decent selectivities in favor of the linear product. With control experiments, a plausible mechanism was suggested involving the addition of a silyl radical, generated at the anode, on the alkyne.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsorginorgau.1c00035>.

Experimental procedures, compound characterization data, ¹H and ¹³C spectra of the products (PDF)

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Author Contributions

T.B. performed all experiments. T.B., P.J., and T.P. conceived the project and analyzed the results. T.P. wrote the manuscript with the input of all the authors.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- Roy, A. K. A Review of Recent Progress in Catalyzed Homogeneous Hydrosilylation (Hydrosilylation). *Adv. Organomet. Chem.* **2007**, *55*, 1–59.
- Troegel, D.; Stohrer, J. Recent Advances and Actual Challenges in Late Transition Metal Catalyzed Hydrosilylation of Olefins From an Industrial Point of View. *Coord. Chem. Rev.* **2011**, *255*, 1440–1459.
- Nakajima, Y.; Shimada, S. Hydrosilylation Reaction of Olefins: recent Advances and Perspectives. *RSC Adv.* **2015**, *5*, 20603–20616.
- Fujii, S.; Hashimoto, Y. Progress in the Medicinal Chemistry of Silicon: C/Si Exchange and Beyond. *Future Med. Chem.* **2017**, *9*, 485–505.
- Franz, A. K.; Wilson, S. O. Organosilicon Molecules with Medicinal Applications. *J. Med. Chem.* **2013**, *56*, 388–405.
- For a recent review, see: Naganawa, Y.; Inomata, K.; Sato, K.; Nakajima, Y. Hydrosilylation of Functionalized Alkenes. *Tetrahedron Lett.* **2020**, *61*, 151513. and references cited herein.
- Obligacion, J. V.; Chirik, P. J. Earth-Abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. *Nat. Rev. Chem.* **2018**, *2*, 15–34.
- Qrareya, H.; Dondi, D.; Ravelli, D.; Fagnoni, M. Decatungstate-Photocatalyzed Si–H/C–H Activation in Silyl Hydrides: Hydrosilylation of Electron-Poor Alkenes. *ChemCatChem* **2015**, *7*, 3350–3357.
- Yu, W. L.; Luo, Y. C.; Yan, L.; Liu, D.; Wang, Z.-Y.; Xu, P.-F. Dehydrogenative Silylation of Alkenes for the Synthesis of Substituted Allylsilanes by Photoredox, Hydrogen-Atom Transfer, and Cobalt Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 10941–10945.

- (10) Wan, Y.; Zhu, J.; Yuan, Q.; Wang, W.; Zhang, Y. Synthesis of β -Silyl α -Amino Acids via Visible-Light-Mediated Hydrosilylation. *Org. Lett.* **2021**, *23*, 1406–1410.
- (11) Zhu, J.; Cui, W.-C.; Wang, S.; Yao, Z.-J. Visible Light-Driven Radical Trans-Hydrosilylation of Electron-Neutral and -Rich Alkenes with Tertiary and Secondary Hydrosilanes. *J. Org. Chem.* **2018**, *83*, 14600–14609.
- (12) Yu, W. L.; Luo, Y. C.; Yan, L.; Liu, D.; Wang, Z.-Y.; Xu, P.-F. Dehydrogenative Silylation of Alkenes for the Synthesis of Substituted Allylsilanes by Photoredox, Hydrogen-Atom Transfer, and Cobalt Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 10941–10945.
- (13) Xu, N. X.; Li, B. X.; Wang, C.; Uchiyama, M. Sila- and Germacarboxylic Acids: Precursors for the Corresponding Silyl and Germyl Radicals. *Angew. Chem., Int. Ed.* **2020**, *59*, 10639–10644.
- (14) Yu, X.; Lübbesmeier, M.; Studer, A. Oligosilanes as Silyl Radical Precursors Through Oxidative Si-Si Bond Cleavage Using Redox Catalysis. *Angew. Chem., Int. Ed.* **2021**, *60*, 675–679.
- (15) Zhu, J.; Cui, W.-C.; Wang, S.; Yao, Z.-J. Radical Hydrosilylation of Alkynes Catalyzed by Eosin Y and Thiol Under Visible Light Irradiation. *Org. Lett.* **2018**, *20*, 3174–3178.
- (16) Liang, H.; Ji, Y.-X.; Wang, R.-H.; Zhang, Z.-H.; Zhang, B. Visible-Light-Initiated Manganese-Catalyzed E-Selective Hydrosilylation and Hydrogermylation of Alkynes. *Org. Lett.* **2019**, *21*, 2750–2754.
- (17) Hou, H.; Xu, Y.; Yang, H.; Chen, X.; Yan, C.; Shi, Y.; Zhu, S. Visible-Light Mediated Hydrosilylative and Hydrophosphorylative Cyclizations of Enynes and Dienes. *Org. Lett.* **2020**, *22*, 1748–1753.
- (18) Pollok, D.; Waldvogel, S. R. Electro-Organic Synthesis – a 21st Century Technique. *Chem. Sci.* **2020**, *11*, 12386–12400.
- (19) Yan, M.; Kawamata, Y.; Baran, P. S. Synthetic Organic Electrochemical Methods Since 2000: on the Verge of a Renaissance. *Chem. Rev.* **2017**, *117*, 13230–13319.
- (20) Mitsudo, K.; Kurimoto, Y.; Yoshioka, K.; Suga, S. Miniaturization and Combinatorial Approach in Organic Electrochemistry. *Chem. Rev.* **2018**, *118*, 5985–5999.
- (21) Waldvogel, S. R.; Janza, B. Renaissance of Electrosynthetic Methods for the Construction of Complex Molecules. *Angew. Chem., Int. Ed.* **2014**, *53*, 7122–7123.
- (22) Wiebe, A.; Gieshoff, T.; Möhle, S.; Rodrigo, E.; Zirbes, M.; Waldvogel, S. R. Electrifying Organic Synthesis. *Angew. Chem., Int. Ed.* **2018**, *57*, 5594–5619.
- (23) Frontana-Urbe, B. A.; Little, R. D.; Ibanez, J. G.; Palma, A.; Vasquez-Medrano, R. Organic Electrosynthesis: a Promising green Methodology in Organic Chemistry. *Green Chem.* **2010**, *12*, 2099–2119.
- (24) Cembellín, S.; Batanero, B. Organic Electrosynthesis Towards Sustainability: Fundamentals and Greener Methodologies. *Chem. Rec.* **2021**, *21*, 2453–2471.
- (25) Lu, L.; Siu, J. C.; Lai, Y.; Lin, S. An Electroreductive Approach to Radical Silylation via the Activation of Strong Si-Cl Bond. *J. Am. Chem. Soc.* **2020**, *142*, 21272–21278.
- (26) Liang, H.; Wang, L.-J.; Ji, Y.-X.; Wang, H.; Zhang, B. Selective Electrochemical Hydrolysis of Hydrosilanes to Silanols via Anodically Generated Silyl Cations. *Angew. Chem., Int. Ed.* **2021**, *60*, 1839–1844.
- (27) Ke, J.; Liu, W.; Zhu, X.; Tan, X.; He, C. Electrochemical Radical Silyl-Oxygenation of Activated Alkenes. *Angew. Chem., Int. Ed.* **2021**, *60*, 8744–8749.
- (28) Zhong, M.; Pannecoucke, X.; Jubault, P.; Poisson, T. Copper-Photocatalyzed Hydrosilylation of Alkynes and Alkenes Under Continuous Flow. *Chem. - Eur. J.* **2021**, *27*, 11818–11822.
- (29) See the [Supporting Information](#) for details.
- (30) H–CH₂OH, BDE = 96 kcal·mol⁻¹; CH₃O–H, BDE = 104 kcal·mol⁻¹; H–CH₂CN, BDE = 92 kcal·mol⁻¹.
- (31) Chatgililoglu, C. Structural and Chemical Properties of Silyl Radicals. *Chem. Rev.* **1995**, *95*, 1229–1251.
- (32) Zhong, M.; Pannecoucke, X.; Jubault, P.; Poisson, T. Copper-Photocatalyzed Hydrosilylation of Alkynes and Alkenes Under Continuous Flow. *Chem. - Eur. J.* **2021**, *27*, 11818–11822.
- (33) Zhong, M.; Gagné, Y.; Hope, T. O.; Pannecoucke, X.; Frenette, M.; Jubault, P.; Poisson, T. Copper-Photocatalyzed Hydroboration of Alkynes and Alkenes. *Angew. Chem., Int. Ed.* **2021**, *60*, 14498–14503.
- (34) Aelterman, M.; Sayes, M.; Jubault, P.; Poisson, T. Electrochemical Hydroboration of Alkynes. *Chem. - Eur. J.* **2021**, *27*, 8277–8282.