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Electrochemically mediated synthesis of trifluoromethylallenes†

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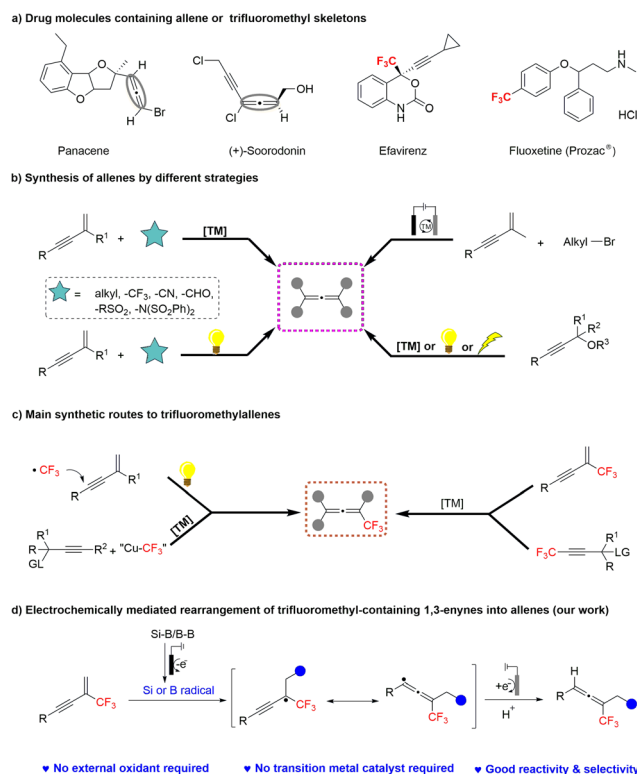
Fluoroalkylated allenes are potential compounds for drug and materials development. Herein, we report electrochemically mediated trifluoromethylallene synthesis through the rearrangement of trifluoromethyl-containing 1,3-enynes under the action of silicon or boron radicals. A series of late functionalization reactions of natural product derivatives were explored to generate corresponding complex allylsilane compounds, and the transformation of homoallenylborates synthesized useful building blocks.

Introduction

Allenes have unique structural characteristics, properties, and versatile chemical reactivity and are thus important structural motifs; they are frequently found in natural products, pharmaceuticals, and organic synthons (Scheme 1a).¹ The efficient and concise synthesis of allenes has attracted considerable interest.² Conventional approaches for accessing allenes typically include 1,2-elimination, Wittig reactions, C–C fragmentation from alkenes, isomerization, substitution, nucleophilic addition, and transition metal-catalyzed cross-coupling with functionalized alkynes.³ The 1,4-bifunctionalization of 1,3-enynes through metal catalysis is the main method for synthesizing various types of allenes.⁴ However, despite their remarkable efficiency for allene derivative preparation, they have limited applications because of the prefunctionalization of substrates and the use of complex and expensive metal reagents. In recent years, allenes have been synthesized by a free radical pathway based on visible light catalysis⁵ because organic reactions through mild radical conversion strategies⁶ are powerful tools for the environmentally friendly and efficient construction of various skeletal structures (Scheme 1b).

The trifluoromethyl (CF₃) group functions as an excellent bioisostere of the methyl group in medicinal chemistry and can improve the metabolic stability, bioavailability, and cellu-

lar membrane permeability of molecules.⁷ Thus, introducing trifluoromethyl groups into molecular skeletons is of great importance. Among many trifluoromethyl substituents, trifluoromethyl-containing allene skeletons are preferred because of their good plasticity. Current methods for synthesizing trifluoromethylated allenes are generally divided into



Scheme 1 Electrochemically mediated synthesis of trifluoromethyl allenes by rearrangement of trifluoromethyl-containing 1,3-enynes.

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two categories: introducing exogenous trifluoromethyl groups⁸ and rearranging alkynes or enynes containing trifluoromethyl groups.⁹

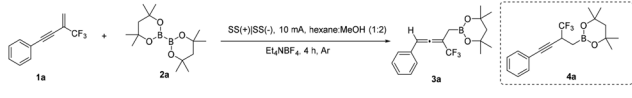
In general, the construction of trifluoromethyl-substituted allene skeletons through an exogenous introduction strategy requires not only transition metal catalysis but also a trifluoromethyl source, which is extremely expensive. A trifluoromethyl source can efficiently facilitate the construction of trifluoromethyl-substituted multifunctional allene skeletons through intramolecular rearrangement. Nevertheless, the rearrangement of enynes containing trifluoromethyl groups is limited to transition metal catalyzed reactions thus far (Scheme 1c).

Organic electrochemical synthesis is an environmentally friendly, mild, and sustainable method for efficient conversion and chemical synthesis.¹⁰ In recent years, Rueping's group has successfully synthesized allenes from 1,3-enynes through organic electrochemistry involving free radicals.¹¹ Thus, trifluoromethyl enynes may be rearranged into trifluoromethyl allenes through the radical addition reaction of silicon or boron radicals. This reaction has been widely reported in unsaturated systems under electrochemical conditions.¹² Herein, a method for synthesizing trifluoromethylated allenes by intramolecular rearrangement through silicon or boron radicals attacking 1,3-enynes is successfully developed. The method does not require metal catalysts or exogenous oxidants and exhibits good chemical and regioselectivity. The introduction of boron promotes the derivatization of trifluoroallenes (Scheme 1d).

Results and discussion

First, 2-trifluoromethyl-1,3-enyne (**1a**) and bis(hexyleneglycolato)diboron (**2a**) were selected as model substrates to optimize the reaction conditions. The reaction was carried out in a MeOH/hexane solution (2 : 1), Et₄NBF₄ was used as the electrolyte (0.05 M), B₂oct₂ was used as the boron reagent, and stainless-steel electrodes had a constant current of 10 mA and charge of 2 F mol⁻¹. We screened a variety of solvents (Table 1, entries 2–5). The optimum reaction result occurred when methanol and hexane were combined. The yield was affected by the methanol content because methanol concentration directly influenced the methoxide anion concentration and intermediate oxidation. No significant change in reaction yield was observed after the amount of **2a** was increased (Table S1,† entries 14 and 15). Different electrolytes considerably influenced the reaction. When LiClO₄ was used as the electrolyte, the target product was not obtained. When tetrabutylammonium bromide was used as the electrolyte, the yield was low (see the details in the ESI†). The use of other electrodes at the cathode and anode was detrimental to the reaction (Table 1, entries 6 and 7). For the electrode materials, the oxidation of the substrate had a high degree of specificity. There have been previous reports of pinacol borane oxidizing on stainless-steel electrodes. When it was added to the reaction, sodium methoxide resulted in a slightly reduced yield

Table 1 Screening of reaction conditions^a

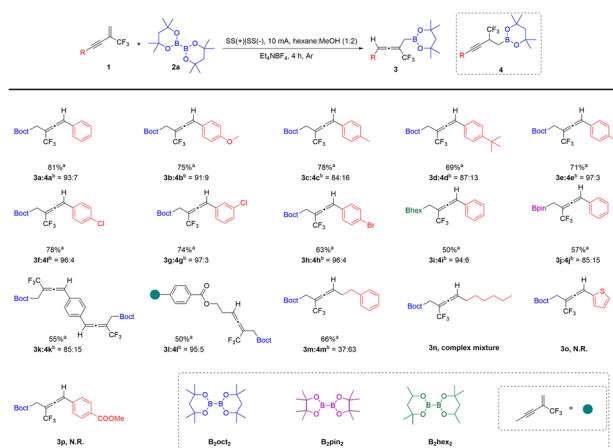


Entry	Variation (from standard conditions)	Yield ^b /%
1	None	81
2	CH ₃ CN instead of hexane : MeOH (1 : 2)	0
3	CH ₃ OH instead of hexane : MeOH (1 : 2)	66
4	1,4-Dioxane/CH ₃ OH(1: 2) instead of hexane : MeOH(1 : 2)	50
5	CH ₃ CN/CH ₃ OH (9 : 1) instead of hexane : MeOH (1 : 2)	30
6	SS (+) Pt (-) instead of SS (+) SS (-)	40
7	SS (+) C (-) instead of SS (+) SS (-)	0
8	1 eq. CH ₃ ONa as base	20
9	ⁿ Bu ₄ NBr instead of Et ₄ NBF ₄	20
10	ⁿ Bu ₄ NPF ₆ instead of Et ₄ NBF ₄	54
11	5 mA instead of 10 mA	50
12	15 mA instead of 10 mA	56
13	6 h instead of 4 h	60
14	8 h instead of 4 h	50
15	No current	0

^a Standard conditions: **1** (0.2 mmol), **2a** (0.4 mmol), Et₄NBF₄ [0.05 M] in hexane/CH₃OH (1 : 2, 6 mL), rt, stainless-steel electrodes (cathode and anode), 10 mA, 2 F mol⁻¹, 5 mA cm⁻², undivided cell, under Ar. ^b Yield of isolated product.

(Table S1,† entries 16–20). When the amount of electricity was constant, either a decrease or an increase in current slightly reduced the yields (Table 1, entries 11 and 12). When the reaction was carried out without current, no product was obtained (Table 1, entry 15).

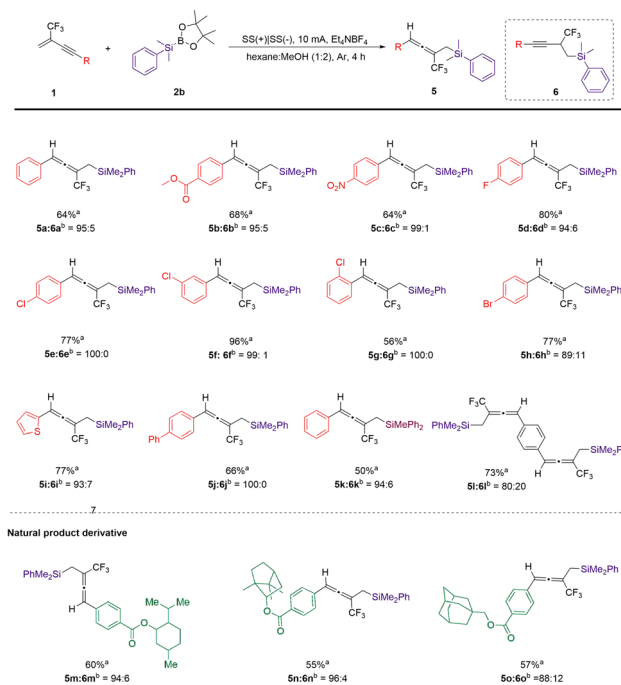
Under the optimized conditions, we examined the scope and the limitations of the electrochemical 1,4-protoborylation of CF₃-substituted conjugated enynes reaction (Scheme 2). The substrate range of electron-donor substituents was expanded.



Scheme 2 Substrate scope for electrochemical 1,4-protoborylation of CF₃-substituted conjugated enynes. ^a Standard reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), Et₄NBF₄ [0.05 M] in hexane/CH₃OH (1 : 2, 6 mL), rt, stainless-steel electrodes (cathode and anode), 10 mA, 2 F mol⁻¹, undivided cell, under Ar. ^b The ratio of **3** to **4** was determined by ¹⁹F NMR analysis.

All the 2-trifluoromethyl-1,3-enynes generated the desired products in good to excellent yields (Scheme 2, **3a–3l**). In addition to simple 2-trifluoromethyl-1,3-enyne, enynes with various substitutions, such as methyl, methoxyl, and tertbutyl, at the *para* site formed the corresponding allenes (**3a–3d**) in high yields (81%–69%). Halogen-containing enynes (**3e–3h**) were obtained in good yields (78%–69%). When a chlorine substituent was in the *para* and *meta* positions, the target products (**3f** and **3g**) were obtained in good yields. Notably, when the chlorine atom was in the *ortho* position, we did not obtain satisfactory results. Therefore, the steric hindrance influenced our reaction. Subsequently, different boranes were tested. B₂hex₂ and B₂pin₂ were converted into the target products (**3i** and **3j**) in moderate yields (57%–50%) under the optimized conditions. Finally, we explored different reaction sites. When the substrate was **1k**, two molecules were generated by the boron-addition rearrangement of the allene product (**3k**). When the reaction substrate was **1l**, **3l** was generated by the addition rearrangement of the alkyl fragment and boron. This result indicated that boron radicals are reactive for alkyl fragments. To further explore the substrates of alkynes containing alkyl substituents, **1m** and **1n** have been selected as the substrates. The experimental results indicate that when **1m** was used, the selectivity to the products was **3m** : **4m** = 37 : 63. When the substrate was **1n**, a complex mixture was obtained. Furthermore, the target product cannot be obtained when the substrate contains heterocyclic and electron-withdrawing substituents (**1o** and **1p**). Therefore, the experimental results indicate that boron radicals preferentially react with higher electron density alkynes, which may be related to the reaction properties of boron radicals themselves.

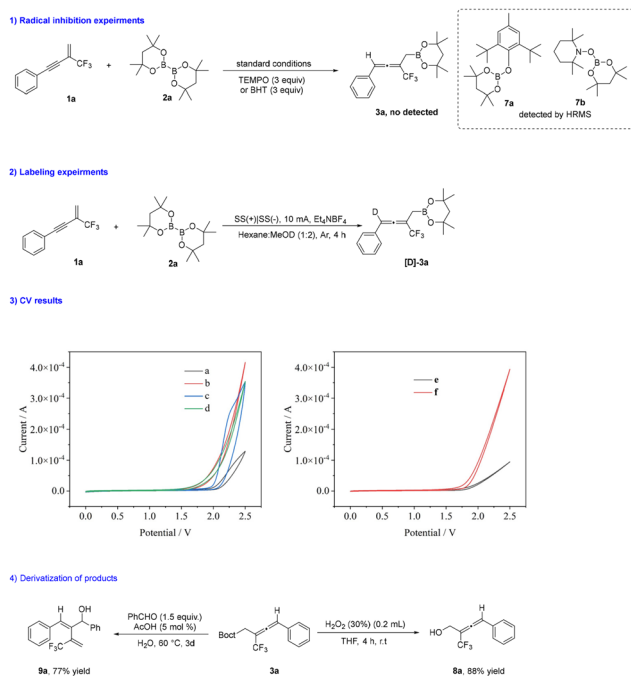
Considering the variability and wide practicality of silicon reagents, we tested the silicon boron reagent **2b** instead of **2a**. Next, we studied the 1,4-protosilylation of trifluoromethyl substituted enynes. The scope of CF₃-substituted conjugated enynes was examined (Scheme 3). Both electron-withdrawing and electron-donating enynes were tolerated under the standard reaction conditions. All the 2-trifluoromethyl-1,3-enynes afforded the desired products in moderate to excellent yields (Scheme 3, **5a–5o**). In addition to simple 2-trifluoromethyl-1,3-enyne, enynes with various substitutions such as ester and nitro at the *para*-position produced allenes (**5b** and **5c**) in good yields (68–64%). When halogen containing enynes were used (**5d–5h**), good yields (96–56%) were obtained. When a chlorine substituent was in the *para*-, *meta*- and *ortho*-positions (**5e–5g**), the target products were obtained in good yields (96–56%). When a chlorine substituent was in the *ortho* position, a single product (**5g**) was obtained, although the yield was not extremely high. This result showed that steric hindrance also had an important influence on the selectivity of the reaction. Then, for enynes containing thiophene or biphenyl, the target products (**5i** and **5j**) could also be obtained in good yield (77–66%). Subsequently, we used a different silicon substrate and obtained a moderate yield (**5k**) with Ph₂MeSi-Bpin. Finally, we used different natural product derivatives, such as menthol, borneol, and adamantyl alcohol derivatives,



Scheme 3 Substrate scope for electrochemical 1,4-protosilylation of CF₃-substituted conjugated enynes.^a Standard reaction conditions: **1** (0.1 mmol), **2b** (0.15 mmol), Et₄NBF₄ [0.05 M] in hexane/CH₃OH (1:2, 6 mL), rt, stainless-steel electrodes (cathode and anode), 10 mA, 2 F mol⁻¹, undivided cell, under Ar. ^b The ratio of **5** to **6** was determined by ¹⁹F NMR analysis.

which produced the corresponding products (**5m–5o**) in good yields (61%–55%).

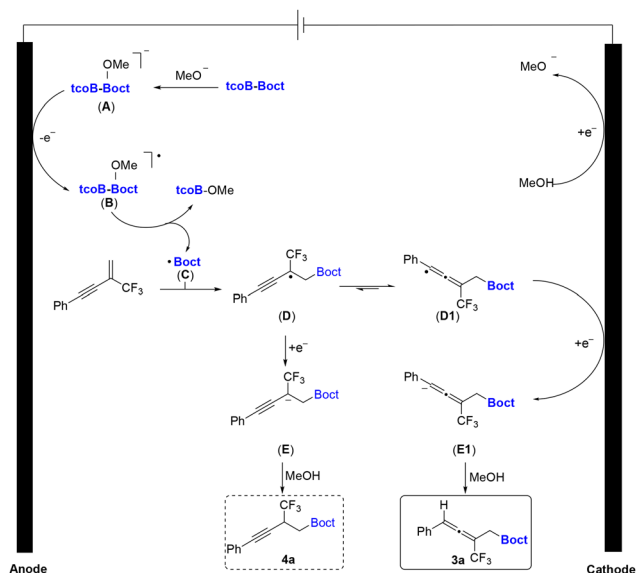
We conducted a series of control experiments to study the mechanism (Scheme 4). When 3.0 equivalents of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl were employed in the reaction, the process was completely suppressed, and **3a** was not detected. Adding 3.0 equivalents BHT into the reaction resulted in the production of trace amounts of **3a** (Scheme 4-1). The HRMS analysis showed that there may be free radical trapping species **7a** and **7b** generated. These results indicated that the reaction may involve a radical pathway. To understand the proton source of hydrogenation in the reaction, we conducted labeling experiments on methanol. The results showed that the proton source of the reaction was methanol (Scheme 4-2). All the results suggested that the boryl radical intermediate was involved in the transformation. We performed cyclic voltammetry (CV) experiments to further understand the details of the oxidation process (Scheme 4-3). First, we tested B₂oct₂ in different solvents. The results showed that methanol was necessary. Subsequently, the solvent under the standard conditions was tested, indicating that hexane promoted the reaction. Second, we tested the CV of 2-trifluoromethyl-1,3-enyne under the standard conditions and without B₂oct₂ in the reaction system. According to the CV experiments, under electrochemical conditions, the results indicate that electrochemical mediated single electron transfer oxidation of silicon boron or boron reagents can easily occur in the form of borate through



Scheme 4 Control experiments, application and cyclic voltammograms in 0.3 mmol B_2oct_2 + 0.05 M Et_4NBF_4 : (a) CH_3CN , 6 mL; (b) CH_3OH , 6 mL; (c) CH_3ONa + CH_3CN , 6 mL; (d) CH_3OH + hexane, 6 mL; (e) no B_2oct_2 ; (f) with B_2oct_2 .

solvent activation.^{12h} Finally, the reaction of homoallenylboronates with benzaldehyde produced dieny alcohol (**9a**). The oxidative derivatization of **3a** afforded the corresponding homoallenol (**8a**) in excellent yield (Scheme 4).

Based on mechanism studies and evidences¹³ regarding the electrochemical borylation reactions, we suggested the following plausible mechanism (Scheme 5). First, the methoxide anion generated by the reduction of methanol at the cathode



Scheme 5 Proposed mechanism.

reacted with bis(hexyleneglycolato)diboron and formed the borate species **A**. The subsequent anodic oxidation of borate **A** generated radical species **B**, which decomposed into octB-OMe and borate radical **C**. Then, the radical rapidly added to the double bond of the 1,3-enyne to produce a highly reactive propargyl radical **D**, which tautomerized with the allenyl radical intermediate **D1**,^{1a,9a} and then the radicals were reduced to negative ions **E** and **E1** at the cathode, which were protonated by the solvent (MeOH), generating the final products **4a** and **3a**. Finally, the main product allene derivatives and alkyne derivatives were obtained by protonation.

Conclusions

In summary, we report an electrochemical method for the preparation of various trifluoromethylated allenes without transition metals. B or Si radicals were introduced. The method was used under mild conditions, and readily available substrates were used. The reaction tolerance to functional groups allows for post-modification of biologically relevant compounds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- (a) H.-J. Miao, J.-H. Zhang, S. Liu, W.-H. Wang, X. Yang, X.-H. Duan and L.-N. Guo, Alkoxy Radical-Mediated Ring Expansion/1,4-Difunctionalization of 1,3-Enynes upon Copper Catalysis, *Org. Lett.*, 2023, **25**, 5563–5568; (b) X. Zhu, W. Deng, M.-F. Chiou, C. Ye, W. Jian, Y. Zeng, Y. Jiao, L. Ge, Y. Li, X. Zhang and H. Bao, Copper-Catalyzed Radical 1,4-Difunctionalization of 1,3-Enynes with Alkyl Diacyl Peroxides and N-Fluorobenzenesulfonimide, *J. Am. Chem. Soc.*, 2019, **141**, 548–559; (c) Y. Liao, X. Yin, X. Wang, W. Yu, D. Fang, L. Hu, M. Wang and J. Liao, Enantioselective Synthesis of Multisubstituted Allenes by Cooperative Cu/Pd-Catalyzed 1,4-Arylboration of 1,3-Enynes, *Angew. Chem., Int. Ed.*, 2020, **59**, 1176–1180.
- S. Yu and S. Ma, How Easy Are the Syntheses of Allenes?, *Chem. Commun.*, 2011, **47**, 5384–5418.

- 3 C. Zhu, H. Chen, H. Yue and M. Rueping, Electrochemical Chemo- and Regioselective Arylalkylation, Dialkylation and Hydro(Deutero)Alkylation of 1,3-Enynes, *Nat. Synth.*, 2023, **2**, 1068–1081.
- 4 (a) Y. Huang, J. del Pozo, S. Torker and A. H. Hoveyda, Enantioselective Synthesis of Trisubstituted Allenyl-B(pin) Compounds by Phosphine-Cu-Catalyzed 1,3-Enyne Hydroboration. Insights Regarding Stereochemical Integrity of Cu-Allenyl Intermediates, *J. Am. Chem. Soc.*, 2018, **140**, 2643–2655; (b) S. Dong, Z. Tian, J. Wang, L. He and J. Li, Organozinc Pivalates for Modular Cobalt-Catalyzed Carbonylation of 1,3-Enynes, *J. Catal.*, 2023, **425**, 350–358.
- 5 (a) Y. Li and H. Bao, Radical Transformations for Allene Synthesis, *Chem. Sci.*, 2022, **13**, 8491–8506; (b) G.-D. Zhang, W. Tan, D. Zhang, K. Wang, P. Gao, S. Wang, S.-L. Liu and F. Chen, Regioselective Hydro(Deutero)Silylation of 1,3-Enynes Enabled by Photoredox/Nickel Dual Catalysis, *Org. Lett.*, 2024, **26**, 536–541; (c) Y. Chen, J. Wang and Y. Lu, Decarboxylative 1,4-Carbocyanation of 1,3-Enynes to Access Tetra-Substituted Allenes via Copper/Photoredox Dual Catalysis, *Chem. Sci.*, 2021, **12**, 11316–11321; (d) C. Cheng, G.-F. Lv, S. Wu, Y. Li and J.-H. Li, Nickel Photocatalyzed Reductive 1,4-Dicarbonylation of 1,3-Enynes with N-Methylamines and Organohalides Enabled by Site-Selective C(sp³)-H Functionalization, *Org. Lett.*, 2023, **25**, 4236–4240; (e) T. Xu, S. Wu, Q.-N. Zhang, Y. Wu, M. Hu and J.-H. Li, Dual Photoredox/Nickel-Catalyzed 1,4-Sulfonylation of 1,3-Enynes with Sulfinates and Aryl Halides: Entry into Tetrasubstituted Allenes, *Org. Lett.*, 2021, **23**, 8455–8459; (f) Y. Chen, K. Zhu, Q. Huang and Y. Lu, Regiodivergent Sulfonylation of 1,3-enynes via Nickel/Photoredox Dual Catalysis, *Chem. Sci.*, 2021, **12**, 13564–13571.
- 6 (a) L. Chen, C. Lin, S. Zhang, X. Zhang, J. Zhang, L. Xing, Y. Guo, J. Feng, J. Gao and D. Du, 1,4-Alkylcarbonylation of 1,3-Enynes to Access Tetra-Substituted Allenyl Ketones via an NHC-Catalyzed Radical Relay, *ACS Catal.*, 2021, **11**, 13363–13373; (b) J.-H. Qin, Z.-Q. Xiong, C. Cheng, M. Hu and J.-H. Li, Electroreductive Carboxylation of Propargylic Acetates with CO₂: Access to Tetrasubstituted 2,3-Allenates, *Org. Lett.*, 2023, **25**, 9176–9180; (c) C.-H. Xu, Z.-Q. Xiong, J.-H. Qin, X.-H. Xu and J.-H. Li, Cobalt-Promoted Electroreductive Cross-Coupling of Prop-2-Yn-1-Yl Acetates with Chloro(Vinyl)Silanes, *Org. Lett.*, 2023, **25**, 7263–7267.
- 7 (a) S. Li, W. Yang, J. Shi, T. Dan, Y. Han, Z.-C. Cao and M. Yang, Synthesis of Trifluoromethyl-Substituted Allenols via Catalytic Trifluoromethylbenzoylation of 1,3-Enynes, *ACS Catal.*, 2023, **13**, 2142–2148; (b) X. Li, N. Li, L. Yang, R. Jiang, Y. He, J. Shi, Z.-X. Jiang and Z. Yang, Switchable Nucleophilic Site Enables Expedient Synthesis of CF₃-Containing Thiazoles and Allenes from 1,3-Enynes, *ACS Catal.*, 2023, **13**, 12755–12765.
- 8 (a) H. Shen, H. Xiao, L. Zhu and C. Li, Copper-Catalyzed Radical Bis(Trifluoromethylation) of Alkynes and 1,3-Enynes, *Synlett*, 2020, **31**, 41–44; (b) Y.-L. Ji, J.-J. Luo, J.-H. Lin, J.-C. Xiao and Y.-C. Gu, Cu-Catalyzed C–H Trifluoromethylation of 3-Arylprop-1-Ynes for the Selective Construction of Allenic Csp²-CF₃ and Propargyl Csp³-CF₃ Bonds, *Org. Lett.*, 2016, **18**, 1000–1003; (c) A. Boreux, G. H. Lonca, O. Riant and F. Gagosz, Synthesis of Trifluoromethyl-Allenenes by Gold-Catalyzed Rearrangement of Propargyl Benzyl Ethers, *Org. Lett.*, 2016, **18**, 5162–5165.
- 9 (a) C. Yang, Z.-L. Liu, D.-T. Dai, Q. Li, W.-W. Ma, M. Zhao and Y.-H. Xu, Catalytic Asymmetric Conjugate Protosilylation and Protoborylation of 2-Trifluoromethyl Enynes for Synthesis of Functionalized Allenes, *Org. Lett.*, 2020, **22**, 1360–1367; (b) S.-H. Yu, T.-J. Gong and Y. Fu, Synthesis of Conjugated Bisallenenes by Cooperative Cu/Pd-Catalysed Boryllenylation of 2-Trifluoromethyl-1,3-Enynes, *Chem. Commun.*, 2022, **58**, 12871–12874; (c) M. Shimizu, M. Higashi, Y. Takeda, G. Jiang, M. Murai and T. Hiyama, Novel Generation of 3,3,3-Trifluoropropynyllithium and Transformation of the Carbonyl Adducts to Trifluoromethyl-Substituted Allenes, *Synlett*, 2007, 1163–1165.
- 10 (a) L. Lu, Y. Wang, W. Zhang, W. Zhang, K. A. See and S. Lin, Three-Component Cross-Electrophile Coupling: Regioselective Electrochemical Dialkylation of Alkenes, *J. Am. Chem. Soc.*, 2023, **145**, 22298–22304; (b) C. Ma, P. Fang, Z.-R. Liu, S.-S. Xu, K. Xu, X. Cheng, A. Lei, H.-C. Xu, C. Zeng and T.-S. Mei, Recent Advances in Organic Electrosynthesis Employing Transition Metal Complexes as Electrocatalysts, *Sci. Bull.*, 2021, **66**, 2412–2429; (c) X. Cheng, A. Lei, T.-S. Mei, H.-C. Xu, K. Xu and C. Zeng, Recent Applications of Homogeneous Catalysis in Electrochemical Organic Synthesis, *CCS Chem.*, 2022, **4**, 1120–1152; (d) H.-T. Tang, Y.-Z. Pan and Y.-M. Pan, Research Progress in Electrochemical/Photochemical Utilization of Methanol as a C1 Source, *Green Chem.*, 2023, **25**, 8313–8327.
- 11 H. Chen, C. Zhu, H. Yue and M. Rueping, Group 14 Elements Hetero-Difunctionalizations via Nickel-Catalyzed Electroreductive Cross-Coupling, *Angew. Chem., Int. Ed.*, 2023, **62**, e202306498.
- 12 (a) X. Chen, Y.-G. Huang, W.-Q. Zhong and J.-M. Huang, Electrochemical Decarboxylative Silylation of α,β -Unsaturated Carboxylic Acids, *Org. Lett.*, 2023, **25**, 4562–4566; (b) L.-Q. Ren, N. Li, J. Ke and C. He, Recent Advances in Photo- and Electro-Enabled Radical Silylation, *Org. Chem. Front.*, 2022, **9**, 6400–6415; (c) L. Lu, J. C. Siu, Y. Lai and S. Lin, An Electroreductive Approach to Radical Silylation via the Activation of Strong Si–Cl Bond, *J. Am. Chem. Soc.*, 2020, **142**, 21272–21278; (d) B. Wang, X. Zhang, Y. Cao, L. Zou, X. Qi and Q. Lu, Electrooxidative Activation of B–B Bond in B₂cat₂: Access to *gem*-Diborylalkanes via Paired Electrolysis, *Angew. Chem., Int. Ed.*, 2023, **62**, e202218179; (e) Y. Cao, C. Huang and Q. Lu, Photoelectrochemically Driven Iron-Catalysed C(sp³)-H Borylation of Alkanes, *Nat. Synth.*, 2024, **3**, 537–544; (f) B. Wang, P. Peng, W. Ma, Z. Liu, C. Huang, Y. Cao, P. Hu, X. Qi and Q. Lu, Electrochemical Borylation of Alkyl

- Halides: Fast, Scalable Access to Alkyl Boronic Esters, *J. Am. Chem. Soc.*, 2021, **143**, 12985–12991; (g) C. Guo, P. Li, S. Wang, N. Liu, Q. Bu, Y. Wang and Y. Qiu, Selective Electroreductive Hydroboration of Olefins with B_2pin_2 , *J. Org. Chem.*, 2023, **88**, 4569–4580; (h) N. Takemura, Y. Sumida and H. Ohmiya, Organic Photoredox-Catalyzed Silyl Radical Generation from Silylboronate, *ACS Catal.*, 2022, **12**, 7804–7810.
- 13 (a) M. Aelterman, T. Biremond, P. Jubault and T. Poisson, γ -Fluoro -Allyl Boronates and Silanes, *Eur. J. Org. Chem.*, 2022, **28**, e202202194; (b) M. Aelterman, P. Jubault and T. Poisson, Electrochemical Borylation of Electron-Deficient Alkenes and Allenates, *Eur. J. Org. Chem.*, 2023, **26**, e202300063; (c) M. Aelterman, M. Sayes, P. Jubault and T. Poisson, Electrochemical Hydroboration of Alkynes, *Eur. J. Org. Chem.*, 2021, **27**, 8277–8282; (d) H.-Y. Zhou, L.-Q. Fei, J.-L. Zhang, Y.-M. Pan and H.-T. Tang, Electrochemical Hydrosilylation of Electron-Withdrawing Alkenes, *Adv. Synth. Catal.*, 2023, **365**, 1591–1595.